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Improved photoelectrochemical performance of electrodeposited ZnO/EosinY hybrid thin films by dye re-adsorption†

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Dye desorption and re-adsorption post treatments on electrochemically self-assembled nanoporous ZnO/eosinY hybrid thin films lead to a large improvement of the dye-sensitized photoelectrochemical performance, achieving an incident photon to current conversion efficiency up to 90%.

Cathodic electrodeposition of ZnO/dye hybrid thin films from aqueous mixed solution of Zn salts and dye molecules has been proposed as a new synthetic route to photoelectrode materials for dye-sensitized solar cells (DSSCs).[1–4] The process is compatible with plastic film substrates, thus leading its future to the realization of flexible DSSCs.[5] The eminent feature of this one-step electrodeposition is that the hybrid crystalline material is built up from the smallest constituents, namely, inorganic ions and molecules, while the more commonly used processes are the methods to form porous films from nanocrystalline particles of semiconductors.[6] The ZnO/eosinY (hereafter called ZnO/EY) hybrid thin films have emerged as especially unique, consisting of highly oriented hybrid crystals in a sponge-like structure, namely, μm-sized ZnO crystals in which three dimensionally interconnected nanopores are formed and eosinY molecules are bound to their surface in high amount.[3,4] The almost perfect crystalline nature of the ZnO/EY hybrid thin film has also been proven by epitaxial electrodeposition of this material on a single crystal GaN substrate.[7]

The unique structure combining high crystallinity and high surface area leads to a high expectation in its application to DSSCs. Its dye-sensitized photoelectrochemical performance,[2–4] however, did not come up to the highest level one can reach by the conventional method,[8] although its fast photocurrent transient response clearly indicated the benefit from the highly crystallized nature of the material.[4] In this communication, we report our new finding that simple dye desorption and re-adsorption post chemical treatments of the electrodeposited ZnO/EY hybrid thin film significantly improve its dye-sensitized photoelectrochemical property. The unparalleled high performance achieved after these treatments has ultimately proven the high potential of the electrodeposited ZnO thin films.

Details of the film synthesis are described elsewhere.[4] Highly transparent and deeply red-colored ZnO/EY hybrid thin films with uniform thickness (3 μm) were electrodeposited at −1.0 V (*vs.* SCE) for 20 min from an aqueous mixed solution of 5 mM $ZnCl_2$ (Merck), 0.1 M KCl (Merck) and 50 μM eosinY (hereafter called EY) disodium salt (Kanto) maintained at 70 °C, on an F-doped SnO_2 (FTO) coated glass (Asahi Glass) substrate mounted to a rotating electrode through a specially designed attachment and set to 500 rpm. EY molecules are electrochemically reduced at this potential and form stable complexes with Zn^{2+} to create the sponge-like crystalline ZnO/EY hybrid thin films.[3,4] When these films are soaked into a dilute KOH solution (pH 10.5), the loaded EY molecules are almost completely (99.8%) desorbed. The film thickness did not change during this treatment, while the surface morphology of the film became slightly more open (Fig. 1 inset). The resulting colorless porous ZnO thin film could be colored again by refluxing the film in dye solutions. About 60% of the initially loaded amount of EY could be re-loaded into the film (Table 1). Dyes other than EY such as coumarin 343 (Sigma, hereafter called C343) and 2,9,16,23-tetrasulfophthalocyaninato-zinc(II)‡ (hereafter called TSPcZn) could also be loaded to furnish the film in yellow and blue, respectively.§ While C343 is loaded as much as EY, TSPcZn is loaded at a much smaller amount, probably due to its large molecular size and/or its low stability of coordination to the surface of ZnO.

Dye-sensitized photoelectrochemical properties are significantly improved by the dye re-adsorption treatment.¶ Incident photon to current conversion efficiency (IPCE) at the absorption maximum of EY increased from 3.7 (as-deposited) to 91% (re-adsorbed) (Fig. 1),

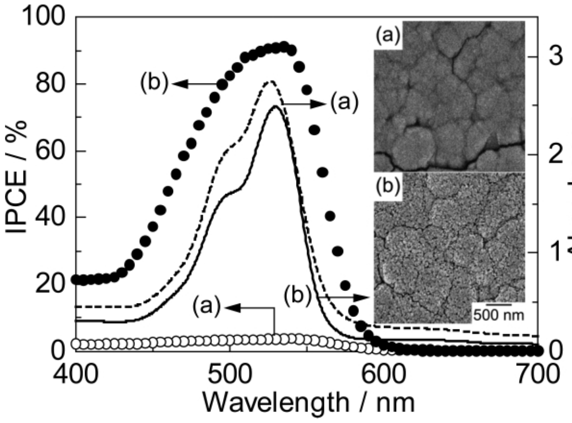

Fig. 1 Surface SEM photographs, Vis absorption spectra and photocurrent action spectra of as-deposited (a) and dye re-adsorbed (b) ZnO/eosinY hybrid thin films.

Table 1 Dye loading and photocurrent density under AM 1.5 irradiation

Dye	Dye loading[a]/nmol cm^{-2}	Photocurrent density/mA cm^{-2}
EY[b]	98	0.33
EY[c]	60	5.9
C343[c]	58	4.0
TSPcZn[c]	3.5	1.1
C343 + EY[c]	34 (C343) 38 (EY)	6.9

[a] Determined by measuring Vis absorption spectra of concentrated ammonia solutions dissolving measured area of ZnO/dye films. [b] As-deposited film. [c] Dye re-adsorbed films.

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while photocurrent density under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) increased from 0.33 to 5.9 mA cm^{-2} (Table 1). On considering the loss of photons caused by surface reflection and absorption by the substrate, the observed high IPCE indicates near 100% efficiencies for electron injection from dye to ZnO as well as collection of the electrons at the back contact.[8] In our preliminary attempt to fabricate a sandwich cell employing a ZnO/EY and a Pt sputtered FTO glass counter electrode, I_{sc} = 6.1 mA cm^{-2}, V_{oc} = 0.59 V, FF = 0.63 and an overall energy conversion efficiency of 2.3% has been achieved under AM 1.5.

As noticed from the increased photocurrent but decreased dye loading for the dye re-adsorbed film (Table 1), aggregates of EY molecules may be formed in the as-deposited film, so that the indirectly bound EY molecules do not inject electrons but lead to non-radiative decay of the excited states. Dye desorption and re-adsorption treatments probably result in ideal monolayer coverage of EY, which should be smaller in amount than that in the as-deposited film. The ultimately high efficiency is thus achieved as all of the EY molecules can act as sensitizers and owing to the very fast electron transporting property of the porous ZnO shown already by detailed photoelectrochemical analysis of the as-deposited ZnO/EY film.[4,9]

Thin films re-loaded with C343 and TSPcZn also exhibit high photoelectrochemical activities (Fig. 2 and Table 1). While C343 marks a high IPCE equivalent to that of EY, only a moderate IPCE of 12.5% is achieved with TSPcZn partly due to the low amount of the adsorbed dye. However, this value is in fact about 100 times higher than that achieved with the ZnO/TSPcZn hybrid thin film prepared by one-step electrodeposition.[10] Quite remarkable is the absence of TSPcZn dimers as evident from both the absorption and the action spectra which are clearly characterized to monomeric TSPcZn. Formation of TSPcZn dimers on ZnO powders refluxed in the dye solution was previously shown[1] and is responsible for its low activity of photosensitization.[10] It is likely that the nanoporous structure formed with EY molecules as templates is so small that it does not allow TSPcZn dimers to enter the film and that only monomers are selectively adsorbed during the re-adsorption.

Nice crossover of the action spectra with the three dyes and their broad coverage of the solar spectrum are recognized from Fig. 2. Combination of the dyes in three primary colors (yellow, magenta, cyan) provides a mean to furnish solar cells in all rainbow colors. At the same time, the spectrum can be broadened for increased efficiencies. Co-adsorption of C343 and EY from their mixed solution at equal concentrations indeed resulted in formation of an orange film. Dye loading of this film shows that the sites for dye adsorption in ZnO are quite equally shared between C343 and EY (Table 1). Further, both the absorption and the action spectra of this film almost reflect the sum of the contributions of the two chromophores (Fig. 3). Especially important is the fact that the high activities of photosensitization are preserved for the two dyes, even when these dyes with different excitation energy levels are co-adsorbed in such a close proximity. As a consequence, a photocurrent density of 6.9 mA cm^{-2} has been achieved, which is higher than those obtained with either one of the two dyes alone.

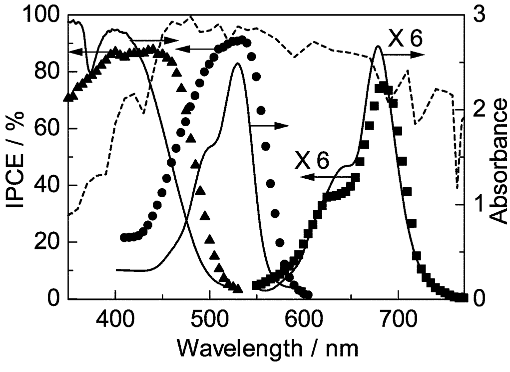

Fig. 2 Photocurrent action and Vis absorption spectra of the electro-deposited ZnO thin film electrodes with C343 (▲), EY (●) and TSPcZn (■, 6 times enlarged for better visibility) re-adsorbed, compared to the AM 1.5 solar spectrum given in a relative energy scale (---).

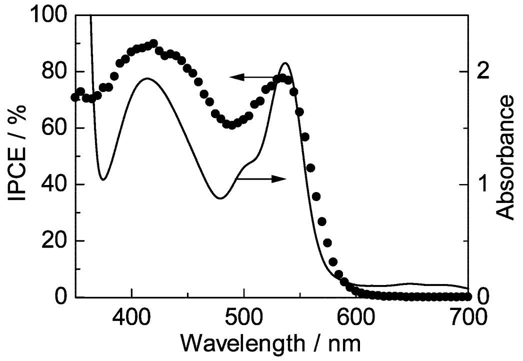

Fig. 3 Photocurrent action and Vis absorption spectra of the electro-deposited ZnO thin film electrode co-adsorbing C343 and EY.

In summary, the simple dye re-adsorption post treatment has been found to fully utilize the potential of the electrodeposited ZnO/EY hybrid thin film. Dye desorption can also be regarded as a way to obtain an efficient porous ZnO electrode. Such a material may also exhibit high performances in applications other than DSSCs. Moreover, the whole process of materials preparation does not involve high temperatures, high mechanical stress nor aggressive chemicals, being perfectly compatible with conductive plastic film substrates. Development of flexible, transparent and colorful solar cells employing electrodeposited ZnO/dye hybrid thin films is under way.

Notes and references

‡ Synthesized according to the method described in literature.[11]

§ Re-adsorption of EY and C343 was carried out in 0.5 and 0.1 mM ethanolic solutions, respectively, while TSPcZn was adsorbed from a 0.25 mM aqueous solution. Co-adsorption of C343 and EY was carried out in an ethanolic mixed solution of 0.1 mM C343 and 0.1 mM EY.

¶ All measurements at the ZnO/dye photoelectrodes were carried out under controlled potentials with respect to a home-made Ag/Ag$^+$ reference electrode (= +0.17 V *vs.* SCE) in a three electrode single compartment cell containing acetonitrile–ethylene carbonate mixed solution (1 : 4 by volume) dissolving 0.5 M tetrabutylammonium iodide and 0.05 M I_2 as redox electrolyte. Light was illuminated from the side of the FTO glass substrate. Photocurrent action spectra were obtained by measuring photocurrent at −0.1 V (*vs.* Ag/Ag$^+$) under monochromatic light illumination with a constant photon number (10^{16} cm^{-2} s^{-1}). Photocurrent density under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) was measured at −0.1 V (*vs.* Ag/Ag$^+$). A Bunko-Keiki CEP-2000 system was used for these measurements.

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