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Zn-Doped SnO2 Nanocrystals as Efficient DSSC Photoanode Material and Remarkable Photocurrent Enhancement by Interface Modification

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Zn-doped SnO2 nanocrystals with different doping concentrations were synthesized and the nanocrystal photoanode based DSSC achieved a PCE of 2.07% with a high Voc (0.67 V). TiCl4 modification of the photoanode greatly improves the charge injection efficiency and charge collection efficiency and the resulting PCE increased to 4.32% despite a decreased dye adsorption. The Zn-doped SnO2 nanocrystals will be of particular interest as photoanode material in DSSCs.

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Experimental

Synthesis of Zn-doped SnO2 nanocrystals.—The SnO2 nanocrystals was prepared by a hydrothermal method. Typically, a 30 mL mixture of equal amount of ethanol and DI water containing 1.0 mmol Zn(CH3COO)2 · 2H2O and 1.0 mmol SnCl4 is used for the synthesis of pure SnO2 nanocrystals. Urea (1.0 g) or HMT (Hexamethylenetramine, 1.0 g) was added to the above solution to achieve the 20% and 30% Zn-doped SnO2 nanocrystals (determined by EDS). The solution was then transferred into a 50 mL Teflon-lined autoclave and was kept at 180°C for 24 hrs. The precipitate was collected after centrifugation and washed with distilled water and ethanol for several times. Finally, the product was dried completely at 70°C.

Electrode preparation and DSSC fabrication.—Paste making and DSSC fabrication were done according to the standard DSSC fabrication procedure. The TiCl4 modification of the Zn-doped SnO2 nanocrystal film was performed by immersing the film into a 40 mM TiCl4 aqueous solution for 30 min at 70°C. Then the electrodes were washed with ethanol and sintered at 500°C in air for 30 min. 0.5 mM of N719 dye was added to a solution with equal amount of tert-butanol and acetonitrile for the dye adsorption (20–24 hrs, room temperature). For counter electrode preparation, Pt catalyst was deposited on cleaned FTO glass by coating with a drop of H2PtCl6 paste for 15 min. Iodide based low viscosity electrolyte with 50 mM of tri-iodide in acetonitrile (AN-50, Solaronix) was used as the electrolyte.

Characterization.—Powder X-ray diffraction (Bruker D8 Advance), field emission scanning electron microscopy (FESEM; JEOL JSM-7600F), EDS, Nitrogen adsorption–desorption (Nova 3200e; quantachrome instruments), UV-Vis (Shimadzu 3600 Uv-Vis Spectrophotometers), Micro-photoluminescence (PL) system (Renishaw Raman Scope 2000) with a He-Cd laser (λ = 325 nm) as excitation source were used to characterize the nanocrystals. Dye desorption was conducted using a 20 mM NaOH solution (equal amount of DI water and ethanol) and by the absorption peak of N719 dye at 511 nm. The current density–voltage (J-V) characterization of DSSCs was performed under 1 sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe, 100 mW/cm²). EIS spectrum were collected using an Autolab potentiostat/galvanostat and the Nova 1.5 software package under illumination provided by a red LED (λ = 627 nm, 19.2 nm FWHM) while the cell was biased at the Voc induced by the illumination.
Results and Discussion

To characterize the morphology of the obtained nanocrystals, FE-SEM images of the different nanocrystals were taken (Fig. 1a-1c). The average sizes of the nanocrystals were obtained by counting the size of 100 nanocrystals and by Gauss fitting (Fig. 1d-1f). The average size of the pure SnO$_2$ nanocrystals was around 22 nm (Fig. 1d). The average sizes of the 20% and 30% Zn-doped SnO$_2$ nanocrystals were smaller and showed a fairly uniform size distribution of about 15 nm (Fig. 1e) and 14 nm (Fig. 1f). The surface area of the pure SnO$_2$, 20% and 30% Zn-doped SnO$_2$ nanocrystals were 91.4, 100.5 and 106.2 m$^2$/g respectively.

XRD patterns of the three kinds of SnO$_2$ nanocrystals (Fig. 2a) can be indexed to tetragonal phase of SnO$_2$ (JCPDS, 41-1445). The peaks of Zn-doped SnO$_2$ nanocrystals showed a slight shift to smaller angles, which was a result of Zn doping. The peaks of the Zn-doped SnO$_2$ nanocrystals broadened in comparison to that of the pure SnO$_2$ nanocrystals. This can be attributed to the decrease in crystal size of the Zn doped SnO$_2$ nanocrystals. The defects induced by Zn doping was evident from the photoluminescence spectrum of the Zn doped SnO$_2$ (Fig. 2b). The photoluminescence intensity of the defect emission increased with increasing Zn doping concentration. The UV-Vis absorption spectrum (Fig. 2c) and the bandgap calculation (Fig. 2d) showed that the pure SnO$_2$ nanocrystals had a bandgap of 4.07 eV, while the 20% and 30% Zn-doped SnO$_2$ nanocrystals showed a much smaller bandgap of 3.24 and 3.42 eV respectively. The reduced bandgap is considered to be caused by the doping effect. The increase of the bandgap with the increase of the doping concentration was reported previously in Zn-doped SnO$_2$ thin films.\textsuperscript{28}

The doping mechanism can be considered as a slow hydrolysis of NH$_3$ given by the additives. When urea or HMT was introduced into the solution, they dissolved and formed ammonium hydroxide. The hydroxide anions in the solution reacted with tin and zinc ions and a white precipitate of ZnSn(OH)$_6$ was formed. Under high temperature and high pressure, further reaction occurred and Zn-doped SnO$_2$ was formed.\textsuperscript{29}

To demonstrate the effect of Zn doping on DSSC performance, the 20% Zn-doped SnO$_2$ nanocrystals was made into paste and used as the photoanode of DSSC (with thickness of 8 and 10 $\mu$m). For both thicknesses, the effect of TiCl$_4$ modification was also studied. The J-V characteristics of the Zn-doped SnO$_2$ nanocrystal DSSCs were
shown in Fig. 3. The $V_{oc}$ of the 20% Zn-doped SnO$_2$ nanocrystals based DSSC (0.68 V) was much higher than the previously reported $V_{oc}$ based on SnO$_2$ (0.52 V; with N719 dye). Since n-type doping causes the Fermi level of SnO$_2$ to shift toward the conduction band, the high $V_{oc}$ obtained here is due to the larger energy level offset between the Fermi level in Zn-doped SnO$_2$ with the reduction potential of $\Gamma^-/I_3^-$. The Zn-doped SnO$_2$ nanocrystal film with a 10 $\mu$m thickness showed a better dye adsorption than the P25 film with the same thickness (1.154×10$^{-7}$ mol/cm$^2$). The obtained PCE prior to TiCl$_4$ modification reaches 2.07% for the 10 $\mu$m thick photoanode, which was much higher than the other SnO$_2$ based systems. After TiCl$_4$ modification of the photoanode, the $V_{oc}$ increases 0.02 V and the current density doubled (from 4.85 to 10.33 mA/cm$^2$) and the highest efficiency reached 4.32%.

Usually, the TiCl$_4$ modification helps to increase the dye loading, and thus helps to improve the light harvesting efficiency. However, the dye adsorbed was found decreased by more than 50% with the TiCl$_4$ modification in the present study (Table in Fig. 3), which is different from most of other studies. Fig. 4a shows the linear relation between the dye concentration and the intensity of the absorption peak of N719 dye at 511 nm. Fig. 4b shows the UV-Vis absorption spectrum of the photoanodes with or without TiCl$_4$ modification. It is clearly shown that the absorption intensity decreased upon TiCl$_4$ modification. Since a thin TiO$_2$ layer formed on the surface of the nanocrystals after TiCl$_4$ modification, the decrease of the dye adsorption is likely due to the drastic reduction in the spacing between the nanocrystals and thus the dye molecules could not penetrate deeper into the photoanode layer. As a result, the light harvesting efficiency decreased.

To study the effect of TiCl$_4$ modification on the kinetics of the charge transport and transfer in the 20% Zn-doped SnO$_2$ nanocrystal photoanode, EIS spectra were obtained and fitted by using ZView software with an equivalent circuit (inset in Fig. 5a) which is based on the general transmission line model of DSSC. The Nyquist plots of the Zn-doped SnO$_2$ nanocrystal photoanode (10 $\mu$m in thickness; without or with TiCl$_4$ modification) based DSSCs at two open circuit voltages. In all the EIS spectra, two well-defined semicircles were observed in the high frequency region (>1 kHz) and in the frequency region of 0.1~100 Hz, respectively. Based on the general transmission line model of DSSC and the equivalent fitting circuit (inset in Fig. 5a), the diameter of the first semicircle in the Nyquist plot is related to $R_{Pt}$, $R_{FTO}$ and $R_{contact}$, which represents the charge-transfer resistance at the counter electrode, the exposed FTO-electrolyte interface and the FTO-SnO$_2$ nanocrystal contact respectively. It is obvious that the diameter of the first semicircle increases greatly with the decrease of the applied voltage from 0.67 V to 0.64 V (Fig. 5a, without TiCl$_4$ modification). While the diameter of

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**Figure 2.** (a) XRD patterns and tetragonal SnO$_2$ (JCPDS, 41-1445) as a reference, (b) photoluminescence spectrum, (c) UV-Vis absorption spectrum, and (d) bandgap calculation of the three kinds of nanocrystals.

**Figure 3.** J-V characteristics of the DSSCs using 20% Zn-doped SnO$_2$ nanocrystals photoanode (8 $\mu$m or 10 $\mu$m) with/without TiCl$_4$ modification under AM 1.5G simulated sunlight with a power density of 100 mWcm$^{-2}$. (The active areas of the photoanodes are 0.2926 cm$^2$.)
Figure 4. (a) Linear relation between the N719 dye concentration and the intensity of the absorption peak at 511 nm. (b) UV-Vis absorption spectrum of the 8 μm and 10 μm thick photoanodes with or without TiCl4 modification.

The first semicircle increases very slowly with the decrease of the applied voltage from 0.67 V to 0.63 V (Fig. 5b, with TiCl4 modification). Compare the cell configurations and the EIS spectrum of the Zn-doped SnO2 nanocrystal photoanode (without or with TiCl4 modification) based DSSCs, the following characteristics can be found. The charge-transfer resistance at the counter electrode (R Pt) is the same for both of the DSSCs with or without TiCl4 modification of the photoanode. Since the electrolyte and the FTO keep unchanged, the charge-transfer resistance at the exposed FTO-electrolyte interface (R FT0) also remains not changed. The only change induced by TiCl4 modification is the charge-transfer resistance at the FTO-SnO2 nanocrystal contact, which is denoted as the contact resistance (R contact). As a result, the change of the diameter of the first semicircle in the Nyquist plot is induced largely by the change of R contact. The contact resistance of the 20% Zn-doped SnO2 nanocrystal films increased largely with the decrease of V oc (Fig. 5c). It is obvious that TiCl4 modification greatly helps to decrease the contact resistance (Fig. 5c). The decrease of the contact resistance will improve the charge collection efficiency. The TiCl4 modification will help to form a very thin layer of TiO2 film on the entire surface of the photoanode. In addition, the TiCl4 modification will definitely help to increase the contact area between Zn-doped SnO2 nanocrystals and FTO substrate, as illustrated in Fig. 5d. As a result, the charge-transfer resistance at the FTO-SnO2 nanocrystal contact (R contact) decreased greatly upon TiCl4 modification.

The second semicircle denotes the electron transfer at the oxide/dye/electrolyte interface. By fitting the Nyquist plot, the electron transfer information can be interpreted. The chemical capacitance (C µ) increased at least 10 times after TiCl4 modification (Fig. 6a). It is considered that the surface states greatly increased due to the TiCl4 modification and these surface states helped to capture the electrons injected by the excited dye molecules rather than facilitate the recombination of injected electrons back to the redox electrolyte.23-32

Figure 5. Nyquist plots of the 20% Zn-doped SnO2 nanocrystal photoanode (10 μm in thickness) based DSSCs without (a) or with (b) TiCl4 modification at different V oc. The inset in (a) is the equivalent circuit used to fit the EIS spectra. The inset in (b) is the enlarged Nyquist plots. (c) The charge-transfer resistance at the FTO-SnO2 nanocrystal contact (R contact) with a function of applied potential. (d) The schematic graphs of the photoanode with/without TiCl4 modification.
Figure 6. (a) The chemical capacitance $C_{\mu}$, (b) the electron lifetime $\tau_{e}$ of the DSSCs using 20% Zn-doped SnO$_2$ nanocrystals photoanode (10 $\mu$m in thickness) with/without TiCl$_4$ modification.

The electron lifetime ($\tau_{e}$) of the Zn-doped SnO$_2$ nanocrystal photoanode DSSC also increased at least 10 times after TiCl$_4$ modification (Fig. 6b). The larger the electron lifetime, the slower the recombination rate. As a result, TiCl$_4$ modification which increased the electron lifetime will make the recombination rate slower. The charge injection efficiency after TiCl$_4$ modification was greatly improved.\(^3\!\!^4\) The Zn-doped SnO$_2$ nanocrystals will be of particular interest as photoanode material in DSSCs. In conclusion, for the first time Zn-doped SnO$_2$ nanocrystals with different doping concentrations were successfully synthesized and were used as a photoanode in DSSCs. Compared to the previous pure SnO$_2$ nanorods based DSSCs with N719 dye as the sensitizer, the present Zn-doped SnO$_2$ nanocrystals based DSSC achieved an efficiency of 2.07% and a high $V_{oc}$ of 0.67 V. TiCl$_4$ modification of the Zn-doped SnO$_2$ nanocrystal photoanode greatly improves the charge injection efficiency (due to increase of electron lifetime) and the charge collection efficiency (due to the reduced contact resistance between the nanocrystals and FTO substrate). As a result, the photocurrent doubled and PCE reaches 4.32% despite a decreased dye adsorption.

Acknowledgments

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References