

## Communications

## Quantum Dot Solar Cells Prepared Using Electrophoretic Deposition

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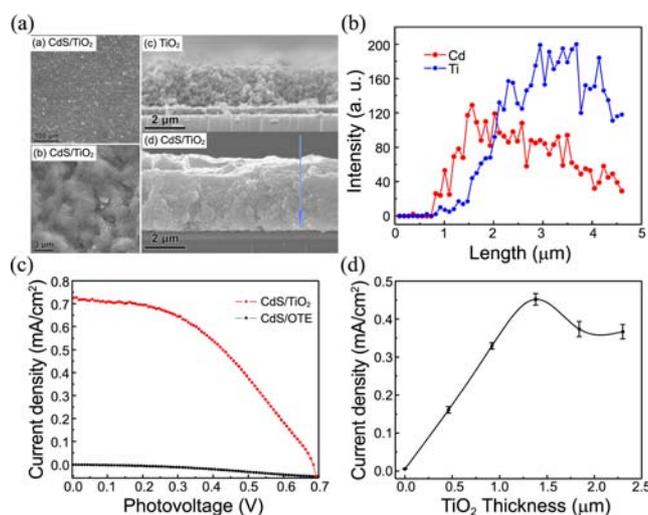
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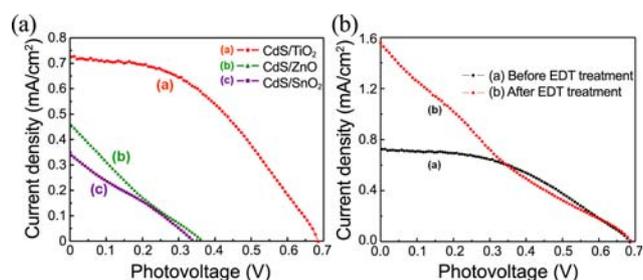
Quantum dot solar cells (QDSCs) have attracted great interest as a next-generation solar energy conversion system.<sup>1</sup> While the conversion efficiency of QDSCs has recently exceeded 5%, they still lag behind their dye-sensitized solar cell analogues. The performance of QDSCs is governed by many factors such as their light harvesting capacity, interfacial charge recombination, the characteristics of the electrolytes, and the electrocatalytic activity of the counter electrode.<sup>2</sup> Among them, the anode characteristics (*i.e.*, light absorption and charge recombination) are intimately associated with the deposition method of the QD sensitizer. Therefore, the development of an effective deposition method is of great importance for highly efficient solar cell fabrication. Commonly used deposition methods include chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), a molecular-linker based approach (MBA), and direct adsorption (DA).<sup>3</sup> CBD and SILAR are based on *in situ* growth of QDs and feature simplicity and high QD coverage. However, they cannot control the QD size and size distribution. MBA and DA, on the other hand, are *ex situ* deposition techniques where pre-synthesized QDs are deposited onto nanoporous oxide substrates. While these methods are superior to CBD and SILAR from the viewpoint of the deposition of monodisperse, highly crystalline QDs, they typically suffer from low coverage and long deposition times. Electrophoretic deposition (EPD) has been demonstrated as a QD deposition method which has advantages of fast deposition with a high loading of monodisperse QDs. To date, most studies have focused on the deposition of QD/carbon composites or QDs on flat oxide substrates, but their performances are not sufficient to meet the requirements of efficient photoelectrodes.<sup>4,5</sup> In this work, we performed EPD of QDs onto nanoporous oxide substrates to result in improved performance and investigated the effects of several factors on the performance of photoelectrodes prepared by EPD.

CdS QDs prepared by a hot injection method (Figure S1) were deposited onto a nanoporous TiO<sub>2</sub> electrode by EPD (see experimental details in Supporting Information). The scanning electron microscope (SEM) images in Figure 1(a) show that the porous nature of the TiO<sub>2</sub> films disappeared

after EPD, revealing that CdS QDs penetrated nanopores into the inner TiO<sub>2</sub> layer during the EPD process. Energy dispersive X-ray spectroscopy (EDS) confirmed that CdS QDs were distributed over the entire TiO<sub>2</sub> layer while a larger amount of QDs were deposited near the top layer of the TiO<sub>2</sub> (Figure 1(b)). Figure 1(c) shows that the CdS/TiO<sub>2</sub> electrode outperformed CdS/OTE, indicating that significantly improved charge separation occurs when the QDs were integrated within the TiO<sub>2</sub> layer. Compared to MBA, which has been widely utilized for the deposition of high-quality QDs, EPD is more effective for constructing efficient photoanodes (Figure S2). To investigate the influence of the TiO<sub>2</sub> thickness, the photocurrent of the electrodes was measured as a function of the TiO<sub>2</sub> thickness. While the photocurrent linearly increased up to a TiO<sub>2</sub> thickness of 1.5  $\mu\text{m}$ , it began to level off as the TiO<sub>2</sub> layer became thicker (Figure 1(d)). This may be attributed to the limited penetration of CdS QDs through the nanopores. With a thicker



**Figure 1.** (a) SEM images of TiO<sub>2</sub> and CdS/TiO<sub>2</sub>, (b) SEM-EDS line analysis along the blue line in SEM image, (c) *I-V* curves of solar cells with CdS/TiO<sub>2</sub> and CdS/OTE anodes (100 mW/cm<sup>2</sup>, 0.1 M Na<sub>2</sub>S electrolyte, Au counter electrode), and (d) photocurrent under illumination (50 mW/cm<sup>2</sup>) as a function of TiO<sub>2</sub> thickness.

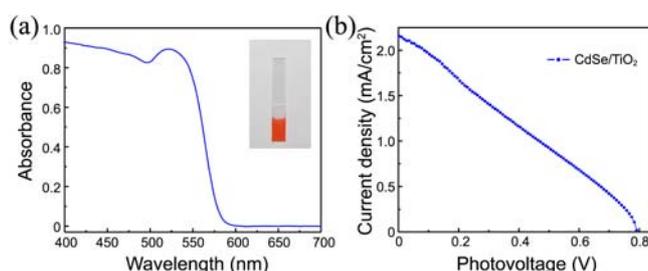


**Figure 2.** (a)  $I$ - $V$  curves of solar cells with CdS/TiO<sub>2</sub>, CdS/ZnO, and CdS/SnO<sub>2</sub> anodes and (b)  $I$ - $V$  curves of CdS/TiO<sub>2</sub> solar cells before and after EDT treatment.

TiO<sub>2</sub> layer, most of the QDs tended to be stacked over its top, which hinders the formation of QD/TiO<sub>2</sub> interfaces for effective charge separation (Figure S3).

The effects of the oxide substrate were also investigated in this study. Three commonly employed oxides (TiO<sub>2</sub>, ZnO, and SnO<sub>2</sub>) with the same thickness of  $\sim 1.5$   $\mu\text{m}$  were employed as EPD substrates. Figure 2(a) compares their solar cell performances, demonstrating that TiO<sub>2</sub> excelled among the three oxides and the solar cells constructed with ZnO and SnO<sub>2</sub> photoanodes suffered from a low open-circuit voltage ( $V_{oc}$ ) and short-circuit current ( $I_{sc}$ ) along with a poor fill factor ( $FF$ ). This observation was supported by the incident photon-to-current efficiency (IPCE) measurements, in which the conversion efficiency of CdS/TiO<sub>2</sub> was superior to its counterparts over the entire visible light spectrum (Figure S4). This result is in good accordance with recent studies of photoelectrodes prepared by MBA,<sup>6</sup> suggesting that oxide substrates have the same influence on the solar cell performance regardless of the deposition method. The CdS/TiO<sub>2</sub> anode was treated with 1,2-ethanedithiol (EDT) to remove the organic stabilizer around the CdS QDs, which results in stronger coupling between CdS and TiO<sub>2</sub>. Figure 2(b) shows that the  $I_{sc}$  dramatically increased after the EDT treatment, which is ascribed to stronger electronic coupling by shortening their distance.<sup>7</sup>

To extend the visible light absorption capability of the photoanode, pre-synthesized CdSe QDs were deposited onto nanoporous TiO<sub>2</sub> films by EPD. Figure 3(a) shows the absorption spectrum of the CdSe/TiO<sub>2</sub> photoelectrode, in which most of the visible light photons were absorbed by the CdSe QD sensitizer. Figure 3(b) displays the  $I$ - $V$  characteristics of the photoelectrode, where the  $V_{oc}$  (0.79 V),  $I_{sc}$  (2.16 mA/cm<sup>2</sup>), and  $FF$  (0.28) were obtained. The overall energy conversion efficiency was found to be 0.48%. It is noteworthy that the  $V_{oc}$  was substantially higher than those observed in reports where other QD deposition methods were employed, which may be attributed to reduced charge recombination. Further investigation is currently underway to elucidate this intriguing observation.



**Figure 3.** (a) Diffuse reflectance UV-Vis absorption spectrum of CdSe/TiO<sub>2</sub> photoelectrode (inset: a photo of the electrode) and (b)  $I$ - $V$  curve of solar cell with CdSe/TiO<sub>2</sub> anode.

In conclusion, we successfully demonstrated that EPD results in the facile and effective deposition of various QDs. The performance of the photoelectrodes was found to be dictated by several factors such as the oxide thickness, type of oxide substrate, and post-treatment. While the EPD process presented in this work has not yet been fully optimized, it led to high  $V_{oc}$  unattainable from other deposition methods, which we believe could be of great benefit for the development of efficient solar cells. Further optimization is in progress to improve the solar cell performance.

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**Supporting Information.** Experimental details; UV-Vis absorption and photoluminescence spectra of CdS and CdSe QDs;  $I$ - $V$  curves of solar cells fabricated by EPD and MBA; SEM image of CdS QDs deposited on a thicker TiO<sub>2</sub> film; IPCE of solar cells with CdS/TiO<sub>2</sub>, CdS/ZnO, and CdS/SnO<sub>2</sub> anodes.

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