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Silver-modified octahedral anatase particles as plasmonic photocatalyst

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ABSTRACT

Octahedral anatase particles (OAPs) were modified with silver nanoparticles (NPs) by photodeposition method. The properties of OAPs influenced the properties of silver deposits, and thus the photocatalytic activity of the obtained silver-modified OAPs. Photocatalytic activities were tested under UV and vis irradiation for oxidative decomposition of acetic acid and oxidation of 2-propanol, respectively. The properties of silver-modified OAPs were investigated by XRD, STEM, DRS, XPS and time-resolved microwave conductivity (TRMC) method. It was found that electron traps (ETs) worked as nucleation sites for silver, resulting in formation of smaller silver NPs on smaller OAPs with larger content of ETs. The modification with silver resulted in enhanced photocatalytic activity under both UV and vis irradiation. It was found that larger crystallite size of silver NPs, and thus larger polydispersity of silver deposits resulted in broad and intense plasmon resonance peak causing enhanced visible activity. The correlation between photocatalytic activity and TRMC data, e.g., slower decay of TRMC signal for more active samples, allowed discussion on property-governed photocatalytic activities of silver-modified titania.

1. Introduction

Energy crisis and environmental pollution have become two serious challenges ahead for human beings. Solar energy has many advantages, e.g., it is a clean alternative to fossil fuels and nuclear power, cost effective, secure, eco-friendly, and especially renewable. Therefore, the effective utilization of solar energy is an advisable way to solve energy crisis. However, development of systems with high efficiency of energy conversion and energy storage is a tough task, and thus still under intensive study. It has been proposed that heterogeneous photocatalysis under solar radiation (solar photocatalysis) can be used for this purpose, as well as for environmental purification [1–3].

Titanium(IV) oxide (titania, TiO_2) is one of the most widely investigated heterogeneous photocatalyst due to high photocatalytic activity, stability, cheapness and nontoxicity (except toxicity of nanomaterials [4]) [5–8]. Moreover, commercial applications of titania have been widely reported, e.g., for self-cleaning and anti-fogging surfaces, disinfection, water purification, wastewater treatment, gas-phase purification, soil treatment, water splitting and solar energy conversion (e.g., dye sensitized solar cells) [9–14]. However, there are two shortcomings of titania usage, i.e., (1) recombination of charge carriers (e^-/h^+) resulting in much lower quantum yield (typical for all semiconducting materials) than that for homogeneous photocatalysis or other advanced oxidation processes (AOPs), e.g., UV/H_2O_2, UV/O_3 [15–19], and (2) only small part of solar energy could be efficiently used due to the wide band-gap of titania (ca. 3–3.2 eV eq. 387–413 nm) [20,21]. Therefore, plenty of studies have been performed to improve photocatalytic performance of titania by, for example, surface modification, doping and heterojunctions with other compounds [22–30], as well as preparation of morphology-controlled titania nanocrystals (faceted particles) [31–38]. It has been proposed that faceted particles retard the recombination of charge carriers, for instance, (i) in the case of decahedral anatase particles (DAPs) selective transfer of electrons and holes to (1 0 1) and (0 0 1) facets, respectively, was proved [35], and (ii) for octahedral anatase particles (OAPs) preferential distribution of shallow than deep electron traps (ETs) resulted in enhanced mobility of electrons [39]. Although photocatalytic activity of titania could be significantly enhanced by morphology control strategies, inactivity of titania under visible light must be overcome by other methods. Recently, modification of titania with NPs of noble metal possessing plasmon resonance feature at visible range of solar spectrum (mainly gold and silver) has been intensively investigated, and those materials

Abbreviations: AOPs, advanced oxidation processes; CDT, time needed for complete deposition of silver; DRS, diffuse reflectance spectroscopy; ETs, electron traps; HT, hydrothermal reaction; LSPR, localized surface plasmon resonance; NPs, nanoparticles; OAPs, octahedral anatase particles; SSA, specific surface area; STEM, scanning transmission electron microscopy; TNWs, potassium titanate nanowires; TRMC, time-resolved microwave conductivity; US, ultrasonication; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy

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are known as plasmonic photocatalysts [40–43].

To obtain photoactive materials under broad range of irradiation, faceted anatase particles of octahedron shape (octahedral anatase particles, OAPs) were modified with NPs of silver and investigated in the present study. Silver (Ag) as a relative cheap noble metal has great potential for the application of plasmonic photocatalysis not only due to its plasmon resonance but also the excellent anti-microbiological (anti-fungal and anti-bacterial) properties.[44–46] In previous study on OAPs it was found that the preparation conditions had important influence on the physicochemical properties of titania (specific surface area, crystallite size, crystallinity, surface composition) including the morphology (the content of faceted NPs), and thus on the photocatalytic activity [47,48]. To investigate how the properties of titania influence the modification with Ag, as well as how the resultant properties of Ag-modified OAPs influence the photocatalytic activity, OAPs samples varied by properties were prepared by ultrasonication-hydrothermal (US-HT) method and then modified with Ag NPs by photodeposition. It was found that an increase in the size of titania nanocrystals resulted in formation of larger silver NPs during photodeposition process. The silver properties (size and oxidation form) had significant influence on the photocatalytic activity, especially under visible light (vis) irradiation, i.e., the larger the size of silver NPs was, the higher was the vis activity.

2. Materials and methods

2.1. Preparation of bare and silver-modified OAPs

Potassium titanate nanowires (TNWs; Earthclean Tohoku Co. Ltd), synthesized by hydrothermal reaction (HT) of Evonik P25 titania (Nippon Aerosil) with potassium hydroxide (17 mol L^{-1}) at 383 K for 20 h [49], were used as the precursor for preparation of bare OAPs, as reported previously [47]. In brief, 267 mg of TNWs were dispersed by ultrasonication (US) in Milli-Q water (40 mL) for 1 h, and the obtained suspension was poured in a 100-mL sealed Teflon bottle. The residue of TNWs was rinsed with an additional portion of Milli-Q water (40 mL) and added to the Teflon bottle. The bottle was inserted into an outer sleeve of a stainless autoclave and then heated in an oven at 433 K for a fixed period of time (3–24 h). The collected suspension after US-HT was dispersed by 10-min US and then centrifugally separated (12000 rpm, 20 min). The white precipitates were collected and dried overnight under vacuum (353 K, 12 h). In total, five titania samples containing OAPs were prepared by varying in duration of HT process, i.e., 3 h, 4.5 h, 6 h, 12 h and 24 h.

For preparation of silver-modified OAPs, the aqueous solution of silver nitrate ($AgNO_3$) was used as metal precursor. 500 mg of each bare titania sample was used for photodeposition. The amount of silver was calculated to be 2.0 wt% to titania. Photoirradiation was carried out for 25 mL of aqueous solution of methanol (50 vol%) containing titania and $AgNO_3$(aq) under magnetic stirring (500 rpm) by a 400-W high-pressure mercury lamp (Eiko-sha; light intensity of 20–22 mW) at 298 K (thermostated water bath). The process of silver deposition on OAPs was carried out for 150 min under deaerated condition, i.e., proceeded by 15-min Ar bubbling to remove oxygen from the tubes. The tubes were sealed with rubber septa and the effectiveness of deaeration was checked by gas chromatography (GC-TCD). During photoirradiation charge carriers (e•/h^+) were formed (Eq. (1)). Holes were scavenged by methanol forming formaldehyde (Eq. (2)), while Ag^+ ions were reduced by electrons to zero-valent Ag (Eq. (3)). Then, hydrogen was formed on deposited Ag NPs (Eq. (4); and Fig. 1a).

$$TiO_2 + h\nu \rightarrow e\bullet + h^+ \quad (1)$$

$$CH_3OH + h^+ \rightarrow HCHO + H^+ \quad (2)$$

$$Ag^+ + e\bullet \rightarrow Ag \text{ (during photodeposition)} \quad (3)$$

$$H^+ + e\bullet \rightarrow 1/2\ H_2 \text{ (on photodeposited Ag NPs)} \quad (4)$$

The H_2 liberation was measured during photodeposition for every 15 min. The obtained photocatalysts were centrifuged, washed with methanol and three times with Milli-Q water and freeze dried. The codes of the samples were defined as follow: HT-duration/Ag, for example, 3HT/Ag meant OAPs-containing titania sample prepared for 3-h HT and then modified with silver.

2.2. Characterization of samples

The morphology of samples was characterized by scanning transmission electron microscopy (STEM, HD-2000). The surface composition and oxidation states of elements were analyzed by XPS on JEOL JPC-9010MC (MgKα X-ray) spectrometer. XRD analysis (phase content, crystallinity and crystallite size of OAP; crystallite size of Ag) was performed using a Rigaku intelligent X-ray diffraction system SmartLab equipped with a sealed tube X-ray generator (a Cu target). Photoabsorption properties were examined by diffuse reflectance spectroscopy (DRS) on a JASCO V-670. Barium sulfate and respective bare OAPs samples were used as references. Electron mobility was evaluated by time-resolved microwave conductivity (TRMC) method, as described in previous reports [39,50,51], under irradiation at two fixed wavelengths, i.e., at 355 nm and 545 nm. The amount of deposited silver was determined by flame atomic absorption spectroscopy (FAAS, Shimadzu AA-6200).

2.3. Photocatalytic activity test

The photocatalytic activity was tested for oxidative decomposition of acetic acid under UV/vis irradiation (the same irradiation system as for silver photodeposition). In each experiment, 50 mg of photocatalyst was suspended in 5 mL of aqueous acetic acid (5 vol%) and then irradiated under magnetic stirring (1000 rpm). Amounts of liberated CO_2 in a gas phase were evaluated by gas chromatography (TCD-GC, Shimadzu GC-8A equipped with Porapak-Q column).

The visible light activity was evaluated for oxidation of 2-proponal to acetone in a sealed testing tubes of 35-mL volume. 50 mg of photocatalyst was suspended in 5 mL of 2-propanol (5 vol%) and irradiated under magnetic stirring (thermostated water bath) in a photoreactor equipped with 300-W xenon lamp (CX-04E Inotech, Japan), a cold mirror, an IR filter (water bath) and a cut-off filter Y45 (Asahi Techno Glass); with vis light intensity of 250–350 μW (lamp spectrum and the photoreactor were described in detail in previous reports [52]). The generated acetone was analyzed in liquid phase (after filtration of 0.3 mL sample through a syringeless filter, (Whatman, PVDF)) by gas chromatography (GC-FID, Shimadzu GC-14B equipped with PEG-20 M 20% Uniport B column, temperature: 80 °C, sample volume: 0.5 μL).

3. Results and discussion

3.1. Preparation and characterization of Ag/OAPs samples

OAPs samples were prepared by varying in duration of HT (3 h, 4.5 h, 6 h, 12 h and 24 h), which resulted in preparation of products with different physicochemical properties, as shown in Table 1. It was found that prolongation of HT duration resulted in higher crystallinity, larger crystallite size, lower specific surface area and lower amount of electron traps (ET density), as described in detail in previous papers [39,47]. In this regard, it has been expected that the properties of titania should influence the course of silver photodeposition as well as the properties of formed Ag NPs. Indeed, the properties of Ag NPs differed in all studied samples, as shown in Figs. 1 and 2. However, the course of hydrogen evolution during Ag deposition did not differ significantly between samples, as shown in Fig. 1a. It is thought that