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Gold nanoparticles supported on cerium(IV) oxide powder for mineralization of organic acids in aqueous suspensions under irradiation of visible light of $\lambda = 530$ nm

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ABSTRACT

Gold (Au) nanoparticles supported on cerium(IV) oxide (CeO_2) were prepared by the photodeposition method. These samples showed strong absorption at around 550 nm due to localized surface plasmon resonance (LSPR) of Au. These Au/CeO_2 samples were used for mineralization of organic acids (formic acid, oxalic acid and acetic acid) in the aqueous suspensions under irradiation of visible light (>ca. 520 nm) and three acids were stoichiometrically decomposed to carbon dioxide. Apparent activation energy for mineralization of formic acid was very small (2.4 kJ mol^{-1}) compared with those by thermocatalytic reactions, and the action spectrum was in good agreement with the photoabsorption spectrum, indicating that the rate-determining step in mineralization of organic acids in the irradiated Au/CeO_2 system was different from the thermal activation process and that this mineralization involved a photoinduced step by LSPR of Au supported on CeO_2. When a green light-emitting diode (center wavelength = 530 nm) was used as the light source of visible light, mineralization of formic acid also occurred. Apparent quantum efficiency of formic acid mineralization increased with decrease in the intensity of the green light and reached 4.7% at 0.4 mW cm^{-2}.

1. Introduction

Many efforts have been devoted to synthesis of photocatalysts that respond to visible light. To the best of our knowledge, these photocatalysts can be roughly classified into four types. The first type is TiO_2 doped with various elements such as nitrogen [1,2], sulfur [3] and transition metals [4]. In the two former cases, the energy levels of nitrogen and sulfur were inserted in the forbidden band of TiO_2, resulting in response to visible light. The second type is a photocatalyst having a narrow band-gap loaded with a co-catalyst. Recently, Abe et al. [5] and Sayama and co-workers [6] reported that platinum- and palladium-loaded tungsten(VI) oxide (WO_3) exhibited a high level of photocatalytic activity for decomposition of organic compounds under irradiation of visible light. The third and fourth types are semiconductors modified with copper ions (Cu^{2+}) utilizing interface charge transfer (IFCT) [7] and TiO_2 samples modified with an inorganic sensitizer such as platinum(IV) and rhodium(III) chlorides [8–14]. The third and fourth types of photocatalysts have various good properties such as high activity, excellent light absorption and high stability because of the varieties of semiconductors, metal ions and sensitizers. Most of the visible light-responding photocatalysts such as doped and modified TiO_2 [3] and tungsten oxide with co-catalysts [1–3] work under irradiation of light of which the wavelength is shorter than about 480 nm. Therefore, development of photocatalysts working under irradiation of light of which the wavelength is larger than about 480 nm is important in order to utilize solar energy efficiently. In our previous communication [15], we briefly reported a new application of CeO_2 as a photocatalytic material, *i.e.*, an excellent supporting material of gold (Au) nanoparticles inducing strong localized surface plasmon resonance (LSPR) of Au at around 550 nm [16–18]. Kowalska et al. [17,18] observed photoinduced oxidation of 2-propanol over Au/TiO_2 under visible light irradiation and proposed the following reaction mechanism: (1) Incident photons are absorbed by Au particles through their LSPR excitation, (2) electrons may be injected from Au particles into the conduction band of TiO_2, and (3) the resultant electron-deficient Au could oxidize 2-propanol to be recovered to the original metallic state. In this paper, we investigated photocatalysis of Au/CeO_2 in detail to further expand of the possibility of Au/CeO_2 and we found that various organic acids were stoichiometrically decomposed to carbon dioxide under irradiation of visible light. Since organic acids are observed as one of intermediates in various processes for degradation of organic compounds in aqueous solutions, the mineralization of organic acids is important for total mineralization of organic compounds.

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2. Experimental

2.1. Preparation of Au/CeO_2

Loading of Au on CeO_2 was performed by the photodeposition method. Commercial CeO_2 powder (Nanotech, 47 $m^2\,g^{-1}$) having a cubic structure was supplied by Kanto Chemical. The CeO_2 powder (198 mg) was suspended in water (10 cm^3) in a test tube and the test tube was sealed with a rubber septum under argon (Ar). Aqueous solutions of citric acid (30 μmol) and tetrachloroauric acid (as 2 mg Au) were injected into the sealed test tube and then photoirradiated at $\lambda > 300$ nm by a 400-W high-pressure mercury arc (Eiko-sha, Osaka) under Ar with magnetic stirring in a water bath continuously kept at 298 K. The Au source was reduced by photogenerated electrons, and Au metal was deposited on CeO_2 particles, resulting in the formation of Au/CeO_2. Analysis of the liquid phase after the photodeposition revealed that the Au source was almost completely (>99.9%) deposited as Au metal on the CeO_2 particles. The resultant powder was washed repeatedly with distilled water and then dried at 310 K overnight under air.

2.2. Characterization

Diffuse reflectance spectra were obtained with a UV–visible spectrometer (UV-2400, Shimadzu, Kyoto) equipped with a diffuse reflectance measurement unit (ISR-2000, Shimadzu) and recorded after Kubelka–Munk analysis. Powder X-ray diffraction (XRD) (Multi Flex, Rigaku, Tokyo) was measured using CuKα radiation and a carbon monochromator and revealed that the sample consisted of cubic phase of CeO_2 (ICDD No. 43-1002). In the XRD pattern of the Au/CeO_2 sample with 1 wt% Au, peaks attributed to Au were not observed, indicating that Au was finely dispersed on the surface of CeO_2. The crystallite size of CeO_2 was calculated to be 22 nm from the half-height width of the 1 1 1 diffraction peak of the cubic phase of CeO_2 using the Scherrer equation; the value of the shape factor, K, was arbitrarily taken to be 0.9. The morphology of Au/CeO_2 was observed under a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV in the Joint Research Center of Kinki University and, in the TEM photograph of 1 wt% Au/CeO_2, fine Au particles of 5–10 nm in size were clearly observed (Fig. S1).

2.3. Mineralization of organic acid in an aqueous suspension of Au/CeO_2 under irradiation of visible light

The dried Au/CeO_2 powder (50 mg) was suspended in distilled water (5 cm^3), bubbled with oxygen (O_2), and sealed with a rubber septum. Organic acid (formic acid, oxalic acid or acetic acid, 100 μmol-C) was injected into the suspension and then irradiated with visible light of a 500 W xenon (Xe) lamp (Ushio, Tokyo) filtered with an O-54 cut-filter (AGC Techno Glass) with magnetic stirring in a water bath continuously kept at 298 K. The amount of carbon dioxide (CO_2) in the gas phases of reaction mixtures was measured using a gas chromatograph (GC-8A, Shimadzu) equipped with Porapak QS columns. In some experiments, a green light-emitting diode (HDMS8G, Hayashi Watch Works, Tokyo, maximum energy at 530 nm, designated green LED hereafter) was also used to evaluate activity of formic acid mineralization under irradiation of visible light coming from a light source other than the Xe lamp. In some condition, the brightness and light intensity on the surface of the test tube were 8000 lx and 1.7 mW cm^{-2}, respectively. To obtain an action spectrum, the full arc from the Xe lamp was monochromated using SM-100 (Bunkoukeiki, Tokyo). Spectra and light intensity of the green LED and Xe lamp (filtered and monochromated) were determined using a spectroradiometer USR-45D (Ushio, Tokyo).

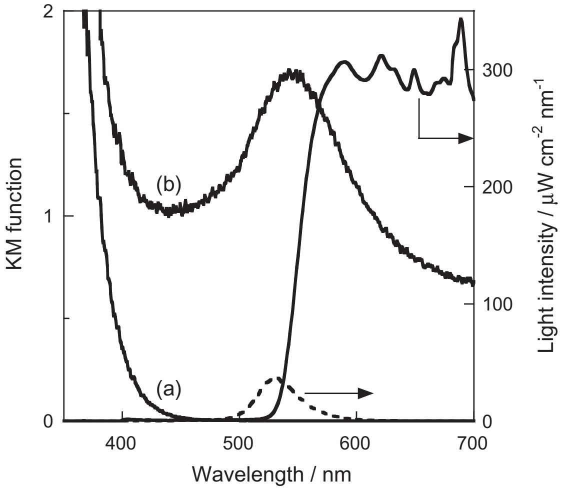

Fig. 1. Absorption spectra of (a) CeO_2 and (b) 1 wt% Au/CeO_2, and visible light irradiated to reaction systems (formic acid in aqueous suspensions of various powders) from a Xe lamp with an O-54 cut-filter (solid line) and green LED (broken line).

3. Results and discussion

3.1. Preparation of Au/CeO_2 and mineralization of formic acid in an aqueous suspension of Au/CeO_2 under visible light irradiation

Fig. 1 shows absorption spectra of CeO_2 and 1 wt% Au/CeO_2. Bare sample, CeO_2, exhibited strong photoabsorption at $\lambda < 410$ nm due to the band-gap excitation. In the spectrum of Au/CeO_2, additional photoabsorption was observed at around 550 nm. Kowalska et al. [17,18] reported that photoabsorption due to LSPR of Au particles supported on TiO_2 was observed at around 550 nm. Therefore, photoabsorption observed in Au/CeO_2 was attributed to LSPR of the supported Au particles.

Fig. 2 shows the time course of evolution of CO_2 from aqueous solutions of formic acid in the presence of 1 wt% Au/CeO_2 under irradiation of visible light from a Xe lamp with an O-54 cut-filter at 298 K. Visible light irradiated to the reaction system is shown

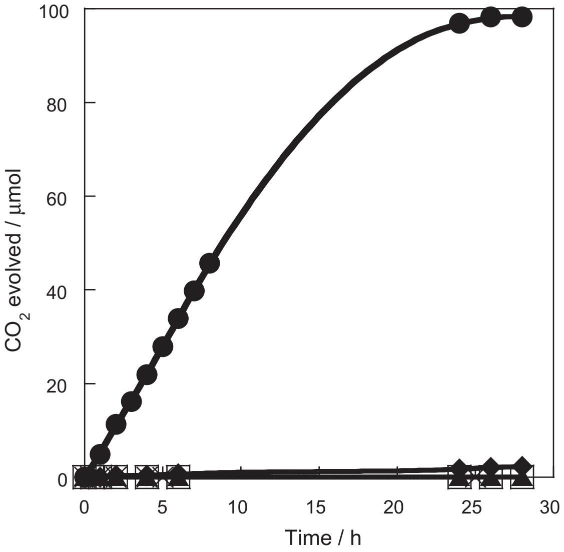

Fig. 2. Time courses of evolution of CO_2 from aqueous solutions of formic acid in the presence of 1 wt% Au/CeO_2 under irradiation of visible light (circles), in the absence of 1 wt% Au/CeO_2 under irradiation of visible light (squares), in the presence of bare CeO_2 under irradiation of visible light (triangles), in the presence of 1 wt% Au/CeO_2 in the dark (diamonds), and in the presence of 1 wt% Au/CeO_2 under irradiation of visible light in the absence of oxygen (crosses).