Sustaining Effect of Gold Colloids on the Amorphous Titanium Dioxide Particles

Mariko Takayanagi, Yoko Imai, and Kazuo Tajima*
Faculty of Engineering, Kanagawa University, Yokohama 221-8686

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We have reported that TiO_2 particles prepared in reverse micelles showed high photocatalytic activity in an amorphous rather than anatase state and that the amorphous state changes easily into the anatase state just by irradiating visible light. So we prepared Au/TiO_2 complex particles which included Au colloids in TiO_2 by the reverse micelle method. We found that Au colloids exhibited the sustaining effect of amorphous TiO_2 particles. Moreover, Au/TiO_2 complex particles showed higher photocatalytic activity than single TiO_2 particles and also could be used repeatedly.

Many researchers had studied on photocatalytic activity of TiO_2 particles, and then a lot of functional materials had been developed until now.[1,2] In particular, these researches had used such particles as TiO_2 combined with other metals or oxide materials for the purpose of developing semiconductor, electrode, and so on.[3,4] We reported that Pt, TiO_2, and SiO_2 particles which formed by the reverse micelle method, showed some peculiar phenomena as those of compared with particle properties.[5] In practice, the amorphous TiO_2 particles prepared by the reverse micelle method had a higher photocatalytic activity than that of anatase with irradiation of visible light ($\lambda \geqq 470\,\text{nm}$).[6] However, the amorphous state of these particles was gradually transformed into stable anatase state with the irradiation of light.

In the present study, we will try to hold back the transition from amorphous into anatase type of TiO_2 particles by plasma oscillation of colloidal Au and then examine photocatalytic activity of Au/TiO_2 complex particles prepared by the reverse micelle, which were formed with pentaoxyethylene dodecyl ether dissolved in cyclohexane. Au/TiO_2 complex particles were prepared as follows: Au colloid was at first prepared by reducing $HAuCl_4$ in water pool of reverse micelle, and subsequently TiO_2 was deposited on the surface of Au colloid by hydrolyzing tetraethyl-*o*-titanate (TEOT) precursor at the reverse micelle surface, according to the established method. Au/TiO_2 complex particles were prepared at various atomic ratio of Ti to Au. Figure 1 shows the XRD patterns (RINT: RIGAKU) for Au/TiO_2 complex particles prepared at different calcination temperatures. These particles were indicative of the same amorphous state for the temperature range from ambient temperature to 473 K as results of XRD measurements. However, as described in previous paper,[6] we found the existence of a local microcrystal even in the amorphous TiO_2 alone by the observations of HR-TEM (JEM-200EX//FX II:JEOL), while any parts of crystallized TiO_2 could not be recognized in the domain of Au/TiO_2. When calcined for 3 h at 673 K, both these particles were transformed into the anatase type (JCPDS No. 21-1272) as shown in Figure 1.

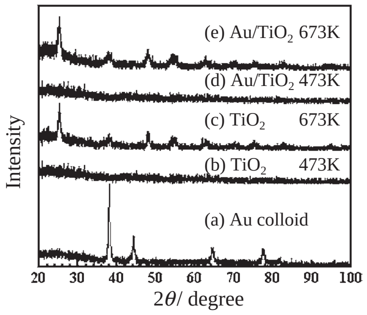

Figure 1. XRD patterns of (a) Au, (b) and (c) TiO_2, (d) and (e) Au/TiO_2 complex particle prepared by reverse micelle method.

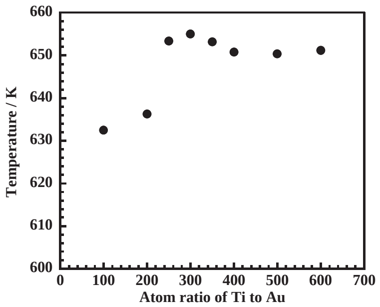

Figure 2. Plots of atomic ratio of Ti to Au vs. transition temperature.

The phase-transition temperature from amorphous into anatase states generated in the TiO_2 domain of the Au/TiO_2 complex particles was observed by TG-DTA (6300: SEIKO) in detail. In addition, the transition temperature of amorphous TiO_2 into anatase was slightly different by the preparation methods; 623 K by sol–gel method, 593 K by reverse micelle method, and 623 K by the thermal decomposition of precursor TEOT. Shown in Figure 2 is the transition temperature as a function of the atomic ratio of Ti to Au in the Au/TiO_2 particles. When the Au/TiO_2 complex particles calcined at 473 K in advance, the transition temperature into anatase increased with increasing atom ratio of Ti to Au in the complex particles. However, when the Au/TiO_2 complex particles calcined over 673 K, the transition temperature could not be observed, because the anatase transition already occurred as shown in Figure 1.

The transition temperature showed the highest value of 657 K at the atom ratio of 300 to 1. From these experimental facts, we consider that Au colloid present in the complex particles works obviously so as to hold back TiO_2 from the phase transition. In practice, it was investigated whether or not the microcrystallization locally appeared in the TiO_2 domain of amorphous Au/TiO_2 complex particles by irradiation of visible-light ($\lambda \geqq 470\,\text{nm}$, $30\,\text{mW/cm}^2$). We found that though amorphous TiO_2 particles were transformed from amorphous into anatase less than one week with irradiation of visible light,[6] the amorphous domain of Au/TiO_2 complex particles was sustainable and unchangeable during a period of four weeks.

Then, the electronic interaction between Au and TiO_2 was

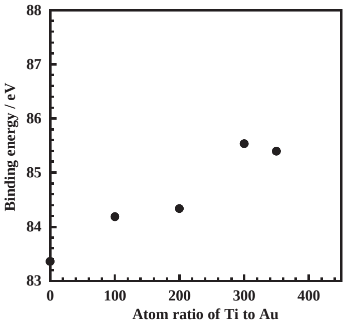

Figure 3. Plots of binding energy vs. atomic ratio of Ti to Au by XPS.

examined by XPS measurement. As shown in Figure 3, binding energy of $Au4f_{7/2}$ in the Au/TiO_2 complex particles was generally higher than that of single Au colloid (83.4 eV) prepared by the reverse micelle method. When the atom ratio of Ti to Au was at 300, binding energy of $Au4f_{7/2}$ had the highest value (85.5 eV). It was worth noting that Au/TiO_2 complex particles obviously took place some electronic interactions between Au colloid and TiO_2 particles induced by plasmon phenomena of Au colloid. This phenomenon was revealed only when TiO_2 deposited so as to contact directly on the surface of Au colloid. Consequently, we found that Au atoms embedded in amorphous TiO_2 particles took an oxidized state as a result of electron transfer from Au to the TiO_2 domain. On the other hands, we found that according to the XANES measurement, the titanium atoms corresponding to the divalent and trivalent states were present in comparable amounts with the tetravalent state. The more precise description related to this will be shown elsewhere. Therefore, the amorphous TiO_2 domain in the Au/TiO_2 complex particles became to be kept in status quo in comparison with the amorphous TiO_2 particles without Au colloid.

If the amorphous TiO_2 could turn out the chemically different states with and without Au colloid, we have to expect to the difference in the band-gap energies ad hoc between the TiO_2 particles and the TiO_2 domain in Au/TiO_2 complex particles, when prepared in reverse micelle and calcinated at 473 K. Their band-gap energies were estimated from UV–vis absorption spectra on these amorphous TiO_2 domains. The band-gap energies were two values for the TiO_2 particle (1.231 and 3.283 eV), and single for the Au/TiO_2 complex particles (0.993 eV) at a Ti/Au ratio of 300:1. Two band-gap energies for the TiO_2 particles prepared in reverse micelles are due to the coexistence of many small crystals with the amorphous domain as described in previous paper.[6] In other words, we believe that the band-gap energies of Au/TiO_2 complex particles could be originated in amorphous state because the amorphous TiO_2 domain is electronically activated and takes somewhat low state of valence electrons by the electron transfer from Au colloid in the Au/TiO_2 complex particles. Therefore, we confirmed that the band-gap energy of Au/TiO_2 complex particles did not have the conventional value of about 3.2 eV. If Au/TiO_2 complex particles were sustainable in amorphous state by the electron transfer based on the Au plasmon phenomena, we could expect the differences in the photocatalytic activities between single TiO_2 particles and Au/TiO_2 complex particles prepared in reverse micelle. In previous paper,[6] we reported that the amorphous TiO_2 alone gave the photocatalytic activity for Methyl Orange (MO) molecules in aqueous solution, though it was short life, irradiated with visible light larger than 470 nm in wavelength. Under the same conditions, we investigated the photocatalytic activity of Au/TiO_2 complex particles. Shown in Figure 4 are the time courses for the photocatalytic activity of Au/TiO_2 complex particles and other particles with irradiation of visible light. MO solution without particles was not decomposed by irradiating of visible light. Fortunately, we could recognized that Au/TiO_2 complex particles decomposed completely the aqueous MO solution for 3 h with irradiation of visible light, and, moreover the rate of decomposition was faster than that by the single amorphous TiO_2 particles prepared in reverse micelle. In the dark, the same Au/TiO_2 complex particles could not entirely decompose MO molecules. From these facts, we emphasized that the catalytic activity of the Au/TiO_2 complex particles performed not as a chemical catalyst but as a photocatalyst activated by means of the Au plasmon resonated with the visible light. The Au/TiO_2 complex particles composed of Ti/Au ratio of 300 to 1showed the highest photocatalytic activity in comparison with that of other atom ratios. The commercial TiO_2 (anatase, Aldrich), however, did not have absolutely any photocatalytic activity as shown in Figure 4. The photocatalytic activity of Au/TiO_2 complex particles was sustained after repeating the fifteen times for decomposition of aqueous MO solution, though the single TiO_2 particles was deactivated after using once time as a photocatalyst.

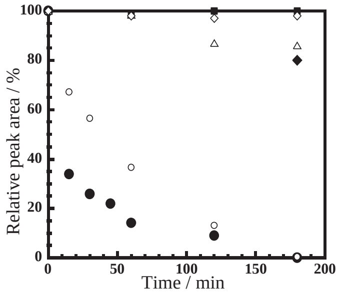

Figure 4. Photocatalytic activity of (●) Au/TiO_2 (1:300) complex particles, (○) TiO_2 prepared in reverse micelle, (△) commercial TiO_2, (◇) Au colloid, (■) MO solution with irradiation of visible light, and (◆) Au/TiO_2 (1:300) complex particles in dark.

In present work, we found that (1) the Au colloid in Au/TiO_2 complex particles could depress the transition of amorphous TiO_2 into anatase state, (2) MO molecules were completely decomposed by the irradiation of visible light for 3 h with the Au/TiO_2 complex particles, (3) the high photocatalytic activity of Au/TiO_2 complex particles prepared in reverse micelle was sustainable with the continuous irradiation of light, and finally (4) TiO_2 particles prepared in reverse micelle was activated by Au colloid.

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