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Effects of the incorporation of carbon powder into nanostructured TiO_2 film for dye-sensitized solar cell

Soon Hyung Kang, Jae-Yup Kim, Yu-Kyung Kim, Yung-Eun Sung *

School of Chemical & Biological Engineering & Interdisciplinary Program in Nano Science and Technology, Seoul National University, Seoul 151-744, Republic of Korea

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Abstract

A nanoporous electrode was prepared by incorporating various amounts of carbon powder (Vulcan X-72) into TiO_2 paste. To remove the black-colored carbon elements, high-temperature (550 °C) thermal treatment was required for a long period of time (from 30 to 50 min). In this way, a nanoporous TiO_2 electrode with a high specific surface area and high porosity was formed after the incorporation of the carbon powder. Especially, the sample containing 1 wt% of carbon powder exhibited the best performance: a V_{oc} of −0.72 V, a J_{sc} of 12.69 mA/cm^2, a fill factor of 62% and an efficiency of 5.6%. Furthermore, the charge recombination between the photoinjected electrons from the excited dye and the I_3^- ions in the electrolyte induced by the enhanced surface was investigated by cyclic voltammetry and dark current measurements. In addition, mechanically stable TiO_2 films were formed in the range of carbon powder contents used in this study. From the above results, it can be concluded that the modification of the TiO_2 electrodes with a suitable carbon powder allows them to be used in dye-sensitized solar cells with improved performance and minor side effects.

Keywords: Carbon-modified TiO_2 electrode; Dye-sensitized solar cell; Porosity; Electron transport; Fill factor

1. Introduction

Since the introduction of anode electrodes composed of nanoporous and interconnected TiO_2 nanoparticles as an electron conductor, as reported by Gratzel's group in 1991 [1], dye-sensitized solar cells (DSSCs) have attracted considerable attention. After sintering at high temperature for a short time, nanoporous and nanocrystalline (nanostructured) films are formed. These films are composed of small and interconnected nanoparticles (typically 5–50 nm in size) and have a high internal surface area, which is 1000 times larger than the projected surface area [2]. This enhanced surface area and interconnection between the particles enhance the efficiency of dye-sensitized solar cells, due to the increased amount of dye adsorbed on the TiO_2 surface [3] and the retardation of electron loss afforded by the formation of a three-dimensional and connected TiO_2 network. As a result, various approaches have been reported to fabricate nanocrystalline and nanoporous metal oxide films.

In order to increase the surface area of nanoporous TiO_2 electrodes, various methods have been tried. Firstly, a metal-oxide (Al_2O_3, ZnO, MgO, Nb_2O_5, etc.) coating with a high band-gap induces the increase of the surface area of the nanoparticulated TiO_2 films [4–10]. Secondly, the $TiCl_4$ treatment (a type of surface treatment) of the TiO_2 electrode was employed to enhance the surface area of the TiO_2 film [11–13]. Thirdly, nanostructured electrodes with various shapes (rod, wire, tube, and suitable mixture of two components) was used to increase the surface area of the nanoporous TiO_2 film [14–17]. Fourthly, a dye-sensitized solar cell using synthesized TiO_2 nanoparticles (3–5 nm in size) by a polymer template was employed to increase the specific surface area and obtain an efficiency of above 8% [18].

Furthermore, to increase the porosity of nanoparticulated TiO_2 film, polymer molecules with a high molecular weight are generally incorporated into the paste, which is deposited by the doctor-blade method. Because the polymer mainly consists of carbon and oxygen elements, the material is then calcinated

* Corresponding author. Tel.: +82 2 880 1889; fax: +82 2 888 1604.
E-mail address: ysung@snu.ac.kr (Y.-E. Sung).

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to form CO_2 gas during sintering at high temperature under air ambient. Then, the space vacated by the carbonized polymer enhances the porosity of the TiO_2 film. The Frank group [19] reported that the larger the amount of polyethylene glycol (PEG) that is incorporated into the paste, the greater the increase in the porosity. However, they also reported that the optimum porosity of the nanocrystalline TiO_2 film used for dye-sensitized solar cells is about 50–65% [20]. In addition, the Gratzel group recently reported the formation of a regular and uniform TiO_2 film using a mixed polymer template and, a high efficiency of 4% was obtained using an organized mesoporous TiO_2 electrode with a thickness of only 1 μm [21].

In a present paper, the formation of porous and nanoparticulated TiO_2 film is presented using carbon powder (Vulcan X-72). In this experiment, we demonstrated that the carbon incorporated TiO_2 electrode has a more uniform pore size than that containing polyethylene glycol (PEG) surfactant. The carbon powder used in this study, Vulcan X-72, has a uniform particle size of 30–40 nm and a structure similar to that of an onion, which gives rise to smooth surface and stable mechanical properties. Conventionally, carbon powders are known to have several advantages [22,23], such as their low cost, which facilitates the commercialization of the resulting products, and the fact that carbon powders with various particle sizes and structures are available. The porosity control of the TiO_2 film can be accomplished by varying the amount of carbon incorporated into the paste, as was confirmed in this study. We also confirmed that the incorporated carbon powder increased the surface area of the TiO_2 films via their reaction with the oxygen molecules originating partially from the air atmosphere and partially from the TiO_2 lattice.

2. Experiment

An optically transparent conducting glass (FTO, Pilkington TEC Glass™, sheet resistance 8 Ω/square, transmittance 77% in the visible range) was used as a substrate. The substrate was cleaned successively in acetone, ethanol and DI water, for 20 min in each step to remove the organic pollutes and dust. To prevent any connection from occurring between the transparent conducting oxide (TCO) substrate and I^-/I_3^- electrolyte, which would otherwise cause the loss of open circuit voltage in the composed cell (cell composed of the TiO_2 electrode with thin thickness), one drop of 0.1 M titanium butoxide in absolute ethanol was spread on the conducting glass (3 cm × 3 cm) and dried at 80 °C for 1 h in an oven [24]. Nanocrystalline TiO_2 powder (P25, Degussa, 0.6 g) and carbon powder (Vulcan X-72, Cabot Corporation, from 0.5 to 3 wt% versus TiO_2 weight) were ground together in a bowl for a few minutes and then, acetylacetone, polyethylene oxide (PEO, M_v: 100,000; 20 wt% versus TiO_2 weight), and solvent (water/ethanol) were added. The nanoporous TiO_2 films were made from the prepared paste by the doctor blade technique using a glass rod, dried for 5 min using a dryer, sintered at 450 °C in air for 1 h and then heated again at 550 °C for 30 or 50 min using a hotplate. The thermal treatment used in the second-step must be conducted, in order to completely remove the incorporated carbon elements through their chemical reaction. In this experiment we varied the amount of carbon powder that was incorporated. The thickness of the TiO_2 films was controlled using transparent adhesive tape (Scotch, nominal thickness: 40 μm) as a spacer and determined by an Alpha-Step 200 apparatus (Tencor Instruments), to be approximately 7.5 μm (±0.5 μm). For the adsorption of the dye, the resulting electrodes were immersed in an ethanol solution of 5×10^{-4} M *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) (Ru535, Solaronix) for at least 12 h at room temperature. Then, the electrode was rinsed with ethanol and dried under an air stream. The redox electrolyte that was employed was composed of 0.5 M LiI, 0.05 M I_2 and 0.5 M-*tert*-butyl pyridine in methoxypropionitrile (MPN). The Pt coated counter electrodes were prepared by spreading a drop of 10 mM H_2PtCl_6 in 2-propanol on the FTO glass and heating it at 400 °C for 20 min under air ambient. The dye-adsorbed TiO_2 electrodes (active area 0.16 cm^2) were assembled using thermal adhesive films (Serlyn, thickness: 50 μm) into the Sandwich-type cell with a counter electrode. A drop of electrolyte solution was injected into the cell through one of two small holes drilled in the counter electrode by capillary action. Then, the holes were sealed using Serlyn and a cover glass. A control sample was prepared by incorporating a PEG surfactant (M_n: 8000, 20 wt% versus TiO_2 weight) into the TiO_2 paste. In this process, the thermal treatment was carried at 450 °C for 30 min under air ambient.

Electrochemical experiments were conducted in a three-electrode potentiostatic system with nanostructured TiO_2 electrodes (geometric surface area 1 cm^2) as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. Then, prior to the electrochemical experiment, a nanostructured TiO_2 film was heated in an oven at 80 °C for 10 min to remove the adsorbed moisture and organics. The electrolyte consisted of 0.2 M $LiClO_4$ solution buffered with 0.02 M K_2HPO_4/KH_2PO_4 (pH 6.4) [25]. Nitrogen bubbling was needed to remove the oxygen present in the electrolyte, which would otherwise influence the potential of the redox reaction, by acting as an oxidizer [26]. To reach equilibrium in the cell, the applied voltage (+0.8 V) was kept constant for 5 min. Then, the potential was scanned from this potential (+0.8 V) to a negative potential (−0.8 V). A scan rate of 5 mV/s was applied.

X-ray diffraction (JOEL 8030) was used to confirm the crystalline phase of the nanoporous TiO_2 film. This was performed with a target voltage and current of 50 kV and 80 mA, respectively, using Cu Kα radiation with an average wavelength of 1.5406 Å. In addition, X-ray photoelectron spectroscopy (XPS) (PHI 5200 mode) was performed to investigate the reactivity between the oxygen originating from the TiO_2 nanoparticles and the incorporated carbon element using an Al Kα X-ray source in an UHV system with a chamber base pressure of $\sim 10^{-10}$ Torr. High-resolution transmission electron microscopy (HR-TEM) (JEOL JEM-2010) was used to study the surface morphology of the modified TiO_2 nanoparticles using an electron microscope operating at 200 keV. To investigate the chemical composition of the modified TiO_2 film, an electron probe microanalysis (JOEL JXA-8900R) was conducted using a qualitative method, and this allowed the absence or presence of remnant carbon elements in