Different depositing amount of CuInS$_2$ on TiO$_2$ nanoarrays for polymer/CuInS$_2$–TiO$_2$ solar cells

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**A B S T R A C T**

This paper reports the deposition of CuInS$_2$ on TiO$_2$ nanoarrays, with different depositing amounts and demonstrates the application of TiO$_2$–CuInS$_2$ composites in polymer-based solar cells. The composites of TiO$_2$–CIS1 and TiO$_2$–CIS2 were prepared by the deposition of CuInS$_2$ on TiO$_2$ with one-step or two-step solvothermal reactions, respectively, and characterized by XRD, SEM, TEM, absorption spectrum and PL spectrum. Results showed that TiO$_2$–CIS1 displayed the higher light-harvesting ability and PL quenching efficiency compared to TiO$_2$–CIS2, although less CuInS$_2$ was deposited on TiO$_2$ surface. As a result, polymer/TiO$_2$–CIS1 solar cells displayed much higher $J_{sc}$ correlated with the increased absorptivity and charge separation efficiency, and the higher $V_{oc}$ was originated from the presence of strong interaction between TiO$_2$ and CuInS$_2$ in TiO$_2$–CIS1 resulting in the effective modification of TiO$_2$ surface by CuInS$_2$.

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1. Introduction

Polymer-based solar cells (PSCs) with conjugated polymers as the electron donor (D) and inorganic semiconductor nanocrystals as the electron acceptor (A) in a hybrid bulk heterojunction (BHJ) structure are attractive at large scale and low-cost because they combine the particular properties of inorganic semiconductors and organic conjugated polymers with unique advantages [1,2]. However, device efficiency is still rather lower than that based on conjugated polymer and fullerene derivatives. One of the important factors influencing device efficiency is the morphology of the nanostructured electron acceptor in PSCs because it affects the processes such as light scattering and charge generation, injection and transport [3]. Superior to the commonly disordered A-phase pathways formed in the simple blends of polymer and nanoparticles, the application of vertically aligned nanoarrays (NAs) provides the PSCs with an ideal BHJ architecture [1,4], which can form the high D/A interfacial area for charge generation and the straightforward nanochannels for electron transportation. TiO$_2$ nanoarrays (TiO$_2$–NAs) are cheap, non-toxic and used to enhance light trapping, in particular, they are highly stable in acidic and basic solutions, as a result, they have been used as electron acceptor in polymer-based solar cells [5–8].

However, the efficiency of polymer/TiO$_2$–NAs is not high owe to the narrow absorption spectrum in the existing conjugated polymers [9–11], which is not match with the maximum photon flux of AM 1.5 solar spectrum [1,12]. Previously, dispersion of quantum dots (QDs) with small band gap inorganic semiconductor matrices may offer composites with complementary absorption range in the visible spectrum [13], as the composites incorporating CdSe [14] or CuInS$_2$ [15] QDs into polymer/PC$_{61}$BM devices, or the application of TiO$_2$–NAs modified with Sb$_2$S$_3$, CdSe or PbS QDs in polymer-based solar cells [16], which achieved the improved device performance mainly originated from the increased light-harvesting ability.

Copper indium disulfide (CuInS$_2$) is a promising light-absorbing material for solar cells, due to its small direct band gap of 1.5 eV, large absorption coefficient ($\alpha \sim 10^5$ cm$^{-1}$) and low toxicity [17–19]. Previously, we deposited zincblende CuInS$_2$ QDs onto TiO$_2$–NAs with cysteine as linkage by solvothermal method, to form the heterogeneous TiO$_2$/CuInS$_2$–core/shell NAs, and the core/shell NAs obtained a much higher performance with wide spectra response range compared to pristine TiO$_2$–NAs in polymer-based solar cells [20]. Different from previous paper [20], we deposited CuInS$_2$ on TiO$_2$ directly by solvothermal method, and the depositing amount of CuInS$_2$ was adjusting with one-step or two-step solvothermal reactions, respectively. QDs-sensitized TiO$_2$–NAs with different CuInS$_2$ crystallization behavior during one-step or two-step solvothermal reactions were obtained. Moreover, the variety in CuInS$_2$ crystallization behavior impacts the qualitative change in device performance of polymer/TiO$_2$–CuInS$_2$ solar cells. The
findings in this work may provide a new strategy for the depositing method of QDs on NAs and the preparation of efficient hybrid PSCs.

2. Experimental

2.1. Materials and chemicals

Titanium isopropanoxylate (J&K Chemicals, 98%), copper (II) chloride (CuCl2) (Acrors, 99%), indium chloride hydrate (InCl3·4H2O, Alfa-Aesar, metals basis 99.99%), 4-bromothiophenol (Alfa-Aesar, 98%), MEH-PPV (average Mn=40,000–70,000, Aldrich) and poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS, Clevios P HC V4, H. C. Starck) were commercially obtained. Other chemicals, including sodium sulfide (Na2S·9H2O, AR), hydrochloric acid (AR), ethanol (AR), tetrahydrofuran (THF) atmosphere overnight (10 mg/mL) under ambient conditions, followed by annealing at 200 °C for 16 h and taken out of the reaction solution, following by thoroughly rinsed with ethanol and dried under N2 stream to provide TiO2–CIS. Moreover, TiO2–CIS1 continued to carry out the same solvothermal reaction for 16 h, forming TiO2–CIS2.

2.2. Synthesis of TiO2–CIS

TiO2–NAs were prepared on the FTO (SnO2:F) coated glass sheet (14 Ω/sq, 400 nm FTO in thickness, Nippon Sheet Glass), as described previously [21]. Then, TiO2–NAs were introduced into the reaction mixtures for the solvothermal growth of zincblende CuInS2 at 200 °C for 16 h and taken out of the reaction solution, following by thoroughly rinsed with ethanol and dried under N2 stream to provide TiO2–CIS1. Moreover, TiO2–CIS1 continued to carry out the same solvothermal reaction for 16 h, forming TiO2–CIS2.

2.3. Device fabrication

A MEH-PPV layer was deposited on top of TiO2–CIS by spin-coating (1000 rpm, 60 s) the polymer solution in chlorobenzene (10 mg/mL) under ambient conditions, followed by annealing at tetrahydrofuran atmosphere overnight first, then heated at 200 °C for 20 min under nitrogen atmosphere. Afterward, a PEDOT:PSS film was spin-coated (1500 rpm, 60 s) over the polymer layer. Before use, the PEDOT:PSS solution with isopropanol (50% in volume) was ultrasonicated for 15 min and filtered with a 0.8 μm filter. After the deposition of PEDOT:PSS, the sample was heated for 15 min at 150 °C under nitrogen atmosphere. Finally, a gold electrode (100 nm thick) was evaporated through a shadow mask to form a top contact of 1 mm × 1 mm so that some of the nanorods could hardly be observed, in which quantum dots were filled into the intervals between the nanorods (Fig. 1e), implying more CuInS2 deposited on the surface of TiO2–NAs successfully.

XRD patterns of TiO2, TiO2–CIS are shown in Fig. 2a. All XRD diffraction peaks of the TiO2–NAs (Fig. 2a) match well with rutile TiO2 (S.G. P4/mmm; JCPDS PCPDFWIN #86-0147, a=b=4.594 Å and c=2.959 Å), compared to the powder diffraction pattern, the diffraction peaks such as (110), (200), (210), (220) and (310) faces are absent and the intensity of (002) face is significantly increased in the TiO2–NAs, indicating that the preferential growth of TiO2 nanorods is along [001] direction [23,24]. After the deposition of CuInS2 on TiO2, additional diffraction peaks as (111), (200) and (220) faces of zincblende CuInS2 appeared in the TiO2–CIS1, suggesting CuInS2 had been deposited on TiO2. It is noted that the diffraction signals of (200), (220) faces are rather weak, which may originate from the depositing amount of CuInS2 is fairly less. However, TiO2–CIS2 prepared with the further deposition of CuInS2 on TiO2–CIS1 produced stronger diffraction peaks as (111), (200), (220) and (311) faces, implying more CuInS2 deposited on the surface of TiO2 successfully. Interestingly, the diffraction peaks of (200) and (220) faces displayed abnormally stronger, implying the different CuInS2 crystallization behavior during the secondary solvothermal reaction. Fig. 2b shows the absorption spectra of TiO2 and TiO2–CIS. Clearly, TiO2 absorbs ultraviolet light, with an absorption edge at ca. 386 nm (3.21 eV) and an absorption peak at 480 nm.

The current–voltage (J–V) properties of the photovoltaic devices were measured on a controlled intensity modulated photo spectroscopy (CIMPS) (Zahner Co., Germany) under ambient conditions with the illumination through FTO glass side, using a light-emitting diode (LED) as the light source (BLL01, λmax=470 nm, spectral half-width=25 nm, Zahner Co.), similar to previous reports [22]. The effective illumination area of a cell was 0.04 cm2 and Au was taken as positive electrode.

3. Results and discussions

3.1. Characterization of TiO2–CIS

Micromorphology of TiO2 and TiO2–CIS is shown as SEM and TEM image (Fig. 1). The TiO2–NAs displayed quite smooth surfaces, with the diameter of 50–60 nm and the length of 500–600 nm (Fig. 1a and d), similar to previous paper [21]. After the deposition of CuInS2 on TiO2, the diameter of nanorod increased obviously with the appearance of rough surfaces (Fig. 1b). TEM results showed the original TiO2–NAs were sensitized by CuInS2, with the irregular attachment of quantum dots (ca. 4–6 nm) on the TiO2 surface, resulting in the diameter of nanorod increased (Fig. 1e). Furthermore, when CuInS2 was deposited on TiO2–CIS1, the diameters of TiO2–NAs increased more obviously and became more roughly (Fig. 1c). It could be observed from TEM that the diameter of nanorod increased to 80–100 nm so that some of the nanorods boundary could hardly be observed, in which quantum dots were filled into the intervals between the nanorods (Fig. 1f), implying more CuInS2 deposited on the surface of TiO2–NAs successfully.

As XRD patterns of TiO2, TiO2–CIS are shown in Fig. 2a. All XRD diffraction peaks of the TiO2–NAs (Fig. 2a) match well with rutile TiO2 (S.G. P4/mmm; JCPDS PCPDFWIN #86-0147, a=b=4.594 Å and c=2.959 Å), compared to the powder diffraction pattern, the diffraction peaks such as (110), (200), (210), (220) and (310) faces are absent and the intensity of (002) face is significantly increased in the TiO2–NAs, indicating that the preferential growth of TiO2 nanorods is along [001] direction [23,24]. After the deposition of CuInS2 on TiO2, additional diffraction peaks as (111), (200) and (220) faces of zincblende CuInS2 appeared in the TiO2–CIS1, suggesting CuInS2 had been deposited on TiO2. It is noted that the diffraction signals of (200), (220) faces are rather weak, which may originate from the depositing amount of CuInS2 is fairly less. However, TiO2–CIS2 prepared with the further deposition of CuInS2 on TiO2–CIS1 produced stronger diffraction peaks as (111), (200), (220) and (311) faces, implying more CuInS2 deposited on the surface of TiO2 successfully. Interestingly, the diffraction peaks of (200) and (220) faces displayed abnormally stronger, implying the different CuInS2 crystallization behavior during the secondary solvothermal reaction. Fig. 2b shows the absorption spectra of TiO2 and TiO2–CIS. Clearly, TiO2 absorbs ultraviolet light, with an absorption edge at ca. 386 nm (3.21 eV) and an absorption peak at 480 nm, in agreement with previous reports [21]. The absorption of TiO2–CIS1 is characterized by a broad shoulder with a trail in the long-wavelength direction typically up to 900 nm, reminiscent of the reported absorption behavior of CuInS2–QDs [22]. It is noted that the absorption band edge gets red-shifted to 340 nm, similar to previous reports [20,21,25], which may originate from the interaction between TiO2 and CuInS2. The oxygen vacancies often occur on the (110) face of rutile TiO2 [26], and the similar chemical properties of oxygen and sulfur atoms favor the formation of the interaction between CuInS2 and TiO2 [27], resulting in the occurrence of oxygen vacancies on TiO2 surfaces by sulfur atoms on CuInS2. However, TiO2–CIS2 displayed largely different absorption characterization, not only at peak position but also at peak
intensity, almost identical to that of pristine TiO₂. The apparently different absorption property may be correlated with the changed crystallization behavior of CuInS₂, which is adverse to the formation of the interaction between sulfur atoms and oxygen vacancies. Therefore, CuInS₂ in TiO₂–CIS₂ compound hardly contributed to the light-harvesting ability.

3.2. Properties of MEH-PPV/TiO₂–CIS composite films

3.2.1. Absorption spectra

As shown in Fig. 3, absorption spectra of MEH-PPV/TiO₂ film are the simple summation of those from MEH-PPV and TiO₂ [21]. However, MEH-PPV/TiO₂–CIS₁ samples exhibit the light-harvesting range from 300 nm to 900 nm which is consistent with the absorption character of CuInS₂ [22], and the absorbance is enhanced significantly compared to that of TiO₂ and MEH-PPV compound. Moreover, the obviously red-shifted TiO₂ absorption peak is resulted from a strong interaction between TiO₂ and CuInS₂, implying the presence of effective contact between CuInS₂ and TiO₂, similar to the absorption spectra of TiO₂–CIS₁. However, absorption spectra of MEH-PPV/TiO₂–CIS₂ displayed largely different, almost identical to that of pristine MEH-PPV/TiO₂ film. Obviously, the further deposition of CuInS₂ on TiO₂–CIS₁ is unexpected to increase the light-harvesting ability of composite film, which may originate from the changed CuInS₂ crystallization behavior adverse to the formation of the interaction between TiO₂ and CuInS₂.

3.2.2. PL spectra

Fig. 4 shows room temperature PL spectra of the MEH-PPV/TiO₂ and MEH-PPV/TiO₂–CIS composites. The PL spectra of MEH-PPV/TiO₂ films display emission profiles similar to that of pristine MEH-PPV (inset to Fig. 4), with obvious decrease in PL emission, indicating an effective energy transfer from polymer to TiO₂ [28,29]. By comparing the maximum emission intensity of MEH-PPV/TiO₂ to that of pristine MEH-PPV film, the quenching efficiency for TiO₂ to polymer PL emission is calculated to be 63.61%. After the deposition of CuInS₂ on TiO₂, the PL quenching efficiency in the MEH-PPV/TiO₂–CIS₁ composites increases to 79.11%, which is possibly due to the presence of CuInS₂ on TiO₂ surface enlarged D/A interface area for exciton dissociation, contributing to the increased PL quenching efficiency. However, compared to MEH-PPV/TiO₂–CIS₁, MEH-PPV/TiO₂–CIS₂ displayed the decreased PL quenching efficiency to 68.61%, which may originate from lots of QDs filled in the intervals between the nanorods, segregating the effective contact between polymer and TiO₂ to decrease the D/A interface area for exciton dissociation.

3.3. Device performance

The J–V curves for the devices MEH-PPV/TiO₂ and MEH-PPV/TiO₂–CIS were measured under monochromatic illumination of

Fig. 1. TEM (a–c) and SEM (d–f) images of TiO₂ (a, d), TiO₂–CIS₁ (b, e) and TiO₂–CIS₂ (c, f) composites.
15.85 mW/cm² at 470 nm (Fig. 5). Table 1 presents the overall photovoltaic performance for each sample. Compared to MEH-PPV/TiO₂ solar cell, the open-circuit voltage ($V_{oc}$) and fill factor (FF) in MEH-PPV/TiO₂–CIS₁ solar cells get slightly increased, whereas the short-circuit current ($J_{sc}$) is improved remarkably, leading to a peak efficiency of 4.09%, which is ca. 4-fold higher than that of the TiO₂ counterpart device. The increase in $V_{oc}$ may be originated from the surface modification of TiO₂ by CuInS₂. As we know, the $V_{oc}$ in MEH-PPV/TiO₂–CIS devices is still dominantly determined by the energy difference between the conduction band edge of TiO₂–NAs and the polymer HOMO level [20,21]. The deposition of CuInS₂ on TiO₂ produced the strong interaction owei to the occupation of oxygen vacancies on TiO₂ surfaces by sulfur atoms on CuInS₂, resulting in the concentration of intraband surface defects (e.g., oxygen vacancies) on TiO₂–NAs decreasing [27], and lots of electrons will accommodate in TiO₂ conduction band with increased energy difference between the quasi-Fermi levels of electrons in TiO₂ and holes in polymer for a higher $V_{oc}$ [30–32]. However, the deposition of CuInS₂ on TiO₂–CIS₂ decreases the $V_{oc}$, even lower than that of pristine TiO₂, which may be correlated with the changed CuInS₂ crystallization behavior adverse to the formation of strong interaction between TiO₂ and CuInS₂, as a result, surface defects of TiO₂ could not be modified effectively. Moreover, the excessive growth and aggregation of QDs boosted the surface defect on the contrary which increased the recombination possibility between electrons and holes [33], resulting in the lower $V_{oc}$ than that of MEH-PPV/TiO₂ device. Compared to MEH-PPV/TiO₂ solar cells, MEH-PPV/TiO₂–CIS₁ solar cells displayed remarkably increased $J_{sc}$. On one hand, MEH-PPV/TiO₂–CIS₁ samples exhibit absorption in the range of 300–900 nm with significantly enhanced absorbance, suggesting the presence of CuInS₂ is an effective complementary light-harvesting materials, contributing to photocurrent. On the other hand, the increased PL quenching efficiency due to the enlarged D/A interface area subjected to the increased nanorod diameter upon the CuInS₂ deposition led to the increased exciton dissociation efficiency, contributing to photocurrent. However, the deposition of CuInS₂ on TiO₂–CIS₂ was unexpected to the decreased photocurrent, even lower than that of pristine TiO₂, which may originate from the overmuch CuInS₂ from the excessive growth and aggregation during the secondary solvothermal process. It would augment the recombination probability of the electrons and holes by the limited efficiency of charge separation and charge extraction [33], decreasing the photocurrent. Obviously, the one-step or two-step solvothermal reactions for the deposition of CuInS₂ on TiO₂

![Fig. 2. XRD (a) and absorption spectra (b) of TiO₂ and TiO₂–CIS composites.](image)

![Fig. 3. Absorption spectra of MEH-PPV (■), MEH-PPV/TiO₂ (●), MEH-PPV/TiO₂–CIS₁ (▼) and MEH-PPV/TiO₂–CIS₂ (◆).](image)

![Fig. 4. PL spectra of MEH-PPV/TiO₂ (■), MEH-PPV/TiO₂–CIS₁ (●) and MEH-PPV/TiO₂–CIS₂ (◆), the inset is PL spectrum of pristine MEH-PPV.](image)

![Fig. 5. The typical $J$–$V$ curves for MEH-PPV/TiO₂, MEH-PPV/TiO₂–CIS₁ and MEH-PPV/TiO₂–CIS₂ solar cells under the monochromatic illumination of 15.85 mW/cm² at 470 nm.](image)

<table>
<thead>
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<th>Device</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV/TiO₂</td>
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<td>0.88</td>
<td>33.74</td>
<td>0.91</td>
</tr>
<tr>
<td>MEH-PPV/TiO₂–CIS₁</td>
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<td>2.73</td>
<td>44.08</td>
<td>4.09</td>
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<tr>
<td>MEH-PPV/TiO₂–CIS₂</td>
<td>0.315</td>
<td>0.46</td>
<td>30.84</td>
<td>0.28</td>
</tr>
</tbody>
</table>
resulted in the different interaction between CuInS$_2$ and TiO$_2$, impacting the qualitative change in device performance.

4. Conclusions

CuInS$_2$ were deposited on TiO$_2$–NAs by one-step or two-step solvothermal reactions to synthesize TiO$_2$–CIS$_1$ and TiO$_2$–CIS$_2$, respectively. Results showed that TiO$_2$–CIS$_1$ displayed stronger light-harvesting ability and PL quenching efficiency, however, TiO$_2$–CIS$_2$ displayed almost unchanged optical properties albeit more CuInS$_2$ was deposited on it. Based on the obvious different properties of composite film, ternary MEH-PPV/TiO$_2$–CIS solar cells displayed the qualitative change in device performance, which may be originated from the different crystallization behavior during the one-step or two-step solvothermal reactions, resulting in the different interactions between TiO$_2$ and CuInS$_2$.

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References