



Tuning of the photocatalytic 1,4-dioxane degradation with surface plasmon resonance of gold nanoparticles on titania

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ABSTRACT

Gold nanoparticles supported on TiO₂ promoted the 1,4-dioxane photocatalytic degradation. This beneficial effect of gold was found to originate from its surface plasmon resonance of which the magnitude is sensitive to both the density and the size of gold nanoparticles. Specifically, various Au–TiO₂ powders, which have a different number density and size of gold nanoparticles, were prepared by a leaching procedure. The highest photocatalytic activity of Au–TiO₂, which is almost two times higher than a commercial TiO₂, was attained at the optimum state of the density and size of gold nanoparticles where the maximum surface plasmon absorption was also obtained.

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1. Introduction

In general, the size and morphology of metal particles in heterogeneous catalysts is thought to be of paramount importance in determining catalytic reactivity. Particularly, the effects of size have been the focus of many studies of gold-based catalysts; nano-scale catalysts are active for catalytic oxidation of, e.g., CO and propene at low temperatures [1–3]. In addition to oxidative catalytic reactions, gold nanoparticles have been highlighted to promote the photocatalytic activity of TiO₂ [4–8]. For example, the gold-capped TiO₂ nanoparticles have been shown to improve photocatalytic efficiency more than 40% for thiocyanate oxidation [5]. It was also reported that TiO₂ modified with nanosized gold reveals higher activity for the mineralization of oxalic acid in an aqueous phase than a commercially available TiO₂ (Degussa P25) [6]. Several studies have also been concerned with the relation between photocatalytic activity and the loading amount and/or size of gold nanoparticles on TiO₂ [7,8].

In order to elucidate the promoting effect of gold nanoparticles toward the photocatalytic activity of TiO₂, three roles of gold nanoparticles have been suggested: (1) the field enhanced light absorption, (2) the assistant for charge separation, and (3) the sensitizer for visible light [9,10]. Surface plasmon resonance originating from the collective oscillations of the electrons on the surface of the gold

nanoparticles was also suggested as the essential factor for these roles. Kamat and co-workers have proved that the enhanced interfacial charge transfer between TiO₂ and gold can be achieved by the negative shift in the Fermi level of the Au–TiO₂ composite resulting from the accumulation of more electrons, due to the surface plasmon resonance [4,5,9]. It was also observed that visible light was absorbed by gold nanoparticles due to the surface plasmon resonance which leads to the photoexcited state of the gold nanoparticles followed by the transfer of the electrons into the TiO₂ [10].

Herein, in order to further investigate the effect of the gold nanoparticles on the photocatalytic reactivity of TiO₂, we tuned the magnitude of the surface plasmon resonance by varying the amount and/or the size of gold nanoparticles on TiO₂ via a leaching procedure [11]. The modified Au–TiO₂ powders were then applied to a photocatalytic degradation of 1,4-dioxane which is widely used as an industrial solvent and as a stabilizer for chlorinated solvent, and is also known as a toxic hazard and is suspected to be a potential carcinogen for humans [12–14].

2. Experimental

A commercial Au(1 wt.%)–TiO₂ (P25) powder (named as-prepared Au–TiO₂) was used in the photocatalytic reactions and the preparation of leached Au–TiO₂ samples as purchased (Mintek). In order to prepare modified Au–TiO₂ samples, the as-prepared Au–TiO₂ was leached off by an aqueous solution of NaCN (1%) at

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room temperature for a specified time maintaining the pH at 12 with NaOH. After immediate filtering and washing of the solution, the sample was dried at 120 °C for 10 h followed by annealing in air at 400 °C for 2 h. TiO₂ powder (Degussa P25) was also used as purchased to compare its photocatalytic reactivity with various Au–TiO₂ powders.

1,4-dioxane (99.9%, Sigma–Aldrich) was used as purchased in the photocatalytic reaction, and the initial concentration of the solution (250 ml) was adjusted to 500 ppm for all reaction experiments. The photocatalytic reaction was carried out in a home-built reactor (10 cm × 5 cm × 10 cm) with a quartz window. During the reaction, TiO₂ and/or Au–TiO₂ powders (0.5 g/l) were suspended by a magnetic stirrer in distilled water. In order to minimize the temperature change during the reaction, an IR filter was installed in front of a light source and cooled by air with a fan, leading to a temperature increase of less than 5 °C during the entire reaction. An Xe-lamp (2 kW) was used as a light source, and its irradiation intensity was calibrated to 100 mW/cm² with a standard reference solar cell (PVM 153, PV Measurements).

During the reaction, 1 ml of solution was collected by a syringe and filtered through a polymer membrane with a pore size of 0.2 μm to remove the TiO₂ or Au–TiO₂ prior to analyzing it by a high performance liquid chromatography (HPLC). The HPLC was equipped with a UV detector and a C18 column (5 μm), with 1.5% acetonitrile in the water as the mobile phase. The structural characterization of the Au–TiO₂ samples was performed by a transmission electron microscopy (TEM, FEI Hong Kong Co. Ltd., Tecnai G2) and an X-ray diffraction (XRD, Shimadzu, XRD-6000). Composition analysis and surface area measurement were achieved by an ICP–AES (Perkinelmer) and a BET (Bel Japan Inc., Belsorp mini II), respectively. Optical properties were measured by a UV–Vis spectrometer (Varian, Cary 1000) with palletized samples very carefully prepared to maintain the same thickness.

3. Results and discussion

As described, we prepared modified Au–TiO₂ (P25) samples by the leaching procedure in which the gold was selectively removed without perturbing the TiO₂. No change in structure of the TiO₂ was confirmed by XRD patterns and TEM images, where the ratio of anatase/rutile and the particle size of TiO₂ were consistent before and after the leaching. There was also no change in the surface area of the samples (~47 g/m²) after the leaching, based on a BET analysis. The amount of carbon impurity (~0.1 wt.%) was also comparable among the samples based on an element analysis.

A remarkable change accompanying the leaching procedure was observed in the UV–Vis absorption behaviors, as seen in Fig. 1. TiO₂ is an oxide semiconductor having a large band gap of ~3 eV; therefore, only UV light (<400 nm) can be absorbed. On the other hand, gold nanoparticles supported TiO₂ generates light absorption (surface plasmon absorption, SPA) in the range of visible light (400–800 nm) due to the surface plasmon resonance. In the UV–Vis absorption data (Fig. 1), the bandwidth of the SPA (FWHM) clearly decreases (~22%) due to the leaching procedure (15 sec) compared to the as-prepared Au–TiO₂, but it does not distinctly vary with up to a 10 min leaching. The SPA peak maximum is also substantially shifted (544 → 572 nm) to a higher wavelength, up to a 30 sec leaching, followed by relatively small shift (572 → 581 nm), up to a 10 min leaching.

Based on the previous studies of SPA with colloidal gold nanoparticles [15–17], our data imply that the size of the gold nanoparticles is increasing with respect to the leaching time of up to 10 min because the bandwidth of the SPA is known to decrease with increasing particle size. Indeed, the TEM data (Fig. 2a–c) revealed that the size of the gold nanoparticles increased with a

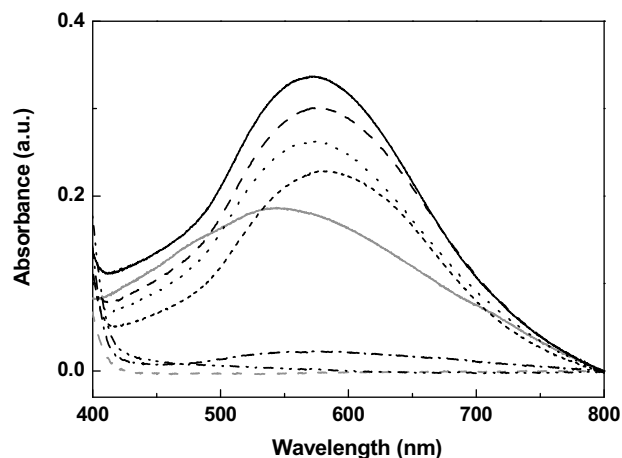


Fig. 1. Absorbance spectra in the range of visible light for a TiO₂ (P25) (gray dash), an as-prepared Au–TiO₂ (gray solid), a leached Au–TiO₂ for 15 sec (black dots), a leached Au–TiO₂ for 30 sec (black solid), a leached Au–TiO₂ for 1 min (black dash), a leached Au–TiO₂ for 10 min (black short dash), a leached Au–TiO₂ for 30 min (black dash-dot), a leached Au–TiO₂ for 13 hr (black dash-dot-dot).

leaching procedure of up to 10 min. The average particle size of the as-prepared Au–TiO₂ was estimated to 2.1 nm, its size distribution was relatively narrow; 85% of the gold nanoparticles are in the size range of 1.5–3 nm, and the gold nanoparticles larger than 5 nm were hardly seen in the TEM images. On the other hand, after the leaching for 30 sec and 10 min, small gold nanoparticles (<3 nm) were not observed in the TEM images, and the average particle size was estimated to 6.6 and 10.4 nm, respectively, indicating the leaching procedure induced particle size growth.

In contrast to the particle size growth, the density of the gold nanoparticles was found to significantly decrease due to the leaching procedure. Even after the 30 sec leaching, only ~2% of the gold nanoparticles were observed compared to the as-prepared Au–TiO₂. The ICP–AES analysis also confirmed that the total amount of gold was diminished by about 63% in a leaching time of 30 sec. The changes of the average particle size and the number density of gold nanoparticles on TiO₂, due to the leaching procedure, is clearly seen in the plot of those with respect to the total amount of gold obtained by ICP–AES analysis as shown in Fig. 2d. The number density and size are average values estimated from three different TEM images, and the error bars indicate the degree of dispersions.

The leaching procedure that used in our experiment consists of three steps; leaching, drying, and heating. In order to further investigate the effect of the leaching procedure on the morphological change of gold nanoparticles on TiO₂, we prepared two the Au–TiO₂ samples by only a vacuum drying at room temperature and further annealing at 400 °C for 2 h after the leaching for 30 sec with a NaCN (1%) solution. The analysis of the TEM images in Fig. 3 indicates that the dramatic decrease (~90%) of the number density of Au nanoparticles occurred after the leaching step with NaCN solution without heat treatment. Simultaneously, the particle size growth was also observed; the average size of Au nanoparticles was estimated to 4.3 nm in diameter which corresponds to twice that of the as-prepared Au–TiO₂. Further particle size increase occurred with the decrease of particle density after the heat treatment at 400 °C indicating the sintering of gold nanoparticles during the annealing process.

In order to investigate the effect of the Au nanoparticles supported on TiO₂ toward photocatalytic reactivity, we applied various Au–TiO₂ powders to 1,4-dioxane photodegradation in an aqueous phase. For comparison, we also tested the reaction with

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