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Preparation of dye sensitized titanium oxide nanoparticles for solar cell applications

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ABSTRACT

A new method for synthesis of titanium dioxide (TiO_2)-dye nanoparticles is reported. TiO_2 nanocrystals were obtained at 150 and 200 °C by using chemically bonded TiO_2-sensitizer dye as a precursor. Titanium tetraisopropoxide was first modified with a dye molecule and then precipitated by dropping into acidic water. A strongly colored precipitate was obtained. Hydrothermal growth of a colloidal solution was carried out in a Teflon-lined stainless steel autoclave. Dye sensitized solar cell efficiencies obtained were comparable and fill factor values were close to the analogous cells prepared by the use of conventional TiO_2 paste techniques. This method allows the use of different substrates together with nanocrystalline TiO_2 for many technological applications.

1. Introduction

Nanocrystalline titanium dioxide (TiO_2) has widespread application in solar energy conversion [1–13]. In particular, dye-sensitized solar cells (DSCs) using mesoporous TiO_2 electrodes are regarded as a promising alternative to silicon-type solar cells because of their low-cost fabrication [1,14]. In order to obtain mechanically stable, uniform, and conductive porous thick films, sintering of TiO_2 paste that contains organic additives, at temperatures ranging from 450 °C to 500 °C is neccessary. An organic binder is used to increase the viscosity of the TiO_2 paste in order to enable the formation of TiO_2 films. High sintering temperatures must be then used to remove the organic binder [15] which increase the production costs and limit the choice of substrates. One of the ways to overcome these problems is try to reduce the annealing temperature [16,17]. Low temperature production allows using polymer substrates to fast and inexpensive roll-to-roll process and reduces the energy consumption.

A variety of methods have been reported that attempt to avoid the use of high sintering temperatures in the production of TiO_2 films, including: adjustment of the viscosity of TiO_2 colloid solution ammonia amount [18]; microwave irradiation of TiO_2 films [19]; mechanical pressing [14,20,21]; hydrothermal preparation of mesoporous TiO_2 films using a solution of TiO_2 powder in ethanol [16]; spin-coating with hydrothermally prepared TiO_2 colloids [22]; utilizing organic/inorganic nanocomposite gels [15]; and electrophoretic deposition of TiO_2 nanoparticles using a solution of TiO_2 dispersed in different solvents [23].

However, preparation of binder-free TiO_2–dye hybrid paste has not been reported yet. Herein, we report the synthesis of TiO_2–dye nanoparticles and producing of a binder free TiO_2 paste. TiO_2 particles were first modified by tethering dye molecules to its surface. Its deposition on the substrate surface was controlled by adjusting the amount of acid. The morphology and photovoltaic properties of TiO_2 films prepared using this procedure are compared to analogous films prepared using conventional techniques.

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2. Experimental section

2.1. Materials and measurements

All chemicals were of the highest purity available and were used as received. Titanium tetraisopropoxide (TTIP, 99.99%) and 4-tert-butylpyridine (TBP) were purchased from Aldrich. $[Ru(dcbpy)_2(NCS)_2](Bu_4N)_2$ (dcbpy=4,4′-dicarboxy-2,2′-bipyridine) (N719) was obtained from Solaronix (Fig. 1a). The thermoplastic polymer, Surlyn-1702 was from DuPont Co. All solvents used were of analytical grade and purchased from Aldrich.

The current–voltage characteristics of samples were performed using KEITHLEY 2400 sourcemeter and Labview data acquisition software under simulated sunlight (AM 1.5 filter, 100 mW/cm^2). The powder X-Ray diffraction pattern of the TiO_2 was analyzed with an X-Ray diffractometer (Philips X′Pert Pro X-Ray Diffractometer, CuKα radiation). Atomic force microscopy (AFM) studies were performed by using Digital Instruments Dimension 3100 in tapping mode. Scanning electron microscopy (SEM) image was acquired using a Zeiss/Supra 55 FE-SEM, and the sample was platinum coated prior to FE-SEM measurements. The films were prepared on transparent conducting oxide (TCO) glass substrates by doctor blade technique and their thicknesses were measured by Ambios XP-1 high resolution surface profiler. Fluorine-doped tin oxide (FTO) (13–15 Ω/sq) coated glass was used as the TCO glass substrate and was kindly provided by Şişecam.

2.2. Preparation of nanoparticles

2.2.1. Preparation of nanocrystalline anatase TiO_2–dye hybrid film (A)

The procedures herein used were previously described in patent application [24]. In a typical preparation of nanoporous TiO_2–dye hybrid paste, TTIP was used as the TiO_2 particle precursor. The commercially available N719 was used as the sensitizer. A 5 mM solution of sensitizer dye was prepared in 0.2 mol dry isopropyl alcohol under inert atmosphere. 0.1 mol TTIP was added to the dye solution under vigorous stirring. The precursor solution was stirred in closed flask for 30 min to achieve a bridge formation (possible chelate, unidentate and/or bidentate formations) between TTIP and N719. The precursor solution was added dropwise to a 10 mol H_2O and a 1 mol acetic acid mixture in an ice bath under vigorous stirring. A strong viscous red-purple colored precipitate was immediately formed. The suspension was stirred for an additional 30 min in order to achieve complete hydrolysis. For peptization, the sol was refluxed at 80 °C for 4 h, and afterward, strongly colored homogeneous TiO_2–dye sol was obtained. The peptized sol was placed in a polytetrafluoroethylene (PTFE) equipped autoclave for hydrothermal crystal growth process. The sample was heated at a temperature of 150 °C or 200 °C for 12 h. It also should be noted that according to previous study these dyes are thermally stable up to 250 °C [25]. The code numbers of samples for different crystal growth temperatures and film thicknesses are summarized in Table 1.

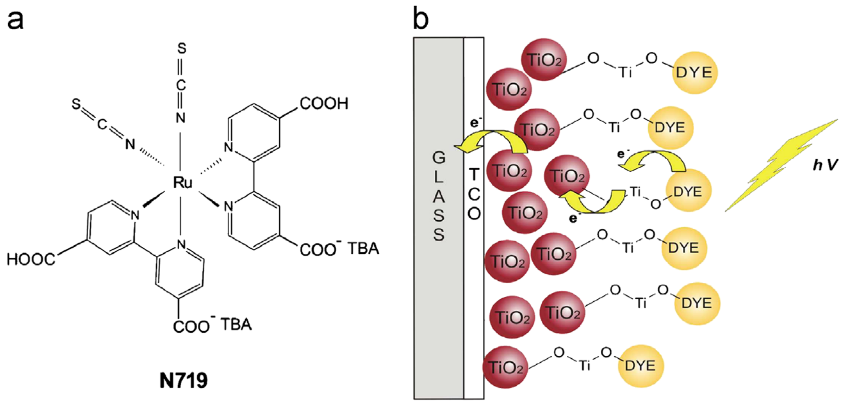

Fig. 1. Molecular structure of the N719 (a), and schematic presentation of the chemically bonded sensitizer dye-nanocrystalline TiO_2 film supported on conducting glass (b).

Table 1
The cell efficiencies and code numbers of samples prepared in different thicknesses and crystal growth temperatures.

Sample code	Crystal growth temp (°C)	Film thickness (μm)	η (%)	V_{oc} (mV)	I_{sc} (mA/cm^2)	I_{mpp} (mA/cm^2)	V_{mpp} (mV)	FF
A1	150	2	0.045	0.44	−0.25	−0.15	0.30	0.41
A2	200	2	0.12	0.49	−0.56	−0.34	0.34	0.42
A3	200	6	1.38	0.66	−4.68	−3.71	0.38	0.45
B1	150	2	0.036	0.46	−0.19	−0.12	0.30	0.42
B2	200	2	1.60	0.63	−4.79	−3.76	0.43	0.53
B3	200	6	2.21	0.65	−5.67	−5.00	0.44	0.60