

Laser processing of nanocrystalline TiO₂ films for dye-sensitized solar cells

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Pulsed-laser deposition and laser direct-write have been applied to deposit dense (30 nm thick) and porous nanocrystalline TiO₂ (nc-TiO₂, 5–20 μm thick) layers incorporated in dye-sensitized solar cells. Laser direct-write is a laser-induced forward transfer technique that enables the fabrication of conformal structures containing metals, ceramics, polymers, and composites on rigid and flexible substrates without the use of masks or additional patterning steps. A pulsed UV laser (355 nm) was used to forward transfer a suspension of TiO₂ (P25) nanopowder onto a F-doped SnO₂ coated glass substrate. In this letter we demonstrate the use of laser transfer techniques to produce porous nc-TiO₂ films required for dye-sensitized solar cells. The dye solar cells fabricated with the laser processed TiO₂ layers on glass showed a power conversion efficiency of ~4.3% under an illumination of 10 mW/cm². © 2004 American Institute of Physics. [DOI: 10.1063/1.1772870]

Over the last decade, dye-sensitized solar cells based on mesoporous, nanocrystalline TiO₂ (nc-TiO₂) films have been extensively studied as possible alternatives to silicon-based solar cells due to their high power conversion efficiencies (~10%) and expected low materials and manufacturing costs.^{1–4} In general, the nc-TiO₂ films have been produced via colloidal synthesis of TiO₂ nanoparticles and subsequent deposition of the TiO₂ colloidal slurry onto substrates by blading^{3,4} or screen printing.⁵ There have also been some efforts to produce the nc-TiO₂ films using spray pyrolysis,⁶ electrochemical deposition,⁷ gas phase deposition,⁸ and sputtering.⁹ However, these processes lack effective control of the TiO₂ film thickness (especially at film thicknesses >10 μm) and they require additional patterning steps.

An alternative approach to address these difficulties with the production of high surface area nc-TiO₂ films is to use a laser direct-write (LDW) technique.¹⁰ LDW is a laser-induced forward transfer process that enables the fabrication of metal oxide (such as nc-TiO₂) conformal thin-film structures on rigid and flexible substrates without the use of masks or additional patterning steps. In addition, this laser processing technique can be combined with *in situ* laser annealing of the films in order to improve the electrical properties of the active TiO₂ layers in dye-sensitized solar cells, without damaging substrates with low glass transition temperatures such as plastics. Recently, we have successfully demonstrated the utility of the LDW technique in producing high surface area, hydrous ruthenium oxide ultracapacitors, and alkaline and Li-ion microbatteries.^{11,12} In this letter, we report on fully operational dye-sensitized solar cells containing nc-TiO₂ films deposited by laser direct-write.

The general structure of a dye-sensitized solar cell used for this work is shown schematically in Fig. 1(a). Dye-sensitized solar cells based on nc-TiO₂ films were fabricated on F-doped SnO₂ (FTO) coated glass (2.5 cm × 2.5 cm; 14 Ω/□; Hartford Glass Co. USA). Prior to the deposition

of the nc-TiO₂ films, a dense TiO₂ film (~30 nm thick) was deposited onto the FTO-coated glass substrates using pulsed laser deposition. This dense TiO₂ film was grown at 450 °C in 50 mTorr of oxygen with a laser fluence of 2 J/cm² using a KrF excimer laser (λ=248 nm).¹³ The purpose of this dense TiO₂ layer was to serve as an electrically isolating barrier between the FTO and the dye sensitized nc-TiO₂ layer in order to minimize short circuit losses in the cell. The

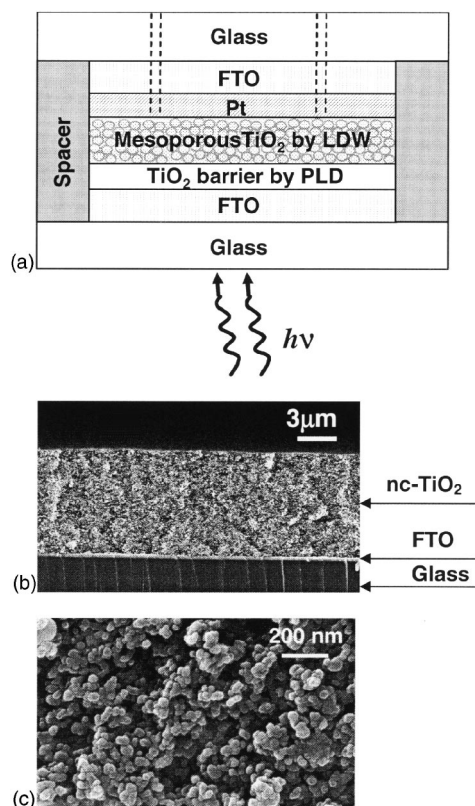


FIG. 1. (a) A schematic diagram showing a cross section of the dye-sensitized solar cell prepared for this work. Dashed lines represent the holes used to add the electrolyte to the cell. SEM micrographs showing (b) the cross section and (c) the surface of a 12-μm-thick mesoporous nc-TiO₂ layer transferred by LDW on TiO₂/FTO coated glass. The film was sintered at 450 °C for 30 min.

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nc-TiO₂ films were deposited from a colloidal TiO₂ paste⁵ onto the dense TiO₂ layer using the LDW technique.

The active nc-TiO₂ layers were deposited onto the TiO₂/FTO coated glass substrates by the LDW technique following previously reported conditions.^{10–12} Briefly, the TiO₂ colloidal paste was cast as a uniform layer of $\sim 2 \mu\text{m}$ thickness (using #4 wire coater, Garner) onto a borosilicate glass plate. The coated side of the borosilicate plate (referred to as the “ribbon”) was held on top of the substrate at a distance of $100 \mu\text{m}$. A frequency-tripled Nd–YVO₄ laser ($\lambda = 355 \text{ nm}$) was focused on the ribbon surface through the back side of the glass plate to transfer the TiO₂ paste to the TiO₂/FTO coated glass substrate. The laser fluence was maintained at about 0.1 J/cm^2 for a spot size of $250 \mu\text{m}^2$. The overall thickness of the transferred nc-TiO₂ layer was controlled by the number of transfer passes conducted. The thickness and the mass of the nc-TiO₂ layers monotonically increase with the number of LDW passes.

The area of the laser transferred nc-TiO₂ films was 0.25 cm^2 . The transferred films were first dried in air and then sintered in air at $450 \text{ }^\circ\text{C}$ for 30 min. The sintered films were impregnated by soaking in a 0.2 M aqueous solution of TiCl₄ overnight ($\sim 10 \text{ h}$), washed with distilled water, and then sintered a second time at $450 \text{ }^\circ\text{C}$ for 30 min. Following the second sintering step, TiO₂ films were dipped while still warm ($\sim 100 \text{ }^\circ\text{C}$) into a $3 \times 10^{-4} \text{ M}$ solution of a dye sensitizer, *cis*-bis(isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N3, Solaronix) in absolute ethanol for 15 h at room temperature.⁵ The resultant dark purple specimens were rinsed with anhydrous ethanol and dried in a dry nitrogen stream. A separate platinum counter electrode was deposited by e-beam evaporation onto a FTO coated glass substrate ($2.5 \text{ cm} \times 2.5 \text{ cm}$) with a Ti ($\sim 30\text{-nm}$ -thick) buffer layer. The thickness and surface resistance of the platinum electrode are 70 nm and $2.8 \Omega/\square$, respectively. The Pt-electrode and the dye-covered TiO₂ electrode were sealed together with a $25\text{-}\mu\text{m}$ -thick Surlyn (1702, Dupont) spacer placed along each edge of the glass substrate. The I₃/I⁻ redox electrolyte ($\sim 5 \mu\text{L}$) was introduced through one of two holes drilled through the Pt counter electrode, shown schematically in Fig. 1(a), and was observed to thoroughly wet the dye-covered nc-TiO₂ film via capillary action. The photovoltaic properties of the fabricated cells were measured using a 150 W xenon arc lamp outfitted with AM 1.5 filters (Thermo Oriel). Incident light intensities at the sample were controlled using neutral density filters and measured using a calibrated silicon photodiode detector (International Light Inc.).

Figures 1(b) and 1(c) show the cross-sectional and surface SEM micrographs of a typical nc-TiO₂ layer deposited by LDW. It is clear from Fig. 1(b) (cross section) that the bottom layer is the glass substrate, the second layer (white color) is the FTO film ($\sim 400 \text{ nm}$), and the top layer is the TiO₂ film ($\sim 12 \mu\text{m}$ thick) prepared with eight LDW passes. Since the LDW passes are conducted as a wet process, no interfacial gaps are formed in the transferred nc-TiO₂ between sequential deposition passes. Figure 1(c) shows that the TiO₂ film is composed of interconnected spherical-shaped particles with an average grain size of $\sim 30 \text{ nm}$. It can also be seen that the particles are distributed homogeneously with a high degree of porosity consistent with a high surface area structure. This three-dimensional network of interconnected TiO₂ nanoparticles provides efficient electron

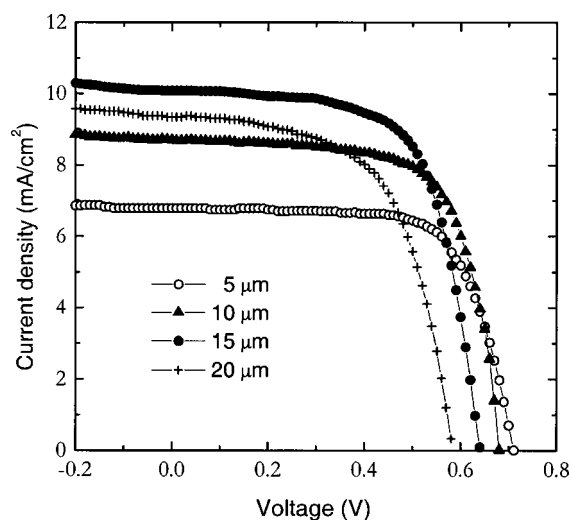


FIG. 2. Current density vs voltage (J - V) characteristics of dye-sensitized solar cells fabricated with different thicknesses of active nc-TiO₂ layers deposited by LDW measured at 100 mW/cm^2 (AM 1.5 simulated solar illumination). The active cell area of all samples is 0.25 cm^2 .

conduction while the high surface area structure maximizes the number density of dye molecules adsorbed on the surface of the nc-TiO₂. Both properties are essential for the fabrication of efficient dye-sensitized solar cells.

Figure 2 shows the current density (J) versus voltage (V) characteristics for several dye sensitized solar cells containing nc-TiO₂ layers of varying thickness. A summary of the J - V characteristics and power conversion efficiencies of different nc-TiO₂ film thicknesses is given in Table I. In these cells, the short circuit current density (J_{sc}) rises from 6.8 to 10.1 mA/cm^2 as the nc-TiO₂ layer thickness is increased from 5 to $15 \mu\text{m}$. Conversely, the open circuit voltage (V_{oc}) in these cells decreases from 0.71 to 0.58 V upon increasing nc-TiO₂ layer thickness from 5 to $20 \mu\text{m}$. The initial increase in J_{sc} with nc-TiO₂ thickness can be related to the increased surface area of the TiO₂ films and hence the concomitant increase in the amount of adsorbed dye. The decrease in V_{oc} with nc-TiO₂ thickness is attributable to an increase in the series resistance⁵ and an increase in the interfacial loss (e^-/h^+ recombination) processes that become more prominent at increased active layer thicknesses.¹⁴ The effects of these recombination loss processes are also manifested in the decrease of the cell J_{sc} from 10.1

TABLE I. Photovoltaic characteristics of dye-sensitized solar cells with different thickness of the light-harvesting active TiO₂ layers. The cell size is 0.25 cm^2 . All curves were collected at 100 mW/cm^2 of AM 1.5 simulated solar illumination. V_{oc} is defined as the voltage at which the photocurrent becomes zero, J_{sc} is defined as the photocurrent at zero voltage, the fill factor (ff) is calculated from the equation $\text{ff} = (J_{max} \times V_{max}) / (J_{sc} \times V_{oc})$, and the power conversion efficiency (η) is calculated from the equation $\eta = 100 (J_{max} \times V_{max}) / P_{in}$, where P_{in} is the power of the incident light.

| Thickness of nc-TiO ₂ layer (μm) | V_{oc} (V) | J_{sc} (mA/cm^2) | ff | η (%) |
|--|--------------|-------------------------------|------|------------|
| 5 | 0.71 | 6.8 | 0.70 | 3.4 |
| 10 | 0.68 | 8.7 | 0.68 | 4.0 |
| 15 | 0.64 | 10.1 | 0.65 | 4.3 |
| 20 | 0.58 | 9.3 | 0.61 | 3.3 |

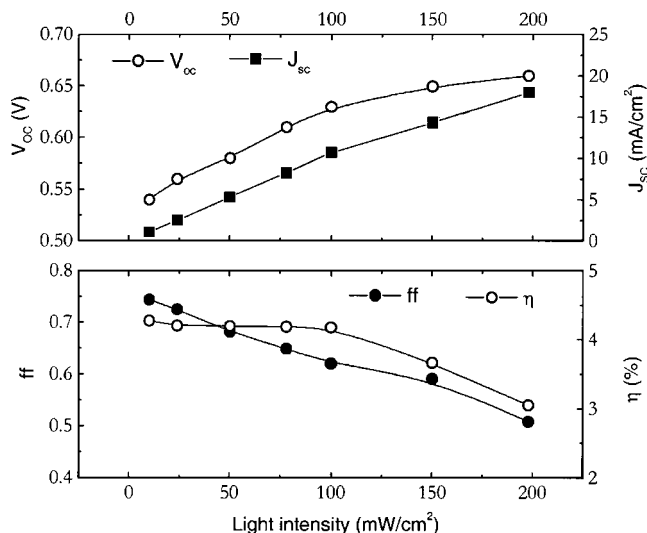


FIG. 3. Photovoltaic properties (V_{oc} , J_{sc} , ff , and η) as a function of the incident light power of the AM1.5 illumination source for a dye-sensitized solar cell fabricated using a laser processed TiO₂ film ($\sim 15 \mu\text{m}$).

9.3 mA/cm² upon increasing the active nc-TiO₂ layer thickness from 15 to 20 μm .

Although the thicker nc-TiO₂ films contain more adsorbed dye molecules and would be expected to produce higher photocurrents, in practice it is found that the very thick nc-TiO₂ films also contain a large number of defect/recombination sites. This rapid increase in the number of defect sites with active nc-TiO₂ layer thickness accounts for the overall decrease in the cell operational characteristics. Because of this, the thickness of the nc-TiO₂ films must be optimized for improving both J_{sc} and V_{oc} parameters simultaneously. In this work, the optimum thickness of the active nc-TiO₂ layer was found to be near 15 μm . The cells made with this optimum thickness (15 μm) exhibited a J_{sc} of 10.1 mA/cm², V_{oc} of 0.64 V, a fill factor (ff) of 0.65, and a white light power conversion efficiency (η) of $\sim 4.3\%$. The observed influence of nc-TiO₂ layer thickness on the J_{sc} and V_{oc} of the present cells is in agreement with earlier studies.¹⁵

The influence of the incident light power density on the photovoltaic parameters has also been investigated. In Fig. 3, V_{oc} , J_{sc} , ff , and η are plotted as a function of the incident light intensity (P_{in}) for the dye-sensitized solar cell fabricated with LDW processed, 15- μm -thick nc-TiO₂ layer. The P_{in} was varied from 10 mW/cm² (0.1 sun) to 200 mW/cm² (2 suns). The V_{oc} is found to increase linearly with increasing P_{in} at lower light intensities ($< 100 \text{ mW/cm}^2$) while increasing more gradually at higher intensities up to 200 mW/cm². The J_{sc} monotonically increases from 1.0 to 10.1 mA/cm² with increasing light intensity from 10 to 100 mW/cm². This near linear dependence of J_{sc} on the incident light power indicates that the photocurrent production is not limited by the diffusion kinetics of I_3^-/I^- ions. This is due to the rapid regeneration of the photo-oxidized dye molecules. At P_{in} values above 100 mW/cm², however, the slope of the J_{sc} versus

P_{in} curve decreases, suggesting that the diffusion of I_3^-/I^- is too slow to efficiently regenerate the oxidized dye molecules resulting in a decrease in the photocurrent. This effect coupled with possible ohmic losses in the TCO support leads to the observed decrease in the fill factor at higher light intensities ($> 100 \text{ mW/cm}^2$). These loss processes have the effect of modulating the power conversion efficiencies of the cells with varying P_{in} . The power conversion efficiency (η) of the 15- μm -thick nc-TiO₂ device ranges from 4.3% at 10–100 mW/cm² to 3.1% at intensities approaching 200 mW/cm² (see Fig. 3).

In summary, a laser direct-write technique has been applied to deposit mesoporous, nanocrystalline TiO₂ films which were incorporated as active layers in dye-sensitized solar cells. The light power conversion efficiency ($\sim 4.3\%$ at 1 sun) of the cells fabricated using this new approach is comparable to those reported earlier for analogous cells fabricated with commercial TiO₂ powders (P25) using standard techniques.^{4,6,16} The ease of device fabrication without the need for patterning and excellent layer thickness control afforded by the LDW technique makes it a very attractive method for the development of conformal dye-sensitized solar cells on flexible and rigid substrates.

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