A novel TiO₂ film photoanode decorated with Spirulina-derived residual groups for enhanced photocurrent in dye-sensitized solar cells

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Abstract

Spirulina-derived residual groups as a special additive to modify the dyed-TiO₂/electrolyte interface are introduced to enhance the photovoltaic performance. The interaction between the spirulina residual groups and surface of TiO₂ films is investigated. It is found that spirulina extracts molecule split into several small fragments as Ti-O-CH₂-OH anchoring on the surface of TiO₂ by thermal treatment. Spirulina residual groups modified TiO₂ photoanodes have a higher light-harvesting capacity and efficient electron transport. As a result, both the V_{oc} and J_{sc} are improved by TiO₂ photoanodes decorated with spirulina derived residual groups, with the short-circuit current of 10.17 mA cm⁻² corresponding to the photoelectric conversion efficiency of 4.26%, which is 33.1% higher than the blank DSSC.

Keywords: Spirulina; Surface modification; Light-harvesting capacity; Dye-sensitized solar cell

1. Introduction

The composite photoanode of dye-sensitized solar cell is among the hot areas

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of current research in photoelectric materials (Hwang et al., 2010; Jiang et al., 2015). The photoanode composite materials are mainly responsible for improving the solar cell performance. Photocurrent generation in dye-sensitized solar cell is achieved by the following steps: The dye adsorbed on TiO_2 thin films plays a central role in harvesting incident sunlight and generates electron-hole pairs. The resulting electrons are injected into the conduction band of the TiO_2 , and then diffuse across inter connecting network of TiO_2 nanoparticles into the electrode and are collected for supply to the external loads (Berglund et al., 2013). Enhancing dye adsorption on the surfaces of semiconductor nanoparticles is an effective method for obtaining high-efficient DSSCs (Honda et al., 2013; Ozawa et al., 2015; Seo & Kim, 2013). To attach the dye molecules to the surface of the photoanode films, anchoring groups that form linkages to the metal oxide are incorporated into the dye sensitizers (Kim et al., 2013). In some modified cases, the dye molecules are adsorbed onto the surface of TiO_2 via the interaction between hydroxyl groups on TiO_2 surface and the carboxylic groups of dye molecules (Nagai et al., 2014). It has been experimented to improve the dye adsorption process by modifying the surface of TiO_2 (Di Carlo et al., 2014; Ye et al., 2014). Most studies focus on treating TiO_2 surface with TiCl_4 (Li et al., 2011) and various acids (Jiang et al., 2015), or coating TiO_2 with inorganic oxide thin layers (Jung et al., 2005; Lee et al., 2012; Menzies et al., 2006; Palomares et al., 2003). Various kinds of co-adsorbents (Hara et al., 2004; Morandeira et al.,

2009; Wang et al., 2004; Wang et al., 2003) are also added to the dye solution to suppress the electron recombination.

Recently, the inorganic materials modified by biomass residuals groups can significantly enhanced adsorption of visible light (Al-Alwani et al., 2015). And microbial synthesis of Cu doped LaCoO_3 (Wang et al., 2015) and palladium supported on TiO_2 photocatalysts modified by biomass *Gardenia* have shown that there are a lot of organic functional groups from biomass for preparation of photocatalysts (Wu et al., 2012). The microalgae biomass as carbon source modified functional materials exhibit good performance (Falco et al., 2012). Microalgae-derived microporous carbons for electrochemical capacitors (Sevilla et al., 2014). Silver nanoparticle embedded CaCO_3 microspheres via microalgae-templated CO_2 biomineralization (Sahoo et al., 2014).

Herein, we introduce a facile method of anchoring a ruthenium dye sensitizer onto the surface of TiO_2 with biomass fragments from extracts of spirulina by thermal Carbonization treatment. The objective is to further investigate the role played by groups of biomass in the preparation of composite photoanode and the process of improving the dye adsorption. This work may pave a new and facile pathway for TiO_2 film photoanode decorated with biomass for high-efficient DSSCs.

2. Experiments

2.1. Fabrication of spirulina extract

Capsule spirulina tablets were purchased and pulverized. Then, made a solution of 0.3 g greenish pulverized spirulina and 100 ml ethanol boiled and centrifuged at 4000 rpm until 3 min and 5 min, respectively. The decanted supernatant 100 ml top-out in dark storage bottle was stored as a feedstock. The resultant supernatant was identified as extract spirulina with ethanol (SP). TiO₂ film was prepared as in our previous literatures (Tian et al., 2013), which was designated T. After soaking in SP until 5 h for proper adsorption, the non-adhered biomass pigment was washed off with ethanol and the films were dried in the air. The resultant film was designated spirulina pigment soaked titanium dioxide (SP-T). Then, the post-sintered SP-T in muffle furnace at 450°C for 30 min was designated SP-C-T.

2.2. Characterization of the photoanode

The visible region extinction spectra of spirulina pigment and photoanodes were recorded on a Varian Cary 5000 UV-vis-NIR. Functional groups were investigated by Fourier transform infrared spectrometer (FTIR) with Nicolet Avatar 330. The elemental composition was examined by X-ray photoelectron spectroscopy (XPS) with a PHI Quantum 2000 Scanning ESCA microprobe consisting of a monochromatized microfocused Al X-ray source. In order to select better materials for the photoanode, material phases were investigated by X-ray diffraction (XRD) with a brand Panalytical pert spathic powder diffractometer with Cu K α radiation. The morphology of the sample films was observed by scanning electron microscopy (SEM) and studied the elements

responsible for dispersion by Energy Dispersive Spectrometer (EDS), model LEO-1530 incorporated electron microscope (Germany). Investigation of compositions likely not suitable for high temperature, was carried out by specified weight loss quantifier thermogravimetry analysis (TGA). Photocurrent density-applied voltage (I-V) and electrochemical impedance spectroscopy (EIS) measurements of the DSSCs were obtained using a home-built setup comprising a xenon lamp, an AM 1.5 light filter, and a CHI660D Electrochemical Analyzer (CHI instruments). The power of the filtered light was calibrated by a China National Institute of Metrology certified silicon reference cell to 100 mW cm⁻².

3. Results and Discussion

3.1. Analysis of spirulina extract

Fig. 1 shows the UV-vis spectra of spirulina extract. It can be divided into two main spectral region, the first one between 330-500 nm, the highest peak at 414 nm, and another between 550-700 nm, the highest peak at 664 nm, which are assigned as the characteristic peak of carotenoids(Sanjay et al., 2007) and chlorophyll A(Wang et al., 2014), respectively.

3.2. XRD analysis

Fig. 2 shows the XRD patterns of the pure TiO₂ and modified TiO₂ photoanodes. The pure TiO₂ photoanode of strong diffraction peaks at 2θ values of 25.33°, 38.61°, 48.10°, 53.92°, 55.14°, corresponding to the (101), (112), (200), (105), and (211) crystal planes of anatase phases, respectively.

Other strong diffraction peaks at 2θ values of 27.44° , 36.08° , 41.24° , 54.32° , 56.63° , 69.01° , corresponding to the (110), (101), (111), (211), (220) and (301) crystal planes of rutile phases, respectively. From the insert, it is obvious that the SP-C-T of the strongest diffraction peak of 2θ value shifts to higher value compared to T and SP-T films. Therefore, it may be that biomass-residual carbon groups in the lattice of TiO_2 , due to difference of ionic radius, resulted to the distortion of TiO_2 crystal lattice.

3.3. FT-IR and TGA analysis

Fig. 3 (a) shows Fourier transform infrared spectra of the TiO_2 nanoparticles. Due to adsorbed supernatant spirulina biomass, SP-T spectrum shows distinct peaks emerged at frequencies of 1736 cm^{-1} and 1458 cm^{-1} corresponding to bending vibration of C=O ester group and C-H alkanes group (R., 2012; Shankar et al., 2003) respectively, the peaks at frequencies of 2924 cm^{-1} and 2858 cm^{-1} corresponding to stretch vibration of C-H ($-\text{CH}_2-$) alkanes group. All these distinct peaks appeared smooth on SP-C-T spectrum; this is evidence of biomass thermal modification. Also, common peak for T and SP-T at frequency of 1095 cm^{-1} corresponding to stretching vibration of C-O ester group (it is anticipated to be carboxylic acid of the biomass) shifted to 1123 cm^{-1} on SP-C-T spectrum. More peaks at frequencies of 3427 cm^{-1} and 1633 cm^{-1} correspond to stretching vibration of -OH groups of TiO_2 /water molecules. Since there are only two visible C-O and -OH groups left on SP-C-T spectrum. This implies that there exist C-O and -OH groups at which new forms could be

Ti-O-CH₂-OH and Ti-OH on the TiO₂ film. The functional groups may contribute to the adsorption of the dye molecules on the surface of titanium dioxide film.

Fig. 3 (b) shows the rapid declination TGA curve of SP-T until at stable temperature of 450°C, properly described quantitative adsorption of organic spirulina biomass extracts. The adsorbed biomass extracts were almost dried up (biomass residue) in post-sintered SP-T, hence, there is tolerable weight loss as seen on SP-C-T profile and it implies that the modification can withstand short disintegration and maintain stability.

3.4. DRS analysis

UV-visible spectroscopy is the most commonly used technique to study the optical properties. Fig. 4 shows the UV-vis spectra of photoanodes after dye sensitization. It is obvious that the biomass-derived residuals groups modified films SP-C-T adsorb more dye and become most excited with highest spectrum. It can be deduced that the adsorbed dye gains advantage of band gap drop in Ti-O-CH₂-OH induced by the thermally treated biomass. Contrary, the competitive molecules of dye and concentrated biomass in SP-T films can hinder the absorptivity leaving its spectrum lowest.

To further gain insight into the absorption changes of materials originate from modification, the dye solution desorption experiment was carried out by the use of a mixed solution of 0.1 M NaOH and ethanol (1:1v/v). The dye-loadings for T, SP-T, and SP-C-T photoanodes are showed in the Table 1, which are very consistent with the absorption spectra. Absorption concentration is

calculated and it is found that the dye-loading of the SP-C-T photoanode ($1.2 \times 10^{-7} \text{ mol cm}^{-2}$) is 1.2 times higher than that in T ($1.0 \times 10^{-7} \text{ mol cm}^{-2}$), which may be due to an increased surface area by the modification of spirulina derived residual groups. Thus we can infer that spirulina derived residual groups modified TiO_2 photoanodes show better performance in dye adsorption, contributing to higher light-harvesting capacity.

3.5. SEM and EDS analysis

Fig. 5 shows the photoanodes SEM images and EDS spectrum. However, the scanned images reveal no discrepancy in morphology appearance. It is seen that there exists relative porosity which essentially good for dye absorption and conductive electrolyte rapid oxidation and reduction cycle. The degree of image smoothness and absence of cracks acknowledges that it is conducive to dye adsorption and the diffusion of the electrolyte in the TiO_2 films. Also, the EDS spectrogram can reveal the fundamental elements (Ti, C, O) are present across the three photoanodes. And the EDS mapping also shows the fundamental elements are almost uniformly distributed (Fig. S1).

3.6. XPS analysis

The XPS analysis was performed with peculiar attention given to the binding energy of O 1s component in order to identify the chemical state of O element in the modified photoanodes. Fig. 6 shows the O 1s region by XPS spectra of the photoanodes. The highest binding energy exists in chemical state curve of O 1s region traced at 533.5 eV in SP-C-T spectrum, which is ascribed to the

bond of C-OH(Zhang et al., 2011), indicating the formation of Ti-O-CH₂-OH. Uniform binding energy exists in the chemical state curves of O 1s region at 532.0 eV, which is attributed to hydroxyl groups (Ti-OH) bond across T, SP-T and SP-C-T spectra. The lattice surface oxygen is represented by the chemical state curves of O 1s region traced at 529.8 eV, 529.7 eV and 529.9 eV respectively. The composites and atomic concentration percentage of thermally treated thin films are shown in Table 2 and it can be seen that the photoanodes SP-C-T have the highest carbon percentage. The phenomenon is in conformity with FTIR result that shows feasibility bond of Ti-O-CH₂-OH in the SP-C-T functional groups.

3.7. EIS analysis

Nyquist map and Bode map are shown in Fig. 7 (a) and (b) respectively. According to the maps, parameters are calculated as listed in Table 3. The radii of semicircles of second impedance are relatively adjacent and relate their transfer resistance. The transfer resistances between TiO₂/dye/electrolyte interfaces are 22.92 Ω, 27.44 Ω and 27.44 Ω respectively. This suggests that biomass residual groups enhance the transmission rate of photoelectron in the TiO₂/dye interface. Also, the intermediate frequency range (electron mobility of TiO₂/dye/electrolyte interfaces associated with the impedance process) at maximum phase Angle corresponding to the maximum frequency $f_{\max}$, could be evaluated with photoelectron longevity equation: $\tau_e = \frac{1}{2 \times \pi \times f_{\max}}$. The outcomes show that SP-C-T has the longest photoelectrons lifetime which

implies that less tedious transmissions occur over a longer distance. Fig. 7 (c) shows Nyquist map under the dark state and bias voltage -0.7 V. The radii of second semicircles show wide discrepancy usually represent the composite resistance of TiO_2 /dye/electrolyte interfaces. The higher value of T could be the natural impedance of TiO_2 before it is altered by biomass which causes lowest impedance, and the biomass residue is considered as optimal tune.

3.8. I-V analysis

The cells of I-V curves under the light and dark condition are shown in Fig. 8 (a) and (b), respectively. The specific parameters are shown in Table 4. From Fig. 8 (b), it can be seen that the SP-T bias voltage is below SP-C-T and T in ascending order, indicating a faster recombination rate of electron-hole pairs of SP-T. The photoanode SP-T are extract spirulina soaked, whose short circuit current drop sharply compared with the blank T. The phenomenon occurs because there is mainly weak physical adsorption between the extract biomass and surface of TiO_2 film and adversely affects the optical performance. Contrary, spirulina derived-biomass residue groups in thermally modified TiO_2 possesses stronger absorption and absorbs higher amount of dye which produces more photoelectron and larger photocurrent. In addition, the residue groups anchoring on the TiO_2 surface provides a direct path of electronic transfer, improves the transmission rate, and prolongs the lifetime of electronic. These advantages make the short circuit current and photoelectric conversion efficiency shoot up to 10.17 mA cm^{-2} and 4.26% in SP-C-T DSSC respectively,

which are improved up to 19.5% and 33.1% respectively, compared to the blank T DSSC.

4. Conclusions

This study has demonstrated that novel biomass-derived residue groups decorated TiO₂ photoanode by thermal treatment can enhance photocurrent, which it has increased from 8.51 mA cm⁻² to 10.17 mA cm⁻², and the SP-C-T-DSSC with an average PCE 33.1% higher than the blank T-DSSC. Avalanche of the spirulina biomass-derived residual groups in thermally modified photoanode stimulated for dye absorption. It is concluded that the promising spirulina biomass-derived modified photoanode is efficacious and potentially ready for further improvements in DSSC researches.

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Figure captions

Figure 1. Uv-Vis spectrum of the extract of spirulina

Figure 2. XRD patterns of the photoanodes

Figure 3. Fourier transforms infrared spectra (a) and the TGA curves (b) of the photoanodes

Figure 4. Adsorption spectra of the photoanodes after dye sensitization

Figure 5. SEM images and EDS spectra of the T (A, a), SP-T (B, b) and SP-C-T (C, c)

Figure 6. The O1s region of XPS spectra of the photoanodes

Figure 7. Nyquist spectra (a), Bode plots (b) and Nyquist spectra in the dark (c) of the DSSCs

Figure 8. I-V curves of the DSSCs under Light (a) and dark (b) condition

Table 1. The amount of dye desorption on the photoanodes

Sample	Amount of dye desorption (mol cm ⁻²)
T	1.0×10 ⁻⁷
SP-T	6.6×10 ⁻⁸
SP-C-T	1.2×10 ⁻⁷

Table 2. XPS generated composites and atomic concentration percentage of thermally treated thin films

Sample	Atomic concentration (%)		
	C	O	Ti
T	68.08	23.83	8.09
SP-T	68.23	24.39	7.38
SP-C-T	81.65	14.87	3.48

Table 3. The electron transport properties determined by EIS analysis

DSSC	R_1 (Ω)	$f_{\max}$ (Hz)	τ_e (ms)	R_1 (Ω) in dark
T	22.92	21.54	7.39	193.3
SP-T	27.44	14.68	10.85	81.58
SP-C-T	21.56	12.12	13.14	100.7

Table 4. The performance characteristics of the DSSCs

DSSC	J (mA cm ⁻²)	V (mV)	FF (%)	η (%)
T	8.51	617	60.9	3.20
SP-T	6.04	614	58.0	2.15
SP-C-T	10.17	657	63.8	4.26