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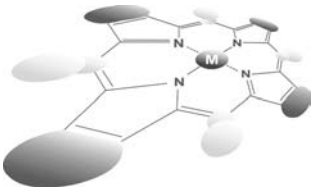

Symmetrically and unsymmetrically substituted carboxy phthalocyanines as sensitizers for nanoporous ZnO films

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ABSTRACT: The photoelectroectrochemical studies of water soluble octacarboxylated oxotitanium (OTiOCPc), zinc (ZnOCPC), hydroxyaluminium ((OH)AlOCPc), dihydroxysilicon ($(OH)_2$SiOCPc), hydroxygallium (OHGaOCPc) and low symmetry zinc monocarboxy (ZnMCPc) phthalocyanines were performed. The dyes were adsorbed to nanoporous ZnO electrodeposited in the presence of eosin Y as structure directing agent (SDA) on FTO substrates by refluxing or soaking the films in a solution containing the dye of interest such that a full surface coverage was achieved. High external (*IPCE*) and internal (*APCE*) quantum efficiencies of up to 50.6% and 96.7% were achieved for the OTiOCPc complex. There was a lower overall cell efficiency for cells sensitized with phthalocyanines containing hydroxyl as axial ligand ZnO/$(OH)_2$SiOCPc, ZnO/(OH)GaOCPc and (OH)AlOCPc because of strong aggregation on the surface of the electrodes. To further suppress dye aggregation, the zinc complex of a new monocarboxylated phthalocyanine sensitizer with bulky naphtho side groups (ZnMCPc) was employed. Among the studied sensitizers, ZnMCPc gave the highest overall cell efficiency of phthalocyanine electrodeposited on ZnO of $\eta = 0.48\%$.

KEYWORDS: octacarboxy phthalocyanine, monocarboxy phthalocyanine, photoelectrochemistry, zinc oxide, eosin Y, photocurrent, photon-to-current conversion efficiency, quantum yield.

INTRODUCTION

Organic dyes show promise as possible sensitizers for semiconductor transition metal oxide photoelectrodes [1]. Considerable attention has been paid to dye sensitized solar cells (DSSC) as they are cheap, effective and environmentally friendly candidates for a new generation of solar power devices [2]. DSSC is a photoelectrochemical device which effectively utilizes a property of nanocrystalline wide bandgap nanoporous semiconductor metal oxide electrode such as ZnO [3] or TiO_2 [4]. Considerable work has been done on TiO_2 as a transparent metal oxide with ruthenium based complexes as photosensitizers [1, 4, 5]. ZnO can serve as an alternative to provide a porous, yet crystalline semiconductor electrode of continuous electrical pathways [3]. It provides similar band edge positions and a similar band gap as TiO_2 and even provides a higher electron mobility compared to TiO_2, making it a very attractive electrode material [6]. ZnO shows larger chemical reactivity at the surface. The larger sensitivity in the UV does not hurt in this context since UV light is excluded by the substrate electrode materials. Its higher chemical reactivity on the other hand allows very detailed structural optimization. In the present work, crystalline ZnO is obtained by electrodeposition from aqueous zinc salt solutions on fluorine doped tin oxide (FTO) [3]. This is a low temperature process and the deposition is therefore compatible with thermally sensitive substrates opening this deposition route for a variety of applications [7–10]. Porosity of the electrodes can be achieved by electrodeposition in the presence of a structure directing agent such as eosin Y [11–13], which can then be easily desorbed from the surface to prepare an open sponge-like structure with a high surface area for further loading of sensitizer molecules [14].

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