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Photosensitization effects of porphyrin on n-Si(111) and n-GaAs(100)

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Abstract

Photosensitization effects of 5,10,15,20-tetrakis-(4-trimethylaminephenyl) porphyrin tetraiodide(TAPPI) on n-Si(111) and n-GaAs(100) were studied by surface photovoltage spectroscopy. n-Si can be sensitized only in the Soret band absorption region of the TAPPI molecule, n-GaAs can be sensitized in the whole irradiation region ($h\nu > E_g$). The diagrams of energetic level correlation between the TAPPI molecule and the two semiconductor substrates were determined by cyclic voltammetric measurement and, on the basis of them, the different photosensitization effects of TAPPI on n-Si and n-GaAs are explained reasonably.

Keywords: Photosensitization; n-Si; n-GaAs; 5,10,15,20-tetrakis-(4-trimethylaminephenyl) porphyrin tetraiodide

1. Introduction

During the last two decades, scientists have conducted extensively the research on dye sensitization of semiconductors — the photoinduced charge injection at the dye molecule and semiconductor interfaces, for the possible applications in many promising fields such as solar light-to-electrical conversion [1,2], photoelectrochemistry [3,4], artificial photosynthetics [5,6], etc. Presently, one of the topics in this study field is focused on maximizing the quantum yield of photoelectric conversion by making the best use of the sensitization function of dye molecules on semiconductors. For example, due to high surface-to-volume ratio and size quantization effect, the nanocrystalline TiO_2 thin film was used as a photosensitized electrode instead of a bulk TiO_2 electrode, and high quantum yield can be obtained [7,8].

Due to its high density of π electrons and good chemical and thermal stability, the porphyrin molecule acts as a kind of typical photoinduced charge transfer sensitizer [9–11]. For the purpose of investigating the influence of semiconductor energy band positions on the dye photosensitization effect, in the present paper we used 5,10,15,20-tetrakis-(4-trimethylaminephenyl) porphyrin tetraiodide(TAPPI) as the probe molecule, n-Si(111) and n-GaAs(100) as the semiconductor substrates, and studied their photoinduced interfacial charge injection processes by surface photovoltage spectroscopy, which is a very simple and precise method for understanding surface charge separation of semiconductors and photoinduced charge injection at organic–inorganic interfaces [12–16]. It is shown that the photosensitization behavior of the TAPPI molecule on n-GaAs is very different from that on n-Si. On the basis of the diagrams of energetic level correlation determined by the cyclic voltammetric method, a new electron injection channel is suggested for the special photosensitization effect of the TAPPI molecule on n-GaAs in comparison with that on n-Si. It may be helpful for the design of a new type of photoelectric conversion device with high efficiency.

2. Experimental details

2.1. Sample preparation

5,10,15,20-tetrakis-(4-trimethylaminephenyl) porphyrin tetraiodide(TAPPI) was synthesized as Ref. [17]. Fig. 1 presents its molecular structure. n-Si(111) and n-GaAs(100) wafers had an area of 11×6.5 mm^2, and were doped with phosphorus (10^{18} cm^{-3}) and silicon (10^{18} cm^{-3}), respectively. n-Si wafers were treated as follows: cleaned with Toluene, diethyl ether, chloroform, acetone and anhydrous ethanol in an ultrasonic agitator for 5 min, respectively; boiled in a mixture of NH_4OH:H_2O_2:H_2O (1:2:5 by volume); boiled in a mixture of HCl:H_2O_2:H_2O (1:2:5 by volume) and then

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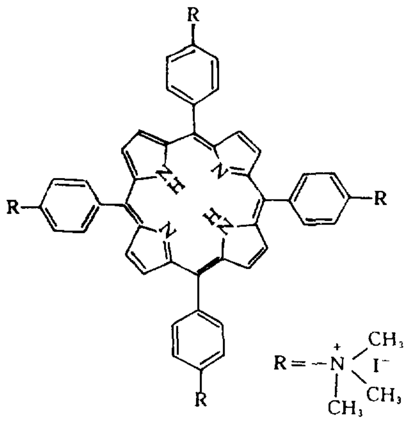

Fig. 1. The molecular structure of TAPPI.

rinsed in deionized water; and etched in a mixture of HF:H_2O (1:10 by volume) for 4 min to reduce the oxide to the minimal and rinsed in bidistilled deionized water. The treated n-Si had a hydrophillic surface. n-GaAs waters were cleaned with chloroform, acetone, anhydrous ethanol and bidistilled deionized water in the ultrasonic agitator for 5 min, respectively, and then rinsed in bidistilled deionized water. The treated n-GaAs wafers had a hydrophobic surface.

TAPPI was dissolved in a mixture of H_2O and C_2H_5OH (1:9 by volume) with a concentration of 1.9×10^{-5} mol l^{-1} in order that the TAPPI solution can be spread quickly and well distributed on the surface of n-Si and n-GaAs. A TAPPI solution of 0.08 ml was spread onto the surface n-Si or n-GaAs by a microsyringe, and then the modified n-Si and n-GaAs wafers were dried in a drier.

2.2. Measurement methods

The absorption spectrum of the TAPPI solution was measured with a UV-3100 spectrometer (Japan). Surface photovoltage spectra were measured with a surface photovoltaic spectrometer [14]. To prevent the measured samples from damaging, a contact-less measurement method was used [15]. The ITO conducing glasses were used as the transparent top and bottom electrodes. Cyclic voltammetric measurement was carried out with a model JSH-I potentiostat/galvanostat coupled to a model DCG-2 multifunction signal generator. Cyclic voltammetric curves were recorded on a TYPE-3086 *X–Y* recorder. A three-electrode cell was utilized, consisting of a 1.0 mm diameter Pt working electrode, a large surface area of platinum electrode (counter electrode), and an Ag/Ag^+ (0.01 mol l^{-1} $AgNO_3$ in acetonitrile (CH_3CN)) reference electrode. 0.1 mol l^{-1} TBAP was used as electrolyte. DMF was used as solvent to prepare 5.0×10^{-4} mol l^{-1} TAPPI solution. High pure Ar gas was used to deoxygenate the solution and keep a positive pressure above the solution during experiment.

3. Results and discussion

3.1. Photosensitization effect of the TAPPI molecule on n-Si(111)

Fig. 2 shows the absorption spectrum of TAPPI solution. The maximum absorption position is at about 413 nm, corresponding to Soret band electron transition from the $a_{1u}(\pi)$ orbital to the $e_g(\pi^*)$ orbital. At the same time, the Q-band transition is relatively weak.

Fig. 3 shows surface photovoltage spectra of bare n-Si and TAPPI-modified n-Si. Distinguishing from that of bare n-Si, the photovoltaic response curve of TAPPI-modified n-Si has a new peak in the Soret band absorption region of the TAPPI molecule. Hence, this new response peak is caused by an electron transition from $a_{1u}(\pi)$ to $e_g(\pi^*)$ orbitals of the TAPPI molecule under illumination. There are two possible resources for this peak: the overlap of photovoltaic responses of TAPPI and n-Si, or the photosensitization effect of the TAPPI molecule on n-Si.

Surface photovoltage is the decrement of surface potential due to illumination on the surface of the measured material. Behaving as a p-type semiconductor [18], bulk state porphyrin has its surface potential barrier opposite to that of a n-type semiconductor. Under illumination, their photovoltaic responses have opposite polarities. If the photovoltaic response of TAPPI-modified n-Si came from the overlap of

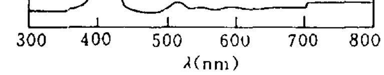

Fig. 2. Absorption spectrum of TAPPI solution in H_2O and C_2H_5OH (1:9 by volume) with a concentration of 1.9×10^{-5} mol l^{-1}.

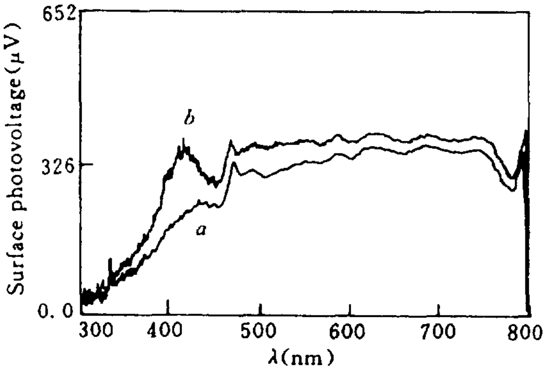

Fig. 3. Surface photovoltage spectra of (a) bare n-Si and (b) TAPPI-modified n-Si.

those of TAPPI and n-Si, the total response strength would be reduced in the Soret band absorption region of TAPPI because of the opposite polarities of the two photovoltaic responses. But this was not the fact, as shown in Fig. 3(b), hence it is sure that the observed peak shows a photosensitization effect of the TAPPI molecule on n-Si, and comes from the photoinduced electron injection form the excited TAPPI molecule into the n-Si substrate.

The most important condition for the photoinduced electron injection at the heterostructure interface is the match of the energetic levels. In order to describe the injection process better, the electrochemical method was employed to determine the energetic level correlation between TAPPI and n-Si. Fig. 4 is the cyclic voltammetric curve of TAPPI; it can be seen that there are two pairs of redox process in the scanning range. **I** is irreversible to some extent and should be assigned to the redox behavior of I^-. **II** is reversible and its $E_{1/2}$ value is 0.76 V vs. NHE, corresponding to the redox behavior of porphyrin ring at ground state. The level of the $a_{2u}(\pi)$ orbital (HOMO) of the TAPPI molecule can thus be determined to be −0.76 eV vs. NHE. Based on this data together with the absorption spectrum of TAPPI and Ref. [19], Fig. 5 gives the diagram of energetic level correlation and interface charge transfer process between the TAPPI molecule and n-Si. It shows clearly the match of energetic levels between the TAPPI molecule and n-Si for the photoinduced electron injection. When the TAPPI molecule is photoexcited, the electron at the $a_{1u}(\pi)$ orbital (NHOMO) is excited to the $e_g(\pi^*)$ orbital (LUMO) and then injected into conduction band of n-Si, resulting in the much greater electron population in the space charge region (electron depletion layer) of n-Si than that of bare n-Si, and the photosensitization effect shown in Fig. 3(b).

3.2. Photosensitization effect of TAPPI on n-GaAs(100)

Fig. 6 presents surface photovoltage spectra of bare n-GaAs and TAPPI-modified n-GaAs. Similar with that of TAPPI-modified n-Si, the photovoltaic response curve of TAPPI-modified n-GaAs has a new peak in the Soret band absorption region of the TAPPI molecule, which is attributed to the photoinduced electron injection from the $e_g(\pi^*)$ orbital of the excited TAPPI molecule into the conduction band of the n-GaAs substrate. But a very distinct difference can be found between Fig. 6 and Fig. 3, i.e. the photovoltaic response strength of TAPPI-modified n-GaAS is increased by more than one order of magnitude in comparison with that of bare n-GaAS in the whole irradiation region. This effect is unseen in the photovoltaic response curve of TAPPI-modified n-Si, which has the same magnitude with that of bare n-Si except for the photosensitization effect in the Soret band absorption region of the TAPPI molecule, meaning that the photoinduced electron injection occurs only from the $e_g(\pi^*)$ orbital of the TAPPI molecule into the conduction band of n-Si.

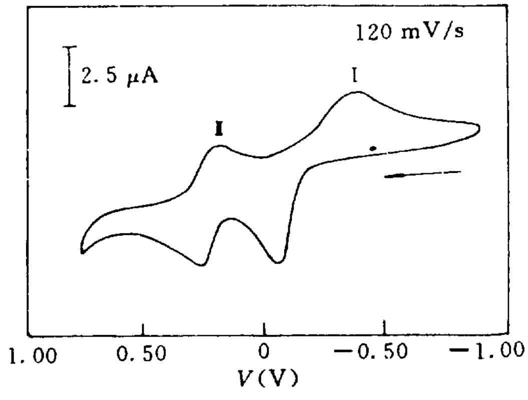

Fig. 4. Cyclic voltammetric curve of TAPPI in DMF with a concentration of 5.0×10^{-4} mol l^{-1}.

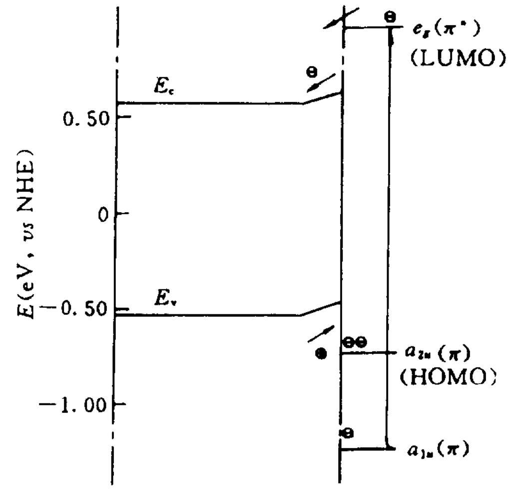

Fig. 5. The diagram of energetic level correlation and interface charge transfer process between the TAPPI molecule and n-Si.

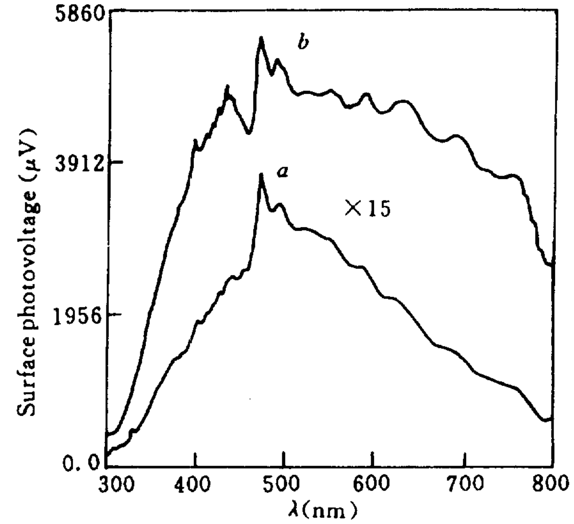

Fig. 6. Surface photovoltage spectra of (a) bare n-GaAs and (b) TAPPI-modified n-GaAs

It can be seen that the increased photovoltaic response of TAPPI-modified n-GaAs keeps the same spectral structure as that of bare n-GaAs in the non-Soret band absorption region of the TAPPI molecule. For an n-type semiconductor illuminated with photon with energy $h\nu \geq E_g$, the photovoltaic response comes from separation of the photogenerated electron–hole pairs from a band-to-band transition under a built-in electric field. The higher the separation efficiency, the more the photogenerated electrons move towards the bulk (and holes towards the surface), and the stronger the surface photovoltaic effect. The band gaps of both n-Si and n-GaAs, 1.1 eV and 1.4 eV, respectively [19,20], are below the lowest incident photon energy ($\lambda = 800$ nm), hence the pronounced photovoltaic response of TAPPI-modified n-GaAs in the whole irradiation region indicates the higher separation efficiency of the photogenerated electron–hole pairs due to the modification of the TAPPI molecule.

Why is the separation efficiency of the photogenerated electron–hole pairs of TAPPI-modified n-GaAs increased in comparison with that of bare n-GaAS? Fig. 7 shows the diagram of energetic level correlation and interface charge transfer models (seeing below) between the TAPPI molecule and n-GaAs [20]. It can be seen that the $a_{2u}(\pi)$ orbital (HOMO) of the TAPPI molecule lies above the top of valence band of n-GaAs about 0.1 eV, from the viewpoint of the match of the energetic levels, it is possible for TAPPI molecule to inject electrons from the $a_{2u}(\pi)$ orbital into the valence band of n-GaAs a at suitable situation. We consider it is this kind of electron injection that enhances the separation efficiency of the photogenerated electron–hole pairs of the modified n-GaAs and photovoltaic response further.

This consideration can be reasonably explained as follows. When n-GaAs is illuminated, the electron is excited from the valence band into the conduction band, and the photogenerated hole in the valence band moves towards surface under a built-in field, it is non-equilibrium and thus prefers to capture and combine with the acceptable electron. The relative energetic level position between the $a_{2u}(\pi)$ orbital of the TAPPI molecule and the valence band of n-GaAs ensures the possibility for the photogenerated hole in the valence band to capture and combine with an electron from the $a_{2u}(\pi)$ orbital of the TAPPI molecule. The top of the valence band of n-GaAs is very close to the $a_{2u}(\pi)$ orbital of the TAPPI molecule, this may cause the effective overlap between them and form the channel for this kind of electron injection. Comparing Fig. 6(b) with Fig. 3(b), one can find that the photosensitization peak corresponding to Soret band absorption of the TAPPI molecule modifying on n-GaAs is much more red-shifted than that on n-Si (437 nm and 421 nm, respectively), which shows the stronger electronic coupling between the TAPPI molecule and n-GaAs substrate.

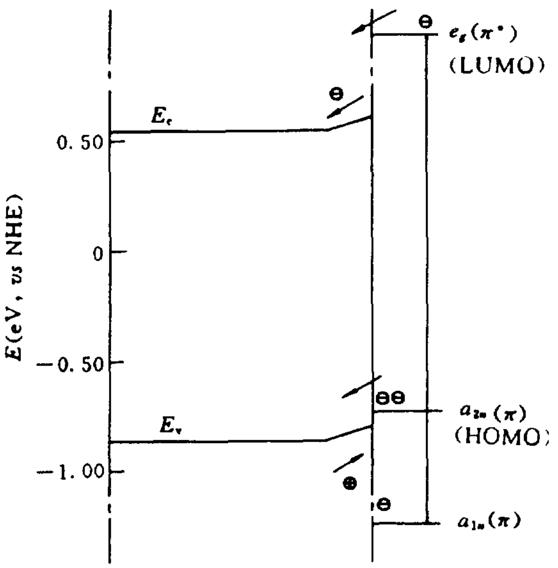

Fig. 7. The diagram of energetic level correlation and interface charge transfer models between the TAPPI molecule and n-GaAs.

Because of this kind of electron injection, the combination rate of the photogenerated electron with the hole in the space charge region of the modified n-GaAs is decreased, resulting in the more efficient photoinduced charge separation efficiency than that of bare n-GaAs, thus photovoltaic response increases pronouncedly. Because this injection process comes from the ground state of the TAPPI molecule and serves to improve the photoinduced charge separation efficiency of the n-GaAs substrate, the photovoltaic response keeps the same spectral structure as that of bare n-GaAs in the non-Soret band absorption region of the TAPPI molecule. The photovoltaic response of TAPPI-modified n-GaAs can be described using a simple formula:

$$\Delta V = \Delta V_1 + \Delta V_2 + \Delta V_3$$

where ΔV is the total photovoltaic response, ΔV_1 the contribution from the photoinduced charge separation of n-GaAs substrate itself, ΔV_2 that from the enhancement of the photoinduced charge separation of n-GaAs by the electron injection from the $a_{2u}(\pi)$ orbital of the TAPPI molecule into the valence band of the excited n-GaAs, and ΔV_3 that from the photoinduced electron injection from the $e_g(\pi^*)$ orbital of the TAPPI molecule into the conduction band of n-GaAs (only when the TAPPI molecule is excited in its Soret band absorption region). For TAPPI-modified n-Si, the $a_{2u}(\pi)$ orbital of TAPPI molecule is below the top of the valence band of n-Si, at least the relative energetic level position is not met for the photoinduced hole in the valence band of n-Si to capture and combine with the electron from the $a_{2u}(\pi)$ orbital of the TAPPI molecule; thus photovoltaic response of TAPPI-modified n-Si has the same magnitude as that of bare n-Si in the non-Soret band absorption region of the TAPPI molecule.

Our consideration is in good coincidence with the photoinduced charge transfer processes in the acceptor–sensitizer–donor (ASD) structure [21], in which, after a π electron of the sensitizer is excited into the π^* orbital and transferred into the acceptor, the emptied π orbital can capture the ground state electron from the donor, and the high charge transfer efficiency can thus be obtained.

Acknowledgements

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References

[1] T.A. Heimer, C.A. Bignozzi, T.J. Meyer, J. Phys. Chem. 97 (1993) 11987.

[2] M.K. Nazeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382.

[3] A. Giraudeau, F.R.F. Fan, A.J. Bard, J. Am. Chem. Soc. 102 (1980) 5543.

[4] R. Memming, Surf. Sci. 101 (1980) 551.

[5] M. Motsumura, K. Mitsuda, N. Yoshizawa, H. Tsubomura, Bull. Chem. Soc. Jpn. 54 (1981) 692.

[6] A.J. Hamnet, M.P. Dave-Edwards, R.D. Wright, K.R. Seddon, J.B. Goodenough, J. Phys. Chem. 83 (1979) 3280.

[7] J. Moser, M. Gratzel, Chem. Phys. 176 (1993) 493.

[8] B. O'Regan, M. Gratzel, Nature 353 (1991) 737.

[9] K. Kalyanasundaram, N. Vlachopoulos, V. Krishna, A. Monnier, M. Gratzel, J. Phys. Chem. 91 (1987) 2342.

[10] A. Kay, M. Gratzel, J. Phys. Chem. 97 (1993) 6272.

[11] H.T. Tien, J. Higgins, J. Electrochem. Soc. 127 (1980) 1475.

[12] H.C. Gatos, J. Lagowski, J. Vac. Sci. Technol. 10 (1973) 130.

[13] M. Leibovitch, L. Kronik, E. Fefer, Y. Shapira, Phys. Rev. B 50 (1994) 1739.

[14] D.J. Wang, W. Liu, H. Tian, Z.Q. Zhu, G.Y. Hong, T.J. Li, Int. Symp. on Hydrogen Systems, Beijing, Vol. 1, China Academic Publishers, Bejing and Pergamon Press Inc., Oxford, 1986, p. 255.

[15] W. Liu, W.S. Yang, T.J. Li, Y.J. Liu, Z.Q. Zhu, Thin Solid Films 179 (1989) 309.

[16] L. Jiang, W. Liu, D.J. Wang, Y.B. Bai, T.J. Li, Thin Solid Films 210/211 (1992) 327.

[17] M. Krishnamurthy, Indian J. Chem. 15B (1977) 964.

[18] K. Yamashita, Y. Harima, H. Iwashima, J. Phys. Chem. 91 (1987) 3055.

[19] M. Gratzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 335.

[20] A. Hagfeldt, M. Gratzel, Chem. Rev. 95 (1995)49.

[21] M. Sakomura, M. Fujihira, Thin Solid Films 243 (1994) 616.