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Photo-Initiated Chemical Vapour Deposition as a Scalable Particle Functionalization Technology (A Practical Review)

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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.

Keywords: Photo-Initiated CVD, PhotoCVD, Photopolymerization, Functionalization, Nanoparticles

Nomenclature

CVD Chemical vapour deposition

$HWCVD$ Hot-wire chemical vapour deposition

$(i)CVD$ Initiated chemical vapour deposition

$LCVD$ Luminous chemical vapour deposition

$MLCVD$ Magneto luminous chemical vapour deposition

$MOCVD$ Metalorganic chemical vapour deposition

$(o)CVD$ Oxidative Chemical Vapour Deposition

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$PACVD$ Plasma- or photo-assisted chemical vapour deposition

$PECVD$ Plasma-enhanced chemical vapour deposition

$(pi)CVD/PICVD$ Photo-induced or -initiated chemical vapour deposition

$TACVD$ Thermally-activated chemical vapour deposition

VDP Vapour deposition polymerization

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 [1]; emerging applications can be found in optics [2], biomedicine [3, 4], heat transfer [5], catalysis [6], architecture [7], energy [8], environment [9] and computer science [10]. 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) [5], 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 [11, 12]. 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 reactant 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 [13]. 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

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for applications that require uniform coating thickness at nanoscale level [13]. 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 [14, 15]. 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 [13, 16, 17]. 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 technique 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.

2. Chemical Vapour Deposition (CVD)

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 [13]. 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

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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 [18].

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 [16]. 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.

3.1. Thermally-activated CVD (TACVD)

Thermally-activated CVD is considered as the conventional CVD process [13] 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 1. This specific technique is sometimes called hot wire CVD (HWCVD) [19]. 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 [13]. 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 1 about here.]

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 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 [11, 20], 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 [13, 16] and books [19, 21, 22], 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 [23, 24, 25], 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 [26].

[Figure 2 about here.]

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 [27]. 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 [28, 29]. Figure 3 illustrates the concept of a PICVD system.

[Figure 3 about here.]

4. Diverging terminologies

Surprisingly, many reviews have been published by different research groups, but without referring to each other [13, 16, 19, 30]. 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.

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. [12, 16, 31, 32, 33, 34]. 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) [19, 13]. 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 [16, 31]. Therefore, the concept of classification of techniques based mechanisms will be kept but consolidated with other used terminologies. Table 1 summarizes Gleason's terminology.

[Table 1 about here.]

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 [13]. 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 [13]. A confusion occurs since PACVD can refer to plasma-assisted CVD in some reports [19, 35]. 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 2 summarizes Choy's terminology.

[Table 2 about here.]

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 [36]. Yasuda [19, 21] 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 [37]. Finally, for Yasuda, CVD without additional acronyms means a thermally-assisted CVD in which the heat is coming from the substrate surface. Table 3 summarizes Yasuda's terminology.

[Table 3 about here.]

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.* [38, 39] and Scherzer [40, 41, 42] 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.* [43] has used this technique to achieve the surface functionalization of nanoparticles.

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 4 describes this new terminology system.

[Table 4 about here.]

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 [44], then took the name of photo-CVD on the two following patents on the subject [28, 29]. 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 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 5 shows the equivalence between terms used by each group.

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[Table 5 about here.]

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.* [16, 31, 33].

5. Comparison of techniques

In order to compare and propose different potential solution, 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 6 about here.]

[Table 7 about here.]

Table 6 shows qualitatively and subjectively how each technique respects the previously presented criteria while table 7 summarizes the advantages and disadvantages of each (i)CVD technique. What can be retained of this study are the following statements:

- 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.

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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.

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 [45, 46, 47, 48]. 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.

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) [49] as well as stability of film by spectrometry [20] is quite useful. The critical issues of PECVD demonstrated by Bunshah [35] coupled with the mass transport considerations proposed by Goyal *et al.* [50] and the critical review from Liston *et al.*[51] can be used to assist in reactor design. Moreover, the kinetic and thermodynamic considerations presented by Choy [13] are valid for all CVD techniques. Finally, the optimal characterization techniques developed by Holländer *et al.* [52], Scherzer *et al.* [40, 41] and Khudyakov *et al.* [53] 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 [54]. Extensive work on the subject has been done around the 1940s [55, 56]. Recently, the photochemistry trend has resurrected vividly, often using acrylates or thiolene acrylates as monomers [38, 42, 57, 58, 59, 60, 61, 62, 63, 64]. 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 [65, 66]. While photopolymerization usually refers to UV emission, it has also been accomplished with visible light [30, 67, 68], and even near-infrared light [69], though these cases required the use of photo-initiators (detailed further on). Some reviews have also been published out on the subject [39, 70]. Pargon *et al.* have compared plasma against VUV [71] 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 [55, 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 [58, 59]. The terms sensitizer and photo-initiator have been interchanged for a long time now [55]. 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 [31].

The field of photopolymerization is growing quickly in terms of its knowledge and comprehension. For example, Andrzejewska [72] and Friedrich [17] 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 [47].

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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 [14]. 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.

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.

8. Acknowledgement

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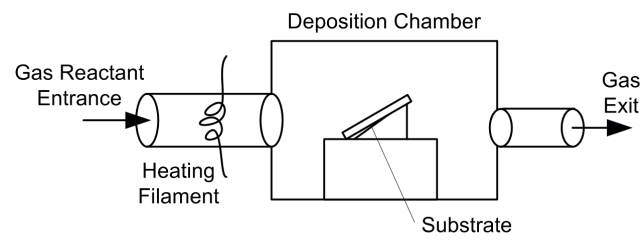
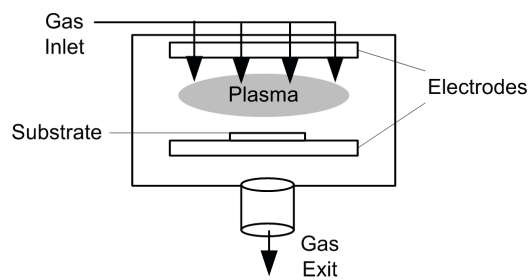## List of Figures

Figure 1: Schematic of a HWCVD setup

Figure 2: Schematic of a PECVD setup
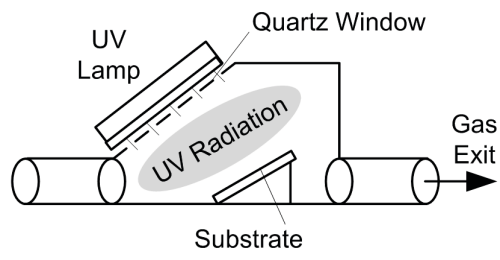
Figure 3: Schematic of a PICVD setup

List of Tables

Table 1: Terminology used by Gleason *et al.*

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

Table 2: Terminology used by Choy

CVD				
CVD	TACVD	PECVD	PACVD	MOCVD

Table 3: Terminology used by Yasuda

TACVD	LCVD			
HWCVD	PP	PACVD	PECVD	MLCVD

Table 4: Terminology used in this paper

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

Table 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

Table 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	[13, 31, 33, 73, 74]
Low capital cost	A	C	A	[13, 16, 31, 32, 48, 74]
Low temperature	C	A	A	[12, 13, 16, 19, 21, 31, 32, 33, 45, 47, 48, 73]
Atmospheric pressure	B	C	A	[12, 13, 16, 19, 21, 31, 32, 45, 48, 73]
Scalability	*B+*	*B-*	*A*	-
Coating quality	A	B	A	[11, 12, 13, 19, 31, 32, 33, 48]
Deposition rate	B	A	B	[11, 13, 21, 31, 33, 48, 73]
Monomer selection	C	A	B	[11, 13, 16, 21, 33]
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 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	[12, 13, 32]
PECVD	High deposition rates Well documented Wide range of monomer usable	Necessity to operate under vacuum High energy consumption Low crosslinking	[11, 13, 19, 21]
PICVD	High crosslinking High control on deposition Can operate at room temperature Can operate at atmosperic pressure	Slower reaction rate than PECVD Gas mixture has to be photosensitive Little work has been done	[16, 45, 46, 47, 48]