Organic Semiconductor Nanoparticles with Heterojunctions Composed of Fullerene C₆₀ and Zinc Phthalocyanine and Their Application to Visible-Light-Responsive Photocatalysts

Shuai Zhang, Toshiyuki Abe, Tomokazu Iyoda, Takayoshi Norimatsu and Keiji Nagai*

*Division of Integrated Molecular Engineering, Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama 226-8503 (Japan)

Fax: 81-45-924-5247, e-mail: nagai.k.ae@m.titech.ac.jp

Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561 (Japan)

Division of Energetic Materials for Photonics, Institute of Laser Engineering (ILE), Osaka University, Suita 565-0871 (Japan)

Composite nanoparticles composed of fullerene C₆₀ and zinc phthalocyanine (ZnPc) were synthesized by injecting their mixed N-methyl-2-pyrrolidone (NMP) solution into water. The nanoparticles have heterojunction structures according to charge-transfer (CT) absorption band of the mixed NMP solution and superior photoanodic current of the composite nanoparticles. The nanoparticles were used as visible-light-responsive photocatalysts without bias potential to decompose organic compounds to CO₂, and heterojunctions are proved to be critical to enhance the photocatalytic activity of the nanoparticles.

Key words: donor-acceptor, heterojunction, nanoparticle, visible-light-responsive photocatalyst

INTRODUCTION

Recently, great efforts have been made to construct low-cost and high-efficiency solar cells based on organic semiconductors with heterojunctions,¹ while their photocatalytic properties are almost overlooked. The few reported researches including CO₂ photofixation² or water splitting³ by organic semiconductors did not involve heterojunctions which are key structures for organic solar cells to achieve efficient charge separation. On the other hand, redox properties of photoelectrodes composed of organic semiconductor bilayers have been reported by Abe and co-workers,⁴ in which photoanodes for water splitting were developed.^{4a} The studies indicate that p-n junctions are necessary to enhance redox capabilities of organic semiconductors. Furthermore, in the study of controlling laser ablation, organic p-n junctions were used for a laser-induced reflection device without electrodes,⁵ indicating that organic p-n junctions can be applied to not only solar cells but also other devices without electrodes. On the basis of these reports, we attempted photodegradation of organic compounds by organic p-n junctions without bias potential.⁶ The results illustrate that the organic p-n junctions can act as highly visible-light-responsive photocatalysts. However, cost of their fabrication method based on vapor deposition is high, and Nafion substrate as an absorbent is necessary to actualize decomposition of the organic compounds, probably due to small surface area of the bilayered photocatalysts. Considering that particulate photocatalysts are prevalent for inorganic semiconductors, which can greatly increase surface area of them, to prepare particulate organic photocatalysts with heterojunctions is indispensable for their practical utilization.

Reprecipitation developed by Kasai and co-workers⁷ is a simple process suitable for preparation of various

organic crystals with size ranging from nanometers to micrometers for constructing electronic and photonic devices. Organic dye clusters synthesized using fullerene and porphyrin or phthalocyanine by reprecipitation have been introduced by Imahori, Fukuzumi, Kamat and their co-workers^{1n-t} as sensitizers of inorganic semiconductors for application as solar cells. The clusters are based on donor-acceptor (D-A) supermolecules, and a maximum photo-to-current efficiency of approximately 60% and a power conversion efficiency of 1-2%^{1p,q} are achieved, whereas photocatalytic properties of the clusters are not studied or discussed in their work.

In this paper, we synthesized D-A complex nanoparticles composed of fullerene C₆₀ and Zinc phthalocyanine (ZnPc) by reprecipitation, and introduce to use them as photocatalysts for the first time. The results show that the nanoparticles with heterojunctions have superior CO₂ generation to only C₆₀ or ZnPc nanoparticles, demonstrating that heterojunctions are also key structures in the application of photocatalysts. Compared to the organic bilayered photocatalysts with p-n junction, the particulate organic photocatalysts have low fabrication cost, and decompose organic compounds to CO₂ without absorbent.

EXPERIMENT

C₆₀ (99%) was obtained from Tokyo Chemical Industry Co. LTD. (TCI), and used as received. ZnPc (TCI) was purified twice by sublimation prior to use. ITO-coated glass plates (resistance: 8 Ω cm⁻²; transmittance: >85%; ITO thickness: 174 nm) were commercially available from Asahi Glass Co., Ltd, and were washed by sonication in water containing detergent, pure water, acetone, and ethanol in that sequence. The plates were dried in air finally before use. All other

solvents and chemicals were of reagent quality, purchased commercially, and used without further purification.

C_{60} , ZnPc or their composite particles were prepared as follows: 50 mL of 0.2 mmol/L C_{60} or/and ZnPc dissolved in N-methyl-2-pyrrolidone (NMP) was injected into 500 mL water with an agitation rate of 750 rpm by a syringe pump with an injection rate of 5 mL/min. After injection, suspensions were kept stirring for 30 min. The suspensions may be used directly for NMP decomposition test, or filtrated to collect particles by adding HCl solution and using hydrophilic PTFE membrane (pore size 0.2 μm). During filtration, NMP and HCl were removed by gently washing with water, and the particles were redispersed in pure water by ultrasonic for characterizations, photoelectrochemical experiments or photodegradation tests.

All the experiments of cyclic voltammogram (CV) were carried out in Ar atmosphere with a standard three-electrode system, which was equipped with a Pt wire counter electrode and Ag/AgCl (in saturated KCl electrolyte) reference electrode. Working electrodes were prepared by simply casting 0.15 mL of a 0.1 mg/mL particle suspension after filtration on an ITO electrode with a surface area of 1 cm^2 , and dried at room temperature. Electrolyte contained 0.1 mol/L KNO_3 and 2 mmol/L trimethylamine (TMA).

Photocatalytic properties of particles were evaluated from photodegradation of organic compounds in water. 5 mL of particle suspension before filtration containing NMP or after filtration (particle concentration: 0.03 mg/mL) containing about 10 wt% ethanal was enclosed into a closed cylindrical Pyrex cell (15 mL) after gas exchange by Ar and O_2 mixed gas (O_2 : 21%). Then, the reactor was irradiated by a 500 W halogen lamp with a sharp cut filter (HOYA, L-42) and a water filter for infrared light to keep the reactor at room temperature. The amount of generated CO_2 was detected by gas chromatography.

RESULTS AND DISCUSSION

The absorption spectra of C_{60} , ZnPc and their mixture in NMP with different concentration are shown in Figure 1. The ZnPc in NMP has a strong Q band absorption with a peak at 670 nm and the NMP solution of C_{60} did not exhibit the characteristic peak at 340 nm⁸ as shown in Figure 1B, probably due to aggregation of C_{60} in NMP.⁹ In Figure 1A, the absorption spectrum of mixed C_{60} and ZnPc solution (c) is compared to mathematic addition (d) of the two respective spectra. It is observed that a charge-transfer (CT) absorption band appears around 700–800 nm, which shall be ascribed to the π complex formed between the C_{60} and phthalocyanine.^{1p, r} In Figure 1B, it is found that the mixed C_{60} and ZnPc solution (c) has more intense absorption band around 300–400 nm and 600–700 nm than that of the mathematic addition (d) of the two respective spectra. The phenomena can be explained as formation of ZnPc dimers in its individual solution and ZnPc- C_{60} CT complex in their mixed solution, considering that ZnPc solution exhibits negative deviation from Lambert-Beer's law when ZnPc dimers are formed.¹⁰

The absorption spectra of C_{60} , ZnPc and their mixture in mixed solvent of NMP and water are shown in Figure. 2

Fig. 1 Absorption spectra of C_{60} (a), ZnPc (b), their mixture (c) in NMP and mathematic addition of a and b (d). $[C_{60}] = [ZnPc] = 0.2 \text{ mmol/L}$ (A) or $4 \text{ }\mu\text{mol/L}$ (B).

Fig. 2 Absorption spectra of C_{60} (a), ZnPc (b) and their mixture (c) in water/NMP (10:1, v/v). $[C_{60}] = [ZnPc] = 0.02 \text{ mmol/L}$.

The C_{60} spectrum shows C_{60} 's characteristic absorption peak around 340 nm and a broad and structureless absorption shoulder in 400–600 nm region which confirms fullerene particle formation;¹¹ the ZnPc spectrum only shows weak and broad absorption, and Soret and Q-bands of ZnPc are hardly identified, in accord with macroscopic ZnPc aggregation in mixed solvent of NMP and water; the mixture spectrum exhibits absorption arising from both C_{60} and ZnPc with broadening and position change of Soret and Q-bands, which would be due to particle formation in the mixed solvent (water and NMP)^{7j} and the intermolecular interactions^{1l}. The results in Figure 2 indicate that C_{60} , ZnPc or their mixture aggregates and forms particles in a mixture of water and NMP, and D-A complex particles are expected to be performed by injecting a mixed solution of C_{60} and ZnPc in NMP into water according

to the results in Figure 1.

The scanning electron microscopy (SEM) images of the C_{60} , ZnPc and their composite particles are shown in Figure 3. All the images show nano-sized particles with irregular shapes. Average size of the ZnPc or the composite nanoparticles is about 40 nm, larger than that of the C_{60} nanoparticles (20 nm). These results indicate that reprecipitation is a good method to prepare nano-sized particles, and filtration may prevent particle's secondary aggregation during solvent evaporation as NMP has been removed.

Fig 3. SEM images of a) C_{60} , b) ZnPc and c) composite particles prepared by injecting 0.2 mmol/L C_{60} or/and ZnPc in NMP into water and after filtration. The scale bar is 50 nm.

Photoanodic properties of C_{60} , ZnPc or their composite nanoparticles were evaluated by CV measurements with nanoparticle deposited ITO as working electrodes as shown in Figure 4. The electrode of ITO/ C_{60} nanoparticles shows a small photoanodic current (Figure 4a), and the electrode of ITO/ZnPc

nanoparticles does not exhibit obvious photoanodic current (Figure 4b), which has been explained elsewhere by Schottky junctions of n-type semiconductor/liquid and p-type semiconductor/liquid interfaces.⁴ It is noteworthy that the electrode of ITO/composite nanoparticles shows a larger photoanodic current than that of either ITO/ C_{60} nanoparticles or ITO/ZnPc nanoparticles (Figure 4c). This result indicates heterojunctions probably arising from D-A complex (vide supra) are formed in the composite nanoparticles, because heterojunctions are key structures to achieve efficient charge separation for organic semiconductors, and our previous studies about p-n junction electrodes also show photocurrent superiority⁴. The photoelectrochemical results demonstrate that heterojunction structures are critical for not only organic solar cells but also organic photocatalysts to enhance their oxidation capabilities.

Fig 4. CV of ITO/ C_{60} nanoparticles, ITO/ZnPc nanoparticles and ITO/composite nanoparticles. Solid line: under light; dot line: in the dark.

To test photocatalytic activities of the nanoparticles in the most direct and simple fashion, NMP or ethanal was chosen as photodegradation substance in water phase. As NMP or ethanal does not have light absorption at visible-light region, direct photodegradation is excluded in the present discussion. As shown in table 1, for the substance of NMP, the composite nanoparticles have the largest CO₂ production in the three samples after 24 h light irradiation. It reaches 2.4×10^{-7} mol, larger than the sum of that for the ZnPc and C₆₀ nanoparticles (1.6×10^{-7} mol), although the composite nanoparticles contain the same amount ZnPc or C₆₀ with that in the ZnPc or C₆₀ nanoparticles. In consequence, the CO₂ generation of the composite nanoparticles does not come from a simple arithmetical addition of that of the ZnPc and C₆₀ nanoparticles. For the substance of ethanal, the same amount of the ZnPc, C₆₀ or composite nanoparticles were used. The CO₂ generation amount of the ZnPc or C₆₀ nanoparticles is still less than that of the composite nanoparticles. The CO₂ generation amount becomes within GC error range in the dark condition or without decomposition substance for all the samples. According to these results, it is demonstrated that: First, the CO₂ generation under light irradiation mainly arises from photocatalytic degradation reactions via comparing its amount under and without light irradiation. Second, the photocatalytic degradation reactions are mainly related to decomposition of the organic substance, because of the neglectable CO₂ generation in the absence of the decomposition substance, which excludes self-decomposition of the nanoparticles under light irradiation. Third, the composite nanoparticles have the largest CO₂ generation, consistent with their superiority of the photoanodic current in Figure 4. It shall be ascribed to heterojunctions in the composite nanoparticles as p-n junctions have been proved to enhance redox capabilities of organic semiconductors in our previous studies.⁴ The external quantum efficiency (EQE) of the composite nanoparticle according to CO₂ generation from ethanal decomposition is calculated to be $5 \times 10^{-3}\%$.

Table 1 CO₂ generation for different particle suspensions or dried particles under different conditions. Concentration of NMP or ethanal is 10 vol% or 10 wt%; light intensity is 30 mW/cm²; irradiation time was 24 h.

Substance& Conditions	CO ₂ generation amount (μmol)		
	C ₆₀ NP	ZnPc NP	Composite NP
NMP with light	0.06	0.1	0.24
NMP in the dark ^a	< 0.05	< 0.05	< 0.05
Ethanal with light	0.09	0.14	0.36
Ethanal in the dark ^b	< 0.05	< 0.05	< 0.05
No substance	< 0.05	< 0.05	< 0.05

^{a,b}Put the samples in the dark for 24 h

For the composite nanoparticles, the process of NMP or ethanal oxidation and CO₂ generation may include oxidation induced by them and autooxidation. The former process shall be related to heterojunctions in the composite nanoparticles. Electrons and holes are

initiated by photoinduced charge separation from ZnPc or C₆₀ excited state to ZnPc-C₆₀ interface. Susequently, electrons and holes may reach to surface of the composite nanoparticles. Finally, NMP, ethanal or their oxidized intermediate product receives the holes from oxidized ZnPc, and O₂ may receive the electrons from reduced C₆₀ through multielectron reduction of it according to the conduction band level of C₆₀.¹²

The stability of the composite nanoparticles was studied by comparing their absorption spectrum before and after visible-light irradiation as shown in Figure 5. It shows that the absorption spectrum after 61 h light irradiation is almost the same with that before light irradiation, demonstrating that the composite nanoparticles are stable under visible-light.

Fig 5. Absorption spectra of composite nanoparticle suspension before and after visible-light irradiation. Light intensity is 30 mW/cm².

In summary, we introduce a photocatalyst based on organic semiconductor nanoparticles with heterojunctions, which can decompose NMP or ethanal to CO₂ under visible-light irradiation. We believe that the present research will open a new research direction for visible-light-responsive photocatalysts.

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REFERENCE

- [1] a) C. W. Tang, *Appl. Phys. Lett.*, **48**, 183-85 (1986). b) D. Wöhrle, K. Meissner, *Adv. Mater.*, **3**, 129-38 (1991). c) D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller, D. Schlettwein, *J. Mater. Chem.*, **5**, 1819-29 (1995). d) Ch. Pannemann, V. Dyakonov, J. Parisi, O. Hild, D. Wöhrle, *Synth. Met.*, **121**, 1585-86 (2001). e) T. Morikawa, C. Adachi, T. Tsutsui, S. Saito, *Nippon Kagaku Kaishi*, **9**, 962-67 (1990). f) M. Hiramoto, H. Fujiwara, M. Yokoyama, *Appl. Phys. Lett.*, **58**, 1062-64 (1991). g) M. Hiramoto, H. Fujiwara, M. Yokoyama, *J. Appl. Phys.*, **72**, 3781-87 (1992). h) P. Peumans, S. Uchida, S. R. Forrest, *Nature*, **425**, 158-62 (2003). i) A. Fujii, T. Shirakawa, T. Umeda, H. Mizukami, Y. Hashimoto, K. Yoshino, *Jpn. J. Appl. Phys.*, **43**, 5573-76 (2004). j) Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka, E. Nakamura, *J. Am. Chem. Soc.*, **131**, 16048-50 (2009). k) Y. Rio, W. Seitz, A. Gouloumis, P. Vázquez, J. L. Sessler, D. M. Guldi, T. Torres, *Chem. Eur. J.*, **16**, 1929-40 (2010). l) G. Bottari, D. Olea, C. Gómez-Navarro, F. Zamora, J. Gómez-Herrero, T. Torres, *Angew. Chem. Int. Ed.*, **47**, 2026-31 (2008). m) D. M. Guldi, A. Gouloumis, P. Vázquez, T. Torres, V. Georgakilas, M. Prato, *J. Am. Chem. Soc.*, **127**, 5811-13 (2005). n) T. Hasobe, H.

- Imahori, S. Fukuzumi, P. V. Kamat, *J. Phys. Chem. B*, **107**, 12105-12 (2003). o) H. Imahori, K. Mitamura, Y. Shibano, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, Y. Araki, O. Ito, *J. Phys. Chem. B*, **110**, 11399-405 (2006). p) H. Imahori, M. Ueda, S. Kang, H. Hayashi, S. Hayashi, H. Kaji, S. Seki, A. Saeki, S. Tagawa, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, M. Shiro, N. V. Tkachenko, H. Lemmetyinen, *Chem. Eur. J.*, **13**, 10182-93 (2007). q) S. Kang, T. Umeyama, M. Ueda, Y. Matano, H. Hotta, K. Yoshida, S. Isoda, M. Shiro, H. Imahori, *Adv. Mater.*, **18**, 2549-52 (2006). r) T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, *J. Am. Chem. Soc.*, **127**, 1216-28 (2005). s) A. Kira, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, M. Isosomppi, N. V. Tkachenko, H. Lemmetyinen, H. Imahori, *Langmuir*, **22**, 5497-503 (2006). t) T. Hasobe, P. V. Kamat, M. A. Absalom, Y. Kashiwagi, J. Sly, M. J. Crossley, K. Hosomizu, H. Imahori, S. Fukuzumi, *J. Phys. Chem. B*, **108**, 12865-72 (2004).
- [2] a) T. Ogata, K. Hiranaga, S. Matsuo, Y. Wada, S. Yanagida, *Chem. Lett.*, 983-84 (1993). b) Y. Wada, T. Kitamura, S. Yanagida, *Res. Chem. Intermed.*, **26**, 153-59 (2000). c) J. R. Premkumar, R. Ramaraj, *Chem. Commun.*, 343-44 (1997).
- [3] a) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **8**, 76-80 (2009). b) K. Maeda, X. Wang, Y. Nishihara, D. Lu, M. Antonietti, K. Domen, *J. Phys. Chem. C*, **113**, 4940-47 (2009).
- [4] a) T. Abe, K. Nagai, S. Kabutomori, M. Kaneko, A. Tajiri, T. Norimatsu, *Angew. Chem. Int. Ed.*, **45**, 2778-81 (2006). b) T. Abe, K. Nagai, M. Kaneko, T. Okubo, K. Sekimoto, A. Tajiri, T. Norimatsu, *Chem. Phys. Chem.*, **5**, 716-20 (2004). c) T. Abe, S. Miyakushi, K. Nagai, T. Norimatsu, *Phys. Chem. Chem. Phys.*, **10**, 1562-68 (2008).
- [5] K. Nagai, K. Morishita, H. Yoshida, T. Norimatsu, N. Miyanaga, Y. Izawa, T. Yamanaka, *Synthetic Metals*, **121**, 1445-46 (2001).
- [6] K. Nagai, Y. Yasuda, T. Abe, JP 2010119996 A, Jpn. Kokai Tokkyo 2010.
- [7] a) H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, H. Nakanishi, *Jpn. J. Appl. Phys.*, **31**, L1132-34 (1992). b) T. Tachikawa, H.-R. Chung, A. Masuhara, H. Kasai, H. Oikawa, H. Nakanishi, M. Fujitsuka, T. Majima, *J. Am. Chem. Soc.*, **128**, 15944-45 (2006). c) Z. Tan, A. Masuhara, H. Kasai, H. Nakanishi, H. Oikawa, *Jpn. J. Appl. Phys.*, **47**, 1426-28 (2008). d) K. Kaneko, K. Furuya, A. B. Hungria, J.-C. Hernandez-Garrido, P. A. Midgley, T. Onodera, H. Kasai, Y. Yaguchi, H. Oikawa, Y. Nomura, H. Harada, T. Ishihara, N. Baba, *J. Electron Microsc.*, **58**, 289-94 (2009). e) H. Kasai, H. Oikawa, S. Okada, H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **71**, 2597-601 (1998). f) H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *Jpn. J. Appl. Phys.*, **35**, L221-23 (1996). g) Y. Kaneko, T. Onodera, H. Kasai, S. Okada, H. Oikawa, H. Nakanishi, T. Fukuda, H. Matsuda, *J. Mater. Chem.*, **15**, 253-55 (2005). h) S. Fujita, H. Kasai, S. Okada, H. Oikawa, T. Fukuda, H. Matsuda, S. K. Tripathy, H. Nakanishi, *Jpn. J. Appl. Phys.*, **38**, L659-61 (1999). i) H. Kasai, H. Kanbara, R. Iida, S. Okada, H. Matsuda, H. Oikawa, H. Nakanishi, *Jpn. J. Appl. Phys.*, **34**, L1208-10 (1995). j) E. Kwon, H. Oikawa, H. Kasai, H. Nakanishi, *Cryst. Growth Des.*, **7**, 600-02 (2007).
- [8] V. L. Aksenov, M. V. Avdeev, E. A. Kyzyma, L. Rosta, M. V. Korobov, *Crystallogr. Rep.*, **52**, 479-82 (2007).
- [9] N. P. Yevlampieva, Yu. F. Biryulin, E. Yu. Melenevskaja, V. N. Zgonnik, E. I. Rjuntsev, *Colloids and Surface A.*, **209**, 167-71 (2002).
- [10] a) X.-F. Zhang, H.-J. Xu, *J. Chem. Soc. Faraday Trans.*, **89**, 3347-51 (1993). b) T. G. Gantchev, J. E. Lier, D. J. Hunting, *Radiation Physics and Chemistry*, **72**, 367-79 (2005).
- [11] H. Hotta, S. Kang, T. Umeyama, Y. Matano, H. Yoshida, S. Isoda, H. Imahori, *J. Phys. Chem. B*, **109**, 5700-06 (2005).
- [12] P. V. Kamat, S. Barazzouk, K. G. Thomas, S. Hotchandani, *J. Phys. Chem. B*, **104**, 4014-17 (2000).