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Cosensitization of a nanostructured TiO_2 electrode with tetrasulfonated gallium phthalocyanine and tetrasulfonated zinc porphyrin

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Abstract

The cosensitization of a nanostructured TiO_2 electrode with the spectral complementary dyes, tetrasulfonated gallium phthalocyanine (GaTsPc) and tetrasulfonated zinc porphyrin (ZnTsPP), is reported. For the liquid junction cell based on a nanostructured TiO_2 electrode cosensitized with GaTsPc and ZnTsPP molecules, cosensitization extends the absorbance into the region 400–750 nm, resulting in an improvement of the light-harvesting efficiency and short-circuit photocurrent on illumination at 35.7 mW cm^{-2}. The photocurrent response at 685 nm, corresponding to the absorbance of the GaTsPc monomer, is strongly enhanced, probably due to the decrease in the surface concentration of GaTsPc molecular dimers and the possible formation of an extended π system in GaTsPc/ZnTsPP heteroaggregates resulting from cosensitization of the electrode. © 1997 Elsevier Science S.A.

Keywords: Cosensitization; Heteroaggregates; Molecular aggregation; Nanostructured titanium dioxide electrode; Photocurrent

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1. Introduction

The nanocrystalline solar cell, recently developed by Grätzel and coworkers [1,2], overcomes the low efficiency of conventional photoelectrochemical cells or solid cells caused by the inefficient separation and transport of the photogenerated charge carriers [3–5] or the low absorbance [6]. The nanocrystalline solar cell is based on a dye-sensitized colloidal TiO_2 film with a very high surface area. As a consequence, a large number of dye molecules can be adsorbed directly onto the electrode surface, with simultaneous direct contact with the redox electrolyte, resulting in efficient separation and transport of the photogenerated charge carriers and efficient and rapid regeneration of the adsorbed dye molecules [1]. If a sufficiently large surface area of the electrode can be provided, even a monolayer of dye molecules adsorbed on the electrode will absorb most of the energy from the incident light photons [2]. In addition, the photogenerated excitons (or charge carriers), resulting from the adsorbed monolayer of dye molecules on the microporous electrode, are directly transported into the conduction band of the semiconductor electrode. This injection mechanism avoids the recombination loss of photogenerated excitons during diffusion towards the junction region, which is encountered in multilayer cells in which photogenerated charge carriers result from exciton dissociation by the built-in field at the junction region.

In our laboratory, transparent and microporous TiO_2 electrodes with a large surface area of 50 have been fabricated [7–9]. By the addition of hydroquinone to a liquid electrolyte solution containing 0.1 M Na_2SO_4, the quantum efficiency of photoelectric conversion of the microporous TiO_2 electrode, sensitized by zinc phthalocyanine substituted with a carboxyl group, reaches about 20% at 690 nm [8], which compensates for the low efficiency or low absorbance of the ruthenium bipyridine complex at the given wavelength [1,2]. Unfortunately, the dimeric absorbance of tetrasulphonated phthalocyanines (MTsPcs; M ≡ Zn, Ga, Co, In, TiO, H_2) does not convert into photocurrent [9], probably due to aggregation and orientation of the MTsPc molecules self-assembled on the nanostructured TiO_2 electrode via electrostatic interaction of the negatively charged sulfonate (SO_3^-). The rapid internal conversion in the phthalocyanine molecular aggregate is believed to be the main deactivation pathway of photogenerated excitons (or charge carriers) [9,10]. In this paper, we report the cosensitization of a nanostructured TiO_2 electrode

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with tetrasulphonated gallium phthalocyanine (GaTsPc) and tetrasulphonated zinc porphyrin (ZnTsPP). Cosensitization results in an improvement of the light-harvesting efficiency and photoelectric conversion of the nanostructured TiO_2 electrode.

2. Experimental details

TiO_2 colloidal solutions were prepared by the hydrolysis of tetrabutyl titanate ($(C_4H_9O)_4Ti$) by a procedure similar to that described in Ref. [7]. The colloidal solution, on addition of 2 wt.% poly(vinyl alcohol) (PVA), was concentrated to the desired density by vacuum rotation evaporation. After the addition of 1.5 wt.% Triton X-100, the concentrated solution (TiO_2 content, 10 wt.%) was spin coated onto a freshly cleaned indium tin oxide (ITO; sheet resistance, 50 Ω/□; transmission, 95% in the visible region) conducting glass substrate. The sheet resistance of the nanostructured TiO_2 electrode, finally obtained by a heating process similar to that described in Ref. [9], was 500 Ω/□. Prior to dye sensitization, the nanostructured TiO_2 electrodes were soaked in HCl solution (pH 2) and dried naturally.

GaTsPc and ZnTsPP were synthesized according to the methods described in Ref. [11] and Ref. [12] respectively; their molecular structures are shown in Fig. 1(a) and (b). For sensitization with GaTsPc or ZnTsPP dye molecules alone, the working electrode was obtained by plunging the TiO_2 electrode into a 5×10^{-5} M solution of GaTsPc or ZnTsPP in dimethyl sulphoxide (DMSO) until the absorbance of the electrode showed no increase. For cosensitization with GaTsPc and ZnTsPP, the working electrodes were obtained by plunging the TiO_2 electrode into a mixed solution of GaTsPc and ZnTsPP in DMSO until the absorbance of the electrode showed no increase. The total concentration of the mixed solution was 5×10^{-5} M. After the typical performance of the cosensitized TiO_2 electrode had been measured, GaTsPc and ZnTsPP on the TiO_2 electrode were washed away using 0.001 M NaOH solution. The resulting solution was used to analyse the amount of GaTsPc and ZnTsPP molecules adsorbed on the electrode.

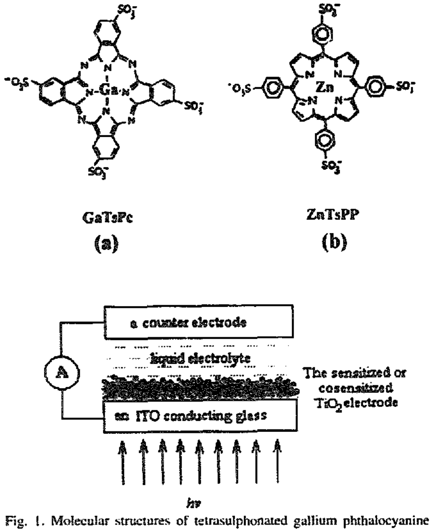

Fig. 1. Molecular structures of tetrasulphonated gallium phthalocyanine (GaTsPc) (a) and tetrasulphonated zinc porphyrin (ZnTsPP) (b) and structure of the liquid junction cell based on the nanostructured TiO_2 electrode sensitized with GaTsPc or cosensitized with GaTsPc and ZnTsPP (c).

As shown in Fig. 1(c), the liquid junction solar cell for measuring the photocurrent consists of a sensitized or cosensitized TiO_2 electrode and a counter electrode separated by an electrolyte solution containing 0.1 M KI and 0.05 M I_2 in 0.001 M $HClO_4$. The counter electrode consists of ITO conducting glass, on which a thin layer of platinum (about 10 nm) has been coated by physical vacuum deposition at 10^{-7} Torr. When light is incident through the counter electrode (the back electrode), ITO conducting glass is used as the back electrode.

The morphology of the TiO_2 electrode was examined by atomic force microscopy (AFM; DI Co., Nanoscope III). The film thickness of the electrode was examined by scanning electron microscopy (SEM; JEOL, JSM-6300). The absorption spectra were recorded with a Shimadzu UV-2201 UV–visible spectrometer. The photocurrent was measured with a potentiostat (model CMBP-1). Monochromatic illumination was obtained using a 500 W xenon arc lamp in combination with a grating monochromator (model WPG3D). The light intensity was calibrated using a model LM-5 laser power meter (National Institute of Metrology, People's Republic of China).

3. Results and discussion

3.1. Spectral characteristics of the nanostructured TiO_2 electrode cosensitized with GaTsPc and ZnTsPP dyes

The nanostructured TiO_2 electrode, characterized by AFM, is composed of interconnected particles (40–60 nm) and pores as shown in Fig. 2 and has a thickness of 10 μm. The specific surface area of the nanostructured TiO_2 electrode is characterized by the dimeric absorbance (see below) in the case of sole sensitization by GaTsPc molecules. Assuming that a monolayer, with an area of 2 nm^2 for each molecule, completely covers the TiO_2 electrode, and that the extinction coefficient of GaTsPc molecules is 3.27×10^7 cm^2 mol^{-1} at 620 nm [13], a specific surface area of the TiO_2 electrode of 370 can be obtained by the formula given in Ref. [2]. The addition of PVA and Triton X-100 prevents the growth of larger TiO_2 crystals and is beneficial to the formation of TiO_2

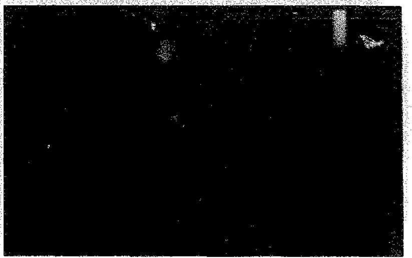

Fig. 2. Surface morphology of the nanostructured TiO_2 electrode by AFM.

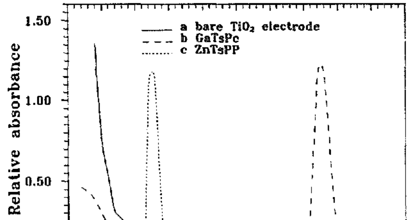

Fig. 3. Absorption spectra of the bare TiO_2 electrode (a), a 5×10^{-5} M solution of GaTsPc in DMSO (b) and a 5×10^{-5} M solution of ZnTsPP in DMSO (c).

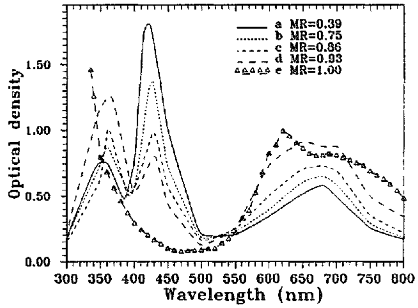

Fig. 4. Absorption spectra of the TiO_2 electrodes cosensitized with GaTsPc and ZnTsPP dyes as a function of the molar ratio of GaTsPc molecules.

nanoparticles and the achievement of a larger specific surface area of the TiO_2 electrode.

The bare nanostructured TiO_2 electrode exhibits the fundamental absorption edge of anatase at 390 nm in the UV region (Fig. 3(a)). Fig. 4 shows the measured absorption spectra of the TiO_2 electrode cosensitized with GaTsPc and ZnTsPP dye molecules. The nanostructured TiO_2 electrode cosensitized with GaTsPc and ZnTsPP dye molecules reveals the characteristic absorption of GaTsPc and ZnTsPP in the visible region, whereas the TiO_2 electrode sensitized with GaTsPc molecules alone reveals the characteristic absorption of GaTsPc between 580 and 750 nm in the visible region; therefore cosensitization of the electrode with GaTsPc and ZnTsPP dyes extends the absorbance of the electrode in the visible region (400–750 nm). The photocurrent response in the visible region results from the absorbance of the dye molecules adsorbed on the TiO_2 electrode. The light-harvesting efficiency, which is defined as the fraction of incident photons absorbed by the dye, is obtained by integration of the spectral overlap between the emission spectrum of the light source and the absorption band of the cosensitized TiO_2 electrode. TiO_2 electrodes sensitized with GaTsPc or ZnTsPP alone harvest only 19.5% or 14.9% of the incident light energy flux, which is smaller than that of the cosensitized electrode. Cosensitization markedly enhances the light-harvesting efficiency of the dye-sensitized TiO_2 electrode, as shown in Table 1.

3.2. *Molecular aggregation of GaTsPc on the cosensitized TiO_2 electrode*

In DMSO, the absorption spectrum of GaTsPc obeys Beer's law over the concentration range 10^{-6}–10^{-3} M. The GaTsPc spectrum at a concentration of 5×10^{-5} M consists of a strong sharp π–π^* absorption between 650 and 710 nm, accompanied by a much weaker vibrationally coupled satellite band at 606 nm as shown in Fig. 3(b). In previous studies, the narrow longer wavelength absorption at 675 nm has been attributed to a monomeric phthalocyanine compound, and the broad partially resolved absorption at 606 nm has been assigned as the characteristic absorption of the GaTsPc dimer [13,14]. The fact that the GaTsPc electronic spectrum in DMSO follows Beer's law shows that GaTsPc exists mainly as a monomer in DMSO.

Compared with the GaTsPc spectrum in DMSO, the absorption spectra of GaTsPc molecules adsorbed and coadsorbed on the nanostructured TiO_2 electrode show striking differences (Fig. 4). When adsorbed or coadsorbed on the electrode, the absorption of the GaTsPc monomer exhibits a red shift of 5–15 nm relative to that in DMSO. The red shift of the GaTsPc monomeric absorbance, given in Table 1, is dependent on the molar ratio ($MR = [GaTsPc]/([GaTsPc] + [ZnTsPP])$) of GaTsPc molecules on the cosensitized TiO_2 electrode. The red shift gradually increases up to a molar ratio of GaTsPc of 0.86. For GaTsPc molecules coadsorbed on the TiO_2 electrode, a second strong, broad and well-resolved π–π^* absorption at 620 nm appears, with a markedly increased intensity relative to the first π–π^* absorption and satellite band; a peak absorbance finally occurs in the case of pure GaTsPc molecules. The π–π^* transition with a broader natural bandwidth is a result of molecular association with cofacial phthalocyanine ring orientation [14,15] (i.e. face-to-face H-type aggregation). These results indicate the

Table 1
Characteristics of the GaTsPc molecules adsorbed or coadsorbed on the nanostructured TiO_2 electrode

Molar ratio of GaTsPc	Light-harvesting efficiency (%)	Short-circuit photocurrent ($\mu A\ cm^{-2}$)	Wavelength (nm)		Optical density		Concentration ($\times 10^{-8}$ mol cm^{-2}) [a]		Molar ratio of dimer to monomer (Γ_d/Γ_m)
			λ_m	λ_d	OD_m	OD_d	Γ_m	Γ_d	
1.00	19.5	110.0	685	620	0.780	0.941	0.605	2.87	9.49
0.93	30.4	246.1	695	620	0.829	0.790	0.643	2.42	7.53
0.86	26.5	370.6	682	620	0.698	0.558	0.541	1.70	6.28
0.75	25.9	460.3	680	620	0.622	0.438	0.482	1.34	5.56
0.39	27.9	771.0	680	620	0.518	0.400	0.402	1.22	6.07
0.0	14.9	605.0	–	–	–	–	–	–	–

[a] $\Gamma(\lambda) = OD(\lambda)/\epsilon(\lambda)$ [1,2], where $OD(\lambda)$ and $\epsilon(\lambda)$ are the optical density and extinction coefficient of the dyes at the given wavelength, respectively. The subscripts "m" and "d" denote the monomer and dimer.

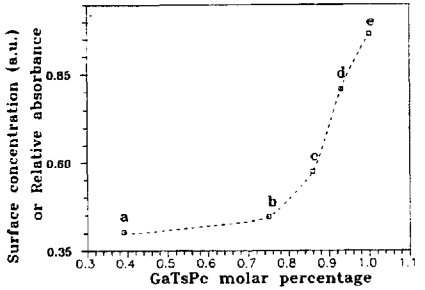

Fig. 5. Absorbance or surface concentration of GaTsPc molecular dimers as a function of the molar ratio of GaTsPc molecules.

occurrence of higher order molecular aggregation of GaTsPc on the nanostructured TiO_2 electrode. Assuming that the dimer is the highest order aggregate and that the extinction coefficient of the GaTsPc monomer is equal to 1.29×10^8 cm^2 mol^{-1} [13], it is concluded that GaTsPc exists mainly as a cofacial dimer adsorbed on the nanostructured TiO_2 electrode. The absorbance or surface concentration is increased with increasing molar ratio of GaTsPc molecules, as shown in Fig. 5. The surface concentration of GaTsPc dimers and the molar ratio of dimers to monomers on the cosensitized TiO_2 electrode are given in Table 1. In general, ZnTsPP doping decreases the surface concentration of the dimer and the molar ratio of dimers to monomers on the cosensitized electrode.

Compared with the absorption of the porphyrin solution in DMSO in Fig. 3(c), that of the film shows a red shift of 5–10 nm in the Soret and Q bands (Fig. 4). This indicates strong interaction between the molecules self-assembled on the TiO_2 electrode. It has been confirmed that the interaction between two porphyrin rings leads to face-to-face molecular aggregation with offset centres in solution and in crystals [16]. On this basis, we conclude that the red shift is due to the adoption of a face-to-face stacking orientation in ZnTsPP molecular aggregates coadsorbed on the nanostructured TiO_2 electrode; an extended and conjugated face-to-face system is formed with π orbital overlap. Such an extended and conjugated system within the molecular aggregates lowers the excitation energy of the π–π^* and n–π^* electron transitions, resulting in a red shift in the Soret and Q band absorption.

3.3. *Photoelectric conversion of GaTsPc molecules on the nanostructured TiO_2 electrode*

Fig. 6 shows the measured short-circuit photocurrent of the TiO_2 electrode cosensitized with GaTsPc and ZnTsPP

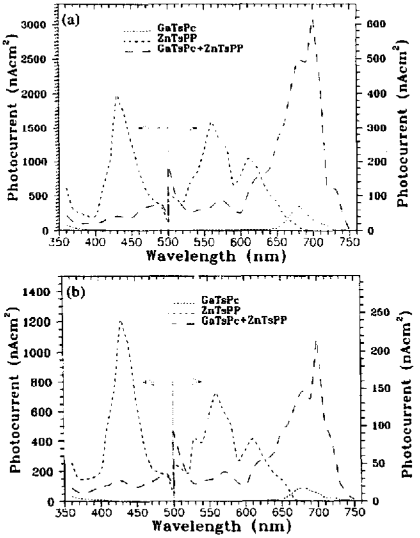

Fig. 6. Photocurrent action spectra of the liquid junction cell based on the cosensitized TiO_2 electrode for light incident through the working electrode (a) and back electrode (counter electrode) (b).

dye molecules as a function of wavelength for light incident through the working electrode and the back electrode. The photocurrent action spectra have been corrected for the absorption of incident light by the ITO conducting glass substrate. The photocurrent for light incident through the working electrode is generally larger than that for light incident through the back electrode, which may be due to the light multi-reflection of the Pt-coated ITO counter electrode and the greater distance of transport of the photogenerated charge carriers towards the TiO_2 electrode in the latter. The photocurrent action spectrum in the former is "in-phase" with that in the latter, indicating that the adsorbed dye molecules exist as a monolayer on the nanostructured TiO_2 electrode or, at least, the thickness of the adsorbed or coadsorbed layer is smaller than the diffusion length (15 nm for phthalocyanine [17]) of the photogenerated charge carriers or excitons. Otherwise, the "in-phase" relation would not be held according to the exciton dissociation theory developed by Ghosh et al. [17]. Therefore it is assumed, reasonably, that the sensitized dye molecules exist as a monolayer self-assembled on the nanostructured TiO_2 electrode. In addition, the "in-phase" relation between the photocurrent action spectra excludes the possibility that the action spectrum of the former results from the filter effect of the adsorbed multilayer of dye molecules.

For the liquid junction cell based on the dye-sensitized TiO_2 electrode, the cosensitization of the nanostructured TiO_2 electrode markedly improves the short-circuit photocurrent, as shown in Table 1, on illumination at 35.7 mW cm^{-2}, and, in particular, the photocurrent response on monochromatic illumination in the wavelength range 580–750 nm (see Fig. 6). The spectral complementarity of the GaTsPc and ZnTsPP dyes in absorption (see Section 3.1) and the photocurrent response improve the photoelectric conversion of the cosensitized TiO_2 electrode. For sensitization with GaTsPc dye molecules alone, the GaTsPc absorbance in the region 430–630 nm is not converted into photocurrent, only that in the region 640–750 nm. For sensitization with ZnTsPP dye molecules alone, the absorbance of the ZnTsPP Soret band in the region 400–470 nm generates a strong photocurrent response and that of the ZnTsPP Q band in the region 500–650 nm shows a weaker photocurrent response. For the TiO_2 electrode cosensitized with GaTsPc and ZnTsPP dye molecules, a photocurrent response in the broader region of 400–750 nm is achieved, although the photocurrent resulting from the absorbance of the ZnTsPP Soret band is smaller than that in the sensitization with ZnTsPP dye molecules alone. Thus an improvement in the photoelectric conversion of the TiO_2 electrode is achieved.

Cosensitization decreases the surface concentration of GaTsPc dimers (see Section 3.2) on the nanostructured TiO_2 electrode and simultaneously enhances the photocurrent response of the GaTsPc monomeric Q band. For light incident through the working electrode or back electrode, the absorbance of the GaTsPc dimer at 620 nm is not converted into photocurrent and only that of the GaTsPc monomer at 685 nm generates a photocurrent for sensitization with GaTsPc dye molecules alone (Fig. 6). This result is in agreement with previous observations [9], and is due to the rapid internal conversion of the photogenerated excitons resulting from phthalocyanine molecular dimers and the anisotropy of charge transport for phthalocyanine compounds [18]. For cosensitization with GaTsPc and ZnTsPP dye molecules, the absorbances at 620 and 685 nm contribute to the generation of a photocurrent. Since, for sensitization with ZnTsPP dye molecules alone, the ZnTsPP absorbance at 685 nm is not converted into a photocurrent, whereas that at 620 nm can generate a photocurrent, the photocurrent response at 685 nm in the cosensitized electrode is attributed to GaTsPc monomeric absorbance. Fig. 7 shows the dependence of the incident-photon-to-current conversion efficiency (IPCE) at 685 nm on the molar ratio of GaTsPc molecules; $IPCE = 1243 I_{SC} \times 100\% / (MR \times \lambda \times P_{in})$, where I_{SC} and P_{in} are the short-circuit current density and the incident light power at the monochromatic wavelength respectively. The IPCE value of 9.8% at MR = 0.39 is eight times higher than that (1.1%) for sensitization with pure GaTsPc molecules alone. However, the surface concentration of the dimer in Table 1 at MR = 0.39 is half that at MR = 1.0, and not eight times smaller. Therefore, in addition to the decrease in surface concentration of the dimer, another mechanism must lead to an increase in the photocurrent at the GaTsPc monomeric absorbance. It is assumed that a heterodimer or heterotrimer is formed between GaTsPc and ZnTsPP molecules during the cosensitization of the nanostructured TiO_2 electrode with a positive charge, although heteroaggregation cannot be observed in the titration of GaTsPc and ZnTsPP in DMSO. It has been confirmed that the face-to-face conformation of heterodimers and heterotrimers appears in supramolecular assemblies of porphyrins and phthalocyanines with oppositely charged, sterically unhindered substituents [19]. The mixed effect may be due to the formation of low-lying charge transfer states [20] in these heteroaggregates as a result of the extended and conjugated face-to-face system with π-

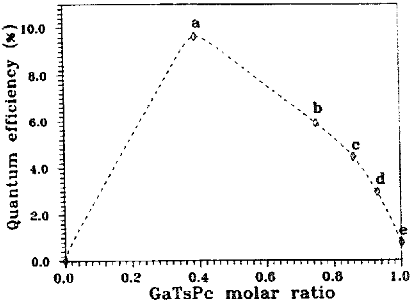

Fig. 7. Quantum efficiency (IPCE) as a function of the molar ratio of GaTsPc on monochromatic illumination at 685 nm for light incident through the working electrode.

orbital overlap between GaTsPc and ZnTsPP. This mechanism needs to be investigated further.

4. Conclusions

Cosensitization with GaTsPc and ZnTsPP molecules extends the absorbance of the electrode, and improves the light-harvesting efficiency and short-circuit photocurrent of the liquid junction cell based on the cosensitized TiO_2 electrode. In particular, the photocurrent response at the GaTsPc monomeric absorbance is strongly enhanced, due to the decrease in the surface concentration of GaTsPc dimers on the cosensitized TiO_2 electrode. This is not sufficient to explain the striking enhancement in the short-circuit photocurrent on monochromatic illumination at 685 nm. Another mechanism may involve the possible formation of GaTsPc/ZnTsPP heteroaggregates during cosensitization.

Acknowledgements

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