Low Temperature Synthesis of Porous Nanocrystalline TiO_2 Thick Film for Dye-Sensitized Solar Cells by Hydrothermal Crystallization

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A crack-free porous thick film of TiO_2 has been fabricated by coating aqueous mixed paste of nanocrystalline TiO_2 powder and $TiCl_4$ and treating it by steam in an autoclave at a temperature as low as 100 °C. The added $TiCl_4$ was hydrolyzed and crystallized into rutile TiO_2 to "glue" the TiO_2 particles. Dye-sensitized solar cell based on this material achieved a high conversion efficiency of 6.23% under illumination by a filtered Xe lamp equivalent to 1 sun intensity.

Porous nanocrystalline TiO_2 electrodes are essential in dye-sensitized solar cells (DSSCs).[1,2] The conventional method of preparation employs TiO_2 paste with organic additives to suppress crack formation, which are removed upon sintering at around 450 °C. When the temperature is not sufficiently high, the remaining organics cause problems in the electron transport. Without organic additives, however, thick films cannot be obtained because of the problems with mechanical stability, thus limiting the amount of adsorbed dye.[3] Glass has therefore been the only choice as the transparent substrate which survives under the typical preparation conditions. Recently, Lindström et al. have successfully prepared nanostructured TiO_2 layers on conductive plastic substrates by mechanical compression of TiO_2 paste without using organic additives.[4] However, the electrical and mechanical connection of the particles in such films are achieved only by physical contact.

It is well known that several Ti(IV) salts and alkoxides can be hydrolyzed and crystallized into TiO_2 at fairly low temperatures under hydrothermal conditions. Such methods are often employed to prepare nanocrystalline TiO_2 powders used in DSSCs.[5,6] Thin films of TiO_2[7] and $BaTiO_3$[8] have been prepared hydrothermally on Si(100) substrates by precipitation from ammonia/H_2O_2/TiO_4^{2-} solution and oxidative conversion of sputtered metallic Ti film in $Ba(OH)_2$ suspension, respectively. Although both films were nicely crystallized in the temperature range below 200 °C, the maximum achievable thickness was less than 1 μm and the films seemed rather dense in structure, making them not suitable for DSSCs.

In this work, we have developed a new method to combine hydrothermal crystallization and the traditional colloid-based method. Hydrothermal crystallization of $TiCl_4$ into rutile TiO_2 has been utilized to chemically "glue" nanocrystalline TiO_2 powders. A crack-free, robust porous thick film of TiO_2 could be prepared at a temperature as low as 100 °C. The DSSCs using the prepared porous electrode have exhibited high performances.

Pure $TiCl_4$ (Kishida) was added dropwise into ice-cold water under vigorous stirring to obtain 1 M (1 M = 1 mol dm^{-3}) solution. It could be stored for more than 6 months in a refrigerator. 0.8 g of nanocrystalline TiO_2 powder (Degussa P25, 30% rutile and 70% anatase, BET surface area 55 m^{2}g^{-1}, particle size 25 nm) was added to 3.2 g of the $TiCl_4$ solution and ground in an agate mortar for about 2 h to get a viscous paste. The paste was spread on an F-doped SnO_2-coated conductive glass (Central Glass, ca. 20 Ω/sq.) by a glass rod and using Scotch tape as spacers. The raw film prepared in this way can easily be dissolved to water. The coated substrate was laid on a sample stage (a glass bottle) which was placed in a teflon-lined autoclave. A small amount of water was added below the level of the sample so that the film is not in contact with water but with steam during the reaction. The autoclave was heated at 100 °C in an oven for 12 h. After the reaction, the film was rinsed with water and dried in air at 100 °C for 1 h prior to dye adsorption. For comparison, the raw film was also directly heated at 100 °C for 12 h. The product films were well-adherent to the substrate and did not dissolve to water. The typical film thickness was about 10 μm but could be varied by the concentration of the paste or the thickness of the spacer. Films as thick as 15 μm could be prepared without causing problems in the mechanical stability. The X-ray diffraction (XRD) patterns of the films were measured on a Rigaku RAD-2R using Cu Kα radiation. The surface morphologies before and after the hydrothermal treatment were observed by a Topcon ABT-150FS scanning electron microscope (SEM).

The dry warm electrodes were immersed in a 0.5 mM $Ru(dcbpy)_2(NCS)_2$ (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid) (Kojima) solution in ethanol and kept overnight at room temperature. A sandwich cell was configured with the dye-modified electrode and a platinized SnO_2 glass counter electrode in face to face and introducing a 3-methoxypropionitrile containing 0.5 M LiI, 0.05 M I_2 and 0.5 M *tert*-butylpyridine. *I–V* curves were recorded under white light illumination from the side of the TiO_2 layer by a 500 W Xe arc lamp with IR-cut and $\lambda > 420$ nm longpass filters (intensity = 100 mW cm^{-2}).

The reaction process has been studied by XRD (Figure 1). When $TiCl_4$ solution without P25 is drop-coated and kept at room temperature, water is evaporated very slowly and leaves a transparent gel film which shows no diffraction peaks (a), indicating that ambient hydrolysis of $TiCl_4$ does not lead to crystallization. Sintering the same sample at 100 °C for 12 h in a dry oven gives a white powdery film, which also does not show any peaks (b). Direct crystallization of $TiCl_4$ into TiO_2 is not possible at 100 °C. However, when the sample is treated with steam at 100 °C for 12 h, broad diffraction peaks of rutile phase arise in the XRD (c). $TiCl_4$ can be hydrolyzed and crystallized into TiO_2 at the solid/gas interface when a hydrothermal condition is applied. The presence of water in the gas phase seems to be crucial to promote the conversion of $TiCl_4$ into TiO_2. Formation of rutile phase is in agreement with the previous finding of hydrothermal crystallization of amorphous TiO_2 in the presence of HCl.[6] The film prepared from the P25 + $TiCl_4$ mixed paste (d) indicates diffraction peaks assignable to both rutile and anatase TiO_2 which are mainly arising from P25, although the added $TiCl_4$ should be converted into rutile TiO_2 in this sample.

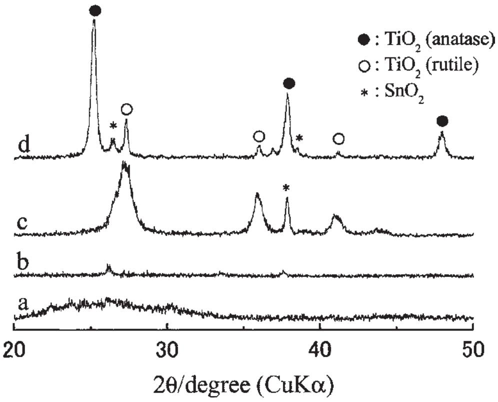

Figure 1. XRD patterns of the films prepared from 1 M $TiCl_4$ aqueous solution after drying in air at room temperature for 12 h (a), after sintering at 100 °C for 12 h (b) and after hydrothermal treatment at 100 °C for 12 h (c); that for a porous TiO_2 film prepared by hydrothermal treatment of $TiCl_4$ + P25 coating at 100 °C for 12 h (d).

The film morphologies before and after the hydrothermal treatment are compared in Figure 2. Particles originating from P25 are recognized for the raw film (a) but are not individually separated as they are seemingly covered with another material. After the treatment (b), the particles apparently become smaller and the film also becomes more open, in fact, looking very similar to the conventional material prepared with heat treatment.[2] It is supposed that $TiCl_4$ is condensed in the raw film to surround the P25 particles, and reduce its volume upon its conversion into rutile TiO_2. The newly formed TiO_2 therefore acts as "glue" to connect P25 particles as well as that between the film and the substrate. No crack was found in the film in its lower magnification SEM image. In the film prepared by direct sintering, on the other hand, amorphous TiO_2 should be present at the boundary as well as on the surface of the particles to form amorphous shell/crystalline core structured films.

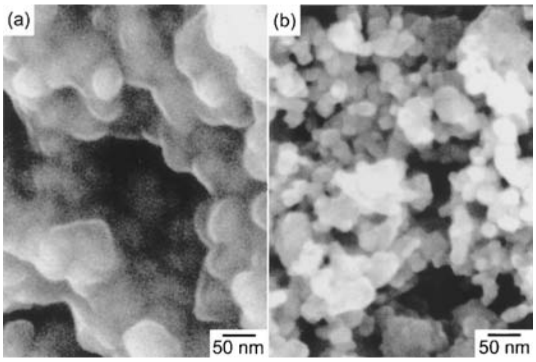

Figure 2. SEM photographs of TiO_2 films prepared from $TiCl_4$ + P25 mixed paste before (a) and after (b) hydrothermal treatment at 100 °C for 12 h.

Both of the prepared porous TiO_2 films became deeply colored after dye adsorption. The dye loading was determined by desorbing the dye in an NaOH ethanol solution and measuring its absorption spectrum.[2] For the 10 μm thick films prepared by the hydrothermal treatment and low temperature sintering, they were 1.5×10^{-7} and 1.1×10^{-7} mol cm^{-2}, respectively, indicating very high surface area of the present materials.

As promised from the favorable features found above, the DSSCs based on these TiO_2 electrodes present high performances. In Figure 3 are shown the I–V curves measured under white light illumination (100 mW cm^{-2}). The cell employing the film prepared by low temperature sintering exhibits a short-circuit photocurrent density (I_{sc}) of 13.1 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 0.65 V, and a fill factor ($F.F.$) of 0.52, achieving an overall light-to-electricity conversion efficiency (η) of 4.4%. It is quite surprising that the film covered with amorphous TiO_2 works as a rather efficient photoelectrode. However, the hydrothermal treatment greatly improved the cell efficiency by almost 50%, achieving the I_{sc}, V_{oc}, $F.F.$, and η of 16 mA cm^{-2}, 0.73 V, 0.54 and 6.23%, respectively. It is supposed that the chemical attachment of the TiO_2 particles with crystalline TiO_2 is effective for their secure electrical contact. The high V_{oc} value is attributable to suppressed charge recombination as often found by post treatment of porous TiO_2 film with $TiCl_4$.[2,9]

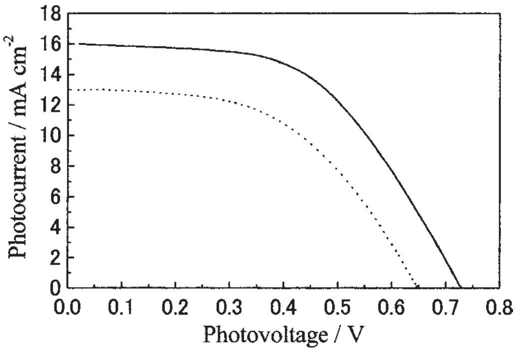

Figure 3. I–V curves measured at the DSSCs based on the porous TiO_2 films prepared by low temperature sintering (dotted line) and hydrothermal treatment (solid line) under white light illumination at 100 mW cm^{-2}.

It has been found in the present study that gas-phase hydrothermal crystallization of $TiCl_4$ in the aqueous mixed paste is a simple and effective way to prepare mechanically stable porous thick film at a low temperature. Since the mixed paste does not contain any organics, the resulting film acts as an efficient photoelectrode even without high temperature sintering. The present method may therefore be applied to conductive plastic substrates for realization of flexible DSSCs.

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