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Formation of mesoporous anatase TiO_2 spheres by hydrothermal method and dye-sensitized solar cells properties

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1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be an alternative energy source for the semiconductor solar cells [1,2]. The power conversion efficiency of over 11 % has been attained so far. The main factors that affect the efficiency are the electron transport in the conduction band of TiO_2 and the interfacial recombination of the charge carreriers at the electrolyte interfaces [3]. The morphology of the photoanode plays an important role in determining electron transport. Generally, the photo anodes are composed of titania nanoparticles with the average size of 15 - 20 nm. The TiO_2 nanoparticles are not considered to be effective for better efficiency DSSCs, because of the random movement of the electrons due to the surface states and grain boundaries. The mesoporous TiO_2 spheres with uniform pore size has a great attention as a photoanode material due to the special function where the interconnected junctions with open pores in the mesoporous structure will speed up electron transport [4]. Since it has the interconnected titania skeleton with regular nanocrystals junctions and internal surface area, it facilitates more adsorption of the dye molecules between the pores and promotes the efficient light harvesting compared with the TiO_2 nanoparticles [5].

There are various methods for the synthesis of the mesoporous TiO_2 spheres. However, the effect of growth period on the formation of mesoporous anatase TiO_2 without the template has not been investigated. In this research, ordered mesoporous TiO_2 spheres were successfully synthesized by the template-free hydrothermal method. The growth period dependence of morphological, structural and optical properties of mesoporous TiO_2 spheres was investigated. Mesoporous TiO_2 spheres at different growth periods were used to prepare the photoanode by spray pyrolysis deposition for DSSCs fabrication using N719 Ruthenium as a sensitizer. The effect of the photoanode active layer thickness on the conversion efficiency was investigated.

2. Experimental procedure

Titanium (IV) isopropoxide (TTIP 97 %), 1-butanol ($CH_3(CH2)_2CH_2OH$) were purchased from WAKO chemicals, Japan and used as received without further purification. TTIP (0.5M) was added to 200 mL in butanol. The solution was maintained at room temperature under vigorous stirring for 30 minutes and 60 mL of deionized water was slowly added to the above solution and stirred for 1 h. Then the white color solution was transferred to the 50 mL Teflon lined stainless steel autoclave at 150 ˚C and the hydrothermal growth was varied for 15, 20 and 25 h, respectively. Finally, the resultant products were collected and annealed at 350 ˚C

The crystalline phase and crystallinity of the samples were measured by a Rigaku (Japan) X-ray diffractometer (RINT-2200, CuKα radiation) at 0.02 ◦/sec as a step interval. Raman characterization was performed with helium – neon laser at room temperature. Surface morphology of the samples were observed with a JEOL JSM 6320F microscope (FESEM). The transmission electron microscope (TEM) images were recorded by a JEOL JEM 2100F microscope at an accelerating voltage of 200 kV. Ultraviolet-visible (UV-vis) spectra were taken by a Shimadzu (Japan) 3100 PC spectrophotometer. X-ray photoelectron spectrum (XPS) was measured by Shimadzu ESCA 3100. The current density and voltage characteristics were measured at 1.5AM (1000 Wm^{-2} simulated sunlight).

3. Results and Discussion

To investigate the elements present in the mesoporous nanoparticles, the XPS measurement was carried out as shown in Fig. 1. The binding energies of the specimen were corrected by referring the Mg peak at 463.8 eV. In Fig. 1 (a), a strong peak at 459 eV corresponded to the Ti $2p_{3/2}$. The broad peak in Fig. 1 (b) was related to O1s, which represented the presence of oxygen in the synthesized material. The main peak located at 530.6 eV was due to the signature of the lattice oxygen in the Ti – O – Ti bonds. The small shoulder peak originated around 532.3 eV may be the cause of physically absorbed oxygen. This peak was more dominated at 25 h compared with 15 and 20 h. It suggested that the material prepared at 25 h had high adsorptive capacity.

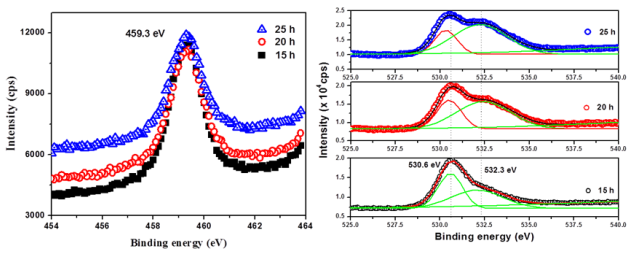

Fig. 1 XPS spectra of mesoporous TiO_2 spheres.

In order to interpret the morphological properties of the synthesized mesoporous TiO_2 spheres, the properties of nanoparticles at various growth periods were analyzed using FESEM and TEM measurements. Figs. 2 (a-c) show the FESEM images of mesoporous TiO_2 at 15, 20, 25h which

illustrated the spherical morphology with the average size of 100 – 200 nm. The TEM images were represented in the Figs. 2 (d-f) which predicted the morphologies of the sample at 15 and 20 h were spherical, however the walls of the sphere were not well defined. The morphology of the samples at 25 h exhibited the determined spherical structure of about 200 nm with the interconnected channels as shown in Fig. 2 (f). Figs. 2 (g-i) present the selected TEM micrographs of mesoporous-TiO_2. These images confirmed the porosity and the interconnectivity nature of the material. The insets are the corresponding HRTEM images at 15, 20 and 25 h. The size of the nanoparticle approximately 5 nm was consistent with the XRD result. It is noted that the sample prepared at the longer growth time 25 h provided a good morphology with the interconnected junctions. It would be more alleviate electron transport through the TiO_2 layer and reduce the recombination process.

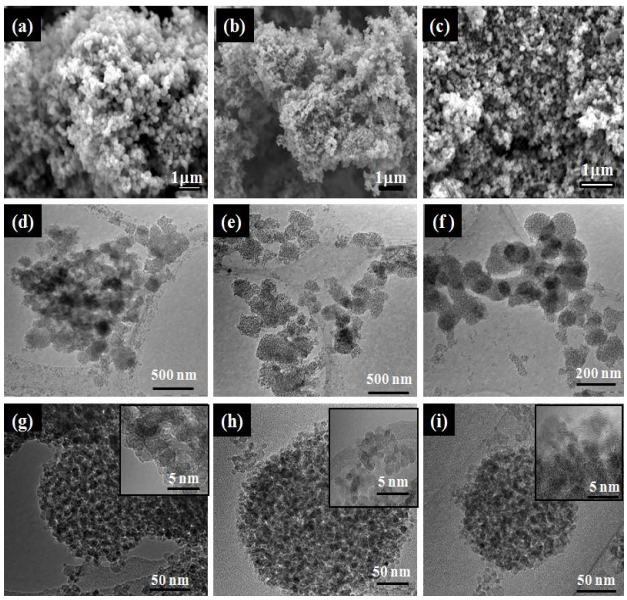

Fig. 2. (a-c) FE-SEM images, (d-f) TEM images, (g-i) magnified TEM images with HRTEM images for the corresponding growth of 15, 20, 25h.

The as-prepared mesoporous TiO_2 spheres at 25 h were used as the photoanodes to fabricate DSSCs. The effect of various thicknesses of the photoanodes on the conversion efficiency was investigated. Fig. 3 (a) depicts the J-V characteristics of 3, 7, 12, 16 and 23 μm thickness of mesoporous TiO_2 spheres. The short-circuit current densities (Jsc) were 3.08, 6.55, 9.23, 13. 11, 8.70 mA cm^{-2}, respectively. The energy conversion efficiencies (η) were 0.56, 2.80, 4.50, 6.4 and 4.07 %, respectively. It indicated that the characteristics of the DSSCs depended on the photoanode thikness. It was affirmed that the Jsc and Voc increased as the thickness increased till 16 μm and decreased at 23 μm. It may be due to the charge recombination process.

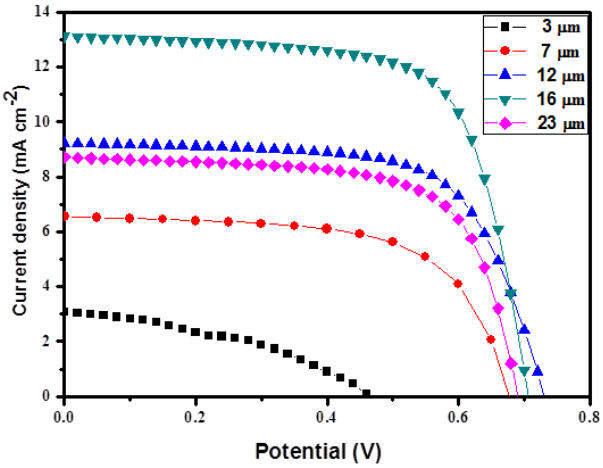

Fig. 3 Illustration of J-V characteristics of mesoporous TiO_2 spheres for various thickness.

4. Conclusion

Mesoporous anatase TiO_2 spheres were successfully synthesized by simple hydrothermal method. The effects of systematic growth periods on the morphological, structural and optical properties of mesoporous TiO_2 spheres were investigated. It was demonstrated the sample prepared at 25 h yielded well interparticle connection with well defined sphere-like morphology compared with the 15 and 20 h growth. Mesoporous TiO_2 spheres at different growth periods were used to prepare the photoanode by spray pyrolysis deposition for DSSCs fabrication using N719 Ruthenium as a sensitizer. The effect of the photoanode active layer thickness on the conversion efficiency was investigated. It was found that the maximum efficiency (η) 6.43 % was achieved for the thickness of 16 μm and attributed to enhance the light harvesting by absorbing the large amount of dye molecules. The mesoporous TiO_2 as photoanode in the DSSCs is beneficial for photo conversion efficiency.

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