Enhanced Photocatalytic Activities of Core–Shell Au–Titanate Nanoparticles

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Recently, a new method to produce Au nanoparticles (Au-NPs) by in situ reduction of a Au salt using 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron) in water was reported. The Au-NPs of 8 nm in the typical average size were adsorbed by ionized Tiron and were dispersed in sol by electrical repulsive force. By addition of titanium butoxide, titanium hydroxide was coated onto Au-NPs via ionized Tiron and, the core–shell particles of Au@titanate were successfully created. Such nanocomposites had high photocatalytic effects for the decomposition of Methylene Blue.

Since photocatalytic splitting of water on titanium oxide (TiO_2) electrode was discovered in 1972, an enormous number of studies on photocatalytic TiO_2-related materials have been carried out[1–3] in order to develop optically functionalized materials for environmental purification, clean habitation, and in amenity space. A fundamental understanding on the photocatalytic properties[4] is that ultraviolet (UV) or near-UV photons create electron–hole (*e–h*) pairs in TiO_2 semiconductor, and subsequently *e–h* pairs migrate to its surface and participate in redox reaction of water. It is now widely accepted that a single component of TiO_2 semiconductor shows a relatively poor photocatalytic effect because of easy recombination of electron and hole. Many researchers reported that composite materials of TiO_2 semiconductors and nanometer-sized metals (Pt, Au, etc.) enhanced the efficiency.[5,6] In this case, metal nanoparticles (NPs) act as an acceptor of electrons so that recombination of *e–h* pairs can be prevented, resulting in a longer hole lifetime and its achievability to TiO_2 surface.

Recently, we reported a novel method for synthesis of Au-NPs by use of organic surfactant, 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt,[7,8] which is called "Tiron" and typically used as a dispersion agent for inorganic materials, such as TiO_2, Al_2O_3, ZrO_2, etc. The chemical foumula is expressed by $(OH)_2C_6H_2(SO_3Na)_2$. Tiron molecules played a role of the reduction reaction of $HAuCl_4$, so that eventually Au-NPs were formed. Moreover, Tiron molecules in ionized form present worked as a dispersant of Au sol, resulting in stable Au sol obtained. Also of importance is that Tiron has an attractive property to combine with above-mentioned ceramics. In this work, to obtain a higher photocatalytic efficiency of titanate materials, we investigate a methodology for preparation of core–shell Au–titanate composites in nanometer size,[9] where the chelating affinity of Tiron molecules for hydrolized titanium hydroxide were utilized. The core–shell type NPs of Au–titanate were examined in photocatalysis for organic dye molecules.

As the starting chemicals, gold(III) chloride acid, tetrahydrate ($HAuCl_4$, $4H_2O$), titanium-*n*-butoxide (TBT), NaOH, ethanol, and 1-butanol were purchased from Kishida Chemical Co., Ltd. Tiron molecules were purchased from Sigma-Aldrich.

Our synthetic process of Au sol and Au–titanate composite is briefly addressed below.[7] At first, aqueous $HAuCl_4$ solution (5.0×10^{-4} M) was boiled. Then, the mixture of Tiron (1.6×10^{-3} M) and NaOH (3.2×10^{-3} M) was added to this solution. The solution immediately turned black and then rapidly changed to transparent orangish red. The Au sol was centrifuged at a speed in the range of 3,000 to 11,800 rpm. The solvent was changed to the mixture of H_2O and ethanol (1:2 volume ratio). After that, 1 wt % TBT solution diluted in 1-butanol was added dropwise into centrifuged Au sols, denoted as Au–TBT sol. The molar ratio of Au to TBT was 1:2. An excess amount of ethanol was added to Au–TBT sol in order to decrease the relative concentration of H_2O in the sol. Then, the same amount of the 1 wt % TBT solution was further added dropwise so that Au/TBT ratio could become 1/4. The sol was called as "2-step added Au–TBT sol." The centrifugation speed in the separation of Au-NPs with Tiron was described in parentheses, e.g., Au(3000)–TBT.

UV–vis spectra were obtained with a spectrophotometer (JASCO, V-570) in the 200–800-nm wavelength range using quartz cells with 1 cm path-length. A transmission electron microscopy (TEM) (JEOL JEM-2010, 200 kV) was used for high-magnification observation of the prepared particles. For an examination of photocatalytic activity, a photolysis of methylene blue (MB), purchased from Kishida Chemical Co., Ltd, was examined. 3 mL of Au(11800)TBT sol was mixed into 30 mL of aqueous MB solution (5.0×10^{-6} M) in 1 cm-quartz cuvette. Before and after UV light irradiation (AS-ONE, SLUV-6: 254 nm, 1 mW/cm^2), optical absorption of MB at 664 nm was examined every 1 h.

Stoichiometrically, 1 mol of $HAuCl_4$ reacts with 1.5 mol of Tiron.[7] As reported previously, however, it was eventually required to add more Tiron molecules than in the stoichiometric ratio. It is a consequence that Tiron molecules did not only work as a reductant of $AuCl_4^-$ but a part of Tiron added also worked in the ionized form as a dispersant of Au-NPs by a repulsive force. The pH value of Au sol was 7.8 with NaOH, which was larger value than pK_{a1} (7.6), and, therefore, unreacted Tiron molecules were present in the ionized form. Each type of Tiron molecules (ionized, oxidized, and natural forms), has a specific absorption band in UV–vis range.[8] Optical absorption peaks of ionized and oxdized Tiron were observed at 305 and 435 nm on a plateau of d–sp interband transition of Au, which are shown in the spectrum of Au sol (dotted line in Figure 1), respectively. In the spectra of centrifuged Au sols, these peaks of Tiron disappeared (solid and broken lines in Figure 1). In order to estimate a relative amount of Tiron, optical absorption intensities of Tiron at 305 and 435 nm to that of surface plasmon resonance (SPR) of Au-NPs (520 nm) were plotted in the insertion of Figure 1. The relative intensity at 435 nm was almost the same after centrifugation, indicating that oxidized Tirons were easily removed by

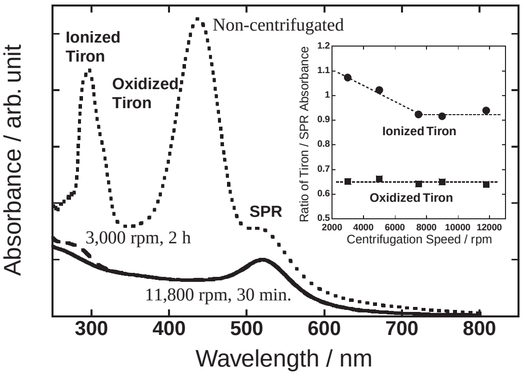

Figure 1. UV–vis absorption spectra for Tiron-coated Au sols before and after centrifugation. The inset shows absorbance at 305 nm (ionized) and 435 nm (oxidized) against SPR as a function of centrifugation speed.

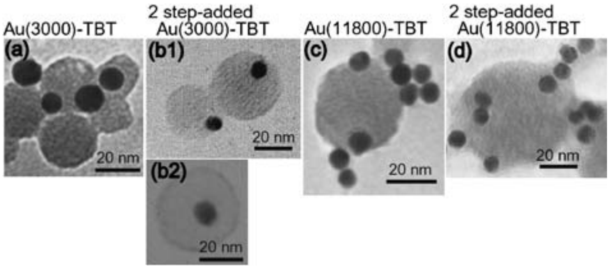

Figure 2. TEM images of Au–titanate nanocomposites; (a,c) Au–TBT and (b,d) 2 step-added Au–TBT with and without ionized Tiron molecules, which were obtained by the centrifugation at the speed of 3,000 and 11,800 rpm, respectively.

centrifugation. Notably, the relative amount of ionized Tiron, corresponding to the 305-nm absorance was decreased with increasing centrifugation speed, and at the speed of more than 7,500 rpm it became almost constant. From these results, it can be found that oxidized and ionized Tiron molecules were separated from Au sol by centrifugation at more than 3,000 and 7,500 rpm, respectively.

After addition of TBT, a red shift in the peak plasmon absorption band was observed from 530 to 533 nm (not shown here), indicating the coverage of An-NPs with titanium hydroxide which has a higher reflective index. In Figure 2, TEM images of Au–titanate composites are depicted. Figure 2a shows the composite containing in Au(3000)–TBT sol. It can be seen that each of Au-NPs well combines with titanium hydroxide, meaning that Au-NPs with ionized Tiron in their surface were preferentially attached with titanium hydroxide. After 2-step addition of hydrolysed TBT, Au–titanate core–shell NPs were obtained, as shown in Figure 2b. Typically the diameter was about 30 nm and the core of Au-NPs was ca. 8 nm size. Furthermore, it should be pointed out that an amount of water contained in the sol affected hydrolysis speed of TBT and coverage area of titanate on Au NPs: A lower water-content sol was effective for the preparation of Au–titanate core–shell NPs. Interestingly, in case of Au-NPs uncapped with ionized Tirons after TBT was added (Au(11800)–TBT), Au-NPs were easily aggregated with less contact area with titanium hydroxide (Figure 2c) and it was hence difficult to form such a core–shell structure. Two-step addition of TBT for Au(11800)–TBT managed to make the titanate coverage on Au-NPs (Figure 2d). On the other hand, if both oxidized and ionized Tiron were incorporated with hydrolized TBT (for noncentrifugated Au sol), no adsorption of Au-NPs with TBT occurred, resulting in bigger titanium hydroxide and self-aggregated Au-NPs (not shown here). It indicated much less occasion of the formation of the nanocomposite Au–titanate.

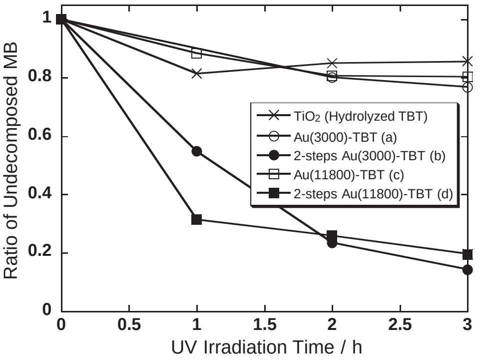

Figure 3. Normalized absorbance of MB at 664 nm, that is the ratio of undecomposed MB, as a function of UV irradiation time in various titanate sols (a–d of Figure 2).

Here, we shall show our recent result on photolysis of MB with these Au–titanate composites. MB has an absorption peak at 664 nm and is not decomposed by itself by UV light irradiation.[10] As well known, in case of UV irradiation to the mixture of MB and crystallized TiO_2, MB is oxidized and the peak intensity at 664 nm is decreased. Figure 3 shows the MB absorbance under UV irradiation as a function of the irradiation time. Two-step added Au–TBT sols (closed circle and square) indicate much higher decomposability than Au–TBT sols (opened circle and square) and TiO_2 (hydrolyzed TBT) sol (cross) independently of centrifugation speed. Two-step addition of TBT promoted TiO_2 formation around Au-NPs because hydrolysis speed was slower in the lower water content sol. It can be seen from this data that the larger contact area between titanate and Au gave rise to a higher photocatalytic properties. Tiron between Au-NPs and TiO_2 did not obstruct photogenerated hole movement.

In conclusion, Au–titanate composites were successfully prepared by using Tiron. By changing the speed of centrifugation, Tiron concentration surrounding Au-NPs could be controlled. It was found that for the preparation of Au–titanate core–shell particles, the presence of ionized Tiron around Au-NPs and the low content of water were needed. By means of two-step addition of TBT to Au sol, Au–titanate composites showed higher photocatalytic effects.

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