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Research Article

Enhanced Efficiency of Dye-Sensitized Solar Cells by Trace Amount Ca-Doping in TiO_2 Photoelectrodes

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Trace amount Ca-doped TiO_2 films were synthesized by the hydrothermal method and applied as photoanodes of dye-sensitized solar cells (DSSCs). To prepare Ca-doped TiO_2 film electrodes, several milliliters of $Ca(NO_3)_2$ solution was added in TiO_2 solution during the hydrolysis process. The improvements of DSSCs were confirmed by photocurrent density-voltage (*J-V*) characteristics, electrochemical impedance spectroscopy (EIS) measurements. Owing to the doping effect of Ca, the Ca-doped TiO_2 thin film shows power conversion efficiency of 7.45% for 50 ppm Ca-doped TiO_2 electrode, which is higher than that of the undoped TiO_2 film (6.78%) and the short-circuit photocurrent density (J_{sc}) increases from 13.68 to 15.42 $mA{\cdot}cm^{-2}$. The energy conversion efficiency and short-circuit current density (J_{sc}) of DSSCs were increased due to the faster electron transport in the Ca-doped TiO_2 film. When Ca was incorporated into TiO_2 films, the electrons transport faster and the charge collection efficiency η_{cc} is higher than that in the undoped TiO_2 films.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on mesoporous nanocrystalline TiO_2 film have achieved photoelectric conversion efficiency (η) up to 13%. In order to develop high performance of DSSCs and commercialize successfully, many nanocrystalline semiconductors such as TiO_2 [1], ZnO [2], and SnO_2 [3] have been used as photoanode materials. Among them, TiO_2 has been proven to be the best semiconductor electrode material due to its high chemical stability [4], excellent charge transport capability, and ideal position of the conduction band edge. It is known to be one of the main components of DSSCs and plays a key role in determining the performance of DSSCs.

In recent years, Doping has been considered as a promising way to improve the properties of TiO_2 photoanode. TiO_2 films doped with metal and nonmetal have been extensively researched, such as Mg-doping [5], La-doping [6], Nb-doping [7], Ta-doping [8], and N-doping [9], which may increase the photoelectric conversion efficiency. In all the applications mentioned above, the TiO_2 films were doped at very high levels (from 0.1% to 10%). However, few studies have been reported about TiO_2 doped at parts per million (ppm) level applied as photoanode of DSSCs. Xie et al. [10] have found that trace amount of Cr-doping TiO_2 films could improve the efficiency of DSSCs. The improvement was ascribed to Cr additions offers more electrons for TiO_2 and increases the property of electron transport for DSSCs. As we all know, doping semiconductors at parts per million (ppm) level is the most common approach for enhancing the Fermi energy level of semiconductors and then increasing their conductivity (for instance, Si).

In this paper, a series of Ca-doped TiO_2 films were synthesized by hydrothermal method and were successfully applied as the photoanode materials in DSSCs, and the short-circuit current densities (J_{sc}) and photoelectric conversion efficiencies of DSSCs were found to be increased by trace amount doping in TiO_2. The change in performance of DSSCs employing Ca-doped TiO_2 films with different concentrations was obvious. We can conclude that the intrinsic increases in the photocurrent and photoelectric conversion efficiency are primarily related to faster electron transport in the Ca-doped TiO_2 film. The effects caused by Ca doping on electron collection, transfer, and recombination of the DSSCs are discussed below.

2. Experimental Section

2.1. Preparation of Undoped TiO_2 and Ca-Doped TiO_2 Pastes. Titanium isopropoxide (TTIP) was used as Ti precursors and calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$) was the Ca sources. Pure TiO_2 and Ca-doped TiO_2 pastes were synthesized by a hydrothermal treatment method. The hydrothermal solutions were synthesized as follows [11].

(i) 2.1 g acetic acid was added dropwise into 10 mL of TTIP. Subsequently, the mixture was added to 50 mL of deionized water mixed with different amounts of $Ca(NO_3)_2{\cdot}4H_2O$ (Ca/TiO_2 molar ratio: undoped, 20 ppm, 50 ppm, 70 ppm, and 100 ppm) with rapid stirring for 1 h. Then, 0.68 mL of nitric acid was added to the obtained mixture solution. After continuous stirring at 80°C for 2~3 h, a transparent mixture solution was obtained.

(ii) The transparent mixture solution was filtered to remove insoluble impurities and transferred into an autoclave at 220°C for 12 h. After cooling to room temperature, 0.4 mL of nitric acid was added into the colloid, using ultrasonicator to disperse.

(iii) The colloid was concentrated to 20 mL by rotary evaporator. Finally, PEG and Triton X-100 were added to form TiO_2 paste. The obtained pastes were denoted as undoped TiO_2, Ca-1: 20 ppm Ca-doped TiO_2, Ca-2: 50 ppm Ca-doped TiO_2, Ca-3: 70 ppm Ca-doped TiO_2, and Ca-4: 100 ppm Ca-doped TiO_2.

Following the procedure described, a total of five pastes with different concentrations of Ca were prepared.

2.2. Fabrication of Photoelectrodes and DSSCs. The FTO glass was used as substrate after careful cleaning. The pure TiO_2 and Ca-doped TiO_2 pastes were coated onto FTO substrates using a doctor-blade method, respectively. Next, the photoelectrodes were sintered at 500°C for 30 min to obtain the mesoporous TiO_2 film photoelectrodes. The thicknesses of these films were around 8 μm measured with a TalyForm S4C-3D profilometer. They were dipped into a 0.5 mM N719 dye solution for 24 h at room temperature, and the excessive dye was washed away by using ethanol, followed by drying at 60°C. The platinum-coated FTO was used as the counter. A drop of electrolyte solution was injected into the photoelectrode and then the counter was clamped onto the photoelectrode; the electrolyte solution consisted of 0.05 mM LiI, 0.03 M I_2, 0.1 M PMII (1-methyl-3-propyl imidazolium iodide), 0.1 M GNCS, and 0.5 M TBP in mixed solvent of acetonitrile and PC (volume ratio: 1/1). A sandwich-type DSSC configuration was fabricated.

2.3. Measurements. Photovoltaic measurements were performed by a CHI660C electrochemical workstation (CH Instruments, Shanghai, China) at room temperature. The irradiated area of each cell was kept at 0.25 cm^2 by using a light-tight metal mask. Electrochemical impedance spectroscopy (EIS) technique [12] was employed to investigate the electron transport in DSSCs.

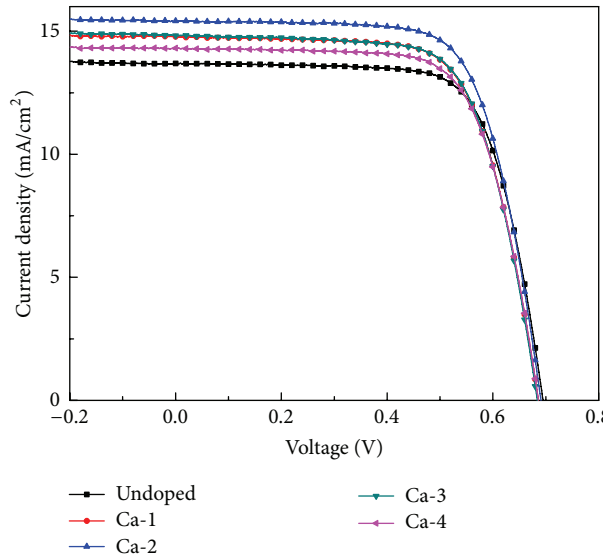

Figure 1: *J-V* characteristics of DSSCs based on the undoped and Ca-doped TiO_2 photoanodes.

3. Results and Discussion

3.1. J-V Characteristics. The photocurrent density-voltage (*J-V*) characteristics of the DSSCs based on the pure TiO_2 film photoelectrodes and Ca-doped TiO_2 film photoelectrodes are shown in Figure 1. The average performance characteristics obtained from multiple cells with the same Ca content were summarized in Table 1, which shows the correlation between the photovoltaic performance parameters and the Ca content in the TiO_2. The best photovoltaic performance was obtained from 50 ppm Ca-doped TiO_2. Obviously, as can be seen from the graph, the energy conversion efficiency (η) went up with the increase of Ca content, which was attributed to the enhancement of the short-circuit current density (J_{sc}). The J_{sc} of DSSCs based on 50 ppm Ca-doped TiO_2 was 15.42 $mA{\cdot}cm^{-2}$, which was 12.7% higher than that of undoped cells. The energy conversion efficiency of 7.58% was achieved for cells based on 50 ppm Ca-doped TiO_2 electrode, which accounts for 9.88% higher than that of undoped cells. The effect on open-circuit voltage (V_{oc}) and fill factor as a result of such a little amount of Ca-doping was negligible. The energy conversion efficiency (η) increases gradually with the increase of Ca content and reaches an optimum value coinciding with Ca quantity of 50 ppm. However, the higher Ca amounts (>50 ppm) cause electron scattering and trap electrons which increase dark current. As a result, the energy conversion efficiency of DSSCs begin to fall.

3.2. Electrochemical Impedance Spectroscopy Analysis of DSSCs. To investigate the difference of the charge transport properties between pure DSSCs and Ca-doped DSSCs, we performed electrochemical impedance spectroscopy (EIS) analysis. EIS has been widely employed to investigate the electron transport in DSSCs, for example, measuring the respective time constants for charge combination and for the

Table 1: Performance of DSSCs based on undoped and Ca-doped TiO_2 photoanodes.

DSSCs	Doping/ppm	V_{oc}/mV	J_{sc}/mAcm^2	FF	η/%	R_{ct}/Ω	η_{cc}
Undoped	0	695	13.68	0.71	6.78	7.34	0.75
Ca-1	20	686	14.78	0.69	7.00	7.32	0.73
Ca-2	50	691	15.42	0.70	7.45	5.24	0.80
Ca-3	70	684	14.82	0.70	7.00	8.09	0.72
Ca-4	100	686	14.32	0.69	6.84	7.30	0.73

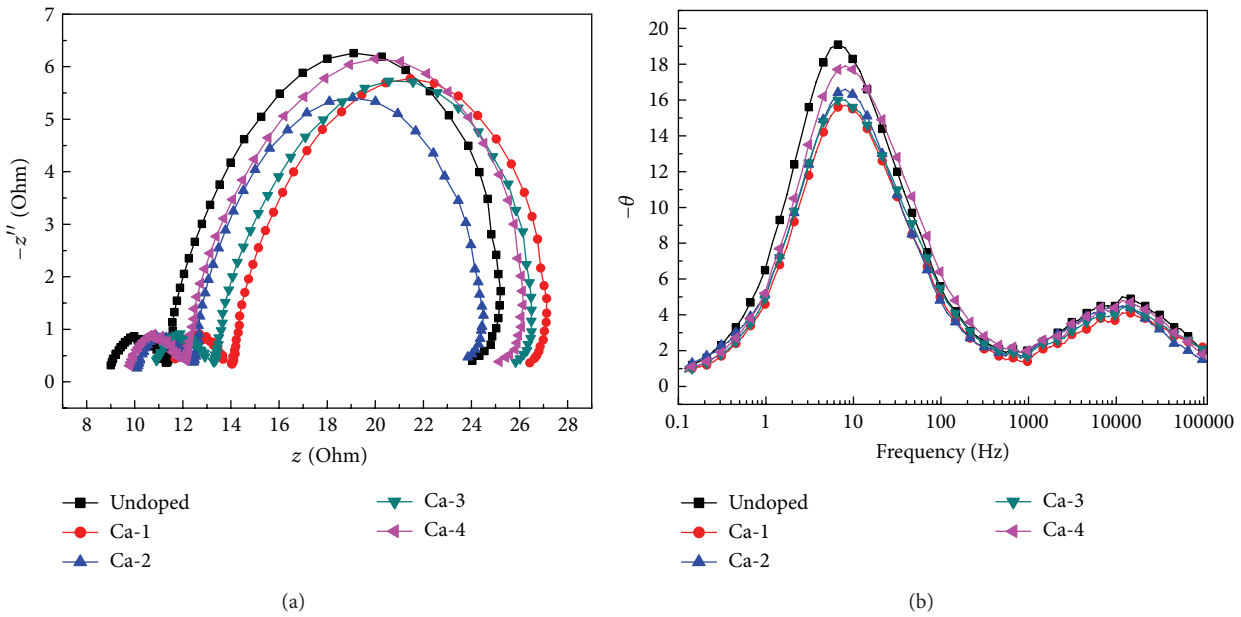

Figure 2: EIS of DSSCs based on the undoped and Ca-doped TiO_2 photoanodes measured in the illumination at the applied bias of V_{oc} (a) Nyquist plots and (b) Bode phase plots.

combined processes of charge collection. From the measured spectra of EIS, we can get reliable value of the parameter. Figure 2 shows the EIS spectra of pure DSSCs and Ca-doped DSSCs, the impedance spectra of DSSCs based on the pure TiO_2 and Ca-doped TiO_2 were measured from 0.1 to 10^5 Hz in the illumination at the applied bias of V_{oc}. The spectra are composed of two semicircles: the small semicircle in the high frequency range of 10^3 to 10^5 Hz fitted to a charge transfer resistance (R_{ct}) at the interfaces of the redox electrolyte/Pt counter electrode and FTO/TiO_2 and the large semicircle in the frequency range of 1 to 10^3 Hz fitted to a transport resistance (R_w), which is related to the charge transport resistance of the accumulation/transport [13] of the injected electrons within TiO_2 film and the charge transport resistance at the TiO_2/redox electrolyte interfaces. This large semicircle is the major concern here. As shown in Figure 2, the large semicircle got smaller with the increase of Ca in TiO_2 films. This change reflected the acceleration of electron transport process in TiO_2 photoanode. The modeled internal resistances of the DSSCs based on five different electrodes are exhibited in Table 2, in which t_r is the electron transport time, t_c is the electron lifetime, R_w is charge transport resistance, and η_{cc} is the charge collection efficiency of DSSCs.

The apparent value of η_{cc} can be estimated on the basis of the t_r and t_c data from the following [14]:

$$\eta_{cc} = 1 - \frac{t_r}{t_c}. \quad (1)$$

The electron transport time constants for Ca-doped TiO_2 films decrease, which indicates the electrons transport faster in the Ca-doped TiO_2 films than the undoped TiO_2 films. This enhanced the charge collection efficiency η_{cc} and led to higher current density (J_{sc}) of DSSCs. The electron life time constants for the Ca-doped TiO_2 films also slightly decrease. The electron lifetime in DSSCs is determined by the characteristic frequency peak in the low frequency (f_{max}) according to the following equation [15]:

$$\tau_e = \frac{1}{2\pi f_{max}}. \quad (2)$$

The shorter electron life time indicates the faster recombination rate in the Ca-doped TiO_2 films, and that could be attributed to impurities of Ca-doping, which acts as a charge trapping site for the electron-hole recombination. The electron lifetime decreases slightly, so we concluded

Table 2: The mean electron life time (t_r), the mean electron transit time (t_c), and the charge collection efficiency (η_{cc}) of DSSCs based on undoped and Ca-doped TiO_2 photoanodes.

DSSCs	Doping/ppm	R_w/Ω	t_r/ms	t_c/ms	η_{cc}
Undoped	0	7.36	0.0350	0.0088	0.75
Ca-1	20	7.32	0.0290	0.0077	0.73
Ca-2	50	5.24	0.0294	0.0059	0.80
Ca-3	70	7.27	0.0290	0.0076	0.72
Ca-4	100	8.09	0.0290	0.0080	0.73

that less photogenerated electrons are captured by empty trap states in the Ca-doped TiO_2 films [16], and this result favors the electron transport. The improvement of electron transport ability was helpful to increase the short-circuit current density (J_{sc}), resulting in higher conversion efficiency.

4. Conclusion

In summary, the Ca-doping TiO_2 nanoparticles were successfully applied as the photoanode material in DSSCs. By comparing the Ca-doping TiO_2 with undoping TiO_2, a faster electron transport and shorter lifetime existed for the Ca-doping DSSCs. Moreover, the higher electron transport rates of Ca-doped TiO_2 photoanode can improve the charge collection efficiency and thus lead to higher short-circuit photocurrent density of DSSCs. The best photovoltaic performance was obtained from 50 ppm Ca-doping with the conversion efficiency of 7.45%. This value was 9.88% higher than that of the undoped device. The short-circuit current density (J_{sc}) was increased due to the faster electron transport in the Ca-doped TiO_2 film. We can conclude that Ca-doped TiO_2 is a better photoanode material and a more promising alternative for high efficient DSSCs than pure TiO_2.

Conflict of Interests

The authors do not have any conflict of interests in their submitted paper.

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