

**HIGHLY EFFICIENT DYE-SENSITIZED SOLAR CELLS BASED ON THE
DISCHARGED TiO₂ NANOPARTICLES**

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Keywords: solar cells, nanoparticles, absorption, transparency

In the past decade, intensive studies have been carried out on the dye-sensitized solar cells (DSSC) because of their high energy conversion efficiency [1]. An efficiency of 10.4% was obtained using a black dye [2] as sensitizer and recently higher efficiency of 11.04% was achieved with modified redox electrolyte [3]. The nanocrystalline mesoporous TiO₂ film is a basic component of DSSC. The fabrication procedure of TiO₂ photoelectrodes includes a synthesis of nanoparticles of a certain size and a crystal structure, deposition of the nanoporous films on the transparent conductive substrates, and activation of the nanoparticles for the dye absorption. Since the performance of the mesoporous solar cells is strongly linked with the interconnection of nanoparticles and their surface activity [4-6], organic binders are usually added to the concentric TiO₂ gel for increasing the viscosity of the colloid and the interconnection of nanoparticles in the films, and the surface treatment was applied for the activation of nanoparticles. However, the viscosity can be increased not only by adding the organic binders but also by changing the pH of the colloid [7]. The slurry is the most viscous at the point of zero charge (PZC) of nanoparticles [7] and the PZC for anatase TiO₂ is at pH 6.2 [8]. The TiO₂ nanoporous films for dye-sensitized solar cells (DSSC) have recently been fabricated at low temperatures by adding the basic ammonia to the binder-free acidic gel [9]. However, the authors achieved the maximum pH 3.6 of the TiO₂ slurry, which is still so far from the charge of the PZC of TiO₂ anatase.

Here we report on the new simplified fabrication technique of highly activated nanocrystalline TiO₂ photoelectrode consisting of discharged TiO₂ nanoparticles. The ammonia hydroxide was used for discharging TiO₂ nanoparticles to reach pH 5 of TiO₂ colloid. AFM and XRD analysis reveals high porosity of the TiO₂ films and the anatase crystal structure of the TiO₂ nanoparticles. The analysis of absorption spectra shows the high transparency of TiO₂ multilayer

photoelectrodes. A conversion efficiency of 9.5 % was achieved on the solar cells based on N719 absorbed TiO₂ photoelectrodes by simulating AM 1.5 solar light (100 mW/cm²).

Experimental: The photoelectrodes were composited from the transparent conductive SnO₂:F(FTO) films deposited on glass which was covered with the nanocrystalline TiO₂ dense thin film followed the nanoporous TiO₂ thick film.

TiO₂ nanoparticles synthesis: The amorphous TiO₂ nanoparticles were synthesized by the sol gel method using titanium alkoxide as the titanium source [10, 11]. The slurry was acitified by HNO₃, which became a translucent blue-white liquid with pH between 0.95-0.98. To complete the peptization, the translucent liquid was heated at 80°C in the oil bath for 8 hours under stirring. The resultant suspensions were treated hydrothermally at 200°C for 12 hours. This autoclaving conditions gave rise to average nanoparticles size of 20 nm. The amorphous TiO₂ nanoparticles were separated from the solvent by centrifuge.

Dense nanocrystalline film deposition: The nanocrystalline TiO₂ films were deposited by a spray pyrolysis method using chromatographic atomizer as described earlier [12]. The titanium acetylacetonate (TAA) precursor was prepared by mixing 0.1M of titanium tetra-isopropoxide and 1.2M acetylacetone AcAc in ethanol. The deposited films were annealed at 500°C for 30 min in the air to complete crystallization of TiO₂ nanoparticles and to remove the remaining organic traces.

Nanoporous electrode fabrication and dye absorption: The pH of the slurry was changed from 2.6 to 5 by adding 0.01M to 0.06M NH₄OH to the centrifuged acidic resultant. The TiO₂ slurry was carefully stirred and immediately printed by doctor-blade technique on the

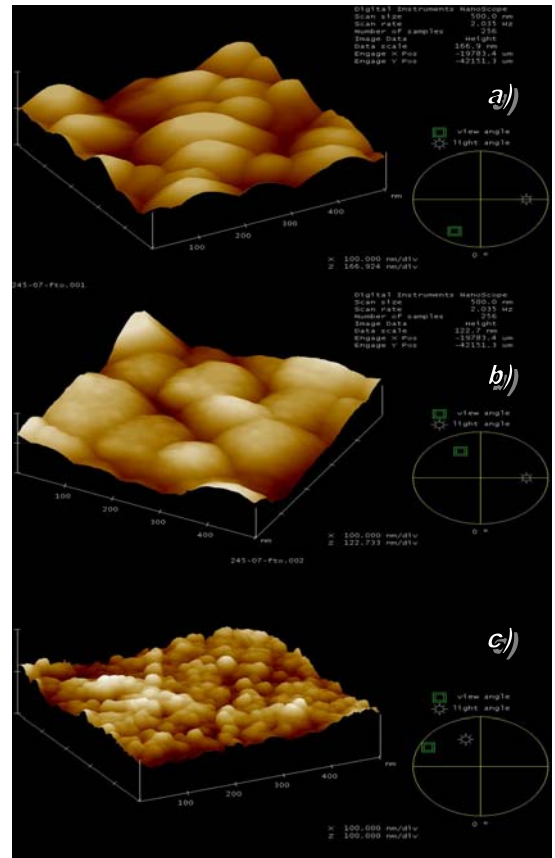


Fig. 1. AFM surface images of a) bare FTO film, b) TiO₂ dense film on the FTO collapses, c) TiO₂ mesoporous film surface image fabricated by doctor-blade technique, followed the at 500°C for 15 min.

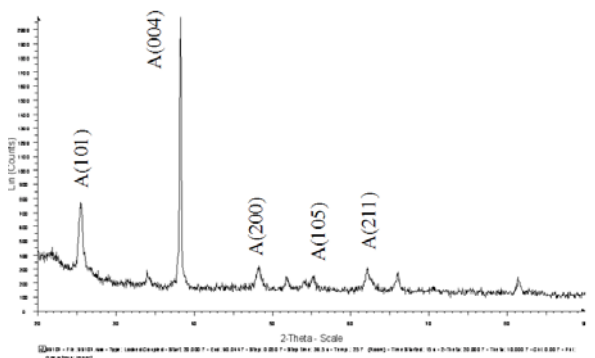


Fig. 2. X-ray diffraction patterns of the TiO₂ nanocrystalline film deposited on the FTO substrate.

substrates covered with the TiO₂ nanocrystalline dense films. After letting to dry in the air for 1 hour, the films were gradually annealed at 500°C for 15 min. The annealed TiO₂ electrodes were cooled down to room temperature and immersed into 0.5 mM D719 dye (Solaronix) in acetonitrile, tertbutanol 1:1 v/v solution for 4 days.

Imaging analysis and characterization: The crystallinity and the phase composition of the TiO₂ nanocrystalline films were examined with Bruker-D8 X-Ray powder diffractometer using CuK_α irradiation. The size of the particles and the morphology of TiO₂ film surface were studied by AFMD3100 Atomic Force Microscope.

The absorption spectra of the multilayer photoelectrodes were investigated with a Varian Cray 50 spectrometer.

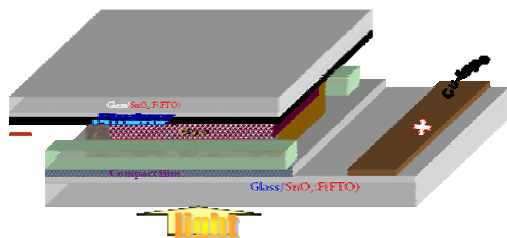


Fig. 3. Dye sensitized solar cell device assembly.

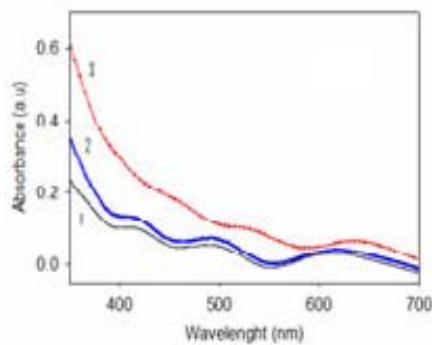


Fig.4. Optical absorption spectra of the FTO and TiO₂ films: 1-bare FTO film, 2-FTO/dense TiO₂ film/mesoporous film multilayer, 3-FTO/dense nanocrystalline TiO₂ film.

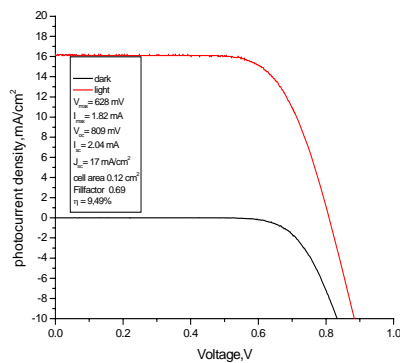


Fig. 5. I-V characteristics of the DSSC's based on the nanocrystalline TiO₂ film fabricated from colloid with pH5.

The current-voltage characteristics of photoelectrodes and solar cells were measured by using Kethley 2440 sourcemeter. An AM 1.5 solar simulator (YSS-50, Yamashita Denso) with a 1000 W Xe lamp was employed as the light source. A calibrated Si cell was used as a reference.

Solar cell assembly: The dye-adsorbed TiO₂ photoelectrodes and the Pt counter electrodes were assembled into sandwich-type cells as shows in Fig. 3. A 60µm-thick polyethylene spacer was used to separate the TiO₂ electrode from Pt counter electrode. The space between the electrodes was filled with the redox electrolyte consisting of 0.6 M 1-Butyl-3-methylimidazolium iodide BMPImI (Merck), 0.1M Guanidinium thiocyanate NH₂C(NH)NH₂HSCN, and 0.03M I₂ in acetonitrile and valeronitrile v/v 4:1 with 0.5M 4-tert-butylpyridine TBP.

Discussion and conclusion: Dense thin nanocrystalline TiO₂ films usually grow to prevent electrical connection of the liquid I⁻/I₃⁻ redox electrolyte with the n-doped FTO conductive electrode. AFM images reveal that after 5-6 consecutive spraying cycles of the TAA diluted

solution on the FTO film, the dense packed layer of TiO₂ nanoparticles fully covers the surface

of the FTO collapses. Figure 1 shows FTO film surfaces before and after spraying of TAA. The size of TiO₂ nanoparticles covering the FTO collapses, shown in Fig. 1b, is seen to be varying 15-30 nm. The average size of nanoparticles in the mesoporous TiO₂ films that coats dense TiO₂ films is 20 nm (Fig. 1c).

XRD analyses show (Fig. 2) the increase in the anatase peaks for the films fabricated from the discharged nanoparticles, when pH of the colloid was 5. The increased intensity of the peaks can be attributed to the co-orientation of the nanocrystallites in the films annealed at higher temperatures. The transparency of the FTO substrates shown in Fig. 4 (black line), is seen to be a little reduced after covering it with the nanocrystalline TiO₂ dense layers (Fig. 4-red line). However, the next deposition of the nanoporous thick TiO₂ film on the dense film is seen to restore the transparency (Fig. 4-blue line) of the photoelectrodes. Figure 5 shows the photocurrent-photovoltage dependence of the DSSC based on the nanocrystalline TiO₂ film fabricated from the colloid with pH5. The parameters of the cells are: open voltage $V_{oc} = 809$ mV, photocurrent density $J_{sc} = 17$ mA/cm², fill factor 69% and conversion efficiency $\eta = 9.5\%$, cell area 0.12 cm² with thicknesses of TiO₂ photoelectrode 18 μ m.

In conclusion, we successfully fabricated the mesoporous nanocrystalline TiO₂ photoelectrodes composited the discharged nanoparticles. Ammonia hydroxide was used for the discharging of TiO₂ nanoparticles. ~9.5% high conversion efficiency was achieved based on these TiO₂ photoelectrodes, and the nature of the TiO₂ nanoparticles in the mesoporous film caused the performance of the DSSC. In addition, this technique simplified the fabrication by avoiding some standard procedures such as adding the binder, treating the nanoporous TiO₂ surfaces, and immersing the hot electrodes into the dye.

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