



Short communication

Enhancement of the generation of photocatalytic active species by loading copper ions on gold-nanoparticle-deposited titanium dioxide



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ABSTRACT

The photocatalytic performance of gold-nanoparticle-deposited titanium dioxide (AuNP/TiO₂) photocatalyst was found to be improved significantly by loading Cu(II) ions, owing to the remarkable enhanced yield of singlet molecular oxygen (¹O₂) and superoxide radical (O₂⁻), which were detected by near-infrared emission and chemiluminescence photometry, respectively. By loading Cu(II) the TiO₂ conduction band electrons caused by the excitation of AuNP are trapped and then the time for reducing O₂ to form O₂⁻ is prolonged. By the electron trap, the lifetime of holes in AuNP becomes also long to promote the formation of ¹O₂ by the oxidation of O₂⁻.

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1. Introduction

To solve environmental hazardous problems, photocatalysis has been recently gathering much attention. Numerous applications to environmental cleanup as well as solar hydrogen production have been proposed and some products have been actually commercialized [1–4]. Recently to utilize sun-light and room-light more efficiently, various visible light responsive photocatalysts have been developed extensively. Among them gold-nanoparticle-deposited TiO₂ (AuNP/TiO₂) is anticipated as one of the promising visible-light responsive photocatalysts [5,6]. Kowalska et al. [6] observed that AuNP/TiO₂ particles could oxidize 2-propanol under visible-light irradiation. They suggested the reaction mechanism that the electron injection from plasmon excited AuNP to TiO₂ should cause the subsequent oxidation of 2-propanol at AuNP [6]. Actually, Furube and coworkers observed the electron transfer from the excited AuNP to the TiO₂ particle by means of the femtosecond transient absorption spectroscopy [7]. However, since the oxidation potential of Au is not so positive as that of TiO₂ valence band holes, some uncertainties still remain in the reaction mechanism.

In photocatalytic reactions, it is well known that active oxygen species such as superoxide radical (O₂⁻), hydroxyl radical, and singlet oxygen (¹O₂) are generated. For bare TiO₂, we measured O₂⁻ and ¹O₂ by a luminol chemiluminescence method [8,9] and near infra-red phosphorescence spectroscopy [10,11] respectively, and demonstrated that O₂⁻ and ¹O₂ are involved in the photocatalytic reactions [8–11]. Recently,

for AuNP/TiO₂ photocatalysts, we presented the evidences of ¹O₂ generation for the first time [12]. Furthermore, we confirmed O₂⁻ generations on AuNP/TiO₂. Then, by analyzing the generations of ¹O₂ and O₂⁻ for the thirteen kinds of AuNP/TiO₂ samples prepared with different kinds of TiO₂ powders, a plausible mechanism of ¹O₂ generation for AuNP/TiO₂ photocatalysts was proposed [13], which could explain the reaction for the photocatalysts more clearly than the other mechanisms suggested previously [14,15]. However, for practical use, the yields of ¹O₂ generated from AuNP/TiO₂ were too small [12,13], due to the recombination between excited electrons and holes. Different from the bare TiO₂ photocatalyst, AuNP/TiO₂ photocatalyst absorbs visible light by surface plasmon resonance. Therefore, the increase in the photocatalytic activity under visible light irradiation has been expected. Then, in the present study, we attempted the Cu(II) loading on AuNP/TiO₂ to accelerate the charge separation to enhance the photocatalytic activity since the loading of Cu(II) on bare TiO₂ was found to enhance the photocatalytic activity in our previous study [16].

2. Experimental

2.1. Sample preparation

Cu-AuNP/TiO₂ samples were prepared by the following procedures. An aqueous solution of 0.2 mM NaAuCl₄ (Wako Co.), containing 40 mM citric acid (Kanto Chemicals) and Cu(I)Cl (Nacalai Tesque Inc.) was vigorously stirred for 10 min at 70 °C, then TiO₂ powder was added into the solution. This colloidal suspension was washed repeatedly with purified water by using centrifugal sedimentation. Finally, the suspension was freeze dried and heat treated at 200 °C. Thus, Cu-AuNP/TiO₂ powder

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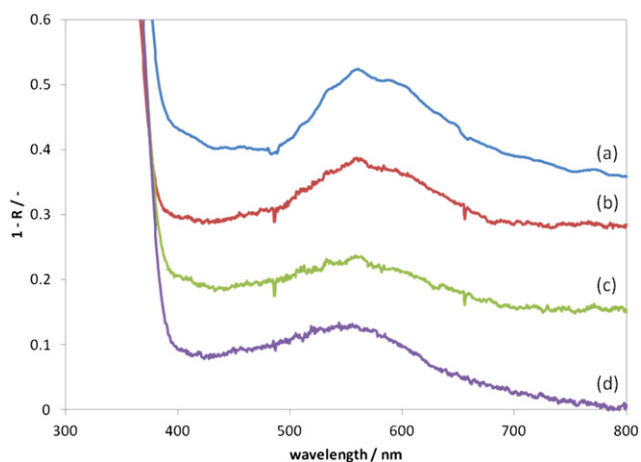


Fig. 1. Diffuse-reflectance spectra of Cu-AuNP/TiO₂ prepared with the CuCl concentration in solution of (a) 0.0, (b) 0.1, (c) 0.2, and (d) 0.4 mM. Actual compositions are shown in Table 1. The base lines of (a), (b), and (c) were shifted for clarity. The absorptivity (1-reflectance) for plasmonic band is shown in Table 1.

Table 1
Amount of AuNP and Cu in Cu-AuNP/TiO₂ samples and the absorptivity of AuNP at 550 nm.

| Samples | Concentration of CuCl in reactant/mM | Amount of Au in Cu-AuNP/TiO ₂ /wt.% | Amount of Cu in Cu-AuNP/TiO ₂ /10 ⁻³ wt.% | Absorptivity of AuNP at 550 nm |
|---------|--------------------------------------|--|---|--------------------------------|
| (a) | 0.0 | 10 | 0.0 | 0.095 |
| (b) | 0.1 | 8.0 | 0.68 | 0.076 |
| (c) | 0.2 | 6.1 | 1.4 | 0.054 |
| (d) | 0.4 | 2.1 | 2.7 | 0.043 |

showing pale violet color was obtained. The CuCl concentration in solution was varied to (a) 0.0, (b) 0.1, (c) 0.2, and (d) 0.4 mM. CuCl was used as the source of Cu(II). When Cu(II) was used initially, it was reduced in place of Au(III), and the preparation of AuNP became difficult. By the heat treatment in air, the adsorbed Cu(I) ions became Cu(II), probably as a form of CuO [17]. TiO₂ used was ST-41 (Ishihara Sangyo Ltd.) because this particular anatase powder showed the highest ¹O₂ and O₂⁻ generation by AuNP loading [13]. The size of AuNP is about 48 nm as was estimated previously [13].

2.2. Detection of ¹O₂ by phosphorescence

The phosphorescence of ¹O₂ was measured for D₂O suspensions (3 ml) of sample powder (40 mg) in a 1 cm × 1 cm quartz cell under

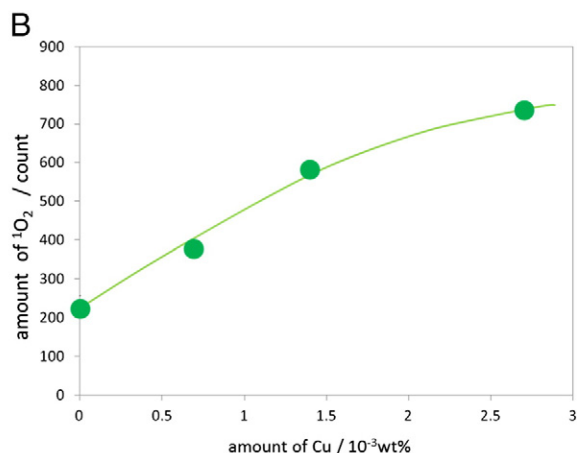
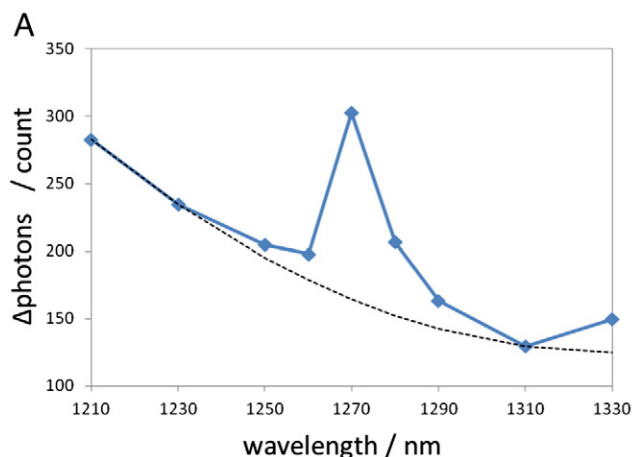


Fig. 2. (A) Emission spectrum for Cu-AuNP/TiO₂ (d) on the excitation at 532 nm. (B) Dependence of ¹O₂ generation on the amounts of Cu(II) loaded on AuNP/TiO₂.

vigorous stirring with a magnetic stirrer. D₂O was used as the solvent, because the lifetime of ¹O₂ in D₂O is prolonged 20 times more than that in H₂O [18]. The front of the cell was alternately irradiated with a DPSS CW laser (Excelsior 532 nm, 100 mW, Spectra Physics) through a light chopper (5584A, NF Electronic Instrument) at the frequency of 10.5 Hz. The emission light was gathered with a convex lens and focused in a monochromator (Shimadzu-BoschLomb), then introduced into a photomultiplier (R5509-41, Hamamatsu) cooled at -73 °C with liquid nitrogen. At the front of the convex lens, a cold mirror filter (CLDM-50S, Sigma Koki) was placed to reduce the obstruction of scattered and/or luminescent light. The signal from the photomultiplier was amplified with a preamplifier (SR445, Stanford Research Systems) and accumulated for 10,000 times with a scalar/averager (SR430, Stanford Research Systems). The difference of the signals caused by the chopped excitation light was measured as the emission intensity.

2.3. Detection of O₂⁻ by chemiluminescence of luminol

O₂⁻ was detected by a luminol chemiluminescence method [19], and the concentration of O₂⁻ was calculated from the intensity of chemiluminescence. The sample powder (15 mg) was suspended in a 1 cm × 1 cm Pyrex cell containing 0.01 M NaOH aqueous solution (3.5 ml). The cell was placed on a magnetic stirrer in a dark box, and kept stirring during the measurements. The solution was irradiated by a 532-nm diode laser (40 mW, ZM18BF, Z-LASER) for 3 to 120 s. Immediately after the laser irradiation, 50 μl of luminol solution was injected into the cell, then, the luminol chemiluminescence was detected through a 430-nm interference filter by a photon counting system (Hamamatsu Photonics) for 20 s.

3. Results and discussion

3.1. Absorption spectra

Diffuse reflection spectra of each sample were measured with a fiber probe spectrometer AvaSpec-2048 with AvaLight-DH-S-BAL (Avantes Inc.) and shown in Fig. 1. All the spectra of the samples showed an optical absorption peak at 550 nm, which is attributed to the surface plasmon resonance band of AuNP. Since the absorption peak wavelength is well known to depend on the size of nano-particles, the same wavelength at the peak position, for the Cu(II) loaded samples ((b)–(d)) indicates that the size of AuNP loaded on each sample is mostly the same.

The decrease of the plasmon absorption by Cu(II) loading indicates the decrease of deposited AuNP. Then, the actual amounts of deposited AuNP and Cu(II) were measured with an ICP optical emission spectrometer (SII Inc, SPS4000). For the sample (d), Au and Cu deposited were 2.1 and 2.7 × 10⁻³ wt.% of TiO₂, respectively. The actual load of both

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