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Germain Rey, N. Karst, Béatrice Doisneau, Hervé Roussel, Patrick Chaudouet,  
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## Morphological and electrical characterization of ZnO nanocomposites in dye-sensitized solar cells

G. Rey,<sup>1,a)</sup> N. Karst,<sup>1</sup> B. Doisneau,<sup>2</sup> H. Roussel,<sup>1</sup> P. Chaudouet,<sup>1</sup>  
V. Consonni,<sup>1,3</sup> C. TERNON,<sup>1,3</sup> and D. Bellet<sup>1</sup>

<sup>1</sup>Laboratoire des Matériaux et du Génie Physique, CNRS – Grenoble INP, 3 Parvis Louis Néel 38016 Grenoble, France

<sup>2</sup>Laboratoire de Science et Ingénierie des Matériaux et Procédés, CNRS – Grenoble INP, 1130 Rue de la Piscine 38402 Saint-Martin d'Hères, France

<sup>3</sup>Laboratoire des Technologies de la Microélectronique, CNRS – UJF – Grenoble INP, 17 Rue des Martyrs 38054 Grenoble, France

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ZnO nanocomposites were fabricated as photoanodes for dye-sensitized solar cells. ZnO nanowires grown by catalyst-free metal-organic chemical vapor deposition were uniformly covered with ZnO nanoparticles by chemical bath deposition. ZnO nanocomposites exhibit the highest cell efficiency of 2.44% with a 16.7 mA/cm<sup>2</sup> short circuit current density due to a higher specific surface area as compared to bare ZnO nanowires. The relatively low open circuit voltage of 0.48 V is associated with a significant decrease in the electron effective life time as shown by electrochemical impedance spectroscopy measurements, pointing out the importance to control the interface quality in dye-sensitized solar cells. © 2011 American Institute of Physics. [doi:10.1063/1.3646762]

Dye-sensitized solar cells (DSSCs) are promising to fabricate low-cost but quite efficient photovoltaic devices. These solar cells are first composed of a nanostructured photoanode of wide band-gap semiconductor.<sup>1</sup> Dye molecules like ruthenium complex are then chemisorbed onto the semiconductor surface in order to absorb the incident photons. After the photon absorption and electron transfer toward the semiconductor, dye molecules are regenerated by an electrolyte containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox species, which carry the charge carriers between the cathode and dye.

TiO<sub>2</sub> or ZnO nanoparticles (NPs) are usually used as photoanode and offer a large specific surface area favoring an efficient dye loading. One way to potentially increase its efficiency would be to enhance the electron transport through the NP network. Indeed, the presence of numerous interfaces between NPs similar to incoherent grain boundaries results in a high density of traps and recombination centers for electrons,<sup>2</sup> which in turn hamper their collection at the photoanode. In order to circumvent such a problem, the use of ZnO single crystal nanowires (NWs) as photoanode has been suggested,<sup>3-5</sup> by taking advantage of the ability of ZnO to grow with the NW morphology by low-cost deposition method.<sup>6</sup> Interestingly, it has been reported that the electron transport is even 100 times faster in NWs than in nanocrystalline films.<sup>4,7,8</sup> However, ZnO NW-based DSSCs have yielded a low efficiency of about 0.5% to 1.5%,<sup>3,4</sup> which is mostly due to the low NW specific surface area. Therefore, nanocomposites were proposed as photoanode, consisting of both ZnO NWs and NPs. The former provide a direct pathway for an efficient electron transport and collection, while the latter increase the specific surface area, which enhances the light harvesting. This approach was first followed by Baxter and Aydil from ZnO NWs grown by metal-organic chemical vapor deposition (MOCVD).<sup>9</sup> ZnO NPs were subsequently deposited by doctor blading, leading to a weak connection and coupling between the NWs and NPs. More recently, ZnO nanocomposites<sup>10,11</sup> were also fabricated by chemical bath deposition (CBD).<sup>12,13</sup> Owing to the direct growth of ZnO NPs onto NWs, the CBD technique

<sup>a)</sup>Electronic mail: germain.rey@grenoble-inp.fr. Tel.: +33 4 56 52 93 54.

leads to well-connected NP/NW networks. Nevertheless, ZnO NWs grown by CBD are associated with lower electron transport properties than ZnO NWs grown by MOCVD.<sup>12</sup>

In this letter, the fabrication of ZnO nanocomposites as photoanode is reported. ZnO NWs with a low bulk density were grown by catalyst-free MOCVD within a self induced approach<sup>14</sup> on fluorine doped tin oxide (FTO) thin films (overall mean visible transmittance = 85%, square sheet resistance = 17  $\Omega/\square$ ), in order to favour an efficient electron transport. Their coverage with ZnO NPs was performed by CBD so as to ensure good interfacial properties.<sup>15</sup> The structural morphology of the resulting nanocomposites was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging as well as x-ray diffraction (XRD) measurements, while the DSSC electrical properties were investigated by J(V) characteristics and electrochemical impedance spectroscopy (EIS) measurements.

The structural morphology of NWs as well as nanocomposites is shown in the SEM and TEM images of Fig. 1. NWs have a film thickness of 3.8  $\mu\text{m}$ . The NW and NP diameter lie in the range of 15–25 nm and 25–30 nm, respectively. Both NWs and NPs present a würtzite type structure while NWs preferentially grow along the c-axis. No sign for the presence of an epitaxial relationship between NWs and NPs is revealed as depicted in Fig. 1(d). After 4 h of CBD, the NP deposit onto NWs is conformal, as seen in Fig. 1(b). For longer time of CBD (22 h), the empty space between NWs is expected to be totally filled, as revealed in Fig. 1(c).

The crystalline structure was investigated by XRD measurements according to the  $\theta/2\theta$  configuration as shown in Fig. 2. A texture coefficient analysis of (100), (002), (101), (102), and (110) Bragg peaks was performed according to the Harris method.<sup>16</sup> In principle, the degree of preferred orientation can vary from 0 (no texturation) to 2 (fully textured along one direction), for a five peak analysis. The degree of preferred orientation was 0.92 for as-grown NWs, while the highest texture coefficient of 2.68 was found for the [002] direction, confirming that ZnO NWs grow along the c-axis. The degree of preferred orientation is smaller than 2 since NWs are not vertically aligned. The covered NWs exhibit a lower texturation with a

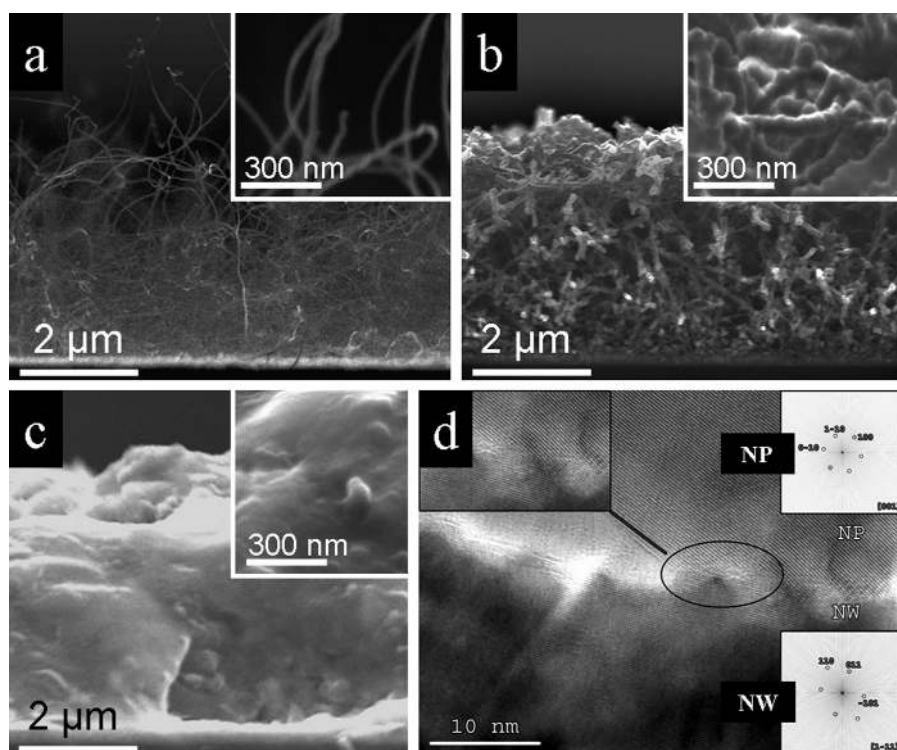


FIG. 1. Cross-sectional SEM images of (a) as-grown ZnO NWs, (b) ZnO NWs covered with ZnO NPs after 4 h of CBD, and (c) ZnO NWs filled with ZnO NPs after 22 h of CBD. TEM image (d) of the NP/NW interface for the covered sample. The insets shown at the top and at the bottom are the fast Fourier transform of the NP and NW, respectively.

degree of preferred orientation and a texture coefficient for the [002] direction falling down to 0.22 and 1.22, respectively. The crystallite size of 27 nm was calculated according to the Debye-Scherrer formula, which is in good agreement with TEM measurements

DSSCs were performed by sensitizing bare ZnO NWs or nanocomposites for 10 min in a 25 mM N719 ethanolic solution. EL-HSE electrolyte supplied by Dyesol was introduced between 25  $\mu\text{m}$  spaced photoanode and cathode. The cathode consists of 100 nm thick platinum film deposited onto glass whereas the solar cell active area was 0.25  $\text{cm}^2$ . For the sake of comparison with standard photoanode morphology, conventional DSSCs derived from doctor bladed ZnO NPs were fabricated following the same procedure. NP films lie in the same thickness range as NWs or composite films.<sup>17</sup>

$J(V)$  characteristics were recorded under AM1.5 filtered Xe lamp illumination with an output set at 100  $\text{mW}/\text{cm}^2$  and are presented in Fig. 3. The short circuit current density  $J_{\text{sc}}$ , open circuit voltage  $V_{\text{oc}}$ , fill factor FF, and overall efficiency are reported in the inset of Fig. 3.

When NPs are deposited in the NW network, the fill factor is almost constant and  $J_{\text{sc}}$  increases more than  $V_{\text{oc}}$  decreases, which shows that the NP addition improves the overall cell efficiency. ZnO composite-based cells show better efficiency than bare ZnO NW- and conventional ZnO NP-based cells, which emphasizes the advantages to combine large specific surface area and good electron transport.

In order to elucidate the effect of ZnO NP addition, the anchored dye amount (ADA) onto ZnO has been determined by desorbing the dye in water and ethanol (1:1) solution of  $10^{-2}$  M NaOH and by measuring the solution absorbance at 540 nm. As expected, the ADA increases with the NP addition due to the surface area increase, as reported in Table I. EIS measurements were performed subsequently at  $V_{\text{oc}}$  under AM1.5 illumination in order to characterize the ZnO/dye/electrolyte interface properties. The Nyquist plots of the impedance spectra are shown in Fig. 4. The charge transfer resistance  $R_{\text{ct}}$  related to ZnO/dye/electrolyte interfaces can be determined from the right semicircle diameter (at the low frequency range) while the electron effective lifetime  $\tau_{\text{eff}}$  is given<sup>18</sup> by the following equation:  $\tau_{\text{eff}} = (2\pi f_{\text{min}})^{-1}$ , where  $f_{\text{min}}$  is the frequency corresponding to the imaginary part minimum.  $R_{\text{ct}}$  and  $\tau_{\text{eff}}$  are reported in Table I: it is shown that the  $R_{\text{ct}}$  decreases when NPs are added since the interface area increases. Correlatively, the decrease in  $\tau_{\text{eff}}$  reveals the degradation of the ZnO/dye/electrolyte interface properties with the NP addition.

$J_{\text{sc}}$  and ADA can be linked by the following relation formula:<sup>19,20</sup>

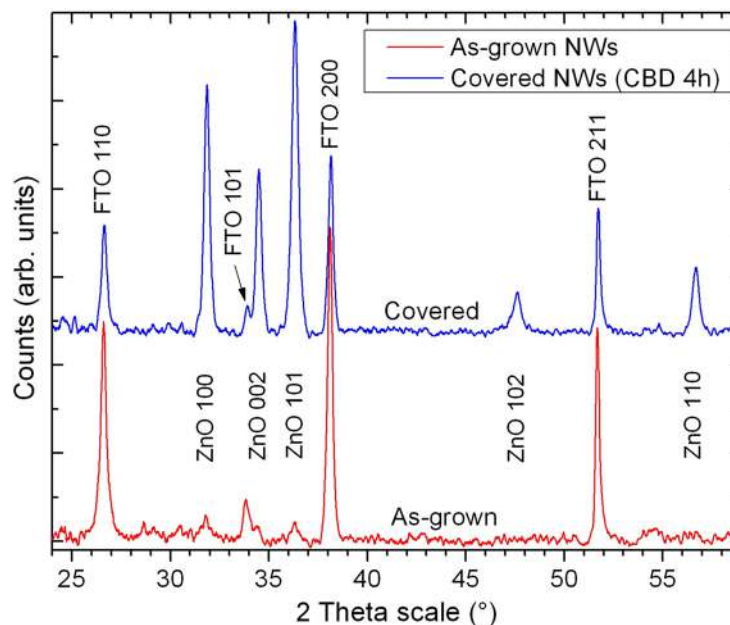


FIG. 2. XRD patterns of as-grown ZnO NWs and ZnO NWs covered with ZnO NPs, on FTO substrate.

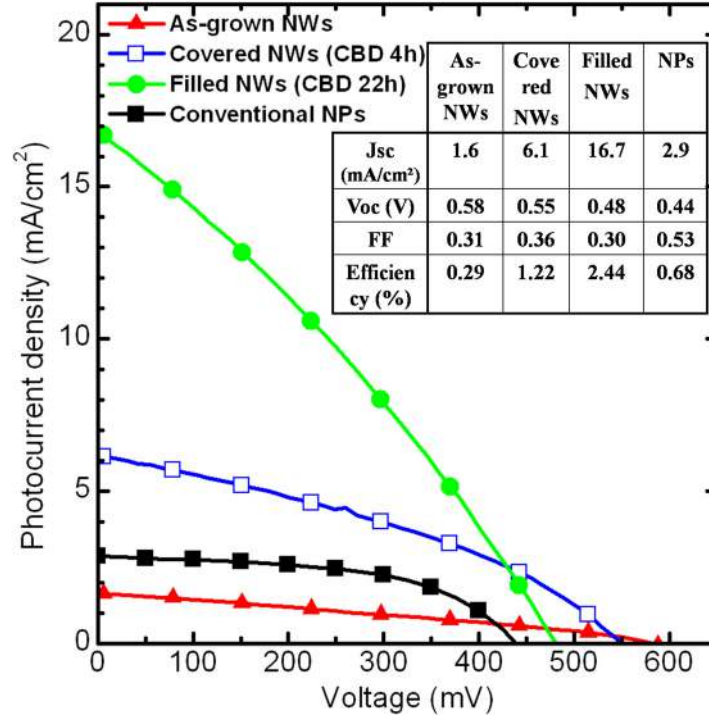


FIG. 3. J(V) characteristics (under AM1.5 illumination) of ZnO NW-, ZnO nanocomposite- and ZnO conventional NP-based DSSCs. The main features are gathered in the inset.

$$J_{sc} = e \int_{\lambda} \Phi(\lambda) \times IQE(\lambda) \times (1 - e^{-\varepsilon(\lambda)ADA}) \times d\lambda, \quad (1)$$

where  $e$  is the elementary charge,  $\lambda$  is the wavelength,  $\Phi$  is the photon flux of the AM1.5 spectrum, IQE is the internal quantum efficiency, and  $\varepsilon$  is the dye molar extinction coefficient. By assuming that the light absorption made by the anchored dye follows the Beer's type law, the term  $1 - e^{-\varepsilon(\lambda)ADA}$  in Eq. (1) refers to the light absorbed fraction (i.e., light harvesting efficiency (LHE)). According to Eq. (1) and to the numerical values given in Table I for  $J_{sc}$  and ADA, the IQE was not reduced when NPs are added into the NW network. This indicated that the interfacial properties between either NPs and NWs or between NPs themselves are relatively good as confirmed by the TEM image in Fig. 1(d). The short distance between NPs and NWs as compared to the electron diffusion length in DSSCs of about 10  $\mu\text{m}$  could be also involved.<sup>21</sup>

The data given in Table I can also be analyzed by taking the ZnO/dye/electrolyte or ZnO/electrolyte interfaces into account. The product  $ADA \times R_{ct}$  can be related to the dye covered ZnO surface fraction  $\eta$  through the formula:

$$\frac{1}{ADA \times R_{ct}} = \frac{S \times \alpha}{\rho_u} \left[ \frac{1}{\eta} + \left( \frac{\rho_u}{\rho_d} - 1 \right) \right], \quad (2)$$

TABLE I. Data deduced from J(V) curves, dye desorption, and EIS measurements.

	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	ADA (M/cm <sup>2</sup> )	$\tau_{eff}$ (ms)	R <sub>ct</sub> ( $\Omega$ )	ADA $\times$ R <sub>ct</sub> ( $\Omega$ mA/cm <sup>2</sup> )
As-grown NWs	0.58	1.6	$1.5 \times 10^{-9}$	25	520	$7.8 \times 10^{-7}$
Covered NWs	0.55	6.1	$5.8 \times 10^{-9}$	9	80	$4.6 \times 10^{-7}$
Filled NWs	0.48	16.7	$16.1 \times 10^{-9}$	7	33	$5.3 \times 10^{-7}$

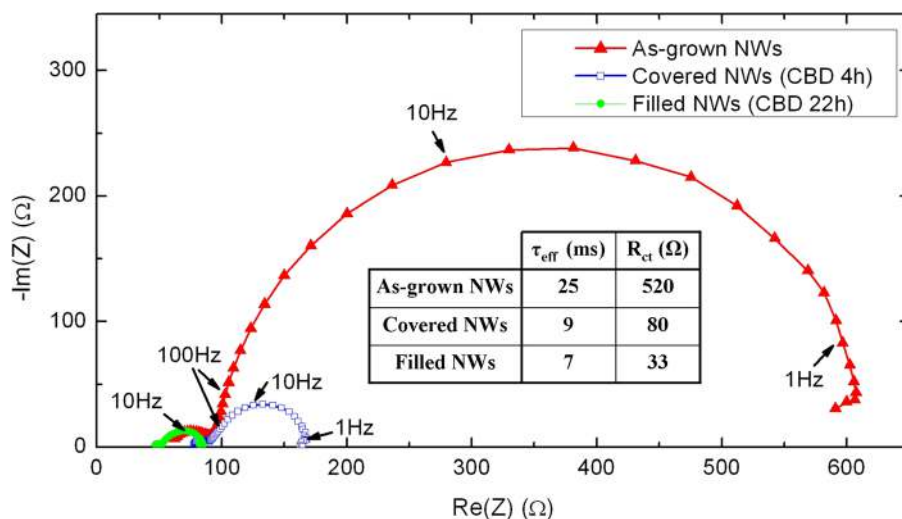


FIG. 4. Nyquist diagram from EIS measurements (under AM1.5 illumination) of ZnO NWs and nanocomposites-based DSSC.

where  $S$  is the sample surface area ( $0.25 \text{ cm}^2$ ),  $\alpha$  is the surface area occupied by one monolayer of one dye mole, whereas  $\rho_d$  and  $\rho_u$  are the interfacial resistivity of dyed or undyed interfaces, respectively. According to the variation of  $\text{ADA} \times R_{\text{ct}}$  as reported in Table I,  $\eta$  is higher for as-grown NWs than for filled or covered NWs which may lead to dye uncoated surfaces in the latter cases. A consequence of these dye free surfaces is a direct contact between ZnO and the electrolyte, leading to electron leakage by charge recombinations at interfaces. This can account for the fall in  $\tau_{\text{eff}}$  and  $R_{\text{ct}}$  and hence in  $V_{\text{oc}}$  when NPs are added in the NW network (see Fig. 3 and Table I).

The dye loading time was set to 3 h instead of 10 min for the NP filled NWs and the  $J(V)$  characteristic was recorded under the same experimental conditions. As expected for a better dye covering, the resulting  $V_{\text{oc}}$  was 0.53 V instead of 0.48 V for 10 min dye loading. However,  $J_{\text{sc}}$  fell to  $7.7 \text{ mA/cm}^2$ , which may be due to the unfavorable formation of the  $\text{Zn}^{2+}$ /dye-complex layer on the ZnO surface. This thin layer is expected to annihilate electron injection from dye molecules into ZnO, as reported for NP structures.<sup>22,23</sup>

In conclusion, ZnO nanocomposites as photoanodes for DSSCs were fabricated by covering ZnO NWs grown by MOCVD with ZnO NPs deposited by CBD. The NP deposit is conformal from the NW bottom to their top and results in a beneficial increase in the specific surface area with respect to bare ZnO NWs. The DSSC efficiency is improved with the NP addition and reaches 2.44% owing to a strong jump of  $J_{\text{sc}}$  up to  $16.7 \text{ mA/cm}^2$ . This indicates that ZnO nanocomposites are very promising to fabricate low-cost and efficient DSSCs. However,  $V_{\text{oc}}$  was decreased when NPs are added since  $\tau_{\text{eff}}$  falls significantly. This emphasizes the occurrences of dye uncovered surfaces and also points out the importance to improve the quality of the ZnO/dye/electrolyte interface properties.

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- <sup>14</sup>Zinc pentane-2,4-dionate hydrate was dissolved (37.5 mM) in propan-1-ol and methanol (19:1). This precursor solution was sprayed in an evaporator heated at 250 °C. The argon flow carried the precursor vapor to the substrate heated at 400 °C under 2.5 Torr.
- <sup>15</sup>The first step consists in the growth of a layered hydroxide zinc acetate (LHZA) by immersing ZnO NWs in a methanolic solution of zinc acetate dihydrate (0.15 M) at 60 °C. The second step allowed transforming the LHZA into ZnO through an air annealing (200 °C during 5 min followed by 450 °C during 10 min).
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