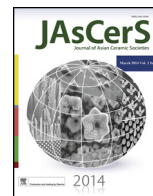




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Full Length Article

A biphasic sol–gel route to synthesize anatase TiO₂ particles under controlled conditions and their DSSC application

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ABSTRACT

A biphasic sol–gel method was introduced to reduce a high hydrolysis rate of metal alkoxides and control a morphological evolution of metal oxides. Titanium tetraisopropoxide (TTIP) was dissolved in an organic solvent which was immiscible with water. The TTIP solution was then contacted with water or pH-controlled aqueous solutions to promote the hydrolysis and the polycondensation reaction through the mass transfer across the organic/aqueous interface. Anatase TiO₂ was formed in any conditions employed in the present work at reaction temperatures of 80 °C or below. The morphology of TiO₂ particles obtained was largely dependent on the kind of organic solvents. It was basically the aggregation of nanoparticles to give submicrometer-sized secondary particles with or without a regular shape. Heptane was found to be suitable to obtain spherical TiO₂ large particles, which were evaluated as a photoanode material in dye-sensitized solar cells. Actually the large TiO₂ particles worked well as the light scattering layer when applying them to a double-layered photoanode, which showed an energy conversion efficiency of 5.67% with a high short-circuit photocurrent density of 14.1 mA cm⁻².

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1. Introduction

A sol–gel method is one of the most widely known liquid processes in fabricating inorganic materials such as glasses and ceramics. When using metal alkoxides as starting materials, they undergo sequentially hydrolysis and polycondensation to form amorphous or crystalline metal oxide fine particles. Titanium alkoxides have been extensively studied to produce both single-component titanium dioxide (TiO₂) materials and titanium-containing complex metal oxide materials including industrially important Pb(Zr,Ti)O₃ and BaTiO₃ ferroelectrics [1,2]. The use of titanium alkoxides needs particular attention because of their higher reactivity towards water. They are often stabilized by adding chelating agents such as acetylacetone to control the hydrolysis reaction [3].

Recently, we have developed a biphasic sol–gel method to reduce the hydrolysis reaction rate of metal alkoxides and synthesize metal oxide materials in a more controlled manner [4–6]. In this method, metal alkoxides are dissolved in organic solvents,

which are subsequently contacted with water or aqueous solutions. If the organic solvents used are immiscible with water, they can form biphasic liquid systems where the hydrolysis reaction is limited to either of the liquid phases or their interface. Our approach was to synthesize morphology-controlled complex metal oxides such as NaNbO₃ [4], CaNb₂O₆ [5], or Ba₂V₂O₇ [6] and, if possible, to improve their physical properties. Actually a luminescence property of the thus synthesized niobate and vanadate was found to be superior to those obtained by a usual sol–gel method with a single-phase liquid system.

In the present work, we attempted to synthesize single-component TiO₂ materials from titanium tetraisopropoxide (TTIP) by using a biphasic sol–gel method. It was expected that the hydrolysis would proceed more gently even at high reaction temperatures without using any stabilizing agents. We then examined carefully experimental conditions such as the combination of TTIP and water-immiscible organic solvents, the concentration of TTIP, the pH value of water or aqueous phases, and the reaction temperature. Our results demonstrated that anatase TiO₂ was formed in any conditions and its particle morphology was dependent on the organic solvents used. Basically the particle morphology was characterized as the aggregation of nanoparticles to give submicrometer-sized spherical secondary particles. Finally, we evaluated the present

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anatase TiO₂ particles as photoanode materials in dye-sensitized solar cells (DSSCs).

2. Experimental

2.1. Synthesis of TiO₂ particles

Two sets of experiments were carried out to synthesize TiO₂ particles through the biphasic sol–gel method. In one set of experiments, a xylene–water system, which had been employed in our former study [6], was used to examine the formation of TiO₂ from titanium alkoxide. TTIP (95.0%, Wako Pure Chemical Industries, Japan) of three different amounts (namely, 1.49, 4.97, or 14.9 mmol) was added to 2.25 mL of ethanol (99%, Amakasu Chemical Industries, Japan). Xylene (Wako) was further added to the respective TTIP solutions until a total volume of 50 mL was reached. The TTIP concentration of the resultant organic solutions was thus adjusted to 0.03, 0.10, or 0.30 M.

In addition to deionized water with pH 7.5, two kinds of aqueous phases were prepared as follows. An acidic aqueous solution with pH 2.9 was prepared by mixing 0.286 mL of acetic acid (99.9%, Wako) and 49.714 mL of deionized water. A basic aqueous solution with pH 11.0 was prepared by mixing 0.389 mL of an ammonia solution (28%, Wako) with 49.611 mL of deionized water. A 7.0 mL aliquot of the respective aqueous phases was placed in a glass container and preheated to 80 °C. Then, 7.0 mL of the above organic solutions was poured into the aqueous phases using a syringe. The resultant biphasic xylene–water systems were kept at 80 °C for 24 h. Precipitates were finally settled at the bottom of the container and collected by removing the solutions, washing with deionized water, centrifuging, and drying at 60 °C for more than 12 h.

In the other set of experiments, the solvents for the biphasic system were changed, aiming at controlling the morphology of precipitates. Xylene was then replaced with other water-immiscible organic solvents such as hexane, heptane, toluene, 1-butanol, 1-octanol, and cyclohexanol (all from Wako). Organic solutions (50 mL each) with the TTIP concentration of 0.10 M were prepared by adding TTIP to the above-mentioned respective solvents. Deionized water (7.0 mL) was placed in the glass container and preheated to 50 °C. The same volume of the above organic solutions was poured into water using a syringe. The resultant biphasic systems were kept at 50 °C for 24 h. The temperature is one of the most important factors influencing chemical reactions in solutions, and in this case the temperature of 50 °C was adopted taking account of the lowest boiling point (68 °C of hexane) of the organic solvents employed. Precipitates settled at the bottom were collected similarly as described above.

Additionally, water in the biphasic system was changed to mixed solvents consisting of acetonitrile (Wako) and water. Five kinds of the mixed solvents with water volume percentages of 2, 5, 20, 50, and 80% were prepared together with the deionized water (100%). An organic solution employed here was a 0.03, a 0.10, or a 0.30 M TTIP solution with heptane as the solvent. The following procedure was the same as that described above, except that the reaction temperature was optimized to 70 °C after preliminary experiments.

2.2. Characterization

Phase identification of the precipitated samples was made by an X-ray diffraction (XRD) analysis (D8 ADVANCE, Bruker AXS) using CuK α radiation. The crystallite size of the samples was calculated with the Scherrer's equation [7], $D = 0.94\lambda / (\beta \cos \theta)$, where D is the crystallite size, λ is the X-ray wavelength, β is the full width at half-maximum of each peak, and θ is the diffraction angle. The

morphology of the samples was observed with a field-emission scanning electron microscope (FESEM; Sirion, FEI) and a field-emission transmission electron microscope (FETEM; TECNAI F20, Philips). Raman spectra of the samples were recorded using a diode laser at 532 nm (Raman–One–CCD, CHROMEX). Diffuse reflectance spectra were recorded with an ultraviolet (UV)–vis spectrophotometer (V-670, JASCO) using an integrating sphere unit (ISN-723, JASCO). A Brunauer–Emmett–Teller (BET) specific surface area was evaluated by a nitrogen gas adsorption/desorption method using an automatic surface area and porosimetry analyzer (Tristar 3000, Shimadzu).

2.3. DSSC measurement

Two TiO₂ samples were chosen for the evaluation as the DSSC electrode; one was synthesized from the xylene–water system at 80 °C (0.30 M TTIP, pH 7.5) and the other from the heptane–water system at 70 °C (0.30 M TTIP, the water volume percentage of 100%). Both the samples were preheated at 500 °C for 1 h to remove unnecessary chemical species. The heated samples (200 mg each) were separately dispersed in 0.70 mL of *tert*-butyl alcohol (Wako), followed by stirring for 5 min and ultrasonication for 10 min. The TiO₂ pastes thus obtained were coated on fluorine-doped tin oxide (FTO)-glass substrates (10 Ω sq⁻¹; Nippon Sheet Glass) by a squeegee method and dried at 90 °C for 10 min. The dried pastes were finally heated at 500 °C for 30 min to obtain TiO₂ films. The films are designated as “Film X” and “Film H” which are originated from the xylene–water and the heptane–water system, respectively.

Next, using commercial TiO₂ nanoparticles (designated as “N”) with an average particle size of 20 nm (Toho Titanium) and the larger TiO₂ particles (“H”) from the heptane–water system, double-layered films consisting of a bottom N layer and a top H layer were fabricated similarly to those described above. Actually, two kinds of the double-layered films were obtained as “Film NH1” and “Film NH2” which were different in the thickness of each layer.

The TiO₂ films on the FTO-glass substrates were immersed in a 0.3 mM RuL₂(NCS)₂:2TBA ($L = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid and TBA = tetrabutylammonium; N719, Solaronix SA, Switzerland) ethanolic solution at 90 °C for 0.5 h. Sandwich-type open cells were constructed with the TiO₂/N719 electrode, a spacer film (50 μ m in thickness), and a counter platinum electrode. An I⁻/I₃⁻ redox couple electrolyte, which was composed of 0.1 M LiI (97.0%, Wako), 50 mM I₂ (99.8%, Kanto Chemical, Japan), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII; Shikoku Chemicals, Japan), 1.0 M 4-*tert*-butylpyridine (96%, Sigma–Aldrich, USA), and 3-methoxypropionitrile (99.0%, Wako), was introduced between the electrodes. An active cell area was fixed at 25 mm² by a mask.

The cell parameters, namely, an open-circuit voltage (V_{OC}), a short-circuit photocurrent density (J_{SC}), a fill factor (ff), and a power conversion efficiency (η), were determined by J – V measurements (J : photocurrent density, V : photovoltage). A 500 W xenon lamp (UXL-500SX, Ushio) was used as a light source to produce the simulated AM 1.5 illumination at 100 mW cm⁻². An AM 1.5 filter, a water filter, and an infrared cut filter (S76-HA50, Hoya) were placed in the light path to regulate the light in a wavelength range of 300–800 nm, reducing a mismatch of the simulated sunlight. J – V curves were measured with a potentiostat (HSV-110, Hokuto Denko) under the simulated sunlight. Dark current–voltage curves were also measured in the same way under a dark condition.

The amount of N719 dyes adsorbed on the TiO₂ electrodes was estimated by removing them in a 0.5 M NaOH ethanol/water ($v/v = 1$) solution. Absorbance of the resultant dye solutions was measured by the UV–vis spectrophotometer and calibrated with a standard solution of N719.

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