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Titanium dioxide paste preparation for dye sensitized solar cell using hydrothermal technique

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The TiO₂ pastes were prepared from commercial P25 titanium oxide powder (sample A) and titanium isopropoxide (sample B) using a hydrothermal technique. The pastes were coated on FTO glass plate and sintered at 500 °C for 30 minutes. The coated films were characterized by XRD, FTIR, SEM, TEM, UV and IV studies. XRD results confirmed that both of anatase and rutile phase were found in the film from sample A but only anatase phase were formed from sample B. The lattice parameters of sample A is a = 3.789 Å and c = 9.526 Å and those of sample B is a = 3.786 Å and c = 9.508 Å. FT-IR studies showed that there is no precursor residue present in both the sample after sintering. The UV-Vis spectrum indicates the amount of dye adsorbed on TiO₂ particle. The conversion efficiency, short circuit current (J_{sc}), open circuit voltage (V_{oc}) is 5.7%, 11.34 mA/cm² and 0.7111 V, respectively, which is high for sample B compared to sample A.

Key words: TiO₂ nanoparticle, Hydrothermal technique, TEM, Conversion efficiency.

Introduction

A dye-sensitized solar cell (DSSC) is a promising device to make use of solar energy to light energy with relatively low production cost compared to those of conventional semiconductor solar cells [1, 2]. The DSSC comprises a dye-adsorbed nanocrystalline TiO₂ layer fabricated on a transparent conducting oxide (TCO) as the working electrode, platinum (Pt) as the counter electrode, and an electrolyte solution with iodide/ triiodide redox reagents. The TiO₂ working electrode is used in a variety of applications like photocatalysis, batteries, optical emission and gas sensing systems other than photovoltaics [3-6]. TiO₂ has been demonstrated as a promising electron-transport material of a dyesensitized, oxide semiconductor solar cell because the crystal structure of TiO₂ governs the electron-transport rates and thus the photovoltaic performance. TiO₂ exists in three polymorphs: anatase, rutile, and brookite. Rutile is the thermodynamically stable phase, whereas anatase and brookite are metastable. Preparing nanosized TiO₂ commonly involves a sol-gel chemistry, which includes hydrolysis, precipitate formation, sol peptization and finally hydrothermal crystallization.

In this work, the nanosized TiO_2 pastes were prepared from two different source, the commercial Degussa P25 and titanium isopropoxide, using an hydrothermal technique at a low temperature of 200 °C. After hydrothermal treatment, the binder is added and ethanol is evaporated to get a good viscous paste. The hydrothermal technique is advantage to proceed under pressurized environment where the crystallization of the particle can be improved because the saturated vapor pressure in an autoclave is temperature dependent. In order to obtain TiO₂ anatase from hydrothermal techniques, titanium alkoxide is very commonly used as a precursor. The obtained pastes were further characterized by XRD, SEM, TEM and electrochemical studies and discussed.

Experimental

Two different TiO_2 paste was prepared by the simple hydrothermal technique using the commercial Degussa P25 powder (sample A) and titanium isopropoxide (sample B). For the preparation of sample A, 0.78 g of P25 powder was mixed in 60 mL of ethanol and followed by the addition of 0.1 mL of acetic acid, 0.3 mL of water and 2 mL of α -terpineol. Sample B was prepared by 3 mL of titanium isopropoxide mixed with 60 mL of ethanol followed by the addition of a 0.1 mL of acetic acid and 0.7 mL of water. Finally α -terpineol was added slowly to the solution. The solution was then heated at 200 °C under hydrothermal technique with vigorous stirring for about 4 hours. After cooling 0.075 g of polyvinyl pyrrolidone dissolved in ethanol were slowly added to the above solution separately and heated in a hot plate at 100 °C for about 10 minutes with vigorous stirring and cooled to room temperature. Then the ethanol was evaporated using a solvent evaporator to obtain a viscous TiO₂ paste.

Electrode assembly

The prepared paste was deposited on an optically

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transparent conducting glass (F-doped SnO₂, 13Ù/sq sheet resistance) by the doctor blade technique. This prepared TiO₂ film was sintered at 500 °C in air for 1 hour. The resulting electrodes were sensitized with an ethanol solution consisting of 3×10^{-4} M cis-bis (isothiocyanato) bis (2, 2'-bipyridy-4, 4'-dicarboxylato) ruthenium (II) bis- (tetrabutylammonium) (Ru 535bisTBA, Solaronix) for 24 hours at room temperature. The Pt counter electrode was prepared by a magnetron sputtering. The dye-adsorbed TiO₂ electrodes were next assembled into a sandwich type model with a Pt-coated counter electrode using thermal adhesive film. An AN-50 iodolyte electrolyte solution was injected into the cell via a hole at the back of the counter electrode. A hot-melt ionomer film (SX 1170, Solaronix) was used to seal the hole covered with glass. Finally, the edge of each side of the FTO glass was cleaned and soldered (ultrasonic soldering system, Model-9200) with alloy #143 (Cerasolza) in order to achieve a good electrical contact for measurement.

Characterization

The crystalline phases of TiO₂ were confirmed using high-power X-ray diffraction (XRD; Rigaku D/MAX 2500 V diffractor) with Cu Kα radiation. The structural characterization of the prepared TiO₂ was characterized by FT-IR spectroscopy with a Nicolet-380 spectrometer using KBr pellets. The surface morphology of the sample was characterized by a field emission scanning electron microscopy (FE-SEM, Hitachi model S-4200). High-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010) was used to examine the morphological structures. UV-Vis spectroscopic analysis was carried out using optizen 3220UV. The photovoltaic performance was measured using a Keithley 2400 at a power of 100 mW/cm² at one sun illumination. The incident light intensity was adjusted with a silicon reference solar cell.

Results and discussion

X-ray diffraction analysis

The XRD spectra of the TiO₂ (sample A and B) are given in Fig. 1. The peaks denoted by stars belong to anatase phase, and symbol 'X' and 'O' indicates the rutile and substrate peaks, respectively. The Degussa P25 powder was used for the preparation of sample A. The results confirmed the presence of anatase TiO₂ phase with small amount of rutile TiO₂ phase for sample A. Sample B was prepared using titanium isopropoxide as a precursor which is in good agreement with that of the anatase structure of TiO₂ [7,8]. The lattice parameters of sample A and B is a = 3.789 Å, c = 9.526 Å and a = 3.786 Å, c = 9.508 Å, respectively. The anatase peak at $2\theta = 25.2$ corresponds to (101) plane and the rutile peak at $2\theta = 27.4$ corresponds to (110) plane, respectively. The XRD patterns are nearly



Fig. 1. XRD patterns of two different TiO₂ paste (sample A and B) sintered at 500°C.



Fig. 2. FT-IR spectra of commercial TiO₂ (P25), sample A and B.

identical. The (101) peaks for sample B is broader than that of sample A, but the intensity of the peaks are inverse. This indicates that the particle size of the sample B is smaller with a low crystallinity compared to sample A.

FTIR analysis

The FTIR studies of sample A and B sintered at 500 °C along with commercial powder TiO₂ (P25 Degussa) is shown in Fig. 2. No considerable changes were detected in all the samples. The large absorption band centered at 3400 cm⁻¹, which is attributed to the stretching vibration of O-H molecules coordinately adsorbed on the surface of Ti⁴⁺ ions and the small peak centered at 1630 cm⁻¹ was due to the H-O-H bending vibration [9-11]. This confirms the presence of hydroxyl group in the TiO₂ film. It may be due to the atmospheric water molecules adsorbed by TiO₂. All spectrum shows stretching vibration at Ti-O-Ti in the low frequency band at the range of 450-900 cm⁻¹. Other than these no peaks were observed. It confirms the assence of organic residues in the both the samples.

Electron microscopy analysis

Fig. 3 shows the SEM images of sample A and B at different magnification. The sample A shows the average particle size is about 24 nm. The surface is smooth and uniform compared to sample B. Even



Fig. 3. SEM images of the TiO₂ film of sample A and B with different magnification (from top-left to bottom-right).



Fig. 4. TEM images of the TiO_2 film of sample B. The inset indicates SAED pattern of sample B.

though sample B does not show the uniform smooth surface, the average particle size is about 12 nm. It has good correlation with TEM analysis. The particle agglomeration is noted in sample B, because of the small particle size. If the particle size is small, the surface area is high. From the SEM analysis, it is confirmed that sample B has the smaller particle size compared to that of sample A. Therefore, the dye adsorption is high with sample B, indicating a good electrochemical performance in DSSC.

Fig. 4 shows the high-resolution TEM (HR-TEM) image of the synthesized TiO₂ at 500 °C of sample B. The TiO₂ nanoparticle size was about 10-13 nm. The crystalline nanoparticles showed visible lattice fringes. Spacing based on 10 planes was calculated to be 3.49 Å for the [101] planes. The inset of each panel in Fig. 4 shows the selected-area fast Fourier transform (FFT) pattern of the crystalline TiO₂ that was identified similar to that of anatase phase.

UV- Vis spectra

The UV-Vis absorption of dye solutions desorbed from TiO_2 films using 0.1 M NaOH aqueous solution is shown in Fig. 5. It showed the measurement of the amount of dye adsorbed onto the TiO_2 film of sample



Fig. 5. UV-Vis spectra of the N719 dye desorbed from TiO_2 film of sample A and B. The inset indicates the photograph of dye adsorbed on TiO_2 prepared from sample A and B.

A and B. The results showed that the absorption intensity of sample B is higher than that of sample A. This is due to the small particle size of the TiO_2 particle of sample B, providing a large surface area for the anchoring of dye molecule. Therefore, the dye adsorption was also very high compared to sample B. The inset figure shows the optical image of dye adsorption on TiO_2 film of sample A and B. The intensity of the color of sample B is very dark red compared to that of sample A. It was qualitatively confirmed by the persistent appearance of its characteristic color to the naked eye. Because of the good adsorption of dye on TiO_2 , the sample B gives good DSSC performance.

J-V curve

Fig. 6 shows the photocurrent-voltage characteristics of the DSSC fabricated using two different working electrodes. The cell fabricated from sample B exhibited the highest short-circuit current density (*Jsc*), outperforming the cell of sample A by ca. 25%. The light-to-electric



Fig. 6. Photocurrent-voltage characteristics of the cell fabricated by the TiO_2 film of sample A and B.

 Table 1. Characteristics of J-V curves of DSSC with different working electrodes prepared from sample A and B.

Sample	Voc (V)	Jsc (mA/cm ²)	Fill factor	Efficiency (%)
А	0.7317	8.4949	72	4.5
В	0.7111	11.3492	70	5.7

energy conversion efficiency (η) and the fill factor (ff) for these cells were also given in the table 1. The conversion efficiency of was also high with sample B (5.7%), because of its large J_{sc} . The efficiency was ca. 21% higher than that of the sample A. Due to the small particle size and high surface area it adsorbs more dye compared to sample A. Therefore, the efficiency was higher than that of sample A. This result indicates that the hydrothermally synthesized TiO₂ paste from titanium isopropoxide gives good performance compared to the paste prepared from commercial TiO₂.

Conclusion

In this work, commercial titanium dioxide (P25) and

titanium isopropoxide was used to prepare TiO₂ paste using a hydrothermal technique. The TiO₂ film was coated on fluorine doped tin oxide (FTO) coated glass surface using doctor blade. The results confirmed the presence of anatase TiO₂ phase with small amount of rutile TiO₂ phase for sample A. Sample B prepared from titanium isopropoxide showed only pure anatase phase of TiO2. The surface morphology of the film for sample A is uniform and smooth compared to that of sample B. The average particle size of the sample B is about 12 nm. It is correlated with TEM analysis. Among the two films, the sample B shows the high dye adsorption and the conversion efficiency of 5.7% compared to sample B. Therefore, it could be concluded that the performance of the paste prepared from titanium isopropoxide using hydrothermal technique is good compared to the paste prepared from commercial TiO_2 .

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