



Weak visible light (\sim mW/cm²) organophotocatalysis for mineralization of amine, thiol and aldehyde by biphasic cobalt phthalocyanine/fullerene nanocomposites prepared by wet process

Prabhakarn Arunachalam^{a,1}, Shuai Zhang^{a,2}, Toshiyuki Abe^b, Motonori Komura^{a,3}, Tomokazu Iyoda^a, Keiji Nagai^{a,*}

^a Division of Integrated Molecular Engineering, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-26 Suzukake-dai, Midori-ku, Yokohama 226-8503, Japan

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

ARTICLE INFO

Article history:

Received 16 July 2015

Received in revised form 7 April 2016

Accepted 14 April 2016

Available online 19 April 2016

Keywords:

Phthalocyanines

Photooxidation

Semiconductors

Cobalt

Nanoparticles

Organophotocatalyst

ABSTRACT

This article describes a visible-light-responsive photocatalyst of cobalt phthalocyanine (CoPc) and C₆₀ nanocomposites synthesized by a reprecipitation process. The full-spectrum-visible-light (420–800 nm) photocatalysis was demonstrated by mineralization under illumination of weak light intensity (in the order of 1 mW/cm²) for aqueous trimethylamine (TMA) and almost agreed with its absorption spectra. Other aqueous volatile molecules of acetaldehyde (AcH) and 2-mercaptoethanol (ME) were decomposed to CO₂. CoPc/C₆₀ nanocomposite exhibited higher photocatalytic activity than independent nanoparticles of CoPc or C₆₀ as well as AlPc/C₆₀ composite. The oxidation power would arise from the hole generated at p/n junction like interface, which was suggested by photoelectrochemical oxidation experiments. The initial external quantum efficiencies of (EQE_{h+}) estimated from CO₂ generation reached to unity under the light intensity of 1 mW/cm², while later EQE_{h+} was \sim 10⁻⁴.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The photocatalytic oxidation of organic substances on a semiconductor photocatalyst is a potential method of removing organic substances from the air and water, to enable us to have comfortable and safe living [1–5]. The most extensively studied photocatalyst, TiO₂, possesses a wide band gap (e_g(anatase) \approx 3.2 eV), which can absorb only the UV light accounting for \sim 4% of total sunlight to generate charge carriers for promoting surface redox reactions [1–6]. In recent years, more attention has been paid for developing new visible-light-active photocatalysts based on molecule [7–9], carbon [10–13], and inorganic solids [14–28], while only few of them are active under interior light illumination.

Organic semiconductors with heterojunctions are widely used to build low-cost and highly efficient photoenergy conversion system in dry state [29–36]. Since Tang's first report in 1986 on organic solar cell composed of Cu-phthalocyanine and a perylene derivative heterojunction bilayer [9], the field has expanded rapidly and is used to construct high-efficiency photoenergy conversion systems in the dry state. On the contrary, primary attempts of organic semiconductor as photoelectrode started more than 30 years ago [37,38]. Oligo *p*-phenylene polymer was used as a sensitizer for photoreduction of not only water molecule to H₂ [39–42] but also CO₂ to CO in the presence of triethylamine (TEA) as a sacrificial electron donor under UV ($\lambda > 290$ nm) irradiation.

Apart from the two research trends, photoelectrochemical catalysis has been used for organic *p*-*n* junction such as a perylene derivative (3,4,9,10-perylenetetracarboxyl-bisbenzimidazole, PTCBI) or fullerene (C₆₀) and metal-free Pc's (H₂Pc) [43–55], Ir-P3HT:PCBM and so forth [56] in the water phase, wherein the evolution of O₂ from the water was found to occur along with hole conduction through the p-type layer under visible-light irradiation [44,57], while the evolution of H₂ from the water was also found with electron conduction through the n-type layer [45,47]. Organic *p*-*n* bilayer undergoes photoinduced redox reaction at the

* Corresponding author.

E-mail address: nagai.k.ae@m.titech.ac.jp (K. Nagai).

¹ Present address: Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.

² Present address: School of Materials and Engineering, Changzhou University, Changzhou, Jiangsu 213164, PR China.

³ Present address: Department of Electrical and Electronics Engineering, Numazu National College of Technology, 3600 Ooka, Numazu, Shizuoka 410-8501, Japan.

solid/water interface along with photophysical events (i.e. light absorption, charge separation at the *p-n* interface, and carrier conduction) in its interior. Moreover, bilayer leads to an efficient carrier generation in comparison with the single layers of Schottky junction [58,59]. An example of the carrier generation without contact electrode is laser-induced reflection for infrared light happened by the photogenerated free electrons in perylene derivative (PTCBI) [60,61].

A visible-light-responsive photocatalyst comprising only organic material based on *p-n* junction has termed to be organophotocatalyst [62,63]. We fabricated an organophotocatalyst composed of a perylene derivative and H₂Pc coated onto a Nafion membrane by the dry process for the photooxidation of trimethylamine (TMA). However, considering the high cost of a dry process (i.e., vapor deposition), it is essential to find an alternative process. A kind of wet process of a reprecipitation from a polar solvent gave biphasic nanocrystals of aluminum phthalocyanine (AlPc) and fullerene [53,64,65], while previous reprecipitation invented by Kasai et al. gave a single component of organic crystals though whose size is controllable between nanometers to micrometers [66–68]. The choice of *N*-methyl-2-pyrrolidone (NMP) [69] as a polar good solvent [53,64] is crucial issue not to form single phase crystal of charge transfer (CT) complex based on electron donor-acceptor interaction, while such single phase D-A complex was obtained by the choice of non-polar good solvent such as toluene for porphyrin-C₆₀ combination [70–73].

Cobalt phthalocyanine (CoPc) is interesting from the view point of oxidation catalysis [74–82], then is expected to be efficient hole consumption. In this study, we will report the synthesis and photocatalytic properties of biphasic nanoparticles comprised of CoPc and fullerene. The photocatalysis properties are evaluated in terms of mineralization of trimethylamine, 2-mercaptoethanol and acetaldehyde to CO₂ under visible-light irradiation (in the order of <1 mW/cm²).

2. Materials and methods

2.1. Materials

C₆₀ (99%) was obtained from Tokyo Chemical Industry Co., Ltd. (TCI) and used as received. CoPc (TCI) was purified twice by sublimation prior to use. Glass substances with ITO coating of 174 nm thickness were commercially available from Asahi Glass Co., Ltd., and were washed by sonication in water-containing detergent, acetone, and ethanol in this sequence. The plates were dried in the air finally before use.

2.2. Synthesis

The C₆₀, CoPc or composite nanoparticles were prepared by dissolving 20 mg of C₆₀, and/or CoPc in 40 mL of NMP as a good solvent. This solution was then injected into 400 mL water by a syringe pump with an injection rate of 5 mL/min. During the injection, the mixture was vigorously agitated with a rate of 700 rpm, which was kept after the injection for 30 min to form a suspension. When the nanoparticles were collected by filtration, 1% (volume ratio) of 1 M HCl was added to the suspension, and the mixture was kept overnight to aggregate the nanocrystals. The particles were collected by filtration (hydrophilic PTFE membrane, pore size 0.2 μm), in which NMP and HCl were removed by gently washing with water 3 times. The nanoparticles were thoroughly washed with distilled water and kept in a deep freezer (−45 °C) for 2 h. Then the frozen nanoparticles were dried with a vacuum of 100 Pa at −10 °C.

2.3. Characterization

UV-vis absorption spectra were recorded using Shimadzu UV-3100S. Transmission electron microscopy (TEM) images were obtained by applying a drop of dilute particle suspension to a carbon-coated copper grid, and they were recorded with Hitachi H-7100. X-ray powder diffraction (XRD) measurements were performed on a Rigaku Rint Ultima+ diffractometer using Cu Kα irradiation. The size distribution of nanoparticles suspension was determined by dynamic light scattering (DLS) using the Malvern Zetasizer Nano ZS at 25 °C. The parameters for the analysis of NMP/water mixture refraction index and the viscosity of the NMP/water are 13.5 and 9.6 Pa s, respectively.

2.4. Photocatalytic oxidation

The photocatalytic oxidation of TMA, 2-mercaptoethanol (ME) or acetaldehyde (AcH) was tested. In a cylindrical Pyrex cell (2 mL), 0.08 mg of the nanoparticles and the aqueous substance (0.4 mL, 1 wt%) was placed. The reactor was irradiated with visible light emitted by a 150-W halogen lamp with an interference filter and a cutoff filter for IR Light. The photon number of almost monochromatic light (FWHM ~ 10 nm) was $3.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ (@1 mW/cm² for 600 nm) which was monitored and adjusted by optical power meter. The irradiation area was 1 cm². The amount of CO₂ generated was detected by a GC-MS (GC; Agilent 7890A. MS; JEOL-JMT-QT400GCP) equipped with a porapak Q column.

2.5. Reusability test

The reusability of the prepared composite nanoparticles was tested by repeating the several cycles of photocatalytic oxidation of AcH. After every cycle, organic substance was removed by argon purging, and fresh AcH was injected into the cell.

2.6. Visible light inorganic photocatalyst test

Splay type WO₃ particles were purchased from Toshiba Lightech (Rene WO₃), and splayed to a sample tube and dried.

3. Results and discussion

3.1. Characterization of particles

The absorption spectra of C₆₀, CoPc and their mixture solutions in NMP are shown in Fig. 1A. The spectrum of C₆₀ (dot line a) exhibited a characteristic shoulder at 340 nm [69], and that of CoPc solution (broken line b) had Q-band absorption with a peak at 675 nm [79]. For the mixture solution of C₆₀ and CoPc (dashed line c), absorption band did not show shift or intensity change compared to the arithmetic sum of two mono-component spectra (solid line d). This indicates that no significant interaction has occurred between C₆₀ and CoPc in the NMP solution as a polar solvent. This observation contrasts with the report on porphyrin/fullerene complex in toluene as a non-polar solvent where a charge transfer band appears at 650–800 nm [70–73].

The reprecipitation process gave nanoparticle suspension. As for the suspension from the mixed solution of C₆₀ and CoPc, composite **c** and **d** denote the nanoparticles of mixing ratios of C₆₀/CoPc = 1/1 and C₆₀/CoPc = 2/1, (wt/wt) respectively. The molar ratios were estimated to be 0.86/1.0 for composite **c** and 1.85/1.0 for composite **d** from elemental analysis (Table S1), while excess H₂O remained. In each of C₆₀, CoPc, and composite **c**, the absorption band of the suspension (lines a–c in Fig. 1B) was broader than that of the corresponding NMP solution (lines a–c in Fig. 1A). This broadening agrees with solidification to be nanoparticle in NMP/water (1/10 = v/v)

Download English Version:

<https://daneshyari.com/en/article/6499100>

Download Persian Version:

<https://daneshyari.com/article/6499100>

[Daneshyari.com](https://daneshyari.com)