Preparation of nano-crystal N–Zn/TiO₂ anode films and the effects of co-sensitization on the performance of dye-sensitized solar cells

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A nano-crystal N–Zn/TiO₂ anode film was prepared using a combined technology. X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and cyclic voltammetry characterizations showed that the two elements N and Zn were doped into nano-crystal TiO₂ successfully. This resulted in a strong redshift in the UV-Visible spectrum. UV-Visible measurements showed that the light absorption of N719 and P3OT were complementary and covered the entire visible region. This led to a high utilization of visible light. Solar cells based on the N–Zn/TiO₂ anode film were co-sensitized using P3OT and N719. The cells have a short-circuit current density of 7.91 mA/cm², an open-circuit photovoltage of 0.659 V, and a photoelectric conversion efficiency of 2.64%. Also, the relationship among the N–Zn/TiO₂-film anode's electric structure, the dye's LUMO, electrochemical impedance, and photoelectric conversion efficiency are discussed in the paper.

dye-sensitized solar cells, nano-crystal N–Zn/TiO₂ anode film, co-sensitization, electrochemical impedance spectroscopy, energy level match, photoelectric properties

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The rapid depletion of fossil fuels and potentially disastrous environmental problems forcing the development of renewable energy resources for our growing energy demands. Fortunately, solar energy has a great potential to fulfill the demand for sustainable energy for future generations. Dye-sensitized solar cells (DSSCs) have attracted increasing attention for their high efficiency, low-cost, flexibility, and fine-tuned materials, since O'Regan and Grätzel first introduced DSSCs in 1991 [1–3].

The most extensively studied DSSCs are based on TiO₂ [4], which is a wide bandgap semiconductor with rutile and anatase phases, and only absorb UV light under 387 nm. Previously, there have been some reports of TiO₂ doped with metal elements or non-metallic elements such as Li, N, Cl, Zn and W [5–9]. However, a nano-crystal N–Zn/TiO₂ anode has not been reported in a DSSC.

Studies on dye sensitizers have been mainly focused on organic metal complexes or pure organic dyes [10–13]. However, there has been no report of dye-sensitized solar cells based on N719 and P3OT (poly(3-octylthiophene)). In this paper, a nano-crystal N–Zn/TiO₂ anode film was prepared by doping N and Zn into TiO₂. Solar cells based on nano-crystal N–Zn/TiO₂ were co-sensitized using P3OT and N719 to improve the performance of the solar cells. The relationships among the microscopic structure of the battery, electrochemical impedance, and photoelectric conversion efficiency were also studied.

1 Experimental

1.1 Preparation of nano-TiO₂

PEG800 (0.5 mL) was added to 0.3 mol/L TiCl₄ (55 mL).

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This solution was stirred vigorously at room temperature. We adjusted the pH of the solution was adjusted to 5–6 by dripping ammonia. The gel was filtered and washed until there were no remaining traces of Cl^- . Then, the gel was transferred into a PTFE autoclave (100 mL) and kept at 240°C for 12 h. Then, the gel was washed using ethanol until almost all the water was removed. The obtained alcogel was transferred into a crucible and dried at room temperature. Finally calcination was performed at 500°C for 1 h. Through this process the nano- TiO_2 was obtained.

1.2 Preparation of nano-N/ TiO_2

The gel (prepared in section 1.1) was filtered and washed with aqueous ammonia (3 mol/L) until all the chloride ions were removed. The N-doped TiO_2 was obtained following the steps in section 1.1.

1.3 Preparation of nano-N-Zn/ TiO_2

PEG800 (0.5 mL) was added to 0.3 mol/L TiCl_4 (55 mL), and was vigorously stirred at room temperature. Aqueous $\text{Zn}(\text{NO}_3)_2$ (0.2 mol/L) was added to the system at the molar ratio, $\text{Ti}:\text{Zn} = 100:0.2$. The N-Zn-doped TiO_2 was obtained following the remaining steps in section 1.1.

1.4 Preparation of P3OT

The conducting P3OT was synthesized using Fe(III) as catalyst, following the method in references [14,15]. In an N_2 environment, chloroform (20 mL) and anhydrous FeCl_3 (0.03 mol) were added to a 100 mL flask, and the mixture was stirred for 15 min. 3-Octylthiophene (0.01 mol) in chloroform (20 mL) was added dropwise to the solution. The reaction temperature of system was kept between $0 - 1^\circ\text{C}$ for 7 h. The product was slowly added to methanol (300 mL), separated from the solvent, and filtered. The remaining black solid was added to chloroform (50 mL) in a conical flask and was stirred for 60 min while being gently heated to 40°C . A chloroform solution remained. After removing the chloroform by distillation, the small amount of viscous liquid residue was slowly added to methanol (200 mL) and a product precipitated. The precipitate was dried in vacuum at room temperature, and then it was subjected to Soxhlet extraction with methanol for 20 h. Finally the polymer was precipitated with methanol (200 mL) and vacuum dried at room temperature. Through this process the target polymer was obtained.

1.5 Preparation of dye-sensitized solar cells

(1) Preparation of TiO_2 anode, N/ TiO_2 anode and N-Zn/ TiO_2 anode. Equal volumes of 4 mol/L TiCl_4 , deionized water and ethanol were mixed to obtain a TiCl_4 solution. In an agate grinding bowl, 0.25 g of TiO_2 powder, 1 mL of

deionized water, 0.05 mL of acetylacetone and 0.15 mL of PEG800 were ground for 20 min to obtain a TiO_2 paste. Four sides of a fluorine doped tin oxide glass were covered with adhesive tape to obtain a 0.5 cm^2 ($0.5\text{ cm} \times 1\text{ cm}$) area. The glass was then coated with a layer of sol- TiCl_4 . We then added some TiO_2 paste to the surface and smoothed the surface using a scraping method. After being dried in air, the tape was removed. The TiO_2 anode was obtained after heating the dried paste at 450°C for half an hour. The N/ TiO_2 anode and N-Zn/ TiO_2 anode were prepared using the same method.

(2) Preparation of Pt electrode. H_2PtCl_6 was placed evenly on another fluorine doped tin oxide substrate. It was then dried at 25°C and calcinated at 380°C for 30 min to prepare Pt electrode.

(3) Sensitization and assembly the DSSCs. We prepared three dyes: 5 mmol/L P3OT in a chloroform solution, 5 mmol/L N719 in an ethanol solution, and mixtures of 5 mmol/L P3OT in a chloroform solution and 5 mmol/L N719 in an ethanol solution with different molar ratios. The N-Zn/ TiO_2 anode thin films prepared using the steps in section 1.5 (1) were soaked in different kinds of dyes at 80°C for 12 h. Dye attached to the surface layer was washed with anhydrous ethanol. The sample was dried at 80°C for 15 min. Through this method the sensitized N-Zn/ TiO_2 anode thin film was prepared. After the dye-sensitized solar cells were obtained, the N-Zn/ TiO_2 anode was packaged with a Pt electrode using an epoxy resin film. Then, we injected the electrolyte (0.5 mol/L LiI, 0.05 mol/L I_2 , 0.3 mol/L DMPH, 0.5 mol/L 4-TBP) into the system and sealed it.

1.6 XRD, XPS, TEM and UV-Vis

X-ray diffraction (XRD) measurements were performed using a Shimadzu HR6000X (Cu target X tube, voltage 40.0 kV, current 30.0 mA, scan angle $20^\circ - 80^\circ$, Kyoto, Japan).

X-ray photoelectron spectroscopy (XPS) analysis was conducted using an ESCALAB 250 (Fisher Scientific, Waltham, MA, USA).

Transmission electron microscope (TEM) measurements were performed on a HITACHI-800 (Tokyo, Japan) to test the power sample.

UV-Visible (UV-Vis) spectra were measured using a Hitachi U-3010 spectrophotometer.

1.7 Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed using a Potentiostat/Galvanostat (EG&G PAR Model 283, Princeton Applied Research, Oak Ridge, TN, USA). The counter electrode was made of platinum, and the reference electrode was non-aqueous Ag/Ag^+ . The CV curves were recorded in acetonitrile with 0.1 mol/L LiClO_4 at a scanning rate of 50 mV/s. Prior to use, all the solutions were insufficient with N_2 for 30 min.

1.8 Testing the DSSCs

Electrochemical Impedance Spectroscopy (EIS) measurements were performed using the Potentiostat/Galvanostat (EG&G PAR Model 283). The measured frequency ranged from 50 mHz to 100 kHz. R_{ct1} , R_{ct2} and R_{diff} were corresponded to the charge transfer processes at the Pt counter electrode, the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface and the Nernst diffusion process of I^-/I_3^- in the electrolyte, respectively.

Current-voltage (I - V) measurements were taken in air at room temperature (25°C) using a Keithley 236 high-current-source power meter (Cleveland, OH, USA) under white-light illumination from a 500-W xenon lamp. The light intensity was about $100 \text{ mW}/\text{cm}^2$ on the sample surfaces, and was measured using a photodetector at 25°C . The tested battery parameters were the short-circuit current density (I_{sc}), the open-circuit photovoltage (V_{oc}), the maximum power (P_{max}), the incident light power P_{in} ($100 \text{ mW}/\text{cm}^2$), and the photoelectric conversion efficiency (η) [16]:

$$FF = P_{max} / (I_{sc} \times V_{oc}),$$

$$\eta = (FF \times I_{sc} \times V_{oc}) / P_{in}.$$

2 Results and discussion

2.1 XRD Characterization of TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$

The XRD traces of the TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ powders are shown in Figure 1. For the TiO_2 particles, the peaks at 25.32° , 37.88° , 48.08° , 53.80° , and 55.04° are assigned to the (101), (004), (200), (105), and (211) lattice planes. These peaks correspond to the anatase phase. There are no N or ZnO diffraction peaks in the XRD spectra, which indicates that doping elements were dispersed in TiO_2 to a high degree. We calculated that the average TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ particles are 22.22, 13.69 and 11.83 nm respectively using the Scherrer formula ($D_{hkl} = k\lambda / \beta \cos\theta$). This indicates the doping of N and Zn can inhibit the growth and increase the surface area of nano- TiO_2 powders. This is favorable for the adsorption of dye molecules in N/

Figure 1 XRD traces of the TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ powders.

TiO_2 and $\text{N-Zn} / \text{TiO}_2$ films.

2.2 TEM measurements of TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$

The TEM images of TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ particles are shown in Figure 2. These images show that the sizes of the particle are 22 nm (a), 14 nm (b), and 12 nm (c). The results are basically the same as those predicted using the Scherrer formula. The doped particles were found to have very good dispersivity. Alcohol exchange during the powder preparation eliminated the liquid surface tension and reduces agglomeration of particles during the calcining process. Therefore, nano-particles with high surface area, small size, and good dispersivity were obtained.

2.3 XPS characterization of $\text{N-Zn}/\text{TiO}_2$

Figure 3(a)–(e) is high-resolution XPS spectra of sample $\text{N-Zn}/\text{TiO}_2$ film. From Figure 3(a), it can be seen that the N and Zn two elements were doped successfully. It can be seen from Figure 3(b) that Ti in $\text{N-Zn} / \text{TiO}_2$ is primarily tetravalent [17]. Figure 3(b) shows a close-up of the scan of the $\text{Ti}2p$ peaks located at 464.62 eV ($\text{Ti } 2p_{1/2}$) and 458.86 eV ($\text{Ti } 2p_{3/2}$) in the $\text{N-Zn} / \text{TiO}_2$ film. Compared with TiO_2 , a high binding energy-shift took place. This is because the radius of Zn^{2+} (74 pm) is larger than that of Ti^{4+} (68 pm), and Zn is difficult to dope into the internal lattice of TiO_2 . This leads to Ti atoms being replaced by Zn atoms to form Ti-O-Zn on the interface of the anatase crystal TiO_2 . In Figure 3(c), two oxygen peaks in the spectra of $\text{N-Zn} / \text{TiO}_2$ at 530.05 and 531.86 eV are shown. The former is attributed to Ti-O and the latter is attributed to Zn-O . Figure 3(d) shows that a close-up of the $\text{Zn}2p$ peaks located at 1044.8 eV ($\text{Zn } 2p_{1/2}$) and 1021.7 eV ($\text{Zn } 2p_{3/2}$). The Zn atoms in $\text{N-Zn}/\text{TiO}_2$ are primarily bivalent and combine with O [18]. The electric binding energy of the $\text{N}1s$ state in $\text{N-Zn}/\text{TiO}_2$ sample is 400.5 eV (Figure 3(e)). N replaces O in the TiO_2 lattice to form Ti-N-O [19].

2.4 UV-Vis spectra of TiO_2 , N/TiO_2 , $\text{N-Zn}/\text{TiO}_2$ and dyes

Figure 4 shows the UV-Vis spectra of TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ anode thin film electrodes. In Figure 4, the UV-Vis absorption spectra show that the maximum absorption wavelengths of TiO_2 , N/TiO_2 and $\text{N-Zn}/\text{TiO}_2$ anode thin films are 249.5, 254.7 and 260.3 nm, respectively. The corresponding absorption wavelengths are 388, 438 and 456 nm. Compared with pure TiO_2 , the significant red-shift took place in $\text{N-Zn}/\text{TiO}_2$ films, which has strong visible light absorption [20].

Figure 5 shows the UV-Vis spectra of P3OT, N719 and P3OT/N719. The three dyes have strong absorption between 200–700 nm. The main absorption peaks of N719 located at 212, 317, 400 and 551 nm, which nearly cover the entire

Figure 2 TEM images of (a) TiO_2 , (b) N/TiO_2 , and (c) N-Zn/TiO_2 .

UV-Vis region. The maximum absorption wavelengths of P3OT are 220 and 518 nm. From Figure 5, it can be seen that N719 has a valley at 490 nm. The absorption peak of P3OT at 500 nm supplements the absorption of N719. The combined absorption of N719 and P3OT can achieve a full absorption of visible light spectrum. Therefore, we used N719/P3OT dye to broaden the light absorption of anode in the visible range to improve the photoelectric conversion efficiency of the system.

2.5 Cyclic voltammetry

CV curves of TiO_2 , N/TiO_2 and N-Zn/TiO_2 nanocrystalline thin film electrodes and different dyes are shown in Figure 6(a) and (b). The frontier orbital and energy gap were listed in Table 1. According to $E_g = 1239.8/\lambda$ (E_g is the band gap, λ is the maximum wavelength of absorption), the maximum absorption wavelengths of TiO_2 , N/TiO_2 and N-Zn/TiO_2 films were 387, 441 and 459 nm, respectively. The results are basically the same with the UV-Vis test.

It can be seen from Figure 7 that the energy gaps of N719 and N719/P3OT are 1.57 and 1.54 eV, respectively. These are smaller than that of P3OT and N719. The electrons in N719/P3OT are easier to excite with light. In addition, the lowest unoccupied molecular orbitals (LUMOs) of N719 and N719/P3OT are 3.11 and 3.12 eV, respectively. It is easier for an electron in the LUMO of N719 or N719/P3OT to transfer to the LUMO of the N/TiO_2 or N-Zn/TiO_2 film electrodes (Figure 7). However, the LUMO

of the N-Zn/TiO_2 film electrode is lower than that of the N/TiO_2 film electrode. Therefore, N719/P3OT matches the LUMO of N-Zn/TiO_2 thin film electrode more closely (Figure 7).

2.6 I-V and EIS

(1) Effects of N-Zn/TiO_2 nanocrystalline thin film electrodes on the performance of dye-sensitized solar cell. Current density-voltage curves for the DSSCs based on the thin film electrodes are shown in Figure 8. The electrodes were sensitized using N719, and are under a constant illumination of 100 mW/cm^2 . The estimated performance parameters are summarized in Table 2. Photoelectric chemical characteristics, such as short circuit current density (J_{sc}) and photoelectric conversion efficiency (η), of the DSSCs based on the N-Zn/TiO_2 film electrode are greater than both of the DSSCs based on the N/TiO_2 and TiO_2 film electrodes. The J_{sc} and η of the DSSC based on the N-Zn/TiO_2 film electrode are 6.22 mA/cm^2 and 2.28%, respectively.

From the EIS spectra (Figure 9), it can be seen that the R_{ct2} of the DSSC based on N-Zn/TiO_2 film electrode is the lowest. We concluded that N719 matches with N-Zn/TiO_2 film electrode the best (Figure 7). The η of the DSSCs based on N-Zn/TiO_2 film electrode is the highest. Also, the particle size of the N-Zn/TiO_2 film is the smallest, and it has with a high surface area. This increases the adsorption for both the dye and anode, which improves the

Figure 3 XPS spectra of the N-Zn/TiO₂ film: (a) survey; (b) Ti 2p_{3/2} and Ti 2p_{1/2}; (c) O 1s; (d) Zn 2p; and (e) N 1s.

photoelectric conversion efficiency.

(2) Effects of co-sensitization on the performance of the dye-sensitized solar cells. Current density-voltage curves for DSSCs sensitized using different dyes are plotted in Figure 10. These measurements were made at a constant illumination of 100 mW/cm². The estimated performance parameters are summarized in Table 3. It can be seen that the performance of the DSSCs co-sensitized using P3OT and N719 is better than that of the DSSCs sensitized using N719 and P3OT. When $n(\text{P3OT}):n(\text{N719}) = 1:2.5$, the dye-sensitized solar cells have a short-circuit current density of 7.91 mA/cm², an open-circuit photovoltage of 0.659 V,

and a photoelectric conversion efficiency of 2.64%. However, photoelectric chemical characteristics, such as J_{sc} , V_{oc} and η , of the DSSCs decrease with increasing N719. This is because the DSSCs become increasingly similar to those sensitized using N719 alone. These findings match those of 3.5, which stated that the P3OT/N719 dye matches the N-Zn/TiO₂ film electrode best. From the EIS spectra (Figure 11), it can be seen that the R_{ct2} of the DSSCs co-sensitized using P3OT and N719 is the lowest when $n(\text{P3OT}):n(\text{N719}) = 1:2.5$. In this case, the short-circuit current density and the photoelectric conversion efficiency are at their highest values.

Figure 4 UV-Vis spectra of TiO_2 , N/TiO_2 and N-Zn/TiO_2 nanocrystalline thin film electrodes.

Figure 5 UV-Vis spectra of P3OT, N719 and P3OT/N719.

3 Conclusion

In this paper, TiO_2 , N/TiO_2 and N-Zn/TiO_2 anode films were prepared using a combination of sol and powder technologies of. DSSCs based on the N-Zn/TiO_2 anode film were co-sensitized using N719 and P3OT.

(1) Anatase N-Zn/TiO_2 was prepared using the hydrothermal method. The XPS measurements showed that the N and Zn elements were doped successfully. From the XRD and TEM characterization, we found that the particles sizes were distributed between 10–13 nm. The doping of N and Zn inhibited the growth of nano- TiO_2 particles.

(2) The TiO_2 , N/TiO_2 and N-Zn/TiO_2 anode films were prepared using a combination of techniques. The UV-vis spectral measurements showed the light absorption of N719 and P3OT could supplement one another and cover the entire visible region. CV measurements showed that the P3OT/N719 matched the N-Zn/TiO_2 film electrode the best.

(3) The co-sensitized solar cell based on the N-Zn/TiO_2 film anode had a short-circuit current density of 7.91 mA/cm^2 , open-circuit photovoltage of 0.659 V, and photoelectric conversion efficiency of 2.64% when $n(\text{P3OT}):n(\text{N719}) = 1:2.5$.

Figure 6 (a) Cyclic voltammetry curves of the TiO_2 , N/TiO_2 and N-Zn/TiO_2 nanocrystalline thin film electrodes, and (b) Cyclic voltammetry curves of P3OT, N719 and P3OT/N719.

Table 1 The frontier orbital and energy gap of TiO_2 , N/TiO_2 , N-Zn/TiO_2 electrodes, P3OT, N719 and P3OT/N719^{a)}

Sample	$\Phi_{\text{ox}}(\text{eV})$	$\Phi_{\text{red}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_{\text{HOMO}}(\text{eV})$	$E_g(\text{eV})$
TiO_2	2.15	-1.05	-3.39	-6.59	3.20
N/TiO_2	2.08	-0.73	-3.71	-6.52	2.81
N-Zn/TiO_2	2.01	-0.69	-3.75	-6.45	2.70
N719	0.24	-1.33	-3.11	-4.68	1.57
P3OT	0.31	-1.62	-2.82	-4.75	1.93
N719/P3OT	0.22	-1.32	-3.12	-4.66	1.54

a) The Φ_{ox} and Φ_{red} potentials (vs. 0.01 mol/L Ag^+/Ag in CH_3CN) were determined using cyclic voltammetry. They were calculated using $E_g = \Phi_{\text{ox}} - \Phi_{\text{red}}$, E_{HOMO} and E_{LUMO} from $E_{\text{HOMO}} = -(\Phi_{\text{ox}} + 4.44) \text{ eV}$ and $E_{\text{LUMO}} = -(\Phi_{\text{red}} + 4.44) \text{ eV}$ [21].

Figure 7 Energy transfer processes of TiO_2 , N/TiO_2 , N-Zn/TiO_2 nanocrystalline thin film electrodes, P3OT, N719 and P3OT/N719.

Figure 8 Photocurrent-photovoltage curves of the DSSCs based on the TiO_2 , N/TiO_2 and N-Zn/TiO_2 nanocrystalline thin film electrodes.

Table 2 Performance parameters of the dye-sensitized solar cells

Sample	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	FF	$\eta(\%)$	$R_{ct2}(\Omega)$
TiO_2	4.40	0.638	0.5785	1.62	33.47
N/TiO_2	4.94	0.637	0.5631	1.77	31.51
N-Zn/TiO_2	6.22	0.636	0.5763	2.28	17.6

Figure 9 EIS spectra of the dye-sensitized solar cells based on the thin film electrodes.

Figure 10 Photocurrent-photovoltage curves of the DSSCs sensitized using P3OT, N719 and P3OT/N719.

Table 3 Performance parameters of the dye-sensitized solar cells.

Dye	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	FF	$\eta(\%)$	$R_{ct2}(\Omega)$
N719	6.22	0.636	0.5763	2.28	17.6
P3OT	0.224	0.440	0.5946	0.06	503
P3OT:N719=1:2	6.72	0.650	0.5174	2.26	21.28
P3OT:N719=1:2.5	7.91	0.659	0.5072	2.64	16.68
P3OT:N719=1:3	6.36	0.638	0.5471	2.22	23.68

Figure 11 EIS spectra of DSSCs sensitized with different dyes.

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