A novel hybrid nanocrystalline TiO$_2$ electrode for the dye-sensitized nanocrystalline solar cells

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The dye-sensitized nanocrystalline solar cells have been extensively studied throughout the last decade, in attempts to make efficient low cost alternatives to the silicon solar cell [1–3]. As the heart of this device, the use of mesoporous nanocrystalline films of the semiconductor increases considerably the effective surface area for dye adsorption [4]. They are typically fabricated by metal oxide nanopowders 5 to 100 nm in size to yield an inter-connected, porous structure [5]. TiO$_2$ is widely used as semiconductor material in dye-sensitized nanocrystalline solar cells, which have achieved solar to electrical energy conversion efficiencies of up to 10.4%, owing to its favorable energetic stability, low price and simple processing [6, 7]. Recently, we reported a hybrid nanocrystalline TiO$_2$ electrode containing a sputter deposited layer and a nanocrystalline TiO$_2$ layer, which exhibited higher energy conversion efficiency than pure sputtering deposited film electrode and larger short-circuit photocurrent even than the sandwich electrode containing a compact layer prepared by sol-gel method [8]. However, the photocatalyze activation is strongly affected by the structure and component of nanocrystalline TiO$_2$ films. The preparation of nanocrystalline films involves controlled hydrolysis of a Ti(IV) salt, which is usually an alkoxide such as Ti-isopropoxide or a chloride followed by peptization [9]. In our work, we exploited a novel nanometer TiO$_2$ powders hydrolyzing from titanyl nitrate, which shows regulable size, controllable crystallite phase, thermal stabilization and very low cost [10].

In this letter, we report the photoelectric behavior of the hybrid nanocrystalline TiO$_2$ electrode sensitized by bis(thio-cyanato)-2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) (known as the N3 dye, purchased from Solaronix of Switzerland) based on these nanometer powders.

The powders of TiO$_2$ I (26 nm, BET 57 m^2/g) and TiO$_2$ II (26 nm, BET 57 m^2/g) were prepared by hydrolysis of titanyl nitrate according to the patent [10]. As shown in Table I, The X-ray diffraction (XRD) patterns of the TiO$_2$ powders indicates that the percentage of anatase is approximately 71% for TiO$_2$ I and 100%

TABLE I. The characters of the typical nanometer TiO$_2$ powders. The contents of anatase were calculated by X-ray, the dimension of the particles were estimated by TEM, the specific surface area of the TiO$_2$ nanoparticles were measured GEM INI 2360 with BET

	Content of Anatase (%)	The mean size (nm)	BET (m^2/g)
TiO$_2$ I	71	26	57
TiO$_2$ II	100	26	57

for TiO$_2$ II. However, the proportion of anatase to rutile of the TiO$_2$ did not change in the process of experiment.

The hybrid TiO$_2$ electrode containing two layers was fabricated as following: The sputter deposited layer was deposited by reactive DC magnetron sputtering in different substrate temperature and different times on the conducting layer of TCO glass. The target is a titanium metal (purity 99.99%) of 6 cm diameter. The deposition rate of the film is about 2 nm· min^{-1}. Another nanocrystalline layer of TiO$_2$ thin films was prepared by the method described below: [11] TiO$_2$ powders were ground in an attritor mill with ethanol containing acetylacetone for 1 h. Then more ethanol and Triton X-100 were added and continuously ground for 3 h. The conducting TCO glass was covered on two parallel edges with adhesive tape (about 40 μm thickness) to control the thickness of the TiO$_2$ film and to provide non-coated areas for electrical contact. Shaking the solution of the TiO$_2$ adequately to produce tentatively a favorable commix, and then the suspension was applied onto the TCO glass by the doctor blade technique at 30 °C. After air-drying, the TCO glass coating TiO$_2$ film was immerged into dry ethanol for 10 min to improve the properties of the nanocrystalline films. Later, it was dried with hot air and then fired for 30 min at 450 °C in air. Coating of the TiO$_2$ surface with dye was carried out by soaking the film for 5 h in a solution of N3 dye in dry ethanol.

Fig. 1 shows the surfaces of these nanocrystalline films obtained by scanning electron microscope (SEM) at different magnifications. The low-resolution image

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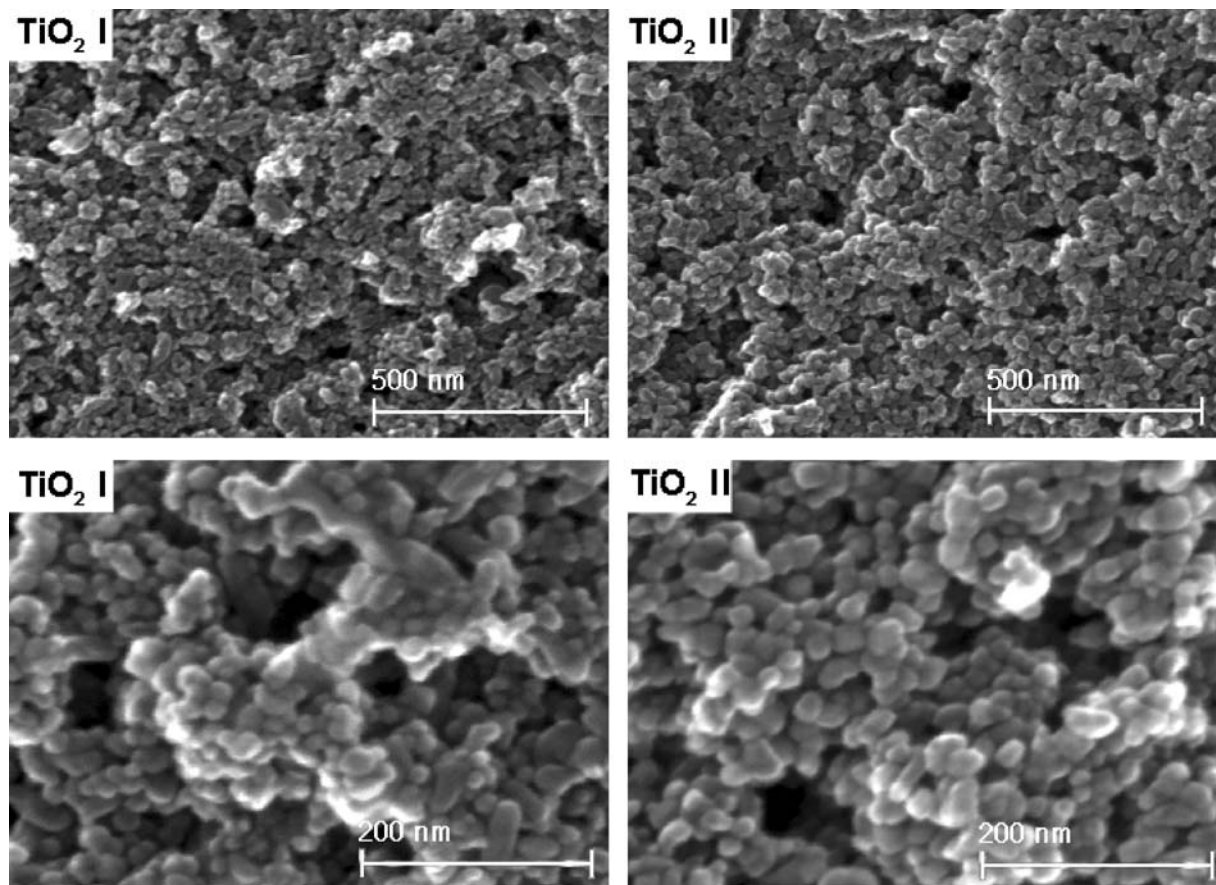
Figure 1 Scanning electron microscope pattern of nanocrystalline films based on different TiO_2 powders.

confirms that the heterogeneous but porous nanocrystalline films were obtained. High resolution (the bottom patterns) reveals clearly the TiO_2 films to be composed of a three-dimensional network of interconnected particles having an average size of approximately 26 nm. Apparently, significant particle growth occurs during the process. These results also indicate that larger surface area of these films can be obtained, which is availability for the deposition of a monolayer dye.

The roughness factor of the nanocrystalline TiO_2 thin films was calculated through the amount of N3 dye absorbing in the TiO_2 films. Due to its unmatched performance in dye staff studied as sensitizer in dye-sensitized nanocrystalline solar cells, this dye has been investigated extensively. The TiO_2 films absorbed the dye of N3 with monolayer was immersed into the solution of 0.5 M sodium hydroxide for about 3 h. UV-visible spectrophotometer was recorded and the number of N3 in the solution was calculated through the optical density of the solution at 306 nm. As each dye molecule occupies an area of 1 nm^2, the inner surface of the films with 1 μm thickness is 86, 80 cm^2 for each 1 cm^2 of geometric surface for TiO_2 I and TiO_2 II, respectively. However, a cubic close packing of the same mean size about 26 nm spheres could be expected to produce the same fold increase in the surface area of the films. The different results could be attributed to the effect of the different crystalloid in TiO_2 powders.

Photoelectrochemical experiments was performed in a two-electrode-system [11] with the Model 2400 Digital SourceMeter (Keithley Instruments Inc., USA), which employed the dye sensitized TiO_2 film incorporated into a thin-layer sandwich-type solar cell. A reflecting counter electrode platinum plate (purity 99.95%) was employed. The counter electrode was placed directly on the top of the dye coated TiO_2 film. Both electrodes were clamped tightly together. A thin layer of electrolyte was permeated into the interelectrode space by capillary forces. The dye coated TiO_2 film was illuminated through the conducting glass support. The conversion efficiencies we reported here are overall yields, which are uncorrected for losses due to light absorption and reflection by the conducting glass support. An Oriel 500-W Xe lamp served as a light source in conjunction with a GG420 filter to remove ultraviolet radiation. The Prinz Optics IR-3 filter was placed in the light beam to simulate AM1.5-type solar emission. A FZ-A irradiatometer (the Optical Co. of Beijing Normal University, Beijing) was used, giving practically identical result.

Fig. 2 shows typical graphs of photocurrent density versus voltage for the photoelectrochemical cells based on the hybrid nanocrystalline TiO_2 electrodes sensitized by N3 under illumination by standard AM1.5 solar light with intensity of 98 mW/cm^2. The highest characters of the photoelectrochemical cells are observed in the hybrid nanocrystalline electrode containing TiO_2 I nanocrystalline layer, which exhibits the light-to-electric energy conversion efficient $\eta = 6.8\%$, short-circuit photocurrents density $J_{sc} = 19.4$ mA/cm^2, open-circuit photovoltage $V_{oc} = 652$ mV, and fill
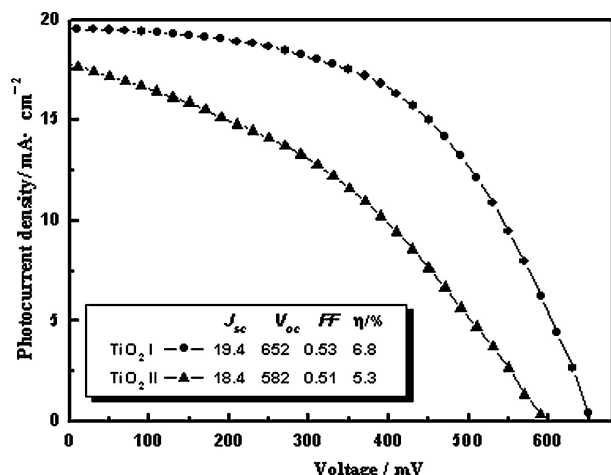
Figure 2 Typical graphs of photocurrent density versus voltage for the photoelectrochemical cells based on the hybrid nanocrystalline TiO_2 electrodes sensitized by N3. Effective area for illumination is 0.5 cm^2. The thickness of the sputter deposited layer and the nanocrystalline layer are 20 nm, 6 μm, respectively. Conditions: electrolyte, 0.5 M LiI + 0.04 M I_2 in propylene carbonate (PC), room temperature, light intensity 98 mW/cm^2, AM1.5 spectral irradiance. Inset: Performance parameters of solar cells.

factor $FF = 0.53$. This indicates that the hybrid electrode prepared by TiO_2 I powders exhibits competitive activation and the cell with this exhibits larger energy conversion. This result was closed to reported [11]. In fact, the photoelectrochemical cell based on the hybrid nanocrystalline TiO_2 electrode containing TiO_2 II nanocrystalline layer exhibited low set of parameters, which are η=5.3%, $J_{sc} = 18.4$ mA/cm^2, $V_{oc} = 582$ mV, FF=0.51. The difference could be attributed to the smaller quantity of N3 in the surface of films and the difference of crystalloid in TiO_2. This indicates that the hybrid nanocrystalline electrode containing a small quantity of rutile is more appropriate for the light-to-electric energy conversion than that of the pure anatase.

In conclusion, two kinds of cheap nanometer TiO_2 powders hydrolyzing from titanyl nitrate containing different content of anatase were used in the hybrid nanocrystalline TiO_2 electrode. Scanning electron microscopy pattern exhibits TiO_2 layers composed of a three-dimensional network of interconnected particles. The photoelectric behaviors of the hybrid electrodes indicate that the photoelectrochemical cells based on TiO_2 powders containing with 71% anatase exhibit larger energy conversion (6.8%), which is higher than that of the electrode composed of the pure anatase. These results also indicate that the cheaper and controllable nanometer TiO_2 powders we used here are available materials for the dye-sensitized nanocrystalline solar cells.

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