

Dye Aggregation Influence on Dye Sensitized Solar Cell Performance in Nanocoral ZnO-Based Thin Film Cells Sensitized with N-719 and Rose Bengal Dyes

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Dye sensitized solar cells were fabricated using ZnO nanostructured photoelectrodes sensitized with N-719 or Rose Bengal dyes. We assessed the device performance as a function of the sensitization time and found a dependence on time for the N-719 and no significant changes for the Rose Bengal. Furthermore, we observe that the structure of the N-719 molecule beneficial for sensitization of TiO₂ may lead to the degradation of the ZnO crystals and a growth of an amorphous shell limiting dye performance in the cells.

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1. Introduction

Dye sensitized solar cells (DSSCs) are a class of photovoltaic devices [1] which has been receiving significant attention due to the possibility of tailoring the absorption properties of the electrodes by sensitizing them using a large family of dyes [2]. The standard electrodes for DSSC consist of mesoporous titanium dioxide (TiO₂) nanostructures which are transparent to the visible light but yield an increased surface area for high dye coverage and efficient photon absorption. Due to the electron mobility in bulk zinc oxide (ZnO) being $\approx 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [3], which is two orders of magnitude higher than in TiO₂ [4], ZnO has been regarded as promising for replacing TiO₂ as the electrode material. Since the electrode morphology is relevant in the electron transport from the dye to the terminal [5] ZnO has an additional benefit of being synthesized in a wide array of nanoscale morphologies [6].

In this communication we report on the application of nanostructured ZnO electrodes in DSSCs which were synthesized by a unique approach of magnetron sputter deposition of nanoporous Zn with postdeposition annealing [7]. Being a large-scale vacuum technique magnetron sputtering enables high throughput stable processing, relevant for potential fabrication. Furthermore, a direct comparison of two most commonly used dyes, the ruthenium complex N-719 and Rose Bengal (RB), in one structure is performed and the properties of their interface with ZnO studied.

2. Experimental

The DSSC is a device consisting of a dye-sensitized photoanode, catalytic counter electrode, redox electrolyte and a seal/spacer. Both electrodes were prepared on fluorine-doped indium tin oxide (FTO) covered

glass. The photoanode was fabricated through deposition of a nanocoral Zn film by magnetron sputtering with subsequent annealing in an oxygen flow at 400 °C for 5 min. To increase its conductivity, it was doped with hydrogen by annealing in an Ar/H₂ flow at 350 °C for 3 s. The photoelectrodes were sensitized by soaking in 0.25 mM ethanol suspensions of the N-719 and RB dyes. The soaking times were in the range of 0.5 to 20 h. The counter electrode was a 5 nm thin Pt film on the FTO-covered glass. Holes were drilled for electrolyte filling in the counter electrode and the cell was assembled by hot pressing the two electrodes together using a 25 μm thick adhesive gasket. Finally, the structure was filled with a iodide/tri-iodide electrolyte and sealed.

We measured the cell performance using a solar simulator under 1 sun 1.5 AM conditions. Areal short circuit current density (J_{SC}) and open circuit voltages (V_{OC}) were determined, along with the filling factor FF and cell efficiency η . A model was fitted to the data to determine the series (R_{s}) and shunt (R_{sh}) resistivities. The model consisted of the photocurrent source, diode and shunt resistor in parallel, connected in series to the series resistor. The morphology of the sensitized photoanodes was imaged using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). High resolution TEM (HR-TEM) along with energy dispersive spectroscopy (EDX) were applied to study in detail the surface of dye-loaded ZnO.

3. Results and discussion

Comparing the performance of the cells sensitized with two dyes, it is evident that both the highest J_{SC} and V_{OC} are obtained with the N-719 dye (see Fig. 1). This may be due to better surface coverage of the semiconductor nanostructures. It is known that the carboxylic acid groups (RCOOH) play a significant role in dye anchoring to the surface of TiO₂ forming relatively strong intimate ester bonds [8]. Their absence in the RB molecule (see insets

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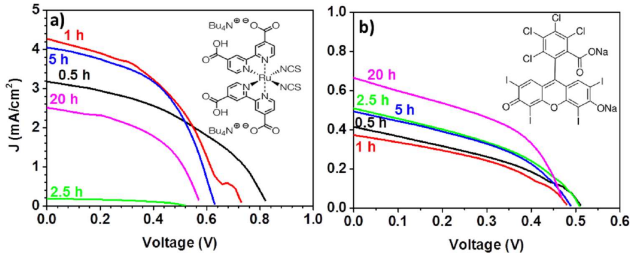


Fig. 1. Current–voltage characteristics of the illuminated cells with electrodes sensitized with (a) N-719 dye and (b) Rose Bengal dye. The insets show the molecular structure of the respective dyes.

in Fig. 1) may be the reason for decreased adsorption in our electrodes. If that would be the case, it would seem that this bond formation is much more relevant in ZnO than in TiO₂ where RB has been successfully used for sensitization.

By changing the sensitization time (t_s) we can obtain different J_{SC} and η . In the N-719 case their dependence on time would show a maximum for 1 h and a decreasing trend for larger t_s (see Table I). For $t_s = 2.5$ h very small currents can be seen and this effect was seen also when we repeated the experiment. From modelling we see that a significant increase in R_{sh} was observed for this sample. However, the reason for such behavior cannot be explained at the moment. For RB the J_{SC} and η shows negligible dependence on t_s . The case with V_{OC} is similar. Its value drops with the increase of t_s but this drop is more evident for N-719 (0.25 V) than for RB (0.05 V). Taking all data into account, including the modelling results, it can be said that the RB efficiency is not significantly dependent on t_s in technologically viable times.

TABLE I

Electrical parameters of the cells sensitized with the N-719 and RB dyes for increasing sensitization times (t_s).

t_s [h]	J_{SC} [mA/cm ²]	V_{OC} [V]	η [%]	FF [%]	R_s [Ω]	R_{sh} [kΩ]
N-719						
0.5	3.19	0.84	1.07	40	48	0.7
1	4.74	0.74	1.37	39	11	0.8
2.5	0.18	0.55	0.04	42	28	7.7
5	4.18	0.64	1.34	50	17	0.6
20	2.51	0.59	0.73	49	5	1.0
Rose Bengal						
0.5	0.83	0.52	0.17	40	77	1.2
1	0.75	0.50	0.15	39	68	1.8
2.5	0.79	0.52	0.17	41	23	1.5
5	0.75	0.50	0.15	41	29	1.4
20	0.84	0.48	0.19	48	17	1.3

From SEM cross-section images of the electrodes we can see that the two dyes show different behavior on the ZnO nanostructures. In the case of RB, we observe no

significant changes in the morphology of individual grains with increasing t_s (see Fig. 2). It is therefore confirming the above hypothesis relating the absence of carboxyl acid groups to low semiconductor adsorption. At the same time, we can see a layer of material aggregating nonuniformly on top of the ZnO electrode for large t_s . This however is not conformal to ZnO and is related to self-aggregation of dye molecules. This aggregation does not block the pores and thus does not change cell performance. On the other hand, for the N-719 dye a conformal shell on the nanostructured ZnO is visible, most notable in the top part of the electrode.

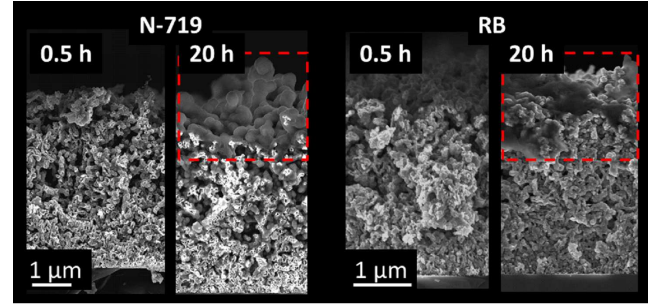


Fig. 2. SEM plan-view images of the ZnO electrode sensitized by N-719 and RB dyes for 0.5 h and 20 h. Red lines mark areas of visible conformal coverage (N-719) and dye self-aggregation (RB).

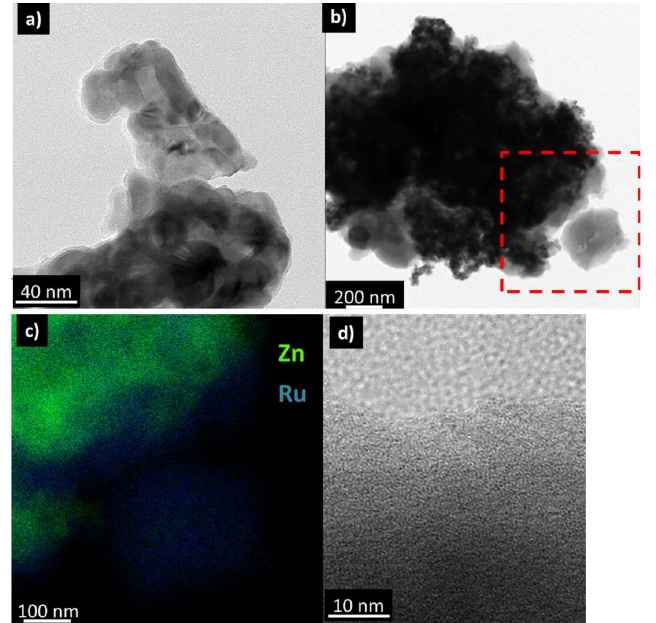


Fig. 3. TEM images of ZnO electrode sensitized for (a) 0.5 h and (b) 20 h. (c) EDX element map of Zn and Ru atoms of the area in (b) marked in red. (d) HR TEM image of the amorphous shell.

We applied TEM investigations to understand the nature of the surface shell in the N-719 samples (see Fig. 3).

The shell grows thicker with sensitization time and by means of EDX mapping we were able to see that there is a small amount of Zn in the Ru-dominant structures. Their microstructure is however atomically amorphous and they can be a product of a reaction between ZnO and the N-719 dye. Most probably the carboxylic acid groups led to dissolution of ZnO and its incorporation into the newly formed compound. Therefore, the same groups that are responsible for the high dye anchoring in TiO₂ may degrade the chemically sensitive ZnO.

4. Conclusions

We fabricated DSSCs with nanocoral ZnO photoanodes fabricated by means of magnetron sputter deposition with postdeposition annealing. We sensitized them with N-719 or Rose Bengal dyes. We assessed the influence of sensitization times of the cell performance finding the highest η for 1 h (1.37%) for N-719 and no significant dependence of η on time for Rose Bengal (0.17%). We relate it to the difference in the chemical structure of the dye molecules. Furthermore, we observe the growth of an amorphous Ru and Zn containing shell on the ZnO nanocrystals in time that we think is related to high ZnO reactivity. Such a shell may limit the cell performance by increasing the dye recharging time from the electrolyte.

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