Dye-sensitized solar cell utilizing TiO_2 -sulphur composite photoanode: influence of sulphur precursor content

M. Y. A. Rahman¹ · S. A. M. Samsuri² · A. A. Umar¹

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Abstract

TiO_2 -sulphur composite films have been prepared and employed as photoanode of dye-sensitized solar cell (DSSC). The influence of sulphur precursor content in terms of thiourea concentration on the structural and optical properties of the sample has been investigated. The anatase and sulphur phases exist in the composite. The secondary phases, namely SO_3 and Ti_3S_4 , also present in the composite. The 0.3 M sample possesses the highest reflection and absorption in visible region. Raman characterization reveals that the peak at 474 cm^{-1} corresponds to the A_{1g} symmetric stretching mode of sulphur. The effect of the sulphur precursor concentration on the performance parameters of the device has also been investigated. The DSSC utilizing the sample with 0.3 M thiourea demonstrates the highest power conversion efficiency, η of 1.80% due to the highest dye loading, the lowest bulk and charge transfer resistance and the longest carrier lifetime. Combining TiO_2 with sulphur in composite form was found as an effective way of enhancing the efficiency of the DSSC.

Keywords Dye-sensitized solar cells · Photoanode · TiO_2 -sulphur composite

1 Introduction

Photoanode in dye-sensitized solar cell (DSSC) serves as a medium for light absorption mainly in visible region and transfers the generated charge carriers to transparent conducting oxide (TCO). Several approaches have been attempted to tune the properties of TiO_2 such as doping with other elemental ions, development of nanocomposites and synthesis of new nanostructures to enhance the performance of DSSC [1]. Improving the optical and electrical properties leads to the enhancement of the performance parameters of the device such as photocurrent and power conversion efficiency. The modifications include coating TiO_2 films with other metal oxide films such as ZnO [2], SnO_2 [3] and ZrO_2 [4, 5]. TiO_2 was also prepared in the form of composite structure with another metal oxide such as TiO_2 - ZnO [6], TiO_2 - SnO_2 [7] and TiO_2 - SiO_2 [8]. It can also be prepared in the form of core-shell structure

such as $\text{SnO}_2/\text{TiO}_2$ and TiO_2/ZnO , respectively [9, 10]. Zinc-doped TiO_2 has been employed as photoanode of DSSC and demonstrated the efficiency of 1.34% [11]. Germanium-doped TiO_2 has been utilized in the device in order to enhance electron transfer and power conversion efficiency [12]. TiO_2 -diamond nanocomposite has been utilized as photoanode of the device [13]. The short-circuit current density and efficiency were found to be improved significantly via these photoanode modifications.

This work is concerned with the modification of TiO_2 by combining it with sulphur in composite form. The new idea of this work is the use of TiO_2 -sulphur composite as a photoanode of the DSSC. So far, there has been no report on the use of TiO_2 -non-metal films composite as photoanode of the device. The goal of this work is to investigate the influence of thiourea concentration on the structural and optical properties of TiO_2 -sulphur composite. The second goal is to study the effect of the sulphur precursor

✉ M. Y. A. Rahman, mohd.yusri@ukm.edu.my; ✉ S. A. M. Samsuri, sitiazah@usm.my | ¹Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia. ²Nano-Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, 11800 Gelugor, Penang, Malaysia.

concentration on the performance parameter of the device especially photocurrent and power conversion efficiency.

2 Experimental

2.1 TiO₂-sulphur composite preparation

TiO₂ films were grown on indium tin oxide (ITO) substrate by liquid-phase deposition method. Firstly, ITO substrate purchased from Kaivo China with a sheet resistance of 16 Ω/square was cleaned in an ultrasonic bath using acetone and 2-propanol in a right sequence. Next, the cleaned ITO was immersed into a growth solution consisting of 7 mL of (NH₄)₂TiF₆ (Sigma-Aldrich) and H₃BO₃ (Sigma-Aldrich) with the molarity of 1.0 M and 2.0 M, respectively, for 15 h. The TiO₂ film was annealed at 400 °C for 1 h in air. The as-prepared TiO₂ sample was then spin-coated with 0.10 M thiourea (CH₄N₂S). This step was repeated with 0.30, 0.5, 1.0 and 2.0 M thiourea. The source of sulphur was thiourea which was purchased from Sigma-Aldrich. The preparation of TiO₂-sulphur composite samples was completed by rinsing the sample with adequate amount of deionized water to remove the agglomerated particles on the surface of the sample and underwent annealing process in air at 100 °C for 1 h.

The phase structure of the samples was characterized using X-ray diffraction (XRD) measurements (Bruker D8 Advance system). The optical properties characterization was carried by using UV-Vis spectrophotometer in diffused reflectance mode (DR) (Hitachi U-3900H). In order to obtain more information about the structure of TiO₂-sulphur composite, Raman analysis at room temperature has been carried out.

2.2 Fabrication and performance study of the DSSC

All TiO₂-sulphur composite samples were sensitized with N719 dye by immersing the samples in a solution containing N719 dye (Solaronix) dissolved in ethanol at temperature of 60 °C for 5 h. The dye loading of the samples was determined by measuring the absorption of the TiO₂-sulphur and TiO₂-sulphur-coated N719 dye at wavelength peak of 530 nm. The absorption of N719 dye in ethanol with the concentration of 0.02–0.25 mM was firstly measured also at the peak wavelength of 530 nm. Then, the difference in the absorption of the TiO₂-sulphur and TiO₂-sulphur-coated N719 dye was then matched with the absorption of N719 dye in order to get the dye loading of the samples. Platinum film with thickness of 20 nm sputtered on the ITO substrate serves as a counter electrode. A DSSC was fabricated by sandwiching a surlyn film between TiO₂-sulphur composite and platinum counter electrode and clamped in order to optimize the interfacial contact between the

TiO₂-sulphur/dye/electrolyte and electrolyte/platinum. The Z-50 electrolyte from solaronix was injected into the space between TiO₂-sulphur/dye and platinum via a capillary action. The surlyn film serves as a separator and electrolyte container. The performance study of the device utilizing the TiO₂-sulphur composite with various thiourea concentrations was carried out by observing the current density–voltage under illumination using an AM 1.5 simulated light with an intensity of 100 mW cm⁻². The active area of the device was 0.23 cm². The current–voltage curves and impedance spectra under illumination were recorded by a Gamry measurement system interfaced with a personal computer.

3 Results and discussion

The XRD patterns for bare TiO₂ and all TiO₂-sulphur composite samples are shown in Fig. 1. For bare TiO₂ film (0.0 M), its XRD spectrum shows an anatase phase with tetragonal structure and lattice plane orientations, (101), (004), (200), (105) and (211) which corresponds with the diffraction angle, $2\theta = 25.56^\circ, 38.27^\circ, 48.29^\circ, 54.42^\circ$ and 55.34° , respectively. All lattice planes of anatase denoted by *T* notation are in good agreement with the standard spectrum of the JCPDS File (No: 01-075-1537). The highest diffraction peak of anatase is at the plane (101) which proves that TiO₂ tends to grow along (101) direction from the ITO surface. The intensity of (101) peak is observed to be decreased upon the addition of sulphur into TiO₂. This signifies that sulphur is well dispersed on TiO₂ with the increase in thiourea molarity, making the TiO₂ phase less detected by XRD [14, 15]. The phase of sulphur denoted by *S* is observed at the diffraction

Fig. 1 XRD spectra of TiO₂-sulphur composite films with various CH₄N₂S concentrations

angles, $2\theta = 23.49^\circ$, 29.24° , 36.61° and 35.74° , corresponding with the plane (113) (223) (-116) and (026), respectively. The intensity of these peaks obviously increases with the concentration of thiourea. All patterns of sulphur can be indexed to a material having a monoclinic structure, which is in good agreement with the one listed in the standard data file (JCPDS No. 01-078-0793). The anatase and sulphur phases exist in all samples as illustrated in the XRD patterns.

Other detected phases belonging to transition complex compound of titanium–sulphur system are SO_3 and Ti_3S_4 . The complex compound phase is also called secondary phase. In Fig. 1, SO_3 and Ti_3S_4 phases are denoted by SO and TS, respectively. SO_3 phase exists at the diffraction angle of 20.23° , 24.13° and 28.63° , and Ti_3S_4 phase presents at the diffraction angle of 36.5° . These two phases are obviously detected in the samples with higher concentrations, namely 1.0 and 2.0 M. The phase of SO_3 and Ti_3S_4 agrees well with the XRD data according to the JCPDS File No. 01-072-0081. These phases might exist due to low annealing temperature used in this work [16].

Table 1 Crystallite size of anatase and sulphur phases with various thiourea concentrations

Concentration (M)	Crystallite size (nm)	
	Anatase (101 plane)	Sulphur (113 plane)
0.0	24.1	–
0.1	24.1	48.1
0.3	23.1	48.3
0.5	22.8	49.1
1.0	40.5	50.2
2.0	65.4	51.8

From Table 1, it is observed that the crystallite size of anatase varies with thiourea concentration with the 2.0 M sample possessing the biggest crystallite size. The 0.5 M sample has the smallest crystallite size. Also, according to the table, the difference in anatase crystallite size between the 0.3 and 0.5 M samples is small that is just 0.3 nm. It can be said that the crystallite size of these samples is similar. However, for sulphur phase, its crystallite size was found to increase with the concentration of thiourea for which the 2.0 M sample exhibits the largest crystallite size. Also, the sulphur crystallite size for the 0.1 and 0.3 M samples is about the same since the difference in the crystallite size is only 0.2 nm.

Figure 2a illustrates the diffused reflection spectra (DRS) for all samples. The sample with 0.3 M $\text{CH}_4\text{N}_2\text{S}$ possesses the highest diffused reflection (80%) in the wavelength range of 500–550 nm which is in the visible region. This indicates that this sample has the best scattering light ability in the visible region. In the infrared region, the samples with the concentration of 0.1 and 0.3 M have the highest scattering property. Good scattering property implies that this sample has high light harvesting efficiency upon incorporation with sensitizer, thus resulting in higher power conversion efficiency when applied in DSSC [17]. The 2.0 M sample has the lowest reflection in the visible region (63%). In other words, the DSSC utilizing the 0.3 M sample has the highest light harvesting efficiency and is expected to demonstrate the highest photocurrent and power conversion efficiency. The absorption spectra of the samples coated with N719 dye are presented in Fig. 2b. According to the spectra, the N719 dye greatly improves the absorption in the visible region, ranging from 400 to 700 nm. All samples coated with N719 possess dominant absorption peak at 530 nm while the sample without dye depicts no peak at that wavelength. From the absorption

Fig. 2 **a** UV–Vis reflection spectra of TiO_2 –sulphur composite films with various $\text{CH}_4\text{N}_2\text{S}$ concentrations and **b** UV–Vis absorption spectra of TiO_2 –sulphur-coated N719 dye with various $\text{CH}_4\text{N}_2\text{S}$ concentrations

Table 2 Photovoltaic parameters and dye loading of the DSSC with various thiourea concentrations

Concentration (M)	J_{sc} (mA/cm ²)	V_{oc} (V)	η (%)	FF	Dye loading $\times 10^{-8}$ (mol cm ⁻²)
0.0	4.45 $\pm$ 0.17	0.58 $\pm$ 0.06	1.20 $\pm$ 0.30	0.46 $\pm$ 0.01	7.39
0.1	5.39 $\pm$ 0.03	0.58 $\pm$ 0.06	1.31 $\pm$ 0.11	0.42 $\pm$ 0.03	8.23
0.3	9.08 $\pm$ 0.11	0.57 $\pm$ 0.08	1.80 $\pm$ 0.23	0.34 $\pm$ 0.04	8.69
0.5	7.11 $\pm$ 0.16	0.54 $\pm$ 0.08	1.16 $\pm$ 0.16	0.30 $\pm$ 0.06	7.21
1.0	3.98 $\pm$ 0.20	0.49 $\pm$ 0.07	0.90 $\pm$ 0.01	0.46 $\pm$ 0.01	6.54
2.0	3.32 $\pm$ 0.14	0.48 $\pm$ 0.04	0.57 $\pm$ 0.01	0.35 $\pm$ 0.05	5.30

Fig. 3 Raman spectra of bare TiO₂ and TiO₂-sulphur composite films with 0.3 M CH₄N₂S

spectra, it can be concluded that TiO₂-sulphur composite film with the concentration 0.1 M and 0.3 M shows the higher absorption peak compared to bare TiO₂ film (0.0 M). The highest absorption peak is owned by TiO₂-sulphur composite film with the concentration 0.3 M corresponding with the dye loading of 8.69×10^{-8} mol cm⁻² (Table 2) while the lowest absorption peak is owned by the TiO₂-sulphur composite film with the concentration 2.0 M with the dye loading of 5.30×10^{-8} mol cm⁻².

Figure 3 displays the Raman spectrum of TiO₂ and TiO₂-sulphur nanocomposite (0.3 M) excited with a 514.5 nm beam of the Ar⁺ laser. Group theory predicts that the typical anatase TiO₂ has six Raman active modes: $I^- = A_{1g} + 2B_{1g} + 3E_g$. For TiO₂, the Raman spectra present four bands at 144 cm⁻¹ (E_g), 390 cm⁻¹ (B_{1g}), 507 cm⁻¹ (A_{1g}) and 628 cm⁻¹ (E_g). All samples that exhibit the characteristic Raman active modes of the anatase TiO₂ phase are in good agreement with the phase structure determined by XRD [18]. For TiO₂-sulphur composite with sulphur precursor concentration of 0.3 M, a small peak at 474 cm⁻¹ corresponds to the A_{1g} symmetric stretching mode of S [19, 20].

Fig. 4 J - V curves of the devices utilizing TiO₂-sulphur composite films coated N719 dye with various CH₄N₂S concentrations

Other bands that present in the spectra might be from the complex compound of TiO₂-sulphur composite system.

Figure 4 depicts the J - V curves of the DSSC employing the samples with various thiourea concentrations. It is found that the area under curves representing the output power generated by the device varies with the concentration of thiourea. The 0.3 M device generates the highest output power, while the 2.0 M device produces the lowest output power. It is also noticeable that the slope of each curve is quite high, signifying the high internal resistance in the devices. The photovoltaic parameters are extracted from the curves and presented in Table 2. According to the table, the J_{sc} and η increase with thiourea concentration until the optimum concentration of 0.3 M and then drops. The 0.3 M device performs the highest J_{sc} and η which is due to the highest dye loading, the lowest R_b and R_{ct} and the longest carrier lifetime. Also from the table, it is observed that the η increases with dye loading. The higher dye loading results in the higher η . The 2.0 M device demonstrates the lowest J_{sc} and η . It is also noticeable that

Fig. 5 Nyquist plots of the devices with various $\text{CH}_4\text{N}_2\text{S}$ concentrations

Table 3 EIS parameters of the DSSC with various thiourea concentrations

Concentration (M)	R_b (Ω)	R_{ct} (Ω)	τ (ms)
0.0	39 ± 3	122 ± 10	6.5 ± 0.1
0.1	38 ± 1	120 ± 8	6.5 ± 0.1
0.3	38 ± 3	118 ± 9	7.7 ± 0.4
0.5	40 ± 2	131 ± 5	7.1 ± 0.5
1.0	42 ± 1	180 ± 1	6.3 ± 0.2
2.0	42 ± 1	210 ± 3	5.1 ± 0.1

Fig. 6 Bode plots of the devices with various $\text{CH}_4\text{N}_2\text{S}$ concentrations

the device utilizing the pure TiO_2 photoanode performs higher J_{sc} than that of 1.0 and 2.0 M devices. The SO_3 and Ti_3S_4 phases lower down the efficiency since according to Table 1; the η of the device utilizing 1.0 and 2.0 M samples is smaller than that of the devices with lower concentrations of thiourea. These two phases exist in the samples with 1.0 and 2.0 M thiourea as observed in the XRD patterns illustrated in Fig. 1. The device utilizing pure TiO_2 also demonstrates higher η than the 0.5, 1.0 and 2.0 M devices. Also, it is observed from the table that the efficiency of the device without sulphur (1.20%) has been improved quite significantly upon combining it with sulphur in composite form. The efficiency has been improved by 50% by modifying TiO_2 films photoanode via sulphur treatment. The highest efficiency of 1.80% was found to be higher than that reported in [10], yielding the efficiency of 0.18% only. This indicates that the highest efficiency obtained from this work is ten times than reported in this literature. Also, it is higher than that of the DSSC utilizing Zn-doped TiO_2 photoanode for which the efficiency was 1.34% [11]. However, it is lower than that of the device utilizing P25 TiO_2 photoanode that was 6.50% [21]. From the table, the FF is low since the internal resistance of the devices is high leading high power loss. The V_{oc} presented in the table is also low. Low FF and V_{oc} lead to low efficiency of the device.

Figure 5 shows the Nyquist plots of the devices utilizing the photoanodes with various thiourea concentrations. The plots display two semicircles for which a smaller semicircle represents bulk resistance and a bigger one denotes charge transfer resistance. From the plots, it is found that the 0.3 M device shows the smallest

semicircles; meanwhile, the biggest semicircles belong to the 2.0 M device. Both resistances are illustrated in Table 3. Figure 6 depicts the Bode plots for all devices. The plots are symmetry about a resonant frequency which was used to compute the carrier lifetime. The 0.3 M device has the smallest frequency leading to the highest lifetime, while the 2.0 M device has the biggest frequency resulting in the shortest lifetime. The improved lifetime of carriers might be due to this reason. The composite sample should be subjected to annealing treatment at high temperature to remove all the organics residues and complexes in order to make sure that the samples are pure TiO_2 -sulphur without the existence of any secondary phase. According to Table 3, the 1.0 and 2.0 samples have shorter carrier lifetime compared with the samples prepared using lower concentrations of thiourea.

4 Conclusions

TiO_2 -sulphur composite films have been prepared via liquid-phase deposition assisted with spin coating technique and employed as photoanode in DSSC. Apart from anatase and sulphur phases, the secondary phase of SO_3 and Ti_3S_4 also exists in the sample. The 0.3 M sample shows the highest reflection and absorption in visible region. The peak intensity at 460 nm decreases with thiourea concentration. The Raman peak at 474 cm^{-1} corresponds to the A_{1g} symmetric stretching mode of sulphur. The efficiency has been improved by 50% by modifying TiO_2 films photoanode with sulphur in composite form. The DSSC utilizing this composite demonstrates the highest power conversion efficiency, η of 1.80% due to the highest dye loading, the lowest bulk and charge transfer resistance and the longest carrier lifetime.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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