



Preparation of dye sensitized titanium oxide nanoparticles for solar cell applications



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ABSTRACT

A new method for synthesis of titanium dioxide (TiO₂)-dye nanoparticles is reported. TiO₂ nanocrystals were obtained at 150 and 200 °C by using chemically bonded TiO₂-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 TiO₂ paste techniques. This method allows the use of different substrates together with nanocrystalline TiO₂ for many technological applications.

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1. Introduction

Nanocrystalline titanium dioxide (TiO₂) has widespread application in solar energy conversion [1–13]. In particular, dye-sensitized solar cells (DSCs) using mesoporous TiO₂ 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 TiO₂ paste that contains organic additives, at temperatures ranging from 450 °C to 500 °C is necessary. An organic binder is used to increase the viscosity of the TiO₂ paste in order to enable the formation of TiO₂ 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 TiO₂ films, including: adjustment of the viscosity of TiO₂ colloid solution ammonia amount [18]; microwave irradiation of TiO₂ films [19]; mechanical pressing [14,20,21]; hydrothermal preparation of mesoporous TiO₂ films using a solution of TiO₂ powder in ethanol [16]; spin-coating with hydrothermally prepared TiO₂ colloids [22]; utilizing organic/inorganic nanocomposite gels [15]; and electrophoretic deposition of TiO₂ nanoparticles using a solution of TiO₂ dispersed in different solvents [23].

However, preparation of binder-free TiO₂-dye hybrid paste has not been reported yet. Herein, we report the synthesis of TiO₂-dye nanoparticles and producing of a binder free TiO₂ paste. TiO₂ 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 TiO₂ 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. $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2](\text{Bu}_4\text{N})_2$ (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/cm²). The powder X-Ray diffraction pattern of the TiO₂ was analyzed with an X-Ray diffractometer (Philips X'Pert Pro X-Ray Diffractometer, CuK α 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 TiO₂–dye hybrid film (A)

The procedures herein used were previously described in patent application [24]. In a typical preparation of nanoporous TiO₂–dye hybrid paste, TTIP was used as the TiO₂ 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 H₂O 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 TiO₂–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.

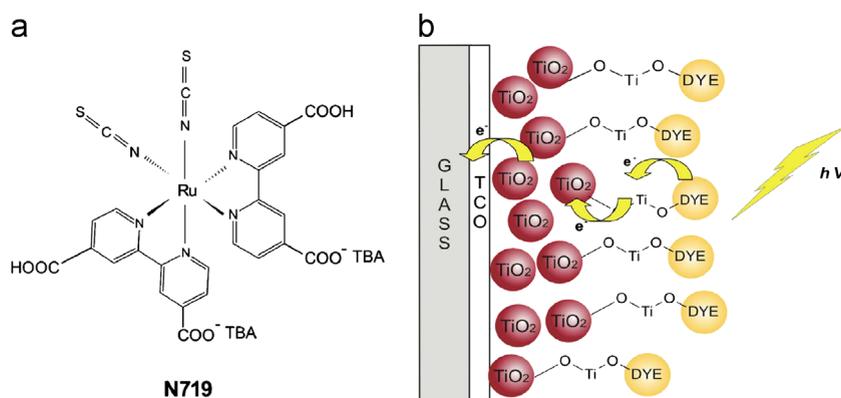


Fig. 1. Molecular structure of the N719 (a), and schematic presentation of the chemically bonded sensitizer dye–nanocrystalline TiO₂ film supported on conducting glass (b).

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

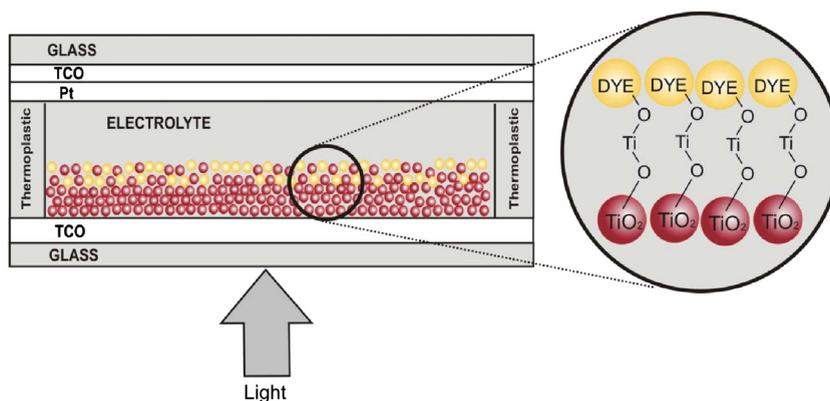


Fig. 2. An illustration depicting the structure of the dye sensitized solar cell. The cell consists of chemically bonded sensitizer dye-nanocrystalline TiO_2 film supported on FTO coated glass as the working electrode, platinum covered conducting glass as the counter electrode and I^-/I_3^- redox electrolyte as the hole conducting medium.

The sol was concentrated to 20% TiO_2 -dye (w/w). The obtained paste was centrifuged to allow solvent exchange; the water and acetic acid mixture was separated, and the precipitate was washed three times with ethanol. The final TiO_2 -dye concentration was adjusted to 15% (w/w). The obtained paste was coated onto the FTO coated glass substrates by doctor blade technique (Fig. 1b). The films were dried first at room temperature and later in the oven at 150°C for 3 h to remove water and acid residues. The obtained films were strongly colored.

2.2.2. Preparation of nanocrystalline anatase TiO_2 film (B)

Anatase nanocrystalline TiO_2 was prepared by the controlled hydrolysis of TTIP without modification with the sensitizer dye at the precursor state. 0.1 mol TTIP was mixed with 0.1 mol acetic acid to achieve a single side modification. All subsequent steps were identical to those described in Section 2.2.1. Two films with different thicknesses, $2\ \mu\text{m}$ and $6\ \mu\text{m}$, were prepared by adjusting the thickness of the spacer used for the doctor blade coating. Films were dried first at room temperature and later in the oven at 150°C for 3 h. Obtained TiO_2 films were sensitized with dye by immersing for 3 h in N719 solution in ethanol, than dried under inert atmosphere.

2.3. Preparation and characterization of DSCs

DSCs were prepared in sandwich geometry as described previously [26] using TiO_2 produced coated TCO glasses as the photoanode and thermally coated platinum TCO glass as the counter electrode (Fig. 2). For the preparation of physically adsorbed TiO_2 -dye films (B1, B2 and B3), nanocrystalline anatase TiO_2 films (B) were immersed in a 1 mM solution of N719 in 1:1 acetonitrile/tert-butyl alcohol overnight, followed by rinsing in ethanol to remove unadsorbed dye. TiO_2 -dye hybrid films (A) were not treated with the dye solution at this step (A1, A2 and A3). The space between the electrodes was filled with electrolyte containing the mixture of 0.5 M LiI, 0.05 M I_2 and 0.5 M TBP in 3-methoxypropionitrile. The cells

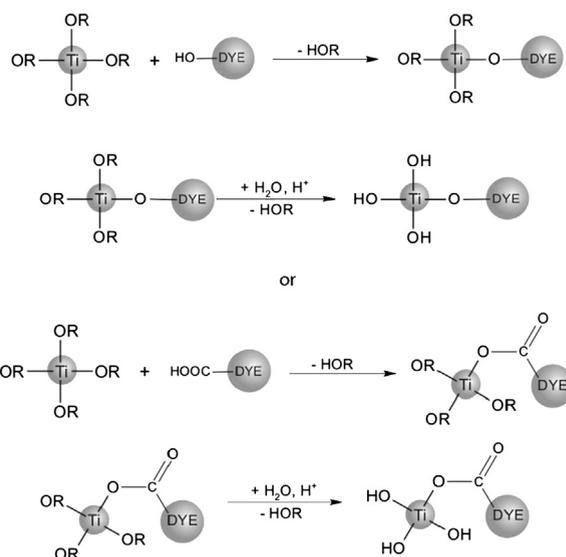


Fig. 3. Schematic presentation of binding reaction between sensitizer dye and TTIP.

were sealed using a commercial thermoplastic material, Surlyn-1702[®] (DuPont Co.).

3. Results and discussion

Dyes containing a carboxylate group can react with titanium alkoxides under the appropriate conditions. The resulting products are titanium-dye hybrid (chelate, unidentate and/or bidentate) formation and alcohol. After modification of the precursor, hydrolysis can be made with the acid and water mixture. As a result of this, colored titanium oxide precipitates immediately. The possible binding positions of carboxylate group on the TiO_2 surface has been studied in detail [27]. The assumed

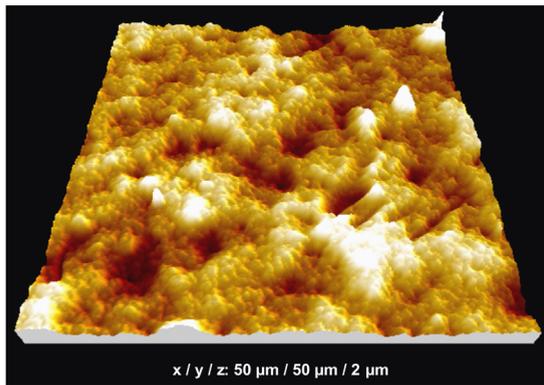
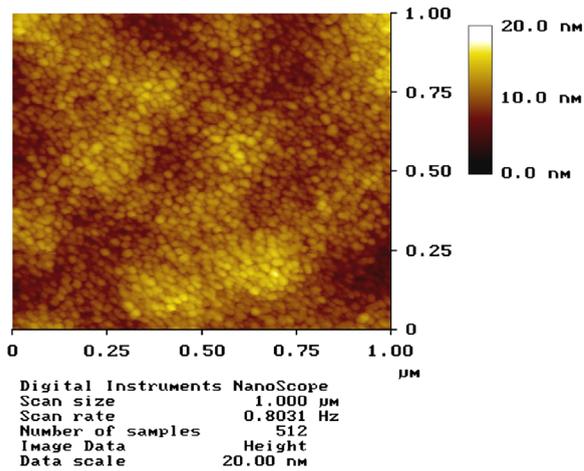


Fig. 4. AFM images of TiO₂-dye hybrid nanoparticles prepared at 200 °C temperature.

binding reactions for these kinds of dyes are presented in Fig. 3.

The morphology and size of TiO₂ nanoparticles obtained was examined using SEM, AFM and X-ray diffraction studies. SEM and AFM measurements demonstrate the sample obtained at 200 °C consists of individual particles, with average particle size of 20–30 nm (Figs. 4 and 5). Samples at earlier growth stages could not be investigated by AFM or XRD as they contained a significant fraction of amorphous material.

The X-ray diffraction pattern of TiO₂-dye hybrid nanoparticles prepared by hydrothermal crystallization is shown in Fig. 6. The XRD profile of fully grown TiO₂ nanoparticles can be indexed by the known standard TiO₂ anatase pattern. Notably, the characteristic line broadening of diffraction peaks points to nanosized crystalline domain. The grain size of the TiO₂-dye film was estimated from the most intensive peak (101) at $2\theta=25.28^\circ$ as 20 nm [26].

The photovoltaic properties of the solar cells were characterized by measuring current-voltage (*I*-*V*) curves in the dark and under white light illumination (simulated AM 1.5, 100 mW/cm²) through the FTO side. DSC performances of the cells prepared using a variety of different cell thicknesses and crystal growth conditions, are summarized in Table 1. The *I*-*V* behaviors of typical cells composed of 2 μm and 6 μm thick films sintered at 150 and 200 °C are shown in Fig. 7. The cell performance was strongly dependent on thickness of the film and the autoclaving temperature, as expected. The short-circuit photocurrent density (*J*_{SC}) (from 0.25 to 0.56 mA/cm² and from 0.19 to 4.79 mA/cm² for A and B, respectively) and the open circuit voltage (*V*_{OC}) both for A1 and B1 cells, increased with a autoclaving temperature of 200 °C when compared to that with the temperature of 150 °C. In other

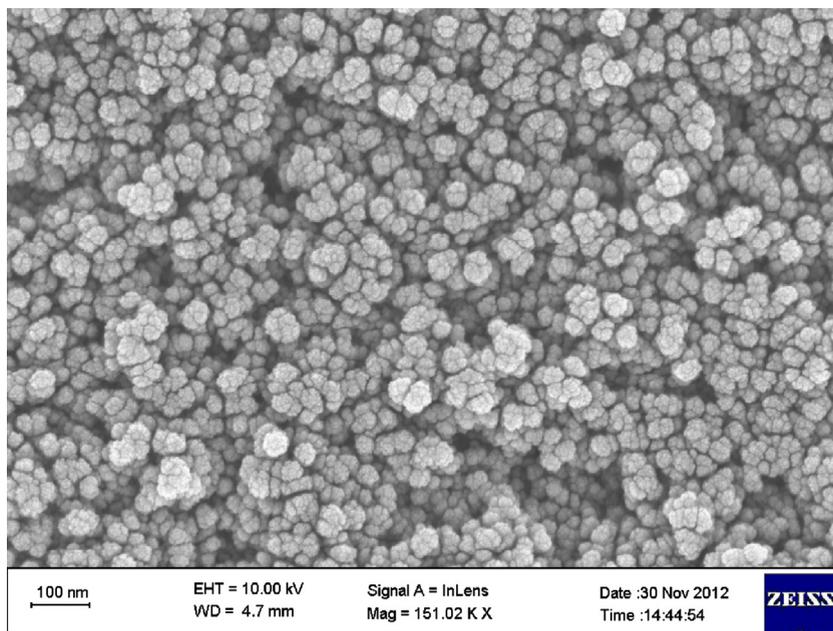


Fig. 5. SEM image of TiO₂-dye hybrid nanoparticles prepared at 200 °C temperature.

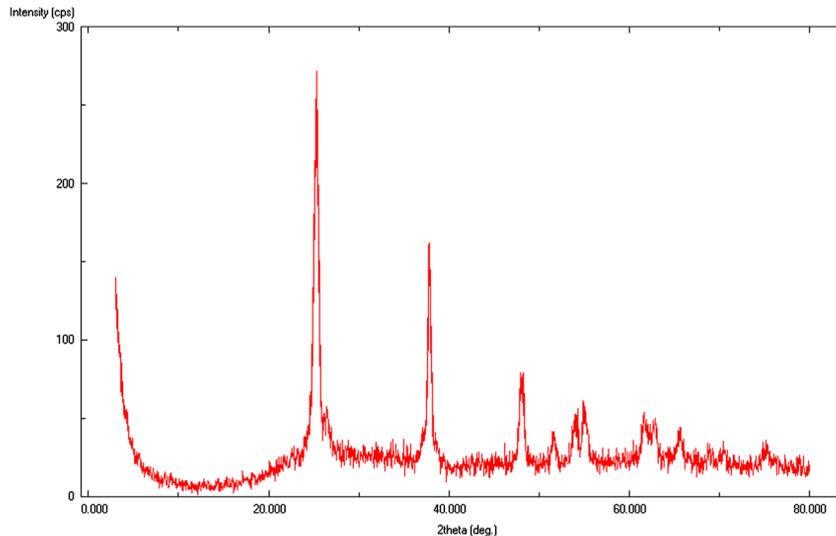


Fig. 6. XRD pattern of TiO₂-dye hybrid nanoparticles prepared by hydrothermal crystallization. The crystal form is anatase.

words, an increase of 50 °C leads to increase the cell efficiencies at the rate of 3 times for A2, and 45 times for B2. Moreover, when the film thickness increased to 6 μm, the cells gave a higher short circuit photocurrent density (J_{sc}) (4.68 mA/cm² and 5.67 mA/cm² for A3 and B3, respectively), resulting in an increase of the efficiency. The improved cell efficiency with increasing the film thickness can be attributed to increase light harvesting efficiency by increasing the amount of dye in the electrodes using thick TiO₂ films (A3). Additionally, the devices employing thicker film gave a higher open-circuit voltage of 0.66 and 0.65 mV for A3 and B3 respectively. As a result, the highest conversion efficiency of 1.38% for A3 and 2.21% for B3 were obtained for the 6 m-thick film.

The existence of dyes that contain anchoring groups such as carboxyls at the preparation step of TiO₂ paste may modulate interaction between neighboring TiO₂ nanoparticles and also change the viscosity of TiO₂ paste that allows the formation of thick TiO₂ films without requiring thermal sintering.

I-*V* characteristics of both A and B type cells are relatively similar, and are comparable to DSCs prepared using TiO₂ films sintered at high temperatures (450 °C). One explanation for the increase in conversion efficiency may be the improved electron/hole migration through the pores of the TiO₂ film that may arise from the high contact area of uniformly arranged TiO₂-dye nanoparticles.

It has been previously observed that TiO₂ nanoparticle surfaces produced at low temperatures contain a large number of recombination sites and that their number can be decreased at the higher sintering temperature [28]. According to our results, this observation can be widened to cover the preparation temperature as it has been increased so did the solar cell conversion efficiency (Fig. 7). Additionally, low preparation temperatures like the ones that were used in this study may show promising results so that the necking between adjacent dyes attached

TiO₂ colloids will presumably be as pronounced as for films sintered at higher temperatures.

4. Conclusions

Porous thick films of nanocrystalline TiO₂-dye hybrid paste have been successfully prepared at 150 and 200 °C without using any polymer binders. The method is simple and scalable to large area applications. Non-heat-resistant substrates such as flexible plastic substrates, paper, and cloth can be used, which should be beneficial not only for DSCs but also for other possible applications. In addition, different dyes could be tried using this method with small modifications. This method can only be limited by thermal stability of the dye, as it requires thermal stability up to 250 °C.

As a result of this processing method, these films have a larger internal surface area resulting in adsorption of more dye for an equivalent film thickness. This effectively can increase the light absorption coefficient and thus can lead to increased photoinduced electron injection efficiency. We also show that, regardless of the sintering temperature, films prepared without organic surfactant tend to adhere better to the underlying TCO substrate, a factor which may be important for the durability of devices made from these films. Further studies toward optimization of the preparation conditions, extension of the method to the preparation of plastic films, and photoelectrochemical analysis of charge transport processes are in progress.

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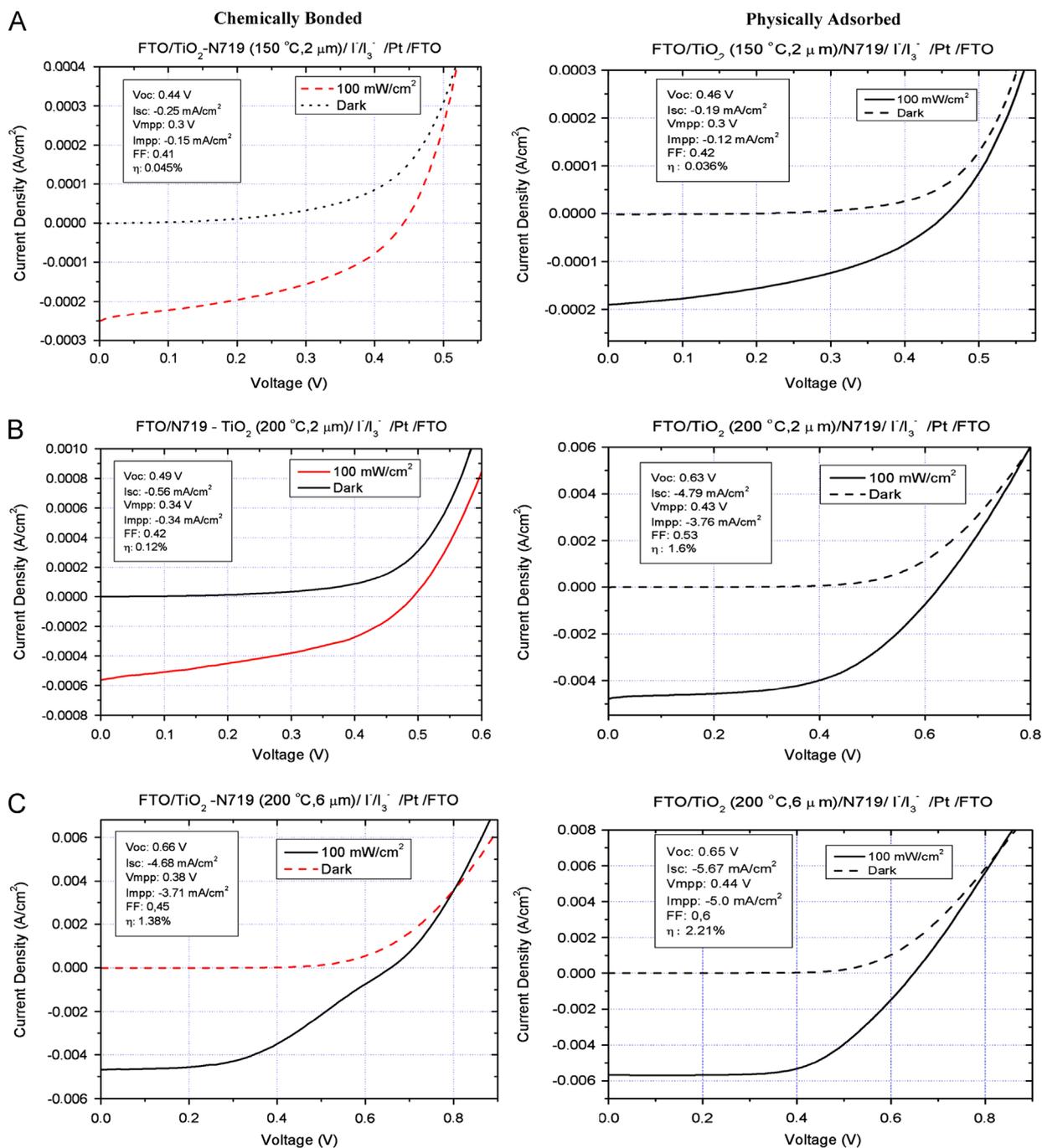


Fig. 7. *J*-*V* characteristics of DSCs that contain chemically bonded TiO₂-dye layer and physically adsorbed TiO₂-dye layer (a) prepared at 150 °C, 2 μm film thickness (A1); (b) prepared at 200 °C, 2 μm film thickness (A2); (c) prepared at 200 °C, 6 μm film thickness (A3) under illumination of 100 mW/cm² light sources and AM 1.5 radiation conditions.

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