Experimental Study of TiO_2 Nanoparticles Fabrication by Sol-gel and Co-precipitation Methods for TiO_2/SnO_2 Composite Thin Film as Photoanode

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ABSTRACT

Sol-gel and coprecipitation methods successfully prepared titanium dioxide (TiO_2) powders with anatase structure. The TiO_2 powders are then used to fabricate pure TiO_2 thin-film or mixed with SnO_2 powders for the TiO_2/SnO_2 composite thin film. Furthermore, the structural, morphological, as well as the optical properties of films were also investigated. The results showed that the synthesized thin-film of TiO_2 powders by sol-gel method obtained better crystallinity and microstructure compared to the synthesized thin film by co-precipitation method. In the DSSC system, these features are needed to increase the electron mobility that responsibility for transport and recombination of photoexcited electrons. SEM images exhibited the smooth surface and uniform in particle size obtained by the addition of SnO_2 powders in composite films. The composite thin film also indicated a higher transmittance value.

Keywords: sol-gel,co-precipitation,anatase, composite.

INTRODUCTION

Dye-sensitized solar cells (DSSC) have been under extensive research to current date (Sathyajothi *et al*., 2017; Park *et al*., 2011;Hamadanian *et al*., 2014) because of their low cost (Sathyajothi *et al*., 2017;Hamadanian *et al*., 2014; Shikoh *et al*., 2017) and simple fabrication (Park *et al*., 201;Singh *et al*., 2014; Bhogaita *et al*., 2016;Gong *et al*., 2017) as a potential alternative for solar energy conventional (Sathyajothi *et al*., 2017;Muniz *et al*., 2011;Tasić *et al*., 2016). DSSC utilize abundant materials resources in nature (Upadhyaya *et al*., 2013). Therefore, they are cheap and easily attained. For instance, the sensitizing material can be obtained from leaves, flowers, and fruits (Hamadanian *et al*., 2014;Singh, Karlo,and Pandey, 2014;Bhogaita *et al*., 2016;Syafinar *et al*., 2015). A sandwich DSSC is composed of nanocrystalline semiconducting oxide films as the photoanode, a sensitizing dye, an electrolyte and a counter electrode (Park *et al*., 2011;Shikoh *et al*., 2017;Su'ait *et al*., 2015). Among these components, photoanode predicted have the most significant impact on the energy conversion efficiency. Therefore, most of this research focuses on the development of the photoanode (Ye *et al*., 2015).

The microstructure and morphology of film photoanodes have a significant influence on solar-to-electrical energy conversion process in DSSC system (Wali *et al*., 2016). Tsai *et al*. explained that a typical nanoporous structure of the film is required to increase dye absorption as well as providing sufficient light absorption due to its high surface area. They also declared that the smooth and homogeneous surface morphology of film photoanodes improve the electron transport between nanoparticles (Lee *et al*., 2011). Significant efforts have been given to fulfill these prerequisites, for example by varying the synthesis method of semiconductor even by modifying two or more the materials used for photoanode fabrication (Liu *et al*., 201;Surya *et al*., 2017).

Semiconducting materials that have been most utilized for photoanode DSSC are Titanium dioxide (TiO_2) (Valencia *et al*., 2010) and Tin dioxide (SnO_2) (Surya *et al*., 2017;Di Paola *et al*., 2013). TiO_2 and SnO_2 had been extensively studied due to its high surface area (Su'ait *et al*., 2015;Essalhi *et al*., 2016), safety and matched energy band structure (Behnajady *et al*., 2011). The optical band gap of TiO_2 is reported at ~3.0, ~3.1 and ~3.2 eV for rutile, brookite and anatase structure, respectively. Whilst, SnO_2 has band gap at ~3.6 eV (Hamadanian *et al*., 2014;Muniz *et al*., 2011;Su'ait *et al*., 2015;Behnajady *et al*., 2011;Yeh *et al*., 2014;Yang *et al*., 2006) with tetragonal cassiterite and orthorhombic phase (Valencia *et al*., 2010;Vijayalakshmi and Rajendran, 2012). Therefore, combining these two materials to build a photoanode is expected could improve the microstructural and morphological characteristics of film photoanodes.

Various methods have been employed to synthesize TiO_2 nanopowders. Choi and Sohn reported that Sol-gel methods are used very often because it does not require high temperatures treatment (Choi and Sohn, 2012), but also Co-precipitation methods can be done because of the easy and simple process (Xu *et al*., 2014).

The main purpose of the study was to compare the crystalline phases, crystallinity, uniformity morphology and optical properties of TiO_2 nanoparticles which obtained by sol-gel and co-precipitation methods. The effect of the addition of SnO_2 on characteristics of film photoanodes will also be investigated. The crystalline phases, crystallinity were characterized by XRD, the morphology of film was observed using SEM imaging. Meanwhile, the opticalproperties of filmswas measured by UV-Vis spectrometer.

METHODS

Preparation of TiO_2 nanoparticles by Sol-gel method

Titanium Isopropoxide (TTIP, Sigma-Aldrich) was slowly dissolved in the Isopropanol (IPA, Sigma-Aldrich) and was then stirred for 30 min. Few drops of HNO_3 were added and stirred for 24 h. Subsequently, TiO_2 powders can be achieved by calcination for 3 h at 400°C.

Preparation of TiO_2 nanoparticles by Co-precipitation method

TiO_2 powders were prepared from Titanium (III) chloride ($TiCl_3$, Sigma-Aldrich) as a titanium precursor. Initially, $TiCl_3$ was mixed with distilled water and stirred for an hour. NH_4OH solution was added dropwise until pH of the mixture reached to 9. Subsequently, the mixture was stirred until resulting white precipitate. The obtained precipitate was filtered and then washed with distilled water, reaching the pH equal to 7. The precipitate was finally calcined at 450°C for 3 h to get the TiO_2 powders.

Preparation of TiO_2 paste

The synthesized TiO_2 powders were blended with distilled water and stirred for 10 min, subsequently added PEG, acetylacetone, acetic acid, and Triton-X to the mixture.

Preparation of SnO_2 paste

Commercial SnO_2 powder was procured from Sigma-Aldrich. The paste solution was made by dissolving ethylcellulose and isopropanol and stirred for 90 min. The paste was obtained by mixing SnO_2 powders with the solution.

Preparation of TiO_2/SnO_2 composite paste

The oxide paste was made from a mixture of SnO_2 and TiO_2 powders that ground using a mortar and then heated at 450°C for 30 min with the solution that has been synthesized by mixing distilled water and ethanol as a solvent with ethylcellulose and terpineol as a binder and kept stirring for 10 min.

Fabrication of Photoanodes

Indium Tin Oxide glass (ITO) was purchased from MianyangProchema Commercial Co., Ltd., China. Removal process of organic impurities such as fat and oils was carried out by washing the ITO glass with a size 1 × 1 cm^2 with alcohol for 60 min in an ultrasonic cleaner. Subsequently, the paste was deposited onto the glass using doctor blade technique.

Immersion of Photoanodes

The dye solution was made by mixing 1.1 mg of N-749 dye powders into 20 mL of ethanol and was then stirred using a magnetic stirrer for 10 min. Immersing the photoanode in the dye solution was done for 24 h, and this process aims to enhance the photosensitivity of the photoanodes.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of TiO_2 powders. The spectra revealed that both patterns are nearly identical and had a polycrystalline structure with a dominant peak (101) appearing around 26 degrees.

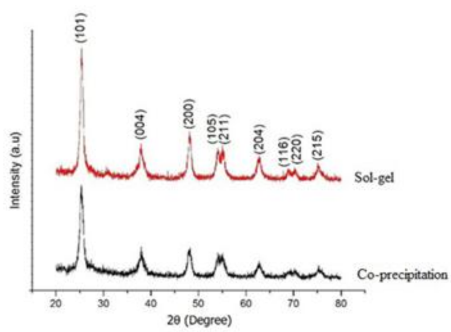

Figure 1. XRD spectra of TiO_2 synthesized by sol-gel and co-precipitation method

This peak reflects an anatase phase with tetragonal structure matched with ICDD data (PDF no 00-078-2486) (Yang *et al*., 2006). Other peaks also identifiedas anatase phase that corresponds to the crystal planes of (004), (200), (105), (211), (204), (116), (220) and (215) at 2θ values 38.3°, 48°, 54°, 55°, 62°, 69°, 71°, and 75° respectively. These results correspond to which obtained by Vijayalaksmi *et al*. and Yeh *et al*. in their investigation (Yeh *et al*., 2014;Vijayalakshmi and Rajendran, 2012).

It can also be seen in Fig. 1; there are a few differences in peak intensity of both patterns. The spectrum of TiO_2 prepared via the sol-gel process (Sol-gel TiO_2) has sharper peaks and can be distinguished easily. The peaks around

70 degrees appeared in the range of TiO_2 obtained by coprecipitation method (Co-precipitation TiO_2) almost look like a single peak due to it has weak peak intensities. The higher and stronger the intensity of diffraction peaks indicate she improved in the degree of crystallinity (Vidyasagar and Arthoba Naik, 2016).

The degree of crystallinity of two powders was summarized in Table 1. The data reveals that the TiO_2 powders synthesized by the sol-gel process have better crystallinity compared to the powders obtained by coprecipitation method (Jian *et al*., 2005).

Table 1. Crystalline parameters of TiO_2 and SnO_2 powders

	TiO_2		SnO_2
	Co-precipitation	Sol-gel	
Amorf (%)	65.12	45.04	37.3
Crystalline (%)	34.88	54.96	62.7
Crystallite Size (nm)	9.8	8.2	29.8
Lattice Parameter (Å)			
a	3.779	3.777	4.716
c	9.476	9.487	1.689

These results also implied the less distinct peaks of TiO_2 that had prepared via co-precipitation process due to the formation of the anatase phase had not been completely formed. This indicates that the chemical bonds are formed less stable so that the interconnection and poor continuity between titania nanoparticles, which in turn decreases the efficiency of electron transfer in photoanode (Adawiyah and Endarko, 2017). Table 1 also showed both TiO_2 powders have crystallite size and lattice constants which are not much different.

Fig. 2 represents the XRD spectra of thin film photoanodes after calcination at 450°C for 90 min.

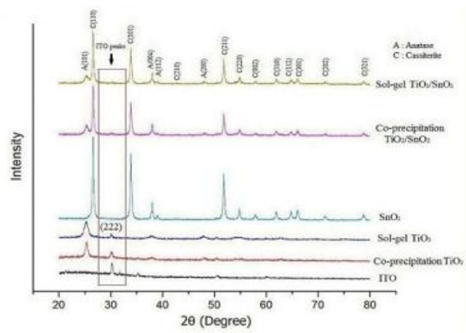

Figure 2**.** XRD patterns of thin-film photoanodes

The pattern confirms that phase transformations did not occur during the heating process hence the anatase phase is still observed in the pure TiO_2 photoanodes. Meanwhile, the composite spectra showed that mixed anatase-rutile phases were formed. It was identified that the presence of rutile phase is a contribution of tetragonal cassiterite structure of SnO_2. The tetragonal SnO_2 peaks at ~26.04, 33.49, 37.45, 51.03 and 54.16 degrees belong to (110), (101), (200), and (211) planes (PDF no 00-077-0447, ICDD). Furthermore, it can also be analyzed that the addition of SnO_2 could reduce the ITO peak (222) in composite photoanodes (Adawiyah and Endarko, 2017). It is intended that only the semiconductor phase will be formed.

Morphological Characteristics

SEM images in Fig. 3 reveals that all samples have spherically shaped particles. It can be seen that the co-precipitation TiO_2 film (a) displays many cracks on its surface. Meanwhile, the sol-gel TiO_2 film (b) exhibits large and intense agglomerations although it also shows free from cracks.

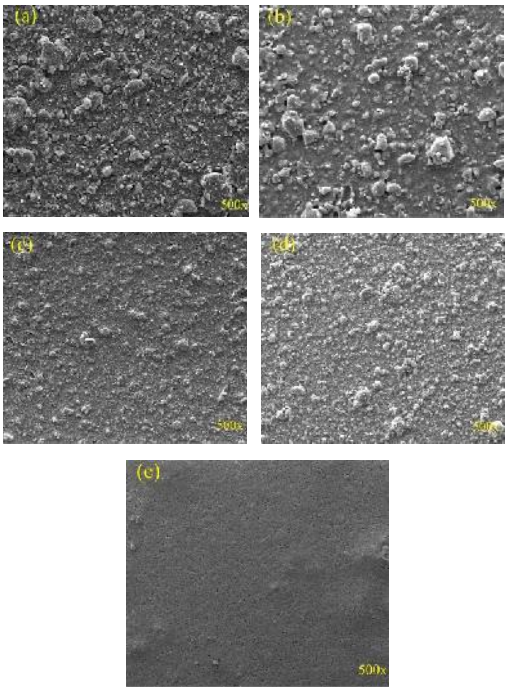

Figure 3**.** SEM micrographs of (a). Co-precipitation TiO_2 film, (b). Sol-gel TiO_2 film (c). Co-precipitation TiO_2/SnO_2, (d). Sol-gel TiO_2/SnO_2 (e). A sno2 film with 500× magnitude

A more uniform distribution of particle size with porous structure was found in both composite images in Fig. 4, which may be due to the addition of SnO_2 (Adawiyah and Endarko, 2017). It can be seen in Fig. 3, a microstructure of SnO_2 film which has a smooth surface with very uniform particle size and its porous structure was exposed in Fig. 4. As also shown by Camacho-López M. A et al. in their SEM pictures (Sociedad Mexicana de Ciencia Superficies y Vacio. *et al*., 2013). The pore structure will allow more dye molecules to be absorbed in the semiconductor, thus will increase the photosensitivity of the photoanode to solar radiation, which means that the dye will inject more electrons. In addition, the homogeneous and crack-free surface of the film will also facilitate the electron flow in the photoanode material thus enhancing the transport and recombination processes in the DSSC system (Ye *et al*., 2015).

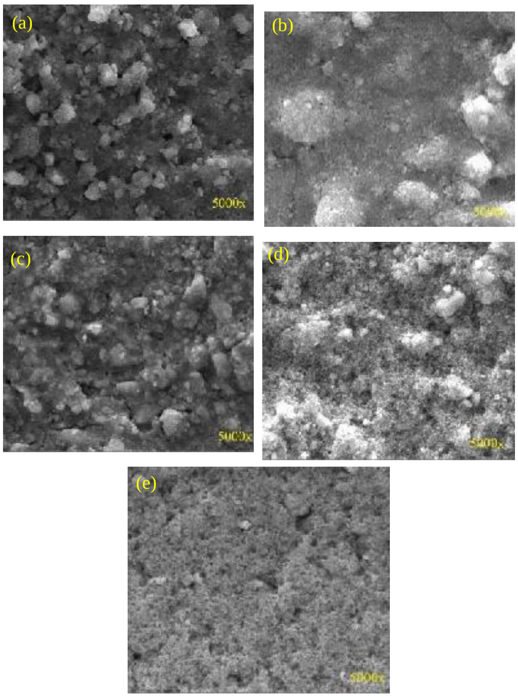

Figure 4. SEM micrographs of (a). Co-precipitation TiO_2 film, (b). Sol-gel TiO2 film (c). Co-precipitation TiO_2/SnO_2, (d). Sol-gel TiO_2/SnO_2 (e). A Sno_2 film with 5000× magnitude

The SEM analysis results also provide information on the particle size of pure TiO_2 films had value in the range of 15–60 nm whereas the composite is smaller in size, which is 10–30 nm. The SnO_2 film shows the surface looks very smooth, flat and rather dense so that the particles are not visible and the particle size determination is difficult to do.

Optical Characteristics

Table 2 gave the optical band gap values (E_g) of the film photoanodes calculated using the Tauc plot method. It was found that the band gap of TiO_2/SnO_2 composites is smaller than the pure TiO_2 film.

Table 2. The energy gap of photoanode immersed in dye N749 for 24 h

Sample	*Eg (eV)*
Co-precipitation TiO_2	3.1
Sol-gel TiO_2	3.2
Co-presipitation TiO_2/SnO_2	3
Sol-gel TiO_2/SnO_2	2.75
SnO_2	3.6
Dye N749	1.47

The result corresponds to the result reported by Essalhi et al. that the addition of SnO_2 may decrease the value of the energy band gap (Essalhi *et al*., 2016). The narrowing of the band gap would increase the probability of electrons being injected into the conduction band of semiconductor (Nguyen, Tran,and Bach, 2014). The higher concentration of electrons in the conduction band will trigger an increase in photocurrent (J_{SC}) value. This condition will undoubtedly lead to an increase in efficiency of DSSC.It appears that the composite bandgap energy value is between the ranges of TiO_2 and SnO_2 band gap energy values.

CONCLUSION

In summary, we fabricated TiO_2/SnO_2 composite DSSC using TiO_2 powders synthesized by sol-gel and co-precipitation methods. The higher crystallinity was obtained through the sol-gel method. The films also showed smooth and crack-free morphology on the surface. Additionally, the mixing TiO_2 and SnO_2 powders result in a composite film with homogeneous surface and porous structure. It explains that SnO_2 addition could be improved the microstructure of the films. Asa consequence, utilization titanate powders obtained by the sol-gel method as a photoanode material followed by SnO_2 addition an effective strategy for enhancing the overall photovoltaic parameters in the future application.

REFERENCES

Adawiyah, S.R., Endarko, 2017. Structural and morphological characterization of TiO_2 - SnO_2 thin film prepared by combining doctor-blade and sol-gel techniques. IOP Conf. Ser. Mater. Sci. Eng. 188, 012062.

Behnajady, M.A., Eskandarloo, H., Modirshahla, N., Shokri, M., 2011. Sol-Gel Low-temperature Synthesis of Stable Anatase-type TiO2 Nanoparticles Under Different Conditions and its Photocatalytic Activity. Photochem. Photobiol. 87, 1002–1008.

Bhogaita, M., Yadav, S., Bhanushali, A.U., Parsola, A.A., Pratibha Nalini, R., 2016. Synthesis and characterization of TiO2 thin films for DSSC prototype. Mater. Today Proc. 3, 2052–2061.

Choi, S.C., Sohn, S.H., 2012. Synthesis and physical properties of TiO2 microparticles coated by a sol–gel method and their application to dye-sensitized solar cells. Powder Technol. 226, 157–164.

Di Paola, A., Bellardita, M., Palmisano, L., 2013. Brookite, the Least Known TiO2 Photocatalyst, Catalysts.

Essalhi, Z., Hartiti, B., Lfakir, A., Siadat, M., Thevenin, P., 2016. Structural and optical properties of TiO_2:SnO_2 thin films prepared by sol gel method. Mol. Cryst. Liq. Cryst. 627, 148–152.

Gong, J., Sumathy, K., Qiao, Q., Zhou, Z., 2017. Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. Renew. Sustain. Energy Rev. 68, 234–246.

Hamadanian, M., Safaei-Ghomi, J., Hosseinpour, M., Masoomi, R., Jabbari, V., 2014. Uses of new natural dye photosensitizers in fabrication of high potential dye-sensitized solar cells (DSSCs). Mater. Sci. Semicond. Process. 27, 733–739.

Jian, L., Shufang, M., Peide, H., Caiyun, S., Bingshe, X., 2005. Synthesis and Characterization of TiO_2 Nanotube [J]. Rare Met. Mater. Eng. 2, 655–659.

Lee, J.-H., Park, N.-G., Shin, Y.-J., 2011. Nano-grain SnO2 electrodes for high conversion efficiency SnO2–DSSC. Sol. Energy Mater. Sol. Cells 95, 179–183.

Liu, Y.-C., Lu, Y.-F., Zeng, Y.-Z., Liao, C.-H., Chung, J.-C., Wei, T.-Y., 2011. Nanostructured Mesoporous Titanium Dioxide Thin Film Prepared by Sol-Gel Method for Dye-Sensitized Solar Cell. Int. J. Photoenergy 2011, 1–9.

Muniz, E.C., Góes, M.S., Silva, J.J., Varela, J.A., Joanni, E., Parra, R., Bueno, P.R., 2011. Synthesis and characterization of mesoporous TiO2 nanostructured films prepared by a modified sol–gel method for application in dye solar cells. Ceram. Int. 37, 1017–1024.

Nguyen, T.T., Tran, V.N., Bach, T.C., 2014. Influences of metallic doping on anatase crystalline titanium dioxide: From electronic structure aspects to efficiency of TiO2-based dye sensitized solar cell (DSSC). Mater. Chem. Phys. 144, 114–121.

Park, J.T., Koh, J.K., Byun, S.J., Kang, S.W., Kim, J.H., 2011. Performance enhancement of dye-sensitized solar cells using nanostructural TiO2 films prepared by a graft polymerization and sol–gel process. Electrochim. Acta 56, 3182–3191.

Sathyajothi, S., Jayavel, R., Dhanemozhi, A.C., 2017. The Fabrication of Natural Dye Sensitized Solar Cell (Dssc) based on TiO2 Using Henna And Beetroot Dye Extracts. Mater. Today Proc. 4, 668–676.

Shikoh, A.S., Ahmad, Z., Touati, F., Shakoor, R.A., Al-Muhtaseb, S.A., 2017. Optimization of ITO glass/TiO2 based DSSC photo-anodes through electrophoretic deposition and sintering techniques. Ceram. Int. 43, 10540–10545.

Singh, L.K., Karlo, T., Pandey, A., 2014. Performance of fruit extract of Melastoma malabathricum L. as sensitizer in DSSCs. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 118, 938–943.

Sociedad Mexicana de Ciencia Superficies y Vacio., M.A., Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales A.C., J.R., Esparza-García, A., Sánchez-Pérez, C., Julien, C.M., 2013. Superficies y vacio., Superficies y vacío. Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales A.C.

Su'ait, M.S., Rahman, M.Y.A., Ahmad, A., 2015. Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). Sol. Energy 115, 452–470.

Surya, S., Thangamuthu, R., Senthil Kumar, S.M., Murugadoss, G., 2017. Synthesis and study of photovoltaic performance on various photoelectrode materials for DSSCs: Optimization of compact layer on nanometer thickness. Superlattices Microstruct. 102, 424–441.

Syafinar, R., Gomesh, N., Irwanto, M., Fareq, M., Irwan, Y.M., 2015. Potential of Purple Cabbage, Coffee, Blueberry and Turmeric as Nature Based Dyes for Dye Sensitized Solar Cell (DSSC). Energy Procedia 79, 799–807.

Tasić, N., Marinković Stanojević, Z., Branković, Z., Lačnjevac, U., Ribić, V., Žunić, M., Novaković, T., Podlogar, M., Branković, G., 2016. Mesoporous films prepared from synthesized TiO2 nanoparticles and their application in dye-sensitized solar cells (DSSCs). Electrochim. Acta 210, 606–614.

Upadhyaya, H.M., Senthilarasu, S., Hsu, M.-H., Kumar, D.K., 2013. Recent progress and the status of dye-sensitised solar cell (DSSC) technology with state-of-the-art conversion efficiencies. Sol. Energy Mater. Sol. Cells 119, 291–295.

Valencia, S., Marín, J.M., Restrepo, G., 2010. Study of the Bandgap of Synthesized Titanium Dioxide Nanoparticules Using the Sol-Gel Method and a Hydrothermal Treatment. Open Mater. Sci. J. 4, 9–14.

Vidyasagar, C.C., Arthoba Naik, Y., 2016. Surfactant (PEG 400) effects on crystallinity of ZnO nanoparticles. Arab. J. Chem. 9, 507–510.

Vijayalakshmi, R., Rajendran, V., 2012. Synthesis and characterization of nano-TiO2 via different methods. Arch. Appl. Sci. Reseacrh 4, 1183–1190.

Wali, Q., Bakr, Z.H., Manshor, N.A., Fakharuddin, A., Jose, R., 2016. SnO2–TiO2 hybrid nanofibers for efficient dye-sensitized solar cells. Sol. Energy 132, 395–404.

Xu, P., Tang, Q., He, B., Li, Q., Chen, H., 2014. Transmission booster from SiO2 incorporated TiO2 crystallites: Enhanced conversion efficiency in dye-sensitized solar cells. Electrochim. Acta 134, 281–286.

Yang, H., Zhang, K., Shi, R., Li, X., Dong, X., Yu, Y., 2006. Sol–gel synthesis of TiO2 nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO2 suspensions. J. Alloys Compd. 413, 302–306.

Ye, M., Wen, X., Wang, M., Iocozzia, J., Zhang, N., Lin, C., Lin, Z., 2015. Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. Mater. Today 18, 155–162.

Yeh, S.-W., Ko, H.-H., Chiang, H.-M., Chen, Y.-L., Lee, J.-H., Wen, C.-M., Wang, M.-C., 2014. Characteristics and properties of a novel in situ method of synthesizing mesoporous TiO2 nanopowders by a simple coprecipitation process without adding surfactant. J. Alloys Compd. 613, 107–116.