Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Seok-Jae Kim, Hyun-Seok Ko, Gil-Ha Jeong, Jae-Jung Yun, Kyung-Hee Park & Eun-Mi Han (2016) The effect of tourmaline additives in TiO_2 photoanode for high-efficiency dye sensitized solar cells, Molecular Crystals and Liquid Crystals, 629:1, 200-205, DOI: 10.1080/15421406.2016.1140300

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1140300

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 629, 200–205
http://dx.doi.org/10.1080/15421406.2016.1140300

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The effect of tourmaline additives in TiO_2 photoanode for high-efficiency dye sensitized solar cells

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ABSTRACT

Tourmaline is a kind of borosilicatemineral and has spontaneous polarization property. Due to this property, it can generate a feeble current around 0.06 mA[1]. We fabricated the TiO_2 photoanode with different wt.% ratio of tourmaline and investigated the effect of tourmaline additive on dye sensitized solar cells (DSSCs). We carried out electrochemical impedance spectroscopy (EIS) and current density-voltage (J-V) measurement. The results showed that the electron lifetime and the power conversion efficiency of the DSSCs with TiO_2 photoanode containing 3wt% tourmaline were enhanced by about 42% and 20%, respectively, as compared to the DSSCs using pristine TiO_2 photoanode.

KEYWORDS

Tourmaline; Photoanode; Life time; Dye Sensitized Solar Cell; Power conversion efficiency

Introduction

DSSCs are a promising alternative to conventional silicon-based solar cells due to their potential low cost, easy fabrication, respectable energy conversion efficiency, and low impact to the environment. Since the breakthrough work was done by Grätzel (1991) [1], DSSCs have been reported around 13% of power conversion efficiency [2]. There were many attempts to achieve high power conversion efficiency. One of these attempts was by using one dimensional nanomaterials, such as nanofibers, nanorods, nanotubes, and nanowires. Modifying the pristine TiO_2 using metals or non-metal elements were also another alternative to achieve high power conversion efficiency and were actively studied [3].

The tourmaline is a kind of borosilicate mineral. Since tourmaline belongs to the trigonal or rhombohedral lattice crystal structures with the space group R3m, tourmaline has unique electrical properties, such as spontaneous polarization, pyroelectricity, piezoelectricity, and ability to generate a feeble current around 0.06 mA [4–6]. Tourmaline has been studied for many applications, such as photosplitting of water [6], photocatalyst [7], electrical/electromagnetic interference shielding [8], and bio-cathode microbial fuel cell [9]. However, there were no reports on the DSSCs application with tourmaline. In this work, the TiO_2

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This paper was originally submitted to *Molecular Crystals and Liquid Crystals,* Volumes 620–622, Proceedings of the KJF International Conference on Organic Materials for Electronics and Photonics 2014.

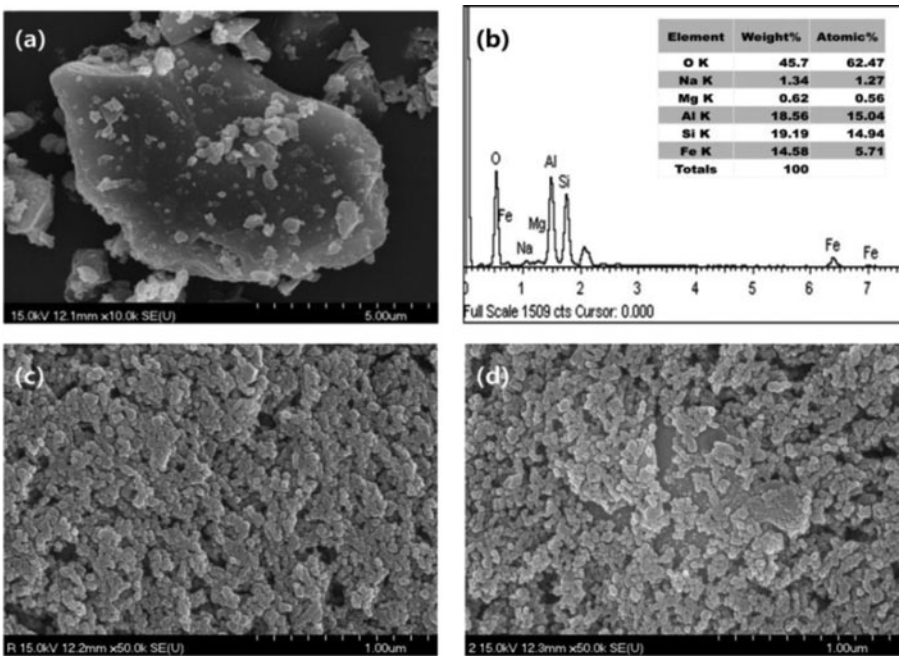

Figure 1. (a) SEM images and (b) EDX analysis data of tourmaline powder and SEM images of (c) pristine TiO_2 photoanode, and (d) TiO_2-tourmaline photoanode.

photoanode with tourmaline additive was expected to have fast electron transport, and a slightly decreased recombination lifetime resulted in the improvement of efficiency because of the unique electrical properties. Therefore, we tried to study the DSSCs with optimized TiO_2-tourmaline composite as a photoanode with different amounts of tourmaline.

Experiments

Photoanodes were fabricated by squeezing the coating colloidal TiO_2-tourmaline (or pristine TiO_2) paste on fluorine-doped tin dioxide (FTO) coated on glass (Pilkington TEC glass, 8 Ω cm^{-2}). A colloidal paste, which consisted of TiO_2 (P25, Nippon Aerosil) or TiO_2-tourmaline mixed powder, polyethylene glycol, Triton X-100, ethanol, acetyl acetone, and deionized water, was mixed at 1350 rpm for thirty minutes by paste mixer. The coated TiO_2-tourmaline and TiO_2 films were dried at 80°C for ten minutes and immediately sintered at 450°C for thirty minutes. Then, the photoanodes were prepared by dipping them in 0.5 mM ethanol solution of N719 dye (Solaronix) for twenty-four hours and dried in an oven. The counter electrode was fabricated by using squeeze coating Pt-Sol (Solaronix) on the FTO glass. The sandwich-type solar cell was assembled by placing a counter electrode on the photoanode. A redox electrolyte solution, EL-HPE (Dyesol), was introduced between the electrodes.

The morphologies of tourmaline powder and TiO_2-tourmaline film were characterized by using Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4700). J-V measurement was performed by using CHI660A electrochemical workstation (USA). The EIS was performed by using Iviumstat electrochemical analyzer. An AM 1.5 solar simulator (Thermo-Oriel) was used as a light source.

Results and discussion

To investigate the tourmaline powder effect on the DSSCs, according to the contents, we fabricated the TiO_2-tourmaline photoanodes with different amounts of tourmaline between 1∼5 wt%. Figures 1(a) and (b) show the SEM images and Energy-dispersive X-ray spectroscopy (EDX) data of the tourmaline powder, respectively. As shown in these Figures, we saw the shape of tourmaline particle and confirmed the elements of tourmaline powder, which consisted of O, Na, Mg, Al, Si, and Fe [4]. SEM images of pristine TiO_2 and TiO_2-tourmaline photoanodes are shown in Figure 1(c) and (d), respectively. TiO_2 particles exhibited homogeneous in the TiO_2 photoanodes. As shown in Figure 1(c), the TiO_2-tourmaline photoanodes showed that tourmaline particles were either covered or surrounded with TiO_2 particles.

Figure 2 shows the J-V characteristics of DSSCs with TiO_2-tourmaline photoanodes and with different amounts of tourmaline. From J-V curve, we obtained performance parameters and summarized then in Table 1: open circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (η). As shown in Figure 2 and Table 1, the DSSCs with TiO_2-tourmaline photoanodes and with different amounts of tourmaline show similar values of V_{oc}, around 0.7 V. However, the J_{sc} increased with increased contents of tourmaline between 1∼3 wt% and decreased with increased contents of tourmaline between 3∼5 wt%. Because of the J_{sc}, the η also increased with increased contents of tourmaline between 1∼3 wt% and decreased with increased contents of tourmaline between 3∼5 wt%. When the DSSC

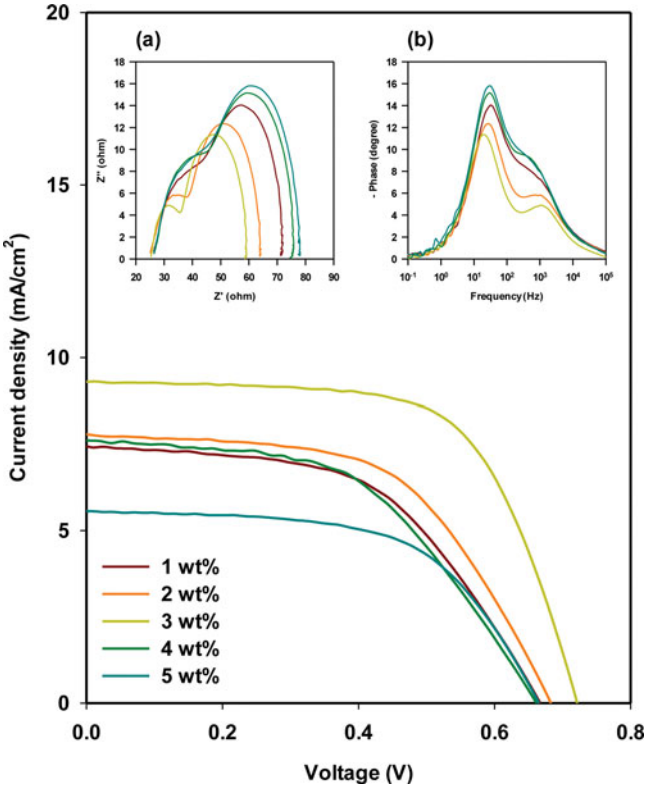

Figure 2. J-V characteristics of DSSCs with TiO_2 photoanode containing different wt.% ratio of tourmaline at 1 sun illumination (100mW/cm2, AM 1.5). The inset illustrates EIS spectra for cells at 1 sun illumination: (a) Nyquist and (b) Bode phase plot.

Table 1. The performance parameters of DSSCs with TiO_2-Tourmaline photoanodes and with different tourmaline contents of 1∼5 wt%.

sample	V_{oc}(V)	J_{sc}(mA/ cm^2)	FF	η(%)	R_{ct}(Ω cm^2)	τ_e(ms)
1 wt%	0.69	7.5	0.51	2.6	7.51	4.96
2 wt%	0.70	7.8	0.54	3.0	6.65	5.91
3 wt%	0.75	9.3	0.62	4.4	5.90	8.38
4 wt%	0.68	7.7	0.49	2.6	7.70	4.96
5 wt%	0.69	4.5	0.56	1.7	8.36	4.96

with TiO_2-tourmaline photoanode contained 3 wt% tourmaline, the record 4.4% of η was the maximum value. We measured UV-Vis reflectance spectra of the TiO_2 photoanode containing different weight ratio of tourmaline to confirm the effect of light scattering to increase light harvesting by the inclution of tourmaline additive. But, there was no enough differences of reflectance to increase the light harvesting.

The inset of Figure 2 shows the EIS spectra for DSSCs with TiO_2 and TiO_2-tourmaline and with different amounts of tourmaline photoanodes. The EIS spectra are typically presented on a Nyquist (a) and Bode phase (b) plot. As shown in Figure 2(a), typically two semicircles were observed in the Nyquist plot. Those semicircles attributed to an impedance-related charge-transfer process. The first circle was related to the charge-transfer between counter electrode/electrolyte interfaces, and the second circle was related to the TiO_2/dye/electrolyte interfaces [10]. For these reasons, the charge transfer resistance (R_{ct}) of TiO_2/dye/electrolyte interface was determined by the second circle, whose values are written in Table 1. The charge transfer resistance decreased with increased contents of tourmaline between 1∼3 wt% and increased with increased contents of tourmaline between 3∼5 wt%. We could confirm that the DSSC with TiO_2-tourmaline photoanode containing 3 wt% tourmaline had the lowest R_{ct} of TiO_2/dye/electrolyte interface.

According to the Bode phase plots in Figure 2(b), the electron lifetime (τ_e) in the TiO_2 film could be derived as equation (1):

$$\tau_e = 1/(2\pi f) \tag{1}$$

where f was the characteristic frequency, corresponding to the peak in intermediate frequency regime [11]. These values are also summarized in Table 1. The electron lifetime increased with increased contents of tourmaline between 1∼3 wt% and decreased at 4 wt%. Likewise for the J-V characteristics, the DSSC with TiO_2-tourmaline photoanode containing 3 wt% tourmaline also recorded the maximum value of τ_e.

To investigate the effect of tourmaline additive, we fabricated the pristine TiO_2 photoanode and compared it with TiO_2-tourmaline photoanode containing 3 wt% tourmaline, which recorded the maximum η in our works.

Figure 3 shows the J-V characteristics and EIS spectra of the DSSCs with different photoanodes, respectively. In Figure 3, the DSSC with TiO_2-tourmaline photoanode showed an improved performance than pristine TiO_2 photoanode, which showed 0.73V of V_{oc}, 7.60mA/cm^2, of J_{sc}, 0.66 of FF, and 3.6% of η while the TiO_2-tourmaline photoanode containing 3 wt% of tourmaline showed 0.75V of V_{oc}, 9.34mA/$cm^2$of J_{sc}, 0.62 of FF, and 4.4% of η. In the terms of J_{sc} and η, the DSSC with the TiO_2-tourmaline photoanode containing 3 wt% of tourmaline showed the higher value for 23% and 20%, respectively, than the DSSC with the pristine TiO_2 photoanode.

Likewise, In the EIS characteristics, the insets of Figure 3, the DSSC with TiO_2-tourmaline photoanode containing 3 wt% of tourmaline showed the 8.38Ω cm^2 of R_c and 8.3ms of τ_e,

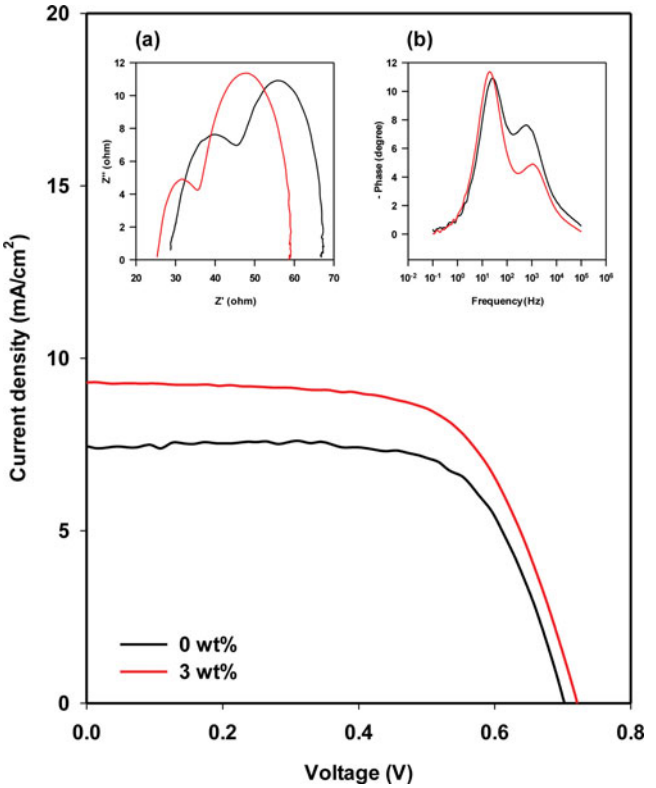

Figure 3. J-V characteristics of DSSCs with pristine TiO_2 and TiO_2-tourmaline photoanode containing 3 wt% of tourmaline at 1 sun illumination (100 mW/cm2, AM 1.5). The inset illustrates EIS spectra for cells at 1 sun illumination; (a) Nyquist and (b) Bode phase plot.

having values that were lower for 0.12 Ω cm^2 and longer for 2.47ms than the DSSC with the pristine TiO_2 photoanode. The DSSC with TiO_2 photoanode recorded 6.02Ω cm^2 of R_{ct} and 5.91ms of τ_e

Conclusions

The DSSCs with TiO_2-tourmaline photoanodes showed that performance parameters, such as R_{ct} τ_e and η, improved with increased contents of tourmaline between 1∼3 wt% and degraded with increased contents of tourmaline between 3∼5 wt%. With 3 wt% of tourmaline content, the DSSCs with TiO_2-tourmaline photoanodes had more superior performance parameters than the DSSCs with pristine TiO_2 photoanode. The 3 wt% of tourmaline in the TiO_2-tourmaline photoanodes had improved power conversion efficiency, which increased 20% higher than the DSSCs with pristine TiO_2 photoanode. These results implied that the DSSCs with TiO_2-tourmaline photoanode would be a promising alternative to achieve high conversion efficiency.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2014R1A2A2A04004950).

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