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Effect of different photoanode nanostructures on the initial charge separation and electron injection process in dye sensitized solar cells: A photophysical study with indoline dyes

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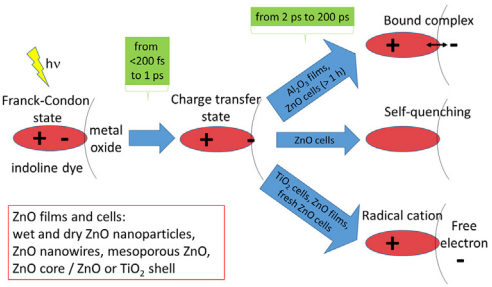
HIGHLIGHTS

- Wide variety of morphologies and preparation methods has been checked for ZnO cells.
- All ZnO cells work worse than TiO_2 ones.
- Effective refractive index might be an additional factor in solar cell performance.
- Excited charge transfer state of indoline dyes participates in the charge separation.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultrafast and fast charge separation processes were investigated for complete cells based on several ZnO-based photoanode nanostructures and standard TiO_2 nanoparticle layers sensitized with the indoline dye coded D358. Different ZnO morphologies (nanoparticles, nanowires, mesoporous), synthesis methods (hydrothermal, gas-phase, electrodeposition in aqueous media and ionic liquid media) and coatings (ZnO–ZnO core–shell, ZnO–TiO_2 core–shell) were measured by transient absorption techniques in the time scale from 100 fs to 100 μs and in the visible and near-infrared spectral range. All of ZnO cells show worse electron injection yields with respect to those with standard TiO_2 material. Lower refractive index of ZnO than that of TiO_2 is suggested to be an additional factor, not considered so far, that can decrease the performance of ZnO-based solar cells. Evidence of the participation of the excited charge transfer state of the dye in the charge separation process is provided here. The lifetime of this state in fully working devices extends from several ps to several tens of ps, which is much longer than the typically postulated electron injection times in all-organic dye-sensitized solar cells. The results here provided, comprising a wide variety of morphologies and preparation methods, point to the universality of the poor performance of ZnO as photoanode material with respect to standard TiO_2.

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1. Introduction

ZnO nanostructures are widely investigated in the group of emerging photovoltaics as promising solutions for pushing the cost-efficiency beyond the reach of contemporary crystalline devices. They are especially explored as photoanodes for dye-sensitized solar cells (DSSC) [1] and n-contacts in both inverted polymer solar cells [2,3] and recently introduced perovskite cells [4,5]. However, in DSSC the predominantly used TiO_2 nanoparticle photoanodes give the record efficiencies of 13% [6], while for the cells based on ZnO the best efficiency is only 7.5% [7]. The difference may seem strange since both oxides share similar energy band properties, with ZnO having much higher carrier mobility (suggesting more favorable transport properties) and an additional useful property of being able to be easily prepared in multitude of morphologies using easy wet methods [1].

Although a large variety of ZnO nanostructures has been proposed to be used as anodes in DSSCs [1], nanoparticles [7,8], nanowire arrays – including more complex variants such multi-branched and hierarchical structures [9–11] – and mesoporous films [12] can be highlighted as those which have attracted most attention. Special interest on the core–shell nanostructures should also be noted [7,13].

In a recent contribution some of us analyzed the performance of ZnO-based DSSC, especially from the point of view of charge separation efficiency within the photoanode on the millisecond time scale [8]. One of the conclusions was that these properties can be at least as good as those of TiO_2 materials. Thus ZnO interaction with dyes and electrolyte is probably the main limiting factor lowering the initial charge injection yield in ZnO-based cells [1,14]. However, the detailed knowledge about such initial charge separation processes in DSSC is still incomplete, especially for the conditions of fully working devices and for a variety of nanostructures. One of the reasons is that the ultrafast dynamics of the interaction of dyes (especially all-organic) with metal oxide nanomaterials, explored by time-resolved laser techniques, is not understood well enough, even for standard TiO_2 nanoparticles.

In this article, the electron injection and dye regeneration dynamics in the most representative architectures of ZnO-based DSSC photoanodes of different morphology (nanoparticles, nanowires, mesoporous, core–shell structures), prepared by different synthesis methods (hydrothermal, gas-phase, electrodeposition in aqueous media and ionic liquid media) [15–17], and sensitized by a fully organic, very absorptive dye are studied. The dynamics and efficiency of these processes is compared to standard TiO_2 nanoparticles with the same dye, i.e. the indoline dye coded D358. Furthermore, as a second objective, an extended analysis of the fundamental processes ongoing during electron injection from the D358 dye and the fingerprints of these processes in transient absorption results, a tool necessary for investigation on ultrashort time scales, is reported. Indoline dyes are a very promising family of all-organic dyes with high extinction coefficient, with best sunlight conversion efficiencies of around 10% [18–20]. The most popular member of this family is D149, which has been recently studied in complete cells by some of us with time-resolved laser spectroscopy techniques [21–23]. In this contribution, its newer modification, D358 dye [24,25], is used. The difference between them is that D358 has two anchoring carboxylic groups and a longer hydrocarbon chain preventing formation of aggregates by steric repulsion. Therefore, both the geometry of the dye attached to the metal oxide surface and the average distance between the dyes might be different for D149 and D358, which can influence e.g. the self-quenching process and electron injection dynamics.

2. Material and methods

The ZnO anodes with different morphologies were prepared by a variety of wet-chemistry techniques, among the most frequently reported to obtain each ZnO nanostructure in particular. Briefly, the ZnO nanoparticles (ZnO NPH) were synthesized by a forced hydrothermal method from reaction of zinc acetate and NaOH in ethanol [26]. The ZnO nanowire arrays (ZnO NW) were electrodeposited from aqueous electrolytes as explained elsewhere [16,27]. The mesoporous ZnO films (ZnO MP) were electrodeposited from ionic liquid-based electrolytes, further details can be found elsewhere [17]. Fig. 1 shows the cross-section FESEM micrographs of the different anodes investigated here.

Some ZnO NW anodes were coated with a thin ZnO or TiO_2 film in order to obtain core–shell nanowires. For ZnO/ZnO core–shell nanowires, the ZnO shell was deposited by the protocol previously reported [16], but varying the number of cycles (i.e. 10 – ZnO NW CS10 and 25 – ZnO NW CS25). For ZnO/TiO_2 core shell photoanodes, the ZnO NW array or ZnO NPH samples were placed in the ALD reactor (Picosun). The TiO_2 thin films were deposited onto the ZnO photoanodes using $TiCl_4$ (titanium tetrachloride) and DI water as ALD precursors. Nitrogen (N_2) flow was used as a carrier and a purging gas. $TiCl_4$ precursor and DI water were evaporated at 20 °C. In this study, the standard cycle consisted of 0.1 s $TiCl_4$ exposure, 3 s N_2 purge, 0.1 s exposure to water and 4 s N_2 purge. The total flow rate of the N_2 was 150 sccm. TiO_2 thin films were grown at 300 °C.

For the comparison, ZnO nanoparticles prepared by gas-phase method (ZnO NPG) were also used, as for the photoanodes in our previous studies for D149 dye [22,23]. Such ZnO films were prepared from a commercial (Evonik) dispersion of hydrophilic nanoparticles of ZnO in water (VP AdNano@Zn20, 35 wt.%) with approximate nanoparticle size of 20 nm. Except the ZnO/ZnO core–shell nanowire arrays, all ZnO anodes were annealed at 420 °C in air before sensitization. TiO_2 solar cell devices were fabricated using films consisting of a layer of 20 nm TiO_2 nanoparticles (Dyesol© paste). Films were deposited onto the conducting glass substrates with the screen printing method, and gradually heated under airflow until 500 °C. After sintering the films, an immersion step in a solution of $TiCl_4$ (40 mM) at 70 °C for 30 min was carried out.

The mean thickness values of the different anodes are the following: 1 μm for ZnO NPG, 2 μm for both ZnO NW and ZnO MP, 3.5 μm for ZnO NPH, and 6 μm for TiO_2. The different film thickness resulted in different absorption of the dye on different photoanodes. Therefore, as will be presented in the next section, the relative photocurrent (divided by the number of absorbed photons estimated from the stationary absorption) was used to compare the performance of the different cells. In transient absorption studies the film thickness was not important because the initial signal is proportional to the number of photoexcited dye molecules, and only the normalized kinetics of different photoanodes were compared.

The photoanodes were prepared by sensitization with the D358 indoline dye (Mitsubishi Paper Mills Limited). The anodes were immersed in a 5×10^{-4} M dye and 7×10^{-4} M chenodeoxycholic acid in acetonitrile/tert-butanol (1:1) solution. The samples remained immersed for 55 min and were subsequently rinsed with the same solvent.

The cells were filled with two electrolytes, both in acetonitrile solvent. The first one (EL1) contains: 0.05 M I_2 (99.5%, Fluka), 0.6 M DMPII (1,2-Dimethyl-3-propylimidazolium iodide, >98%, Iolitec), 0.1 M LiI (99%, Aldrich), 0.5 M TBP (4-tert-butylpiridine, 96%, Aldrich) and 0.1 M GuSCN (guanidine thiocyanate, Aldrich). The second electrolyte (EL2) does not contain TBP and was used for several samples to check the effect of shifting metal oxide conduction band towards more positive potentials. It contains: 0.05 M

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