Ink-jet-printed $(ZnO)_{1-x}(TiO_2)_x$ composite films for solar cell applications

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Ink-jet printing technique is used to prepare porous $(ZnO)_{1-x}(TiO_2)_x$ composite films on indium tin oxide-coated glass substrates. Dye-sensitized solar cells were fabricated using well-characterized printed films of thickness ~20 and 30 μm, respectively. It is found that the photovoltaic performance of the cells is dependent on the film thickness and the concentrations of ZnO. The obtained results are compared with those of pure ZnO- and TiO_2-based cells prepared by the same route to optimize the device efficiency. This study suggests that ink-jet printers promise an inexpensive and simple technology for manufacturing solar cell composite films.

I. INTRODUCTION

Dye-sensitized solar cell (DSSC) is a type of photoelectrochemical cell that provides more than 11% power conversion efficiency of solar energy. DSSC is composed of a dye-modified wide band gap semiconductor electrode, a counter electrode, and an electrolyte containing a redox couple (I^-/I_3^-). Under sunlight illumination, the dye molecules adsorbed on the wide band gap semiconductor surface absorb light and become excited. Subsequently, an electron is injected from the excited state of the dye to the conduction band of semiconductor and then transfers to the transparent oxide. Finally, the electron flows through the external circuit.[1–4] Recently, nanocomposite films have been of particular interest for DSSC device development owing to their controlled binary components and porosity. Preparation of a film on flexible organic substrates can make DSSC a commercially competitive technology as it allows the control of flexibility, weight, and overall device thickness. For example, DSSCs based on TiO_2 films are regarded as low cost alternative cells for conventional semiconductor devices, which makes them of academic and practical interests.[5–9]

Various methods have been proposed for preparing semiconductor films on a flexible substrate, such as sol–gel dip coating,[10,11] spin coating,[12,13] sputtering,[14,15] spray pyrolysis,[16,17] atomic layer deposition,[18,19] chemical vapor deposition,[20,21] and electrodeposition.[22] Ink-jet printing technique is considered as a potential candidate that can provide mass production of low cost and uniform film deposition. This technique has been studied extensively as a research tool in materials and devices development due to the advantages of high reproducibility and easy production automation in comparison to dip coating techniques.[23–26]

TiO_2 is a well-known oxide because of its remarkable optical and electronic properties. Nanocrystalline TiO_2 thin films are proved to have various applications in sensors, photocatalysis, and solar cells.[27,28] The problem of TiO_2 is its inefficient charge transfer where the electron hops through the TiO_2 thin films and exhibits a slow nonexponential current and charge recombination.[29,30] ZnO is another important semiconductor that has been widely investigated for its catalytic, electrical, optical, photochemical properties,[31–34] and for applications in blue/ultraviolet optoelectronic devices and in piezoelectric devices. It is known that semiconductors composites like $(ZnO)_{1-x}(SnO_2)_x$,[35] $(CdS)_{1-x}(MgO)_x$,[36] and $(SnO_2)_{1-x}(MgO)_x$[37] show a lower power conversion efficiency than that observed for TiO_2 film alone in a cell.

The combination of TiO_2 with ZnO in a composite film is expected to reduce recombination rate by providing an energy barrier at the electrode/electrolyte interface leading to a reduced recombination of photoinduced electrons.[38–40] In this paper, we present a new approach, using ink-jet printing technique to produce the films. The DSSC is investigated by replacing TiO_2 film with composite $(ZnO)_{1-x}(TiO_2)_x$ films with $x = 0$, 0.2, 0.5, 0.8, and 1 to elucidate the probable induced effect on the efficiency of the base DSSC.

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II. EXPERIMENTAL

The semiconductor layers were printed by ink-jet technology from 1 M inks with multiprint passes. Five inks containing (i) 0.025 mol ZnO particles, (ii) 0.02 mol ZnO and 0.005 mol TiO_2 particles, (iii) 0.0125 mol ZnO and 0.0125 mol TiO_2 particles, (iv) 0.005 mol ZnO and 0.02 mol TiO_2 particles, and (v) 0.025 mol TiO_2 particles were added into 2-isopropoxyethanol (IPE) to form 25 mL suspensions for printing $(ZnO)_{1-x}(TiO_2)_x$ films where $x = 0$, 0.2, 0.5, 0.8, and 1, respectively. The five mixtures were ultrasonically agitated for 30 min in order to obtain suitable monodispersed suspensions for printing. The indium tin oxide glass substrates, used as the transparent conductive anode, were sonicated in acetone for 10 min followed by rinsing in isopropanol and dried by nitrogen gas to remove the acetone and unwanted contaminations. The substrates were heated to 80 °C before and during printing. The inks were deposited on the substrates by a piezoelectric shear mode drop-on-demand ink-jet printer using Xaar XJ126/50 printhead (XaarJet AB, Järfälla, Sweden). The as-deposited layers were dried in tens of seconds because of the substrate temperature (80 °C). To obtain films with suitable thickness for DSSC fabrications, the inks were printed layer by layer. We fabricated $(ZnO)_{1-x}(TiO_2)_x$ composite films consisting of 20 and 30 layers, respectively. The as-deposited films were then sintered in air at 600 °C for 1 h to completely evaporate the IPE solvent and condense the films.

The overall thickness of the $(ZnO)_{1-x}(TiO_2)_x$ film was determined by a dual beam focused ion beam/scanning electron microscope (FIB/SEM; FEI Nova 600 Nanolab, FEI Europe NanoPort, Eindhoven, Netherlands). X-ray diffractometer (XRD; Siemens D5000, Siemens AG, Karlsruhe, Germany) was used to detect the constituents of the semiconductor layer using Cu K_α irradiation ($\lambda = 0.154$ nm). The diffraction data were collected over a range of $20° \leq 2\theta \leq 70°$ with a scan speed of 0.01°/step and 2 s/step.

The printed $(ZnO)_{1-x}(TiO_2)_x$ films were activated at 550 °C and left to cool down to 80 °C and immersed overnight in 3×10^{-4} M N3 dye solution (purchased from Solaronix Solaronix SA, Aubonne, Switzerland) in pure isopropanol. They were washed thoroughly by deionized water and then absolute ethanol and left to dry. The photoelectrode was sandwiched with Pt counter electrode prepared by magnetron sputtering and filled with liquid electrolyte consisting of concentration 0.5 M KI and 0.05 M I_2 in ethylene glycol, over an area of 1.26 cm^2. The fabricated cells were connected to variable resistors by aluminum wires, and the current/voltage of the cell was monitored by a multimeter.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD intensity patterns of the 30-layer printed $(ZnO)_{1-x}(TiO_2)_x$ composite films with different molar ratio of ZnO to TiO_2. The scans were taken under the same condition, and therefore, the intensity of the peaks should be related to the quantity of the constituents. It is clear from Fig. 1 that as the ZnO molar concentration is increased, the relative intensity of diffraction peaks from ZnO [Joint Committee on Powder Diffraction Standards (JCPDS) No. 01-079–2205] is enhanced, while the relative intensity of diffraction peaks from TiO_2 (anatase, JCPDS No. 00-002–0387) is reduced. The observed other titanium oxide phases (e.g., Ti_nO_{2n-1}) in the films, we believe, come from the chemical source of TiO_2 particles.

Figure 2 shows the typical SEM images and the FIB cross-sectional image of the 20-layer ink-jet-printed TiO_2 film. From the images, the size of TiO_2 particle was detected to be in a range of 70–400 nm with an average value of ~170 nm. It is clearly seen from the cross-sectional image [Fig. 2(b)] that the film is uniform with thickness of ~19.4 μm. The porous structure is observed in both the surface morphology and the cross-sectional images of the prepared films, which displays the large surface area for dye adsorption.

The effect of $(ZnO)_{1-x}(TiO_2)_x$ films thickness on the properties of solar cell has been investigated. Figure 3 shows the photocurrent density versus photovoltage (J-V) curves of solar cells prepared from 20- and 30-layered films for different constituent concentrations. For certain concentration solar cells, the short circuit photocurrent density (J_{SC}) of the 20-layer samples is larger than that observed value for the 30-layer samples, while their open circuit voltage (V_{OC}) is smaller. The film thickness dependence of J_{SC} is related to: (i) the number of dye molecules adsorbed in the semiconductor films. The buildup of dye molecules in thicker film can generate more photoelectrons and thus result in higher J_{SC}. (ii) The charge recombination between the ejected electrons and the I_3^- ions in the electrolyte. In thicker films, more photoelectrons are recombined with the electrolyte during the transport to the transparent conductive anode, which can decrease the J_{SC}.[41] We observed an increase of V_{OC} with the thickness for all the films, especially for ZnO-dominate $(ZnO)_{1-x}(TiO_2)_x$ films

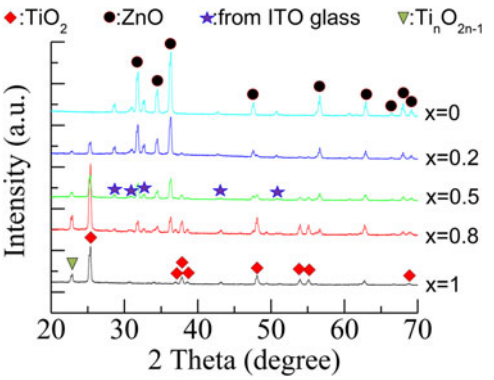


FIG. 1. XRD intensity patterns of $(ZnO)_{1-x}(TiO_2)_x$ composite films with varied x values.

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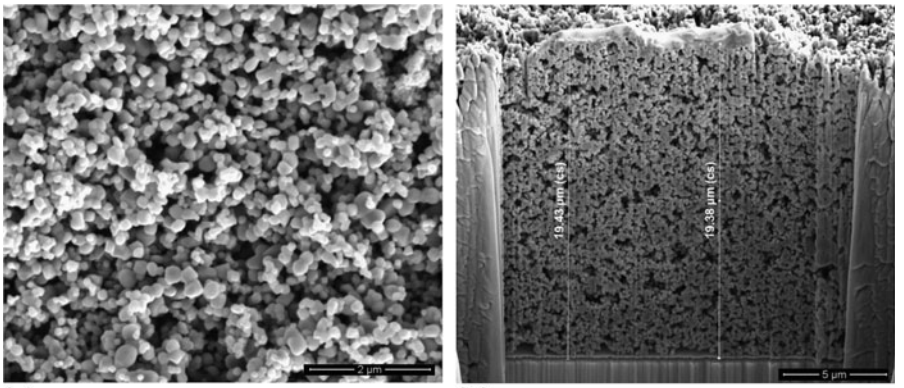


FIG. 2. SEM morphology (a) and the FIB cross-sectional image (b) of TiO_2 film.

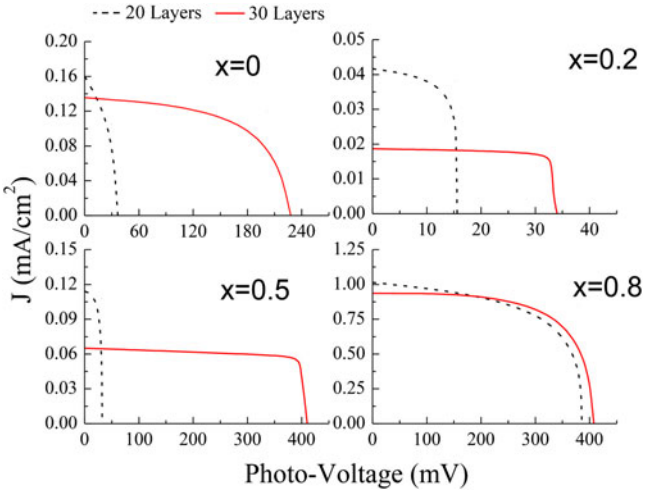


FIG. 3. *J-V* characteristics of fabricated solar cells using 20- (dash lines) and 30-layer (solid lines) $(ZnO)_{1-x}(TiO_2)_x$ films, printed with different components concentration.

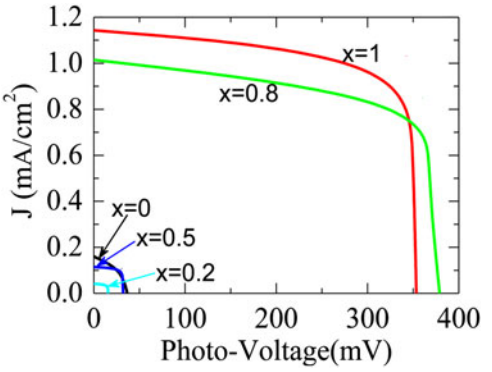


FIG. 4. Comparison of *J-V* curves of the solar cells fabricated from 20-layer $(ZnO)_{1-x}(TiO_2)_x$ films.

$(x \leq 0.5)$. In thicker films, electrons transport along a longer path to complete the circuit. This increases the resistance of the cell, the charge recombination rate,[41] and the possibility of back electron transfer.[42] In addition, the photon localization[43] inside a thick film is more serious than in a thin film. These result in the V_{OC} decrease with the thickness. On the other hand, it is known that in thick films, the capture of photons is better than in thin films. With the buildup dye molecules, the photovoltaic effect can be enhanced.

It is clearly seen from the curves that the *J-V* properties of solar cell depend on the molar ratio of ZnO to TiO_2 in the films. In Fig. 4, we compare the photocurrent density–voltage (*J-V*) curves of solar cells fabricated from 20-layer $(ZnO)_{1-x}(TiO_2)_x$ films with different molar ratio of the components. It shows that the photovoltaic response of ZnO-dominated cells is much less than that of TiO_2-dominated cells. The fill factor (FF) and the power conversion efficiency (η) were calculated according to:

$$FF = \frac{P_{max}}{V_{OC} J_{SC}}, \eta = \frac{P_{max}}{P_{input}} \quad ,$$

where P_{max} is defined as maximum power, P_{input} is the intensity of sunlight during the measurements (650–750 W/m^2). Figure 5 shows the FF and the energy conversion efficiency of the cells with different ZnO molar concentration in 20-layer $(ZnO)_{1-x}(TiO_2)_x$ composite films. It demonstrates that ZnO decreases the energy conversion efficiency, from 0.52% for pure TiO_2-based solar cell to 0.46% for the cell with $(ZnO)_{0.2}(TiO_2)_{0.8}$ and finally less than 0.01% for ZnO-dominated solar cells. The dramatic influences of the component of the semiconductor layer on the performance of DSSCs could be attributed to the following: (i) the instability of ZnO in dye solution. It is reported that the acidic dye could dissolve Zn atoms and form Zn^{2+}/dye complex resulting in insufficient dye adsorption and photoelectron generation and thus resulting in a poor performance of DSSCs.[43] (ii) Unlike the chemisorption in TiO_2, pure ZnO layers do not easily absorb enough amount of the ruthenium complex dye. (iii) Even though the TiO_2 and ZnO have similar band gap

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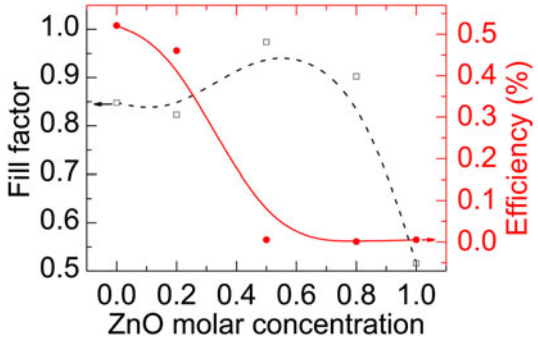


FIG. 5. Plot of FF (dash line) and energy conversion efficiency (solid line) versus the molar concentration of ZnO (the value of $1-x$) in $(ZnO)_{1-x}(TiO_2)_x$ films.

TABLE I. Photovoltaic properties of ink-jet-printed solar cells based on $(ZnO)_{1-x}(TiO_2)_x$ films.

$(ZnO)_{1-x}(TiO_2)_x$	Printed layers	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	Efficiency (%)
$x = 0$	20	0.160	36.7	0.516	0.005
	30	0.136	202.0	0.780	0.034
$x = 0.2$	20	0.042	15.5	0.902	0.001
	30	0.019	34.0	0.721	0.001
$x = 0.5$	20	0.114	32.2	0.974	0.005
	30	0.065	399.8	0.858	0.033
$x = 0.8$	20	1.014	379.0	0.823	0.460
	30	0.937	382.7	0.931	0.508
$x = 1$	20	1.143	353.4	0.848	0.521
	30	1.171	399.6	0.602	0.375

energy, their conduction band structures are different: Ti^{4+} has empty $3d$ orbitals ($1s^2\ 2s^2 2p^6\ 3s^2 3p^6$), while Zn^{2+} has empty $4s$ orbitals ($1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}$). Therefore, their density states and the electronic coupling strength with dye adsorbate are different. This results in the differences in electron injection rate from dye to their conduction band. For instance, the ejection time scale of photoelectron into ZnO conduction band is 1.5–150 ps (10^{-12} s), while for TiO_2, it takes <100 fs (10^{-15} s).[44] The faster electron injected into the conduction band of TiO_2 can reduce the recombination of electrons with the I_3^- ions in the electrolyte, and hence, the electron injection efficiency is higher and cell performance is better. (iv) The advantage of using ZnO in DSSC is the higher electron mobility than in TiO_2 (2 order of magnitude higher), which may improve the performance of the cell by minimizing the charge recombination during the transport of the photoelectrons.[45]

Notice that the 30-layer $(ZnO)_{0.2}(TiO_2)_{0.8}$ film-based cell has a higher power conversion efficiency than that of pure TiO_2-based cell (Table I). This might be caused by proximity effect of ZnO among TiO_2 particles and retard charge.

IV. CONCLUSIONS

$(ZnO)_{1-x}(TiO_2)_x$ composite films with nanosized porous structure have been prepared from ZnO and TiO_2 nanoparticles via ink-jet printing. By changing the molar ratio of ZnO to TiO_2 in the ink, the constituent concentration of $(ZnO)_{1-x}(TiO_2)_x$ films has been successfully modified. Based on these films, solar cells have been fabricated and the cell performances have been measured. The results indicate that the solar cell fabricated with thinner $(ZnO)_{1-x}(TiO_2)_x$ films have higher short circuit current density but lower open circuit voltage than thicker films. On increasing the ZnO concentration in $(ZnO)_{1-x}(TiO_2)_x$ films, the power conversion efficiency of the cell is found to decrease. Possible reasons for such a decrease are discussed.

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