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Research Article

Natural Dye-Sensitized Solar Cells Based on Highly Ordered TiO_2 Nanotube Arrays

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The dye-sensitized solar cells (DSSCs) have been fabricated using highly ordered TiO_2 nanotube arrays as photoelectrode and natural dyes as photosensitizers. The natural dyes were extracted from the abundant plants in the tropical region, such as *Tradescantia zebrina*, kapok, and pitaya. The dyes could chemically couple with TiO_2 nanotubes and effectively convert visible light into electricity in DSSCs. A power conversion efficiency could be achieved up to 0.3% in the solar cell sensitized by the extracts from kapok with a short-circuit current of 0.86 mA/cm^2. Furthermore, the influences of the crystal structure of TiO_2 nanotube arrays on the performance of the natural DSSCs were discussed.

1. Introduction

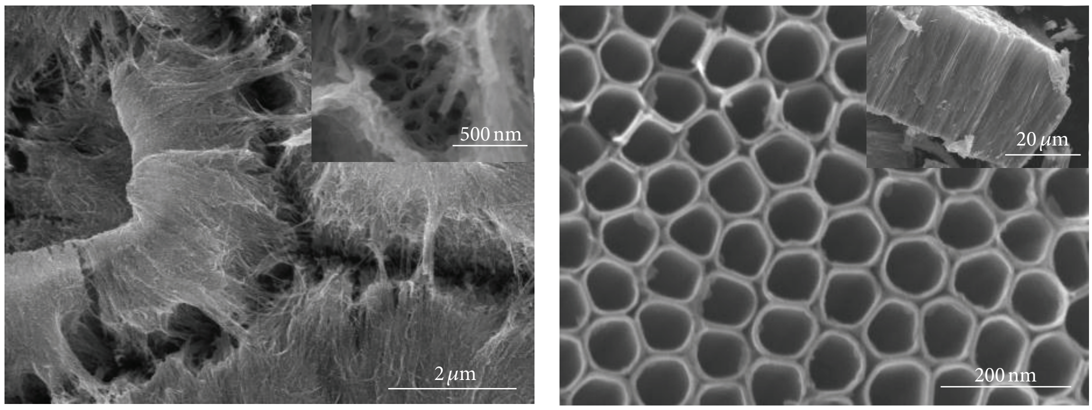
Photosensitized wide-band gap metal-oxide semiconductors are used to convert visible light into electricity [1, 2]. In most dye-sensitized solar cells (DSSCs), nanocrystalline TiO_2 films are used as photo-electrode due to their impressive properties when compared to other metal-oxide semiconductors. Most recently, different TiO_2 nanostructures (nanotubes, nanorods, nanowires, nanoparticles, etc.) are explored as dye carriers [3–8]. Compared to other nanostructures, TiO_2 nanotubes (TNTs) enhance much visible-light scattering and absorption due to their high length-to-diameter ratio and large surface area and facilitate electron transportation to the electrodes due to their unique geometry [9–12].

One of the key elements in DSSCs is photosensitizer. The most successful photo-induced electron transfer sensitizers employed so far in DSSCs are ruthenium (II) polypyridyl complexes. The ruthenium complexes in DSSCs have exhibited power conversion efficiencies up to 12% [13]. Due to the high cost of ruthenium complexes and the scarce availability of those noble metals, looking for cheaper, simpler, and safer sensitizers becomes a scientific challenging problem [14]. Natural pigments, including chlorophyll, anthocyanin, nasunin, and carotenoids, can fulfill those requirements, and sensitization of TiO_2 by natural pigments has been reported [15–19]. Experimentally, natural dye-sensitized TiO_2 solar cells have reached an efficiency of 7.1% [17].

Natural pigments extracted from leaves, flowers, and fruits of plants have advantages over rare metal complexes and other organic dyes. The natural dyes are readily available, easy to extract, of less cost, and environmentally friendly. In this work, we have made an attempt to collect red pigments from *Tradescantia zebrina*, kapok, and pitaya, as these plants are abundant in Hainan, the tropical island of China. The natural dyes were used to sensitize the highly ordered TiO_2 nanotube arrays fabricated by chemical anodization technique. Then DSSCs were assembled, and the photoelectrical properties were investigated.

2. Experimental

2.1. Preparation of Natural Dye-Sensitized TiO_2 Solar Cells. Ti foils (0.5 mm thickness, 99.4% purity) were sequentially cleaned in acetone, ethanol, and deionized (DI) water. Anodization was then performed in a two-electrode configuration with titanium foil as the working electrode and a stainless steel foil as the counter electrode [11, 12, 20]. A direct current power supply was used as the voltage source to drive the anodization. The electrolyte consisted of 0.3 wt% NH_4F and 2 vol% H_2O in ethylene glycol. The anodization



(a) (b)

Figure 1: Top view SEM images of TiO_2 nanotube arrays (a) before and (b) after the ultrasonic treatment. The inset in (a) is the image with high magnification, while the inset in (b) shows the cross-sectional view of the nanotube arrays after ultrasonic treatment.

was conducted at 60 V for 2 h at room temperature. After anodization, the samples were annealed at 500°C or 600°C for 2 h in air with the temperature rising rate of 2°C/min.

All the fresh fruits and flowers were harvested in Hainan, the tropical island in China. The extracts of *Tradescantia zebrina*, kapok, and pitaya were obtained according to the similar steps as followed. The fresh fruits or flowers well cleaned (200 g) were crushed and soaked in 95% ethanol (50 mL) and then kept for 24 h in dark at room temperature. The residual parts were filtered. The clear solutions were centrifuged and diluted HCl was added to adjust the pH value. The solution with the extracts became red in color, and the natural dyes were ready to use as sensitizers in DSSCs.

TiO_2 nanotube array electrodes were immersed at room temperature for 12 h in dark in the solution with the extracts, respectively. To evaluate the photovoltaic performance, TiO_2 nanotube array electrode and Pt counter electrode were assembled to form a DSSC. The electrolyte was injected into the space between the two electrodes. The redox electrolyte with $[I^{-3}]/[I^{-}] = 1:9$ was prepared by dissolving 0.5 M LiI and 0.05 M I_2 in acetonitrile solution.

2.2. Characterization of Natural Dye-Sensitized TiO_2 Solar Cells. The morphology and crystal structure of TiO_2 nanotube-array electrode were characterized by field-emission scanning electronic microscopy (FESEM, Hitachi S4800, Japan) and X-ray diffraction technique (XRD, Bruker D8, Germany), respectively. The absorption spectrum of three kinds of natural extracts in solution and adsorbed onto TiO_2 photoanode were measured by UV-visible absorption spectra measurements (Persee, TU-1901). Photocurrent-photovoltage characteristics of the natural dye-sensitized solar cells were measured by the electrochemical workstation (Zahner 6.0, Germany) with a xenon source with intensity of 50 mW/cm^2. The effective cell area was 1.0 cm^2.

3. Results and Discussion

3.1. Characteristics of TiO_2 Nanotube-Array Electrode. Figure 1(a) shows the SEM image of the sample without ultrasonic treatment. The surface is covered with a layer of grassy residual and the nanotubes underneath are visible as shown in the inset of Figure 1(a). The grassy layer could block the infiltration of the dye and the redox electrolyte into the nanotubes. Thus it must be removed before the nanotubes are assembled into the DSSC [9]. Ultrasonic treatment can remove the grassy layer and expose the underneath nanotubes, as shown in Figure 1(b). The nanotubes are well defined. As the nanotubular structure provides a high specific surface area, the nanotubes can absorb more dyes on the electrode surface as compared with the planar film.

Before being assembled into DSSCs, the samples were annealed for crystallization of the TiO_2, since a large number of localized states in the amorphous structure without annealing can act as traps and recombination centers [21]. Figure 2 shows the XRD patterns of TiO_2 nanotubes annealed at different temperatures. It is evidenced that TiO_2 transforms from amorphous phases to crystalline anatase phases and rutile phases after the annealing at 500°C. When the temperature increased to 600°C, the peaks relate to rutile phase increase.

3.2. Spectroscopic Characterization of Natural Photosensitizers. Figure 3(a) presents the absorption spectra of the red pigments in acid solutions, which were extracted from *Tradescantia zebrina*, kapok, and pitaya, respectively. The absorption peaks of the extracts from *Tradescantia zebrina* in visible-light region have maximums at 540 nm and 584 nm, which show typical absorption of anthocyanin [22]. For the extracts from kapok in solution, the maximum of the absorption intensity in visible-light region is located at 406 nm and 508 nm, which correspond to the absorption of carotenoid [18, 23] and anthocyanin, respectively. And the absorption peak obtained for extracts from pitaya in visible-light region is at 400 nm. As shown in Figure 3(a), these red pigments in solution have maximum absorption peaks at 350 nm and 380 nm in ultraviolet region. The same locations of the absorption peaks mean that they contain similar compounds.

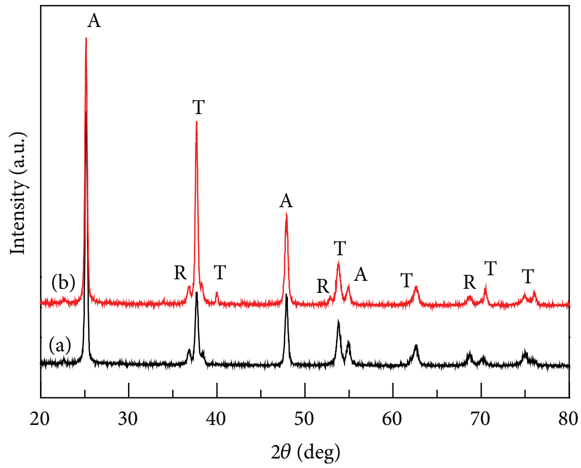


FIGURE 2: XRD patterns of (a) the TiO_2 nanotube arrays ample annealed at 500°C and (b) the TiO_2 nanotube arrays ample annealed at 600°C. A, R, and T represent anatase, rutile, and titanium, respectively.

Figure 3(b) shows the absorption spectra of the extracts adsorbed on TiO_2 electrodes, which were compared with that of TiO_2 electrode without any dye sensitization. The bare TiO_2 electrode cannot respond to the visible light due to its large band gap of 3.2 eV [24]. However, a broad absorption peak in visible-light region extending from 380 to 680 nm was observed for the electrodes sensitized with the extracts of tradescantia zebriza, kapok, and pitaya. The natural dye sensitizers are thus found to effectively increase the absorption of the visible light, which dominates the terrestrial solar spectrum.

A close look at Figure 3 could found that the UV-vis absorption peaks of the dyes adsorbed on TiO_2 electrodes are broadened and the peak positions are redshift, compared to those in solution. Such phenomenon can be explained as follows. Anthocyanin has a high absorption coefficient in the visible part of the solar spectrum. The binding between anthocyanin molecules and TiO_2 semiconductor takes place through the carbonyl and hydroxyl groups. The chemical attachment could affect the energy levels of the highest occupied molecular level and the lowest unoccupied molecular level of the anthocyanidin molecules [25], which eventually affects the band gap and results in a shift of the absorption peak in the absorption spectra. Besides, the redshift of the visible-light absorption peaks could also be due to the complexation with metal ions [15].

3.3. Photoelectrochemical Performance of DSSCs Sensitized with Natural Dyes. Figure 4 shows the photocurrent-photovoltage (*J-V*) characteristics of the DSSCs. The photoelectrochemical parameters evaluated from Figure 4 are summarized in Table 1. The photoenergy conversion efficiencies (η) of the DSSCs sensitized with tradescantia zebriza, kapok, and pitaya are 0.23%, 0.3%, and 0.17%, respectively, and the short-circuit photocurrent densities (J_{SC}) are 0.63 mA/cm^2, 0.87 mA/cm^2, and 0.50 mA/cm^2, respectively. The values of η and J_{SC} after natural dye sensitization are effectively

TABLE 1: Photoelectrochemical parameters of DSSCs sensitized with three kinds of natural dyes, compared with the solar cell without dye sensitization.

Sensitizer	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
Without dye	0.023	0.3	0.494	0.006
Tradescantia zebrina	0.63	0.35	0.52	0.23
Kapok	0.87	0.36	0.49	0.3
Pitaya	0.50	0.33	0.52	0.17

TABLE 2: Photoelectrochemical parameters of DSSCs based on TiO_2 nanotube arrays annealed at different temperatures.

Annealing temperature	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
500°C	0.64	0.35	0.52	0.23
600°C	0.15	0.41	0.26	0.03

enhanced in comparison to that without dye sensitization with the value η of 0.006% and J_{SC} of 0.023 mA/cm^2, while the open-circuit voltages and the fill factor are similar. This suggests that the chemical adsorption of the natural dye molecules on TiO_2 electrodes takes place. The hydroxyl and carboxyl groups on anthocyanin are easy to chelate with Ti (IV) on TiO_2 surface [25]. This helps the excited electron quickly transfer from anthocyanin molecules to the conduction band of TiO_2.

It can be seen from Table 1 that the DSSC sensitized with the extracts from kapok exhibits the best value of η among the three kinds of dyes. This might be due to the higher intensity and broader range of the visible-light absorption of the extracts from kapok in comparison to the others as shown in Figure 3(b). Furthermore, stronger interaction between TiO_2 and the dye molecules of the extracts of kapok also might lead to charge transfer quickly.

The stability of the natural dyes was further studied by continuous irradiation in the sunshine for 2 h and no significant changes were observed.

3.4. Effect of TiO_2 Crystal Structure on the Performance of DSSCs. To further investigate the effect of TiO_2 nanotube crystal structure on the natural DSSCs, characteristics of DSSCs at different annealing temperature were measured. As shown in Figure 5 and Table 2, the values of J_{SC} and η for DSSCs based on TiO_2 annealed at 500°C outperformed those annealed at 600°C. According to Figure 2, TiO_2 nanotube arrays annealed at 500°C were major anatase phase with minor rutile ones. The electrode possesses the mixed crystal structure. When the temperature increased to 600°C, the sample has more obvious rutile peaks than the one annealed at 500°C. The results here suggest that the performance of DSSC based on TiO_2 nanotube arrays depends on the proportion of anatase to rutile for TiO_2 crystal structure. Besides the crystal structure, the geometric structure of TiO_2 nanotube arrays can affect the photoelectrical properties and thus the performance of the DSSCs [11], which requires further experimental investigation.

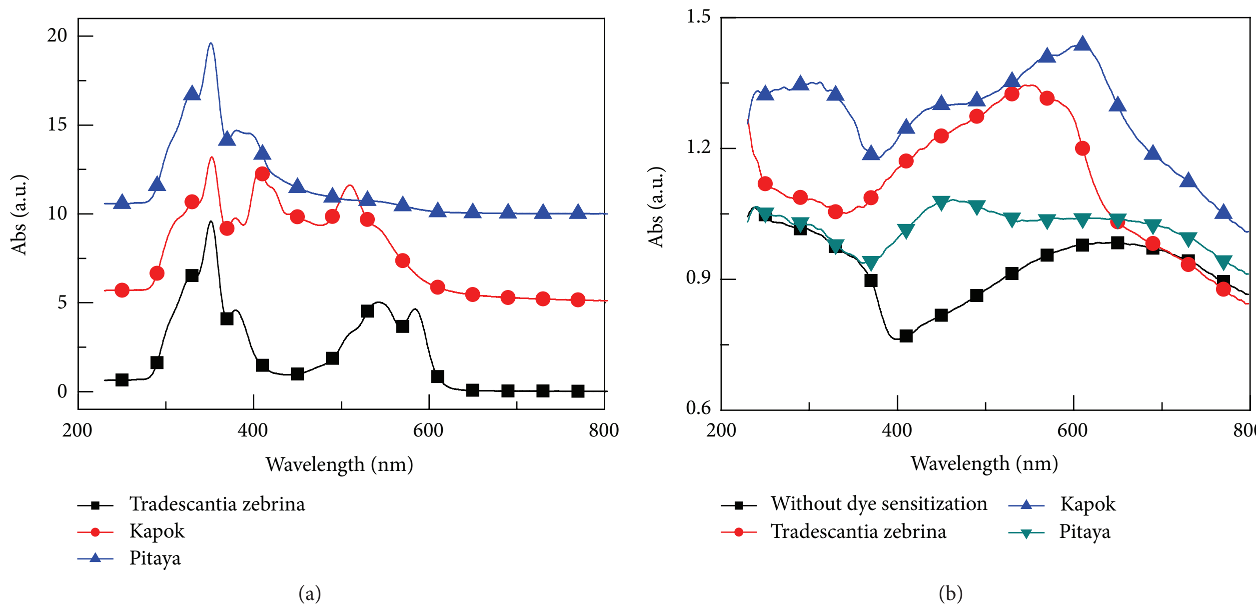


Figure 3: Comparison of the absorption spectra of the natural extracts: (a) in acid solution; (b) adsorbed on TiO_2 electrode.

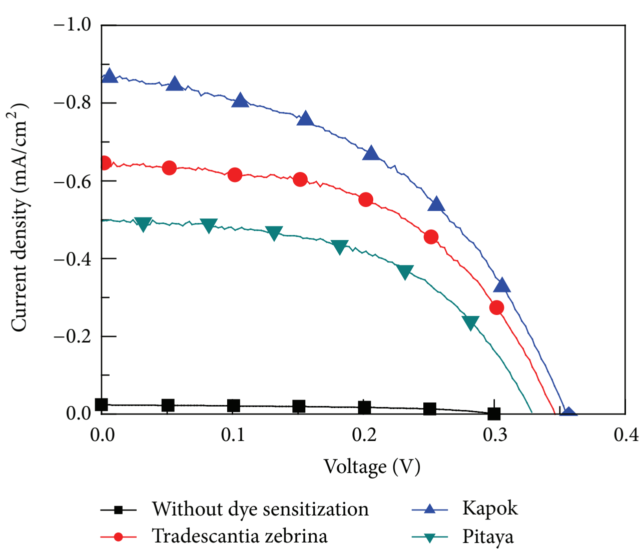


Figure 4: *J-V* characteristics of DSSCs sensitized with three kinds of natural dyes under illumination of 50 mW/cm^2, compared with the solar cell without dye sensitization.

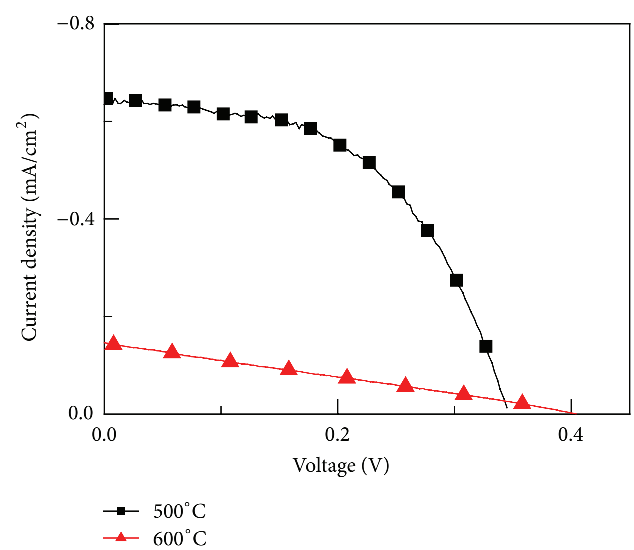


Figure 5: *J-V* characteristics of DSSCs sensitized with extracts of *Tradescantia Zebrina* based on TiO_2 nanotube arrays annealed at different temperatures.

4. Conclusions

The feasibility of assembling DSSCs with TiO_2 nanotube arrays sensitized with three kinds of natural dyes has been demonstrated. Successful conversion of visible light into electricity was achieved. The efficiencies of the solar cells sensitized with the extracts of Tradescantia zebrine, kapok, and pitaya skin were up to 0.23%, 0.3%, and 0.17%, respectively. Crystalline phases of TiO_2 significantly affect the photoenergy conversion parameters of DSSCs. Although our best values of DSSCs using kapok pigments are still lower than those obtained for the reference solar cells using the chemical dye N719, the simple extraction procedure, low cost, wide availability, and environmentally friendly nature make natural dyes as the promising sources of sensitizers for DSSCs. Through improving extraction method, refining natural dyes, and optimizing the geometric and crystal structures of TiO_2 nanotube arrays, we believe that better results will be achieved.

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