HYDROTHERMAL GROWTH AND SQUEEGEE METHOD IN THE FABRICATION OF MIXED-PHASE TiO_2 NANOSTRUCTURES

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ABSTRACT

In this work, the modification of TiO_2 nanostructures based on its morphology and crystallinity phase were fabricated using a simple method. Hydrothermal growth method was used to synthesize nanorods and nanoflowers, while nanoparticles was applied using squeegee method. The average length and diameter of the as-grown nanorods were 3.5 and 46-215 nm, respectively. Meanwhile, the average total thickness and band gap value of mixed-phase TiO_2 nanostructures were 15.98-24.54 nm and 2.84 eV, respectively. Based on its structural and electrical properties, the fabricated film has great potential to be applied as photoanode semiconductor layer for dye-sensitized solar cells application.

Key words: TiO_2, Nanostructures, Mixed-phase, Hydrothermal, Squeegee.

ABSTRAK

Dalam penelitian ini, modifikasi struktur nano TiO_2 berdasarkan morfologi dan fase kristalinitasnya difabrikasi menggunakan metode sederhana. Metode pertumbuhan hidrotermal digunakan untuk mensintesis batang nano dan bunga nano, sementara untuk partikel nano diterapkan menggunakan metode squeegee. Rata-rata panjang dan diameter batang nano adalah masing-masing 3,5 dan 46-215 nm. Sementara itu, total rata-rata ketebalan dan nilai *band gap* dari fase campuran struktur nano TiO_2 adalah masing-masing 15,98-24,54 nm dan 2,84 eV. Berdasarkan sifat struktural dan listriknya, film yang dibuat memiliki potensi besar untuk diaplikasikan sebagai lapisan semikonduktor fotoanoda untuk aplikasi sel surya *dye-sensitized*.

Kata kunci: TiO_2, struktur nano, fase campuran, hidrotermal, Squeegee.

INTRODUCTION

Titanium dioxide (TiO_2) becomes the most investigated metal oxides materials due to its wide range of applications and suitable for many experimental techniques (Diebold, 2003). TiO_2 has several nanostructures, such as nanoparticle, nanorod, nanoflower, nanowire, nanotube, and hollow hemisphere. Meanwhile, anatase, rutile, and brookite are the crystallinity phase known for TiO_2. Each nanostructures and crystallinity phase have its own advantages and disadvantages. Brookite is known as metastable phase thus rarely used, while rutile is known as the most stable phase among other phases and has larger grain size as compared to anatase. The smaller grain size of anatase becomes an advantage due to the larger surface area as compared to rutile. Anatase also has the widest band gap (E_g) among other phases which is useful in electronic applications [Lei, *et.al.,* 2016]. Based on those facts, the synthesis of mixed-phase TiO_2 between rutile and anatase could yield a better electrical performance (Mehmood, *et.al.,* 2014). Some methods to synthesize TiO_2 are pulsed laser deposition, hydrolysis method, hydrothermal growth, and solvothermal method.

Photocatalyst material, gas sensor, corrosion-protective coating, optical coating, Li-based batteries, and electrochromic devices are some of the applications which utilize TiO_2. In addition, TiO_2 is also used in paint industries and cosmetic products as white pigment and even in medical as bone implant (Diebold, 2003). Among those applications, TiO_2 as photocatalyst material gains a lot of interest since the invention of dye-sensitized solar cells (DSSCs) in 1991 (O'Regan and Grätzel, 1991; Ahmad, *et.al.,* 2015; Zhang, *et.al.,* 2006; Lee, *et.al.,* 2014). Based on several investigations, TiO_2 shows better performance as compared to ZnO and SnO_2 which are usually used as photoanode semiconductor layer (Han, *et.al.,* 2009; Fukai, *et.al.,* 2007; Bauer, *et.al.,* 2002). Moreover, the properties of TiO_2 which are chemically and physically stable, low-cost, good electronic properties, non-toxic, and large effective surface area are needed in dye adsorption process and suitable as well as become the advantages for DSSCs application (Lei, *et.al.,* 2016, Qin, *et.al.,* 2015; Tamilselvan, *et.al.,* 2012; Hwang, *et.al.,* 2012). The adsorption process becomes an important factor in DSSCs process which affect the DSSCs energy conversion efficiency (η). The η value is affected by the amount of flowing electrons through the circuit indicated by short current density (J_{SC}) value. The morphology and crystallinity phase of TiO_2 absolutely affect the J_{SC} value thus their crystallinity need to be greatly considered in terms of structural optimization (Mehmood, *et.al.,* 2014; Zhu, *et.al.,* 2014; Gong, *et.al.,* 2012). Another important factor is the chosen substrate which should have high electrical conductivity and optically transparent. Sima et al. (Sima, *et.al.,* 2010) investigated the DSSCs performance by comparing indium-doped tin oxide and fluorine-doped tin oxide (FTO) as substrates. Based on the result, FTO shows a lower sheet resistance and thermally-stable thus it is recommended for DSSCs application.

In this work, we synthesize rutile TiO_2 nanorods−nanoflowers and mix them with anatase TiO_2 nanoparticles. Nanorods and nanoflowers were synthesized using hydrothermal growth (Ahmad, *et.al.*, 2015), while nanoparticles was synthesized using squeegee method (Zhang, *et.al.*, 2006).

MATERIALS AND METHODS

FTO substrate was cut into 2×1 cm^2 dimension and cleaned using acetone, methanol, and deionize (DI) water for 15 minutes, respectively. The substrate was then placed on autoclave with the conductive surface facing upward. Hydrothermal solution for TiO_2 nanorods and nanoflowers growth were prepared based on previous study conducted by Ahmad, et al. [Ahmad, *et.al.*, 2015]. 120 ml of hydrochloric acid and 120 ml of DI water was stirred for 5 minutes until well-mixed before adding 6 ml of titanium butoxide dispersing drop by drop to the solution. Clear hydrothermal solution was obtained after stirring for another 10 minutes and directly poured into autoclave. Hydrothermal growth process was performed at 150℃ for 5 hours. The grown films were then taken out from the autoclave after cooled down to room temperature followed by rinsing using DI water and drying in room temperature.

The second layer of the film was produced by applying TiO_2 paste based on simple squeegee method (Zhang, *et.al.*, 2006) on top of the as-grown TiO_2 nanorods and nanoflowers. 7.5 ml of ethanol was poured into 1.75 g titanium (IV) oxide and stirred until a paste formed followed by adding0.25 ml of titanium (IV) isopropoxide and stirred until the prepared paste became well-mixed with low agglomeration. The obtained paste was sonicated for 5 minutes in room temperature and rolled over the fabricated film's first layer using glass rod and heated in electric oven for 10 minutes at 150℃. The films was annealed at 450℃ for 1 hour before processing with physical characterizations. Several characterization, such as field emission scanning electron microscopy (FESEM), micro-Raman spectroscopy, energy dispersive X-ray (EDX), and UV-Vis spectroscopy were used to investigate the morphology, lattice crystallinity, and electrical performance of the fabricated film.

RESULTS AND DISCUSSIONS

FESEM images of the as-grown TiO_2 nanorods are presented in Fig. 1. Based on Fig. 1 (a), it can be shown that the synthesized nanorods was grown uniformly and densely. The crystal structure of nanorods was in tetragonal shape with diameters range of 46−215 nm as shown in Fig. 1 (b). Cross section image of fabricated film's first layer in Fig. 1 (c) reveals the perpendicular direction and high-density nanorods grown on FTO substrate. The results was in good agreement with Ahmad et al.(Ahmad, *et.al.*, 2015). Several size of nanoflowers which grow rarely in some spot of nanorods were also observed. The average length of nanorods was 3.5 nm, which was a bit longer compared to the previous result (Ahmad, *et.al.*, 2015). Anatase TiO_2 nanoparticles was also seen to be uniformly spread and completely covered nanorods as shown in Fig. 1 (d). The large surface area of nanoparticles due to the small grain size of particles gives an advantage if it

is applied as photoanode semiconductor layer which increase the dye adsorption. The study reveal that the maximum dye adsorption led to the increment of electron excitation thus improve the J_{SC} value. As a result of this, high η will be achieved. A closer view in Fig. 1 (e) shows a closely interconnected particles which is believed to give an advantage in electrons transfer to the nanorods. The shape and direction of as-grown nanorods perpendicular to the substrate makes the electrons directly and easily move to FTO substrate. Fig. 1 (f) shows the cross section view of fabricated film thickness. Based on the image, the film thickness range from 15.98 to 24.54 μm. EDX analysis as shown in Table 1 confirms titanium and oxygen as element compound of fabricated mixed-phase TiO_2 nanostructures.

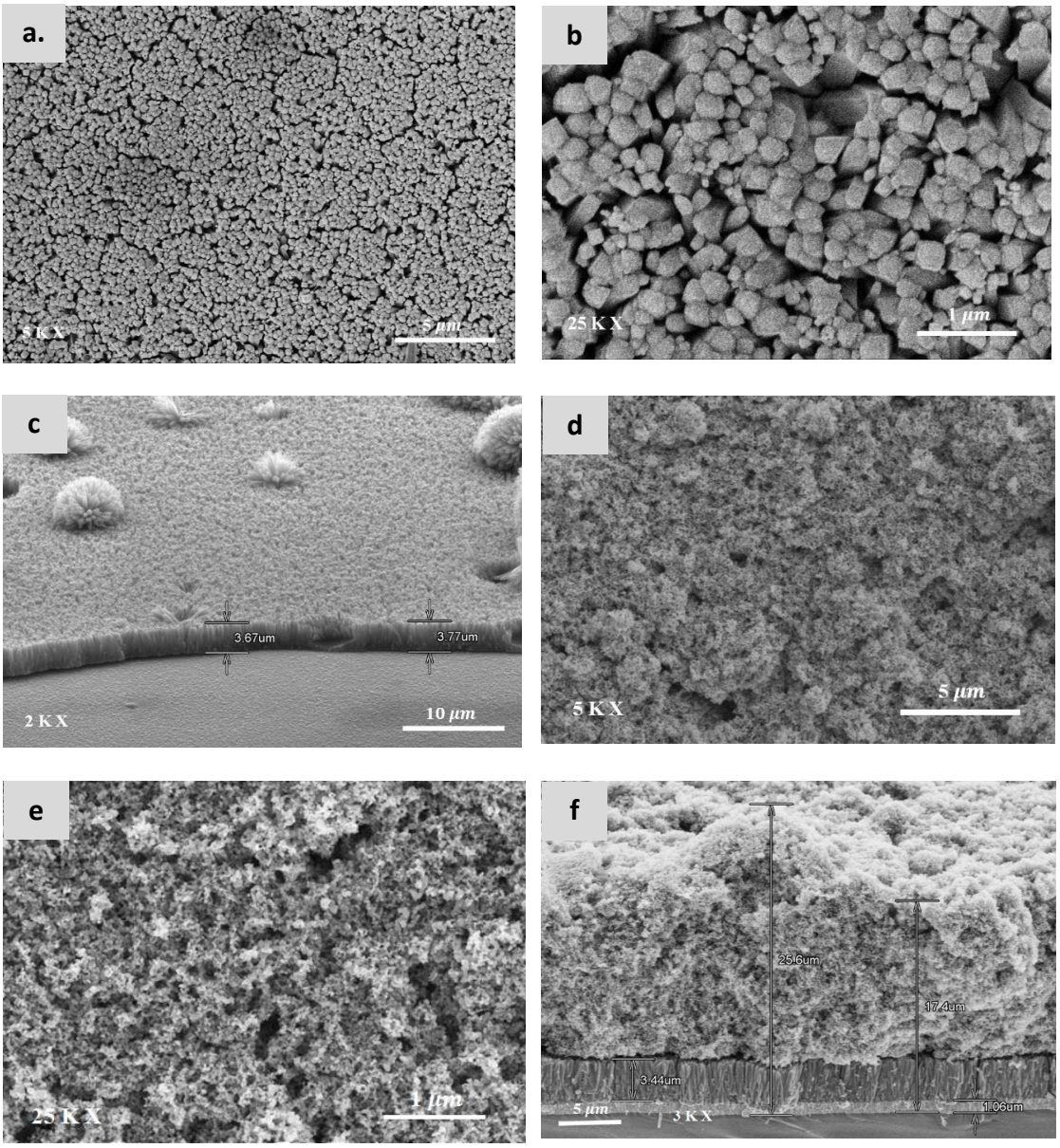

Fig. 1. FESEM images of fabricated mixed-phase TiO_2 nanostructures; (a)-(b) TiO_2 nanorods top view and (c) its cross section which contains nanoflowers, (d)-(e) TiO_2 nanoparticles top view and (f) fabricated film thickness cross section.

Table 1. EDX analysis of fabricated mixed-phase TiO_2 nanostructures.

Element compound	Weight (%)	Atomic (%)
Titanium (Ti)	56.05	29.87
Oxygen (O)	43.95	70.13

Fig. 2 shows micro-Raman spectra for both nanorods and mixed-phase of TiO_2 nanostructures films. Based on Fig. 2 (a), the synthesized TiO_2 nanorods was confirmed in rutile phase shown by four major peaks at 117, 237, 444, and 607 cm^{-1}. Two prominent peaks at 444 and 607 cm^{-1} shows a high intensity indicated that there were lots of nanorods compared to nanoflowers which confirm the analysis by FESEM. The micro-Raman spectra of mixed-phase TiO_2 did not shifted much after nanoparticles were applied on top of the nanorods as shown in Fig. 2 (b). The additional peaks at 144 and 516 cm^{-1} are known as anatase phase which confirmed that the synthesized film are in mixed-phase of rutile and anatase phase. The two prominent peaks of rutile phase in Fig. 2 (b) also slightly shifted to higher wavelength and its intensity also decreases which might be caused by nanoparticles that covers the nanorods (Balachandran and Eror, 1982; Aprile, *et.al.*, 2008; Luo, *et.al.*, 2014; Ahmad, *et.al.*, 2016).

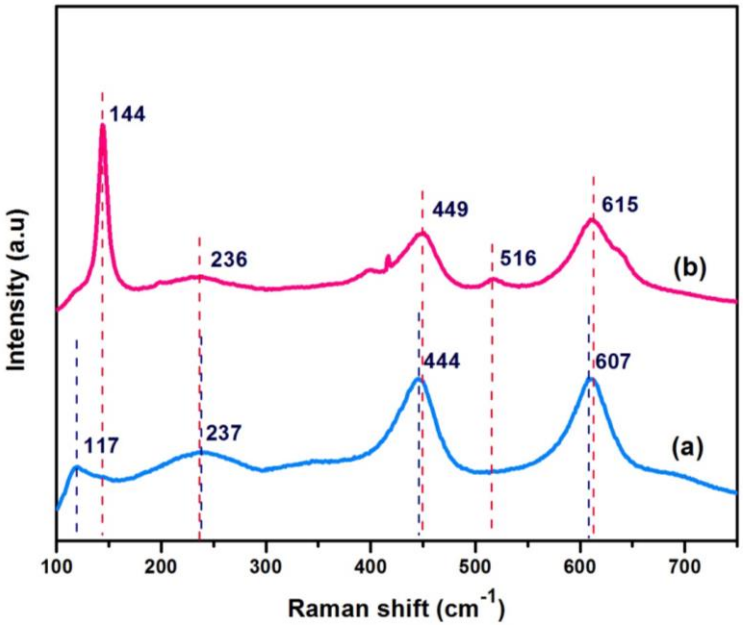

Fig. 2. Micro-Raman spectra of; (a) TiO_2 nanorods and (b) mixed-phase TiO_2 nanostructures.

The E_g value of fabricated TiO_2 nanostructures were calculated from UV-Vis data. The plotted graph shown in Fig. 3 shows the large difference of E_g value between rutile TiO_2 nanorods and mixed-phase TiO_2 nanostructures.

The calculated E_g for rutile TiO_2 nanorods is 3.06 eV while the mixed-phase TiO_2 is 2.84 eV which is in the range of TiO_2 band gap. The obtained E_g value of pure rutile is similar with previous report (Lei, *et.al.*, 2016).

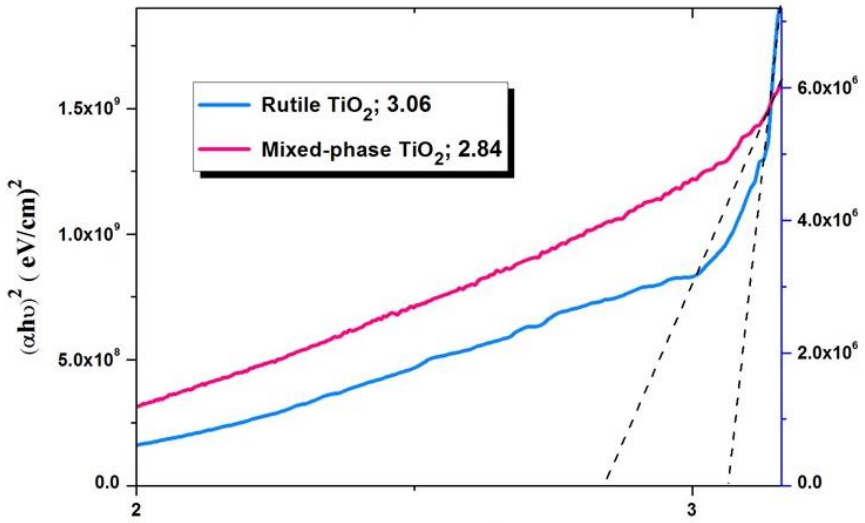

Fig. 3. Band gap value of TiO_2 nanorods and mixed-phase TiO_2 nanostructures.

CONCLUSION

In this study, we successfully synthesized mixed-phase TiO_2 nanostructures which contains bilayer TiO_2 nanorods-nanoflowers and nanoparticles. The rutile nanorods-nanoflowers and anatase nanoparticles were synthesized using hydrothermal growth and squeegee method, respectively. The average length of as-grown nanorods were 3.5 nm with the diameter range of 46-215 nm. Meanwhile, the average total thickness and band gap value of mixed-phase TiO_2 nanostructures were 15.98-24.54 nm and 2.84 eV, respectively. This value is acceptable and the synthesized film has great potential to be applied as photoanode semiconductor layer for DSSCs application.

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