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Switching redox site of photocatalytic reaction on titanium(IV) oxide particles modified with transition-metal ion controlled by irradiation wavelength

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ABSTRACT

Titanium(IV) oxide (TiO_2) particles were modified with several kinds of transition-metal ions (iron(III), copper(II), nickel(II) and chromium(III) ions). Photocatalytic activity for acetaldehyde decomposition over metal-ion-modified TiO_2 showed higher photocatalytic activity than bare TiO_2 under ultraviolet (UV) as well as visible-light irradiation. The mechanism of photocatalytic reaction over metal-ion-modified TiO_2 was investigated by double-beam photoacoustic (DB-PA) spectroscopy, which enables observation of electron migration in the TiO_2 particles. DB-PA measurements suggested that metal ions on TiO_2 surface acted differently depending on the wavelength of photoirradiation, i.e., as electron acceptors under UV irradiation and as electron injectors under visible-light irradiation.

1. Introduction

Titanium(IV) oxide (TiO_2) is one of the most attractive materials for a semiconductor photocatalyst with advantages of photostability, oxidation ability and availability [1]. TiO_2 photocatalysts required ultraviolet (UV) irradiation, the amount of which corresponds to only 3% of total solar energy, for generation of photoexcited electrons and positive holes. However, a large proportion of them recombine with each other without being utilized in chemical reactions. Thus, it is important to prevent recombination in order to make efficient use of the photoexcitation. One conventional method for preventing recombination is utilization of noble metal catalysts, e.g., platinum and rhodium, which are capable of collecting a large number of electrons and enhancing reduction activity, though the use of noble metals as co-catalysts is a problem from the viewpoints of cost and shortage.

Recently, we have succeeded in enhancement of photocatalytic activity of sulfur-doped TiO_2 (S-TiO_2) by adsorption of iron(III) ion (Fe^{3+}) as an electron acceptor [2,3]. Transition-metal ions with more positive redox potential than the conduction band of TiO_2, such as Fe^{3+}, can act as electron acceptors, resulting in an increase of reduction rate. Such electron acceptors are expected to have a larger influence on rutile TiO_2 than anatase TiO_2 because reduction activity of rutile TiO_2 is thought to be inferior to that of anatase TiO_2 due to less negative potential of the conduction band. On the other hand, some studies have indicated that rutile TiO_2 shows superior activity to that of anatase TiO_2 for some oxidative reactions [4,5]. Therefore, the photocatalytic activity of rutile TiO_2 has greater potential than that of anatase TiO_2 to be enhanced with the aid of electron acceptors because it is difficult to enhance oxidation activity of TiO_2 photocatalysts with a co-catalyst.

Furthermore, some metal ions are also capable of working as sensitizers for visible light by formation of a metal complex, such as a ruthenium complex, which is a well-known sensitizer for dye-sensitized solar cells [6]. However, development of visible-light response photocatalyst by modification of sensitizer on TiO_2 has been failed because of poor stability under photoirradiation. Recently, Kisch et al. reported a new type of visible-light response photocatalyst developed by modification of platinum(IV) chloride surface complex [7–10]. The photocatalyst has attracted much attention because of simple preparation without any impurity doping, which causes formation of defects in a semiconductor and reduces photocatalytic activity under UV irradiation.

In this study, TiO_2 particles were modified with various inexpensive transition-metal ions, including iron(III) ion (Fe^{3+}), copper(II) ion (Cu^{2+}), nickel(II) ion (Ni^{2+}) and chromium(III) ion (Cr^{3+}), by the impregnation method. Photocatalytic reaction and electron migration on TiO_2 modified with metal ions under UV and visible-light irradiation were investigated.

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2. Experimental

2.1. Materials and instruments

TiO_2 (MT-600B) particles having a rutile phase were obtained from TAYCA. The specific surface area of MT-600B was 27 $m^2\ g^{-1}$. Acetaldehyde (CH_3CHO) was obtained from Aldrich, and other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The crystal structures of TiO_2 particles were determined from X-ray diffraction patterns measured with an X-ray diffractometer (JEOL, JDX3500) with a Cu target Kα-ray (λ = 1.5405 Å). The specific surface areas of the particles were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). The diffuse reflection (DR) spectra were measured using a Shimadzu UV-2500PC spectrophotometer equipped with an integrating sphere unit (ISR-240A). X-ray photoelectron spectra (XPS) of the TiO_2 particles were measured using a JEOL JPS90SX photoelectron spectrometer with an Mg Kα source (1253.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard.

2.2. Sample preparation

An aqueous suspension composed of rutile TiO_2 particles and an aqueous solution of iron(III) chloride ($FeCl_3$), iron(III) nitrate enneahydrate ($Fe(NO_3)_3\cdot 9H_2O$), copper(II) chloride dehydrate ($CuCl_2\cdot 2H_2O$), nickel(II) chloride hexahydrate ($NiCl_2\cdot 6H_2O$), chromium(III) chloride hexahydrate ($CrCl_3\cdot 6H_2O$), the amount of which corresponds to 0.1 wt% modification of metal, was stirred for 3 h under an aerated condition at ca. 80 °C. The residue was washed with deionized water several times until pH of the filtrate was ca. 7. The particles were dried under reduced pressure at 60 °C for 12 h. Then metal-ion-modified TiO_2 (M^{n+}/TiO_2) was obtained.

2.3. Photocatalytic decomposition of acetaldehyde

The photocatalytic activity of a M^{n+}/TiO_2 sample was evaluated by photocatalytic decomposition of acetaldehyde. One hundred milligrams of TiO_2 particles was spread on a glass dish, and the glass dish was placed in a Tedlar bag (As one) with a volume of 125 cm^3. Five hundred parts per million of gaseous acetaldehyde was injected into the Tedlar bag, and the photoirradiation was carried out at room temperature after acetaldehyde had reached an adsorption equilibrium. A 500-W xenon lamp (Ushio, SX-UI501XQ) was used as a light source and the wavelength of photoirradiation was controlled by UV-35 and L-42 filter (Asahi Techno Glass Co.). Concentrations of acetaldehyde and carbon dioxide (CO_2) were estimated by gas chromatography (Shimadzu, GC-8A, FID detector) with an PEG-20 M 20% Celite 545 packed glass column and by gas chromatography (Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and methanizer (GL Sciences, MT-221), respectively.

2.4. Double-beam photoacoustic spectroscopic measurement

A gas-exchangeable photoacoustic (PA) cell equipped with two valves for gas flow was used, and a TiO_2 sample was placed in the cell. The atmosphere was controlled by a flow of artificial air or N_2 containing ethanol vapor (air + EtOH, N_2 + EtOH), and the measurements were conducted after shutting off the valves, i.e., in a closed system at room temperature. A light-emitting diode (LED) emitting light at ca. 625 nm (Luxeon LXHL-ND98) was used as a probe light, and the output intensity was modulated by a digital function generator (NF DF1905) at 80 Hz. In addition to the modulated light, a UV-LED (Nichia NCCU033, emitting light at ca. 365 nm, 2.5 mW cm^{-2}) and a blue-LED (Luxeon LXHL-NB98, emitting light at ca. 470 nm, 8.1 mW cm^{-2}) were also used as simultaneous continuous irradiation for photoexcitation of M^{n+}/TiO_2. The PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier (NF LI5640). Detailed setups of double-beam photoacoustic (DB-PA) spectroscopic measurements have been reported [11].

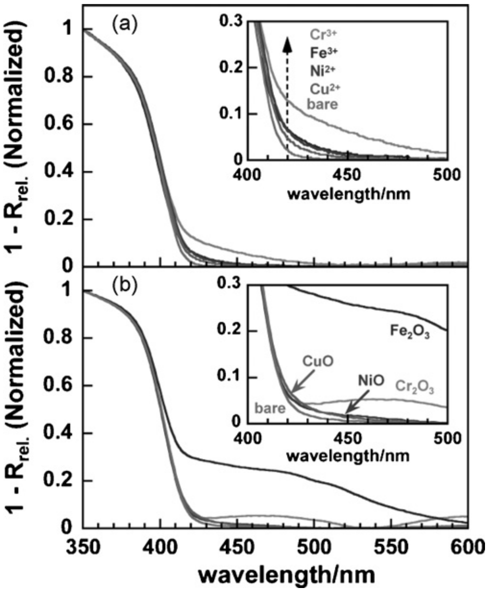

Fig. 1. DR spectra normalized at 350 nm ($R_{rel.}$: relative reflection) of (a) M^{n+}/TiO_2 and (b) a mixture of TiO_2 and metal oxide.

3. Results and discussion

3.1. Photoabsorption properties of M^{n+}/TiO_2 sample

The color of M^{n+}/TiO_2 samples was changed by modification with metal ion and depended on the kind and amount of metal ion adsorbed on TiO_2. Fig. 1a shows DR spectra of bare TiO_2 and M^{n+}/TiO_2 samples. The absorption edge of M^{n+}/TiO_2 samples shifted to a longer wavelength region of 500–550 nm, but the range of red shift depended on the kind of metal ion ($Cr^{3+} > Fe^{3+} \sim Ni^{2+} > Cu^{2+}$ at 420 nm). Fig. 1b shows DR spectra of a mixture of TiO_2 and metal oxide fine particles, the amount of which corresponds to 0.1 wt% of metal atom. Similar DR spectra were observed between M^{n+}/TiO_2 and TiO_2 particles physically mixed with NiO and CuO fine particles, while rather large differences were observed in the DR spectra for TiO_2 particles physically mixed with Fe_2O_3 and Cr_2O_3 fine particles. This suggests that state of Fe^{3+} and Cr^{3+} on the TiO_2 surface was very different from the bulk state of metal oxide.

3.2. Photocatalytic reaction of M^{n+}/TiO_2 sample under UV–vis irradiation

Fig. 2 shows the time course of CO_2 evolution of acetaldehyde decomposition under UV–vis irradiation. M^{n+}/TiO_2 showed a higher photocatalytic activity than that of the bare sample. As suggested by our previous studies [2,3], a metal ion possibly prevents an excited electron from recombining with a positive hole by acting as an electron acceptor. Moreover, the activity depended on the kinds of metal ion ($Fe^{3+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$), and the order of photocatalytic activity coincided with the order of redox potential (Fe^{3+}/Fe^{2+} = 0.771 V, Cu^{2+}/Cu^{+} = 0.159 V, Ni^{2+}/