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Synthesis of Macro-Porous SnO_2 for Dye-Sensitized Solar Cells

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Macro-porous SnO_2 was synthesized using the template method and its electrical properties were investigated for applications as an electrode in dye-sensitized solar cells (DSSCs). Polystyrene (PS) spherical nano beads in a colloidal solution were used as a template for the synthesis of macro-porous SnO_2. Macro-porous SnO_2 was synthesized by mixing the precursor and polystyrene colloid. The concentration of tin chloride ($SnCl_4$) used as the precursor ranged from 0.025 to 0.1 M. The surface area and crystallinity of macro-porous SnO_2 increased with increasing concentration of the $SnCl_4$ solution. The crystalline SnO_2 electrode in a DSSC produced a high short circuit current (J_{sc}) owing to its high surface area. Overall, macro-porous SnO_2 can be applied to electronic devices because of its high performance, such as electron mobility.

Keywords macro-porous SnO_2; dye-sensitized solar cells; and polystyrene colloidal solution

1. Introduction

Titanium oxide has been used in various applications, such as the electrode for DSSCs [1, 2], a photo-catalyst [3–9] and a reflective coating material, owing to its photoelectric properties. DSSCs generally consisted of a TiO_2 layer over a FTO thin layer used as a transparent electrode, a mono-dispersed dye over TiO_2 particles, and an electrolyte [1, 2, 10]. The electrons from the photo-sensitive dye coated over the solid oxide particles used as the electrode are excited by UV-Visible light. The excited electrons move into the conduction band and are transferred to electrode layer. These electrons flow to the counter electrode through the FTO layer. The electrolyte provides electrons to the positive holes of the excited dye through oxidation, and is reduced to accept electrons from the counter electrode. Because the electrical current is obtained by the circuit of excited electrons, the transfer of electrons from the electrolyte is enhanced by increasing the contact area

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between the electrolyte and photo-sensitive dye. In particular, if a solid-state electrolyte is used for DSSCs, the contact area needs to be considered when attempting to increase the short current circuit (J_{sc}). Therefore, in this study, a macro-porous solid oxide electrode was fabricated and the diffusion of an electrolyte into the electrode layer was assessed. Nano crystalline SnO_2 and ordered meso-porous SnO_2 have been applied as an electrode in DSSCs by various researchers [11, 12].

Macro-porous SnO_2 is expected to have high photoelectric properties as an electrode for dye sensitized solar cells (DSSCs). The advantages of macro-pores are the 'good diffusion of the liquid electrolyte' and 'reduction of the shadow effect'. The shadow effect occurs when the UV and visible light are blocked by the surface layer over the bulk SnO_2 film. Because UV light is not transmitted into the electrode bulk layer, the dye over the internal SnO_2 particles in the bulk film is not sensitized. On the other hand, UV light is transmitted into the macro-porous SnO_2 bulk layer. Macro-porous SnO_2 was synthesized using a matrix-assisted method to improve the internal diffusion of the liquid phase electrolyte in the bulk electrode layer and reduce the shadow effect.

To synthesize the ordered type macro-porous SnO_2, polystyrene nano beads were used as the template material for the formation of macro-pores. The polystyrene colloidal solution was mixed with a SnO_2 paste and the pore-density was controlled by changing the concentration of the SnO_2 precursor solution. The morphology of the macro-porous SnO_2 layer prepared from the precursor solution was observed by scanning electron microscopy (SEM) and the cell efficiency of the DSSCs prepared from the macro porous SnO_2 as an electrode was investigated using a solar simulator.

2. Experiment

Synthesis of Polystyrene Colloidal Solution

Polystyrene (PS) nano spherical beads were synthesized by the polymerization of a styrene monomer in water used as a solvent. Distilled water (500 ml) was placed in a round flask and styrene monomer (11 g) was injected through the syringe. The round flask used as the reactor was purged with alternate cycles of nitrogen and vacuum, and was finally left under a nitrogen atmosphere before injecting the initiator. The temperature of the solution in the flask was maintained at 80°C using a water bath. The solution was stirred at 350 rpm using a magnetic bar. The polymerization of styrene was initiated by injecting an initiator(Potassium persulfate) through the stem, and was carried out for 12 h.

Synthesis of Macro-Porous SnO_2

The synthesis of macro-porous SnO_2 was carried out in a vacuum oven. The mixture solution (100 ml), which consisted of a $SnCl_4$ solution (0.025–0.1 M) and a PS colloidal solution, was placed in a glass container with an internal diameter of 50 mm. The volumetric ratio of the $SnCl_4$ and PS colloidal solution was fixed to 1/1. A glass substrate was placed in the bottom of the glass container. The solvent of the mixture solution, water, was removed by vacuum evaporation at 50°C. After sufficient evaporation of the liquid solvent in the mixture solution, the solid mixture, which consisted of polystyrene spherical nano beads and $SnCl_4$, over the glass substrate, was dried at 150°C for 12 h. The coated glass substrate was then calcined at 600°C for 4 h to thermally decompose PS used as the template.

Characterization of Macro-Porous SnO_2

The surface morphology of the macro-porous SnO_2 was observed by SEM (HITACHI S-4800) and its crystal phase was analyzed by X-ray diffraction (XRD, PANalytical, MPD for bulk). The surface area of macro-porous SnO_2 was investigated using the nitrogen adsorption method (Quanta Chrom, AutoSorb-1).

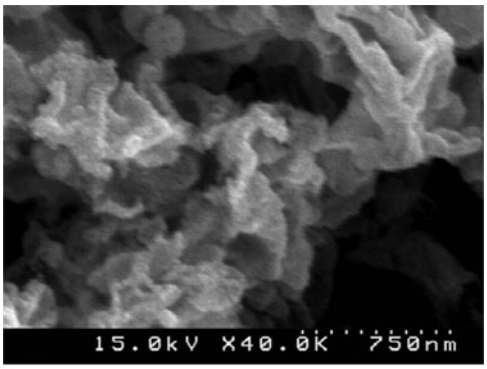
Preparation of DSSCs

The macro-porous SnO_2 solution was coated over a FTO glass substrate and the macro-pores were formed by thermal treatment of the mixture coating layer at 600°C. The cells of the DSSCs using macro-porous SnO_2 as an electrode were manufactured to assess the photoelectric properties of the synthesized SnO_2. The efficiency of the different DSSCs fabricated from an electrode comprised of macro-porous SnO_2 prepared from Sn-precursor solutions at different concentrations was compared. The transparent nanocrystalline-SnO_2 layer was coated on fluorine-doped tin oxide (FTO, sheet resistance: 10 Ω per square) glass plates by screen printing and then heated gradually in air at 325°C for 5 min. To obtain the dyes adsorbed onto the surface, the resulting electrode was immersed into the N3 dye solution (0.3 mM of N3 in ethanol solution, Solaronix) at room temperature for 24 h. The dye-adsorbed TiO_2 electrode and FTO glass were assembled into a sealed sandwich-type cell. Subsequently, a drop of the electrolyte solution (AN50, Solaronix) was placed on a drilled hole in the counter electrode of the assembled cell and was driven into the cell by vacuum backfilling. Finally, the hole was sealed with an additional cover glass. The cell efficiency of the DSSCs prepared with the macro-porous SnO_2 as the electrode was investigated using a solar simulator.

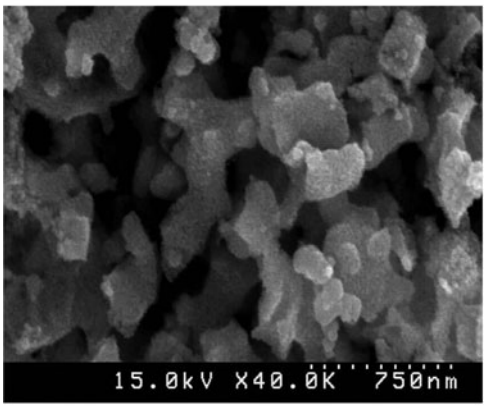
3. Results and Discussion

SEM Analysis of Macro-Porous SnO_2

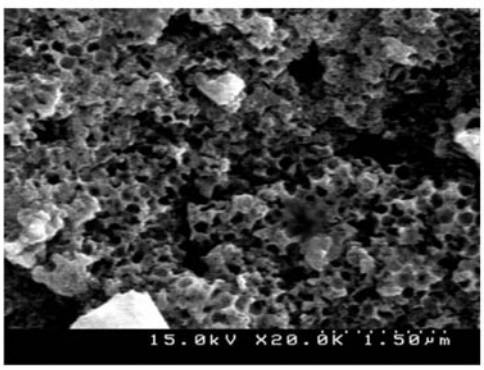
The morphology of the surface of macro-porous SnO_2 prepared by changing the concentration of the precursor solution was examined by SEM, as shown in Fig. 1. After removing the moisture from the PS colloid and tin chloride mixed solution by vacuum evaporation, solid PS-$SnCl_4$ formed as a shiny white lump. In this step, PS spherical beads agglomerated to a homogeneous state and the Sn-precursor is impregnated on the surface of the PS spherical beads. The content of $SnCl_4$ impregnated over the polystyrene beads can be controlled by changing the concentration of the precursor solution. The Sn-precursor over the PS beads was converted to SnO_2, and the PS was decomposed thermally during the thermal treatment step. The macro-pores were created in SnO_2 lumps by the thermal decomposition of PS at 600°C. The [PS]/[$SnCl_4$] ratio was fixed to 1/1 and the $SnCl_4$ concentration was controlled in the range of 0.025–0.1 M. Macro-pores were well formed in the SnO_2 bulk powder, as shown in Fig. 1, and were observed in SnO_2 synthesized under most conditions. On the other hand, the morphology of these macro-porous SnO_2 differed considerably with increasing concentration of the precursor solution. The ordered type SnO_2 was formed with increasing concentration of the precursor solution; this structure is called the opal structure. The sample synthesized with the 0.1 M $SnCl_4$ solution contained homogeneous macro-pores, as shown in Fig. 1(c).



(a)



(b)



(c)

Figure 1. SEM images of macro-porous SnO_2 prepared with different $SnCl_4$ solution concentrations using a template method, (a) 0.025 M, (b) 0.5 M, (c) 0.1 M.

Changing of Surface Area with Concentration of Sn-Precursor Solution

The surface area of the macro-porous SnO_2 was measured using the N_2-adsorption method. The concentration of the $SnCl_4$ solution used as the precursor was controlled for the ordered type macro-porous SnO_2 and the effect of concentration on the surface area was

Table 1. Surface area of macro-porous SnO_2 synthesized with different concentrations of $SnCl_4$

Concentration of $SnCl_4$, M	Surface area, m^2/g
0.025	19
0.05	32
0.1	45

investigated. The surface area of the electrode coated on FTO glass is very important because the amount of the photosensitized dye deposited over the solid oxide electrode is dependent on the surface area of the electrode. The surface area of macro-porous SnO_2 changed according to the concentration of the $SnCl_4$ solution. A high surface area was obtained at high $SnCl_4$ concentrations. When a 0.1 M $SnCl_4$ solution was used, the surface area of the resulting SnO_2 was 45 m^2/g, as shown in Table 1.

XRD Analysis

The crystal structures of macro-porous SnO_2 prepared from the 0.025 – 0.1 M $SnCl_4$ solutions were investigated by XRD, as shown in Fig. 2. SnO_2 treated thermally at 600°C exhibited a typical XRD pattern for SnO_2 (27°, 33°, 38°, 52°, 54° and 57° 2θ) with a high peak intensity in their XRD peak patterns. The FWHM (Full Width at Half Maximum) of the XRD peaks was higher than that of non-porous SnO_2 because the SnO_2 synthesized in this study has an ordered macro-porous structure. The FWHM(Full width at half maximum) of the XRD peaks increased with the synthesis of macro porous SnO_2. The growth of SnO_2 crystallites can be inhibited because the Sn precursor material was dispersed over polystyrene nano beads. To grow SnO_2 crystallites, sufficient Sn must be supplied in a

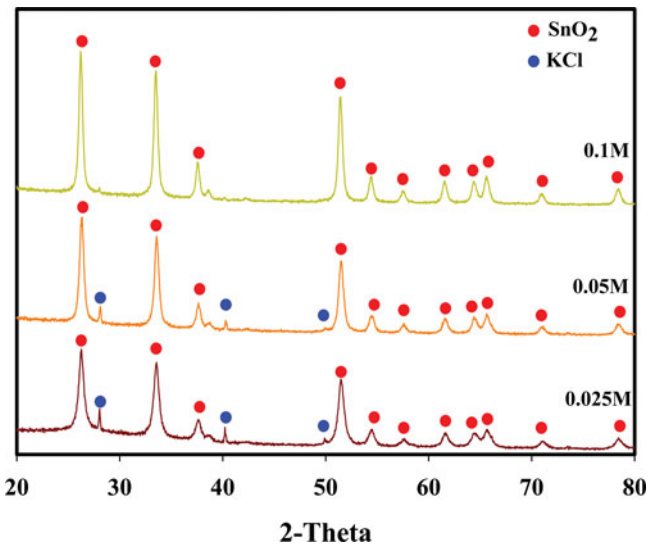


Figure 2. XRD peak patterns of macro-porous SnO_2 with different $SnCl_4$ solution concentrations using a template method.

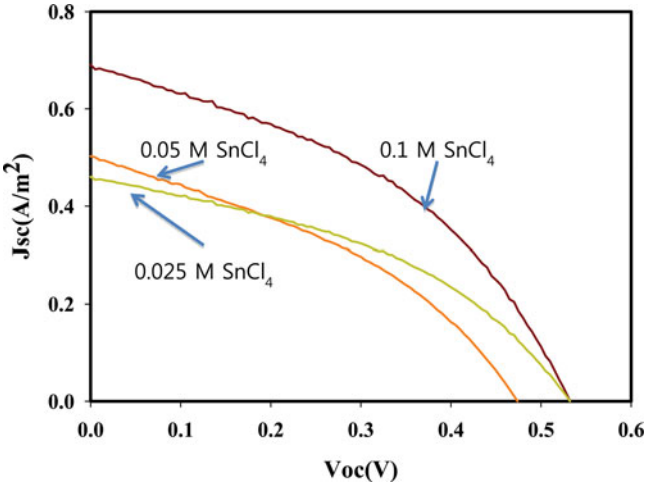


Figure 3. I-V curves of DSSCs manufactured by macro-porous SnO_2 synthesized with different $SnCl_4$ solution concentrations using a template method.

single crystal. On the other hand, the supply of Sn elements was restricted because the Sn precursor material was dispersed over the polystyrene nano beads. Hence, the growth of SnO_2 crystallite was inhibited by the polystyrene nano beads used for the synthesis of macro-porous SnO_2. Therefore, the size of crystallite in the macro-porous SnO_2 decreased due to the high dispersion of the Sn-precursor over PS spherical beads. The peaks for KCl in the XRD pattern were observed at 28°, 40° and 50° 2θ because of a reaction between the chlorine in the precursor and potassium in the initiator used for the polymerization of polystyrene during the synthesis of macro-porous SnO_2. The peak intensities increased with increasing concentration of the Sn-precursor solution. An increase in peak intensity means an increase in crystallinity and size of the SnO_2 crystallites. The growth of crystallites was confirmed by SEM, as shown in Fig. 1. The XRD patterns were well matched with the results of SEM.

Photoelectric Property of Macro-Porous SnO_2

DSSCs cells were assembled with macro-porous SnO_2 as the electrode to investigate the photoelectric properties the macro-porous SnO_2 synthesized by the template method. The cell efficiency of the DSSCs was also measured using a solar simulator, and the I-V curves were obtained, as shown in Fig. 3. The cell efficiency of the DSSCs manufactured in this study differed according to the concentration of the Sn-precursor solution used in the synthesis of macro-porous SnO_2. The cell efficiency of the DSSCs increased with increasing concentration of the polystyrene colloidal solution, because the macro-pores in the SnO_2 layer were formed from the decomposition of the polystyrene nano-size spherical beads. The transmittance of light into the SnO_2 layer used as the electrode for the DSSCs increased with increasing macro-pores because the macro-porous SnO_2 synthesized at a suitable Sn-precursor concentration exhibited ordered type macro-pores. The efficiency of the cells increased with increasing concentration of the $SnCl_4$ solution used as a precursor. The N_2 adsorption method and XRD confirmed that the surface area of macro-porous SnO_2 increased with increasing $SnCl_4$ solution concentration and its

Table 2. Efficiency of the DSSCs manufactured by macro-porous SnO_2 synthesized with different $SnCl_4$ solution concentrations using a template method

Concentration of $SnCl_4$, M	Jsc(A/m^2)	Voc(V)	FF(%)	Efficiency(%)
0.025	0.45	0.53	36.77	0.89
0.05	0.50	0.47	40.58	0.96
0.1	0.69	0.54	41.42	1.53

crystallinity increased. An increase in surface area of the electrode leads to an increase in the amount of photosensitive dye deposited over the electrode. The electro-conductivity of SnO_2 can be enhanced by increasing its crystallinity. Therefore, the electrical current over the electrode could be enhanced by the use of macro-porous SnO_2, which has a high surface area and high crystallinity. The short circuit current (J_{sc}) increased with increasing $SnCl_4$ solution concentration, as shown in Fig. 3 and Table 2.

4. Conclusion

Macro-porous SnO_2 was prepared using a matrix assisted method with polystyrene nano sized beads as the template. The optimal conditions for the synthesis of macro-porous TiO_2 were determined by controlling the precursor concentration. The crystallinity and the surface area of the macro-porous SnO_2 increased with increasing concentration of the precursor solution. The DSSC efficiency increased with increasing precursor solution concentration. The cell efficiency increased because the surface area and crystallinity of macro-porous SnO_2 were enhanced by controlling the precursor content. The cell efficiency of macro-porous SnO_2 as an electrode in DSSCs was enhanced due to the good diffusion of methylene blue and the good transmission of UV-light into the macro-pores.

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