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Aggregation and the photoelectric behavior of tetrasulfonated phthalocyanine adsorbed on a TiO_2 microporous electrode

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Abstract

Absorption spectroscopy of tetrasulfonated Zn, Co, Ga, In, TiO and metal-free phthalocyanine on a transparent titanium dioxide film electrode, which is made up of interconnected particles and pores characterized by scanning electron microscopy, has been reported. The chemical modification of the TiO_2 microporous electrode with tetrasulfonated phthalocyanine (MTsPc) extends its absorbance into the visible region. The tetrasulfonated phthalocyanine mainly exists as the dimer on the TiO_2 microporous electrode. The photocurrent action spectroscopy shows that only the absorbance of the MTsPc monomer contributes to the photocurrent while that of the MTsPc dimer does not generate a photocurrent.

Keywords: Tetrasulfonated phthalocyanine; Dimer; Photocurrent; Titanium dioxide; Solid–electrolyte interface

1. Introduction

Organic photovoltage solar cells have been intensively investigated. The major advantages of organic cells in which an organic dye layer is used to extend the absorbance of a solar cell into the visible region are the full use of solar energy and the ease of fabrication and low cost. These devices conventionally have a sandwich structure in which an organic layer is interposed between the metal and semiconductor (or metal) electrode [1–4]. So far, however, the power conversion efficiency is poor at about 1%. Whether in the form of a photoelectrochemical cell or a solid cell, the low efficiency in the organic photovoltaic cell is due to the low efficiency of charge carrier separation and transport if the dye layer is thick [3,4] or due to the low absorbance if the dye layer is thin [5]. The conventional approach to improve the energy conversion efficiency is to increase the conduction of the dye by doping with an appropriate sensitizer such as iodine or AgI [3,6]. Recently, a Swiss research group has developed several concepts in order to overcome the above two limitations. The surface area of the transparent electrode was increased so that a large number of dye molecules can be adsorbed directly on the electrode's surface and simultaneously be in direct contact with the redox electrolyte, which results in efficient separation and transport of the photogenerated charge carrier [7]. If a sufficiently large surface area of the electrode can be provided, even a monolayer of dye molecules adsorbed on the electrode could absorb most of the incident photons [8]. In our laboratory, a microporous electrode with a large surface area had been fabricated [9]. The quantum efficiency of the microporous electrode sensitized with zinc phthalocyanine reaches about 20% at 690 nm [10]. However, we found that the absorbance of the tetrasulfonated phthalocyanine (MTsPc) dimer does not convert into a photocurrent. In this paper, we first report the photoelectric behavior of the MTsPc aggregation, especially for the dimeric phthalocyanine adsorbed on the TiO_2 microporous electrode in detail.

2. Experimental details

TiO_2 colloidal solution were prepared by hydrolysis of tetrabutyl titanate ($(C_4H_9O)_4Ti$) by a similar procedure to that described in [7]. The colloidal solution on addition of 2% poly(vinyl alcohol) was then concentrated to a desired density through vacuum rotation evaporation. The concentrated solution was spin-coated on a conducting glass (indium tinoxide (ITO), 50 $\Omega/\square$) substrate. This was heated in air in a furnace in which the temperature was increased gradually to 723 K and then keep at 723 K for $\frac{1}{2}$h. The conductivity (500 $\Omega/\square$) of the film can be achieved by finally annealing at 823 K under nitrogen gas flow for another $\frac{1}{2}$h.

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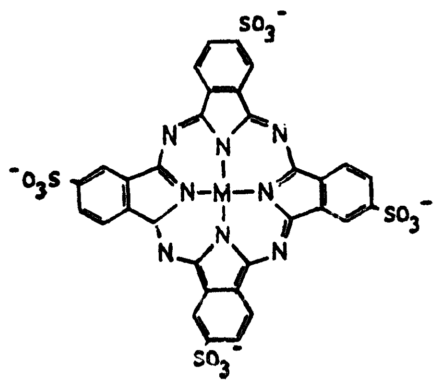

M=Zn,Ga,Co,In,TiO,H$_2$

Fig. 1. The molecular structure of tetrasulfonated phthaloyanine (MTsPc), M = Zn, Co, Ga, In, TiO or H_2.

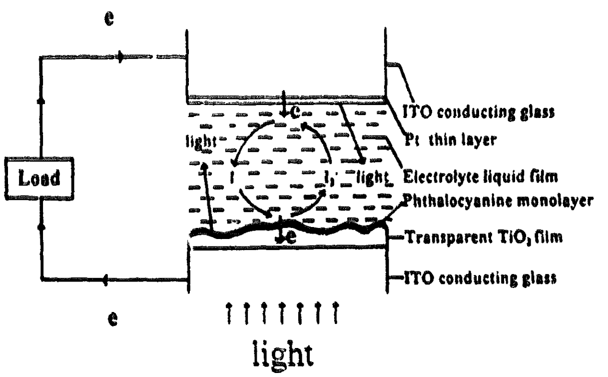

Fig. 2. The structure of the microporous TiO_2/MTsPc/electrolyte liquid junction cell.

The tetrasulfonated Zn, Co, Ga, In, TiO, and metal-free phthalocyanines were synthesized by us according to the method in [11], and the molecular structures are shown in Fig. 1. The working electrode was obtained by plunging the above TiO_2 electrode into a 5×10^{-4} M solution of the tetrasulfonate phthalocyanine in dimethyl sulfoxide (DMSO).

To form the final cell, a drop of liquid electrolyte, which contained 0.1 M KI and 0.05 M iodine in 0.001 M $HClO_4$ solution, is placed on the film to percolate into the pores of the microporous electrode. A counter electrode of ITO conductive glass, on which a thin layer of platinum has been physically vacuum deposited at 10^{-7} Torr, is placed on top and the sandwich is illuminated through the TiO_2 support as shown in Fig. 2.

The morphology of the TiO_2 electrode was examined by scanning electron microscopy (SEM) (Fig. 3). The absorption spectra of the MTsPc/TiO_2 electrode were recorded with a Shimadzu UV-2201 UV-visible spectrophotometer. The photocurrent and photovoltage were 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 intensity was calibrated using a model FP-3 radiometer-photometer.

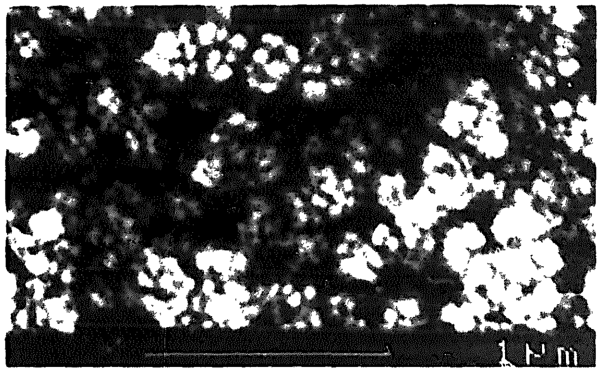

Fig. 3. Morphology of the TiO_2 microporous electrode.

3. Results and discussion

3.1. Absorption spectroscopy of the MTsPc/TiO_2 microporous electrode

The absorption spectra of the TiO_2 electrode with and without a coating of MTsPc have been measured and are shown in Fig. 4. The bare TiO_2 films are transparent and colorless, displaying fundamental absorption onset of anatase at 390 nm (band gap energy, 3.2 eV) in the UV region. The MTsPc/TiO_2 electrodes all reveal the characteristic absorption between 580 and 750 nm in the visible region, indicating that the sensitization of the TiO_2 electrode with MTsPc dye molecules could extend the absorbance of the electrode into the visible region. The electrode, characterized by SEM, is composed of interconnected particles (50–70 nm) and pores as shown in Fig. 3 and is found to have a thickness of 10 um. The specific surface areas of TiO_2 microporous electrode have been listed in Table 1, which can be derived from a similar method to that described in [8] by assuming complete monolayer coverage on TiO_2 electrode and a 2 nm^2 area for each molecule. At $\lambda = 615$ nm, the optical density of the ZnTsPc/TiO_2 electrode and the extinction coefficient of the ZnTsPc dye are about 1.08 and 2.7×10^8 cm^2 mol^{-1} [12] respectively. For the ZnTsPc/TiO_2 microporous electrode, a specific surface area of 50 is obtained, which is the maximum for the MTsPc/TiO_2 electrodes.

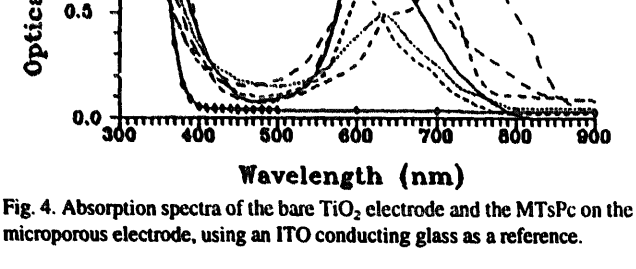

Fig. 4. Absorption spectra of the bare TiO_2 electrode and the MTsPc on the microporous electrode, using an ITO conducting glass as a reference.

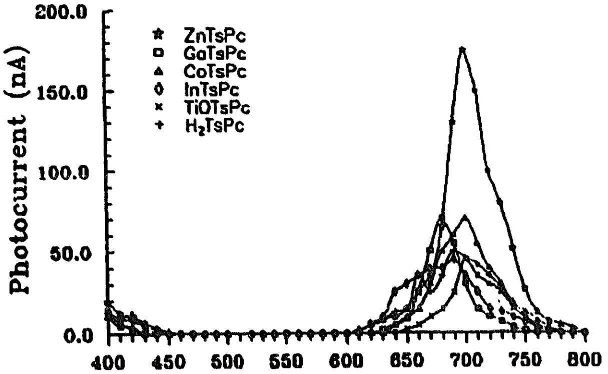

Fig. 5. Photocurrent spectra of the liquid junction cell based on the MTsPc/TiO_2 electrode.

In DMSO, the MTsPc spectra obeyed Beer's law over the accessible concentration range ($10^{-6}-10^{-3}$ M). The MTsPc spectra at a concentration of 5×10^{-4} M consist of a strong sharp π–π^* absorption of MTsPc between 650 and 710 nm accompanied by a weaker vibrational coupled satellite band at around 610 nm, indicating that there is weaker intermolecular interaction and MTsPc exists mostly as a monomer in DMSO. On the TiO_2 microporous electrode, however, shoulders at around 690 nm, which generally could be assigned as the monomeric MTsPc Q band, were observed while the peak at around 610 nm is strikingly enhanced except for InTsPc, indicating the occurrence of molecular aggregation of MTsPc on the TiO_2 electrode [13]. The peak at around 610 nm can be assigned as the dimeric MTsPc Q band [14], which has a blue shift of 30–50 nm relative to the monomeric characteristic absorption. Hence, MTsPc exists mainly as the dimer on the TiO_2 microporous electrode with a minority of the MTsPc monomer except for InTsPc.

3.2. *Photocurrent (or incident–photon-to-current conversion efficiency) action spectroscopy*

Fig. 5 shows the measured short-circuit photocurrent of the MTsPc/TiO_2 electrode as a function of wavelength. The spectra have been corrected for the absorption of incident light by the conducting glass substrate. The incident–photon-to-current conversion efficiency (IPCE), as listed in Table 1, is calculated from IPCE = $1243I_{sc}\times100\%/\lambda P_{in}$ [7], in which I_{sc} and P_{in} are the short-circuit current density and the incident light power at the monochromatic wavelength respectively. Considering the actual part R_{ab} of the incident light absorbed by the dye molecules, the quantum efficiency η can be derived from η = IPCE/R_{ab} at the monochromatic wavelength as listed in Table 1. In contrast with the absorption spectra, it is found that the maximum of the short-circuit photocurrent occurs only at around 690 nm whether the maximum absorbance of the MTsPc/TiO_2 electrode is at around 690 nm or not. Although the maximum absorbance of the MTsPc/TiO_2 electrode in the case of the Zn, Co, Ga, TiO and H_2 compounds is at around 610 nm, the short-circuit photocurrent at around 610 nm is almost zero. Hence, it is generally concluded that only the absorbance of the MTsPc monomer adsorbed on the TiO_2 microporous electrode generates the photocurrent while that of the MTsPc dimer does not convert into the photocurrent.

3.3. *Exciton model*

The photoelectrical behavior of the MTsPc aggregation adsorbed on the TiO_2 microporous electrode can be explained as follows. The MTsPc monomer adsorbed on the surface of the TiO_2 electrode are nearly all in direct contact with the TiO_2 particle. Because the energy level of the singlet is located above the TiO_2 conduction band as shown in Fig. 6, the band energies of which are taken from [15,16], the photogenerated carriers can be easily transported into the conduction band of the TiO_2 semiconductor, forming the photocurrent collected by the ITO electrode.

Tetrasulfonated phthalocyanine is adsorbed on the TiO_2 particle by a chemical bond with sulfonate (SO_3^-) rather than with the central metal because there are excess positive charges on the TiO_2 electrode. The adsorption of metal-free tetrasulfonated phthalocyanine on the TiO_2 electrode substantiates this assumption. Thus the Pc planar ring is tilted to the spherical TiO_2 particle and is not tangent to the TiO_2 particle. The photogenerated charge carriers resulted from the dimer preferably transfer to the electrolyte (I_3^-/I^-) in the electrolyte solution along the stacking direction of the

Table 1
The performance characteristics of the MTsPc/TiO_2 microporous electrode

Species	Wavelength λ (nm)	Optical density OD_d	Specific surface area	Wavelength λ (nm) [a]	Optical density OD_m	Photocurrent I_{sc} (nA)	IPCE (%)	Quantum efficiency (%)
ZnTsPc	615	1.08	50	(700)	0.34	175	2.1	5.7
GaTsPc	620	0.94	42	688	0.78	70	0.82	1.1
CoTsPc	628	0.72	32	(700)	0.50	70	0.84	1.7
InTsPc	645	0.46	20	697	0.69	45	0.30	0.43
TiOTsPc	635	0.45	20	(690)	0.23	45	0.30	1.3
H_2TsPc	609	0.52	23	(700)	0.22	50	0.33	1.5

OD_d, optical density of monomer; OD_m.
[a] With shoulders in parentheses.

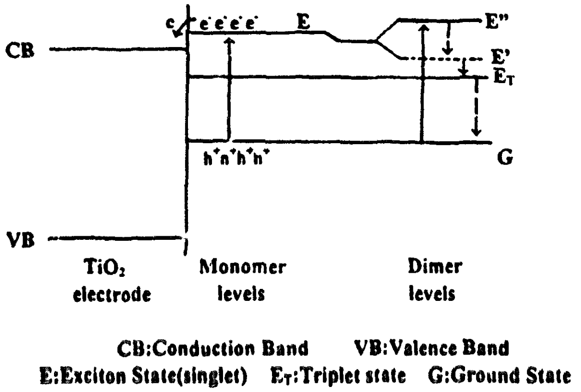

Fig. 6. Energy level diagram of the TiO_2 electrode, MTsPc monomer and dimer: CB, conduction band; VB, valence band; E, exciton state (singlet); E_T, triplet state; G, ground state.

dimeric molecules [17] rather than transport into the conduction band of TiO_2 semiconductor because of the overlap between the intermolecular π conjugated electron orbital in the MTsPc dimer. In addition, the overlap of the intermolecular π conjugated electron orbital within the phthalocyanine dimer leads to a band split [18] as shown in Fig. 6, which explains well the blue shift of the absorbance in the dimer with respect to that in the monomer in the visible spectra. The absorbance of the dye molecules at around 610 nm (corresponding to a photon energy of 2.04 eV) can cause electron transfer to the excited state E'' because transitions from the ground state to the excited state E' are forbidden while transitions from the ground state to the excited state E'' are allowed [18]. In terms of the rapid internal conversion between singlet states, the excited electron in the exciton state E'' transfers to the exciton state E', whose energy level is located under the conduction band of TiO_2 semiconductor. The subsequent radiationless transition from the exciton state E' to the lower triplet state E_T quenches the excited electron. The absorbance at around 610 nm can be attributed to the dimerization of dye molecules [13]. So the dimeric absorption cannot generate the photocurrent.

Only the absorbance of the MTsPc monomer adsorbed on TiO_2 microporous electrode contributes to the photocurrent while that of the MTsPc dimer on TiO_2 electrode does not convert into a photocurrent. So increasing the absorbance of the MTsPc monomer and decreasing the density of the MTsPc dimer on the TiO_2 microporous electrode are efficient means of improving the energy conversion efficiency.

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