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UNIVERSITÉ DE MONTRÉAL

DÉPOSITION PHOTOCHIMIQUE DU GAZ DE SYNTHÈSE (CO ET H_2) POUR LA FONCTIONNALISATION EN SURFACE À CONDITIONS AMBIANTES

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Ce mémoire intitulé :

DÉPOSITION PHOTOCHIMIQUE DU GAZ DE SYNTHÈSE (CO ET H_2) POUR LA FONCTIONNALISATION EN SURFACE À CONDITIONS AMBIANTES

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À Jason,
Celui-ci est le premier d'une longue série...

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RÉSUMÉ

Le phénomène d'agglomération des nanoparticules reste un obstacle technique à leur mise en œuvre à leur plein potentiel. Bien que les agents tensioactifs peuvent résoudre ce problème dans le cas de suspensions dans des liquides, cette solution facile n'est pas applicable à toutes les situations. Le problème est que les agents tensioactifs ont tendance à se désorber de la surface lorsqu'amenés à des températures au-delà de 70°C. De nombreux usages nécessitent d'atteindre des températures plus élevées que ce seuil, soit au cours de leur durée de vie utile (par ex. : nanofluides) ou au cours de leur processus de fabrication (par ex. : nanocomposites, soit des nanoparticules dispersées dans une matrice polymère). Une autre façon de contrer cet effet consiste à attacher des groupes fonctionnels à la surface des particules grâce à une forte liaison covalente (un processus connu sous le nom fonctionnalisation), modifiant ainsi leurs propriétés de surface. Bien qu'applicables à certaines applications à forte valeur ajoutée, les méthodes actuelles de fonctionnalisation à base de liquides sont souvent trop coûteuses pour permettre leur utilisation en contexte industriel. Notre groupe de recherche a étudié l'aspect coût versus efficacité et propose la déposition de vapeur photochimique (PICVD) comme un candidat potentiel pour la fonctionnalisation de particules à grande échelle. Le PICVD utilise la lumière UV comme initiateur de polymérisation radicalaire en phase gazeuse, afin de déposer des groupes fonctionnels sur la surface. Les avantages de cette technique sont non négligeables : faible consommation d'énergie, opération à des conditions normales et utilisation de matériel et de réactifs communs. Alors que le souci premier relié à l'utilisation du PICVD est son faible taux de déposition, cette crainte n'est pas fondée dans le cas de la fonctionnalisation en surface, puisque la charge de surface est un principe purement surfacique et aucunement volumique.

La possibilité d'utiliser le PICVD pour la fonctionnalisation en surface a été étudiée. Les essais ont été effectués sur des substrats macroscopiques plats afin d'éliminer les facteurs reliés aux phénomènes de transfert de masse, ainsi qu'à la manipulation souvent complexe des nanoparticules. Les propriétés de surface ont été caractérisées par goniométrie ainsi que par FTIR, alors que la composition de l'effluent gazeux de sortie a été mesuré par GCMS. Les résultats obtenus ont confirmé que les surfaces peuvent être traitées par PICVD, mais invitent aussi à penser que les propriétés de surface peuvent être finement ajustées en contrôlant la cinétique impliquée dans le réacteur. Un modèle empirique a été développé reliant l'angle de contact aux paramètres expérimentaux du système. De plus, l'addition de peroxyde d'hydrogène en tant que promoteur a permis l'extension des plages de valeur obtenues pour l'angle de contact, soit de 30-100° à 5-118°.

Des substrats de polymères ont également été testés suivant le même procédé, mais cette fois en visant uniquement les revêtements hydrophobiques. Les résultats démontrent que le concept s'applique également sur des substrats de polymère. L'addition de peroxyde d'hydrogène a entraîné la formation de revêtement hautement hydrophile (angles de contact autour de zéro), et ce, à des conditions généralement connues pour donner des revêtements hydrophiles.

L'étude a conclu que le PICVD est en effet un candidat potentiel pertinent pour la fonctionnalisation en surface. Par contre, cette étude ne peut formuler aucune conclusion quant à son efficacité directement appliquée aux nanoparticules. Des recommandations pour des travaux futurs incluent un contrôle plus fin des températures locales dans le réacteur. Par exemple, le refroidissement du substrat ainsi que le préchauffage du précurseur pourraient améliorer considérablement la qualité des revêtements, notamment en encourageant la condensation et l'adsorption sur la surface ainsi qu'en accélérant la cinétique dans le gaz du même coup. Le mémoire se termine sur des idées d'applications industrielles potentielles pour cette nouvelle technologie.

ABSTRACT

Agglomeration of nanoparticles remains a technical barrier to their implementation at their full potential. While surfactants can address this problem for nanoparticles in liquid suspensions, this quick fix is not applicable to every situation, since surfactants tend to desorb from the surface at temperatures as low as 70°C. Many usages require reaching higher temperatures either during the course of their useful life (i.e. nanofluids) or during their fabrication process (i.e. nanocomposites like nanoparticles dispersed in polymer matrix). Another way to counter this effect consists to attach functional groups to the surface of the particles through a strong covalent bound (a process known as functionalization), therefore changing their surface properties. While valid for some high-added value applications, current, mainly liquid-based functionalization methods are often too expensive to allow for their use in industrial context. Our research group has considered the cost-efficiency aspect and proposes the gas-phase photo-initiated chemical vapor deposition (PICVD) approach as a potential candidate for scalable particle functionalization. PICVD uses UV light as an initiator for gas phase radical polymerization that deposits functional groups on the surface. The advantages of this technique are tremendous: lower energy consumption, operation under normal conditions (room temperature and atmospheric pressure) and usage of common material and reactants. While the main concerns of this technique is about its low deposition rates (compared to the plasma-enhanced equivalent), we have good reasons to believe that the deposition rates offered by PICVD would be sufficient for the current purpose.

The feasibility of using PICVD for the functionalization of surfaces has been investigated using syngas as precursor. In order to characterize the method properly, benchmark tests have been run on copper flat macro-scale substrates. This strategy allowed us to neglect the effect of mass transfer limitations, but also to avoid the complexity associated to nanoparticle handling. Surface characterization focuses on FTIR spectroscopy and goniometry (water contact angle) analysis giving, respectively, the composition and wettability of the surface. The exiting gas has been also analyzed through gas chromatography (GC-MS) in order to better understand the gas-phase reactions taking place through the reactor. The results obtained confirmed that surfaces can be treated through PICVD, but also suggest that the surface properties can be finely tailored by controlling the kinetics involved in the reactor. More specifically, a strong correlation between the composition of the exiting gas and the surface properties has been observed; depending on which reaction set is dominant, the surface can be set as hydrophilic or hydrophobic. An empirical model has been derived from the data relating the contact angle to the process parameters. Hydrogen peroxide was added

into the system as a reaction promoter and it successfully widened the range of contact angle obtained from 30-100° to 5-118°.

Polymer substrates have also been tested with the same method, but this time aiming hydrophobic coatings only. It has been found that the method also worked for the polymer substrates. The coating process indeed increased the measured water contact angle on substrates. The addition of hydrogen peroxide was also tested but gave unexpected results: the coated surfaces were highly hydrophilic (contact angle near zero) at process parameters that were expected to achieve hydrophobic coatings.

This study concluded that PICVD does show promises as a scalable gas phase functionalization process for surface treatment. However this study cannot reach any conclusion related to its efficiency for the surface functionalization applied to nanoparticles. Recommendations for future work include a finer control of temperature inside the reactor, therefore promoting adsorption and condensation on the surface by cooling down the substrate, while improving the kinetics by preheating the precursors. The master thesis closes on some ideas of potential industrial applications of this new technology.

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CVD	Chemical vapour deposition
HWCVD	Hot-wire chemical vapour deposition
(i)CVD/iCVD	Initiated chemical vapour deposition
LCVD	Luminous chemical vapour deposition
MOCVD	Metalorganic chemical vapour deposition
MLCVD	Magneto luminous chemical vapour deposition
(o)CVD	Oxidative Chemical Vapour Deposition
P	Pression dans le réacteur
PACVD	Plasma- or photo-assisted chemical vapour deposition
PECVD	Plasma-enhanced chemical vapour deposition
(pi)CVD/PICVD	Photo-induced or -initiated chemical vapour deposition
PET	Polyethylene Terephtalate
Pos	Position dans le réacteur
PP	Polypropylène
r	Ratio de gaz H_2/CO (Molaire)
TACVD	Thermally-activated chemical vapour deposition
VDP	Vapour deposition polymerization

CHAPITRE 1

INTRODUCTION

Ce mémoire discute du traitement de surface par déposition chimique en phase vapeur visant à contrer le problème d'agglomération des nanoparticules. Plus particulièrement, ce travail fait appel à la photo-initiation du gaz de synthèse pour effectuer sa déposition chimique. Ce projet de maîtrise discute également de l'utilisation de l'analyse multivariée afin de modéliser de manière empirique le comportement des surfaces observées en fonction des paramètres expérimentaux.

1.1 Définitions et concepts de base

1.1.1 Nanoparticules, agglomération et tension de surface

Bien qu'ils fassent l'objet de bien des discussions, les nanoparticules ne sont pas aussi répandues dans nos technologies qu'elles pourraient l'être. Pourtant, leur petite taille leur attribue bien des propriétés qui sont considérées intéressantes, puisqu'à cette échelle, les propriétés de ces particules diffèrent de leurs propriétés théoriques (*"bulk"*) [36]. C'est d'ailleurs en raison de leurs très petites tailles qu'elles possèdent une énergie de surface aussi importante qui se traduit en un phénomène d'agglomération [43]. Ce phénomène d'agglomération est considéré comme problématique, dans le sens où les agglomérats formés simulent une taille de particule plus grande, et ainsi perdent leur intérêt. Un exemple d'utilisation des nanoparticules est de les disperser dans une matrice, soit solide ou liquide, pour former respectivement ce que l'on appelle des nanocomposites ou des nanofluides. Dans ce document, il sera discuté des différentes méthodes actuellement employées pour contourner ce problème, ainsi que de leurs avantages et inconvénients. La méthode utilisée dans ce projet de maîtrise s'appelle fonctionnalisation en surface et consiste à attacher des groupements fonctionnels (soit des molécules possédant différentes charges) à ces surfaces afin d'en changer leur charges apparentes. Une méthode simple et peu coûteuse pour mesurer cette charge consiste à déposer des gouttes de liquide (dans le cas présent, de l'eau) sur la surface et à mesurer ce que l'on appelle l'angle de contact à l'aide d'un appareil nommé goniomètre. L'angle de contact est une manière élégante de mesurer la tension de surface, car elle donne l'heure juste quant aux affinités de ce système à trois (3) phases, ces phases étant l'air ambiant, le liquide et la phase solide. Ce bilan des forces indique si la surface solide préfère être mouillée par l'air ou par le liquide. L'air ambiant étant généralement considéré constant en composition, la mesure

de l'angle de contact est souvent considérée comme étant une indication de l'affinité entre le solide et le liquide. Pour changer la mouillabilité d'une surface, on peut, soit mécaniquement modifier la rugosité de cette surface, ou bien recouvrir la surface avec un matériau qui possède la mouillabilité désirée [53].

1.1.2 Le gaz de synthèse

Le gaz de synthèse (*"syngas"* en anglais) est un mélange de gaz combustible issu du procédé de gazéification. La gazéification est un procédé où l'on fait la combustion partielle de matières organiques (telles que du bois, du charbon, ou encore des substances végétales), en introduisant un oxydant en quantité insuffisante comparativement à ce qui est stoichiométriquement requis pour accomplir la combustion complète. Bien que le gaz de synthèse puisse contenir d'autres composés tels que de l'eau (H_2O), du méthane (CH_4), ainsi que du dioxyde de carbone (CO_2), le terme gaz de synthèse est souvent associé à un mélange pur de monoxyde de carbone (CO) et de dihydrogène (H_2). Actuellement, le gaz de synthèse peut être utilisé soit comme combustible ou encore comme matière première pour la synthèse d'hydrocarbures, notamment grâce au procédé Fischer-Tropsch [84].

1.1.3 La déposition chimique en phase vapeur

La déposition chimique en phase vapeur est utilisée pour produire des dépôts de couches minces sur des substrats à partir d'un ou des réactif(s) présent(s) dans la phase gazeuse. Les réactifs impliqués dans la réaction (souvent appelés précurseurs) sont des monomères qui, sous l'effet d'une initiation, entrent dans une réaction en chaîne de polymérisation [1]. Les précurseurs commercialement utilisés sont souvent liquides aux conditions ambiantes, mais sont distribués dans la phase gazeuse par la tension de vapeur typiquement en opérant dans une chambre sous vide. L'utilisation de molécules gazeuses aux conditions ambiantes est très rare, puisqu'en raison de leur petites tailles, ces dernières tendent à engendrer des taux de déposition plus lents. La nouvelle molécule formée, une combinaison de plusieurs monomères l'un à la suite de l'autre, se dépose sur le substrat. Ceci a pour effet de former une couche mince sur celui-ci. L'initiation, quant à elle, consiste en un apport d'énergie suffisant pour atteindre l'énergie d'activation de la réaction et peut être fournie sous plusieurs formes : plasma, rayonnement et chaleur étant les plus courantes. La déposition chimique est une technique considérée comme très propre, principalement parce qu'elle est opérée en phase

1. Cette étude s'intéresse uniquement aux procédés CVD dits "organiques". Cependant la déposition chimique en phase vapeur peut également se produire à l'aide de silanes [100] et de composés organométalliques [78]. Ces derniers impliquent des mécanismes réactionnels bien différents de ceux impliqués dans ce mémoire. Pour cette raison, ils ne seront couverts par cette revue de littérature.

gazeuse, ce qui facilite la séparation précurseur-substrat après déposition [16]. L'industrie du semi-conducteur est actuellement la plus grande utilisatrice de cette technologie [55].

Voici une compilation de faits pertinents à propos du CVD :

- La plupart des procédés CVD sont des systèmes ouverts où les précurseurs entrent et réagissent, alors que les molécules non-réagies ressortent.
- Il n'y a pas d'équipements standards, les designs sont adaptés aux besoins spécifiques de l'application.
- Alors que le CVD est fondamentalement un procédé très complexe, son application est très simple.
- D'un point de vue théorique, les aspects thermodynamiques, cinétiques ainsi que les phénomènes de transfert de masses jouent des rôles importants.
  - Thermodynamique : la réaction des précurseurs vers le produit désiré doit être thermodynamiquement possible (minimisation de l'énergie de Gibbs).
  - Cinétique : la température et la pression ont un effet majeur sur les taux de réaction.
  - Transfert de masse : de manière à ce que la déposition se fasse, les patrons d'écoulements et la diffusion interne dans le substrat sont des aspects à considérer.
- Les principaux paramètres sont la température, la pression, la concentration du réactif dans la phase gazeuse, les ratios de réactifs (lorsque mélange de réactifs).
- Ces paramètres doivent être surveillés et contrôlés étroitement.
- L'opération sous vide est généralement favorable, car elle facilite l'adsorption en profondeur dans les pores du substrat, en plus de contribuer à l'évaporation du précurseur dans le cas d'un précurseur liquide. La plupart des procédés CVD peuvent tout de même opérer à pression ambiante au besoin.
- Afin d'améliorer l'uniformité du revêtement, l'opérateur peut, soit pivoter le substrat, l'incliner ou encore améliorer le mélange en introduisant des turbulences.
- Les réactions CVD sont souvent identiques à leurs homologues en polymerisation de radicaux libres. Non seulement la stoichiometrie est la même, mais les mécanismes réactionnels sont généralement les mêmes également.

1.1.4 La photo-initiation

La photo-initiation est une forme d'initiation qui utilise la lumière pour fournir l'énergie nécessaire pour amorcer une réaction. Cette source n'est pas souvent utilisée car elle possède le désavantage d'être moins énergétique que l'initiation par plasma (en anglais *"Plasma Enhanced CVD"* ou PECVD) et plus capricieuse que l'initiation thermique (en anglais *"Thermally Activated CVD"* d'où l'accronyme TACVD) puisque le mélange doit être photosensible [5]. De ce fait, le PICVD une variante du CVD injustifiablement sous-estimée, car elle s'avère

beaucoup moins dispendieuse que le PECVD alors qu'elle ouvre la porte à des systèmes de réactions chimiques autrement impossibles à atteindre par TACVD [16]. La sélection d'une forme d'initiation doit donc se faire au cas par cas, en fonction des objectifs visés et des contraintes et/ou ressources présentes, et non en fonction des courants et tendances. Fait intéressant, la photo-initiation a déjà été utilisée pour promouvoir la cinétique de réaction avec le gaz de synthèse dans le cadre d'un procédé Fischer Tropsch [80].

1.1.5 L'analyse multivariée

L'analyse multivariée[2] est une technique qui a gagné énormément en intérêt dans les dernières années dans le milieu industriel [44]. Cette approche est populaire en raison de sa capacité d'extraire l'essentiel de l'information d'un système complexe en modélisant de manière empirique les paramètres dominants et en ignorant simplement les autres [51]. La première étape consiste à normaliser toutes les données ainsi que les réponses. La normalisation est une opération mathématique qui consiste à soustraire toutes les valeurs d'un groupe de données par la moyenne de ce groupe, puis en divisant ces nouvelles valeurs par l'écart-type de ce groupe. Ceci a pour effet d'amener les différents groupes de données sur une base comparable. Ce prétraitement permet non seulement de réduire le bruit associé aux incompatibilités entre les différentes échelles et unités, mais permet en plus de mettre en évidence l'importance relative des paramètres. Une fois les données normalisées, il devient raisonnablement facile de dériver des modèles empiriques en tenant compte des variables qui ont une corrélation importante avec la réponse et en éliminant les autres. L'approche propose de commencer par un modèle multilinéaire, et puis d'augmenter le niveau de complexité du modèle si nécessaire. Bien entendu, un paramètre a besoin d'au moins trois (3) niveaux (-, 0, +) pour passer d'un modèle linéaire à un modèle polynomial. Évidemment, un design d'expérience à deux niveaux réduit le nombre nécessaire d'expériences, mais implique que l'on assume une relation linéaire entre le paramètre et la réponse.

1.2 La problématique

Les récents travaux de Buongiorno et al. [12] ont démontré que si les nanofluides présentent en effet une augmentation des propriétés de transfert de chaleur (à savoir, la conductivité thermique) par rapport au fluide de base, il n'y a pas d'amélioration "anormale" de la conductivité thermique telle que réclamée par les premiers ambassadeurs des nanofluides. Des conclusions similaires en ce qui concerne les propriétés mécaniques des nanocomposites

2. Également nommée l'analyse multivariable. Les deux termes sont acceptés par la banque de données terminologiques et linguistiques du gouvernement du Canada (Termium)

polymères ont également été formulées. Toutefois, cette absence d'amélioration anormale de valeur ajoutée n'écarte pas la validité de l'incorporation de nanoparticules dans des matrices liquides ou polymères, mais elle nous incite néanmoins à trouver des moyens pour réduire le coût de synthèse ainsi que les méthodes de traitement des nanoparticules nécessaires pour leur utilisation. Actuellement, le coût des nanoparticules se situe entre 150 $ à 2000 $ par kilogramme, dépendamment de la nature du matériau (métaux, oxydes métalliques et matériaux exotiques ci-exclus, http ://www.nanoamor.com). Tandis que les chargements de particules requises peuvent être relativement faibles (typiquement entre 0,5 % à 5 % pour les nanofluides), ce coût demeure suffisament élevé pour rendre l'incorporation de nanoparticules à des matrices non rentable à grande échelle.

En outre, ces prix ne représentent que le coût pour synthétiser des nanoparticules et ne prennent pas en compte le coût du traitement des nanoparticules nécessaire pour leur dispersion dans un milieu. L'approche traditionnelle à faible coût utilisée pour contrer l'agglomération des nanoparticules afin d'en faciliter la dispersion est d'utiliser des agents tensioactifs. Cependant, ces composés tensioactifs présentent des lacunes importantes, notamment en ce qui concerne leur stabilité thermique [25]. La stabilité thermique est un critère important à considérer si l'on cherche à élargir la plage de température pour laquelle un nanofluide, par exemple, peut être utilisé. Cet argument est également valide pour empêcher l'agglomération lors de la dispersion des nanoparticules dans des matrices de polymères à haute température. La fonctionnalisation en surface, qui permet la formation d'une liaison chimique entre la surface des nanoparticules et les groupes fonctionnels désirés, peut actuellement être réalisée au moyen de diverses méthodes, allant de la chimie à base de solvant [7], à des procédés électrochimiques [26] ou à des techniques de déposition chimique en phase gazeuse souvent basées sur une technologie plasma [49, 79]. Celles-ci ont obtenu beaucoup de succès, en permettant la synthèse d'un revêtement de particules thermiquement stables (voir la figure 1), mais le coût de la mise en œuvre de ces techniques à base de plasma est assez élevé, notamment en raison de l'opération à basse pression et de l'importante consommation électrique de ces technologies.

Il semble donc impératif de trouver une solution qui permettra d'attaquer le problème d'agglomération des nanoparticules afin de simplifier leur intégration aux procédés actuels. Pour être pertinente, cette solution se devra de répondre à certains critères de base :

- Être abordable : autant en terme de matières premières, qu'en coûts d'opération. Par exemple, tout procédé qui implique la mise en solution des particules risque d'engendrer des frais subséquents liés à la séparation solide-liquide en fin de procédé. Les procédés opérant sous vide engendrent également des coûts supplémentaires. De plus, les procédés continus sont généralement plus rentables que les procédés *"batch"* d'un point de vue

économique.
- Être stable : le traitement de surface de la particule, peu importe sa nature, devra être capable de résister aux variations de température ainsi qu'au temps.
- Être transposable à grande échelle.

À la lumière de ces critères, une présélection peut déjà être faite. D'abord, par souci de stabilité thermique, la direction de la fonctionnalisation en surface semble à prioriser. Afin d'éviter la séparation solide-liquide qui est très coûteuse, une méthode en phase gazeuse semble un choix judicieux. Idéalement, l'opération se ferait à pression et température ambiante plutôt que sous vide. Les matières premières utilisées seraient peu coûteuses et faciles d'accès. Cette présélection mène à une famille de procédés qui s'appelle la déposition chimique en phase vapeur, soit en anglais le *"Chemical Vapour Deposition" ou CVD*. La revue de littérature présentée au chapitre 3 couvre les différentes variantes de cette technique et identifie une d'entre elles comme étant une solution potentielle.

1.3 Objectifs de recherche

Les objectifs de recherche poursuivis lors de la maîtrise sont énumérés ci-dessous :
- Effectuer une revue exhaustive de la littérature afin d'évaluer les différentes technologies de fonctionnalisation en surface.
- Identifier une technologie prometteuse pour le traitement des nanoparticules possiblement transposable à l'échelle industrielle à faible coût.
- Construire un montage à l'échelle laboratoire et prouver le concept identifié précédemment en posant des hypothèses simplificatrices valides.
- Évaluer le potentiel de la technologie testée à partir des résultats obtenus et proposer des avenues de recherche pour les travaux futurs.
- Communiquer à la communauté scientifique la démarche logique employée, les résultats de l'investigation, de même que les conclusions émises.

1.4 Plan de mémoire

Le mémoire a été conçu avec l'intention d'offrir une suite logique d'idées. Le lecteur sera rassuré par le fait que, bien que le mémoire incorpore du matériel rédigé en dehors du cadre du mémoire (articles et demande d'application de brevet), le mémoire porte en soit un fil conducteur solide. Les sous-sections suivantes décrivent le déroulement du mémoire en prenant un pas de recul sur ses parties constituantes.

L'introduction L'objectif de cette introduction était d'abord de définir la problématique et ensuite d'amener le lecteur à considérer des avenues potentielles en fonction des indices amenés. Une première piste de départ y est dévoilée. Pour ce faire, des critères de base sont énumérés pour la sélection d'une technologie, ce qui dirige le lecteur dans la direction du projet de recherche. Du même coup, ce premier aperçu des concepts de base permet de préparer le lecteur en vue de l'exhaustive revue de la littérature qui est offerte dans le chapitre 3. Puis, les objectifs de recherche viennent définir l'ensemble de règles avec lequel le projet de maîtrise a été composé. Finalement, ce présent plan de mémoire explique brièvement le déroulement du mémoire.

La revue de littérature Bien que l'essentiel de la littérature soit revu au chapitre 3, ce chapitre vient compléter l'information. En effet, l'article du chapitre 3 couvre principalement l'aspect procédé du CVD et du PICVD, mais couvre plus superficiellement l'aspect chimique au niveau moléculaire. Le chapitre 2 présente des mécanismes réactionnels d'applications connexes qui pourraient s'avérer pertinentes pour l'étude en cours. Entre autres, cette section fait des parallèles entre un exemple de photochimie du monoxyde de carbone, la catalyse Fischer-Tropsch ainsi que la formation de réseaux hautement réticulés par photopolymérisation. Le chapitre conclut sur les transferts de masse qui pourraient jouer un rôle important en raison de la présence d'un système réactionnel gaz-solide.

Les chapitres 3 et 4 Ce mémoire contient deux (2) articles, dont un est publié et l'autre soumis. La présence de ces articles dans ce mémoire semblait essentielle puisque ces derniers couvrent la quasi-intégralité de la matière, soit autant l'aspect théorique que pratique, et le font de manière concise et élégante. Ce mémoire n'est donc pas une simple juxtaposition d'articles, mais une suite naturelle logique. Alors que le premier article constitue la revue de littérature sur lequel se base tout le projet de recherche, le second article poursuit sur les conclusions et recommandations du premier article pour débuter son travail pratique, en plus de synthétiser l'ensemble des résultats obtenus lors de la maîtrise.

Le chapitre 5 Le chapitre 5 quant à lui, traite sur un point soulevé dans la conclusion du second article (chapitre 4), soit à savoir si la modification de surface fonctionnait également avec d'autres matériaux comme substrat, ou si le phénomène est propre au cuivre, ou encore aux métaux. Or, le chapitre 5, basé sur un travail à l'origine extra-curriculaire provenant du domaine alimentaire, explore la méthodologie développée sur des substrats en polymère, ce qui amène des éléments de réponse à l'interrogation soulevée par l'article du chapitre 4, en plus de soulever des doutes sur des hypothèses précédemment posées.

La discussion générale et la conclusion La discussion générale regroupe les notions et conclusions des chapitres 3 à 5 et cherche à formuler des hypothèses quant aux règles régissant la technologie développée. Elle fait également la lumière sur les concepts qui apparaissent encore flous. La conclusion traite ensuite de la problématique mentionnée à l'introduction et situe le projet de recherche par rapport à la problématique initiale, puis dans sa globalité. Le corps du mémoire se termine sur une ouverture, soit des idées d'applications industrielles qui découlent naturellement de l'essence même du projet de maîtrise.

L'annexe : Application de brevet Le travail effectué au cours de la maîtrise s'est avéré être suffisamment innovateur pour faire l'objet, d'abord d'un rapport d'invention puis, d'une demande de brevet. Alors que le brevet est davantage un document légal qu'un document scientifique, sa présence dans le mémoire amène néanmoins une profondeur qui semblait nécessaire. En effet, la demande de brevet vient renforcer la pertinence de la technologie développée en raison de son innovation. La demande contient également certains détails, tels que des données brutes, qui auraient alourdi le corps du texte, mais qui peuvent demeurer pertinents pour le lecteur curieux. À l'inverse, le lecteur contraint par le temps sera libre d'ignorer cette section sans pour autant perdre l'essence du mémoire.

CHAPITRE 2

REVUE DE LITTÉRATURE

Alors que l'article du chapitre suivant traite de manière exhaustive l'aspect procédé des technologies CVD et plus spécifiquement le PICVD, il aborde de façon détaillée l'aspect chimique au niveau moléculaire de ces dernières. Pourtant, les aspects à considérer sont nombreux dans un tel système réactionnel. Au niveau moléculaire, le PICVD est un procédé complexe qui fait intervenir des réactions de polymérisation de radicaux libres dans un système hétérogène gaz-solide photo-initié pour former une structure solide à partir d'un gaz. Dans le cas plus spécifique de ce projet, il est question d'utiliser de petites molécules simples pour produire un solide au réseau dense et hautement réticulé. Face à cette difficulté, il n'est pas possible de prédire avec précision les réactions qui auront lieu dans un réacteur de PICVD en présence de gaz de synthèse à la longueur d'onde testée. Cette revue de littérature a pour but de présenter les différents aspects chimiques incluant les mécanismes réactionnels proposés tirés de la littérature qui pourraient s'avérer utile dans le contexte de ce mémoire et ce, dans l'unique but de fournir des pistes à suivre pour la proposition d'un mécanisme réactionnel viable. Finalement, un court passage discute également des phénomènes de transferts de masse qui pourraient jouer un rôle important dans les réactions au niveau moléculaire.

2.1 Photochimie du gaz de synthèse

Bien que plusieurs articles se soient penchés sur la photochimie du monoxyde de carbone et de l'hydrogène indépendemment, il n'y a pas vraiment d'article qui se soit attardé à la photochimie du gaz de synthèse en tant que mélange gazeux. Cela pourrait d'abord s'expliquer par le fait que le gaz de synthèse est un concept relativement récent, qui gagne en intérêt grâce à l'essor des techniques de gaséification. Finalement, une autre explication plus pratique pourrait venir du fait que la théorie ne prédit pas de réactivité hors du commun pour ces deux gaz indépendemment lorsqu'ils sont soumis à des lampes de faible énergie.

L'hydrogène seul en photochimie n'a pas grand intérêt puisque les combinaisons de réactions possibles sont très limitées. La molécule de dihydrogène requiert une énergie de 4.478 eV et pourrait donc théoriquement être dissociée par une lampe à 254 nm. Par contre, l'hydrogène absorbe la lumière que dans un très court intervalle de longueur d'onde, soit entre 85 et 110 nm.

Dans le même ordre d'idées, toute formation de produits photochimiques à partir de

monoxyde de carbone à l'aide d'une lampe de longueur d'onde supérieure à 111 nm, s'il y a lieu, devrait forcément être due à la formation de radicaux [58], puisque l'énergie requise pour dissocier la molécule est 11.09 eV [1]. Cet état électroniquement excité ($a^3\pi$), permet néanmoins de produire des réactions qui autrement n'auraient pas lieu. Par exemple, le CO est connu pour produire du C_3O_2 en présence de lampes de krypton (605 nm) et de xénon (185 nm), qui ne possèdent pas l'énergie suffisante. Les produits de réaction du CO $a^4\pi$ sont le CO_2 et le C_3O_2 [58]. Le mécanisme proposé est le suivant[99] :

$$CO \xrightarrow{hv} CO* \tag{2.1}$$

$$CO* + CO \rightarrow CO_2 + C \tag{2.2}$$

$$C + CO \rightarrow C_2O \tag{2.3}$$

$$C_2O + CO \rightarrow C_3O_2 \tag{2.4}$$

Il est intéressant de noter que les deux dernières étapes du mécanismes rappellent le comportement d'une polymérisation cationique [30] :

$$M^+ + M \rightarrow MM^+ \tag{2.5}$$

$$MM^+ + nM \rightarrow M[M_n]M^+ \tag{2.6}$$

Ce qui impliquerait que la croissance du produit pourrait se résumer de la manière suivante le cas échéant :

$$C_nO_{n-1} + CO \rightarrow C_{n+1}O_n \tag{2.7}$$

Il est tout à fait possible que certaines étapes des mécanismes présentés précédemment soient transposables à la photochimie du gaz de synthèse. Par exemple, vu la présence d'hydrogène, il serait tentant de penser que l'oxygène avec le doublet d'électrons libres pourrait réagir avec l'hydrogène pour former de l'eau qui est un produit très stable. La réaction pourrait ensuite poursuivre son cours tel que précédemment.

$$CO \xrightarrow{hv} CO* \tag{2.8}$$

$$CO* + H_2 \rightarrow C^+ + H_2O \tag{2.9}$$

$$C + CO \rightarrow C_2O \tag{2.10}$$

$$C_2O + CO \rightarrow C_3O_2 \tag{2.11}$$

1. Ce qui correspond à environ 111 nm à 100% d'absorption

Un autre effet potentiel de la présence d'hydrogène pourrait être que les carbones de la chaîne auraient tendance à se saturer. Ceci laisse penser qu'une réaction photochimique impliquant le gaz de synthèse aurait le potentiel de produire de grandes molécules de la forme $C_xH_yO_z$ ainsi que de l'eau (H_2O). Ceci pourrait favoriser la production de groupements -OH, qui sont généralement désirés lors du traitement hydrophile d'une surface.

2.2 Analogies avec la synthèse Fischer-Tropsch

Puisqu'il est question de générer des composés à chaînes longues à partir du gaz de synthèse, il est difficile d'ignorer la comparaison avec la synthèse Fischer-Tropsch. La synthèse Fischer-Tropsch a été développée par les Allemands lors de la première guerre mondiale qui, n'ayant pas facilement accès aux carburants fossiles, cherchaient à produire du diesel à partir du gaz de synthèse. Encore aujourd'hui, cette réaction suscite beaucoup d'intérêt pour la recherche, car elle constitue une alternative aux carburants fossiles à considérer.

La réaction Fischer-Tropsch peut être exprimée de la manière générale suivante :

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{2.12}$$

Cette réaction est exothermique et requiert un catalyseur afin d'abaisser l'énergie d'activation nécessaire à son déroulement. Voici le mécanisme réactionnel généralement accepté, où S représente un point d'attachement sur la surface [84] :

$$CO + 2S \rightarrow C \cdot S + O \cdot S \tag{2.13}$$

$$C \cdot S + H_2 \rightarrow CH_2 \cdot S \tag{2.14}$$

$$2(C \cdot S) + 3H_2 \rightarrow 2(CH_3 \cdot S) \tag{2.15}$$

$$R - CH_2 \cdot S + CH_2 \cdot S \rightarrow R - CH_2 - CH_2 \cdot S + S \tag{2.16}$$

$$R - CH_2 - CH_2 \cdot S \rightarrow R - CH = CH_2 + S \tag{2.17}$$

$$2(R - CH_2 - CH_2 \cdot S) + H_2 \rightarrow 2(R - CH2 - CH_3) + 2S \tag{2.18}$$

Il est pertinent de mentionner que Tavasoli *et al.* ont expérimenté la réaction Fischer-Tropsch en présence d'une lampe UV. Le groupe a rapporté que la présence de lumière avait plus que quadruplé l'activité apparente du catalyseur par rapport aux tests de contrôle sans lumière. Le groupe a également rapporté une différence avec les tests de contrôle au niveau de la sélectivité des produits. En effet, la présence de lumière semblait déplacer la sélectivité en direction des produits à longueurs de chaîne entre C_5 et C_{11}, au détriment des C_{12+} [80]. Il

est important de mentionner que ces expériences ont été conduites en présence de catalyseurs solides dans les deux cas (avec et sans lumière), bien que le groupe utilise le terme "photo-catalyse". Les catalyseurs solides utilisés était tous des catalyseurs à base de cobalt dont le matériau support variait. Les matériaux supports testés étaient l'alumine (Al_2O_3), la silice (SiO_2), ainsi que le dioxyde de titane (TiO_2). Les auteurs ont déterminé que les catalyseurs supportés par le dioxyde de titane ressentaient la plus nette amélioration causée par la lumière en terme d'activité.

Ce dernier point mène naturellement à se questionner quant à savoir si la présence de métaux dans un réacteur de PICVD pourrait agir en tant que catalyseur. Dans le cadre du projet de recherche actuel, il est question d'utiliser des substrats de cuivre pour effectuer la preuve de concept du PICVD appliqué au traitement de surface. Bien que le cuivre en tant que tel ne soit pas un catalyseur courant pour le Fischer-Tropsch, des études ont testé l'effet du cuivre en tant que promoteur dans un catalyseur Fischer-Tropsch. Les chercheurs sont venus à la conclusion que non seulement l'ajout du cuivre améliore le rendement général, mais aurait aussi tendance à favoriser la production d'alcènes versus celle d'alcanes [101].

Ces derniers constats peuvent laisser présager qu'une réaction Fischer-Tropsch, à la fois photo-assistée et en présence de cuivre, aurait le potentiel de donner des résultats hors du commun. Également, d'un point de vue thermodynamique, l'existence de la réaction Fischer-Tropsch est encourageante quant à la faisabilité de la réaction photo-initiée du gaz de synthèse.

2.3 Réactions d'un procédé PICVD

Baxamusa *et al.* ont proposé un mécanisme réactionnel pour le PICVD, se basant sur la théorie de réaction initiée par radicaux [8]. La première étape indique que la lumière décompose le monomère organique en radicaux. Les auteurs spécifient que cette étape peut être achevée autant en phase gazeuse qu'une fois le gaz adsorbé à la surface. Dans les deux cas, les radicaux présents à la surface réagissent avec les monomères absorbés afin de croître en produits polymérisés. Dans le cas présent, l'étude ne mentionne aucune réaction en phase gazeuse autre que la formation de radicaux et laisse donc sous-entendre que la réaction PICVD aurait besoin de la surface pour catalyser la réaction.

Il est aussi connu que les radicaux peuvent être la force motrice de cyclisation [38], ce qui laisse indiquer que la présence de cycles dans des produits issus du PICVD ne serait pas surprenante.

Finalement, Andrzejewska explique dans son excellent article "Photopolymerization kinetics of multifunctional monomers" que les dépôts produits par photoinitiation offrent un

très haut taux de réticulation. Toujours en raisons de la présence des radicaux libres, les propagations se poursuivent en suivant trois (3) chemins différents, soit :

1. L'addition d'un autre monomère ;
2. L'addition d'une molécule complexe voisine (réticulation inter-moléculaire) ;
3. Une réaction de cyclisation (réticulation intra-moléculaire).

Tout cela mène à la formation d'un réseau complexe hautement interrelié. La figure 2.1 illustre les propos décrits plus haut.

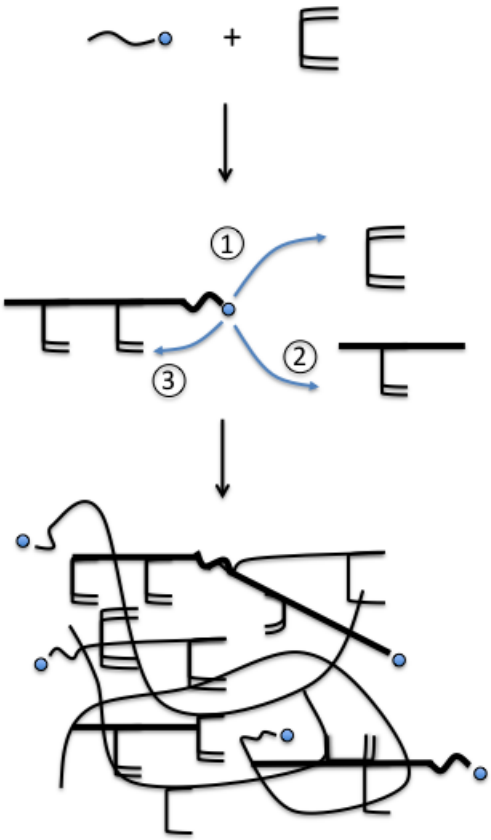

Figure 2.1 La formation de réseaux (réticulation), telle que décrite par Andrzejewska, en tant que combinaison de trois (3) mécanismes de propragation advenant simultanément. De la première à la seconde étape, un groupement radical réagit avec le monomère de plusieurs manières pour former quelques produits intermédiaires de base. De la seconde à la dernière étape, un amalgame de réaction vient créer un réseau aléatoire hautement réticulé.

2.4 Phénomènes de transfert de masse

Il est difficile de parler de systèmes réactionnels gaz-solide sans mentionner les effets des phénomènes de transfert de masse. Par définition, le procédé CVD est une réaction de surface. La vitesse de réaction n'est donc pas uniquement fonction de la cinétique intrinsèque, mais bien de l'ensemble des étapes menant à la réaction, incluant les transferts de masse internes et externes. En d'autres mots, avant de réagir à la surface, les molécules doivent d'abord se rendre au site actif. Bien que ce concept puisse sembler simple théoriquement, cette étape s'avère être souvent celle limitante dans le cas de réactions surfaciques. Ceci peut également engendrer plusieurs problèmes pratiques dans le cas du CVD[32, 59]. Par exemple, si la fonctionnalisation de surface de nanoparticules est pour être conduite dans un lit fluidisé, la théorie affirme qu'il faut augmenter la vitesse superficielle pour contrer les effets de transfert de masse externe [28]. Or, ceci risque fort de causer l'entraînement des particules par l'effluent gazeux. Également, dépendamment de leur géométrie et porosité, les nanoparticules pourraient également être soumises à des phénomènes de transfert de masse interne. Les paramètres principaux influençant la qualité du transfert de masse dans un réacteur selon Choy [16] sont énumérés ci-dessous :

1. La température moyenne ainsi que les profils de températures dans le réacteur ;
2. La pression dans le réacteur ;
3. Débit de gaz ;
4. Les caractéristiques du gaz (tel que la densité, viscosité, etc.) ;
5. La géométrie du réacteur.

Ce dernier aspect est très critique, car il peut être la cause de patrons d'écoulement qui peuvent jouer sur plusieurs aspects, dont l'uniformité d'un dépôt photochimique.

CHAPITRE 3

ARTICLE 1 : PHOTO-INITIATED CHEMICAL VAPOR DEPOSITION AS A SCALABLE PARTICLE FUNCTIONALIZATION TECHNOLOGY (A PRACTICAL REVIEW)

Par C.A. Dorval Dion et J.R. Tavares.
Publié dans le journal Powder Technology d'Elsevier en mai 2013

Ce premier article se trouve à couvrir une grande partie de la revue de littérature. Publié en mai 2013, l'article se révèle être une revue pratique des différentes technologies pouvant être utilisées pour le traitement de surface des nanoparticules. Plus précisément, il focalise sur les variantes des technologies CVD dans le but de trouver un candidat potentiel adéquat qui répond convenablement aux critères proposés. Pour ce faire, l'article dresse un portrait complet de ces technologies pour ensuite les comparer entre elles. Les critères de sélection pour faciliter la prise de décision mettent l'emphase sur les aspects coûts et potentiel de mise à l'échelle. L'article en conclut que le PICVD s'avère être un candidat sous-estimé, mais néanmoins très attrayant pour la problématique en jeu.

Abstract

Chemical vapour deposition (CVD), and its variants, is a more viable technology than the addition of surface active agents to modify nanoparticle surfaces. While thermally-activated CVD simply works by initiating the monomers using heat, some other techniques are more powerful and versatile. Indeed, higher energy CVD methods open up possibilities to a wider range of monomers. Unfortunately, different terminology and classifications due to parallel work have led to confusion. This paper presents and explains the different techniques as well as their equivalent terminologies to clarify the big picture. While the demand for functionalized nanoparticles grows rapidly, current functionalization methods are still too expensive for most applications. This paper is intended to be a practical review of the gas phase methods available in order to identify a potential candidate for large scale functionalization of nanoparticles. This study identifies Photo-Initiated CVD (PICVD) as an ideal solution for scalable particle functionalization technology.

3.1 Introduction

Due to their high surface/volume ratio, nanoparticles exhibit properties that differ greatly from their bulk ones, which makes them popular in almost every field of natural science [27]; emerging applications can be found in optics [56], biomedicine [60, 63], heat transfer [25], catalysis [35], architecture [93], energy [92], environment [20] and computer science [91]. For the same reason, nanoparticles also possess extremely high surface energy. Thus, the particles strive towards a lower-energy thermodynamic state through agglomeration, leading to larger effective particle sizes. In terms of nano range applications, this phenomenon is usually undesirable since the properties attributable to individual nanoparticles are lost or diminished. Traditionally, agglomeration phenomena have been overcome effectively through the use of surface-active compounds such as surfactants. Despite the apparent efficiency of this method, it has been found to be inapplicable for a wide range of application due to the poor thermal stability of surfactants. In fact, many surfactants desorb from nanoparticle surfaces at temperature as low as 350K (70 °C) [25], leading to particle agglomeration. This makes surfactants unusable for several applications where tolerance to high thermal cycling is required (e.g.: nanofluids, thermoset polymer nanocomposites, etc.).

Where thermal stability can be an issue, the best way to counter the agglomeration is through covalent functionalization of the particles with organic or inorganic groups in order to change their surface charge [46, 79]. Nanoparticle functionalization can be achieved following two different methods, both based on *in situ* polymerization. The first is classical wet chemistry method (also known as sol-gel), which may upon first inspection appear quite simple, but is limited to small quantities due to the use of multi-step reactions requiring specialized knowledge and, most importantly, the high cost of downstream separation. Moreover, potentially toxic solvents and/or reactants are typically involved, further limiting scalability. The second method is through gas phase techniques, usually called either vapour deposition polymerization (VDP) or chemical vapour deposition (CVD). Vapour deposition methods allow for a higher purity surface coating without the use of organometallic compounds [16]. Currently, CVD seems to be the most promising technology for the functionalization of nanoparticles on an industrially-relevant scale. Multiple variants of this method exist, such as thermally-activated, plasma-enhanced, photo-initiated and oxidative, to name just a few. It is generally accepted that gas phase polymerization is cleaner and by definition more adequate for applications that require uniform coating thickness at nanoscale level [16]. Even if several papers have already been published on the scientific relevance of these techniques, there is still no gas phase method that is economically viable at a large scale for the coating of nanoparticles. Despite this, the industrial demand for functionalized

nanoparticles continues to grow, extending its field to new markets, such as nanocomposites and biomedical applications [88, 98]. The limiting step between the research and the development appears to be cost-effectiveness. Despite the interesting results obtained in laboratory, the value gained is still not always economically balanced and leveraged to a useful scale. New solutions have to be proposed. This paper is not intended to be an extensive review from a fundamental point of view since this work has already been done many times by different groups [16, 30, 78]. However, by reading those reviews, one can be easily be distracted by the terminology which lacks standardization and classification. This can be due to the fact that those different research groups tend not to share the same vision or point of view of gas-phase deposition mechanisms. This paper will attempt to unify these diverging terminologies and concepts into more objective point of view or at least a bigger picture of vapour deposition methods. Some equivalencies will be proposed in order to position the reader. Hopefully, this will allow for greater innovation in the field of particle functionalization by levelling the playing field. An overview of three initiated CVD ((i)CVD) techniques will be presented as well as a comparison of those techniques and their potential as nanoparticle coating system at large scale. Knowledge gaps will be identified and resources will be presented in order to potentially fill these gaps.

3.2 Chemical Vapor Deposition (CVD)

3.2.1 Overview

Chemical vapour deposition is a chemical process that consists in reacting volatile precursors in the gas phase to form a solid compound that deposits on surfaces. This technique is widely used in the semiconductor industry to produce dense thin films.

In terms of mechanism, chemical vapour deposition can occur in two different ways. The gaseous species can either polymerize in the gas phase and then adsorb to the surface, or adsorb first on the surface and then polymerize *in situ* using the substrate as a foundation. The first case has been demonstrated to create poorer coating adhesion compared to the second one [16]. A third possible mechanism could be the combination of the previous two; There is no apparent reason why the polymerization process could not begin in the gas phase and continue to growth once adsorbed onto the surface.

CVD processes are often achieved under low-pressure conditions for two reasons. First, the monomers used as reactants are often liquid under normal conditions. The amount of monomer gas flow is then directly dependant of the evaporation rate achieved through pressure decrease. Though thermal energy may be supplied to further increase the evaporation rate, temperature will be limited by the types of monomer used, as will be discussed further.

Secondly, it is often desired that the reaction occur onto the substrate rather than in the gas phase for reasons mentioned previously (the lower the pressure, the lower the probability of gaseous species colliding and reacting with each other in the gas phase). This means that if using gaseous monomers at normal conditions coupled with a tolerance to reaction in the gas phase, it could be possible to operate at atmospheric pressure. This would have a tremendous effect on the feasibility as well as the operational cost of an industrial-scale system.

As mentioned previously, reactions occurring in the gas phase can be used for functionalization, but adherence to the substrate may be weakened. However, some polymers and resins that can be formed exhibit very strong adhesive properties, depending on the monomers used [33].

3.3 Description of (i)CVD techniques

The concept of initiated CVD was introduced by Gleason *et al.* to describe the general mechanism of polymerization that needs the formation of radicals to occur [78]. This radical formation can be achieved by adding energy to the system in the form of heat (thermal), electricity (plasma), light (photo) or a combination thereof. The current section describes more specific details for each technique.

3.3.1 Thermally-activated CVD (TACVD)

Thermally-activated CVD is considered as the conventional CVD process [16] and consists of initiating the monomers by means of heat. The heat source can come from one or different sources such as infrared radiation, inductive heating, or electrical resistivity. In most cases, a resistive hot wire is used to induce the reaction as shown in figure 3.1. This specific technique is sometimes called hot wire CVD (HWCVD) [95]. Usually, the gas phase is heated in order to create reactive species and promote the kinetics. Alternatively, the substrate temperature may also be increased independently to promoted surface reactions. However, substrate temperature is critical, since there are two phenomena competing against each other: increasing the temperature will increase the polymerization kinetics, but also promote desorption. TACVD has been used extensively in industry for surface coatings though not for nanoparticle functionalization. Examples of application are thin films for semi-conductors, protective coatings for ceramics and fiber coatings. Major drawbacks of this technique are the limited range of monomers that can be used, since some monomers will degrade when exposed to heat, and its poor thermal transfer efficiency [16]. Moreover, while the heating methods do not necessarily require a large capital investment, high temperature operation tends to increase operating cost namely as a result of poor efficiency, especially when heating gases.

The major advantage of TACVD is its simplicity along with the fact that it can be operated at normal pressure. However, it might be necessary to increase the temperature tremendously to make the environment reactive, which can play important role on the materials used and, thus, the capital cost of the equipment.

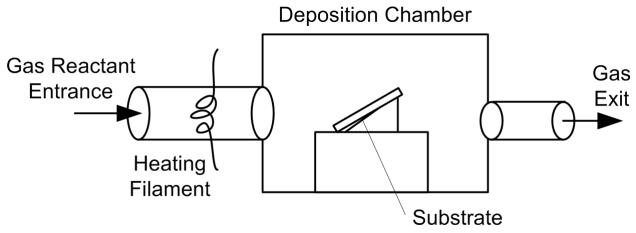

Figure 3.1 Schematic of a HWCVD setup

3.3.2 Plasma-enhanced CVD (PECVD)

Plasma-enhanced CVD (PECVD) uses non-equilibrium or "cold" plasma to initiate the polymerization reaction, through a combination of light emission, typically ultraviolet (UV), radical formation and ionization. Figure 3.2 illustrates the principle of a PECVD setup. Only a small percentage of electrons are excited to a level sufficient to drive forward chemical reactions. A great deal of energy is wasted on lower energy electron, which makes the technique poor in terms of efficiency. Nonetheless, due to its high energy transfer to the reactive species, PECVD is the most powerful CVD technique. PECVD has been proven to functionalize nanoparticles very efficiently [68, 79], but tends to make reaction happen too quickly, resulting in unstructured coatings with low crosslinking. A variant of this technique consists in pulsing the plasma in order to allow the functional coating to restructure itself between pulses. Pulsed-PECVD tends to increase the density of the coating though the trade-off is a decrease in the deposition rate. Choy, Gleason and Yasuda have contributed greatly to diffuse the knowledge acquired through extensive reviews [16, 78] and books [94, 95, 96], and PECVD can now be described as a well-known technique. However, this technique has tremendous practical limitations; since it typically operates under vacuum, one can expect the scale-up to be costly. Moreover, the operating cost versus the equipment size usually increases exponentially for plasma systems. While it is possible to operate "cold" plasma discharges at atmospheric or near-atmospheric pressures [18, 50, 57], discharge volumes are severely limited and thus not appropriate for large-scale particle functionalization. Recently, PECVD has also been used for the growth of carbon nanotube [54].

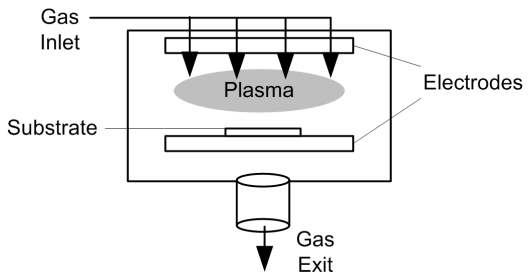

Figure 3.2 Schematic of a PECVD setup

3.3.3 Photo-initiated CVD (PICVD)

Photo-initiated CVD uses the light to initiate the polymerization reaction through the formation of radicals. Unfortunately, there is still very little information available on PICVD, beyond that of the groups presented in the previous section. This can be explained by the fact that CVD techniques have been mainly developed to respond to semiconductor industry demands, which is more focused on high deposition rates. PICVD is very close to PECVD since they share common basics; a UV lamp is simply an arc or a glow discharge plasma confined in a bulb that is transparent to UV, such as quartz. Indeed, the energy supplied by the UV lamp is inferior to that supplied by plasma since ionization and radical formation through electron bombardment are not available to stimulate the reaction. The main advantages of PICVD are clear; it is more efficient in terms of energy consumption (lamps have been optimized), the reactor can operate under normal conditions and, most importantly, the polymers formed are more structured than with unpulsed PECVD. However, because the initiation caused by the plasma is not introduced, only its UV content, the reactive mixture has to be photosensitive. Therefore, the reactive mixture has to be photosensitive. This reduces the range of monomers that can be used, but can lead to a better control on the reaction. As previously discussed, PECVD can be sometimes too energetic: the polymerization process moves too fast to allow the molecules on the substrate to restructure, which is not usually the case with PICVD. By this very fact, PICVD will tend to produce more crosslinked structures. For applications that do not require the polymerization of heavy monomers at high deposition rate, UV radiation should be adequate [6]. A technical barrier of this technology is the need for transparent-to-light reactor walls. Moreover, as mentioned in two patents on PICVD, the polymerized compounds tend to stick to the window of the reactor and block further radiation, but solutions to counter this effect exist [64, 89]. Figure 3.3 illustrates the concept of a PICVD system.

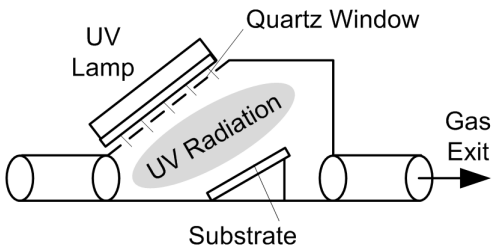

Figure 3.3 Schematic of a PICVD setup

3.4 Diverging terminologies

Surprisingly, many reviews have been published by different research groups, but without referring to each other [14, 16, 78, 95]. Another interesting fact is that these groups, even if they are working in same field, do not share the same terminology. This review intends to reduce the gap between the different fields that have been working in parallel until now by combining the different terminologies into a more consistent system.

3.4.1 Gleason et al.

Gleason's research group has published many relevant article on the subject of CVD, focusing namely on particle encapsulation and electrically-conductive thin coatings. [1, 45, 46, 78, 82, 83]. Gleason *et al.* have developed their own terminology. Their nomenclature philosophy is based on adding a lower case acronym, describing the nature of the technique, contained between parentheses as a prefix to CVD. More precisely, (i)CVD and (o)CVD stand for initiated and oxidative CVD, respectively. PECVD is an exception to this rule and is considered as a category by itself. Furthermore, they use the term VDP to describe a CVD that does not require additional heating nor any other form of intiation, while usually other reseach groups consider CVD and VDP as synonyms. (pi)CVD, which stands for photo-initiated CVD, is included in (i)CVD, but (i)CVD refers to thermally-activated CVD most of the time, more specifically using heating filament that is refered elsewhere by hot wire chemical vapour deposition (HWCVD) [16, 95]. Based on the inclusion of (pi)CVD, PECVD could also have been categorized as a type of (i)CVD, but it is not, for unknown reasons. It is important to not confuse the term initiated from (i)CVD with photo-initiator, which will be detailed later in this paper.

The interesting aspect of this terminology is the classification based on mechanism type. On the other hand, the actual system shows some inconsistencies between categories and techniques. Moreover, this terminology is not often used outside of their research group [1, 78]. Therefore, the concept of classification of techniques based mechanisms will be kept

but consolidated with other used terminologies. Table 3.1 summarizes Gleason's terminology.

Table 3.1 Terminology used by Gleason *et al.*

CVD			
VDP	PECVD	(i)CVD (pi)CVD	(o)CVD

3.4.2 Choy

In 2003, Choy has published an extensive review on the field, stemming from work on process-structure-properties relationships, especially with regards to nanomaterials processing [16]. From Choy's point of view, the conventional CVD method is thermally-activated CVD (TACVD). Therefore, other techniques are considered as variants of TACVD, altogether under the general CVD label. Choy's terminology uses PECVD and PACVD to describe plasma-enhanced and photo-assisted CVD, respectively [16]. A confusion occurs since PACVD can refer to plasma-assisted CVD in some reports [11, 95]. Choy also presents other, more exotic variants such as metalorganic (MOCVD) and flame-assisted (FACVD). The first can be related to (o)CVD (from Gleason's group), while flame-assisted could be considered as a Gleason (i)CVD technique. From Choy's point of view, CVD without initiation does not exist. Choy's nomenclature is widely used in the field. As such, it serves as the principal resource for the terminology developed in this work. Table 3.2 summarizes Choy's terminology.

Table 3.2 Terminology used by Choy

CVD				
CVD	TACVD	PECVD	PACVD	MOCVD

3.4.3 Yasuda

Even if Yasuda's field of interest is mainly focused on plasma polymerization methods, his knowledge is very useful for the purpose of this article. Contrary to Choy, PACVD stands for plasma-assisted rather than photo-assisted in Yasuda's work [97]. Yasuda [94, 95] introduced the term luminous CVD (LCVD) to describe every technique that actively uses plasma in the reaction. Counter-intuitively, LCVD does not include photo-induced methods; if it does, it is implicit that every potential source of light is coming from a plasma source. Also, Yasuda makes a distinction between plasma polymerization, plasma CVD, plasma-assisted CVD and

plasma-enhanced CVD which are the same technique with the exception that the substrate is heated in the case of PECVD and PACVD. The use of a heated filament (HWCVD) is referred to the traditional CVD method. More recently, Yasuda has added the magneto luminous polymerization (MLP) to his vocabulary which he describes as the "process of dielectric breakdown of gas molecules under the influence of a magnetic field" [96]. Finally, for Yasuda, CVD without additional acronyms means a thermally-assisted CVD in which the heat is coming from the substrate surface. Table 3.3 summarizes Yasuda's terminology.

Table 3.3 Terminology used by Yasuda

TACVD	**LCVD**			
HWCVD	PP	PACVD	PECVD	MLCVD

3.4.4 Other terminologies

Many other authors use an amalgam of all terminologies mentioned earlier or different ones without being systematic or consistent in their usage. Also, other authors, such as Wertheimer *et al.* [67, 87] and Scherzer [72, 73, 75] use the term photopolymerization to describe the use of vacuum-ultraviolet (VUV) radiation to achieve the functionalization of a surface. Those articles do not mention the term CVD. This is surprising because the term photopolymerization by itself describes the polymerization reaction by the use of light, but does not necessarily implies a coating process. From a more technical point of view, the major disadvantage of the use of VUV is its absorption in the air. Since very few materials are transparent to those wavelengths, its usage requires exotic and sensitive materials such as MgF_2 or LiF_2 (the only materials transparent to UV light below 200 nm) as reactor window. Therefore, this technique introduces high costs and would be difficult to integrate in common industrial context.

Another term, FACVD, that sometimes stands for flame-assisted CVD and sometimes for flame aerosol CVD, consist to spray the monomer into a flame. This technique can be seen as a hybrid between PECVD and TACVD. Pratsinis *et al.* [81] has used this technique to achieve the surface functionalization of nanoparticles.

3.4.5 This paper

In an attempt to unify the terminology, some aspects of each terminological system have been retained, with consistency between terms as main objective. Table 3.4 describes this new terminology system.

Table 3.4 Terminology used in this paper

CVD			
(i)CVD			*(or)CVD*
TACVD	PECVD	PICVD	MOCVD

The basis of this new terminology is that all chemical reactions require energy to move forward, even if this energy source is as weak as the heat available at room temperature. Therefore, the term VDP has been discarded. The technique of using light as initiator was originally named photo-assisted CVD on its first patent [2], then took the name of photo-CVD on the two following patents on the subject [64, 89]. To avoid any confusion between the possible meanings of PACVD (photo- or plasma-assisted), this acronym has been discarded. PhotoCVD would have been an appropriate choice, but since it is not based on acronyms, it has been rejected for the sake of uniformity. Since the use of light to achieve the chemical vapour deposition can be called both photo-initiated and photo-induced, the PICVD acronym seems a fair choice. This term is very close to the (pi)CVD acronym proposed by Gleason *et al.*, but without the use of parentheses since it is not consistent with other specific techniques. Since PECVD is the most common term for plasma enhanced polymerization, it is retained. As mentioned earlier Wertheimer *et al.* used photopolymerization to describe PICVD. For the purpose of this paper, it is preferred to consider photopolymerization as part of photochemistry, which is a related but distinctive field. It is true however, that photopolymerization and PICVD share a basic common knowledge. This aspect will be discussed later in this paper. The lower capital acronym between parentheses has been kept for general CVD categories. (or)CVD stands for oxidative or reductive CVD and has replaced (o)CVD in order to include metalorganic CVD (MOCVD) that occurs under reductive conditions. With this new system, as shown in table 3.4, CVD, (i)CVD and (or)CVD do not correspond to specific techniques but to categories of techniques. In doing so, a great deal of confusion is thus avoided. Table 3.5 shows the equivalence between terms used by each group.

Table 3.5 Summary: Equivalence between terms

Yasuda	**Choy**	**Gleason *et al.***	**This paper**
-	-	VDP	CVD
HWCVD	CVD	(i)CVD	TACVD
-	PACVD	(pi)CVD	PICVD
LCVD	PECVD	PECVD	PECVD

From this point, the proposed terminological system will be used. The following sections

will primarily on (i)CVD-based methods. For further information on (o)CVD, please refer to Gleason *et al.* [1, 78, 83].

3.5 Comparison of techniques

In order to compare and propose different potential solutions, it is pertinent to define some key guidelines related to the context. To be satisfactory, the selected method for nanoparticle functionalization should meet the following criteria:

- Low processing cost
- Low capital cost
- Operate at low temperature
- Operate at normal pressure

These first 4 criteria are unified under the term *scalability*.

- Produce dense uniform high quality coatings
- Allows for acceptable deposition rate
- Able to process a range of monomers wide enough to offer an interesting selection of functional properties that can be transferred to the coated material

These last 3 criteria are unified under the term *versatility*.

Table 3.6 Comparison of different (i)CVD techniques by means of subjective grades.(A=excellent, B=good, C=mediocre).*

Criteria	**TA**	**PE**	**PI**	**References**
Low operating cost	B	C	A	[1, 16, 23, 59, 83]
Low capital cost	A	C	A	[1, 10, 16, 23, 45, 78]
Low temperature	C	A	A	[1, 9, 10, 16, 45, 46, 59, 78, 83, 94, 95, 100]
Atmospheric pressure	B	C	A	[1, 10, 16, 45, 46, 59, 78, 94, 95, 100]
Scalability	*B+*	*B-*	*A*	-
Coating quality	A	B	A	[1, 10, 16, 45, 46, 79, 83, 95]
Deposition rate	B	A	B	[1, 10, 16, 59, 79, 83, 94]
Monomer selection	C	A	B	[16, 78, 79, 83, 94]
Versatility	*B+*	*A-*	*B+*	-
Average	**B+**	**B**	**A-**	-

**To evaluate the resulting grades for the major categories ("Scability", "Versatility"), numerical values to each letter grade have been assigned (A=3, B=2, C=1) and calculated an average of the criteria grades for each category. The final average corresponds to the average of all grades.*

Table 3.6 shows qualitatively and subjectively how each technique respects the previously presented criteria while table 3.7 summarizes the advantages and disadvantages of each (i)CVD technique. What can be retained of this study are the following statements:

Table 3.7 Comparison of different (i)CVD techniques by means of technical aspects

Techniques	Advantages	Disadvantages	References
TACVD	Simplicity Well documented	Low energy Necessity to operate under vacuum	[16, 45, 46]
PECVD	High deposition rates Well documented Wide range of monomer usable	Necessity to operate under vacuum High energy consumption Low crosslinking	[16, 79, 94, 95]
PICVD	High crosslinking High control on deposition Can operate at room temperature and atmosperic pressure	Slower reaction rate than PECVD Gas mixture has to be photosensitive Little work has been done	[9, 10, 31, 78, 100]

- TACVD can be good under certain circumstances but remains the weakest form of (i)CVD methods.
- PECVD is the most versatile (i)CVD method, but its implementation is not realistic due to its pressure constraints and high scaling costs.
- PICVD seems to be the only (i)CVD technique that has the potential to respect the criteria.

It can be concluded from this comparison that PICVD seems to be a promising avenue of research for the functionalization of nanoparticles at large scale.

3.6 Knowledge gap and avenues of research

While a wide range of publications has been published on the coating of nanoparticles, it is unexpected to see that so little work has been conducted to investigate the use of PICVD as a potential solution. The authors truly believe that more work has to be done in that direction since, as shown earlier, PICVD seems to be the best compromise for the functionalization of surfaces. It seems obvious that there is a knowledge gap to be filled. This paper aims to provide key resources needed to get started.

3.6.1 Avenues of research

Zhang *et al.*, from the University of Minnesota, have demonstrated the feasibility of using PICVD to deposit coatings on nanoparticles [9, 10, 31, 100]. Surprisingly, it is the only research group that have reported work on the subject that the authors are aware of. More

precisely, the papers reported the growth of organic coating on sodium chloride and silicon dioxide nanoparticles.

3.6.2 Current knowledge gap

As mentioned before, there is still little knowledge about PICVD. However, the PICVD technique inherits a solid theoretical background from related fields. To close the gap of information available for PICVD, the actual review will draw its resources from PECVD and photopolymerization knowledge.

From PECVD PECVD and PICVD have a lot in common. If the deposition rates may differ, the mechanisms would, at least in part, be similar. For example, the functional coating will be subject to the same problems. Therefore, work conducted by Wertheimer *et al.* on coating aging (hydrophobic recovery) [86] as well as stability of film by spectrometry [68] is quite useful. The critical issues of PECVD demonstrated by Bunshah [11] coupled with the mass transport considerations proposed by Goyal *et al.* [32] and the critical review from Liston *et al.*[52] can be used to assist in reactor design. Moreover, the kinetic and thermodynamic considerations presented by Choy [16] are valid for all CVD techniques. Finally, the optimal characterization techniques developed by Holländer *et al.* [34], Scherzer *et al.* [72, 73] and Khudyakov *et al.* [41] can be re-used as well. Those techniques includes photo differential scanning calorimetry (photo-DCS) (Khudyakov), real-time fourier transform infrared spectroscopy (Scherzer), fluorescence dye fluram and several chemical analysis (Holländer).

From Photopolymerization and Photochemistry A great deal of PICVD knowledge comes from photopolymerization and photochemistry. In fact, the idea of coating surfaces by this method is not young. The book "Photopolymerization of coating surfaces" is a great example that came out in 1982 [65]. Extensive work on the subject has been done around the 1940s [48, 66]. Recently, the photochemistry trend has resurrected vividly, often using acrylates or thiolene acrylates as monomers [15, 17, 19, 21, 47, 67, 74, 75, 76, 102]. The field has garnered renewed interest in the two last decades, mainly due to its application to many fields such as coatings and adhesives. More specifically, this trend is going in the direction of self-initiating monomers [37, 69]. While photopolymerization usually refers to UV emission, it has also been accomplished with visible light [13, 14, 29], and even near-infrared light [71], though these cases required the use of photo-initiators (detailed further on). Some reviews have also been published out on the subject [70, 87]. Pargon *et al.* have compared plasma against VUV [61] on chemical modification of surface and reported similar results for both technologies.

In order to be able to initiate the polymerization process, a bond has to adsorb enough energy to break itself and create a free-radical site through light-initiated means. Ideally, the absorption spectrum of the compound would match perfectly the lamp emission spectrum. Unfortunately, this is rarely, if not ever, the case. Often, the actual emission frequency does not exceed the energy required to break the bond. Sometimes, the desired reactant is almost transparent to UV. In those cases, photosensitizers or photo-initiators can be added to the gas phase.

Photopolymerization in the presence of diverse photo-initiators has been studied extensively. When the retained monomer is transparent to the emission spectrum of the light, the photo-initiators becomes a prerequisite. In other cases, the photo-initiators accelerated the reaction kinetics. Ideally, the photopolymerization process would not need the assistance of a photo-initiator since the use of photo-initiator contaminates the final product [66, 70]. Moreover, commonly used photo-initiators are rather expensive or toxic, if not both [70]. More recently, the trend is in the direction of photo-initiator-free reaction solutions [21, 74]. The terms sensitizer and photo-initiator have been interchanged for a long time now [66]. As a main distinction, while photo-initiators are consumed in the reaction and thus generate by-products, photosensitizers are not. This means that photosensitizers are simply sensitive to the light used, without being a reactant. This subtlety makes a difference in terms of contamination of the polymer generated. Photosensitizers are further distinguished from photo-initiators by the mechanism by which they act; indeed, photosensitizers are compounds that absorb the light radiation used and convert it either to a wavelength that can be absorbed by the reactant or to thermal energy to stimulate the reaction.

Another important consideration is the polymerization mechanism itself. It can be either step or chain growth. Chain growth is the most common and consists of similar monomers adding one by one, forming a chain. Co-polymerization can also be considered as chain growth (one monomer is alternated with another). Step growth, on the other hand, is more chaotic and can include several reactions forming intermediate products that will form the polymer that is obtained at the end. Alf *et al.* seem to imply that every CVD process is based on chain growth, but this position is not clearly stated nor demonstrated [1].

The field of photopolymerization is growing quickly in terms of its knowledge and comprehension. For example, Andrzejewska [4] and Friedrich [30] wrote impressive reviews exclusively on the photopolymerization kinetics. Boies *et al.*, from the same research group as Zhang, have recently published a kinetic study of the PICVD applied to the coating of silver nanoparticles in the gas phase [9].

Among the monomers tested, many studies have been focused on photopolymerization of acrylates. The choice of this monomer is based on the fact that it offers high deposition

rates without requiring photoinitiators [88]. Most of the work on photopolymerization has been done on liquids, not on gases. Therefore, there is still a lot of work to be done. To be optimal, PICVD should use reactants that either strongly absorb in the lamp emission range or include photosensitizers or, if contamination can be tolerated in the targeted application, photo-initiators.

3.7 Conclusion

In summary, gas-phase polymerization is a more viable technology than the addition of surfactant agent for the dispersion of nanoparticles in fluids. Among these gas-phase reactions, called CVD, many versions exist. While the traditional method (TACVD) simply works by initiating the monomers using heat, some other techniques are more versatile. Higher energy CVD methods (such as PECVD and PICVD) allow for a wider range of monomers. Unfortunately, different terminology and classifications due to parallel work have led to confusion. The present work attempted to present and explain the different techniques and nomenclatures available to clarify the big picture. Indeed, the most versatile subcategory of CVD is the PECVD due to its high-energy state (ionization, electron bombardment) combined with its rich UV content radiation. In terms of surface functionalization, the effectiveness of PECVD is proven. However, some technical constraints are limiting its adoption by the industry, especially in the case of lower value-added products. While some technologies might be scaled up quite easily, it is not the case of PECVD. As demonstrated in this paper, PICVD using UV lamps seems to be a good compromise with regards to particle functionalization on a large scale. Basically, the use of UV lamps consists of decoupling the plasma source from its reactor, therefore allowing the reactor to operate under more gentle conditions. While the range of reactants that can be used is slightly reduced, the cost effectiveness rises tremendously. Further work in the field of PICVD is thus warranted, and this work can build on an existing foundation in the fields of photopolymerization and, more generally, photochemistry.

Acknowledgement

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CHAPITRE 4

ARTICLE 2: PHOTO-INITIATED CHEMICAL VAPOR DEPOSITION OF THIN FILMS USING SYNGAS FOR THE FUNCTIONALIZATION OF SURFACES AT ROOM TEMPERATURE AND NEAR-ATMOSPHERIC PRESSURE

Par C.A. Dorval Dion, W. Raphael, E. Tong et J.R. Tavares.
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Ce second article, soumis en octobre 2013, est une suite logique de l'article précédent puisqu'il reprend les conclusions de celui-ci comme point de départ. Après avoir revu les technologies CVD de manière exhaustive, l'article précédent était venu à la conclusion que le PICVD était la technique la mieux adaptée à la problématique. Cet article se trouve à être l'investigation expérimentale du PICVD pour la fonctionnalisation en surface, soit la preuve de concept réclamée en 3.7. Si l'article précédent s'attaquait principalement à l'aspect procédé du projet, celui-ci couvre majoritairement l'aspect expérimental de celui-ci. Cette investigation utilise le gaz de synthèse comme précurseur et vise l'opération aux conditions ambiantes pour traiter des substrats plats macroscopiques en cuivre.

Abstract

Hydrophilic and hydrophobic thin films have been deposited onto flat metallic substrates through photo-initiated chemical vapour deposition (PICVD), using syngas a as precursor, and affordable UVC germicidal lamps as a source of light. This study is the first experimental investigation of what has been previously concluded to be the potential solution to the current widespread nanoparticle functionalization problem. This study addresses the current limiting factor, namely the cost issue, by using simple gas precursors, by using an affordable initiation source and operating under normal condition. This approach differs from the current approaches which use expensive solvents as precursors, energy consuming-sources of initiation (e.g. high temperature, plasma and VUV) and operate under high vacuum and/or high temperatures. While the current paradigm is to target the peak absorption of a molecule, the present study indicates that long chain polymerized products can be formed from off-peak wavelength. It has been found that photo-initiated deposition occurs and that a wide range of surface, from 5° to 118° properties can be obtained by manipulating the experimental

conditions. A multilinear empirical model has been derived, and it predicts fairly well the contact angles obtained as a function of the different experimental parameters.

4.1 Introduction

Due to their high surface/volume ratio, nanoparticles exhibits interesting properties that promise a brillant future for many applications such as adsorption, absorption and heat transfer [27]. However, even if nanoparticles have mobilized the attention of scientists, they are still not adopted industrially as much as they could be. Among the reasons behind this is the fact that particle agglomeration issues remain an important practical limitation. Typical approaches to counter this problem are through the use of surfactant. While the use of surfactants possesses numerous advantages (cost, simplicity, efficiency), these compounds are simply adsorbed to the surface and not chemically attached to it. Weak adsorption bonds imply that surfactants can detach from the surface when heated above temperatures as low as 70°C [25]. While this solution has allowed the use of nanoparticles for a limited range of room-temperature applications, a new solution is still required for high-temperature applications such as nanofluids, nanocomposite preparation, etc. This new solution would benefit from being based on a strong covalent bond between the functional compound and the particle, instead of simply counting on weak physical adsorption. Also, nanoparticle manufacturing already being a costly process, to make sure of its adoption, a functionalization technology must not only be reliable but also affordable and scalable.

Surface functionalization through chemical vapour deposition shows great promises as a potential solution. The advantages of gas phase methods are considerable: these processes are considered as cleaner and simpler as they do not involve liquids. Dry processes simplify also the downstream separation. It is also recognized as a method that is highly capable of producing dense and pure materials on complex shapes. Another advantage of the gas phase method is that it can be operated as a continuous process instead of a batch process. This can have a tremendous effect on the profitability of an industrial scale system [42]. Different variations of the chemical vapour deposition technique exists, such as thermally activated-, plasma enhanced- and photo initiated- chemical vapour deposition (respectively TACVD, PECVD and PICVD), and each of them has strengths and weaknesses. Our research group previously concluded that PICVD was showing potential as a large scale gas phase treatment for the surface functionalization of nanoparticles at normal conditions and low cost [24]. Since large scale nanoparticle synthesis is usually accomplished in the gas phase, it would make sense if the following functionalization process was also a gas phase process. We thus present an experimental proof of concept of PICVD for surface functionalization on flat substrates.

4.2 Theoretical Framework

4.2.1 Chemical Vapor Deposition Theory

The fundamental aspects of CVD will not be reviewed in depth here, since this has been done thoroughly already [16, 78, 94]. Also, the different forms of CVD applicable to the current situation have already been reviewed and compared in our previous paper [24].

Baxamusa *et al.* have previously reported that PICVD was able to produce thin films (100 nm) near room temperature under unspecified "mild" vacuum conditions. They also indicated that the technique would be suitable for coating particles having diameters as small as 5 microns [8]. However, nothing indicates that it could not be done with finer particles. They reported that PICVD was a more "gentle" method than PECVD, which explains their choice to go with PICVD for the coating of sensitive sensors such as protein detectors. Due to a slower deposition rate as well as the presence of UV light, the curing is achieved by default during the whole operation. This explains why PICVD is able to produce such crosslinked structures. Baxamusa *et al.* reported to be even able to "tune" the crosslink density, which means that the mechanical properties of the film could be tailored.

PICVD typically refers to systems using vacuum ultraviolet (VUV), which is low wavelength/high energy UV light. It is important to mention that the cost is very high in that situation, namely for two reasons: first, the system has to operate under high vacuum because the radiation is intensely absorded by gases and secondly, the reactor window, in order to let these wavelengths pass through must be made of highly expensive exotic materials such as MgF_2, LiF and CaF_2.

Most of the work done with PICVD has targeted acrylates precursors, mainly because of their high photosensitivity. Those compounds are usually liquid at ambiant conditions, and thus operation under low pressure or heating to vaporize small amounts become a prerequisite, using gas precursors is a way to curtail this requirement. To be able to polymerize from gases, it is usually required to have both a polymerization backbone (a source of carbon) and a source of hydrogen to saturate the carbons atom to the needed degree. Carbon sources in the gas domain tend to be very small for obvious reasons, such as CH_4, C_2H_6, C_3H_8. Zhang et al. [100] used short-chain hydrocarbons, mainly alkanes. For the present study, the objective being to introduce functionality to the surface, there is a need of oxygen in the reactor. Knowing that CO and H_2 is a common gas combination resulting from gasification processes, this gas mixture seemed pertinent. Here are other reasons making CO and H_2 an interesting choice:

– The simple fact of having two gases instead of one opens up the possibility to produce a wide range of different products. Different kinetics and stoichiometry should result

into different compounds.

- CO and H_2 being a mix of gases often present together in industry (e.g. product of the gaseification process), it could be very convenient to use those products as process inlet.
- Fischer-Tropsch synthesis (FTS) is a similar reaction that consists to reconstruct long chain of carbons from syngas. First, it proves that the reaction is feasible thermodynamically, and second, knowledge gaps can be filled by borrowing information from those researches. Even Tavasoli *et al.* has already enhanced FTS with UV light [80].
- Finally, the CO bonds are known to produce radicals under UV light [58]. The gas mixture could thus react without the need for a photoinitiator or photosensitizer.

The bond dissociation energies of CO and H_2 are respectively 11.09 eV and 4.478 eV. Since the main wavelength emitted by the UVC lamp is 254 nm, which corresponds to 4.88 eV, even at complete absorption only the hydrogen would be dissociated. However, it is worth mentioning that the radiation can nevertheless open constituent π bonds, thus electronically exciting the CO molecule and therefore contributing to the kinetic enhancement of the reaction. Further, it is known that carbonyl species tend to decompose into radicals under UV light below 267 nm [8], which is close to the CO configuration. It is worth mentioning that standard 254 nm germicidal lamps also have an emission peak around 185 nm.

Scott *et al.* has previously shown that 254 nm germicidal lamps were effective in eliminating gaseous contaminants such as carbon monoxide and VOCs [77]. They discussed the importance of the ratio 185 nm versus 254 nm necessary to eliminate low concentration of CO in gas stream. Commercially available low-pressure mercury-vapor lamps emit about 86% of their light at 254 nm, the rest being mainly attributed to 185 nm. Although 185 nm may provide more energy, the quartz glass used in commercially available lamps are more opaque to 185 nm than 254 nm [90].

4.3 Methodology

4.3.1 Materials

Copper substrates were multipurpose copper (Alloy 110) sheets supplied by McMaster-Carr trimmed to 1.5 cm by 1 cm coupons. Argon (HP+), CO (Pur T-44) and H_2 (UHP T-30) were supplied by Air Liquide. The reactor was made of two custom built 45 cm long quartz tubes with standard 24/40 taper joints and supplied by Technical Glass Products. All experiments were conducted with a dual-bulb 254 nm UVC germicidal lamps of 96 cm in length supplied by Cole-Parmer which offers 5.5×10^{-4} W/cm^2 of light intensity. The light intensity was measured with an International Light Technologies ILT 1700 Research

Radiometer. The joints were sealed using standard clips and high vacuum laboratory grease (Dow Corning). The massflow controller were part of the 5850E Brooks series and calibrated for each gas. The sandpaper used for substrate polishing was 2500 grit supplied by McMaster-Carr.

4.3.2 Experiment

The experimental setup is shown in figure 4.1. The gas mixture is fed to custom made quartz tube, where the gas is to be irradiated by the UV lamp. The flat copper substrates to be treated were placed into the reactor onto a custom made holder having a capacity of 5 coupons. The H_2 and CO gas ratio was controlled by adjusting each gas individual massflow controller. The experiment duration was fixed to 1 hour. Before any experiments, the copper coupons were thouroughly polished using deionized water and sandpaper. An 18 cm long and 1.5 cm wide holder was used to insert the freshly polished substrates into the reactor. A total of 5 copper substrates, spaced 3.5 cm apart, could be inserted at the same time. The coupon were inclined with an angle of 45°.

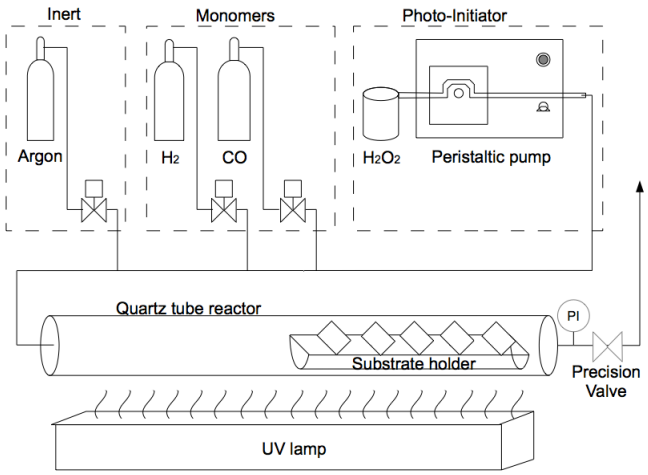

Figure 4.1 Experimental setup

Copper was used because it has been known to work with PECVD [79], so a comparative standard exists. The temperature inside the reactor was monitored with an IR temperature sensor with an emissivity factor of 0.75. The operating pressure in the reactor was controlled via a 3-way valve placed at the output. One of the two outputs of the valve was linked to a vacuum line, while the second was leading to a fume hood. This configuration allowed a pressure range from +/- 10 kPa gauge. The quartz tubes were previously cleaned by submerging them in a solution of NaOH 5.0M for 24 hours. They were then rinsed with distilled water and air dried. Before any experiments, argon was used to purge the reactor

for 3 minutes. The reactor was then covered with standard commercial aluminium foil. When the experiments were completed, each copper substrates were carefully taken out of the reactor and placed in a plastic container filled with argon.

Experimental conditions The effects of the following parameters have been tested:

- H_2/CO molar ratio (varying from 1/16 to 4),
- Total flow rates (varying from 260 to 1000 mL/min),
- Position in the reactor from 1 to 8 (8 arbitrary positions uniformly spaced apart from each other in the second tube, spacing being 1/8 of the tube length)
- Pressure in the reactor (varying from -10 to +10 kPa gauge),
- Delay before analysis (in number of days after deposition of the coating),
- Order of experiment (to identify and control for cumulative effects over time, for example lamp degradation)
- Light intensity (increased by partially or totally enclosing the lamp together with the reactor using aluminium paper). Note: this also has the effect of increasing the reactor temperature as well by about 30°C.

A secondary objective was to test the capacity of H_2O_2 to act as a photoinitiator because of its absorption peak that falls directly onto the 254 nm wavelength, which corresponds exactly to the lamp emission. For these experiments, 0 to 10 mL/h was injected in to the reactor by the mean of a peristaltic pump. H_2O_2 used was 50% concentrated and was supplied by Fischer Scientific.

4.3.3 Modeling methodology

Design of experiment and multivariate analysis As the present study represents an investigation of a wholly new process, experimental design was applied to determine the effect of a large variety of parameters and trends were extracted through a multivariate analysis. The first step of this method consists in normalizing the data, as well as the response (here being the contact angle). Once normalized, it becomes fairly easy to derive emperical models, usually starting by trying multilinear regression, then increasing the complexity if needed. Having three levels (-, 0, +) per parameters helps to determine either if the relationship between the parameter and the response is linear or better approximated by a polynomial. Also, sometimes some parameters by themselves do not have effect, but do have an effect when combined with another factor.

The modeling was achieved following a multilinear approach using the Microsoft Excel solver to find the parameter coefficients. The approach consisted of trying to model with parameters individually, and then trying combined effects.

4.3.4 Characterization

The treated copper substrates were analyzed by goniometry with distilled water, Fourier transform infrared spectroscopy (FTIR) (Spectrum 65 from Perkin Elmer) and field emission scanning electron microscopy (FESEM) (JEOL JSM7600F). The exiting gases were captured through an acetone (A18P-4, Fischer Scientific) bubbling column for analysis by GCMS. The acetone was Chromasolv for HPLC grade ($\geq$ 99.9 % purity) and supplied by Sigma Aldrich. The GCMS system was a Agilent 7890A matched with a HP-88 column with the quadrupole Agilent 5975 detector operated at a helium flow rate of 1.5 mL/min. The light intensity was monitored by a Ocean Optics USB2000 spectrophotometer. The goniometry measurements were achieved by placing 4 μL of distilled water on every copper samples. The sessile drop water contact angle being relatively stable on the minute time frame, one measurement per location was taken immediately for 5 locations per sample. Figure 4.2 represents a typical sample and shows the 5 locations where measurement were taken.

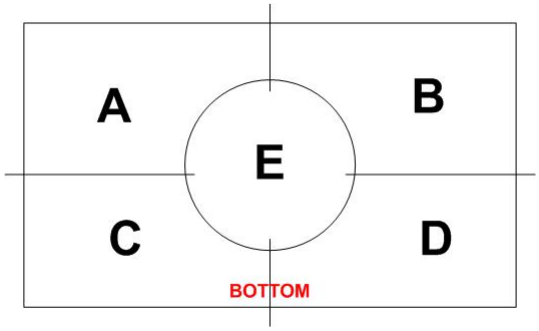

Figure 4.2 Goniometry measurements

4.4 Results

The results showed that, indeed, PICVD was able to functionalize the surface of copper substrate using syngas as precursor. Figure 4.3 demonstrates the before and after effect of such coating.

4.4.1 Modeling results

The modeling of the PICVD process has been made in two steps. The first one being an overall mapping of the conditions and process parameters, while the second one was a refinement of the first one. This approach helped to eliminate the non-significant parameters and, at the same time, gave indication about what direction to go in order to push the boundaries, and therefore expand the validity of the model. As a result, the model's coefficient

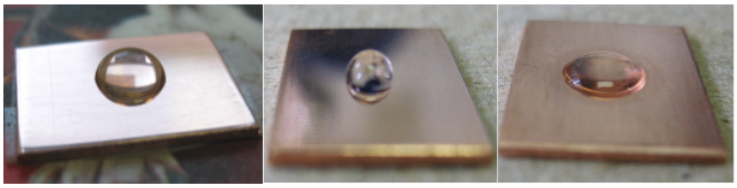

Figure 4.3 Water contact angle of samples, respectively untreated, hydrophobic and hydrophilic

readjusted a little, and some parameters, like the delay before analysis, could be excluded simply by adapting the procedure.

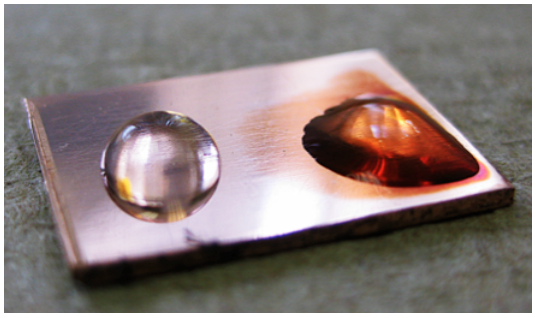

Figure 4.4 Water contact angle of samples, respectively untreated, hydrophobic and hydrophilic

Due to the non-uniformity of the coating, some data had to be removed from the data set. Previously, figure 4.2 shown the sampling procedure for the goniometry analysis. Looking at some visible coatings that were obtained (figure 4.4), it can be noticed that surface coverage is non-uniform, therefore measuring the contact angle of very thin or non-existant coating instead of the evident "sweet spot". Since the objective is to model the contact angle of the coating, and not the surface in average, the data must be filtered accordingly. The measurement procedure can be easily readjusted when the coating is visible, but data filtering can be more complicated when the coating is invisible, which was the case most of the time. First, the measurement corresponding to the copper's native water contact angle were dismissed right away. Futhermore, figure 4.5 shows that the coating usually has a fade with multiple shade of colors, and indeed the contact angles varied accordingly.

This lack of uniformity can be due to the flow dynamics of the system. As a first proof of concept, the emphasis were put on the most extreme value, assuming that uniformity is an issue that can be addressed subsequently. In other words, this study focused on what was achievable rather than on an average uniformity-biased efficiency. The following multilinear empirical model has been derived from the data:

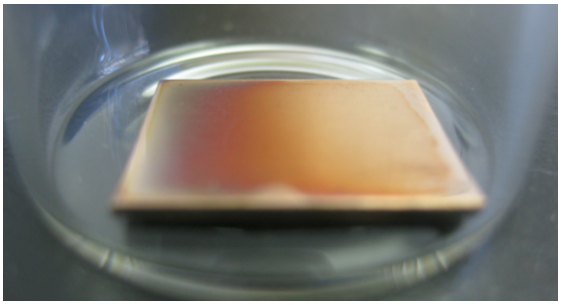

Figure 4.5 The red spot seem to cure into a blue color

$$Angle(^\circ) = 1.75 \cdot P + 3.58 \cdot pos - 0,83 \cdot P \cdot r + 0.15 \cdot P \cdot pos + 39 \tag{4.1}$$

Where P is the relative pressure in the reactor in kPa; "Pos" is the position in the reactor (an integer dimensionless parameter between 1 and 8) and r is the H_2/CO molar ratio (also dimensionless). The normalized model had a coefficient of determination (R^2) of 0.91, the model presented in equation 4.1 is an adapted version using real life conditions and has a coefficient of determination of 0.89. This difference can be explained by the fact that normalization helps attenuating noise caused by scale and unit mismatch. For the current study, multilinear modeling seemed to fit the data well. The analysis of residues have shown that noise is dispersed randomly and evenly accross the spectrum, which means that pushing the model's complexity might have only resulted in modeling noise. This experiment have allowed for reaching contact angles from 30° to 100°, without the addition of photoinitiator or sensitizers, simply by mapping the experimental conditions.

Following the previous statement, it is tempting to conclude that the hydrophilic/hydrophobic "switch" could, in fact, be attributed to the regime where the reaction had taken place. Reaction occuring in the gas phase might encourage hydrophobic behavior of the coating, while coating growth onto the surface would tend to be hydrophilic.

Another aspect that is to be looked into is if the reaction is adsorption limited or not, which is commonly observed for initiated-CVD (iCVD) polymers. A good way to verify this is by increasing temperature to see if the reaction rates improves. If not, it can be considered as adsorption limited. The effect of pressure mixed with a tight optimization of temperature profile in the reactor could tremendously improve the system's performance. While this study was a proof of concept of the feasibility of using PICVD, further investigation are obviously required in this regard.

It is still to early to determine if the reaction is a step growth or a chain growth. However the following hypothesis can be formulated, when there is the presence of an initiator as well

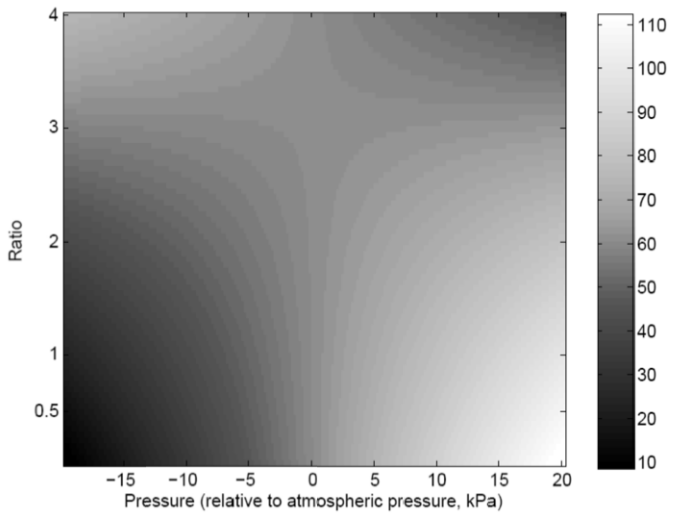

Figure 4.6 Empirical mapping of water contact angle as a function of CO/H_2 ratio and relative pressure

as the presence of light, it is probable that the reaction is a chain polymerization one. UV light has been demonstrated to form free radical, which are the very core of a chain growth polymerization [39].

From a photopolymerization stand of view, it is usually accepted that those reactions requires a photo-initiator [70]. The present experiment have shown however that syngas was able to self-initiate in the presence of UV light, probably because of the formation of radicals. Experiments with H_2O_2 did promote the reaction by pushing the boundaries of contact angles measurements. The addition of hydrogen peroxide as a photoinitiator increased the range of water contact angles to 5° to 118°, and the angles seemed to be highly correlated with its flow rate. It is worth noticing that the total pressure is the dominant factor with this configuration. Generally, pressures slightly below 1 atm translates into hydrophilic surfaces, while pressures slightly higher than 1 atm resulted into hydrophobic surfaces. This could be interpreted as a transition between a kinetic controlled reaction to a mass transfer controlled reaction. As described in a previous paper [24], a chemical vapor deposition reaction can occur either in the gas phase or on the surface of the substrates. If the kinetic rate is high, the reaction will occur in the gas phase, and the resulting compound will tend to deposit on any solid surfaces present in their pathway. To get in this regime, either high temperatures or high pressures must be reached. The second way of proceeding is through adsorption on the surface, promoted at lower pressures.

4.4.2 Characterization

GCMS Samples of the outlet gas were analyzed by GCMS. The deposited compound has been identified as a close match to the bis(2-ethylhexyl)-phtalate. A sample GCMS spectrum is shown in figure . This characterization of species in the gas phase provides information on 2 fronts. First, it gives insight into the reactions taking place in the reactor - the molecule formed are rich in double-bonds and aromatics, and can have a relatively long chain length. Second, it provides information with respect to secondary products formed, which is key for eventual scale-up.

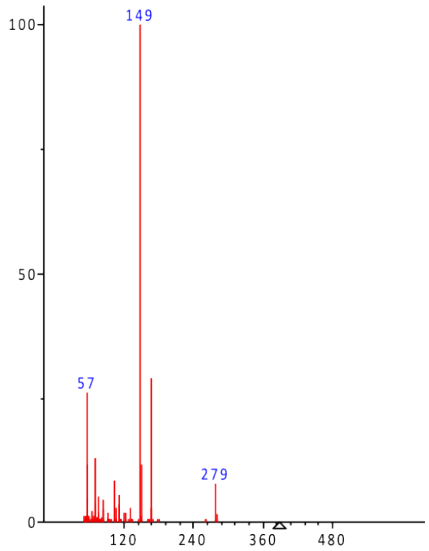

Figure 4.7 Mass spectrometry with peak retention time of 17.4 min

FTIR The FT-IR was operated in attenuated total reflectance mode (ATR) in order to characterize the species present on the surface. With the available database, the closest match was phenol formaldehyde resin. Interestingly, the coating shared some properties with this family of resins, like its resistance to dissolution in solvents and its susceptibility to strong bases. That is the reason why NaOH was used for tube cleaning steps. While the match was not perfect, this indicates at least that the coated molecule is highly crosslinked and has a high concentration of C=C bonds. A sample FTIR spectrum is shown in figure 4.8. In this figure, the first peak on the left can be associated with O-H bonds without doubt. The 1585 cm^{-}1 one can be associated with C=O in the case of carboxylate conformation. The 1414 cm^{-1} peak indicates the presence of C=C bonds in the case of aromatics. 1263 cm^{-1} and 1104 cm^{-1} peaks both suggest C-O bond but from potentially different structures. It

would be tempting to guess that the peak corresponds to the bond between copper and the polymer, which would also explain the strenght of the peak. The presence of a carboxylate group is interestingly similar to the Bis(ethylhexyl)phtalate where a carbon chain links to two different oxygen atoms.

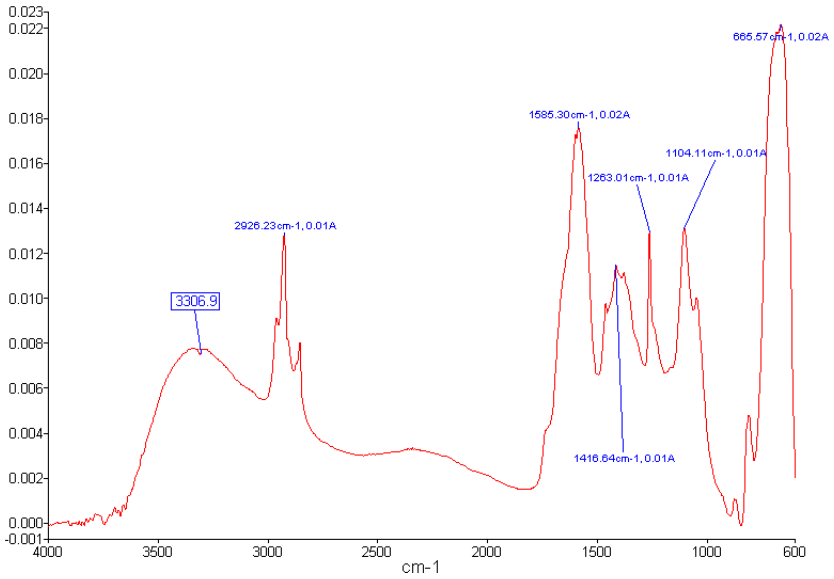

Figure 4.8 FTIR absorption spectrum (H_2/CO=2, P=0 kPa)

FESEM FESEM images helped to determine the general morphology of the sample's surface. The coated samples consisted of tiny circular islands of approximately 40 nm of diameter. The fact that those islands appear as being white means that they are made of an electrically non-conductive material, which is consistent with the hypothesis of a polymer or a resin. It is expected that increased treatment time would lead to merging of these polymer islands on the surface. Figure 4.9 shows the scan of a coated surface.

Visual inspection It is worth mentioning that the presence of red spots appeared in some cases and not in others. However, after investigation of the different parameters, this phenomenon was not significantly correlated to any of them. Those red spots tended to be superhydrophilic ($\leq 10°$), more so than their transparent conterparts for the same experimental conditions. Over a hundred experiments have been conducted in order to find a pattern leading to such results. Despite the efforts, these red spots seemed to appear randomly and therefore, could not be statistically associated with any combination of known parameters. For the time being, figure 4.10 illustrates fairly well the appearance of these spots. Some

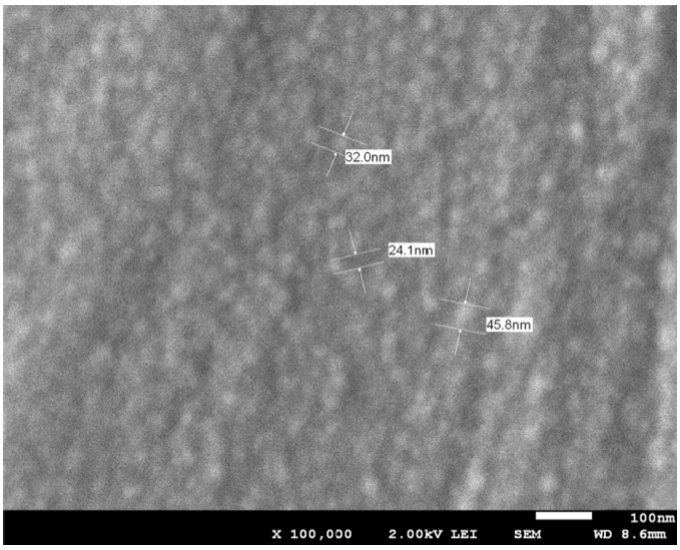

Figure 4.9 Scanning Electron Microscopy of Coated Sample

variants appeared as shown in figure 4.5, where the red eventually evolved into a blueish color.

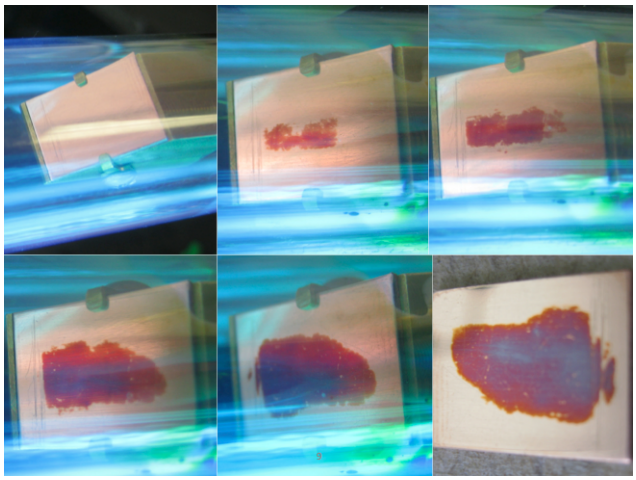

Figure 4.10 A growth progression of red spots over an hour

Hydrophobic recovery Another concern that remains is the hydrophobic recovery, which consists of a hydrophilic surface that loses its property over time. During the experiment, it has been noticed that hydrophilic surfaces lose a great deal of their hydrophilicity over a short period of time (within 24 hours). For that reason, the water contact angles were measured in the hour following the deposition. According to Anderson and Ashurst hydrophobic recovery would be due to the migration of bulk material to the surface [3]. On the other hand,

Figure 4.11 The spots exhibits very small contact angles

Wertheimer *et al.* affirm that hydrophobic recovery was due to hydrogen molecules which rotate inward caused by the attraction of hydrogen bond [85]. It has been observed that hydrophobic surfaces remained stable over time since no significant changes in measurement a week after was noticed.

4.5 Conclusion

The current process was able to produce both hydrophilic and hydrophobic coatings on copper surface. The feasability of using PICVD with simple gases such as H_2 and CO (syngas) for the functionalization of surfaces has been studied. In the tested conditions, it has been determined that syngas can be photopolymerized by UVC germicidal lamp to deposit functional groups onto copper. The deposited compound has been identified as being very similar to phenol formaldehyde resin. The gas sample analysis identified the bis(2-ethylhexyl)-phtalate as being produced in the reactor.

The current results seems to indicate that the potential of applications could be more numerous than originally planned. Also, the possibility to trigger a very specific water contact angle from a wide range between highly hydrophilic to highly hydrophobic opens up the possibilities even more. In other words, the wettability of a material can be tailored.

With a highly scalable method, it has been possible to produce high quality and dense coating in deposition temperature as low as room temperature and atmospheric or near-atmospheric pressures. While the effect of different process parameters remains to be optimized, the current results suggest that PICVD shows promises as a scalable and affordable technique for the functionalization of nanoparticles, as well as for any other surfaces. However, it is certain that more work has to be done to confirm the validity of PICVD for large scale applications. This technology being completely novel, experimental parameters, reactor design, as well as the scaling up are aspects that deserves to be investigated further.

A great start for future work would be to control more locally the temperature. In the case of this experiment, the substrate holder did not possess any cooling system and the whole reactor was assumed as being isothermal. It might have affected the deposition rate substantially. Precursor preheating might also help initiate the reaction. Since high deposition rate nor thickness is the objective for the purpose of surface functionalization, an enhancement of kinetic would rather translate into a decreased processing time. Other

materials should be investigated as substrate in order to determine if the surface selection has an effect or not on the produced coating.

Also, the evaluation of the required concentration functional group on a surface that is necessary to have a positive effect onto the surface is another study that needs to be conducted. Finally, while the coating seemed very hard to remove from the surface, this study did not investigated the mechanical properties of the coating.

Acknowledgements

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CHAPITRE 5

TRAITEMENT DE SURFACE SUR DES SUBSTRATS POLYMÉRIQUES POUR LE DOMAINE ALIMENTAIRE

5.1 Mise en contexte

Le chapitre précédent soulève dans sa conclusion une interrogation quant à savoir si le même processus pouvait être applicable à d'autres substrats que le cuivre. Alors qu'à l'origine il n'était pas prévu d'inclure l'effet du substrat dans la preuve de concept du PICVD pour le traitement de surface, l'opportunité s'est présentée sous la forme d'un contrat provenant de l'externe. Le projet en question consistait à tester la méthode PICVD pour la modification en surface de substrats de polymères, plus précisément le polypropylène (PP) et le polytéréphtalate d'éthylène (PET) pour une application dans le domaine alimentaire. Il est important de souligner que l'objectif dans le cas présent était de viser l'hydrophobicité uniquement. La motivation du client était de rendre l'intérieur des contenants en polymère hydrophobe de manière à faciliter l'écoulement du contenu en créant une répulsion entre la phase aqueuse et le polymère.

5.2 Méthodologie

Pour se faire, la méthode, le montage ainsi que le modèle empirique développés lors de l'investigation expérimentale du chapitre 4 ont été utilisés pour atteindre l'objectif en question. La présente investigation s'est basée sur certaines hypothèses :

1. À moins que les dépôts soient uniformes et couvrent entièrement la surface, l'effet du substrat sera ressenti sur l'angle de contact mesuré. Il n'est donc pas attendu que le modèle obtenu pour le cuivre prédise les angles obtenus pour les substrats de polymères.
2. Il est néanmoins attendu que les tendances décrites par le modèle soient conservées. En d'autres mots, les conditions expérimentales menant à des surfaces hydrophobes sur le cuivre devraient également produire des surfaces hydrophobes sur les substrats de polymères. D'un point de vue pratique, une pression légèrement positive favorise le dépôt de revêtements hydrophobes, alors qu'une pression légèrement négative favorise un revêtement hydrophile.
3. Tel que formulé dans le chapitre précédent, il est attendu qu'en augmentant le temps de traitement, l'effet du revêtement sur l'angle de contact soit davantage ressenti. Cette

affirmation s'explique premièrement par le fait que le revêtement avec le montage actuel ne produit pas de revêtement uniforme et que deuxièmement, le taux de déposition est assumé comme étant linéaire pour des techniques de déposition CVD [1][22, 88].

4. Toujours en reprenant les connaissances acquises lors de l'investigation faite au chapitre 4, l'ajout de peroxyde d'hydrogène dans le système devrait permettre d'étendre la plage de valeurs accessibles. Ceci revient à dire qu'un temps de déposition plus long maximise les chances que la goutte posée sur le substrat ne ressente pas la propriété de surface du substrat.

En premier lieu, les conditions optimales pour obtenir un dépôt hydrophobe sur le cuivre ont été appliquées aux échantillons de polymères. Ces conditions correspondent aux coordonnées de la zone plus foncée sur la figure 4.6, soit un ratio H_2/CO de 1/8 et une pression légèrement inférieure à -10 kPa.

À des fins de comparaisons, les angles de contact respectifs pour le PP et le PET ont été mesurés avant et après traitement afin d'être présentés au client en terme d'amélioration d'hydrophobicité [2] plutôt qu'en terme d'angles de contact bruts. Le temps alloué pour ce projet étant limité, l'approche utilisée consistait à aller droit au but. Pour ce faire, deux séries d'expériences ont été poursuivies, soit avec et sans peroxyde d'hydrogène. Ces deux expériences ont été soumises aux conditions définies comme étant optimales pour le traitement hydrophobe sur le cuivre. Le temps de traitement a été conservé à une (1) heure par expérience.

5.3 Résultats

5.3.1 Sans peroxyde d'hydrogène

Les résultats obtenus pour les essais sans peroxyde d'hydrogène sont plutôt fidèles à ce que l'on pouvait s'attendre. En effet, les angles de contact, qui étaient en moyenne 69° et 75° pour le PP et le PET respectivement avant traitement, ont augmenté de manière significative grâce au traitement. En moyenne, les échantillons de polymère possédaient 84° (PP) et 99° (PET), mais il est encore plus intéressant de noter que des angles de 111° (PP) et 115° (PET) ont été obtenus. La figure 5.1 présente les résultats en terme d'amélioration de l'angle de contact, tel que présenté au client. Ces derniers résultats démontrent qu'en effet, des angles relativement élevés peuvent être obtenus grâce à la méthode en utilisant le gaz de synthèse comme précurseur.

1. Ceci semble faux lors des premiers nanomètres déposés, probablement parce que l'initiation n'est pas un phénomène linéaire. Néanmoins, dépassé ce point, la règle linéaire s'avère très exacte.

2. On définit par "amélioration" la différence d'angle de contact moyen avant et après traitement pour un polymère donné.

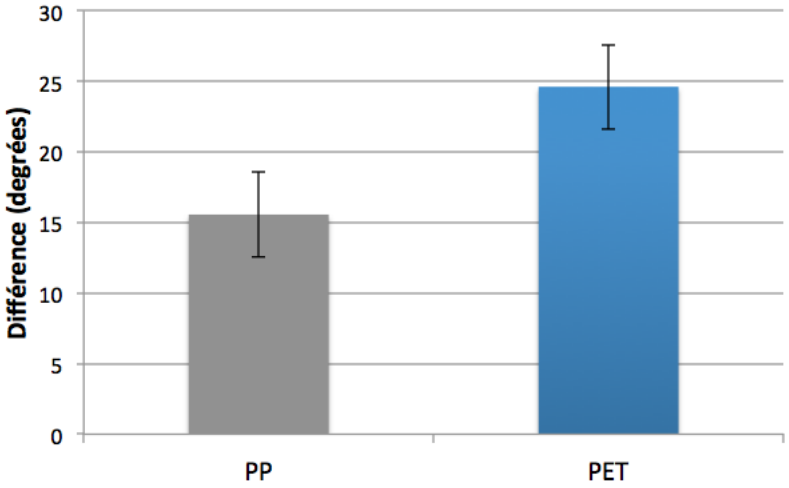

Figure 5.1 Améliorations moyennes des angles de contact

5.3.2 Avec peroxyde d'hydrogène

Les résultats obtenus lors des essais avec le peroxyde d'hydrogène ont différé de ce qui était attendu. Tel que mentionné précédemment, l'addition de peroxyde d'hydrogène devrait permettre d'étendre la plage d'angles de contact atteignables. Dans le cas présent, travaillant à des conditions propices à la production de revêtements hydrophobes, ceci impliquait une augmentation de l'angle de contact. Par contre, les résultats obtenus viennent contredire cette hypothèse. En effet, des angles de contacts entre 0° et 5° ont été obtenus. Ce qui suggère que le rôle du peroxyde d'hydrogène dans la réaction est plus complexe qu'une simple promotion cinétique.

5.3.3 Effet du rayonnement sur le polymère et l'angle de contact

L'inquiétude de la détérioration du polymère par la lumière a été soulevée lors de l'expérimentation. Pour vérifier si l'exposition du polymère à la lumière allait avoir une répercussion sur les propriétés de surface, des réplicats des expériences sans peroxyde d'hydrogène ont été effectués, mais cette fois-ci en coupant le substrat de l'exposition à la lumière. Cette expérience a permis de conclure qu'il n'y avait aucune différence statistiquement significative entre les deux groupes d'expériences.

5.4 Conclusion

En conclusion, bien que cette investigation de courte durée n'ait aucun lien avec les nanoparticules, elle a néanmoins permis d'en apprendre davantage sur le procédé. Plus précisé-

ment, l'investigation a permis de déterminer que le phénomène de modification de propriétés de surface par le gaz de synthèse sous rayonnement UV n'est pas un phénomène propre à des substats de cuivre. L'investigation n'a pas infirmé l'hypothèse quant à savoir si les tendances prédites par le modèle empirique développé dans le cadre de l'étude du chapitre 4 étaient transposables à d'autres substrats. L'investigation a également soulevé une importante incertitude quant à la capacité du peroxyde d'hydrogène à étendre la plage d'angles de contact atteignables. L'étude réalisée a démontré que bien que le peroxyde d'hydrogène semble avoir un effet positif sur la réaction de déposition, sa participation dans la réaction est plus complexe que prévue et son effet est, pour l'instant, imprévisible quant au caractère hydrophile ou hydrophobe du revêtement déposé. De plus, l'étude réalisée ne permet aucunement d'apporter des conclusions quant à l'efficacité de ces revêtements pour faciliter l'expulsion de fluide de leur contenant dans le domaine alimentaire. Finalement, l'étude a démontré que la modification de surface par PICVD était applicable à des substrats non seulement non-métalliques, mais aussi de nature polymériques.

CHAPITRE 6

DISCUSSION GÉNÉRALE

6.1 Synthèse des travaux

6.1.1 Identification d'une technologie prometteuse

Ce projet de maîtrise avait pour objectif, à la suite d'une revue de littérature exhaustive, d'identifier et d'investiguer expérimentalement une technologie de traitement de surface, dans le but ultime de contrer le phénomène d'agglomération des nanoparticules. Les critères de sélection initiaux priorisaient une technologie basée sur la fonctionnalisation en surface, peu coûteuse (autant en frais d'opération, que d'installation) et transposable à l'échelle industrielle. Ces derniers pointaient naturellement en direction des technologies de déposition en phase gazeuse, soit le CVD et ses multiples variantes. Ces technologies ont été revues et comparées dans le premier article (chapitre 3) pour la fonctionnalisation industrielle de surface de nanoparticules à faible coût. Cette étude est arrivée à la conclusion que la déposition chimique en phase vapeur (PICVD) serait un candidat intéressant pour l'application envisagée.

6.1.2 Preuve de concept

Le second article, présenté au chapitre 4, utilise les conclusions obtenues par l'article précédent et en investigue la faisabilité sous la forme d'une preuve de concept. Cette preuve de concept ne s'est pas attaquée directement à la fonctionnalisation en surface sur des nanoparticules car cette démarche aurait entraîné beaucoup de facteurs à tenir compte à la fois. L'étude s'est penchée sur la fonctionnalisation en surface sur des substrats plats non poreux, ce qui a permis de dissocier le principe de fonctionnalisation en surface des effets de transfert de masse interne et externe causés par les nanoparticules, qui auraient complexifié le problème sans raisons valables. L'objectif était de démontrer si le PICVD, en utilisant des précurseurs gazeux et peu coûteux, pouvait induire des fonctionnalités à des surfaces. Toujours dans l'optique d'une mise à l'échelle commercialement viable, les précurseurs gazeux permettent d'opérer à pression et température ambiante [1] comparativement à des précurseurs liquides qui doivent être évaporés. De plus, les gaz utilisés devaient être photosensibles, polymérisables en chaînes carbonées comprenant des groupements -OH et disponibles en grande quantité à faible coût. Le gaz de synthèse, un mélange gazeux de monoxyde de carbone (CO) et de dihydrogène

1. Plus ou moins 10 kPa relatif à la pression atmosphérique pression ainsi plus ou moins 10°C relatif à 22°

(H_2) a été utilisé car il correspondait à un mélange de gaz disponible industriellement, qui n'a pour l'instant pas de valeur autre qu'énergétique par sa combustion. Ce mélange de gaz est connu pour être polymérisable (procédé Fischer Tropsch) et les sous-produits issus de ces réactions contiennent souvent des groupements -OH.

L'étude a permis de démontrer que des groupements fonctionnels peuvent être attachés à des surfaces de cuivre et qu'en plus, l'énergie de surface peut être ajustée en manipulant les variables du procédé. Le tableau 6.1 résume les connaissances acquises au fil des expériences quant aux effets des paramètres sur différents aspects de la déposition. À l'aide d'une analyse multivariée, un modèle empirique a pu être dérivé afin de relier l'énergie de surface (par le biais de l'angle de contact) aux conditions opératoires. Le paramètre le plus influent du modèle est, de loin, la pression dans le réacteur. Il a été constaté qu'une pression positive favorise la déposition de revêtements hydrophobes, alors qu'une pression négative favorise la déposition de revêtements hydrophiles. L'effet de la pression sur les propriétés de surface obtenues est un résultat intéressant en soi. En effet, selon la théorie du CVD, l'opération à basse pression permet d'éviter que la réaction ne se déroule dans la phase gazeuse plutôt qu'à la surface du substrat. Inversement, une pression supérieure encouragerait la cinétique dans la phase gazeuse, suivie de la condensation du produit sur la surface. Il serait tentant d'attribuer le changement de comportement de mouillabilité à un changement de régime (réaction en phase gazeuse versus réaction à la surface).

Tableau 6.1 Effets des différents paramètres

Parameter	**Haut**	**Bas**
Ratio H_2/CO	Hydrophile	Hydrophobe
Pression	Taux de réaction élevé	Favorise l'adsorption
Température	Taux de réaction élevé	Favorise l'adsorption
Débit	Taux de déposition élevé	Revêtement plus dense (*"crosslinked"*)

De plus, dans certains cas, des dépôts colorés ont été observés. Cependant l'apparition de ces dépôts n'a pu être associée à aucune combinaison spécifique de paramètres expérimentaux. Ces dépôts colorés ont été observés comme étant hautement hydrophiles, ayant des angles de contact entre 0 et 5°. L'ajout de peroxyde d'hydrogène comme agent promoteur a permis l'extension de la plage de valeur des angles de contact pouvant être atteints par la méthode, soit de 30-100° à 5-118°. Cependant celle-ci demeure relativement restreinte. L'investigation ne permet d'établir aucune garantie quant à l'efficacité du traitement sur des nanoparticules donc, pour ce faire, une étude subséquente devra s'attaquer à ce problème. Néanmoins, la méthode développée dans le cadre de cet article a été considérée suffisamment pertinente pour faire l'objet d'abord d'une déclaration d'invention, puis d'une application de brevet (inclus

en annexe).

6.1.3 Extension de la preuve de concept

Bien que l'investigation de l'effet du matériau du substrat n'était pas envisagée à l'origine, une étude commandée de l'externe a amené ce facteur à l'étude. La méthode précédemment développée a été testée sur des substrats de polymères (PET et PP) en visant l'application d'un caractère hydrophobique à la surface. Les conditions opératoires ont été sélectionnées en se basant sur l'optimisation de la prédiction offerte par le modèle développé au chapitre 4, en tenant pour acquis que si les angles prédits ne seront pas exacts, les tendances, quant à elles, devraient se maintenir. L'étude a démontré que la fonctionnalisation en surface par PICVD du gaz de synthèse n'était pas un cas qui se limitait uniquement au cuivre, ni aux métaux. Les échantillons traités ont démontré une augmentation de l'angle de contact d'en moyenne 15° pour le PP et 24° pour le PET. L'ajout de peroxyde d'hydrogène comme agent promoteur a amené des résultats inattendus, soit des surfaces hautement hydrophiles (angles de contact virtuellement nuls) lorsque traitées à des conditions connues pour favoriser des revêtements hydrophobes.

6.2 Limitations de la solution proposée

6.2.1 Nouveauté

La méthode étant nouvelle, beaucoup de limitations sont liées au manque de connaissances du procédé. Bien que le concept de modification de l'angle de contact sur la surface soit une preuve de concept intéressante en soi, cette étude donne très peu d'indications quant aux limites des bornes supérieures et inférieures pouvant être atteintes. Il est difficile de dire si la plage de valeurs d'angles obtenus est optimale ou non pour ce procédé et l'effet de la nature du substrat ainsi que le rôle du peroxyde d'hydrogène dans la réaction demeurent des mystères à élucider. Comme aucun test de résistance mécanique n'a été effectué, il est difficile de prédire si le revêtement saura résister aux conditions de l'application pratique sur le long terme. Pour terminer, les résultats préliminaires sont encourageants quant au potentiel du PICVD pour la traitement de surface, mais des études plus approfondies seront requises pour confirmer ce fait.

6.2.2 Revêtement de fenêtre

Durant les tests préliminaires, un phénomène souvent associé au PICVD a été remarqué, soit le revêtement de la fenêtre. Sous certaines conditions, ce phénomène était présent sans

nécessairement être nuisible à l'expérience. Il était parfois nécessaire de nettoyer les tubes. Ce revêtement qui était normalement visible à l'oeil nu, apparaissait sous la forme d'une teinte jaunâtre qui graduellement tournait au brun, probablement en raison de l'épaisseur du revêtement. Ce revêtement s'est avéré comme non soluble dans les solvants communs, mais soluble à l'aide de soude caustique (NaOH). Les tubes étaient submergés toute la nuit avant d'être rincés à l'eau déionisée. Cette limitation pourrait être facilement contrée à l'aide d'un design de réacteur en conséquence. La configuration actuelle (forme cylindrique, petit diamètre, long) s'avère loin du cas idéal en relation à ce problème et pourtant, ce phénomène n'est pas apparu comme intrusif. En prenant l'industrie du semi-conducteur comme exemple, des tailles de chambres très grandes comparativement aux échantillons traités sont priorisées. Ce genre de design permet de minimiser le contact avec les murs de la chambre en augmentant sa surface et en refroidissant le substrat de manière à favoriser la déposition sur celui-ci.

6.2.3 Rétablissement du caractère hydrophobe

Une autre limitation dénotée concerne la stabilité des revêtements déposés. Un enjeu important relié à cette stabilité concerne le rétablissement du caractère hydrophobe d'une surface qui a subi un traitement hydrophile. Durant les expériences, il a été remarqué que les surfaces hydrophiles perdaient une grande partie de leur hydrophilicité sur une période de très courte durée[2]. Par contre, il a été reporté que les revêtements demeurent stables lorsque conservés en solution [8]. À l'inverse, les surfaces ayant reçu des traitements hydrophobes n'ont démontré aucun changement significatif de tension de surface lorsque mesurées à nouveau une semaine après traitement.

2. On parle d'une disparition quasi-totale des propriétés attribuées en 24 heures.

CHAPITRE 7

CONCLUSION

7.1 Retour sur le travail accompli

La possibilité d'utiliser le PICVD pour la fonctionnalisation en surface a été étudiée. Les essais ont été effectués sur des substrats macroscopiques plats afin d'éliminer les facteurs reliés aux phénomènes de transfert de masse, ainsi qu'à la manipulation souvent complexe des nanoparticules. Les propriétés de surface ont été caractérisées par goniométrie ainsi que par FTIR, alors que la composition de l'effluent gazeux de sortie a été mesuré par GCMS. Les résultats obtenus ont confirmé que les surfaces peuvent être traitées par PICVD, mais invitent aussi à penser que les propriétés de surface peuvent être finement ajustées en contrôlant la cinétique impliquée dans le réacteur. Un modèle empirique a été développé reliant l'angle de contact aux paramètres expérimentaux du système. De plus, l'addition de peroxyde d'hydrogène en tant que promoteur a permis l'extension des plages de valeur obtenues pour l'angle de contact, soit de 30-100° à 5-118°.

Des substrats de polymères ont également été testés suivant le même procédé, mais cette fois en visant uniquement les revêtements hydrophobiques. Les résultats démontrent que le concept s'applique également sur des substrats de polymère. L'addition de peroxyde d'hydrogène a entraîné la formation de revêtement hautement hydrophile (angles de contact autour de zéro), et ce, à des conditions généralement connues pour donner des revêtements hydrophiles.

L'étude a conclu que le PICVD est en effet un candidat potentiel pertinent pour la fonctionnalisation et cette avenue requiert davantage d'investigation.

7.2 Travaux futurs

Optimisation : Un bon départ pour des travaux futurs serait de contrôler la température plus localement. Tel que discuté précédemment, le refroidissement du substrat favoriserait la déposition sur la surface en encourageant les phénomènes de condensation et d'adsorption. Également, le préchauffage pourrait aider l'initiation de la réaction. Ce contrôle raffiné de température, même en restant près de la température ambiante, pourrait avoir un effet considérable sur la qualité des revêtements. Également, l'utilisation d'une source de lumière circulaire entourant le réacteur serait plus adéquate qu'une radiation unidirectionelle linéaire. Dans le cas où ces ajustements ne s'avèreraient non suffisants, l'idée de remplacer le gaz de

synthèse pourrait être à considérer. Une fois le procédé de fonctionnalisation en surface bien rodé, la prochaine étape de mise à l'échelle sera envisageable.

Mise à l'échelle : Puisque cette étude s'est basée sur des substrats plats non poreux, le prochain pas en direction de l'objectif ultime consisterait à investiguer des méthodes de recouvrement de nanoparticules, probablement en utilisant un lit fluidisé. À ce point, il sera nécessaire de déterminer quelle est la quantité nécessaire de groupements fonctionnels à la surface afin d'éliminer le phénomène d'agglomération.

Application finale : Il sera impératif de tester si la fonctionnalisation en surface par PICVD permet de contrer ou non le phénomène d'agglomération des nanoparticules. Des tests pratiques devront également être effectués dans les conditions d'applications réelles afin de déterminer si la résistance mécanique ainsi que la stabilité du revêtement sont suffisamment bonnes pour justifier davantage d'investigations dans cette technologie.

7.3 Applications futures

Alors que le projet a démarré avec la problématique de la fonctionnalisation de nanoparticules en tête, la présente étude semble indiquer que l'invention ci-présente possède un potentiel dont l'étendue est beaucoup plus grande qu'originalement envisagée. En effet, bien que le PICVD ait été identifié pour un besoin bien spécifique, il s'avère que la preuve de concept ouvre la porte à toutes surfaces où l'aspect coût est critique.

Bien que l'objectif initial de ce projet visait un traitement hydrophile, plusieurs domaines industriels s'intéressent sérieusement aux traitements hydrophobes [53]. L'application du chapitre 5 en est un exemple concret : une industrie du domaine alimentaire est intéressée à traiter l'intérieur des contenants afin de faciliter l'expulsion du contenu. Un autre exemple est l'industrie du textile : parce que le textile a tendance à absorber les liquides, un traitement hydrophobe permettrait d'éviter les tâches et de conserver les vêtements secs [40]. L'industrie cosmétique a également démontré de l'intérêt envers la technologie pour le traitement de l'intérieur, simplifiant ainsi le nettoyage des cuves. Finalement, Paxson *et al.* ont récemment affirmé que le traitement hydrophobe des condenseurs de vapeur utilisés pour la génération d'électricité permet d'accroitre l'efficacité énergétique de manière substantielle [62].

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ANNEXE A

METHODS FOR THE PHOTO-INITIATED CHEMICAL VAPOR DEPOSITION (PICVD) OF COATINGS AND COATINGS PRODUCED BY THESE METHODS

(PATENT APPLICATION)

ABSTRACT OF THE DISCLOSURES

Methods for producing coatings on substrates are provided. These methods comprise the steps of introducing the substrate in a photo-induced chemical vapor deposition reactor, introducing a gas precursor in the reactor, irradiating said gas precursor with UV radiation at a given wavelength to photodissociate the gas precursor. In one method, the gas precursor is a mixture comprising carbon monoxide and hydrogen. In another method, the pressure in the reactor is between about 0.75 and 1.25 atm and the gas precursor has an absorption cross section of about $5x10^{-16}$ cm^2/molecule or less at said given wavelength.

FIELD OF THE INVENTION

[0001] The present invention relates to methods of producing coatings on substrates. More specifically, the present invention is concerned with methods for producing hydrophobic and hydrophilic coating by PICVD.

BACKGROUND OF THE INVENTION

[0002] The need for organic surface modification arises from the desire to develop materials capable of serving multiple functions beyond their native properties. For example, while one may require the mechanical strength-to-weight ratio and corrosion resistance of stainless steel to build reactors in the cosmetics industry, one also needs the surface to repel the often sticky formulations from the reactor wall - properties that are not native to the base material - while ensuring that the product is not in any way contaminated.

[0003] In the field of nanomaterials, the exceptional conductivity of carbon nanotubes makes them ideal materials to form conductive nanocomposites for the aeronautics industry; at the same time, their homogeneous dispersion in a polymer matrix requires that they be

imparted with a significant surface charge and functional groups that are stable over a wide range of processing temperatures. Further, surface treatment for nanoparticles may also be required to avoid agglomeration.

[**0004**] Surface modification can currently be achieved through two main streams: adsorption and functionalization.

[**0005**] Surface adsorption is the simplest method to impart a charge or steric hindrance to a surface by using compounds known as surfactants. These are widely used in the field of colloids to promote dispersion of small particles in a host fluid. On macroscopic surfaces, these compounds can also be used to form self-assembled monolayers (SAMS) that can, for example, alter the wettability of a surface. Various functional moieties can also be applied using SAMS. However, the basic functionalities achievable through surface adsorption face a severe limitation: the coating is not bonded to the surface and is thus prone to thermal or mechanical desorption (surfactants are known to desorb at temperatures as low as 70°C).

[**0006**] On the other hand, functionalization allows for the formation of a strong covalent bond between the functional moiety and the substrate. Functionalization can be achieved through solvent-based chemistry or gas-phase deposition.

[**0007**] The currently favoured liquid-based methods can be fairly problematic: achieving the desired functionality requires knowledge about the specific reactions or reaction mechanisms (often complex and multi-step, and involving potentially toxic solvents and reactants). Moreover, it can be quite difficult to identify the appropriate medium through which to conduct the functionalization reactions (the substrates and the functionalization reagents may not be compatible with the same solvent). Furthermore, in the case of nanoparticle functionalization, the separation of the functionalized particles from the leftover reagents, undesirable by-products and solvents typically requires significant downstream processing, thereby leading to efficiency loss which limits the potential for scale-up and increases the overall cost of treatment. These difficulties are compounded when attempting to form multi-functional "smart" surfaces, given the increased number of reagents and possible products involved. These methodological shortcomings are generally dodged in the literature.

[**0008**] Solvent-free gas-phase methods, typically referred to as chemical vapour deposition (CVD), do not face these particular issues: gases are miscible (at normal pressures) and readily separate from solid substrates. In a typical CVD process, a substrate is exposed to one or more volatile precursors (gas), which react and/or decompose on the substrate surface

to produce a coating. The advantage of this technique is that it allows a rapid deposition, consistent and clean coating. CVD is typically stimulated by one (or a combination) of three energy sources: heat, plasma or light.

[0009] Thermally activated CVD (TACVD) is mostly reserved to inorganic coatings, as the high temperatures required to achieve the desired reaction activation energy are incompatible with most organic compounds. This limitation can be curtailed in some cases through the use of initiator compounds.

[0010] Plasma-enhanced CVD (PECVD) allows for the creation of a non-thermal highly reactive environment through ionization, which leads to strong electron and UV light bombardment of organic species. PECVD has been extensively used to form thin organic coatings (often referred to as "plasma polymerization"). The possibility of using PECVD for tailoring wettability of surfaces by adjusting the process parameters of plasma enhanced CVD has been demonstrated. It was also shown that UV light was contributing to PECVD's efficiency. While this technique is successful for organic surface functionalization, it suffers from a processing point of view. Indeed, it requires specialized equipment and, in most cases, that processing occurs under low pressure, thus limiting treatment volumes and throughput. Moreover, the use of certain electronegative compounds, such as oxygen, can rob PECVD of its efficiency. This technique is therefore best suited for high value-added applications.

[0011] Photo-initiated CVD (PICVD) allows for a decoupling of the useful components of plasma processing (such as UV radiation and use of small organic precursor compounds) from the process itself. Thus, specific plasma processing conditions, such as operating under vacuum, can be avoided. Indeed, UV lamps (typically glow discharge plasmas) are separated from the process by a UV-transparent window, thereby allowing for the functionalization process to operate under atmospheric or near-atmospheric conditions. Photochemical reactions have been used to grow SiO_2 layers in the semi-conductor industry and to deposit certain organic coatings on macroscopic surfaces.

[0012] These processes typically resort to high-energy, low-wavelength vacuum UV (VUV, <200 nm) or extreme UV (EUV, <121 nm) sources such as D_2, Hg or excimer lamps, or custom-made plasma sources. In fact, PICVD efforts have almost all relied on the use of such VUV and EUV sources. This is due to the fact that, at such low wavelengths, it is possible to specifically target certain molecular bonds and break them. This favors large coating thickness and fast deposition kinetics, which are the main focus of the semi-conductor industry, from which most PICVD studies arise. In fact, there is an established consensus

in the PICVD literature that it is necessary to use a light source emitting radiation close to the peak absorption of the gas precursor used for PICVD to be useful. Therefore, light sources are chosen so as to emit at a wavelength at which the gas precursor used exhibit a significant absorption cross-section. However, it should be noted that VUV and EUV sources can be very costly. In addition, they require the use of specific window materials to allow for light transmission. In fact, MgF_2, LiF, and CaF_2 are the only common materials with significant transparency below 200 nm, and these materials must typically be maintained under inert atmosphere at all times, which complicate VUV and EUV PICVD. In the absence of a light source with the appropriate emission wavelength, the literature teaches to use a photosensitizer sensitive to the wavelength of the light source. See references 1-5 in the section entitled "References" below.

[0013] PICVD has only sparsely been used for the coating of nanomaterials, but it has been shown to have potential as a gas phase nanoparticle treatment.

[0014] On another subject, syngas (also called synthesis gas) is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and very often some carbon dioxide. It is combustible, but has less than half the energy density of natural gas. Syngas is a product of several processes, including steam reforming and waste destruction processes such as gasification. Generally, syngas is converted into hydrocarbons or alcohols via various catalytic processes or is burned in a turbine to produce energy (with average to low efficiency).

[0015] On yet another subject, UVC light sources have been used in the field of photochemistry to stimulate polymerization reactions (curing), to degrade harmful organics in wastewater (photocatalysis), for lithography and, recently, for nanomaterials synthesis.

SUMMARY OF THE INVENTION

[0016] In accordance with the present invention, there is provided:

1. A method for producing a coating on a substrate, the method comprising the steps of:
   - introducing the substrate in a photo-induced chemical vapor deposition reactor,
   - introducing a gas precursor in the reactor so that the pressure in the reactor is between about 0.75 and 1.25 atm, and
   - irradiating said gas precursor with MUV radiation at a given wavelength to photodissociate the gas precursor,
   - the gas precursor having an absorption cross section of about $5x10^{-16}$ cm^2/molecule or less at said given wavelength.

2. The method of item 1, wherein the absorption cross section is of about $1x10^{-16}$ cm^2/molecule or less.
3. The method of item 2, wherein the absorption cross section is of about $7x10^{-17}$ cm^2/molecule or less.
4. The method of item 3, wherein the absorption cross section is of about $5x10^{-17}$ cm^2/molecule or less.
5. The method of item 4, wherein the absorption cross section is of about $2x10^{-17}$ cm^2/molecule or less.
6. The method of any one of items 1 to 5, wherein the gas precursor is an organic gas, ammonia, hydrogen, nitrogen, oxygen, carbon dioxide, or carbon monoxide, or a mixture thereof.
7. The method of item 6, wherein the gas precursor is a C_{1-12}-alcohol (such as methanol, ethanol, propanol, butanol, glycerol, phenol), a C_{1-12}-alkane (such as methane, ethane, propane, butane, pentane, hexane, heptane), a C_{1-12}-alkene (such as ethylene), a C_{1-12}-alkyne (such as acetylene), acetic acid, acetone, acrylic acid, ammonia, carbon dioxide, carbon monoxide, ethylene glycol (including oligomers and polymers thereof), formaldehyde, hydrogen (H_2), methanal, methyl methacrylate, nitrogen, a nitrogen oxide, oxygen, ozone, peroxide, sulfur oxide, water, or a mixture thereof.
8. The method of item 7, wherein the gas precursor is a mixture of carbon monoxide and hydrogen.
9. The method of item 8, wherein the gas precursor is syngas.
10. The method of any one of items 1 to 9, wherein said given wavelength is about 254 nm.
11. The method of any one of items 1 to 10, wherein the MUV radiation is emitted by a low pressure germicidal lamp.
12. The method of any one of items 1 to 11, wherein the gas precursor is heated at a temperature above room temperature
13. The method of any one of items 1 to 12, wherein the substrate is held at a temperature between about 30 and 50°C.
14. A method for producing a coating on a substrate, the method comprising the steps of:
    - introducing the substrate in a photo-induced chemical vapor deposition reactor,
    - introducing a gas precursor in the reactor, the gas precursor being a mixture comprising carbon monoxide and hydrogen, and
    - irradiating said gas precursor with UVC radiation to photodissociate at least one of the carbon monoxide and the hydrogen.

15. The method of item 14, wherein the gas precursor is syngas.
16. The method of item 14 or 15, wherein the UVC radiation has a wavelength of about 254 nm.
17. The method of any one of items 14 to 16, wherein the UVC radiation is emitted by a xenon lamp, a krypton lamp, an excimer xenon lamp, a deuterium hydrogen lamp, or a germicidal lamp.
18. The method of item 17, wherein the UVC radiation is emitted by a low pressure germicidal lamp.
19. The method of any one of items 14 to 18, wherein the pressure in the reactor is between about 0.75 and 1.25 atm.
20. The method of any one of items 14 to 19, wherein the gas precursor is heated at a temperature above room temperature.
21. The method of item 20, wherein the gas precursor is heated at a temperature between about 20 and about 70C,
22. The method of any one of items 14 to 21, wherein the substrate is held at a temperature between about 20 and about 80°C.
23. The method of item 22, wherein the substrate is held at a temperature between about 20 and about 30°C.
24. The method of item any one of items 14 to 23, wherein the hydrogen (H_2) and the carbon dioxide (CO) are present in a H_2/CO ratio varying between about 1/16 to about 4.
25. A coating produced by the method of any one of items 14 to 24.
26. The coating of item 25 being hydrophilic.
27. The coating of item 25 being hydrophobic.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In the appended drawings:

- Figure 1 show the calculated contact angle (shades of grey) as a function of the pressure in the reactor and the H_2/CO ratio;
- Figure 2 is a schematic of the PICVD setup used;
- Figure 3 is a graph of the contact angle measured as a function of the pressure in the reactor;
- Figure 4 is a graph of the contact angle measured as a function of the position in the reactor;

- Figure 5 is a graph of the contact angle measured as a function of the H_2/CO Ratio*Pressure;
- Figure 6 is a graph of the contact angle measured as a function of the Pressure*Position;
- Figure 7 shows an embodiment of an hydrophobic coating;
- Figure 8 shows an embodiment of an hydrophilic coating; and
- Figure 9 is a SEM micrograph of a coating according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

PICVD Coating at High Pressure with a Gas Precursor of Low Absorption Cross Section

[0018] Turning now to the invention in more details, in a first aspect of the invention, there is provided a method for producing a coating on a substrate, the method comprising the steps of: (A) introducing the substrate in a photo-induced chemical vapor deposition reactor, (B) introducing a gas precursor in the reactor so that the pressure in the reactor is between about 0.75 and 1.25 atm, and (C) irradiating said gas precursor with MUV (Middle Ultraviolet) radiation at a given wavelength to photodissociate the gas precursor, the gas precursor having an absorption cross section of about $5x10^{-16}$ cm^2/molecule or less at said given wavelength. Herein, "MUV" radiation refers to "middle UV", that is radiation having a wavelength between 200 and 300 nm.

[0019] As discussed above, in PICVD, it is customary to specifically target certain molecular bonds in the gas precursor to break them. To do so, it is necessary to use a light source emitting radiation close to the peak absorption of the gas precursor. In other words, the gas precursor must have a large absorption cross section at the wavelength of the MUV irradiation used.

[0020] The absorption cross section is a measure of the probability of an absorption process. It represents the ability of a molecule to absorb a photon of a particular wavelength. The Beer-Lambert Law for gases expresses the absorbance of a gas at a given wavelength (A') as a function of the absorption cross section at that wavelength (σ), the path length (l) and density of the gas molecules (N, for example expressed as a number of molecules per cubic centimeter) as follows:

$$A^{'} = \sigma l N \tag{A.1}$$

[**0021**] In PICVD, the gas precursor absorbs the MUV radiation. This causes the photodissociation (photolysis) of the gas precursor molecules and produces radicals (or ions). These radicals are very reactive and, when they contact the substrate, will react (photopolymerize) to form a coating on it. The more gas precursor molecules are present in the reactor (i.e. the higher the pressure in the reactor), the higher the likelihood of a newly formed radical encountering and reacting with another gas precursor molecule or another radical rather than reacting with the surface of the substrate to be coated. Therefore, it is common knowledge to conduct PICVD at low pressures (i.e. a few Torrs or less) to ease coating formation. If higher pressures were to be used, it would appear necessary to the skilled person to generate more radicals to produce the desired coatings. In other words, at higher pressures, higher absorption of the radiation by the gas precursor molecules is needed, which means that the absorption cross section of the gas precursor must be higher than when the PICVD is conducted at lower pressures.

[**0022**] This aspect of the invention is based on the inventors' surprising finding that a coating can be effectively produced on a substrate at high pressure even if the gas precursor has a relatively low absorption cross section at the wavelength of the MUV radiation used. It should be noted that this is achieved without using a photosensitizer. Therefore, in embodiments of the methods of the invention, the irradiation is carried out in the absence of a photosensitizer.

[**0023**] The nature of the substrate to be coated is not crucial. The substrate may for example present a metallic surface, a quartz surface, an oxide surface or a polymeric surface. In embodiments, the substrate is made of copper. Furthermore, the substrate may be macroscopic (reactors surfaces, textiles, polymeric nets, bottles, wafers and the like) or it can be a nanomaterial (nanoparticles, nanotubes, etc.).

[**0024**] The photo-initiated chemical vapor deposition reactor to be used is not restricted in form or material. It should comprise a chamber to hold the substrate and contain the gas precursor at a given pressure. This chamber should be provided with appropriate gas inlet(s) and outlet(s) as well as with a means to introduce and remove the substrate. Further, at least part of the chamber should be transparent to MUV radiation at the wavelength used to allow for irradiation of the gas precursor molecules. Alternatively, the chamber should be designed such that light source may be installed within it. In embodiments, the chamber is a quartz tube.

[0025] Finally, the reactor should be provided with a light source emitting MUV radiation at a proper wavelength. This means that the main emission peak (the emission peak with the highest intensity) of this light source should be in the MUV range. In addition, the light source may emit light at other wavelengths.

[0026] In embodiments, the light source is a germicidal lamp, such as a low pressure germicidal lamp. Low pressure germicidal lamps are a common type of germicidal lamp. They generally look similar to ordinary fluorescent lamps but the tube contains no fluorescent phosphor. In addition, rather than being made of ordinary borosilicate glass, the tube is made of fused quartz. These two changes combine to allow the 253.7 nm ultraviolet light produced by a mercury arc to pass out of the lamp unmodified (whereas, in common fluorescent lamps, this UV light causes the phosphor to fluoresce, producing visible light). Germicidal lamps produce MUV radiation at a wavelength of 253.7 nm (commonly rounded to 254 nm), and often have a secondary emission peak at 185 nm. Therefore, in embodiments, the wavelength used in the above method is 253.7 nm or about 254 nm. In this particular regard, the method of the invention differs significantly from the high-energy, low-wavelength light sources typically used. Indeed, it makes use of high-wavelength commercial anti-microbial lamps. MUV light sources have never been used to promote surface functionalization. Such sources are not used because of the established belief in the field of CVD that photo-stimulated coating and functionalization processes can only occur if the selected precursor compounds have very high absorbance (absorption cross section) at the retained wavelengths. Indeed, most organic compounds have poor absorbance at 253.7 nm, thus bond-breaking efficiency is fairly low and deposition kinetics are decreased. Nonetheless, it has been found possible to use MUV to generate reactive radicals or ions that can be used for surface functionalization, though at a reduced rate with respect to more energetic sources.

[0027] In the method of the invention, the pressure in the reactor is between about 0.75 and about 1.25 atm. In embodiments, this pressure is about 0.75, 0.8, 0.85, 0.90, 0.95, or 1 atm or more and/or 1.25, 1.20, 1.15, 1.10, 1.05 or 1 atm or less.

[0028] As explained above, the gas precursor has a relatively low absorption cross section (about $5x10^{-16}$ cm^2/molecule or less). In embodiment, the absorption cross section is of about $3x10^{-16}$ cm^2/molecule or less, about $1x10^{-16}$ cm^2/molecule or less, about $7x10^{-17}$ cm^2/molecule or less, about $5x10^{-17}$ cm^2/molecule or less, or about $2x10^{-17}$ cm^2/molecule or less. Apart from that, the nature of the gas precursor is variable. There is no lower limit for the absorption cross section, although it should be understood that the irradiation time

required to form a coating of a given thickness is inversely proportional to the absorption cross section.

[0029] In embodiments, the gas precursor is an organic gas, ammonia, hydrogen, nitrogen, oxygen, carbon dioxide, or carbon monoxide, or a mixture thereof. Herein, an "organic gas" is a gaseous chemical compound whose molecules contain one or more carbon atoms, excluding carbon-containing carbides, carbonates, simple oxides (CO and CO_2), and cyanides, as well as the allotropes of carbon (e.g. diamond and graphite).

[0030] In embodiments, the organic gas is as defined above, but is free of metal atoms (such as Si, Cu, Al, etc.).

[0031] In embodiments, the gas precursor is a C_{1-12}-alcohol (such as methanol, ethanol, propanol, butanol, glycerol, phenol), a C_{1-12}-alkane (such as methane, ethane, propane, butane, pentane, hexane, heptane), a C_{1-12}-alkene (such as ethylene), a C_{1-12}-alkyne (such as acetylene), acetic acid, acetone, acrylic acid, ammonia, carbon dioxide, carbon monoxide, ethylene glycol (including oligomers and polymers thereof), formaldehyde, hydrogen (H_2), methanal, methyl methacrylate, nitrogen, a nitrogen oxide, oxygen, ozone, peroxide, a sulfur oxide, water, or a mixture thereof.

[0032] In embodiments, the gas precursor is a mixture of carbon monoxide and hydrogen, including syngas (see below for more details).

[0033] The gas precursor is irradiated with MUV radiation. This irradiation is to be carried out until enough molecules of the gas precursor have been photodissociated and have reacted (photopolymerized) with the substrate to form the desired coating. The exact irradiation time needed for each coating will depend on the thickness of coating desired, the extent of surface coverage desired, the absorption cross section, flow rates and pressure of the gas precursor(s), the temperature of the gas precursor and of the substrate and the power of the light source used.

[0034] In embodiments, the gas precursor in the reactor and the substrate are at room temperature.

[0035] Increased gas temperature beneficially speeds photodissociation rates. Therefore, in embodiments, the gas precursor temperature is above room temperature, for example at a temperature of between about 20 and about 70°C, such as between 30 and 50°C. This can

be achieved by recuperating the heat emitted by the MUV lamp (when applicable) or by any other means known to the skilled person.

[**0036**] Increased substrate temperature also increases reaction kinetics. However, the desorption rate may also undesirably be increased. The temperature of the substrate can be adjusted depending on the exact reactions at play. Therefore, the substrate may be at the same temperature, hotter, or cooler than the gas precursor. This can be achieved using, for example, a temperature regulating system, such as a water circulation system placed near the support holder.

[**0037**] The method of this aspect of the invention is very versatile. It can be used to impart various surface functionalities to various types of substrates. It is applicable to any surface, including nanomaterials.

[**0038**] The method is quite simple and inexpensive. For example, it uses relatively affordable equipment. Indeed, no high vacuum equipment is needed. In some embodiments, no heat is required as the coating can be produced at room temperature. This could open the field of gas-phase surface modification to industries that could benefit from thin films, but could not historically benefit from traditionally expensive CVD techniques

[**0039**] The method shows significant potential for:

- the growth of thin, tailored surface coatings at atmospheric pressure and low temperature with a wide range of possible functionalities;
- the solvent-free formation of multi-functional surfaces; and
- the functionalization of powders and nanoparticles at much larger scales than is currently possible.

[**0040**] With regard to the use of MUV light, it should be noted that it has many advantages:

- MUV light can be transmitted readily through common materials such as quartz;
- it has little to no absorbance in air, and does not generate ozone; and
- MUV lamps (in particular low pressure germicidal lamps) are cheap and commercially available, requiring no specialized equipment beyond standard lighting ballasts.

PICVD Coating of Carbon monoxide and Hydrogen Mixtures

[**0041**] In another aspect, the present invention provides a method for producing a coating on a substrate, the method comprising the steps of (A) introducing the substrate in a photo-

induced chemical vapor deposition reactor, (B) introducing a gas precursor in the reactor, the gas precursor being a mixture comprising carbon monoxide (CO) and hydrogen (H_2), and (C) irradiating said gas precursor with UVC radiation to photodissociate at least one of the carbon monoxide and the hydrogen.

[0042] When the wavelength of the UVC radiation is such that the carbon monoxide and the hydrogen both have a low absorption cross section (i.e. about $5x10^{-16}$ cm^2/molecule or less) and when the pressure in the reactor is between about 0.75 and 1.25 atm, this method is an embodiment of the method described as the first aspect of the invention. This is the case when the UVC radiation used has a wavelength of about 254 nm (corresponding to that emitted by a low pressure germicidal lamp). However, the method of the second aspect of the invention is not so limited and can be carried out at all UVC wavelengths and at other pressures, in particular smaller pressures. Herein, "UVC" radiation refers to UV radiation of subtype C, that is, UV having a wavelength between 10 and 300 nm (including the middle, the far and the extreme UV).

[0043] This aspect of the invention is based on the inventors' finding that a mixture comprising carbon monoxide and hydrogen could surprisingly be used to produce coatings exhibiting a wide range of hydrophilicity (and conversely hydrophobicity). As will be seen below, the exact properties of the coating depend on a few process parameters.

[0044] In embodiments of this method, the gas precursor is a mixture of carbon monoxide and hydrogen only. In embodiments, the gas precursor is syngas.

[0045] The nature of the substrate to be coated is not crucial. The substrate may for example present a metallic surface, a quartz surface, an oxide surface or a polymeric surface. In embodiments, the substrate is made of copper. Furthermore, the substrate may be macroscopic (reactors surfaces, textiles, polymeric nets, bottles, wafers and the like) or it can be a nanomaterial (nanoparticles, nanotubes, etc.).

[0046] The photo-induced chemical vapor deposition reactor to be used is not restricted in form or material. It should comprise a chamber to hold the substrate and contain the gas precursor at a given pressure. This chamber should be provided with appropriate gas inlet(s) and outlet(s) as well as with a means to introduce and retire the substrate. Further, at least part of the chamber should be transparent to UVC radiation at the wavelength used to allow for irradiation of the gas precursor molecules. In embodiments, the chamber is a quartz tube.

[0047] Finally, the reactor should be provided with a light source emitting UVC radiation at a proper wavelength. This means that the main emission peak (the emission peak with the highest intensity) of this light source should be in the UVC range. In addition, the light source may emit light at other wavelengths.

[0048] In embodiment, the main emission peak of the light source is between about 100 nm and about 300 nm, for example, between about 120 nm and about 260 nm. In embodiments, the light source is a xenon lamp (147 nm), a krypton lamp (123 nm), an excimer xenon lamp (172 nm), a deuterium hydrogen lamp (160 nm) or a germicidal lamp, such as a low pressure germicidal lamp (253.7 nm often with a secondary emission peak at 185 nm).

[0049] The gas precursors are irradiated with MUV radiation. This irradiation is to be carried out until enough molecules of at least one of them have been photodissociated. It is not necessary that both precursors be photodissociated by the MUV radiation. Photodissociation of one precursor produces reactive species that can react with molecules of the other precursor and cause their dissociation. The reactive species of both precursors can then react (photopolymerize) with the substrate to form the desired coating. The exact irradiation time needed for each coating will depend on the thickness of coating desired, the extent of surface coverage desired, the absorption cross section, flow rates and pressure of the gas precursor(s), the temperature of the gas precursor and of the substrate and the power of the light source used.

[0050] In embodiments, the carbon monoxide and the hydrogen in the reactor and the substrate are at room temperature.

[0051] Increased gas temperature beneficially speeds photodissociation. Therefore, in embodiments, the gas precursor temperature is above room temperature, for example at a temperature of between about 20 and about 70°C, such as between 30 and 50°C. This can be achieved by recuperating the heat emitted by the MUV lamp (when applicable) or by any other means known to the skilled person.

[0052] Increased substrate temperature also increase reaction kinetics. However, the desorption rate may also undesirably be increased. Therefore, in embodiments, the substrate is at the same temperature or cooler than the gas precursor. This can be achieved using, for example, a temperature regulating system, such as a water circulation system placed near the support holder. In embodiments, when producing a hydrophilic coating, the substrate

can be at a temperature between about 20 and about 80°C, preferably between about 20 and about 30°C.

[0053] As stated above, the wettability of the coating produce can be tailored to be hydrophilic (with a contact angle with water of less than 90) to hydrophobic (with a contact angle with water of more than 90) by adjusting certain process parameters. These parameters are the pressure of the gas precursor in the reactor, the H_2/CO ratio, and the position of the substrate in the reactor.

[0054] The influence of the position in the reactor will depend on reactor design. It will simply be noted here that more hydrophilic coatings tend to be produced closer to the gas precursor inlet, while more hydrophobic coatings tend to be produced farther from the inlet.

[0055] In embodiments, the pressure in the reactor is between about 0.75 and about 1.25 atm. In embodiments, this pressure is about 0.75, 0.8, 0.85, 0.90, 0.95, or 1 atm or more and/or 1.25, 1.20, 1.15, 1.10, 1.05 or 1 atm or less. In other embodiments, the pressure in the reactor is lower than 0.75 atm.

[0056] In embodiments, the H_2/CO ratio varies between about 1/16 to about 4. It can be for example, 1/16, 1/8, 1/4, 1/2, 1, 2, 3, or 4.

[0057] Figure A shows the calculated contact angle (shades of grey) as a function of the pressure in the reactor and the H_2/CO ratio. The contact angles were calculated using the model discussed below for an average position in the reactor, that is one at which both hydrophilic and hydrophobic coatings can be produced (more specifically position 6 discussed below). Therefore, the pressure and the H_2/CO ratio can be selected so as to tailor the properties of the coating produced. It is to be understood that the exact contact angle produced for a given set of parameters may vary from a PIVCD setup to another. However, Figure 1 provides trends to be used to set the process parameters.

[0058] The method of this aspect of the invention is very versatile as it is applicable to any surface, including nanomaterials.

[0059] The method is quite simple and inexpensive. For example, it uses relatively affordable equipment. Indeed, when carrying out deposition around normal pressure, no high vacuum equipment is needed. In some embodiments, no heat is required as the coating can

be produced at room temperature. This could open the field of gas-phase surface modification to industries that could benefit from thin films, but could not historically benefit from traditionally expensive CVD techniques

[**0060**] This method also offers possibilities for the valorisation of syngas, which instead of being burned can be used as a raw material to produce value added materials.

Substrate with Hydrophilic or Hydrophobic Carbon Polymer Coating

[**0061**] In another aspect, the present invention provides a material produced through the method described in the second aspect of the invention.

[**0062**] This material is thus a substrate (of various natures) with a carbon polymer coating. It is believed that this carbon polymer could have a chemical structure akin to phenolic resin.

[**0063**] This coating can be hydrophilic (having a contact angle with water of 90 or less) or hydrophobic (having a contact angle with water of 90 or more). In fact, the surface wettability of this coating can be tailored from hydrophilic to hydrophobic by varying the process parameters as explained above.

[**0064**] It should be noted that after being coating, the material still has the mechanical properties of the substrate, but has advantageously gained different surface properties, which makes it a value added material.

Definitions

[**0065**] The use of the terms ”a” and ”an” and ”the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

[**0066**] The terms ”comprising”, ”having”, ”including”, and ”containing” are to be construed as open-ended terms (i.e., meaning ”including, but not limited to”) unless otherwise noted.

[**0067**] Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it

were individually recited herein. All subsets of values within the ranges are also incorporated into the specification as if they were individually recited herein.

[0068] Herein, an "alkane" is a saturated aliphatic hydrocarbon of general formula C_nH_{2n+2}. An "alkene" is an aliphatic hydrocarbon similar to an alkane except that it comprises at least one double bond. An "alkyne" is a aliphatic hydrocarbon similar to an alkane except that it comprises at least one triple bond. It is to be noted that, unless otherwise specified, the hydrocarbon chains of these compounds can be linear, branched or cyclic. Further, unless otherwise specified, these groups can contain between 1 and 12 carbon atoms, between 1 and 6 carbon atoms, between 1 and 3 carbon atoms, or contain 1 or 2 carbon atoms.

[0069] Herein, an "alcohol" is a saturated or unsaturated aliphatic (linear, branched or cyclic) or aromatic hydrocarbon compound comprising one or more -OH groups, for example two or three such groups. Unless otherwise specified, the alcohol can contain between 1 and 12 carbon atoms, between 1 and 6 carbon atoms, between 1 and 3 carbon atoms, or contain 1 or 2 carbon atoms.

[0070] All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context.

[0071] The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed.

[0072] No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0073] Herein, the term "about" has its ordinary meaning. In embodiments, it may mean plus or minus 10% or plus or minus 5% of the numerical value qualified.

[0074] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0075] Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of specific embodiments thereof, given by way of example only with reference to the accompanying drawings.

Description of Illustrative Embodiment

[**0076**] The present invention is illustrated in further details by the following non-limiting examples.

Example 1 - Hydrophilic and Hydrophobic Coatings Prepared by PICVD of Syngas

[**0077**] We describe herein the coating of high quality hydrophilic and hydrophobic deposits on flat copper substrates by photo-initiated chemical vapour deposition (PICVD). The monomers used for the photopolymerization consisted of a mixture of hydrogen (H_2) and carbon monoxide (CO), which is commonly called syngas.

Experimental

[**0077**] Figure A shows a schematic of the PICVD setup used.

[**0078**] H_2 and CO were supplied in gas bottles (10 and 12) and the gas ratio was controlled by adjusting each gas individual massflow controller (16, 18). Argon for flushing the reactor as needed was also supplied in a gas bottle (14) fitter with a massflow controller (20). The gas mixture was fed to a quartz tubular reactor (22) which was partially transparent to UV in the 254 nm range. The reactor was made of two quartz tubes joined end to end and custom built with standard 24/40 taper joints. The joints were sealed using standard laboratory grease. All experiments were conducted using a dual-bulb 254 nm UV germicidal lamp (24) 1.5 m wide. The experiments duration was fixed to 1 hour.

[**0079**] Flat copper substrates (26) of 1.5 cm per 1 cm were used for all experiments and the substrate holder (28) could hold 5 such substrates at a time (only three of which are shown in Figure 2 for clarity). The position of the substrates in the reactor was noted using integers ranging from 1, which was the position closest to the end of the reactor where the gas entry was located (on the left in Figure 2), to 8, which was closest to the other end of the reactor (on the right in Figure 2). These positions are indicated on the grey ruler (not part of the actual PICVD setup) in Figure 2. In this figure, substrates (26) from left to right are shown at about positions 5, 6, 7, respectively.

[**0080**] The temperature inside the reactor was taken through an IR temperature measurement with an emissivity factor of 0.75. The operating the pressure in the reactor was controlled via a 3-way valve (28) placed at the output by dosing the constriction. One of the

two outputs of the valve was linked to a vacuum line, while the other led to a vent. This configuration allowed obtaining pressures ranging from -20 kPa to +10 kPa gauge (relative to atmospheric pressure).

[0081] Once coated, the copper substrates were analyzed by goniometry to measure their wettability. More specifically, the contact angle formed by a drop of water was measured (conditions = 1 min, 5 points). Some coatings where also observed by SEM.

[0082] The effects of the following parameters have been tested in 1 hour duration experiments and statistically analysed:

- H_2/CO molar (or volume) ratio (varying from 1/16 to 4),
- individual and total flowrates (the total flowrate varying from 260 to 1000 mL/min),
- position in the reactor (from 1 to 8),
- pressure in the reactor (expressed as the difference with atmospheric pressure and varying from -20 to +10 kPa),
- delay before analysis (in number of days after deposition of the coating),
- order of experiment (to identify and control for cumulative effects over time, for example lamp degradation), and
- light intensity (increased by partially or totally enclosing the lamp together with the reactor using aluminium paper). NB. This increased temperature in the reactor as well.

[0083] For each experiment, 4 samples were held in the reactor at 4 specific positions. The experimental design is shown in Table A.1

Table A.1 Experimental plan

H_2/CO ratio	Pressure
-1	-1
1	1
1	-1
-1	1

Results

[0084] Table A.2 shows the effect of some of the experimental parameters varied on the reaction observed and the coating produced.

Table A.2 Effects of experimental parameters on the reaction observed and the coating produced

Parameter	**High**	**Low**
Pressure	High reaction rate	Promote in-depth adsorption
Gas precursor temperature	High kinetic rate	Low kinetic rate
Substrate temperature	High desorption rate	Low desorption rate
Flowrates	High deposition rate	High coating density

[0085] Statistically, the following parameters have been found to have no significant effect on the wettability observed:

- individual and total flowrates,
- light intensity,
- order of experiments, and
- H_2/CO ratio (though this parameter had an effect when combined with pressure as explained below).

[0086] On the other hand, the following parameters have been found to have a significant effect on the surface properties:

- pressure in the reactor,
- position in the reactor (more hydrophilic towards 1 and more hydrophobic towards 8), and
- delay before analysis.

[0087] In view of the effect of the delay before analysis on the surface properties, the surfaces were analyzed on the same day they are produced in order to eliminate uncertainties in the data analysis.

[0088] Figure A shows the influence of the pressure in the reactor on the contact angle measured for a series of experiments at various positions in the reactor.

[0089] Figure A is a graph of the contact angle measured as a function of the position in the reactor for a series of experiments (with various pressures in the reactor).

[0090] Finally, it has been found that some parameters have an effect on the surface properties when they are combined (through multiplication of one by the other):

- H_2/CO Ratio*Pressure, and
- Pressure*Position.

[0091] Figure A is graph of the contact angle measured as a function of H_2/CO ratio*Pressure for a series of experiments at various positions in the reactor.

[0092] Figure Ais graph of the contact angle measured as a function of Pressure*Position for a series of experiments at various H_2/CO ratios.

[0093] Table A.3 summarizes the effect of the above parameters alone and in combination.

Table A.3 Summary the effect of the above parameters alone and in combination

	Hydrophilicity	**Hydrophobicity**
Pressure* H_2/CO Ratio	increased	decreased
Position*Pressure	increased	decreased
Pressure	decreased	increased
Position	decreased	increased

[0094] Using the above setup, contact angles ranging from 30° to 100° have been obtained simply by mapping the experimental conditions. By slightly varying the setup, coatings with contact angles from about 5 to about 110 were obtained.

[0095] Figures A to A show no clear tendencies. This is because many parameters were varied simultaneously. Therefore, the above data only make senses when all parameters are considered together. For this reason, a model of the contact angle versus the above parameters has been used to fit the data.

[0096] The following empirical model describes the behavior of the PICVD system used by relating contact angle to the above parameters:

$$Angle(^\circ) = 1,75P + 3,58 \cdot pos - 0,83P \cdot R + 0,15P \cdot pos + 39 \tag{A.2}$$

where:

- P is the pressure in the reactor, relative to atmospheric pressure (in kPa),
- Pos is the position in the reactor (an integer from 1 to 8), and
- R is the H_2/CO molar (or volume) ratio (dimensionless). The correlation coefficient $R^2$for this model is 0,89 (due to the noise introduced by the different order of magnitude between parameters). A higher coefficient R^2(0,91) was obtained for a normalized model.

[**0097**] The above model can predict accurately the contact angle obtained using a given set of experimental parameters and the above experimental, while a simple study of the individual tendencies shown in the figures could not. The position parameter would be expected to vary from one setup to another, but the influence of the pressure and the ratio on the contact angle is expected to follow similar trends independently of the experimental setup.

[**0098**] This model shows that the parameters favoring hydrophobic coatings are higher pressure combined with lower H_2/CO ratio, while the opposite favors hydrophilic surfaces.

[**0099**] Figure A is a picture of one of the hydrophobic coatings produced with a H_2/CO Ratio of 1/8, at a pressure 10 kPa above normal pressure, and at position 2 in the reactor. It can be seen that a drop of water on the coating does not spread. The contact angle for this coating was about 95°.

[**0100**] Figure A is a picture of one of the hydrophilic coatings produced with a H_2/CO Ratio of 1/8, at a pressure 10 kPa below normal pressure, and at position 4 in the reactor. It can be seen that a drop of water on this coating spreads. The contact angle for this coating was about 5°.

[**0101**] It should be mentioned that hydrophobic coatings have been found to be more stable with time than hydrophilic coatings.

[**0102**] It was observed that increasing the temperature in the reactor by covering part the reactor and the UV lamp with aluminum paper tended to favor hydrophobic coatings. It also increased the rate of deposition up to a point. Then, when too much of the reactor was covered, the increased desorption lowered the deposition rate to a level below that observed at room temperature (i.e. without aluminum paper). It was observed that a cooling system used to cool the substrate holder countered this effect and increased the deposition rate.

[**0103**] Finally, it has also been observed that some coatings produced under conditions for generating hydrophilic coatings presented red spots. The wettability was at its highest on these red spots. Contact angles as low as 5° were observed. Figure A is a SEM micrograph of such a red spot. The small white circles on the surface are believed to represent nano structures that have been coated on the surface. The average diameter of those circles appears to be in the order of 30 nm. The conductivity of the red spots was very low (127 times lower than copper alone).

[0104] The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

REFERENCES

[0105] The present description refers to a number of documents, the content of which is herein incorporated by reference in their entirety. These documents include, but are not limited to, the following:

1. K.L. Choy. Chemical vapour deposition of coatings. Progress in Materials Science 48 (2003) 57-170 (in particular section 12.3.2).
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8. J.H. Rhieu. Photo-cvd system, June 1 1993. US Patent 5,215,588.
9. Jason Tavares, Edward J. Swanson, and Sylvain Coulombe. Plasma Synthesis of Coated Metal Nanoparticles with Surface Properties Tailored for Dispersion. Plasma Processes and Polymers, 5(8):759{769, OCT 14 2008.
10. S. Tsuo and A.A. Langford. Method and apparatus for removing and preventing window deposition during photochemical vapor deposition (photo-cvd) processes, March 28 1989. US Patent 4,816,294.
11. US Patent no. 4,435,445.
12. US Patent no. 5,215,588.

CLAIMS

1. A method for producing a coating on a substrate, the method comprising the steps of:
   – introducing the substrate in a photo-induced chemical vapor deposition reactor,
   – introducing a gas precursor in the reactor so that the pressure in the reactor is between about 0.75 and 1.25 atm, and
   – irradiating said gas precursor with MUV radiation at a given wavelength to photodissociate the gas precursor,
   – the gas precursor having an absorption cross section of about $5x10^{-16}$ cm^2/molecule or less at said given wavelength.
2. The method of claim 1, wherein the absorption cross section is of about $1x10^{-16}$ cm^2/molecule or less.
3. The method of claim 2, wherein the absorption cross section is of about $7x10^{-17}$ cm^2/molecule or less.
4. The method of claim 3, wherein the absorption cross section is of about $5x10^{-17}$ cm^2/molecule or less.
5. The method of claim 4, wherein the absorption cross section is of about $2x10^{-17}$ cm^2/molecule or less.
6. The method of any one of claims 1 to 5, wherein the gas precursor is an organic gas, ammonia, hydrogen, nitrogen, oxygen, carbon dioxide, or carbon monoxide, or a mixture thereof.
7. The method of claim 6, wherein the gas precursor is a C_{1-12}-alcohol (such as methanol, ethanol, propanol, butanol, glycerol, phenol), a C_{1-12}-alkane (such as methane, ethane, propane, butane, pentane, hexane, heptane), a C_{1-12}-alkene (such as ethylene), a C_{1-12}-alkyne (such as acetylene), acetic acid, acetone, acrylic acid, ammonia, carbon dioxide, carbon monoxide, ethylene glycol (including oligomers and polymers thereof), formaldehyde, hydrogen (H_2), methanal, methyl methacrylate, nitrogen, a nitrogen oxide, oxygen, ozone, peroxide, sulfur oxide, water, or a mixture thereof.
8. The method of claim 7, wherein the gas precursor is a mixture of carbon monoxide and hydrogen.
9. The method of claim 8, wherein the gas precursor is syngas.
10. The method of any one of claims 1 to 9, wherein said given wavelength is about 254 nm.
11. The method of any one of claims 1 to 10, wherein the MUV radiation is emitted by a low pressure germicidal lamp.

12. The method of any one of claims 1 to 11, wherein the gas precursor is heated at a temperature above room temperature
13. The method of any one of claims 1 to 12, wherein the substrate is held at a temperature between about 30 and 50C.
14. A method for producing a coating on a substrate, the method comprising the steps of:
    – introducing the substrate in a photo-induced chemical vapor deposition reactor,
    – introducing a gas precursor in the reactor, the gas precursor being a mixture comprising carbon monoxide and hydrogen, and
    – irradiating said gas precursor with UVC radiation to photodissociate at least one of the carbon monoxide and the hydrogen.
15. The method of claim 14, wherein the gas precursor is syngas.
16. The method of claim 14 or 15, wherein the UVC radiation has a wavelength of about 254 nm.
17. The method of any one of claims 14 to 16, wherein the UVC radiation is emitted by a xenon lamp, a krypton lamp, an excimer xenon lamp, a deuterium hydrogen lamp, or a germicidal lamp.
18. The method of claim 17, wherein the UVC radiation is emitted by a low pressure germicidal lamp.
19. The method of any one of claims 14 to 18, wherein the pressure in the reactor is between about 0.75 and 1.25 atm.
20. The method of any one of claims 14 to 19, wherein the gas precursor is heated at a temperature above room temperature.
21. The method of claim 20, wherein the gas precursor is heated at a temperature between about 20 and about 70°C,
22. The method of any one of claims 14 to 21, wherein the substrate is held at a temperature between about 20 and about 80°C.
23. The method of claim 22, wherein the substrate is held at a temperature between about 20 and about 30°C.
24. The method of claim any one of claims 14 to 23, wherein the hydrogen (H_2) and the carbon dioxide (CO) are present in a H_2/CO ratio varying between about 1/16 to about 4.
25. A coating produced by the method of any one of claims 14 to 24.
26. The coating of claim 25 being hydrophilic.
27. The coating of claim 25 being hydrophobic.

Figure A.1 Calculated contact angle as a function of the pressure in the reactor and the H_2/CO ratio

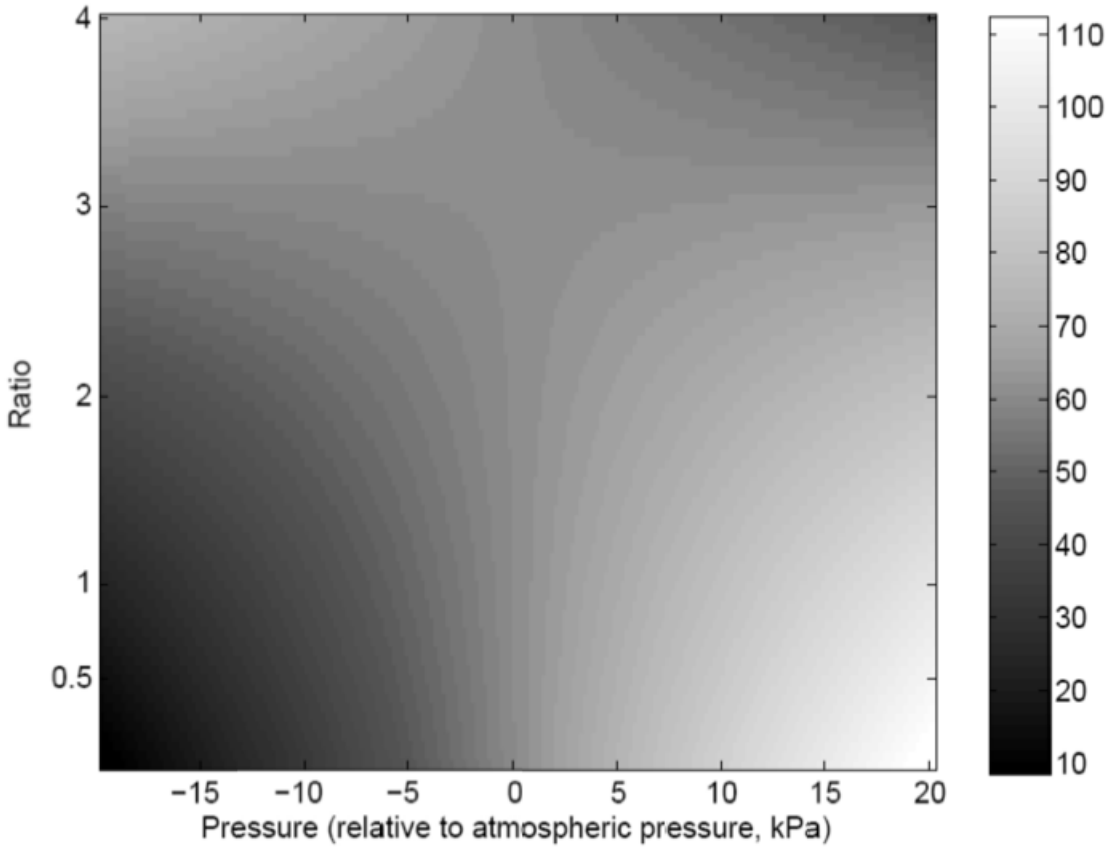

Figure A.2 Schematic of the PICVD setup used

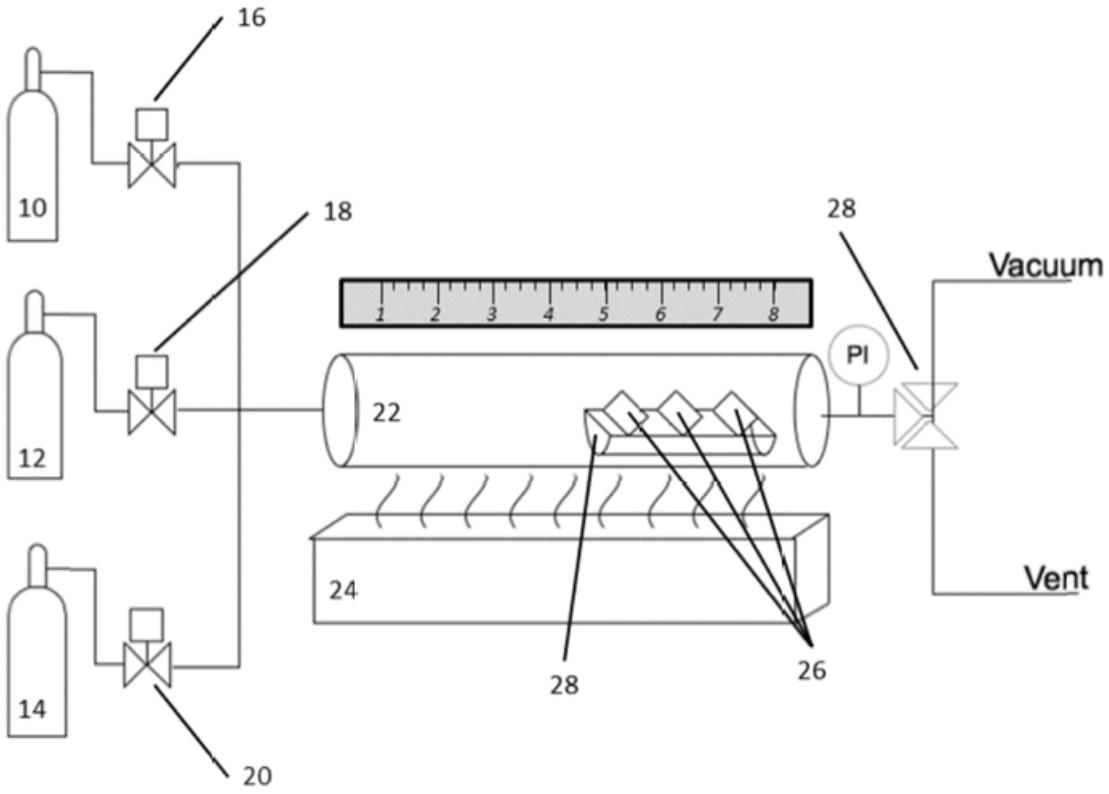

Figure A.3 Influence of the pressure in the reactor on the contact angle

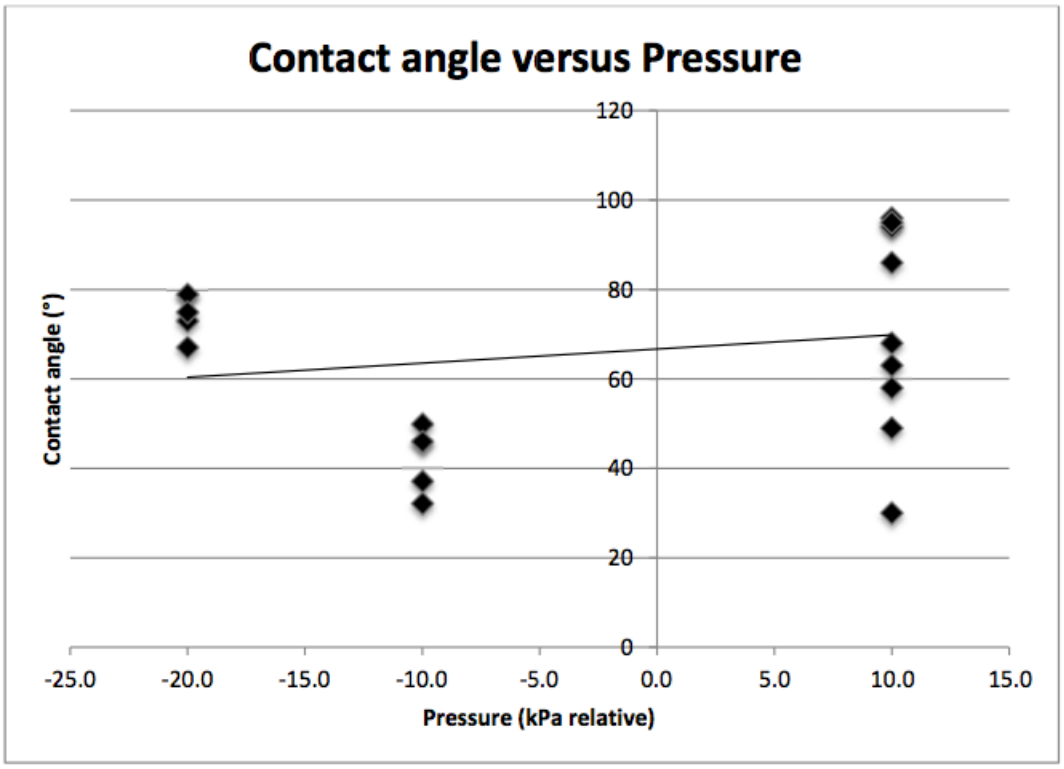

Figure A.4 Contact angle measured as a function of the position in the reactor

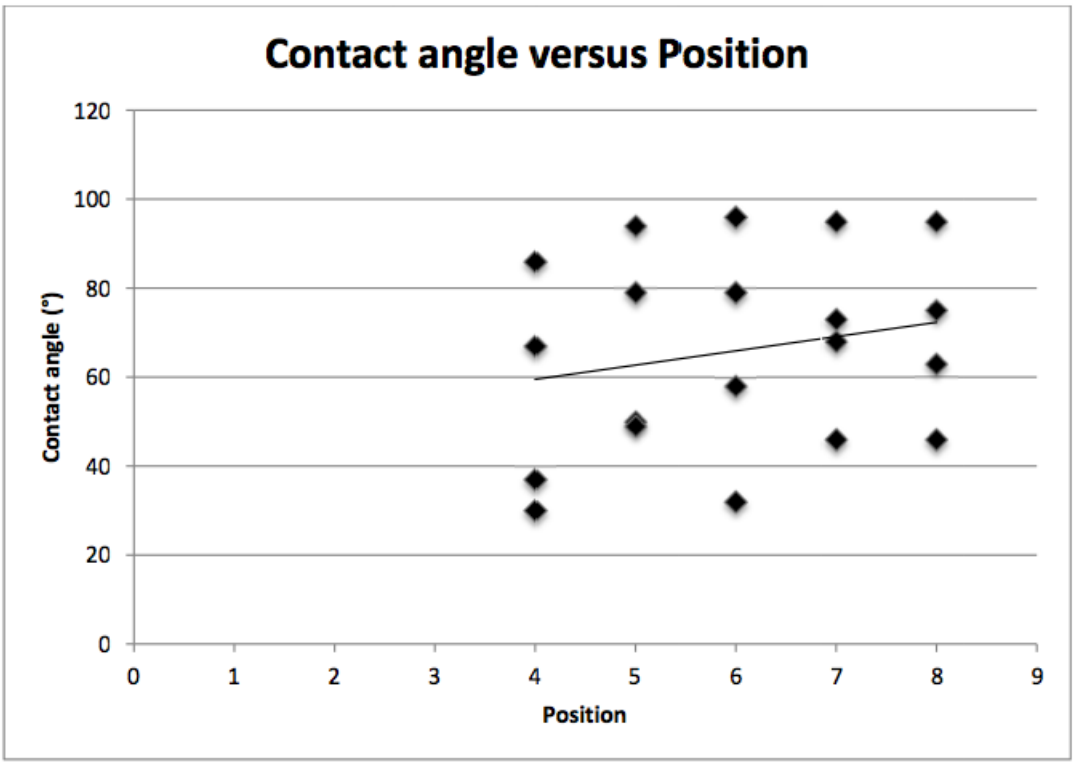

Figure A.5 Contact angle measured as a function of H_2/CO ratio*Pressure

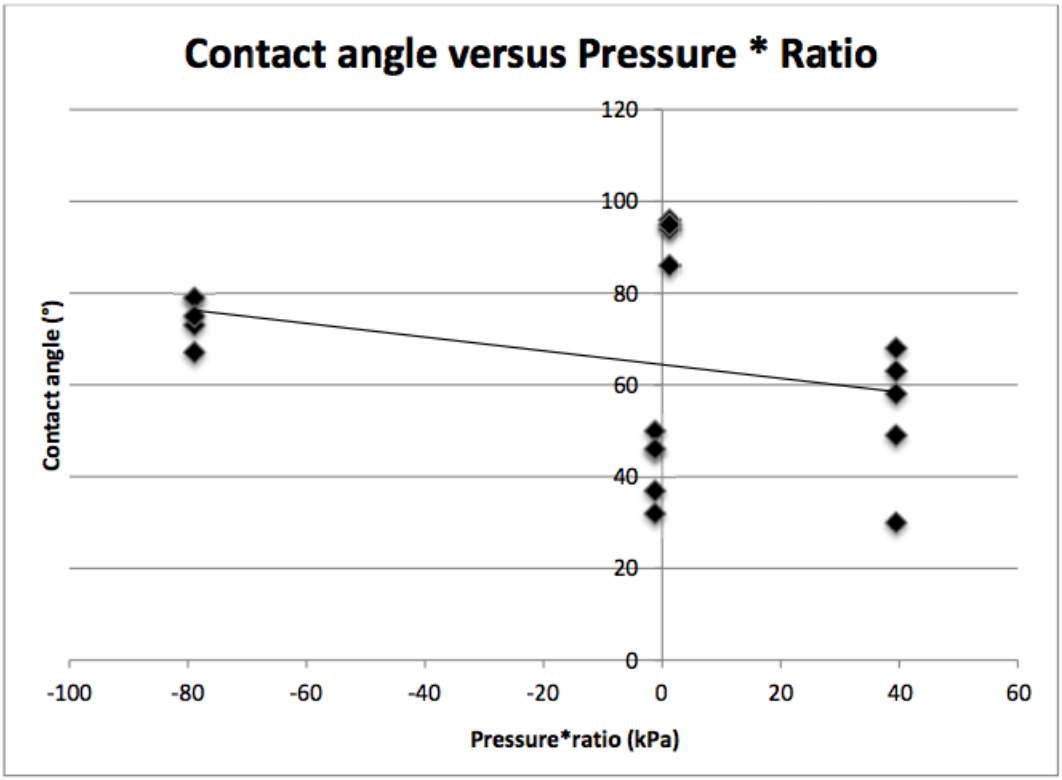

Figure A.6 Contact angle measured as a function of Pressure*Position

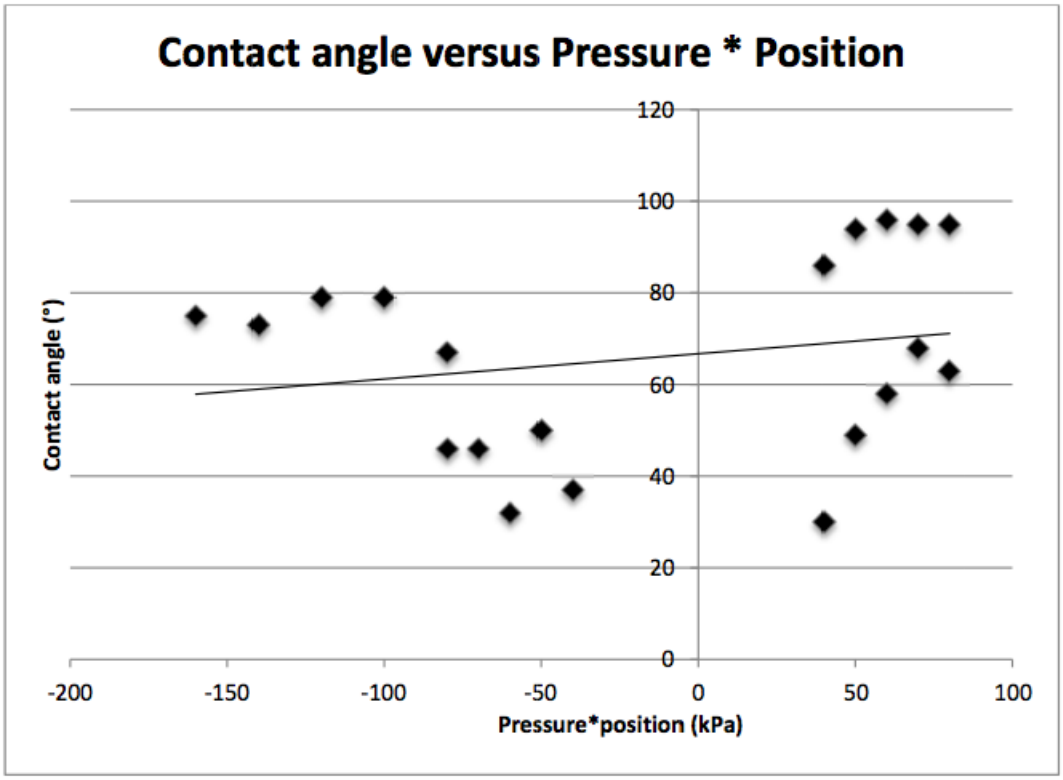

Figure A.7 Hydrophobic coating produced with a H_2/CO Ratio of 1/8, at a pressure 10 kPa above normal pressure

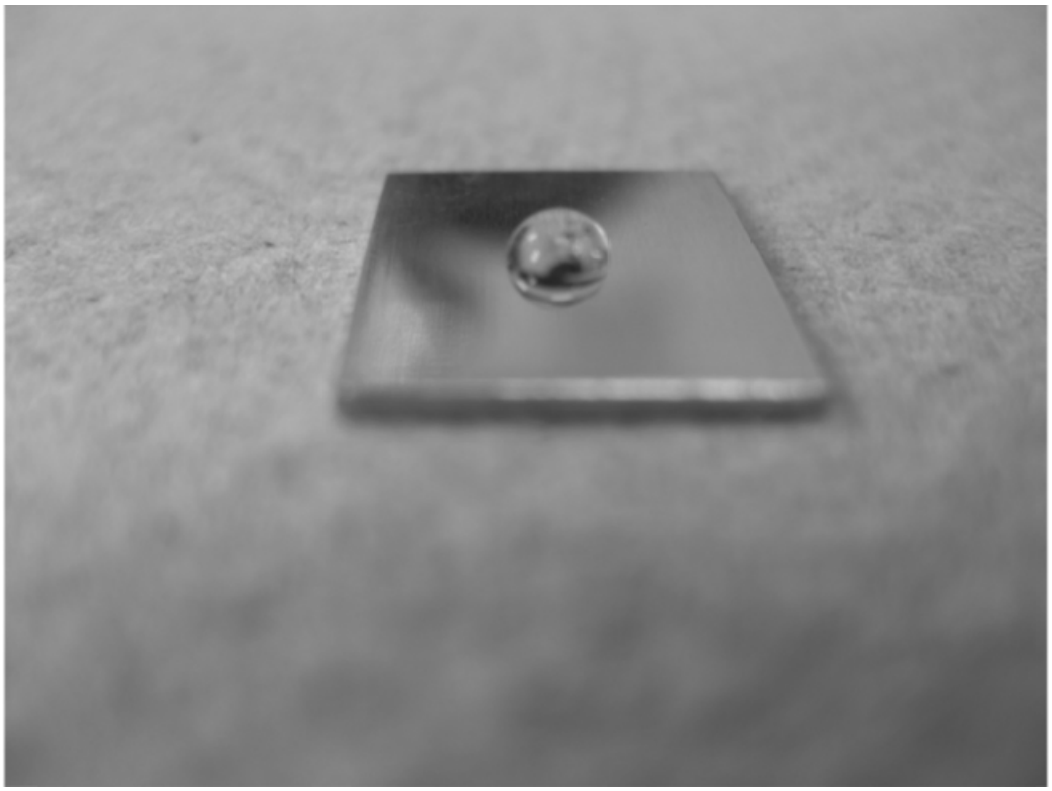

Figure A.8 Hydrophilic coatings produced with a H_2/CO Ratio of 1/8, at a pressure 10 kPa below normal pressure

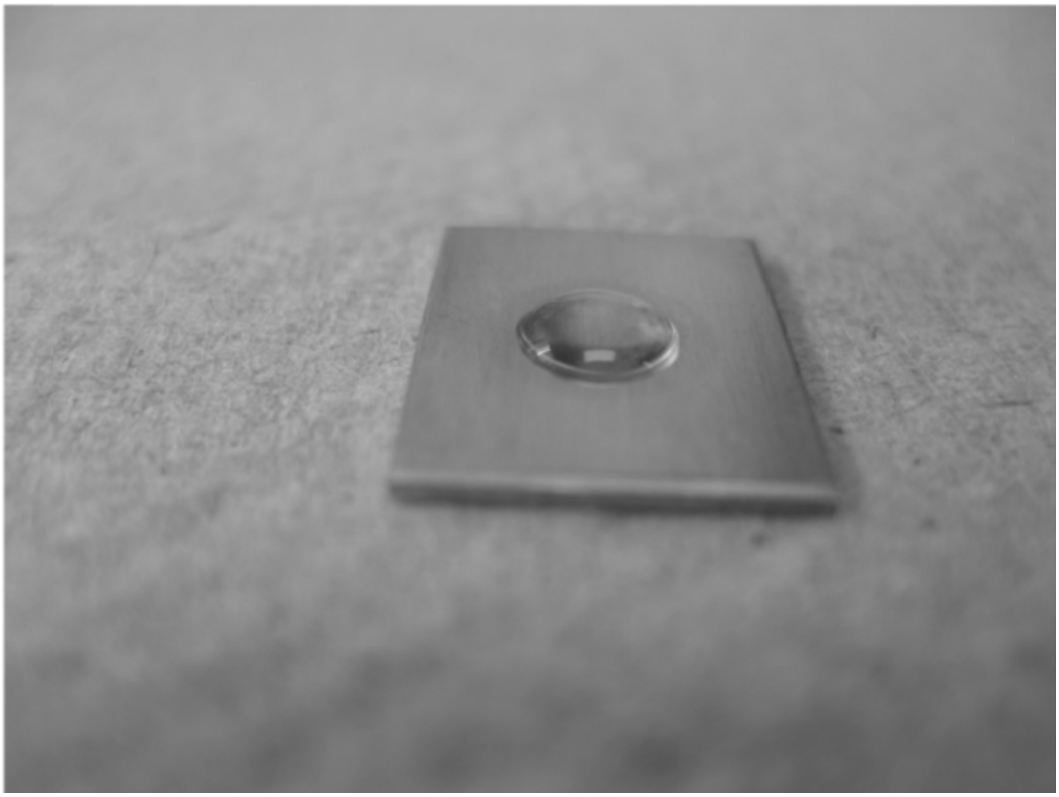

Figure A.9 SEM micrograph of a red spot