



Research Paper

Size-controlled gold nanoparticles on octahedral anatase particles as efficient plasmonic photocatalyst



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ABSTRACT

Octahedral anatase particles (OAPs), prepared by ultrasonication-hydrothermal reaction (US-HT), were modified with 2 wt% of gold by photodeposition. Conditions of US-HT process such as durations of US and durations of HT were varied to obtain OAPs products different by physicochemical and morphological properties. Au/OAPs samples were characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRS). The photocatalytic activity was tested under UV irradiation for decomposition of acetic acid (CO₂ system) and dehydrogenation of methanol (H₂ system) under aerobic and anaerobic conditions, respectively, and for oxidation of 2-propanol under visible light irradiation. Photodeposition of gold was very fast for all OAPs samples (0.5–10 min) under Ar atmosphere, and the clear correlation between the content of electron traps (ETs) and the induction period, during which nanoparticles (NPs) of gold are formed, indicates that ETs in titania samples are a key-factor for rapidity of gold photodeposition on titania surface. It was found that better morphology of titania (larger content of faceted particles) resulted in formation of larger gold NPs, while small gold NPs were deposited on structural defects. Modification of OAPs with gold NPs resulted in significant enhancement of photocatalytic activity, being e.g., 1.5 (CO₂ system), 7.7 (H₂ system), and even more than 40 under vis irradiation. It was found that both the properties of titania and gold are crucial for resultant photocatalytic activity, but a direct correlation between one structural/physical property and photocatalytic activity could not be obtained since all structural properties changed simultaneously when conditions of photocatalyst preparation (US-HT) were changed. Therefore, gold NPs of controlled sizes were deposited on OAPs product with the best morphology by modified photodeposition method. Clear correlation between photocatalytic activity under visible light and the size of gold NPs indicates that gold properties are decisive for visible light activity rather than titania properties. 3D-FDTD simulations confirm that an increase in the size of gold NPs results in extended surface areas with field enhancement.

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1. Introduction

Semiconductor photocatalysis has been extensively studied for more than forty years for environmental purification [1–3], anti-fogging/self-cleaning surfaces [4], water splitting [5] and solar energy conversion [6]. It is expected that solar photocatalysts (semiconductor photocatalysis driven by the Sun) could help in solving the most emerging humanity problems, i.e., (1) energy, (2) water and (3) environment (three of “Top Ten Problems of Human-

ity” proposed by Prof. Smalley [7]), where abundant and clean energy would enable the resolution of all other problems. Solar energy conversion into electricity and fuel (e.g., H₂, CH₃OH) by novel photocatalytic systems has recently been extensively studied, e.g., inspired by nature, two-step photoexcitation systems, the so-called “artificial photosynthesis” [8].

Titanium(IV) oxide (titania) is one of the most often used semiconductor photocatalysts because of its high photoreactivity, chemical stability, high availability and non-toxicity (except possible nanomaterial toxicity [9]) [10]. However, two shortcomings for its application should be overcome, i.e., recombination of charge carriers (e⁻/h⁺, typical for all semiconducting materials) and inactivity in the visible range of the solar spectrum (due to its wide

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band-gap, ca. 3.2 eV depending on polymorphic form). Therefore, plenty of studies have been performed to improve the performance of titania photocatalysts by morphology arrangements [11,12], surface modification [13,14], doping [15–17], and coupling with other semiconductors [18]. Noble metals in the form of adsorbed complexes [19–21] and metallic deposits [22–27] have been extensively investigated for improvement of photocatalytic activity of titania under UV irradiation [28,29]. Enhancement of photocatalytic activity comes from prolongation of lifetime of charge carriers [25] since noble metals serve as electron sinks [30], and thus accelerate the transfer of electrons from titania to substrates, e.g., protons to evolve hydrogen [31,32].

Over the last decade another property of noble metals (Au, Ag), i.e., absorption of visible light due to plasmon resonance, has been used to activate titania [33,34] and other wide band-gap semiconductors (CeO₂ [35,36], ZnO [37]) towards visible light. Plasmonic photocatalysts (photocatalysts which use plasmonic properties of noble metals) have been considered as a good candidate for efficient conversion of solar energy to chemical energy (solar fuel) and/or electrical energy (by solar cells), and purification of environment [34,38–41]. Although plasmonic properties of noble metals were observed 100 years ago, explained more than 30 years ago and commercially used in many fields (biosensors [42], chemical sensors [43,44], nano-lithography/nano-photonics [45,46], surface enhanced Raman spectroscopy (SERS) [42,44], medicine (drug delivery, cancer therapy) [44] and optical data storage [47]), the examination of their usage for photocatalysis was started ca. ten years ago [33]. Despite the novelty of plasmonic photocatalysis, a large number of studies have already been performed to improve photoactivity and stability as well as to clarify the mechanism under irradiation with visible light, i.e., energy transfer, electron transfer, plasmonic heating [48–50]. A few reviews on plasmonic photocatalysis have also been published [38,39,51–53].

The large majority of research has been performed using commercial titania nanoparticles (NPs) as a support for plasmonic NPs (mainly P25 composed of anatase and rutile crystallites and amorphous titania [54]), which makes discussion on plasmonic photocatalysis quite complex, e.g., due to impurities, irregular morphology, and possible transfer of charges between phases [55]. Our recent study indicates that faceted titania of octahedron shape (octahedral anatase particles, OAPs) of high-level photocatalytic activity (due to preferential distribution of shallow than deep electron traps resulting in high mobility of electrons [11]) is a good support for NPs of noble metal such as gold, silver and copper [56]. It has been found that gold-modified titania showed the best photocatalytic activity under visible light irradiation among tested metals. Therefore, OAPs have been selected as a support for gold NPs in the present study. It has been expected that preparation conditions of titania, resulting in the change of surface properties (crystalline size, specific surface area, crystallinity) and content of OAPs in the final product (morphology) [11,57], as well as method of gold deposition should influence the final properties of gold NPs (size, shape and distribution on OAPs), and thus resultant photocatalytic activity. Accordingly, the influence of titania morphology and properties of gold deposits on photocatalytic activity was investigated and is presented in this paper.

2. Experimental details

The detailed procedure for synthesis of OAPs has been reported elsewhere [11,58]. In brief, OAPs were prepared by hydrothermal reaction (HT, at 433 K for 3–24 h) of titanate nanowires (TNWs). Prior to HT, ultrasonication (US, 0–4 h) was used to homogenize TNWs suspension as well as to influence the morphology of TNWs (by their shortening) and thus to change the morphology of the

final product (content of OAPs). Gold was photodeposited on OAP samples (prepared at various US-HT conditions) under UV/vis irradiation ($\lambda > 290$ nm) in the presence of methanol (MeOH) as a hole scavenger and under argon (Ar) atmosphere to avoid scavenging of photogenerated electrons by oxygen (O₂) [59]. In brief, five hundred mg of an OAP product was used for each photodeposition, and the amount of gold was calculated to be 2 wt% of titania. The weighed OAP powder was put into a Pyrex glass tube equipped with a magnetic stirrer, to which 25 mL of MeOH (50 vol%, MilliQ water) was added. Then, the aqueous solution of chloroauric acid was slowly dropped while being stirred. The suspension was Ar-sparged for 15 min. The tube was sealed with a rubber septum and photoirradiated with magnetic stirring (500 rpm) by a 400-W high-pressure mercury lamp (Eiko-sha) under thermostatic control at 298 K (details presented elsewhere [60]). The codes of gold-modified OAPs samples were defined according to conditions of US-HT process, e.g., 1US/1HT means gold-modified sample, in which OAPs were obtained for 1-h US and 1-h HT at 433 K (in total nine different OAP samples were modified with gold). After photodeposition, samples were washed (three times with methanol and then three times with Milli-Q water), centrifuged and freeze dried.

To control solely the size of gold NPs (keeping the properties of titania the same), modified photodeposition method was used for OAP sample of the best morphology, i.e., prepared for 1 h of US and at 433 K of HT for 6 h [11]. Three modified photodeposition systems were used: (1) without Ar prebubbling (initial aerobic conditions): MeOH/air sample and (2) for O₂-saturated MeOH suspension (15-min O₂ prebubbling): MeOH/O₂ sample; in those two systems (MeOH/air and MeOH/O₂) photogenerated electrons were firstly consumed by O₂ hindering formation of gold NPs, and (3) in the presence of 2-propanol (IPA; 50 vol%) as a hole scavenger (instead of methanol) under Ar atmosphere: IPA/Ar sample. The gold-modified sample (1US/6HT) prepared at standard conditions (under Ar from deaerated MeOH suspension) was named as MeOH/Ar (for easier comparison between those four samples).

Photocatalysts were characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM, HITACHI HD-2000), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRS). XRD analysis was performed using the Rigaku intelligent X-ray diffraction SmartLab system equipped with a sealed tube X-ray generator (a Cu target). Crystallite sizes of anatase and gold were estimated from the corrected width of an anatase 101 and gold 200 diffraction peaks using the Scherrer equation. Crystallinity was estimated using highly crystalline nickel oxide as an internal standard, and experimental details were presented in previous paper [57]. XPS analysis was conducted on a JEOL JPC-9010MC (MgK α X-ray) spectrometer. DRS measurements were performed on a JASCO V-670 spectrophotometer equipped with a PIN-757 integrating sphere. Barium sulfate and respective bare OAP products were used as references.

Finite difference time domain (FDTD) method was used to calculate light-field distributions and extinction spectra (total extinction losses, due to light absorption and scattering). For this purpose, the structure was surrounded by a total-field scattered-field broadband source, extending from 200 nm to 1500 nm wavelength, and two monitor boxes recording the total extinction cross-section and the scattering cross-section of the structure. Another monitor recorded the E-field intensity distribution in the total-field domain to give the field maps showing the hotspot distribution around the geometry.

Photocatalytic activities were tested under UV-vis irradiation for oxidative decomposition of acetic acid (CO₂ system) and anaerobic dehydrogenation of methanol (H₂ system). In each experiment, 50 mg of the photocatalyst was suspended in 5 mL of aqueous solution containing 5 vol% acetic acid (CO₂ system) or 50 vol% methanol

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