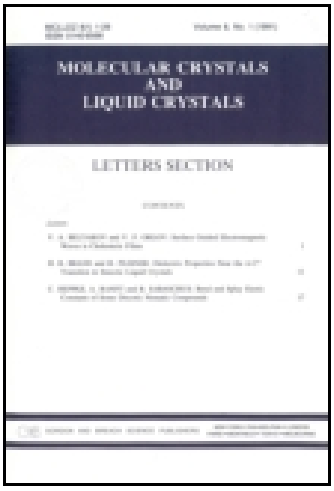

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Formation of Ordered Macro Porous TiO_2 Layer with Polystyrene Nano-Beads over FTO Glass DSSCs

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The macro porous TiO_2 applied as the electrode materials were prepared by a matrix-assisted method in this study. The matrix for the preparation of the macro porous materials was used polystyrene nano spheres. The precursor for a preparation of TiO_2 was used $TiCl_4$. The morphology of TiO_2 synthesized by a matrix-assisted method was the macro-porous material of the ordered type. In this study, the ordered type macro-porous TiO_2 layer as the solid oxide electrode was formed over FTO glass for high efficient DSSCs. TiO_2 synthesized in this study was applied as the electrode for dye sensitized solar cells (DSSCs). The cell efficiency of DSSCs with the macro-porous TiO_2 was investigated and the cell efficiency was enhanced with increasing density of macro pores. These results were concluded, because the shadow effect of the macro porous materials under photo radiation decreased.

Keywords Macro-porous TiO_2; dye-sensitized solar cells; and polystyrene colloidal solution

1. Introduction

Titanium oxide has been used in various application parts, such as the electrode for DSSCs [1, 2], the photo-catalyst [3–9], and the reflective coating material etc., due to its photoelectric properties. As well known, DSSCs is consisted of the TiO_2 layer over FTO thin layer used as a transparent electrode, the mono-dispersed dye over TiO_2 particles, and electrolyte [1, 2, 10]. The electrons of photosensitive dye coated over TiO_2 particle are exited with UV-Visible light and the exited electrons moved into conduction band are transferred to TiO_2 electrode layer. These electrons flowed to count electrode through FTO layer. Meanwhile, the electrolyte provides the electron to the positive hole of exited dye by their oxidation, and is reduced to accept the electrons from the count electrode. Since the electrical current is obtained by the circuit of excited electrons, the transfer of electrons from the electrolyte is enhanced with increasing contact area of between the electrolyte and the photo-sensitive dye. Specially, if the solid-state electrolyte is used for DSSCs, the contact area can be

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considered for the increase of short current circuit (J_{sc}). Therefore, the synthesis of macro-porous solid oxide electrode was researched for well diffusion of electrolyte into the TiO_2 layer in this study.

Meanwhile, it is expected that the macro porous TiO_2 has the high photoelectric property as the electrode for dye sensitized solar cells (DSSCs). The advantages of macro pore are 'well diffusion of liquid electrolyte' and 'reduction of shadow effect'. Shadow effect is that irradiated UV and visible light are to black by the surface layer over bulk TiO_2 film. Since UV light is not transmitted into the electrode bulk layer, the dye over the internal TiO_2 particles in the bulk film is not sensitized. However, UV light transmitted into the macro porous TiO_2 bulk layer. The macro porous TiO_2 was synthesized by a matrix assisted method in order to improve the internal diffusion of liquid phase electrolyte into the bulk electrode layer and to reduce the shadow effect.

In order to synthesize the ordered type macro-porous TiO_2, the polystyrene nano beads were used as the template material for the formation of macro-pores. The polystyrene colloidal solution, which is consisted of polystyrene nano particles of approximately 250 nm and solvent, was mixed with TiO_2 paste and the pore-density was controlled with changing TiO_2 precursor solution/polystyrene colloidal solution volumetric mixing ratio. The mixture solution was coated over FTO glass and the macro-pores were formed by the thermal treatment of mixture coating layer at 600%. The morphology of macro-porous TiO_2 layer prepared with mixing ratio of mixture solution was observed by SEM and their cell efficiency was investigated by solar simulator.

2. Experiment

2.1. Synthesis of Polystyrene Colloidal Solution

Polystyrene nano spherical beads were synthesized by the polymerization of styrene monomer in water used as a solvent. The distilled water of 500 ml was contained in the round flask and styrene monomer of 11 g was injected by the syringe. The concentration of styrene monomer was controlled in a range of 0.05–0.15 M. The round flask used as the reactor was purged with alternate cycles of nitrogen and vacuum, and was finally left under nitrogen atmosphere before the injection of initiator. The temperature of solution in the flask was maintained at 80°C by the water bath. The solution was mixed by the magnetic bar stirred to 500 rpm. Polymerization of styrene was begun from the injection of initiator through the stem, and was carried out for 12 h.

2.2. Synthesis of Macro-Porous TiO_2

The synthesis of macro porous TiO_2 was carried out in the vacuum oven. The mixture solution of 100 ml, which is consisted with $TiCl_4$ solution of 0.01–0.5 M and polystyrene colloidal solution, was contained in the glass container made with I.D of 50 mm. The volumetric ratio of $TiCl_4$ and polystyrene colloidal solution was controlled to 1/10, 1/5, 2/5 and 3/5. The glass substrate was placed in the bottom of glass container. The solvent of mixture solution, which is a water solution, was removed by the vacuum evaporation at 50°C. After the enough evaporation of liquid solvent in the mixture solution, the solid mixture, which is consisted polystyrene spherical nano beads and $TiCl_4$, over the glass substrate was calcined at 500°C for 4 h in order to thermally decompose polystyrene used

Figure 1. Synthesizing steps for the macro-porous TiO_2 by matrix assisted method.

as the template. The glass substrate of 10 mm × 10 mm size was used as the electrode material for the fixation of macro porous TiO_2.

2.3. Characterization of Macro-Porous TiO_2

The surface morphology of macro-porous TiO_2 was observed by scanning electronic microscopy (SEM, HITACHI S-4800) and its crystal phase was analyzed by x-ray diffraction meter (XRD, PANalytical, MPD for bulk). The particle size of P25 and the macro porous TiO_2 was investigated by transmittance electronic microscopy (TEM, HITACHI H-7600).

2.4. Preparation of DSSCs

The cells of DSSCs, which employed the macro-porous TiO_2 as an electrode, was also manufactured for assessing the photoelectric property of synthesized TiO_2. The efficiency of DSSCs was compared with relation to different particle size of TiO_2 synthesized by a matrix assisted method. The transparent nanocrystalline-TiO_2 layer was coated on the Fluorine-doped Tin Oxide (FTO, sheet resistance: 10 Ω per square) glass plates by screen printing and then gradually heated under the atmosphere at 325°C for 5 min. In order to get the dyes adsorbed onto the surface, the resultant 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 means of vacuum backfilling. Finally, the hole was sealed with an additional cover glass.

3. Results and Discussion

3.1. Size Control of Spherical Polystyrene Beads

In this study, polystyrene spherical beads were used as the template in order to control the size of macro pore and the size of polystyrene nano beads were controlled with changing concentration of styrene monomer used as the raw material for the synthesis of polystyrene. When the concentrations of styrene monomer were 0.05, 0.1 and 0.15 M in its polymerization, the size of polystyrene nano spheres were approximately 280, 360 and 540 nm, respectively, as show in Fig. 2. Since the reaction rate for polymerization can be depended on the concentration of monomer, these results mean that the size of polystyrene nano-beads

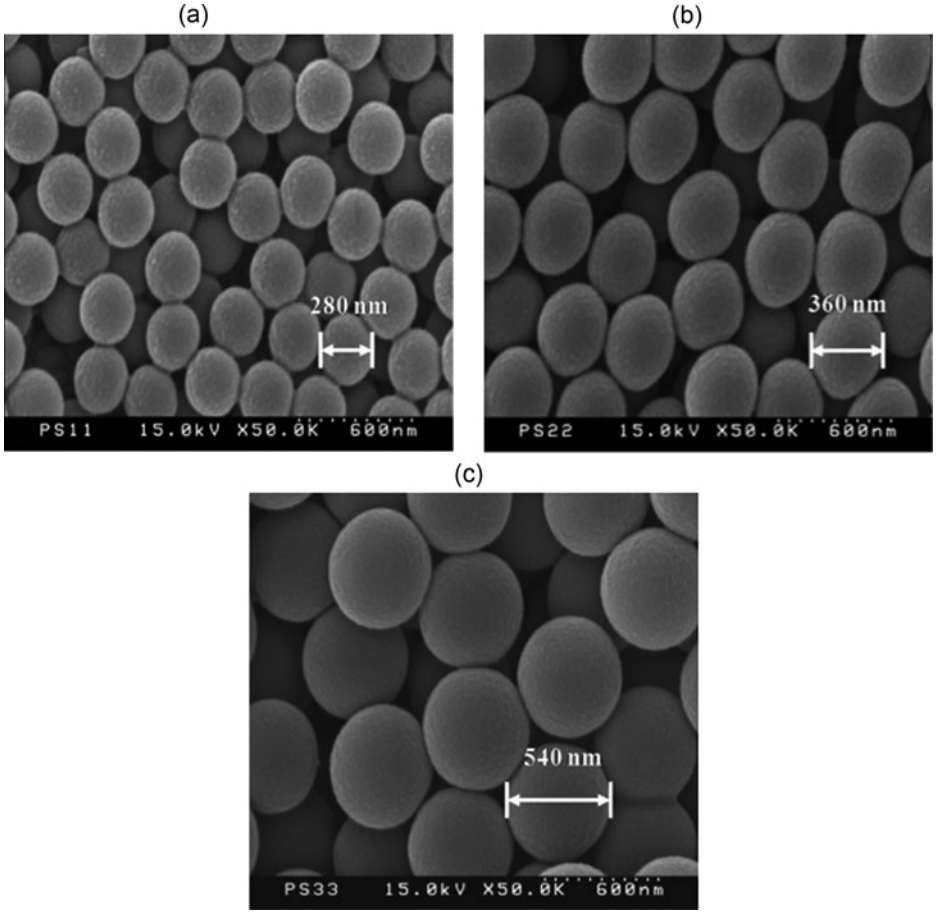

Figure 2. Size of polystyrene spherical beads changed with the concentration of styrene, (a) 0.05 M, (b) 0.1 M, (c) 0.15 M.

is changed with the content of styrene added in the solvent of 500 ml. The morphology of polystyrene nano-beads was the complete spherical type and their sizes were homogeneously, as show in Fig. 2. Therefore, it was concluded that the polystyrene nano-beads are a suitable template for the formation of ordered macro porous materials.

3.2. Effect of Styrene Monomer Concentration

The morphology over the surface of macro-porous TiO_2 prepared with changing concentration of precursor solution was investigated and its images analyzed by SEM were observed as shown in Fig. 3. After the moisture of mixture solution mixed with polystyrene colloidal solution and titanium precursor solution was removed by a vacuum evaporation, PS-$TiCl_4$ of solid state, which is a shiny white lump, was formed as explained in Fig. 1. In this step, polystyrene spherical beads are agglomerated to homogeneous state and the Ti-precursor is impregnated on the surface of polystyrene spherical beads. The content of $TiCl_4$ impregnated over polystyrene beads can be controlled with the changing concentration of precursor

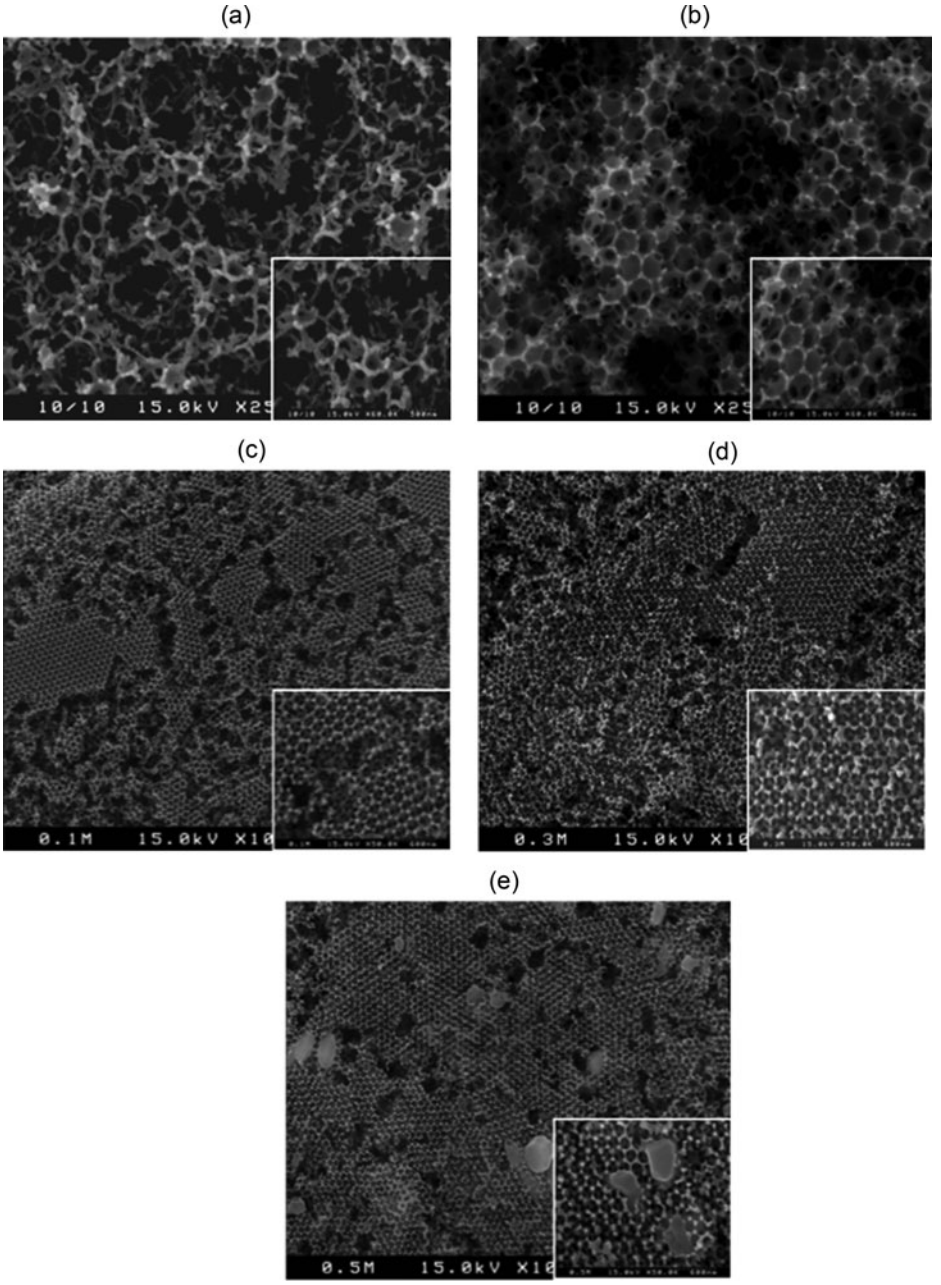

Figure 3. SEM images of macro porous TiO_2 prepared with changing concentration of $TiCl_4$ solution by matrix assisted method, (a) 0.01 M, (b) 0.02 M, (c) 0.1 M, (d) 0.3 M, (e) 0.5 M.

solution. Ti-precursor over polystyrene beads is converted to TiO_2 and polystyrene is thermal decomposed during the calcinations step. The macro-pores are created in TiO_2 lumps by the thermal decompose of polystyrene at 600°C. [PS]/[$TiCl_4$] ratio was fixed to 2/5 and the concentration of $TiCl_4$ was controlled in range of 0.01–0.5 M. The macro pores were

well formed in TiO_2 bulk film, as shown in Fig. 3, and were observed in TiO_2 synthesized under most conditions. However, the morphology of these macro porous TiO_2 was considerably differed with the concentration of precursor solution. The ordered type TiO_2 was formed with increasing concentration of precursor solution and this structure is called the opal structure. It was concluded that ordered type TiO_2, as channel structure, was formed because the density of metal oxide increased from the increase of $TiCl_4$ concentration. If the macro porous materials have a structure of channel type, the improvement of UV-Vis light transmission and diffusion of liquid electrolyte into electrode bulk layer for DSSCs can be expected. The structure of channel type in TiO_2 bulk leads the improvement of cell efficiency due to the transmission of irradiation into the bulk TiO_2 structure.

3.3. Effect of [PS]/[$TiCl_4$] Volumetric Ratio

The morphology of TiO_2 bulk structure was investigated with the change of [PS]/[$TiCl_4$] mixing ratio for the macro porous TiO_2. The concentration of $TiCl_4$ used as a precursor was fixed at 5 M in this experiment. The volumetric mixing ratio of polystyrene colloidal solution and precursor solution was controlled to 1/10, 1/5, 2/5 and 3/5 for the formation of macro porous TiO_2. The SEM images of macro porous TiO_2 formed from four kind samples were showed in Fig. 4. The different morphology of macro porous TiO_2 was observed with the change of its volumetric ratio. When the low volumetric content of polystyrene was used

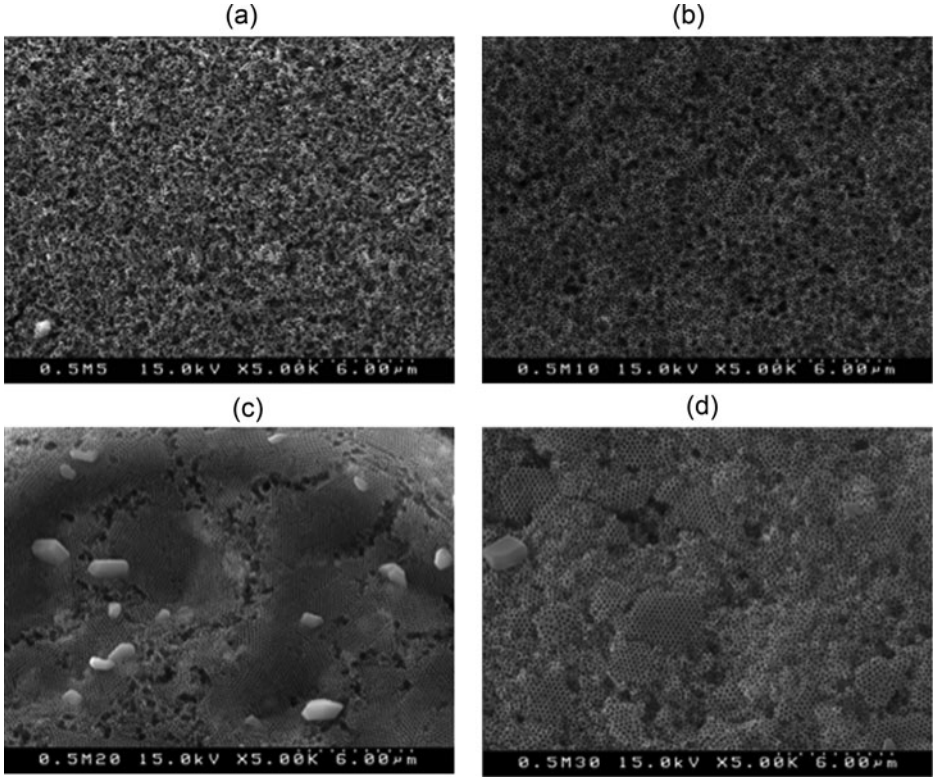

Figure 4. SEM images of macro porous TiO_2 prepared with changing [PS]/[$TiCl_4$] ratio by matrix assisted method, (a) 1/10, (b) 1/5, (c) 2/5, (d) 3/5.

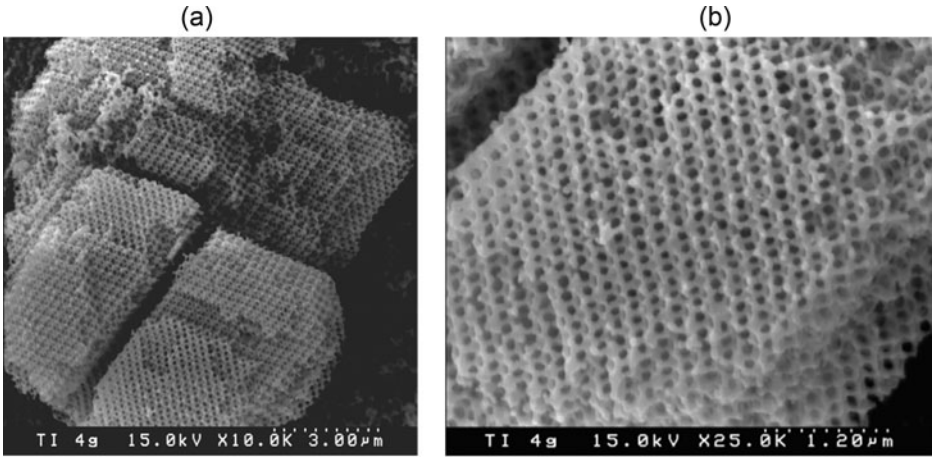

Figure 5. SEM images of multi-channel type TiO_2 prepared with PS-$TiCl_4$ mixture solution, [PS]/[$TiCl_4$] ratio = 2/5, [$TiCl_4$] = 5 M, (a) x 10,000, (b) x 25,000.

in these experiments, the macro porous TiO_2 of uniform size was formed to the random arrangement in TiO_2 bulk, as shown in Fig. 4(a) and Fig. 4(b). However, the macro pores were homogeneously line up to ordered type structure with increasing volumetric content of polystyrene colloidal solution, as shown in Fig. 4(c) and Fig. 4(d). The ordered macro pores of TiO_2 bulk were formed over TiO_2 bulk film when [PS]/[$TiCl_4$] volumetric ratio is above 2/5. It was confirmed that the pore structure of multi-channel type, which is created by the connection of ordered type pores could be prepared with the arrangement of polystyrene, as shown in Fig. 5.

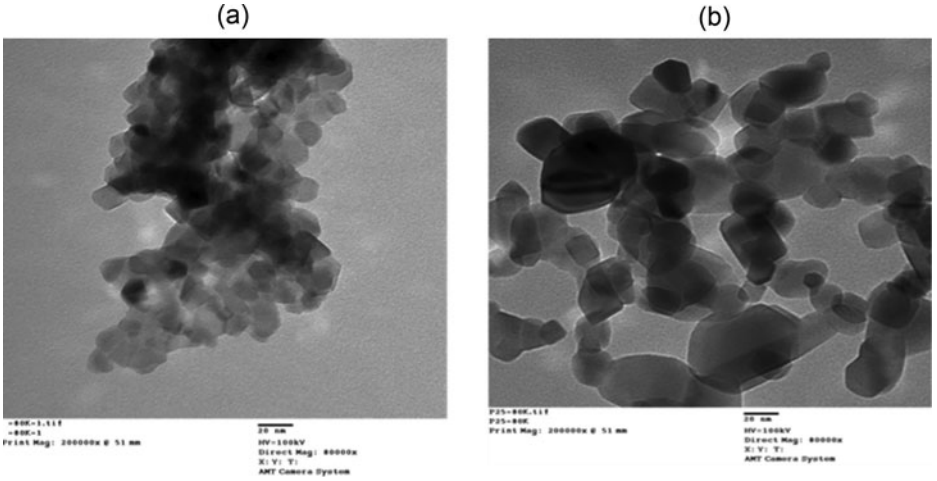

Figure 6. TEM images of (a) macro porous TiO_2 and (b) P25.

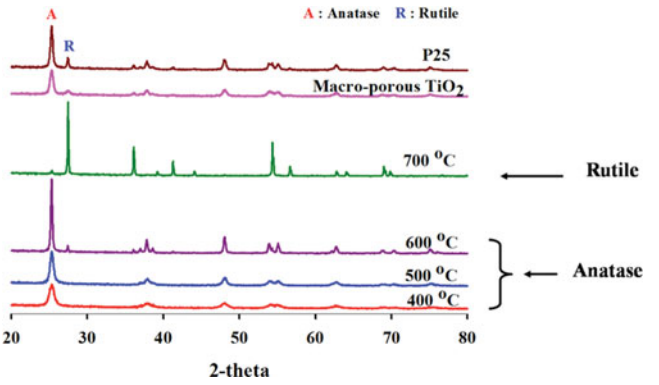

Figure 7. XRD peak patterns of various TiO_2.

3.4. TEM and XRD Analysis

The particle size of the commercial TiO_2, which is P25 produced by Daegusa, and the macro porous TiO_2 synthesized in this study was analyzed by TEM. It was confirmed that the particle size of macro porous TiO_2 was lower than that of P25, as shown in Fig. 6. These particles were formed to the uniform size of approximately 15 nm. The surface area

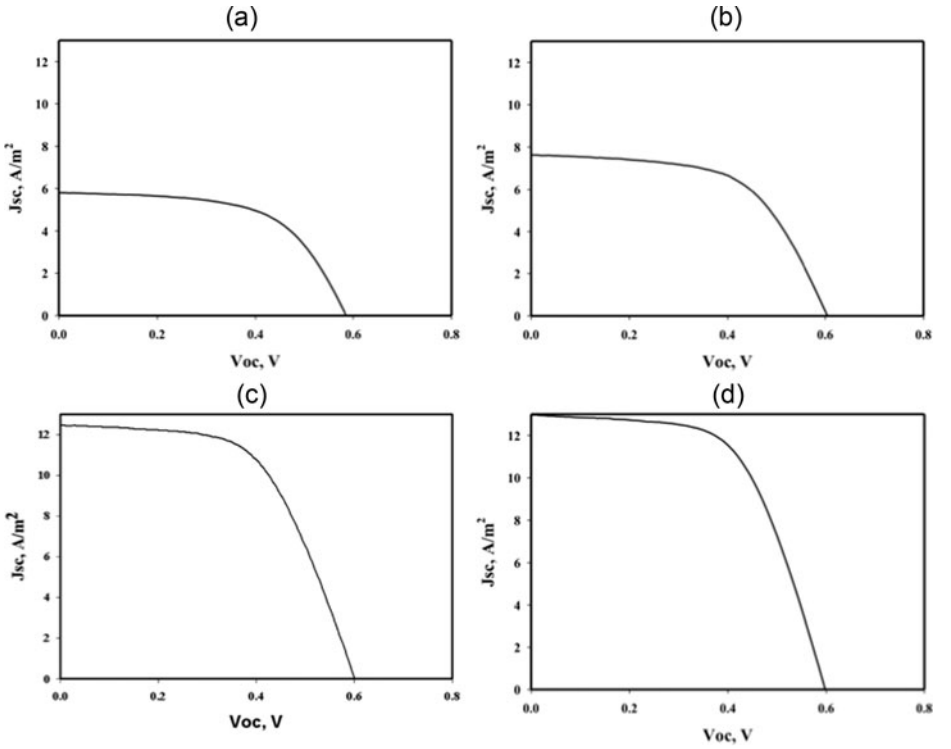

Figure 8. I-V curves of DSSCs manufactured by macro-porous TiO_2 synthesized with changing [PS]/[$TiCl_4$] volumetric ratio, (a) 1/10, (b) 1/5, (c) 2/5, (d) 3/5.

Table 1. Efficiency of DSSCs manufactured by macro-porous TiO_2 synthesized with changing volumetric ratio of [PS]/[$TiCl_4$] mixture solution by a matrix-assisted method

[PS]/[$TiCl_4$] volumetric ratio	Jsc, A/m^2	Voc, V	Fill factor	Cell efficiency, %
1/10	5.78	0.5844	0.5843	1.973
1/5	7.62	0.6012	0.5708	2.616
2/5	12.63	0.5962	0.5467	4.11
3/5	13.08	0.5950	0.5682	4.421

of solid materials can be changed with the size of particles. Therefore, it was expected that the macro-porous TiO_2 synthesized in this study had the higher cell efficiency than that of P25.

The peak pattern of macro porous TiO_2, P25, and other TiO_2 samples prepared by hydrothermal method was investigated by XRD analysis, as shown in Fig. 7. TiO_2 treated at 600° after the preparation by hydrothermal was exhibited to a high peak intensity of anatase structure (2 theta = 25°) and low peak intensity rutile structure (2 theta = 27°) in their XRD peak patterns. P25 and the ordered macro porous TiO_2 synthesized in this study also exhibited similar XRD peak pattern. Therefore, it was concluded with the consideration of its XRD pattern that two TiO_2 have the similar chemical and physical property.

3.5. Photoelectric Property of Macro Porous TiO_2

In order to investigate the photoelectric property the macro porous TiO_2 synthesized by matrix-assisted method, DSSCs cells were assembled with the macro-porous TiO_2, which is the opal structure. The cell efficiency of DSSCs was also measured by solar simulator and I-V curves were obtained in these tests as shown in Fig. 8. DSSCs manufactured in this study exhibited the different cell efficiency with [PS]/[$TiCl_4$] volumetric ratio changed in the synthesis process of macro-porous TiO_2. The cell efficiency of DSSCs increased with increasing content of polystyrene colloidal solution, because the macro pores in TiO_2 layer is formed with polystyrene nano-size spherical beads. It was concluded that the transmittance of light into the TiO_2 layer used as the electrode for the cell efficiency of DSSCs increased with increasing macro pores, because the macro-porous TiO_2 synthesized at the high [PS]/[$TiCl_4$] volumetric ratio exhibited the morphology of ordered type macro-pores. Meanwhile, the content of TiO_2 in the electrode layer can be reduced with the increase of polystyrene spherical beads under the same thickness of electrode layer. Since the content of mono-dispersed photosensitive dye over the electrode material is depended on the content of TiO_2 in the electrode layer, the cell efficiency can be reduced with the formation of macro pores. Therefore, the thickness of TiO_2 layer was controlled by several times coating in order to maintain the similar content of TiO_2 in the electrode layer. The macro-porous TiO_2, has the ordered type macro pores, exhibited the higher cell efficiency despite the long thickness, as shown in Table 1. The increase of short circuit current (J_{sc}) means the increase of excited electron on the photosensitive dye. It was concluded that the macro pores of ordered type enhance the transmittance into the electrode layer.

4. Conclusion

The macro porous TiO_2 was prepared by a matrix assisted method with polystyrene nano sized beads used as the matrix. The optimum conditions for the synthesis of the macro porous TiO_2 were selected with the control of precursor concentration and [matrix]/[precursor] volumetric ratio. The crystallinity and the surface area of the macro porous TiO_2 were lower than that of P25 (commercial material). However, its photo-catalytic activity was high than that of P25. From these results, it was concluded that the cell efficiency of macro-porous TiO_2 for DSSCs was enhanced due to the well diffusion of methylene blue and the well transmission of UV-light into the macro-pores.

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