Dye-sensitized Solar Cells Using Brookite Nanoparticle TiO_2 Films as Electrodes

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Mesoporous brookite-based TiO_2 films, consisting of a certain amount of anatase, with thickness of about 2 and 5 μm were prepared by dip coating and screen printing techniques, respectively. Dye-sensitized solar cells based on both of these mesoporous brookite films using as electrodes, showed that the conversion efficiency of 2.6% and 4.1%, respectively.

Dye-sensitized mesoporous TiO_2 solar cells (DSC) have been regarded as a potential alternative to silicone solar cells because of their high efficiency, simple fabrication and low production cost.[1] The conversion efficiencies of the cells are known to be affected by the crystal phase and size of nano-structured TiO_2 particles, whose surface can be anchored by the sensitizing dye molecules, and by the mesoporous space in the films, which is constructed of the nano-TiO_2 and is filled with the iodide electrolyte.[2,3]

TiO_2 has three crystal phases, anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic).[4–6] Among them, rutile is the most common phase, and brookite is the rarest. Until now, many researches focused on the studies of anatase mesoporous TiO_2 film for DSC.[1–3,7–9] Recently, Park et al. reported photoelectrochemical properties of the solar cells based on rutile TiO_2 used as electrodes.[10] However, there is no report of usage of brookite TiO_2 as electrode in DSC, because nobody reported the synthesis of brookite nanocrystallites with suitable size (>10 nm) and shape (cubic or spherical) to get thick film (~ 10 μm).[11,12] In this letter, TiO_2 mesoporous films of brookite-based 10 nm-sized particles which contain a certain amount of anatase were prepared by dip coating and screen printing techniques on optically transparent conducting glasses, and the stability of crystal phase was checked using XRD in different sintering temperatures. The conversion efficiencies of solar cells, using the mesoporous brookite films as electrodes, were investigated.

A commercial brookite TiO_2 sol (NTB-1, a mixture of ca. 75% brookite and 25% anatase; TiO_2 solid content of 10% in the water) was supplied from Showa Denko. The size distribution of TiO_2 particles dried at r.t. from the sol is as from 10 to 35 nm determined by SEM. The thickness of TiO_2 film on a conducting glass prepared by dip coating of the sol as received was of 2.0 μm measured by a profiler (dektak^3, Sloan). To prepare thicker film, the same volume of diaceton alcohol (Nacalai, EP) as water was added into the above-mentioned sol, and then water was removed out from the sol by rotary evaporation at 40 °C. Using this sol, 5.0 μm film was obtained by screen printing technique (screen: AISI304, plane weaving, 150 mesh, Mesh Industrial).

The morphology of the brookite TiO_2 film sintered at 380 °C for 30 min were recorded by a nitrogen adsorption-desorption apparatus (Autosorb-1, Quantachrome), and determined using the BJH method of nitrogen desorption measurements. BET surface area, total volume, and pore distribution of the film were $118\ m^2 \cdot g^{-1}$, $0.38\ mL \cdot g^{-1}$, and 8–40 nm with average of 13 nm, respectively. The crystallinity and crystal phase of the TiO_2 films were evaluated by a powder X-ray diffractometry (RINT 2000/PC9 using Cu Kα radiation, Rigaku). Figure 1 reveals the surface SEM micrograph of the dip coated brookite TiO_2 film sintered at 380 °C for 30 min. The film was composed of cube-like particles with diameter distribution of 10–30 nm with average of 20 nm. Figure 2 shows the XRD patterns of the TiO_2 films that are obtained from the sol dried at different temperatures for 30 min. Obviously, brookite phase is dominant from the XRD patterns with characteristic peaks at $2\theta = 25.3°$, $30.7°$ and $36.2°$, but there

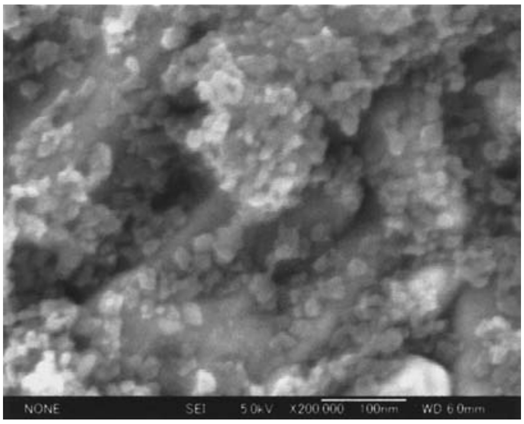

Figure 1. SEM image of brookite-based nanocrystalline TiO_2 film sintered at 380 °C for 30 min.

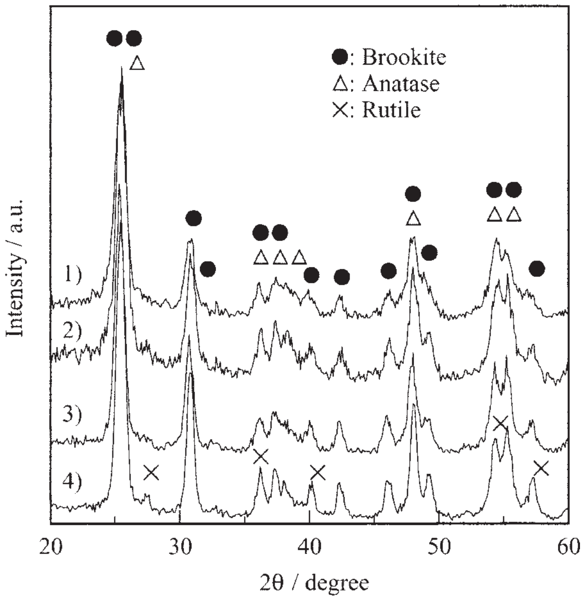

Figure 2. XRD patterns of brookite-based nanocrystalline TiO_2 films sintered for 30 min at 1) r.t., 2) 380 °C, 3) 500 °C, and 4) 550 °C.

is a certain amount of anatase, which can be proved by the following facts: 1. The intensity ratio of characteristic peaks of brookite at 25.3° assigned to the composite of two peaks of (120) and (111), and at 30.7° assigned to (121) was quite large as 2 : 1, which suggest that the 25.3° peak of brookite could be overlapped with (101) peak of anatase at 25.3°. 2. No obvious change of XRD pattern was observed up to 500 °C sintering, but the peaks were narrowed. Mean diameter calculated by Scherrer equation from the FWHM of (121) peak was changed from 10.3 nm for r.t. to 12.3 nm for 500 °C. Thus a little amount of amorphous component on the surface could be crystallized on sintering. When the sintering temperature increased to 550 °C, a peak at 27.3° assigned to (110) of rutile grew, suggesting that some amount of brookite transfer to rutile. Ye et al. reported that particle size of bulk brookite TiO_2 increased with sintering temperature, but the phase almost didn't change until 652 °C.[13] Thus nanosized brookite TiO_2 is stable up to 500 °C, but much easier to transfer to rutile phase at higher temperature compared with bulky particles.

The above-mentioned electrodes with 2 and 5 μm thick brookite films with projection area of 0.2 cm^2 prepared on conducting glasses were dried in air condition about 20 min, and then fired at 380 °C for 30 min before cooling to r.t. The electrodes were immersed overnight in an ethanolic solution of ruthenium dye $\{(Bu_4N^+)_2Ru(II)(dcbpy)_2(SCN^-)_2$; dcbpy = 4,4′-dicarboxy-2-2′-bipyridine$\}$ with 3×10^{-4} M (1 M = 1 mol·dm^{-3}) concentration. The resulting dye absorbed film was assembled with a Pt-sputtered conducting glass to form a sandwich-type dye cell. The electrolyte solution was composed of 0.1 M LiI, 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M I_2 and 0.5 M *tert*-butylpyridine in acetonitrile. The performances of DSCs with different thickness were studied by recording the photocurrent-voltage characteristics of the cell under an illumination of AM 1.5 (1 Sun, 100 mW·cm^{-2}) using a solar simulator (YSS-80, Yamashita Denso). The detailed description for the measurement was given elsewhere.[8] The results were shown in Figure 3, in which the conversion efficiencies were uncorrected for losses due to light absorption and reflection by the conducting glass. For the electrode with 2 μm thick TiO_2 film, conversation efficiency is about 2.6%, short-circuit photocurrent density J_{sc} is 5.2 mA·cm^{-2}, open-circuit voltage V_{oc} is 0.71 V, and fill factor *ff* is 0.68. J_{sc} increased approximately linearly to the film thickness from 5.2 to 8.9 mA·cm^{-2} but V_{oc} and *ff* decreased to 0.68 V and 0.66, respectively. Thus, the resulting conversion efficiency of 5 μm film showed 4.1%. These values on the cells with brookite films were comparable to the results obtained in anatase and rutile films with similar thickness.[8,10] For the improvement of the performance, further increase in film thickness should be done by changing the conditions of the sol, such as adding additives of polymer, and coating technique.

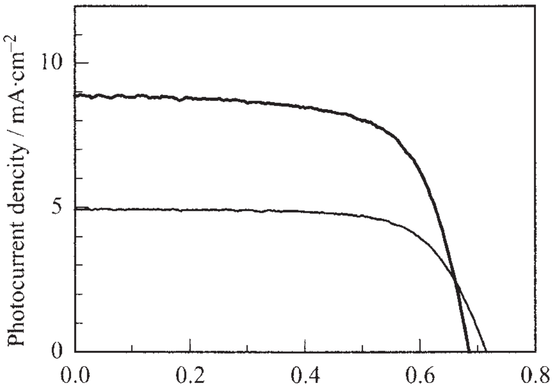

Figure 3. Photocurrent-voltage characteristics of dye-sensitized solar cells based on brookite-based TiO_2 films with 2.0 (thin) and 5.0 (bold) μm thickness under AM 1.5 illumination.

In conclusion, brookite-based TiO_2 mesoporous films on conducting glasses were successfully prepared. XRD studies show no phase transition under the sintering temperature up to 500 °C, but some amount of brookite transfer to rutile at 550 °C. The performance of the dye sensitized solar cell based on the electrodes of brookite-based TiO_2 film was comparable to those for anatase or rutile TiO_2 films.

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