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A Novel Nanocrystalline TiO_2 Thin Film Electrodes Prepared at Low Temperature

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Abstract: Nanocrystalline TiO_2 thin films were successfully prepared by a new "water-cooked" method on both conductive glass substrates and flexible substrates at low temperature. Dye-sensitized solar cells based on these films have exhibited high overall light-to-electricity conversion efficiencies of 4.67 % and 1.94 % on conductive glass substrate and flexible substrate, respectively, under the illumination at 100 mW/cm^2.

Keywords: Tetrabutyl titanate, low temperature synthesis, nanocrystalline TiO_2 dye-sensitized solar cells, flexible solar cells.

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 thin film electrodes have been attracting a lot of interests due to high energy conversion efficiencies and low production cost[1-3]. Nanocrystalline TiO_2 thin film electrodes are commonly prepared by coating TiO_2 colloid with organic additives on conductive glass substrates and annealing at high temperature of 450℃-500℃ to remove organic additives and connect TiO_2 particles to form mechanically stable film. However, use of glass substrates with heavy weight and frangibility limits manufacture process and practical application of DSSCs. Therefore, flexible DSSCs have attracted much attention[4-6]. Flexible substrates have advantages over glass substrates, *e. g.* lower weight, non-breakable and easy integrity[7]. But flexible electrodes could not withstand high temperature above 150℃[8]. Some efforts have been made to overcome this problem such as using low temperature annealing[9], mechanical compressing of crystalline particles[8, 10] and chemical deposition[11]. However, such prepared electrodes exhibited larger inherent resistance[6]. Recently, D. S. Zhang *et al.* reported a novel method based on hydrothermal crystallization at the solid / gas interface to prepare nanocrystalline TiO_2 film[7]. The conversion efficiency of the cell prepared on glass substrates was 4.2 %. However, this method needs special devices and take long reaction time of about 12 h[7].

In this work, we have developed a new "water-cooked" method to prepare nanocrystalline TiO_2 thin film electrodes at low temperature and optimized Ti (Ⅳ) precursors and the solvents. The used precursor could not damage flexible substrates.

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The DSSCs using these electrodes exhibited high light-to-electricity conversion efficiencies.

0.8 g of commercial nanocrystalline TiO_2 powder (Degussa P25 70 % anatase and 30 % rutile) was mixed with 3.6 g of a 1 mol/L *n*-butanolic solution of tetrabutyl titanate [$Ti(OC_4H_9)_4$] and stirred in a closed glass container for about 2 h to obtain a paste of appropriate viscosity. The raw films were produced by coating the paste with doctor-blade method on the glass substrates (FTO, square resistance: 30 Ω/cm^2, Heilongjiang Hake New Energy Co. Ltd.) and on the flexible substrates (PET/ITO, square resistance: 90 Ω/cm^2, Shenzhen Angzhi Film Technology Co. Ltd.) and then dried at room temperature. The raw films can be treated either by hydrothermal method[7] or cooked in a container full of water at 100℃ for 4 h.

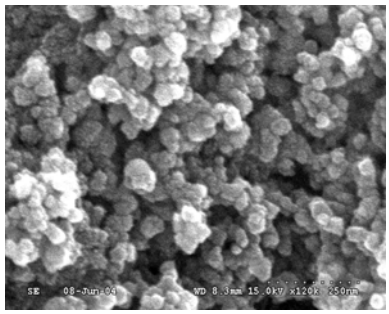
The raw and treated films were heated at 100℃ for 1 h, then immersed in a 5×10^{-4} mol/L ethanol solution of $Ru(dcppy)_2(NCS)_2$ (dcbpy: 2,2′-bipyridine4, 4′-dicarboxylic acid) dye overnight at room temperature. The dye loading of the films were measured according to the referenced literature[12]. The cells employed dye adsorbed films as the working electrodes and platinum foils as the counter electrodes to assemble the sandwich DSSCs. The electrolyte was consisted of 0.5 mol/L LiI, 0.05 mol/L I_2 and 0.5 mol/L *tert*- butylpyridine in methoxypropionitrile. I-V curves of the cells were measured with Potentiostat / Galvanostat Model 273 (EG & G) under the light intensity at 100 mW/cm^2 by halogen tungsten lamp, and the active area was 0.2 cm^2. The surface morphology of the films was observed by a Hitachi S - 4300F field scanning electron microscope. The thickness of the films measured by thickness meter (LG-1) was about 9 μm.

The photovoltaic performances of the cells based on the raw and treated films were shown in **Table 1**. Different from the films reported in the literature[12], our raw films have good mechanical stability and non-solubility in water, ethanol and electrolyte, which is very beneficial to “water-cooked” treatment. The cell based on the raw film thus still exhibited good performance of 3.17 % conversion efficiency. However, the cell performances were obviously improved by treating the raw films. The highest conversion efficiency of 4.67 % has been achieved for the cell based on the film treated by “water-cooked”. The difference of the efficiency arises mainly from that of V_{oc} and I_{sc}. The V_{oc} of the cell with “water-cooked” film dramatically increased about 60 mV comparing to that of the cell with untreated raw film or hydrothermally treated film. It implied that amorphous hydrolysis products of tetrabutyl titanate in the raw films could be recrystallized during “water-cooked” treatment. Moreover, this recrystalization could easily take place on the defects and surface states of the films, which could reduce the back reaction at defects and surface states and therefore increase V_{oc}. The great increase of the I_{sc} for the cell with “water-cooked” films may be attributed to the increase of dye loading and good electric connection between TiO_2 particles as well as between TiO_2 particles and substrates.

Table 1 Photovoltaic performances and the dye loading of the TiO_2 films on glass substrates treated by the different methods.

treatment method	I_{sc}/mAcm^{-2}	V_{oc}/V	FF	η /%	Dye loading/molcm^{-2}
no treatment	6.30	0.68	0.74	3.17	1.1×10^{-7}
hydrothermal	7.15	0.68	0.75	3.67	1.2×10^{-7}
water-cooked	8.60	0.74	0.73	4.67	1.8×10^{-7}

Figure 1 SEM picture of TiO_2 film prepared from P25 + Ti $(OC_4H_9)_4$ on FTO after "water-cooked" treatment.

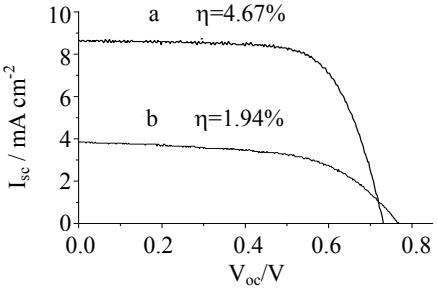


As seen from the SEM image in **Figure 1**, the film after "water-cooked" treatment was consisted of particles about 20 nm and highly porous so that more dye molecules could be absorbed (see **Table 1**). At the same time, the electrolyte can easily penetrate into the TiO_2 film.

Based on the high performance of the cell with TiO_2 films treated by "water-cooked", this treatment was also applied to PET/ITO substrates. I-V curves of the DSSCs with FTO and PET/ITO substrates were presented in **Figure 2**. The cell with PET/ITO substrates showed lower I_{sc}, FF and higher V_{oc}. The decrease of I_{sc} was caused by slower charge transport between PET/ITO substrates and TiO_2 thin film. The slower transfer rate of the electrons between PET/ITO substrates and the electrolyte decreased charge recombination, resulting to the higher value of V_{oc}. The higher resistance of PET/ITO substrates obviously decreased FF of the cell. Therefore, the conversion efficiency of the cell based PET/ITO was lower than that of the cell on FTO. The performance improvement of the flexible cells has been making based on the present results.

The optimization of Ti (Ⅵ) precursors and the solvents have made TiO_2 films strong enough to withstand the "water-cooked" treatment. The "water-cooked" treatment method was proved to be a low-cost, less time-consuming, successful and convenient method to produce nanocrystalline TiO_2 electrodes at low temperature. The recrystallization process during the "water-cooked" treatment may play an important role in improving the photovoltaic performances of the cells.

Figure 2 I-V curves of the DSSCs based on "water-cooked" TiO_2 electrodes prepared on FTO (a) and PET/ITO (b) at illumination of 100 mW/cm^2.



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