Research Article

Interconnected TiO₂ Nanowire Networks for PbS Quantum Dot Solar Cell Applications

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We present a simple method for the fabrication of an interconnected porous TiO₂ nanostructured film via dip coating in a colloidal suspension of ultrathin TiO₂ nanowires followed by high-temperature annealing. The spheroidization of the nanowires and the fusing of the loosely packed nanowire films at the contact points lead to the formation of nanopores. Using this interconnected TiO₂ nanowire network for electron transport, a PbS/TiO₂ heterojunction solar cell with a large short-circuit current of 2.5 mA/cm², a Voc of 0.6 V, and a power conversion efficiency of 5.4% is achieved under 8.5 mW/cm² white light illumination. Compared to conventional planar TiO₂ film structures, these results suggest superior electron transport properties while still providing the large interfacial area between PbS quantum dots and TiO₂ required for efficient exciton dissociation.

1. Introduction

Lead chalcogenide colloidal semiconductor nanocrystals can be promising materials for low-cost, large-area, and efficient photovoltaic devices, due to a large Bohr radius, size-effect tunable bandgap across the near-infrared region and large absorption cross-section, as well as the solution processability [1–7]. Over the last few years, Schottky solar cells based on PbS, PbSe, or PbSₓSe₁−ₓ quantum dots with power converting efficiencies over 3% have been demonstrated [3, 5, 7]. More recently, the depleted-heterojunction quantum dots solar cells based on the PbS/TiO₂ nanocrystals have achieved an unprecedented efficiency of 5.1% [1], and PbS/ZnO photovoltaic devices have exhibited excellent air stability for 1000 h of continuous illumination under ambient atmosphere [2].

In general, the power conversion efficiency of the QDs solar cells is primarily determined by three factors: exciton generation, exciton dissociation, and carrier collection efficiencies. Indeed, it was shown previously that the structure and morphology of the TiO₂ layer can play the key role in achieving efficient extraction and transport of minority carriers in dye- and QDs-sensitized solar cells [8]. The TiO₂ layer requires large surface areas for quantum dots attaching, as well as rapid electron transport across the film to ensure efficient electron collection by the conductive substrate. The widely used mesoporous TiO₂ nanostructured films can be employed to significantly increase the contact area between TiO₂ and the active quantum dot layer, thus facilitating exciton dissociation before radiative recombination and allowing efficient carrier collection. However, the electronic transport suffers from slow electron diffusion rates and low electron mobility in the structurally disordered TiO₂ mesoporous films [8, 9].

Fabrication of TiO₂ films from one-dimensional nanowire and nanotube structures has proven to be an effective way to improve the overall efficiencies of the devices [9–12]. The one-dimensional nanostructure allows diffusion free electron transport along the axial direction to improve electron collection, while the light scattering effect from the subwavelength features can enhance the effective absorption thickness of the quantum dots layer. Nevertheless, one major concern with lateral nanowires is the smaller surface areas it presents for dye and quantum dot sensitization [8].

In this paper, we report the fabrication of superior TiO₂ film structures for QD solar cells formed by dip coating and annealing of ultrathin TiO₂ nanowire films. This interconnected nanowire network structure maintains the large
surface-to-volume ratio from traditional porous TiO₂ films, while allowing efficient electron transport along the nanowires. As we show, the electron transport and carrier extraction in the TiO₂/PbS heterojunction solar cell can be significantly improved using this porous interconnected TiO₂ nanowire network film. A superb low-cost solar cell was fabricated with a large short-circuit current of 2.5 mA/cm², a Vₐₙₜ of 0.6 V, and a power conversion efficiency of 5.4% achieved under 8.5 mW/cm² illumination.

2. Experiments

2.1. Chemicals. Titanium (IV) butoxide 99% (TBT, Aldrich), oleic acid (90%, Aldrich), titanium (IV) isopropoxide (TTIP, Aldrich, 99.999%), poly(acrylic acid) (M 450,000, Aldrich), ethyl acetate (Aldrich, Anhydrus 99.8%) (EAcAc), ethanol (ACS reagent, ≥ 99.5% (200 proof, absolute), 1-octadecene (90%, Aldrich), lead oxide (99.99%, Aldrich), hexamethyldisilathiane (Fluka) are used.

Preparation of TiO₂ Sol-Gel [13]. PAA (0.035 g) and EAcAc (1.7998 g) were mixed and sonicated at room temperature for 5 minutes. Ethyl alcohol (42.3429 g) was added and left reposed for 20 minutes. Finally, TBT (13.7489 g) was added to the mixture and was reposed for another 20 minutes, and distilled water (0.5457 g) was added to start the reaction. The solution was continuously stirred for 8 hours and then aged for 24 hours to form the TiO₂ sol-gel.

Synthesis of TiO₂ Nanowires [14]. The TiO₂ nanowires were synthesized through the nonhydrolytic ester elimination reaction of titanium isopropoxide and oleic acid. TTIP (3.5 mL) was added to 10 g of OA at room temperature under nitrogen atmosphere. The resulting mixture was heated to 280°C for a period of 20 min and was kept at this temperature for 2 h. The light-yellow solution gradually turned dark brown and then white. The solution was then cooled down to room temperature, excess acetone was added, and the solution was centrifuged to precipitate the nanowires.

PbS Quantum Dot Synthesis [15]. Lead oxide (0.45 g), octadecene (10 g), and oleic acid (1.34 g) are added to a three-neck flask. The mixture is then heated and kept at 80°C for two hours under vigorous stirring in vacuum to degas the solution and dissolve the mixture. Then, the temperature is kept at 110°C under nitrogen flow for 30 min. Subsequently, a solution made of 210 μL of hexamethyldisilathiane diluted in 4 mL of octadecene is quickly injected into the reaction flask under vigorously stirring. The heating was immediately removed and the reaction solution was allowed to cool down slowly to room temperature. Finally, the colloidal PbS quantum dots are collected by quick injection of the reaction solution into excess amount of acetone (with ratio ~ 1: 4) for centrifugation. The precipitates are dried in vacuum and redispersed in hexane. To ensure adequate removal of the reaction solvents, precipitation and redispersion are repeated. The quantum dot solution is filtered with 0.2 μm polytetrafluoroethylene filters before device fabrication.

Fabrication of Solar Cells. The ITO glass was cleaned using a sequence of ultrasonic baths of deionized water, acetone and isopropanol. Then, the substrate was dipcoated into the TiO₂ sol-gel for 10 seconds and then withdrawn at 200 mm/min to form a thin layer of planar TiO₂ layer (∼35 nm), in order to prevent any shorting of the device. This sol-gel TiO₂ layer was annealed at 500°C for 1 hour in a tube furnace to improve its crystalline structure and its conductivity. After that, the porous TiO₂ layers were fabricated by dip-coating the substrate (immersed in the nanowire solution for 10 seconds, and then withdrawn at 200 mm/min) into the TiO₂ nanowires solution in hexane (∼35 mg/mL), followed by another annealing at 500°C for 1 hour in the furnace. To make the porous TiO₂ layer thicker, another layer of TiO₂ nanowire was dip-coated on top and then annealed. The PbS quantum dots are then deposited using the layer by layer spin-coating method [1]. For each cycle, the PbS quantum dot solution (25 mg/mL in hexane) is spin-coated (2000 rpm) on the substrate, then the diluted ethanedithiol solution in acetonitrile (0.02 M) is subsequently spin-coated on top to crosslink the quantum dot and make the quantum dot indissolvable in the original solution, and finally, hexane was spin-coated on the substrate to rinse the quantum dot solid film obtained. For both devices, eight layers of quantum dots are deposited. Finally, gold is thermally evaporated on top as the back contact electrode. The solar cell was measured with devices placed on top of an integrated sphere under 8.5 mW/cm², white light illumination. The integrating sphere is connected to a fiber illuminator, and the light was uniformly coupled out from the top port of the integrate sphere.

3. Results and Discussions

As shown in Figure 1(a) the free-standing TiO₂ nanowires are typically 100–200 nm in length and 3–4 nm in diameter. As shown in Figure 1(b), the high-resolution TEM analysis of the TiO₂ nanowires confirms their sound crystalline structure. The FFT shown in the inset of Figure 1(b) indicates the nanowires are TiO₂ anatase, and it was imaged with its [100] direction parallel to the electron beam. Here, the long 18-carbon-atom stabilizing surfactant (oleic acid) plays a crucial role in passivating the nanowires to prevent agglomeration; thus a uniformly and loosely compacted TiO₂ nanowires film can be deposited by dip coating the substrate into the nanowire solution, as shown in Figure 2(a).

The TiO₂ nanowire fuse with each other at the contact point via sintering. On the other hand, the one-dimensional nanowire will reduce the aspect ratio and spheroidize owing to surface energy reduction [17]. When the spheroidization stops at the contact points of the nanowires, the porous structure is formed. Thus, a high-surface-area, interconnected porous TiO₂ nanostructure is fabricated using the facile dip-coating and annealing process, as shown in the SEM image in Figure 2(c). Large quantities of pores are distributed randomly on both the surface and the interior of the TiO₂ nanostructure. A high-resolution secondary electron SEM image in Figure 2(d) clearly resolved the porous structure of the film. The irregularly distributed nanopores
are interconnected by spheroidized NWs after thermal annealing process, with average diameter of $13.2 \pm 4.7$ nm and average pore area of $117 \pm 123$ nm$^2$. Since the quantum dots used in these devices are typically 3-4 nm in diameter, the relatively larger nanopores can create additional volume for QDs attaching, as well as provide large surface areas to achieve efficient electron extraction.

The SEM image in Figure 3(a) shows the structure of the resulting solar cell device, while the band alignment is shown in Figure 3(b). All the fabrication steps except the evaporation are done in ambient atmosphere. The thickness of the planar TiO$_2$ is $\sim 35$ nm, the porous TiO$_2$ nanowire layer is $\sim 60$ nm, while the PbS quantum-layer is $\sim 320$ nm.

Figure 4 compares the current density-voltage (J-V) characteristics of a standard PbS quantum dot-sensitized TiO$_2$ heterojunction solar cell using a planar TiO$_2$ film formed by conventional sol-gel chemistry with the same solar cell using the thick nanoporous interconnected TiO$_2$ nanowire network previously deposited on a thin planar TiO$_2$ film. Here, small PbS quantum dots of relatively large bandgaps and with their conduction bands well above that of TiO$_2$ were used, so as to achieve efficient electronic transfer from the quantum dots to the TiO$_2$ [18]. For comparison, both the planar and porous TiO$_2$ heterojunction solar cells have equally thick PbS nanocrystalline layers and both were crosslinked using EDT. In contrast with the planar device, the TiO$_2$ nanowire device exhibits a superb short-circuit current ($J_{sc}$) of 2.5 mA/cm$^2$, a large open-circuit voltage ($V_{oc}$) of 0.6 V, a fill factor of 33%, and a power-converting efficiency of 5.4%. These results suggest that the large surface area in the porous TiO$_2$ nanostructured film, as well as an efficient carrier transport along the longitudinal axis of TiO$_2$ nanowires, appears to be critical to achieve high $J_{sc}$ in the heterojunction solar cell architecture. The near-ideal rectifying J-V characteristics of the TiO$_2$ nanowire device under dark directly confirm the formation of a high-quality p-n heterojunction between PbS and TiO$_2$. In contrast, the planar TiO$_2$ solar cell device suffers from a much smaller short-circuit current ($J_{sc}$), in addition to a significantly lower fill factor of 14%. Moreover, the current drops down rapidly as the voltage starts to increase. Most likely, this can be attributed to the inefficient electron transport in the planar TiO$_2$ layer. Otherwise, it is also possible that pin holes are generated in the planar TiO$_2$ film during annealing, thus ruining the performance of the device and explaining the much larger currents observed under forward bias. Since the open-circuit voltage of the devices is mainly determined by difference of the quasi-Fermi level between the PbS nanocrystals and the TiO$_2$ layer, both devices exhibit a similar $V_{oc}$ around 0.6 V.

To better understand the exciton dissociation and electron extraction from the PbS quantum dots to the TiO$_2$ we studied the absorption and photoluminescence of EDT-treated nanocrystalline films deposited on glass, planar TiO$_2$, and porous TiO$_2$ nanowire network films. Indeed, the electron transfer from small PbS nanocrystals to the TiO$_2$ can be monitored through the shift and quenching of the absorption and photoluminescence spectra [19, 20]. The conduction band of the small quantum dots lies well above that of the TiO$_2$ thus the high-energy excitons generated upon the absorption of high-energy photons in small QDs can rapidly dissociate with electrons injected to the TiO$_2$ layer. The porous TiO$_2$ nanowire structure provides large interfacial areas between QDs and TiO$_2$, thus enables efficient electron transfer [21]. This rapid relaxation of high-energy excitons can in turn improve the absorption of high-energy photon by rapid depopulating the excitons in the QDs. As seen in Figure 5(a), the absorption spectrum of the PbS nanocrystals deposited on porous TiO$_2$ nanowire structure displays a stronger absorption on the high-energy side and an obviously blue shift compared to the QDs deposited on planar TiO$_2$.

Meanwhile, the photoluminescence of the quantum dots is quenched owing to hot electron transfer to TiO$_2$. Figure 5(b) compares the photoluminescence of monolayer of nanocrystals deposited on glass, on planar TiO$_2$ and on the porous TiO$_2$, nanowire network. Due to the photoluminescence quenching at the high energy side, the photoluminescence of the PbS quantum dots exhibits a 24 nm red-shift on planar TiO$_2$, compared with a remarkable 76 nm red shift.
on the porous TiO₂ nanowire network film. The strong absorption on the high-energy side combined with the significant quenched and red shifted photoluminescence indicates that efficient electron transfer is achieved between the PbS quantum dots and the porous TiO₂ nanowire. This is also consistent with the superb short-circuit current observed for the porous TiO₂ nanowire-based devices owing to its large interfacial areas and strong electron extraction ability.

4. Conclusions

In summary, we fabricated a high-performance porous TiO₂ film for nanocrystal-sensitized solar cell using an interconnected TiO₂ nanowire network. This facile all-solution-based method simply relies on dip coating and annealing of ultrathin TiO₂ nanowires. This unique nanostructured film provides large interfacial area allowing efficient electron extraction from quantum dots and uses the one-dimensional morphology of the TiO₂ nanowires to favor direct electron transport along the long axial direction to improve electron collection. The heterojunction solar cells using this porous interconnected TiO₂ nanowire network films exhibit a superb $J_{sc}$ of 2.5 mA/cm², a large $V_{oc}$ of 0.6 V, and a power conversion efficiency of 5.4% under 8.5 mW/cm² white-light illumination. Through the absorption and photoluminescence study of the same PbS quantum dots deposited...
Figure 3: (a) SEM image showing the cross-section of the PbS-TiO$_2$ heterojunction solar cell device. (b) Band diagram of the device.

Figure 4: Comparison of the current density-voltage (J-V) characteristics under illumination for a standard PbS quantum-dot-sensitized TiO$_2$ heterojunction solar cell using a planar TiO$_2$ film formed by conventional sol-gel chemistry with the same solar cell using our thick nanoporous interconnected TiO$_2$ nanowire network previously deposited on a thin planar TiO$_2$ film. Both devices are measured under a uniform 8.5 mW/cm$^2$ white-light illumination. The inset shows the dark I-V characteristics for both devices.

Figure 5: (a) Absorption spectrum for the same PbS nanocrystals deposited on planar TiO$_2$ and porous interconnected TiO$_2$ nanowire network film. (b) Photoluminescence from a monolayer of the same EDT-treated PbS nanocrystals deposited on glass, on planar TiO$_2$, on a porous TiO$_2$ nanowire network film.

on various TiO$_2$ substrates, we demonstrated a significantly improved electron-transfer efficiency using the TiO$_2$ nanowire network structure instead of a conventional planar TiO$_2$ film structure.
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References
