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Preparation of TiO_2 Double-Layer Films with Echinoid-Like Particles on Nanorods Array for Dye Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) were intensively studied in the last two decays as alternatives to conventional silicon-based solar cells due to its low cost and relatively high power conversion efficiency.[1] TiO_2 is used as a semiconductor layer in DSSCs and the structure influences on the power conversion efficiency significantly. One of the causes which lower the power conversion efficiency is recombination; generally occur on the surface of TiO_2 nanoparticles. Many strategies have been reported to reduce the recombination. One is passivation of TiO_2 surface by coating with metal oxides as a barrier, such as Nb_2O_5,[2] metal oxide,[3] MgO,[4] and another is preparation of 1-dimensional (1D) semiconductor structures, such as nanorods, nanotubes, for the fast electron transfer.[5-8] However, when 1D semiconductor structures were used as working electrodes, low power conversion efficiencies were obtained because their specific surface area was small, resulting in less adsorption of dye.[9,10]

In this study, we report a double-layer structure for DSSCs consisting of TiO_2 nanorods array (TRA) and echinoid-like particles. This double-layer structure satisfies both fast electron transfer rate and large surface area which are important factors for the high power conversion efficiency.

TRA film was prepared by hydrothermal method, reported in the literature.[7] In brief, 15 mL D. I. water, 15 mL HCl, and 0.5 mL titanium(IV) isopropoxide (TTIP) were mixed and stirred. FTO glass was placed in the teflon-lined stainless steel autoclave and the prepared solution was added. The hydrothermal synthesis was conducted at 150 °C for 10 h, and then, the sample was washed with D. I. water and dried at 70 °C.

TiO_2 echinoid-like TiO_2 particles were synthesized as a same process reported earlier by our group.[11] 0.6 g poly (vinyl alcohol) (PVA) was dissolved in 18 mL dimethyl sulfoxide (DMSO) and TTIP was added to 30 mL 2-propanol. The PVA/DMSO solution and TTIP/2-propanol solution were added dropwise to 600 mL acetic acid under vigorous stirring and the resultant solution was refluxed at 100 °C. After 4 days, the synthesized particles were centrifuged and washed with acetone several times and dried at 70 °C.

For the formation of the double-layer film, the TiO_2 echinoid paste was prepared by using α-terpineol, dibutyl phthalate, lauric acid, and ethyl cellulose. The paste was deposited on the TiO_2 array film by doctor blade method and the resultant was annealed at 450 °C for 30 min. The prepared working electrode was immersed into N719 dye in the mixture of acetonitrile and *tert*-butanol for 18 h. Pt-coated FTO glass was used as a counter electrode, and the electrolyte was prepared with 1-propyl-3-methylimidazolium iodide (PMII), I_2, LiI, *tert*-butylpyridine, and acetonitrile. The active area was 0.25 cm^2.

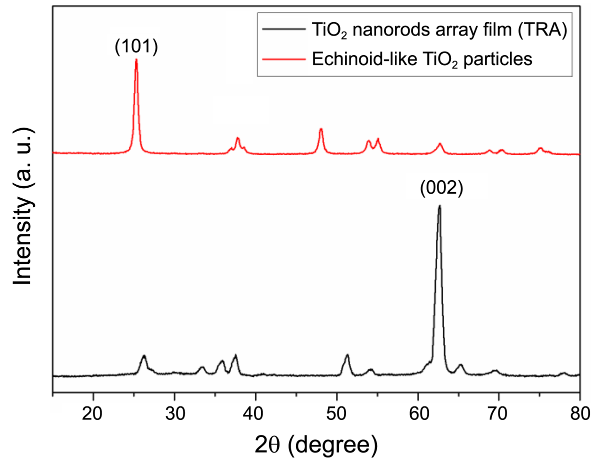

Figure 1. XRD patterns of TRA film and echinoid-like TiO_2 particles.

The XRD patterns of TRA film and echinoid-like TiO_2 particles are shown in Figure 1. According to the XRD patterns, the crystal structures of TRA film and echinoid-like TiO_2 particles are rutile and anatase, respectively. As shown in Figure 1, (002) peak of TRA film is significantly enhanced and this is attributed to the fact that TiO_2 nanorods are well aligned on the FTO glass vertically, and grew in the [001] direction.[7]

Figure 2 shows FE-SEM images of TRA film, echinoid-like TiO_2 particles, and double-layer films. The nanorods are well aligned on the surface of FTO vertically with few misoriented nanorods, and they cover the surface of FTO uniformly, as shown in Figure 2(a). The length and diameter of nanorods are about 4.5 μm and 100 nm, respectively. In Figure 2(b), the echinoid-like TiO_2 particles are successfully synthesized and the size of echinoid-like particles is about 600-1200 nm. The specific surface area of them is 82.81 m^2/g, which is measured by BET as a powder, and this value is comparable with that of 18.6 nm-sized-nanoparticles.[11] Therefore, it is expected that the amount of adsorbed dye can

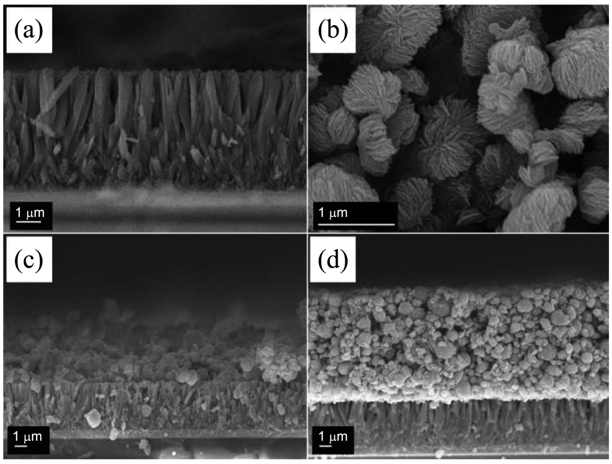

Figure 2. FE-SEM images of TRA film (a), echinoid-like TiO_2 particles (b), and TRE1 (c), TRE2 (d) films.

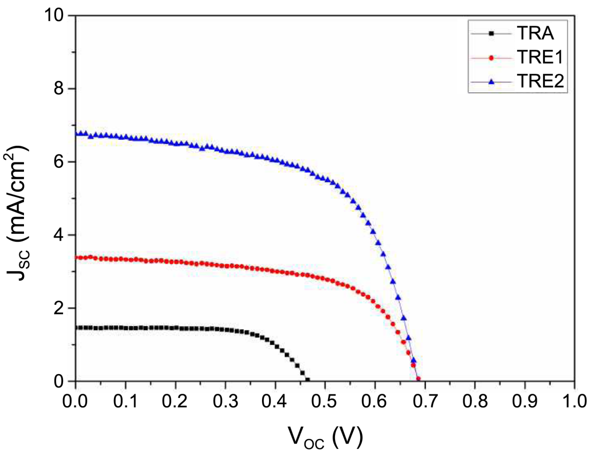

Figure 3. J-V curve of the cells using TRA, TRE1, and TRE2 film.

be increased by the large surface area. Double-layer films are prepared with different thicknesses of echinoid-like TiO_2 particles; Figure 2(c) and (d) represents 1 and 2 layers of echinoid-like TiO_2 particles on the TRA film, respectively. The samples are named as TRE1 and TRE2 according to the thickness of echinoid-like TiO_2 particles.

Photovoltaic performances of the cells using TRA, TRE1, and TRE2 films are measured under AM1.5 and their results are shown in Figure 3 and summarized in Table 1. The cell using TRA film shows the lowest power conversion efficiency because of the small amount of adsorbed dye. TRE1 and TRE2 films show relatively high power conversion efficiency, and when the thickness of echinoid-like TiO_2 particles increases, the efficiency also increases. This is attributed to the fact that the amount of adsorbed dye is very high, which is resulted from the large specific surface area of the echinoid-like TiO_2. However, comparing the cell using TRE1 film with that using TRA film, when the adsorption amount of dye is increased about 4.57 times, power conversion efficiency is increased only 1.49 times. This is expected that the weak connectivity between TRA film and echinoid-like TiO_2 particles layer leads to the difficult transfer of the electrons from upper layer to the under layer, as a result, interfacial resistance increases.

In this study, double-layer films for DSSCs consisting of TRA film and echinoid-like TiO_2 particles were prepared. Power conversion efficiencies of the cells using echinoid-like TiO_2 particles did not increase as much as the increase of adsorbed dye, because of the weak connectivity between TRA film and echinoid-like TiO_2 particles layer. However, the enhancement of dye adsorption compensate difficult electron transfer, and the overall power conversion efficiencies were improved.

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Table 1. The adsorption amount of dye and photovoltaic parameters of the cells using TRA, TRE1, and TRE2 films

Samples	Adsorption amount of dye (10^8 mol/cm^2)^a	Film Thickness (im)	V_{OC} (V)	J_{SC} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
TRA	0.56	4.5	0.466	2.27	67.2	0.71
TRE1	2.56	9.23	0.688	3.38	60.7	1.41
TRE2	4.32	13.1	0.686	6.77	60.2	2.80

^{a}Adsorption amount of dye was measured by the method mentioned in the literature.[12]