THE STRUCTURAL PROPERTIES OF ZnO/TiO_2 BILAYER THIN FILM AS PHOTOANODE

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ABSTRACT

The ZnO/TiO_2 bilayer was fabricated on the fluorine-doped tin oxide (FTO) substrate. The ZnO nanorods and TiO_2 nanoparticles were developed as photoanode material that were fabricated by using sol-gel immersion and squeegee method. The structure of ZnO/TiO_2 bilayer showed a good properties for photoanode in DSSCs application. The ZnO/TiO_2 bilayer has large surface area that could increase a dye loading and performance of photoanode. Meanwhile, the micro-Raman spectra of ZnO/TiO_2 bilayer indicated a good crystallinity. Therefore, the ZnO/TiO_2 bilayer showed a good structure for photoanode in DSSCs application.

Key words: ZnO nanorods, TiO_2 nanoparticles, ZnO/TiO_2 bilayer, Photoanode

ABSTRAK

Lapisan ZnO/TiO_2 difabrikasi di atas substrat oksida timah yang di doping florin (FTO). Batang nano ZnO dan partikel nano TiO_2 dikembangkan sebagai material fotoanoda yang difabrikasi menggunakan metode pencelupan sol-gel dan *squeegee*. Struktur lapisan ZnO/TiO_2 menunjukkan sifat fotoanoda yang baik dalam aplikasi DSSCs. Lapisan ZnO/TiO_2 memiliki luas permukaan yang besar yang bisa meningkatkan muatan *dye* dan performa fotoanoda. Sedangkan spktrum mikro-Raman lapisan ZnO/TiO_2 mengindikasikan kristalinitas yang bagus. Oleh karena itu, lapisan ZnO/TiO_2 menunjukkan struktur yang baik untuk fotoanoda di dalam aplikasi DSSCs.

Kata Kunci: batang nano ZnO, partikel nano TiO_2, lapisan ZnO/TiO_2, fotoanoda

INTRODUCTION

Recently, the semiconductors such as zinc oxide (ZnO) and titanium dioxide (TiO_2) have received wide attention due to their outstanding optical and electrical properties (Kwiatkowski, et al, 2015). The semiconductor materials are included in wide band gap (~3 eV) and good absorption in UV range. The band gap of ZnO is around ~3.37 eV (Wu, et al, 2013) and TiO_2 is around ~3.2 eV (Lee, et al, 2010). The ZnO is widely used in photovoltaic devices due to its high electron mobility of 200-300 cm^2Vs^{-1} for bulk ZnO, meanwhile for single crystal ZnO nanowires its electron mobility is much higher at ~1000 cm^2Vs^{-1} (Ozgur, et al, 2005). For the TiO_2, it has low electron mobility (0.1-4 cm^2Vs^{-1}) (Tang, et al, 1994). The ZnO is a good candidate as photoanode in dye sensitized solar cells (DSSCs) application due to its low cost, nontoxicity

(Umar, et al, 2008), strong exciton binding energy (60 meV) (Kim, et al, 2010), chemical and thermal stability (Zeng, et al, 2009). However, ZnO has a low energy conversion efficiency in photovoltaic performance.

Therefore, the TiO_2 is also developed as photoanode material because of its high performance in energy conversion efficiency. The TiO_2 is used to improve the properties of ZnO and increase the performance of photoanode in DSSCs application. Then, the TiO_2 is fabricated on the ZnO thin film to produce photoanode properties much better. The structures of ZnO such as nanorods (Wu, et al, 2013), nanowires (Fan, et al 2013), nanotubes (Han, et al, 2010) and nanosheets (Li, et al, 2012) are usual morphology used as photoanode in DSSCs application. However, among all these the ZnO nanorods structure are widely used in photoanode due to their high energy conversion efficiency and better electron transport (Kislyuk, et al, 2008). The ZnO nanorods are usually grown on the seeded catalyst such as magnesium (Mg) (Zhou, et al, 2011), aluminum (Al) (Malek, et al, 2016) and aurum (Au) (Xu, et al, 2013). Among those mentioned seeded catalysts, Mg is preferable catalyst for ZnO nanorods growth due to its similar ionic radii (0.72 Å) to Zn^{2+} (0.74 Å) which later gives less lattice distortion when Zn^{2+} is replaced with Mg^{2+} (Lien, et al, 2014).

The ZnO nanorods can be grown by using sol-gel immersion method (Malek, et al, 2013), solvothermal (Wu, et al, 2013) and hydrothermal (Tan, et al, 2013). Among these methods, sol-gel immersion shows the best method to grow aligned ZnO nanorods due to its low cost and simple fabrication. Afterwards, the TiO_2 nanoparticles can be fabricated either by using squeegee method (Zainun, et al, 2012), hydrothermal (Yune, et al, 2013) or screen printing (Valsaraj, et al, 2016). However, the squeegee method is preferred to fabricate TiO_2 nanoparticles on ZnO nanorods in conjunction of its simple fabrication and low cost production. In this paper, the ZnO/TiO_2 bilayer as photoanode was fabricated on FTO substrate. The structural properties of ZnO/TiO_2 bilayer were carried out by using field emission scanning microscopy (FESEM), energy dispersive X-ray (EDX) and micro-Raman spectroscopy. From the analysis done, it shows that the ZnO/TiO_2 bilayer is potential to be used as photoanode for DSSCs application.

MATERIALS AND METHODS

The ZnO/TiO_2 bilayer fabrication involved 3 steps. (1) First, the magnesium zinc oxide (MgZnO) seeded catalyst was fabricated by mixing zinc acetate dehydrate (Zn $(CH_3COO)_2$ $2H_2O$; 99.5% purity; EMSURE) as precursor and magnesium nitrate hexahydrate (Zn $(NO_3)_3$. $6H_2O$; 99% purity; Across Organic) as dopant which were mixed into 2-metoxyethanol ($C_3H_8O_2$) solvent. Then, mono-ethanolamine (C_2H_7NO) as stabilizer was added in the solution. Afterwards, the 0.4 M of MgZnO solution was prepared by using 0.88 g of zinc acetate dehydrate, 0.44 g of magnesium nitrate hexahydrate and the 0.25 ml of mono-ethanolamine then mixed with 10 ml of 2-methoxyetanol. The MgZnO solution was then coated on 2x1 cm^2 FTO substrate by using spin coating technique and annealed at 500˚C for 1 hour.

(2) Second, the ZnO nanorods were grown on MgZnO seeded catalyst by using sol-gel immersion method (Suriani, et al, 2016). The ZnO solution was prepared by mixing of 2.975 g zinc nitrate hexahydrate and 1.409 g of hexamethylenetramine (HMT) into 200 ml of DI water. The ZnO nanorods were synthesized in water bath for 4 hours at 95˚C. Then, the ZnO was annealed at 500˚C for 1 hour. (3) Next, the TiO_2 nanoparticles on ZnO nanorods (ZnO/TiO_2 bilayer) was coated by using squeegee method (Yune, et al, 2013). The TiO_2 paste was prepared from 3.5 g of commercial titanium (IV) oxide nanopowder (Sigma Aldrich, particle size ~21 nm), 0.5 ml titanium tetraisopropoxide (TTIP) and 15 ml ethanol. The ZnO/TiO_2 bilayer were then annealed at 450˚C for 1 hour. The ZnO/TiO_2 bilayer was characterized by using FESEM-Hitachi Su8020, EDX-Horiba EMAX and micro-Raman spectroscopy (Renishaw InVia micro-Raman System).

RESULTS AND DISCUSSIONS

The FESEM images (Fig. 1) show the morphology of ZnO/TiO_2 bilayer by sol-gel immersion and squeegee method. The MgZnO image shown in Fig. 1(a) that demonstrated nanoparticles structure and the grains size were around 15-35 nm. Meanwhile, the white agglomerations of MgZnO nanoparticles in the surface were shown by the arrow and these were caused by the inhomogeneous MgZnO solution. Fig. 1(b)-(c) show the top and side view of vertically aligned ZnO nanorods that were grown on MgZnO nanoparticles. Then, the existence of HMT in the ZnO solution produced ZnO with a hexagonal-shaped. The diameter and thickness of ZnO nanorods were around 675-794 nm and 2.89-5.13 µm, respectively. The different thickness of ZnO nanorods was believed and resulted from an uneven of MgZnO seeded catalyst (Suriani, et al, 2015). The thickness of MgZnO seeded catalyst was measured to be around 1.15 µm as shown in Fig. 1(c).

Fig. 1(d)-(e) show the top and side view of ZnO/TiO_2 bilayer where the TiO_2 nanoparticles were coated on top of ZnO nanorods. The approximate thickness of TiO_2 nanoparticles on ZnO nanorods was measured to be at around 9.72-13.2 µm. However, the overall TiO_2 nanoparticles thickness were seen to be uneven which may be attributed to low amount of dye adsorption on the TiO_2 surface when used as photoanode later on. The photo-excitation of electrons in the photoanode was influenced by the amounts of dye adsorption. Therefore, low dye adsorption by uneven TiO_2 sample may results in low energy conversion efficiency if they are applied for DSSCs application. Nonetheless, large surface area of TiO_2 itself was believed that it could absorb dye optimally as compared to pristine ZnO as photoanode.

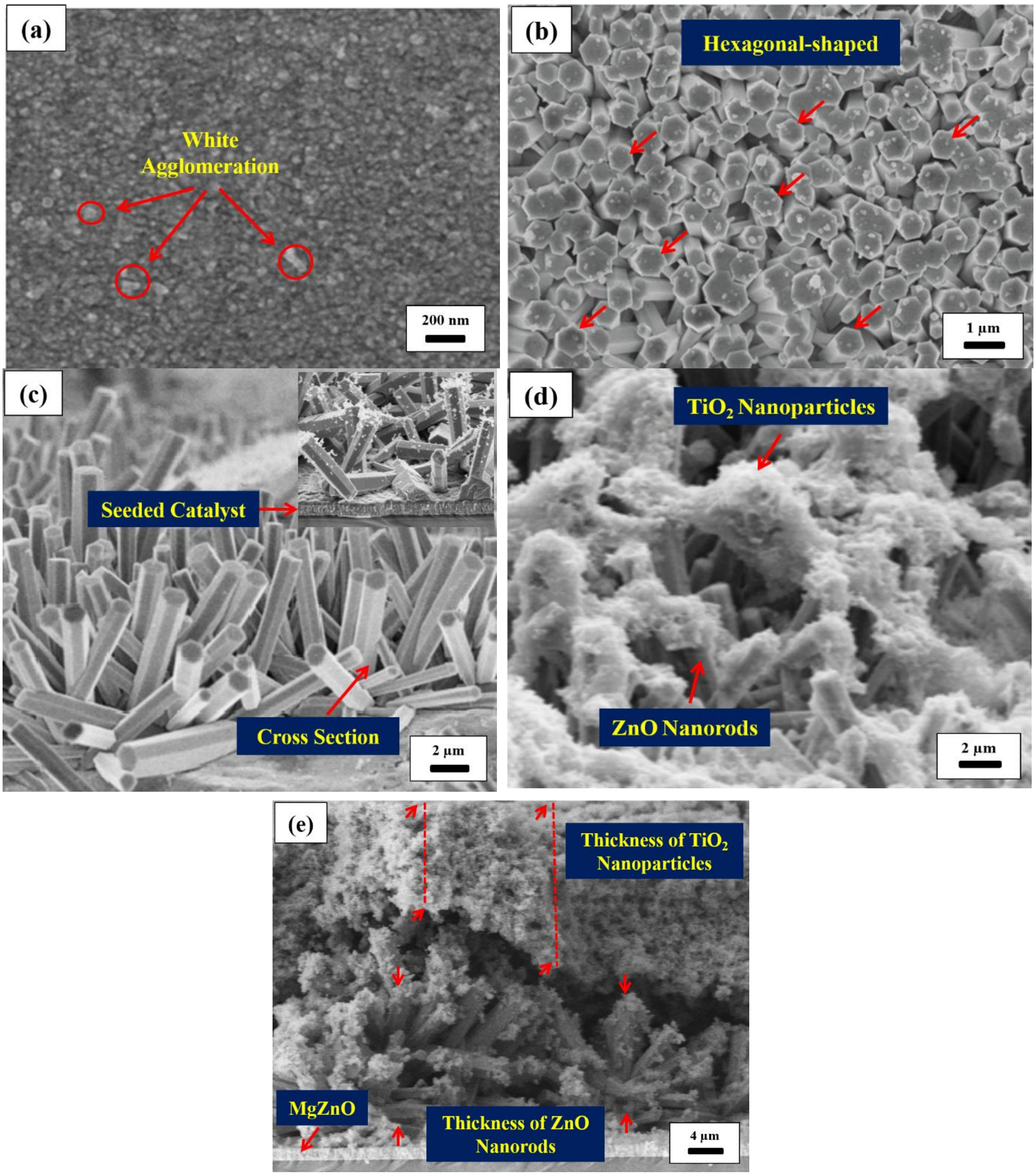

Fig. 1. FESEM images of (a) MgZnO seeded catalyst, (b) top and (c) side view of ZnO nanorods, (d) top and (e) side view of ZnO/TiO_2 bilayer.

Next, the composition of ZnO/TiO_2 bilayer was examined by using EDX as hown in Fig. 2. Fig. 2(a) shows the EDX spectra of MgZnO seeded catalyst that has atomic % of ~5.28% Mg, ~16.21% Zn and ~74.48% O. These results were consistent with the previous research (Suriani, et al, 2015). Meanwhile, the EDX spectra of ZnO is shown in Fig. 2(b) that has atomic content of ~39.61% Zn, ~0.85% Mg and ~59.55% O. Fig 2(c) shows the EDX spectra of ZnO/TiO_2 bilayer which confirmed the Mg, Zn, Ti and O in the ZnO/TiO_2 bilayer thin film. This result proved that the highest atomic content was Ti (~27.69%). The highest atomic % of TiO_2 content detected from EDX consistent with FESEM analysis as Ti was thicker than Zn with the difference thickness value around 4-8 µm.

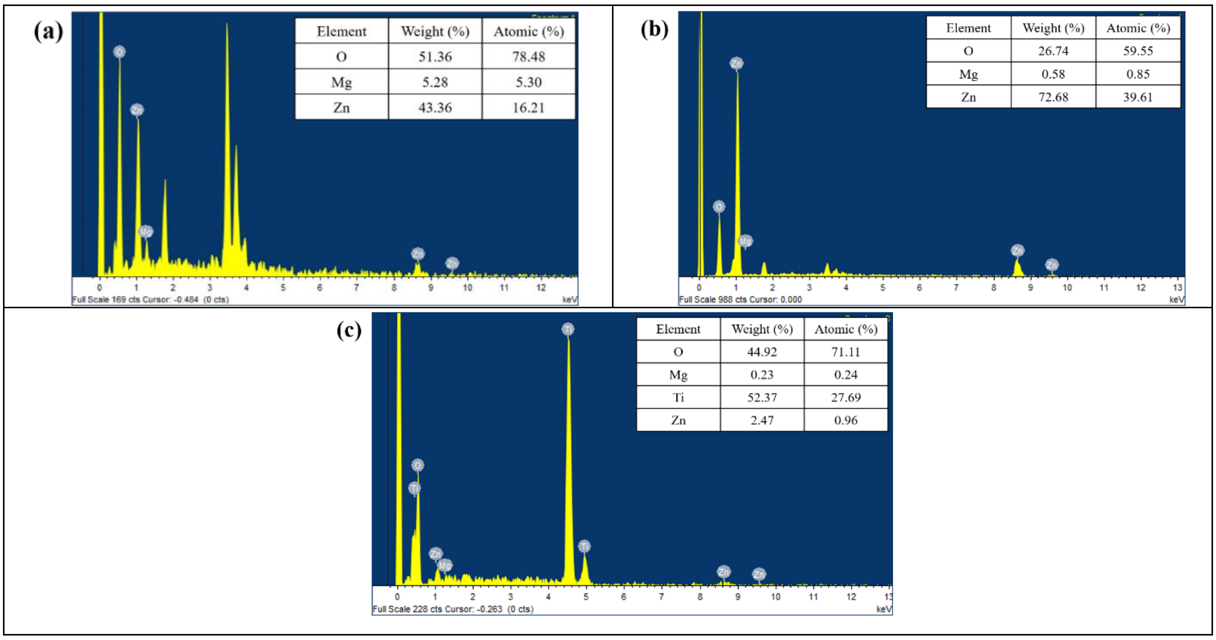

Fig. 2. EDX spectra of (a) MgZnO seeded catalyst, (b) ZnO and (c) ZnO/TiO_2 bilayer.

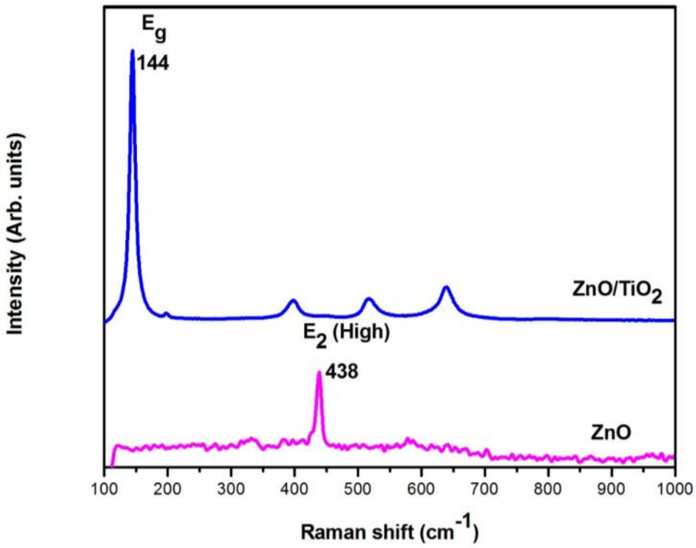

Fig. 3. Raman spectra of ZnO and ZnO/TiO_2 bilayer.

The structural properties were further analysed by micro-Raman spectroscopy as shown in Fig. 3. Based on Raman analysis, it shows peaks and phases of ZnO and ZnO/TiO_2 bilayer which could determine the defects and qualities of crystal (Ahmed, et al, 2011). The ZnO nanorods have peak at 438 cm^{-1} E_2 (high) that explained a wurtzite phase in ZnO structure. This Raman spectra also explained the peaks of ZnO/TiO$_2$ bilayer which has prominently intense peak at 144 cm^{-1} (Ohsaka, et al, 1980).

CONCLUSION

The ZnO/TiO$_2$ bilayer was successfully fabricated as photoanode for future application in DSSCs. The structural properties of ZnO/TiO$_2$ bilayer had been investigated by using FESEM, EDX and micro-Raman spectroscopy. The FESEM images show that the structure of ZnO/TiO$_2$ bilayer had large surface area in nanoparticles surface to increase the dye loading in photoanode. Whereas, the EDX spectra confirmed that the ZnO/TiO$_2$ bilayer thin film had the Mg, Zn, Ti and O elements. Then, the micro-Raman spectra explained the crystallinity structure of ZnO/TiO$_2$ bilayer. Therefore, according to the structural properties of ZnO/TiO$_2$ bilayer, it showed that ZnO/TiO$_2$ bilayer can be applied for photoanode in DSSCs.

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