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Title:

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Date: 2015

Type: Article de revue / Article

Référence: Vu, T. T. D., Patel, J., Mighri, F., Do, T.-O., & Aji, A. (2015). The effect of TiO₂ surface modification on the photovoltaic properties of hybrid bulk heterojunction solar cells based on MEH-PPV/CdS/TiO₂ active layer. *Green Processing and Synthesis*, 4(2), 79-90. <https://doi.org/10.1515/gps-2014-0092>
Citation:

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Document issued by the official publisher

Titre de la revue: Green Processing and Synthesis (vol. 4, no. 2)
Journal Title:

Maison d'édition: de Gruyter
Publisher:

URL officiel: <https://doi.org/10.1515/gps-2014-0092>
Official URL:

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The effect of TiO₂ surface modification on the photovoltaic properties of hybrid bulk heterojunction solar cells based on MEH-PPV/CdS/TiO₂ active layer

Abstract: In this work, we present the synthesis details of uniform shape and size-controlled titanium dioxide (TiO₂) nanorods followed by the deposition of cadmium sulfide (CdS) quantum dots on their surface. The achieved surfactant-capped-TiO₂ nanorods as well as CdS/TiO₂ nanocomposites were dispersed in nonpolar solvents, which enabled an easy solution blending with poly (2-methoxy, 5-(2-ethyl-hexy-loxy)-p-phenyl vinylene) (MEH-PPV) conjugated polymer to prepare the active layer of bulk heterojunction solar cells (BHJSCs). The properties of the synthesized capped-TiO₂ nanorods, CdS/TiO₂ nanocomposites, as well as those of their corresponding blends with MEH-PPV were characterized using transmission electron microscopy (TEM), thermogravimetric analysis (TGA), UV-Visible spectroscopy, and photoluminescence (PL) technique. The characterization of the effect of the surfactants (oleic acid, OA, olyamine, OM, and 6-aminohexanoic acid, 6AHA) left on TiO₂ surface and CdS surface modification on BHJSC photovoltaic power conversion efficiency (PCE) showed that: i) for the same surfactants, when CdS was added on the surface of TiO₂ nanorods, the PCE increased due to the higher efficiency of CdS compared to MEH-PPV; and ii) the best PEC was obtained with CdS/

OA-6AHA-capped-TiO₂ nanocomposite due to the shortest length of the carbon-chain of 6AHA, leading to higher charge carrier mobility.

Keywords: bulk heterojunction solar cell; cadmium sulfide; nanocomposite; titanium dioxide.

DOI 10.1515/gps-2014-0092

Received November 12, 2014; accepted December 17, 2014; previously published online February 2, 2015

1 Introduction

Over the last decade, hybrid bulk heterojunction solar cells (BHJSC) using soluble conjugated polymers and inorganic nanoparticles have become attractive for use as large area, physically flexible and low-cost solar cells [1–3]. Conjugated polymers can exhibit both electronic and optical properties, and they are well known for their mechanical properties and intrinsic processing advantages, which makes the fabrication of BHJSCs easy, leading to a low manufacturing cost. However, conjugated polymers have low mobility of charge carriers, particularly electrons, which results in insufficient charge generation and transportation. Therefore, the introduction of inorganic nanomaterials into polymer matrix would further increase the performance and the efficiency of the organic solar cell by using the high electron mobility of the inorganic phase. Currently, the most common conjugated polymers used as hole transporting materials in solar cells are 2-methoxy, 5-(2-ethyl-hexy-loxy)-p-phenyl vinylene) (MEH-PPV) [4–7], poly (3-hexylthiophene) (P3HT) [8, 9], and poly (2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV) [9]; while different types of inorganic nanoparticles and nanoparticle systems such as CdS [4], CdTe [7, 10], CdSe [11, 12], ZnO [13–15], TiO₂ [16–18], CdSe-CdTe [19], PbS/TiO₂ [20] have been reported.

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Due to the difference of electrical and optical properties of the two materials, the photogenerated excitons can diffuse to the interface between the conjugated polymer and the inorganic nanomaterials, but the charge transportation through the nanocrystalline network can be strongly affected by surface defects and adsorbed species on nanocrystals surface, which acts as surface traps. Therefore, these traps can affect the mobility of charge carriers and probably can cause their recombination, thus affecting the power efficiency conversion (PEC) of the solar cells. Therefore, by controlling the particle crystallinity as well as their surface properties, we could help to enhance the PEC of BHJSCs.

In this work, we present an original low temperature solvothermal synthesis process recently developed in our lab to synthesize surfactant-capped-TiO₂ nanorods using different capping surfactants. The shape and size of these TiO₂ nanorods were adequately controlled and optimized in nano-scale range for BHJSC application, which is considered as a first original idea. We also propose an original two-step-synthesis process to deposit CdS nanoparticles on the surface of the synthesized TiO₂ nanorods to obtain CdS/TiO₂ collide systems of high absorption properties in the visible light region, which is needed for photovoltaic applications. As a final step, both capped-TiO₂ nanorods and CdS/TiO₂ nanocomposites were separately blended with MEH-PPV polymer. The blend solution was used as a new route to develop the active layer of BHJSC prototypes by using the spin-coating method at room temperature. The photovoltaic properties of these prototypes were then characterized and the effect of TiO₂ surface modification on these properties was studied.

2 Materials and methods

2.1 Materials

Commercially titanium (IV) butoxide (TB, 97%), oleic acid (OA, 90%), oleyl amine (OM, 70%), 6-aminohexanoic acid (6AHA), cadmium acetate dehydrate, thioamide, nitrosonium tetrafluoroborate solution (NOBF₄), 2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene (MEH-PPV) with the average molecular weight of 150,000–250,000, and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) were purchased from Sigma-Aldrich Chemical, Oakville, ON, Canada. Indium-tin-oxide (ITO) glass substrate 25×25 mm was purchased from Delta Technologies, Loveland, CO, USA. Absolute (pure) ethanol (EtOH), from Commercial Alcohols Inc., Brampton, ON, Canada, N,N-dimethylformamide (DMF), dichloromethane, dichlorobenzyl, and hexane, from Fisher Scientific, Ottawa, ON, Canada, and toluene, from Anachemia, Lachine, QC, Canada, were all of analytical grade. All chemicals were used as received without further purification or distillation.

2.2 Synthesis of OA and OM or 6AHA capped TiO₂ nanorods

OA, OM or 6AHA capped anatase TiO₂ nanorods were synthesized at low temperature by the hydrolysis of TB using OA and OM or 6AHA as surfactants followed by the steps that we already described in our previous work [21, 22]. Typically, 1 mmol of TB was added to a mixture of 7 mmol of OA, 3 mmol of OM or 6AHA, and EtOH. The system was then heated at 140°C for 18 h. The resulting TiO₂ nanocrystals were washed with toluene and EtOH 95% several times then dried at room temperature.

2.3 Synthesis of CdS modified TiO₂ nanorods

It is important to mention that the use of surfactants during the synthesis of TiO₂ nanorods results in the presence of capping molecules on the surface of these nanorods. These capping molecules create an insulating barrier around each nanorod and block the access to its surface. Therefore, in order to deposit CdS nanoparticles on the surface of TiO₂ nanorods, the latter must undergo a surface treatment, typically by replacing the original ligands with specifically designed species through a ligand-exchange process. For this, NOBF₄ was used in our study. This strategy helps to enable sequential surface modification of TiO₂ nanorods without affecting their size and shape, and also to increase the access to their surface.

Basically, surfactants-capped-TiO₂ nanorods dispersed in hexane solvent were added into 5 ml of dichloromethane solution of NOBF₄ (0.01 M). The mixture was well shaken; the precipitation of TiO₂ nanorods was then observed just after few minutes. Precipitated nanorods were collected then washed by using a mixture of toluene and EtOH 95%.

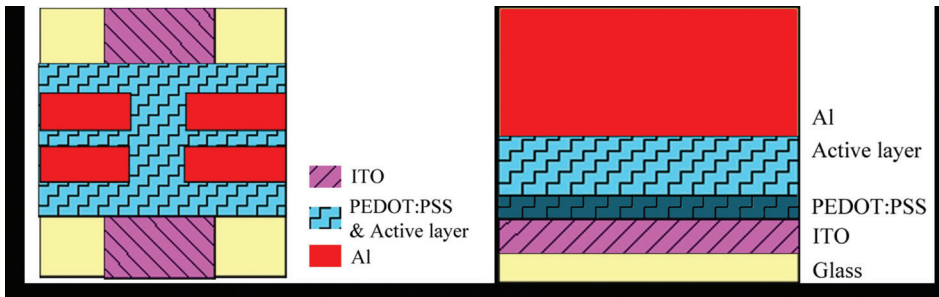
As a final step, 4.5 mmol of the above treated TiO₂ nanorods were dispersed in 10 ml of DMF and 9 mmol of cadmium acetate dihydrate then stirred under room temperature for 2 h. Subsequently, 9 mmol of thioamide were added to the mixture and let under stirring overnight. The precipitated CdS/TiO₂ nanocrystals were washed few times using toluene and EtOH 95%, and then collected by centrifugation.

2.4 Preparation of MEH-PPV/capped-TiO₂ and MEH-PPV/CdS/TiO₂ blend solutions

Mixtures of MEH-PPV and TiO₂ or CdS/TiO₂ were prepared by solution blending in dichlorobenzyl solvent with a mole ratio MEH-PPV:TiO₂ or MEH-PPV:CdS/TiO₂ of 1:3. The blend solutions were continuously stirred overnight under dark. Ultrasonic agitation was applied to disperse nanoparticle agglomerates in the solvent and to ensure dispersion homogeneity.

2.5 Fabrication of BHJSC devices

The fabrication process consisted in developing a sandwich structure, as shown in Scheme 1, composed of i) ITO/PEDOT:PSS anode, ii) MEH-PPV/CdS/TiO₂ nanocomposite active layer, and iii) aluminum cathode [23]. A 25×25 mm ITO glass substrate with a sheet resistance of 15 Ω/



Scheme 1 Architecture scheme of a BHJSC device.

square was ultrasonically cleaned with soap, followed by acetone then isopropanol solvents. A thin layer of PEDOT:PSS was then spin-coated on the cleaned ITO glass substrate, then baked at 80°C for 5 min to remove any possible contamination. Being a highly hole-conducting metal-like polymer, PEDOT:PSS eases the conduction of holes from the active layer to the ITO layer by lowering the intrinsic energetic barrier between the ITO work function and the highest occupied molecular orbital (HOMO) of the active material. So this layer acts as a semi-permeable membrane for holes only and blocks the extraction of electrons on the ITO side. Therefore, PEDOT:PSS layer helps to reduce electron-hole recombination phenomena. In addition, it also allows ITO surface smoothing, which is usually quite rough, and hence reduces the risks of shortcuts within the BHJSC. The composite CdS/TiO₂/MEH-PPV solution already prepared, which constitutes the active layer, was then deposited over the PEDOT:PSS layer by the same spin-coating technique. Finally, four aluminum cathode layers (700 Å in thickness) were then thermally evaporated in a vacuum chamber at a pressure below 3×10^{-4} Pa. The final device is then composed of four heterojunction cells with individual active area of 0.24 cm².

2.6 Characterization

Powder X-ray diffraction (XRD) characterization was done using a Bruker SMART APEXII X-ray diffractometer equipped with a Cu K α radiation source ($\lambda=1.5418$ Å) in the 2θ range of 5–20° at a scan rate of 1.0°/min. All samples were dried at 65°C overnight to eliminate guest solvent molecules on the surface of particles before the XRD scan. Fourier transform infrared (FTIR) characterization was done using a FTS 45 infrared spectrophotometer in the spectral range of 4000–400 cm⁻¹. The characterization was done at room temperature using atmosphere as background. The thermal characterization of the developed TiO₂ nanorods, CdS nanoparticles and hybrid CdS/TiO₂ nanocomposites was carried out at a heating rate of 10°C/min up to 900°C under an oxygen flow using a Perkin-Elmer TGA thermogravimetric analyzer (TGA). The UV-visible spectra of the developed nanostructures were recorded on powder samples using a Cary 300 Bio UV-visible spectrophotometer; pure toluene was used as a blank. Room temperature photoluminescence (PL) characterization was done by using an optical spectrum analyzer (ANDO AQ6317, Japan). Electronic transport in the BHJSC device was studied via current density-voltage (I-V) characterization using a 2400 Keithley source meter. The voltage was varied from -0.5 to 2.0 V. I-V curves were taken both in the dark and under white illumination provided by a halogen source through the ITO electrode.

3 Results and discussion

3.1 Analysis of synthesized capped-TiO₂ nanorods

3.1.1 Transmission electron microscopy characterization

Figure 1A and B show representative transmission electron microscopy (TEM) images of the as-synthesized TiO₂ nanoparticles using respectively OA/OM and OA/6AHA as surfactant combinations. In both cases, the shape of TiO₂ nanoparticles was in the form of nanorods of 4–5 nm in diameter and 20–40 nm in length. The morphologies of TiO₂ nanoparticles were closely controlled by the presence of OA/OM and OA/6AHA surfactants. According to the literature, these surfactants play important roles during the hydrolysis process as they generate water resulting from the acid-base pair catalyst. The more water they generate, the faster the hydrolysis process, leading to larger nanoparticle dimensions. Besides, the presence of surfactant lowers the surface tension, which allows particles to grow further in the surfactant direction. For the case of the addition of TB precursors into the reaction solution, the early formation of TiO₂ truncated octahedral bi-pyramid seeds were expected. These seeds terminated by {001} faces, which have high surface energy, and {101} faces with relative low energy. When the hydrolysis process increases, the final shape of TiO₂ nanoparticles is more controlled by the competition between the relative surface energies of the {001} and {101} faces and, therefore, the growth rate ratio between [001] and [101] directions [21, 24–26]. Hence, with the utilization of OA surfactant, which is more likely to bind strongly to TiO₂ {001} faces, and amines like OM or 6AHA that weakly bind on {101} faces, this leads to a more progressive TiO₂ growth along [001] direction than along [101] direction. Therefore, this oriented growth leads to TiO₂ nanorods instead of TiO₂ nanospheres or nanorhombics, as presented in our previous work [21].

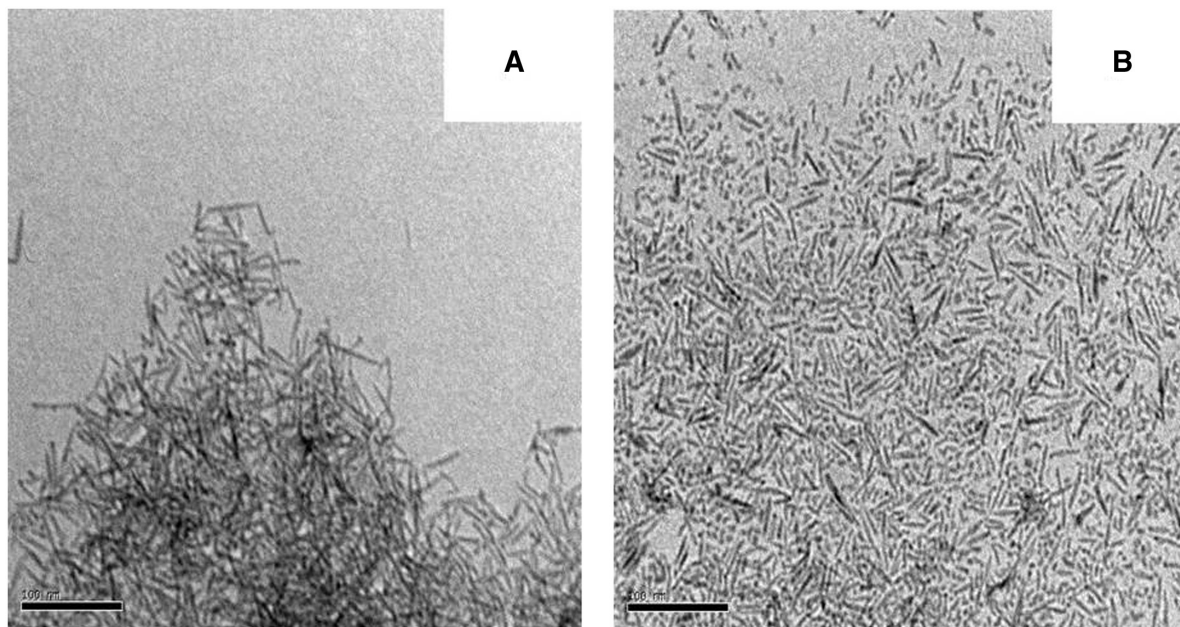


Figure 1 TEM of TiO₂ nanorods synthesized using (A) OA/OM, and (B) OA/6AHA surfactants combinations.

3.1.2 XRD and FTIR characterizations

Figure 2 shows XRD spectra of OA/OM-capped-TiO₂ and OA/6AHA-capped-TiO₂ nanoparticles. Both spectra show strong diffraction peaks at 25° and 48°, indicating TiO₂ anatase phase with typical anisotropic growth pattern along the [001] direction [Joint Committee on Powder Diffraction Standards (JCPDS) no: 88-1175 a-nd 84-1286].

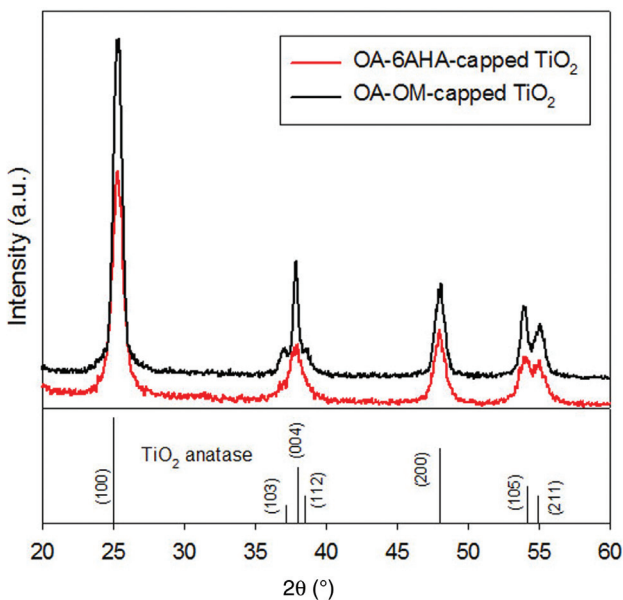


Figure 2 Powder XRD patterns of OA-OM-capped-TiO₂ and OA-6AHA-capped-TiO₂ nanoparticles.

In order to understand the surface properties of TiO₂ nanorods, FTIR characterization was carried out. The FTIR of pure OA, OM, and 6AHA surfactants were also analyzed for comparison. The corresponding results are shown in Figure 3. The FTIR bands at 2850–2920 cm⁻¹ are attributed to the asymmetric and symmetric C–H stretching vibrations of methylene groups, the vibration at 1465 cm⁻¹ is a characteristic of -(CH₂)_n- chains with n>3, the small peaks at 3004 cm⁻¹ correspond to the stretching of =C-H bond [27–29]. Furthermore, it was observed that the vibration bands at 1710 and 1285 cm⁻¹, which are the characteristic bands of carbonyl -C=O- and -C-O- stretch in the carboxyl

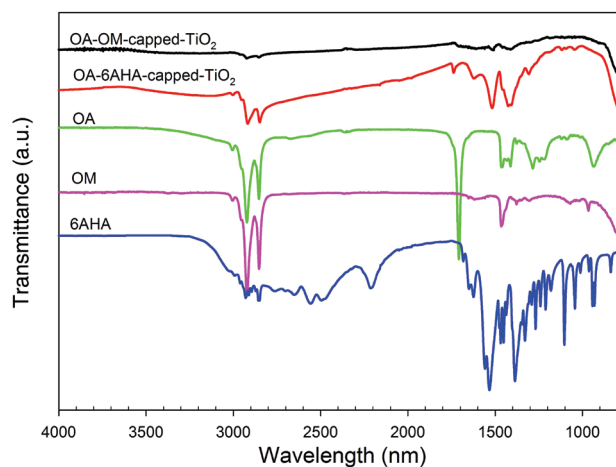


Figure 3 FTIR spectra of OA-OM-capped-TiO₂ (A1), OA-6AHA-capped-TiO₂ (A2) nanoparticles, pure OA, OM, and 6AHA.

acid of OA, appear weak on the spectrum (A2) of OA-6AHA-capped-TiO₂ nanoparticles and that of OA-OM-capped-TiO₂ nanoparticles (A1). This indicates in both cases the chemisorptions of OA onto the surface of TiO₂ nanorods [30]. However, the intensities of those absorption bands are all reduced compared to the absorption bands of pure OA, OM and 6AHA. This is due to the fact that only small amounts of surfactants are expected to be left on the surface of TiO₂ nanoparticles. Also, the FTIR spectrum (A1) of OA-OM-capped-TiO₂ nanoparticles shows a vibration band at 1379 cm⁻¹, which is identical to that observed on the FTIR spectrum of pure OM [31]. This indicates the presence of OM on the surface of OA-OM-capped-TiO₂ nanoparticles. A close look to the spectrum shows two peaks at 1536 and 1560 cm⁻¹ corresponding to the symmetric and asymmetric stretching vibrations of uncoordinated -COO- group [32]. These two peaks are observed to be absent on the spectrum (A2) of OA-6AHA-capped-TiO₂ nanoparticles. The latter spectrum also shows a band at 1386 cm⁻¹ corresponding to C-N stretching mode of AHA molecules, and two vibration peaks at 1622 and 1506 cm⁻¹, which are anti-symmetric and symmetric deformation peaks of NH₃⁺. These results prove the binding of amino groups on the surface of TiO₂ nanorods and show that i) only the amino (-NH₂) group of AHA molecules capped on the surface of TiO₂ nanorods and ii) the free carboxylic (-COOH) terminus was oriented outward [33]. Finally, the broad band at around 3000 to 3600 cm⁻¹ is due to the presence of adsorbed water on surface of the sample. This band also appears on spectrum (A1) of OA-OM-capped-TiO₂ nanoparticles but with a lower intensity, which is an indication that the amount of water on OA-OM-capped-TiO₂ was less than that on OA-6AHA-capped-TiO₂. This will also be confirmed in by TGA characterization presented in the following section.

3.1.3 TGA characterization

TGA curves of capped-TiO₂ nanorods, obtained at a heating rate of 10°C/min under O₂ atmosphere, are shown in Figure 4. For both surfactants combinations, an initial weight loss starting from 50°C was observed. The most significant weight loss occurred between 200 and 480°C, which is a clear indication of the presence of surfactants OA/OM and OA/6AHA surfactants on the surface of TiO₂ nanorods. For higher temperatures (>480°C), the small weight loss is attributed to the decomposition of residual product traces that forms a sheath over the TiO₂ nanoparticles [34]. By calculating the weight loss difference from 200 to 480°C, the weight proportions of OA/OM and OA/6AHA surfactants were around 9% and 16%, respectively. These

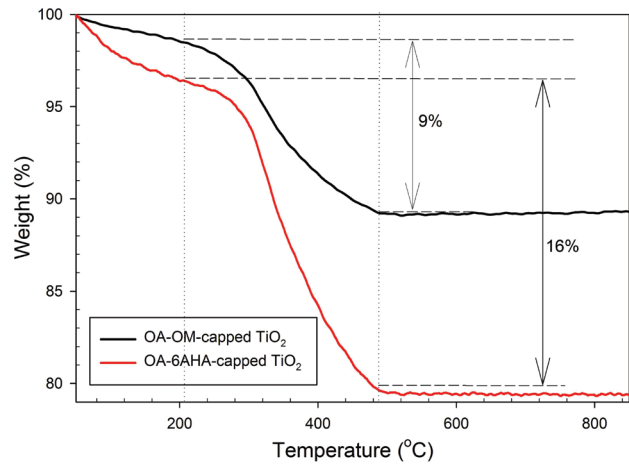


Figure 4 TGA spectra of OA-OM-capped-TiO₂ nanoparticles (A1) and OA-6AHA-capped-TiO₂ nanoparticles (heating rate: 10°C/min, O₂ atmosphere).

results are all in agreement with those already obtained in our previous work [21]. In addition, according to the TGA spectrum, the amount of water absorbed on the surface of TiO₂ nanoparticles, which was already observed above by FTIR characterization, was around 1.4% for OA-OM-capped-TiO₂ and 3.5% OA-6AHA-capped-TiO₂.

3.1.4 UV-vis characterization

The UV-vis absorption spectra of both OA/OM and OA/6AHA surfactant-capped-TiO₂ nanorods are shown in Figure 5. As shown, their corresponding absorption band edges were around 370 and 380 nm, which are approximately similar to the gap energy of bulk anatase

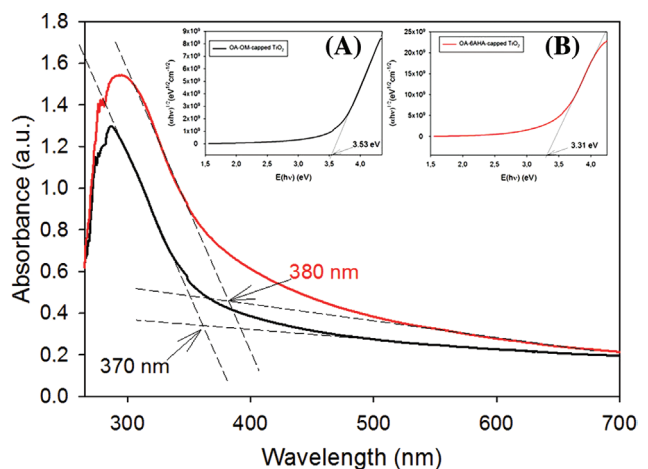


Figure 5 UV-vis characterization of capped-TiO₂ nanoparticles (A) OA-OM-capped-TiO₂, (B) OA-6AHA-capped-TiO₂. The insets show their respective band gap energy plots.

TiO₂ (385 nm). It is important to mention that, for small TiO₂ nanoparticles (size <20 nm), Ti atoms at the surface of the nanoparticles adjust their coordination environment (compression of the Ti-O bond) in order to accommodate the curvature of the nanoparticles [35]. Then, the hybrid localized defect sites could enhance the selective reactivity of TiO₂ nanoparticles towards bidentate ligands binding. As a consequence, the chelation of Ti atoms on the surface with electron donating bidentate ligands changes the electronic properties of TiO₂ nanoparticles. Then, the absorption of light by the charge-transfer complex yields to the excitation of electrons from the chelating ligand directly into the conduction band of these nanoparticles [36]. By using different surfactants during the synthesis process, different capping ligands were observed to bind on the surface of TiO₂ nanoparticles, which results in different charge-transfer processes from the chelating ligand into the conduction band for the different types of TiO₂ nanoparticles. Therefore, a red shift of the UV-vis absorption spectra is expected for both OA/OM and OA/6AHA surfactant-capped-TiO₂ nanoparticles. Hence, UV-vis spectra show that the charge transportation is better for OA-6AHA-capped-TiO₂ nanoparticles than for OA-OM-capped-TiO₂ nanoparticles. The energy band gap was evaluated from the following Tauc relation:

$$(\alpha h\nu)^{1/2} \sim E_g - h\nu \quad (1)$$

where α (cm⁻¹) is the absorption coefficient, h (J.s) is the Plank constant, ν (Hz) is the frequency of radiation, and E_g (eV) is the energy band gap for direct band gap semiconductor. By drawing the tangent line on the linear part of the curve $(\alpha h\nu)^{1/2}$ versus the photon energy, $h\nu$, the intercept of this line with the photon energy axis gives the value of E_g (see the insets of Figure 5) [37]. Based on that, the energy band gaps for OA-OM-capped-TiO₂ and OA-6AHA-capped-TiO₂ nanoparticles were respectively 3.53 and 3.31 eV.

3.2 Analysis of the synthesized CdS modified TiO₂ nanorods

3.2.1 FTIR characterization

FTIR characterization was done for the CdS/TiO₂ nanocomposite samples in order to analyze their surface properties. Figure 6 shows the corresponding spectra, together with those of pure OA, OM, 6AHA and NOBF₄. As shown, after doing the surface treatment with NOBF₄ and depositing CdS on the surface of TiO₂ nanorods, the essential peak characteristics of -C-H, =C-H, -C=O-, -C-O-,

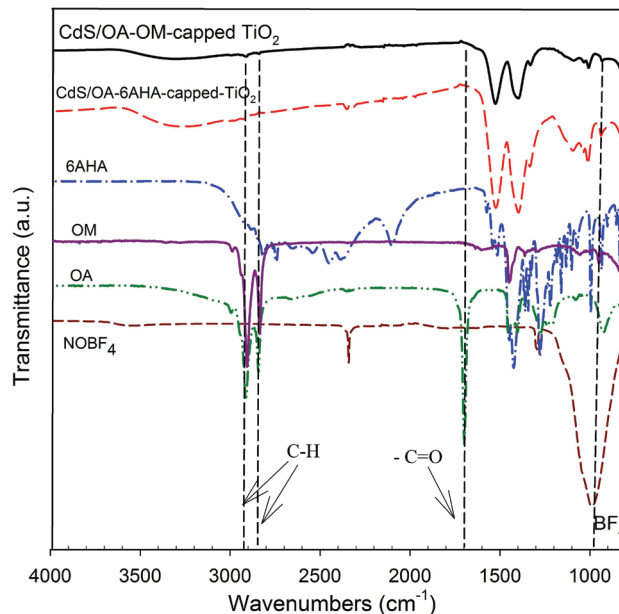


Figure 6 FTIR curves of the two developed CdS/TiO₂ nanocomposites, together with those of pure OA, OM, 6AHA and NOBF₄.

and -NH₂ stretching vibration of the different surfactants either disappeared or appeared very weak. This is an indication that NOBF₄ treatment process was able to remove a big part of OA, OM and 6AHA molecules attached to TiO₂ nanorod surface.

3.2.2 TGA characterization

Figure 7 shows the TGA curves of both CdS/TiO₂ nanocomposites and that of bulk CdS. The weight losses below

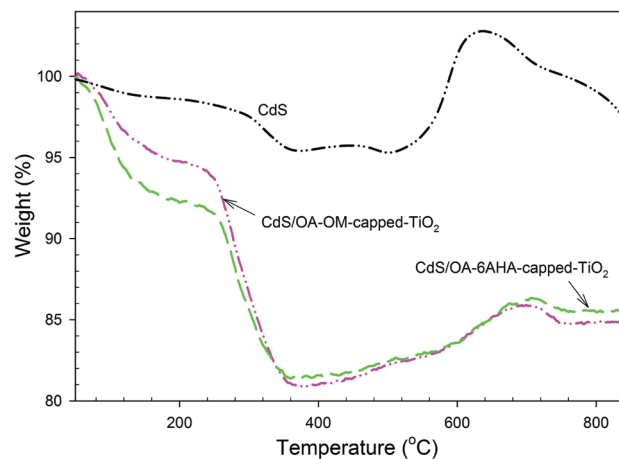


Figure 7 TGA spectra of CdS/OA-OM-capped-TiO₂ (A1) and CdS/OA-6AHA-capped-TiO₂ (A2) (heating rate: 10°C/min, O₂ atmosphere).

200°C were attributed to water absorbed on the surface of the nanocomposites, while the weight losses from 200 to around 400°C were attributed to the loss of OA/OM and OA/6AHA surfactants from the surface of capped-TiO₂ nanoparticles. As seen in the figure, a non-negligible gain in mass was observed between 380 and 750°C for both CdS and CdS/TiO₂ nanocomposites. This surprising gain in mass is due to the formation of cadmium sulphate (CdSO₄), which started at around 380°C for both bulk CdS and CdS/TiO₂ nanocomposites [38]. Moreover, the significant increase in mass at 750°C of CdS alone compared to CdS/TiO₂ could be related to the loading of CdS in these samples.

3.2.3 UV-vis characterization

As reported before, TiO₂ nanoparticles with their characteristic band gap of around 3.2 eV had no absorption band in the visible region. They only show a characteristic absorption spectrum (absorption of Ti-O bond) in ultraviolet light range up to 400 nm. However, as clearly shown in Figure 8, the addition of CdS on the surface of TiO₂ nanorods can effectively shift the absorption range of TiO₂ into visible light region of 400–550 nm due to the narrow band gap of CdS (2.4 eV). Compared to the spectra of CdS and both capped-TiO₂ nanoparticles, the spectra of CdS/TiO₂ nanocomposites are basically a combination of those of CdS and capped-TiO₂, where the absorption bands around 330 nm were from TiO₂, and the broad absorption bands around 530 nm were from CdS. The red shift of absorptions bands of the CdS/TiO₂ nanocomposites were due to the coupling between TiO₂ and CdS. This also leads to the decrease of surface defects

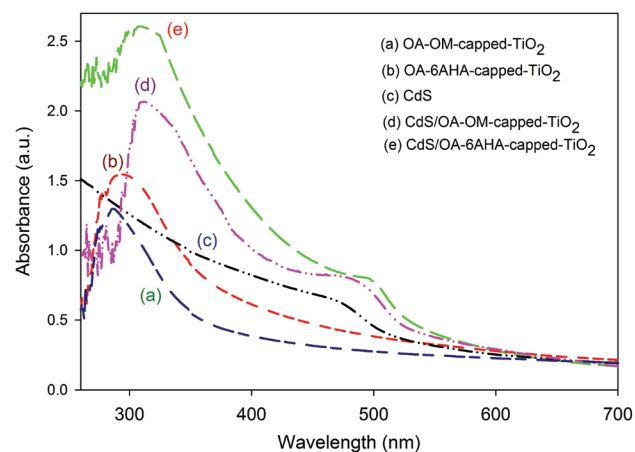


Figure 8 UV-vis characterization of capped-TiO₂ nanoparticles, CdS, and CdS/TiO₂ nanocomposites.

[39]. With these shifts in absorption bands, the light-harvesting efficiencies of CdS/TiO₂ nanocomposites were larger than those of TiO₂ nanoparticles in the visible light region, which is beneficial for the photovoltaic activity. As shown, the highest was observed for CdS/OA-6AHA-capped-TiO₂ nanocomposite.

3.3 Characterization of BHJSCs with active layers based on MEH-PPV/capped-TiO₂ or MEH-PPV/CdS/TiO₂

3.3.1 Scanning electron microscopy characterization

Figure 9 shows the typical scanning electron microscopy cross thickness images of BHJSC devices prepared using different active layer materials (blends A1, A2, S1, and S2). BHJSC whole thickness was around 0.5 μm, which is composed of 70 nm aluminum cathode, 100 nm ITO glass, and around 330 nm of PEDOT:PSS and photoactive layers. The thickness of the photoactive layer plays an important role in the final device efficiency. It should be thick enough to absorb all the maximum incident-light but would not burden the charge transportation. Therefore, a careful optimization of layer thicknesses is necessary to place the maximum of the optical field in the photoactive material and maximize the absorption of incident photons [40, 41].

3.3.2 TGA characterization

The TGA characterization of MEH-PPV/capped-TiO₂ (active layer blends A1, A2) and MEH-PPV/CdS/TiO₂ (active layer blends S1 and S2) are presented in Figure 10. As all the blends of MEH-PPV with TiO₂ nanoparticles or with CdS/TiO₂ were prepared using the blending solution method, in which there is no chemical bonding up between two materials, their corresponding TGA curves are expected to be the combination of those of pure MEH-PPV and TiO₂ nanoparticles and CdS/TiO₂ nanocomposites. As the surfactant-capped-TiO₂ nanorods used in blends A1 and A2 had, respectively, OA/OM and OA/6AHA surfactants on their surfaces, consequently the weight loss difference between the blend A1 (around 18%) and the blend A2 (around 24%) was not far from the weight loss difference between the two surfactant-capped-TiO₂ nanorods themselves (~7%). However, as shown in the figure, the TGA curves corresponding to the blends S1 and S2 show no big loss difference, due to the effective reduced residues of OA, OM and 6AHA molecules on TiO₂ nanorod surface.

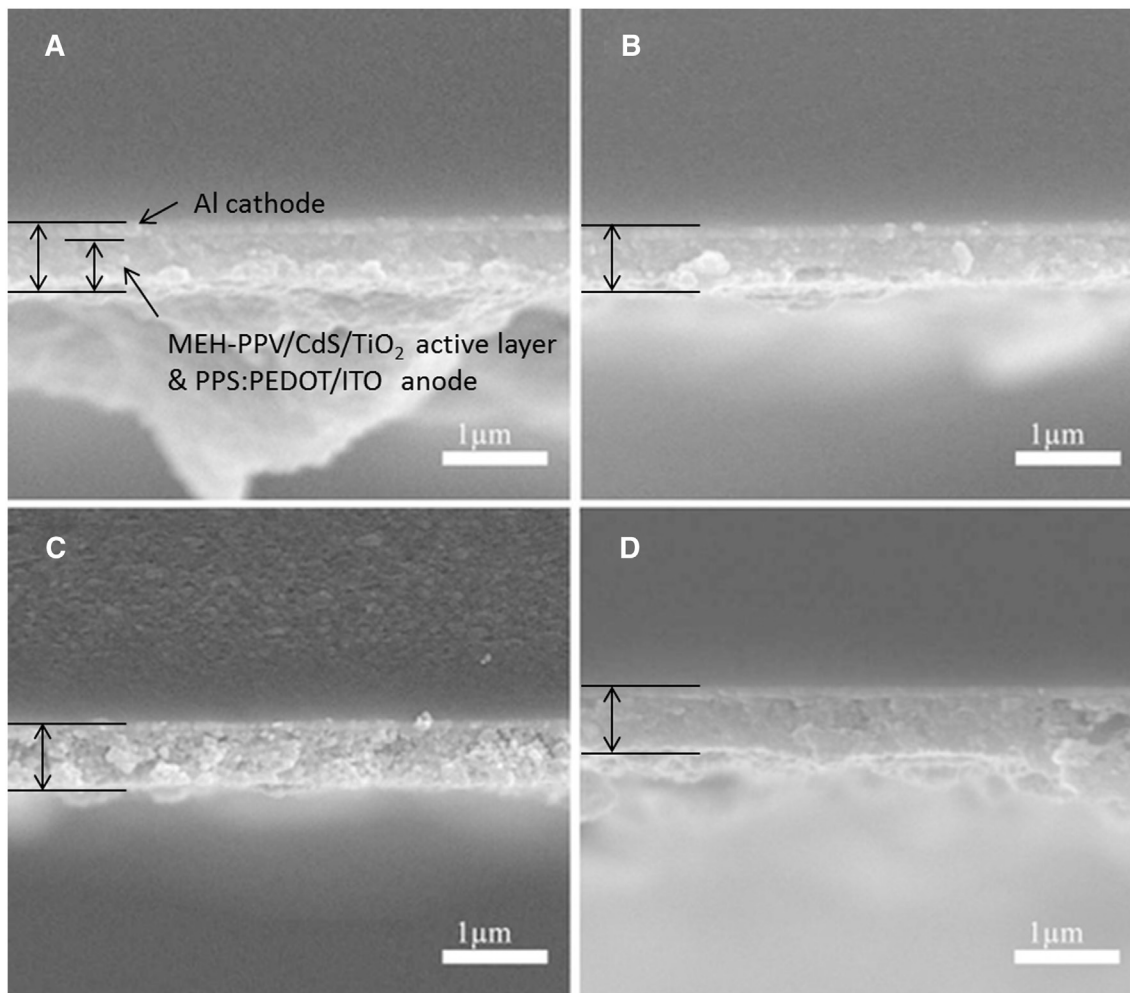


Figure 9 SEM pictures of BHJSC active layer blends: A1 (A), A2 (B), S1 (C), and S2 (D).

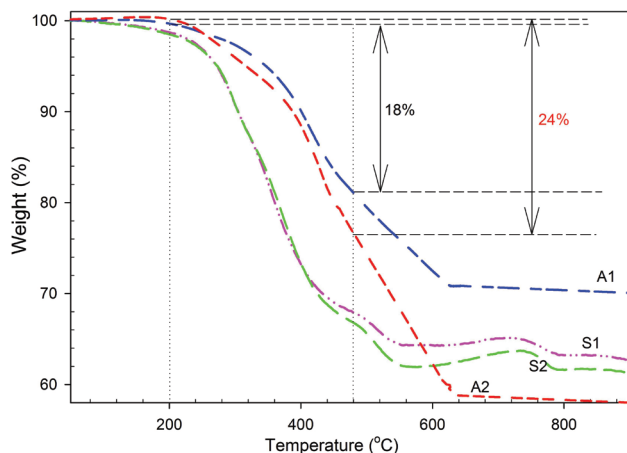


Figure 10 TGA spectra of BHJSC active layer blends A1, A2, and S2 (heating rate: 10°C/min, O₂ atmosphere).

3.3.3 UV-vis characterization

Figure 11 shows the UV-vis spectra of MEH-PPV/capped-TiO₂ (active layer blends A1, A2) and MEH-PPV/CdS/TiO₂ (active layer blends S1 and S2) together with the spectrum of pure MEH-PPV conjugated polymeric matrix. As shown, the UV-vis spectrum of pure MEH-PPV consists of three absorption peaks at ~500, 330 and 240 nm in the region between 220 and 800 nm. These peaks correspond to PPV-derivatives; also, the spectrum shows a sharp onset near 590 nm (2.1 eV). The absorption peak observed near 500 nm (in the visible region) is related to the transition $\pi-\pi^*$ of the MEH-PPV conjugated polymer [6, 42]. The figure shows that this peak remained at approximately the same position when MEH-PPV was blended with

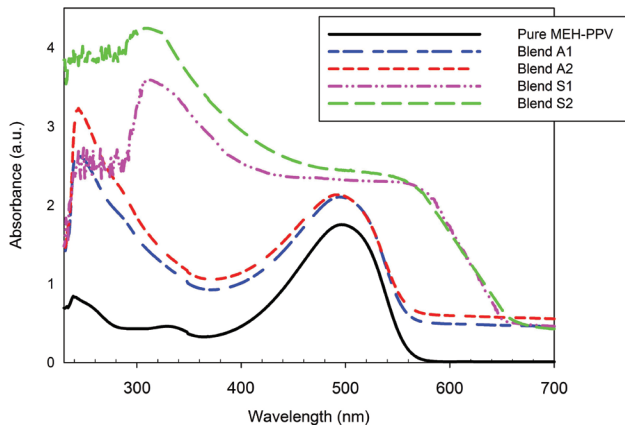


Figure 11 UV-vis of pure MEH-PPV and BHJSC active layer blends A1, A2, S1, and S2.

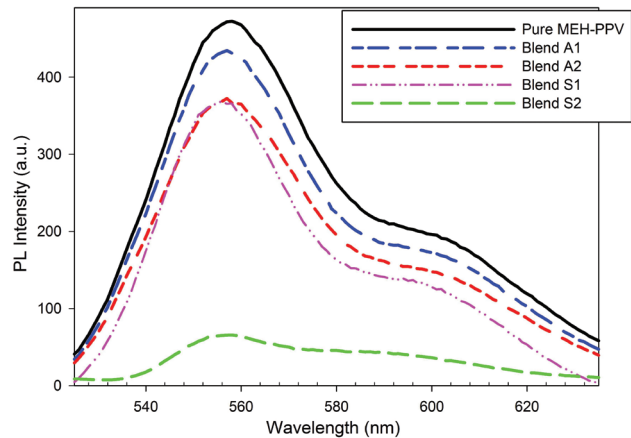


Figure 12 Photoluminescence (PL) of pure MEH-PPV and BHJSC active layer blends A1, A2, S1, and S2.

capped-TiO₂ nanoparticles (blends A1 and A2). However, when MEH-PPV was blended with CdS/TiO₂ nanocomposites (blends S1 and S2), this peak was broadened, red shifted and extended to 525–530 nm range. This is due to the fact that MEH-PPV and CdS/TiO₂ nanocomposites have complementary absorption spectra and light harvesting, while the absorption spectra in the visible region of MEH-PPV/capped-TiO₂ mostly correspond to the absorption of the MEH-PPV matrix [43]. Furthermore, in the region between 300 and 750 nm, all the blends show no new peaks; the absorption is almost the overlap of their pure components, indicating no chemical bonding between the MEH-PPV matrix and capped-TiO₂ nanoparticles or CdS/TiO₂ nanocomposites.

3.3.4 PL characterization

The efficiency of charge trapping and recombination of photo-induced electrons and holes in the developed composites could be verified by the PL characterization. Figure 12 shows the PL emission spectra for pure MEH-PPV, MEH-PPV/TiO₂ (active layer blends A1 and A2), and MEH-PPV/CdS/TiO₂ (active layer blends S1 and S2) in dichlorobenzyl at room temperature under light excitation at a wavelength of 495 nm. It can be observed that a significant quenching of the emission intensity of MEH-PPV occurs with the addition of TiO₂ nanorods or CdS/TiO₂ nanocomposites. According to PL spectra of all the samples, MEH-PPV/CdS/TiO₂ blends exhibited much weaker intensity of peaks than MEH-PPV/capped TiO₂ blends. Though the emission features of the polymer are not affected by the presence of CdS/TiO₂ nanocomposites, the significant quenching in the emission intensity

could be ascribed to the effective charge transfer from MEH-PPV to CdS then to TiO₂ surface, and also to the lower recombination probability of photo-induced electrons and holes in MEH-PPV. In addition, this degree of PL quenching is an indication of how well the nanoparticles are mixed in the polymer and the quality of the interface between the MEH-PPV matrix and the dispersed nanoparticles [44].

It is well known that surfactants are very important to stabilize and control the shape and size of TiO₂ nanorods during the synthesis step. Also, they are very useful to increase the dispersion of particles inside the polymer matrix. However, these useful surfactants could be a major hurdle to the charge transfer between the MEH-PPV matrix and TiO₂ nanorods or CdS/TiO₂ nanocomposites. As shown in Figure 12, the presence of different surfactants capped on the surface of TiO₂ nanorods led to a significant difference in the PL quenching of their corresponding blends. The PL quenching of the blends A2 and S2 were respectively higher than those of the blends A1 and S1. This could be due to the nature of the capping agent itself that affects the efficiency of charge transfer between TiO₂ nanoparticles and also within the nanoparticle itself. In fact, both A1 and S1 blends were based on OA-OM-capped-TiO₂ nanorods, while A2 and S2 blends were based on OA-6AHA-capped-TiO₂ nanorods. Only the surfactant OM (used for A1 and S1 blends) that was replaced by 6AHA for A2 and S2 blends. The main difference between these two surfactants is that the length of the carbon-chain of 6AHA is much shorter than that of OM. It was reported in the literature that carriers' mobility decreases exponentially with increasing ligand length [45]. Hence, the probability for electrons and holes recombination is higher with using OM as surfactant rather than 6AHA due to the lower carrier

mobility, which explains the lower PL quenching of A1 and S1 blends compared to A2 and S2 blends.

3.3.5 Current density-voltage (I-V) characterization of BHJSCs

Figure 13 shows the I-V curves under dark and under 100 mW/cm² (AM 1.5 G) illumination for four different BHJSC devices with the active layer composed of A1, A2, S1 and S2 blends. The corresponding photovoltaic parameters [(open-circuit voltage (V_{oc}), short-circuit current density (I_{sc}), fill factor (FF) and the PCE⁻] are summarized in Table 1. As shown by the insets of both figures, the I-V curves in the dark of all the devices pass through the origin, which is currently reported for heterojunction solar cells.

As mentioned in the literature [46] for an active layer composed of MEH-PPV/TiO₂ blend, due to the fact that the

Table 1 Summary of the photovoltaic parameters of BHJSC devices with active layer blends A1, A2, S1, and S2.

Active layer	V_{oc} (V)	I_{sc} (mA)	FF (%)	PEC (%)
MEH-PPV/OA-OM-capped-TiO ₂ (A1)	0.06	0.19	24.4	0.003
MEH-PPV/OA-6AHA-capped-TiO ₂ (A2)	0.32	0.1	28.0	0.010
MEH-PPV/CdS/OA-OM-capped-TiO ₂ (S1)	0.89	0.16	33.9	0.05
MEH-PPV/CdS/OA-6AHA-capped-TiO ₂ (S2)	0.95	0.36	31.5	0.11

work function of TiO₂ anatase is 5.1 eV, which is closed to the work function of ITO (4.8 eV) and the HOMO of MEH-PPV, the transportation of electron-holes is not effective, leading to a poor PEC. In our case, the first BHJSC device has an active layer composed of MEH-PPV blended with OA-OM-capped-TiO₂ nanorods (blend A1). This device showed a PCE of 0.003%, which is very low. When OM is replaced by 6AHA as surfactant (blend A2), the PCE was tripled. As expected from UV-vis and PL characterizations of the four blends A1, A2, S1 and S2, an increase in V_{oc} , I_{sc} , and PCE could be obtained by using an active layer composed of MEH-PPV blended with the CdS/capped-TiO₂ composite (blends S1 and S2). This increase is due to the higher efficiency of CdS compared to MEH-PPV; so more electrons from MEH-PPV would be able to travel faster to CdS [47]. Therefore, more electrons from the MEH-PPV matrix would be transported to the photoanode via CdS, TiO₂ and ITO. Moreover, the best results were observed with the S2 blend.

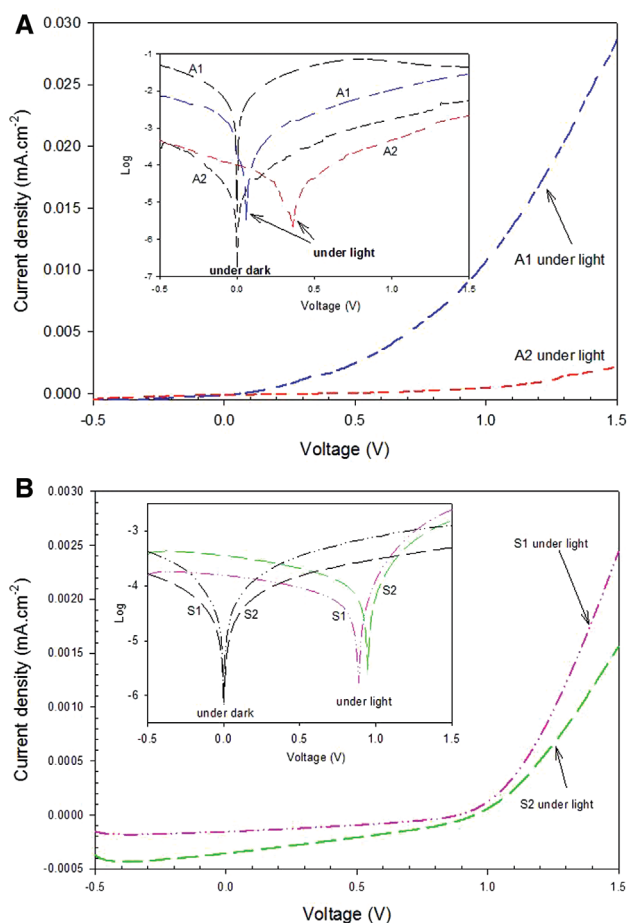


Figure 13 I-V Characterization under light illumination (1.5 AM) of BHJSC devices with the active layer blends (A) A1 and A2, and (B) S1 and S2. The insets are their corresponding log I-V properties in the dark and under light illumination.

4 Conclusion

In summary, the synthesis of TiO₂ nanorods has been proposed using OA, which is more likely to bind strongly to TiO₂ {001} faces, and OM or 6AHA that weakly bind on {101} faces. OA/OM and OA/6AHA combinations led to an oriented TiO₂ growth to form TiO₂ nanorods. The UV-vis characterization of the developed capped-TiO₂ nanorods showed that the charge carrier was better for OA-6AHA-capped-TiO₂ nanorods than for OA-OM-capped-TiO₂ nanorods due to shorter 6AHA chain length, compared to that of OM. Further optimization of the developed TiO₂ nanorods was done by doping CdS nanoparticles on TiO₂ surface. UV-vis characterization of the developed CdS/TiO₂ nanocomposites showed red shift of absorptions bands due to the coupling between TiO₂ and CdS, which is beneficial for their photovoltaic activity. When blended with MEH-PPV conjugated polymer, photoluminescence characterization showed that the developed MEH-PPV/

CdS/TiO₂ blends presented improved the charge transfer from MEH-PPV to TiO₂ surface.

Finally, the same trend was also observed when the MEH-PPV/capped-TiO₂ blends and MEH-PPV/CdS/TiO₂ blends were used as BHJSC active layers. The BHJSC devices made from the latter blends showed greater improvement in their PEC. This improvement is due to the increase of electron mobility thanks to the presence of CdS quantum dots on TiO₂ surface, as mentioned above. Also, the obtained PEC results showed that the combination of OA/6AHA surfactants was better than that of OA/OM.

Acknowledgments: The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work.

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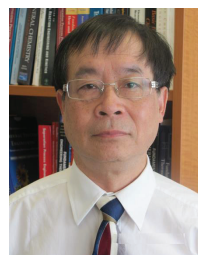
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