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Preparation of TiO$_2$-Supported Twinned Gold Nanoparticles by CO Treatment and Their CO Oxidation Activity

Junya Ohyama,*a,b Taiki Koketsu,a Yuta Yamamoto,c Shigeo Arai,c and Atsushi Satsuma *a,b

We found that twinned gold nanoparticles (T-AuNPs) are generated at a high probability by CO treatment of TiO$_2$-supported Au(III) at room temperature. Because of the formation of T-AuNPs, the Au/TiO$_2$ prepared by the CO treatment showed higher catalytic activity for CO oxidation than Au/TiO$_2$ prepared by conventional H$_2$ treatment.

Structure dependent catalytic activity of gold nanoparticles (AuNPs) has been attracted intense attention, since the discovery of remarkable catalytic activity of supported AuNPs for CO oxidation.1, 2 The catalytic activity of supported AuNPs usually depends on their size, and drastically increases when the size decreases less than 3 nm. The size dependent catalytic activity can be largely explained by variation of perimeter of AuNPs on interface with support; however, the catalysis is also affected by the other factors such as chemical state,4–7 low coordinate site,7, 8 and dimension (number of Au layer). 9, 10 In addition, crystal structure of AuNPs, more specifically, twinning, also have an effect on their catalysis.11-16 It has been reported that twinned AuNPs (T-AuNPs) show higher catalytic activity for CO oxidation reaction than single crystal AuNPs (S-AuNPs).11, 12 In the case of selective hydrogenation of an unsaturated aldehyde, T-AuNPs shows lower catalytic activity and selectivity than S-AuNPs.13 Although change of crystal structure can cause unique catalysis, there are still a few studies on synthesis and catalysis of T-AuNPs.

Supported T-AuNPs have been synthesized by controlling their preparation conditions: pH for deposition and precipitation of Au ions on supports,13 calcination temperature and time;13 heating and quenching (cooling) rate;12 addition of magnesium citrate.15 The T-AuNPs prepared in the previous studies has large size (> 5 nm) or constitutes small percentage (< 20%) of all AuNPs including S-AuNPs. In other words, there is no study presenting selective synthesis of supported small T-AuNPs. Herein, we report that TiO$_2$ supported small T-AuNPs (ca. 2 nm) are selectivity (> 50%) synthesized by CO treatment at room temperature (r.t.). We also demonstrate that twinning of AuNPs enhances the catalytic activity for CO oxidation reaction.

We prepared 1 wt% Au/TiO$_2$ by a deposition-precipitation method (Details in SI). To a suspension containing 1 mM of HAuCl$_4$ and 300 mg of TiO$_2$ (JRC-TIO8, anatase phase), a NaOH was added to control the pH to 7. After removal of the aqueous phase by centrifugation, the remaining slurry was washed with water and dried in a desiccator containing dry silica gel for 48 h at r. t. The Au loading of the catalysts was determined to be 0.66 wt% by using inductively coupled plasma spectroscopy. The specific surface areas determined by the BET method were 62 m$^2$ g$^{-1}$ for Au/TiO$_2$-CO and 63 m$^2$ g$^{-1}$ for Au/TiO$_2$-H. Thus, the difference in the preparation condition did not affect the surface area. In addition, the X-ray diffraction patterns and the X-ray photoelectron spectra indicated that the crystalline phase and the chemical state of TiO$_2$ cause little change by the preparation condition (Figs. S1 and S2).
The diffuse reflectance UV-vis spectrum of Au/TiO$_2$-CO is shown in Fig. 1(a). Au/TiO$_2$-CO exhibited large and broad adsorption of visible light, although the as-prepared Au/TiO$_2$ did not show such large absorption of visible light (Fig. 1(d)). The spectrum of Au/TiO$_2$-CO was similar to that of Au/TiO$_2$-H show in Fig. 1(b). The large and broad absorption is assignable to surface plasmon band of AuNPs, indicating that Au(III) on TiO$_2$ were reduced to form AuNPs by CO treatment at r.t. On the other hand, as shown in Fig. 1(c), the as-prepared Au/TiO$_2$ treated under H$_2$ at r.t. showed almost the same spectrum as the as-prepared Au/TiO$_2$. The result indicates that Au(III) are not reduced by the H$_2$ flow at r.t. Therefore, the CO treatment at r.t. caused reduction of Au(III) and formation of AuNPs, but the H$_2$ treatment at r.t. did not. The higher reactivity of Au(III) with CO could be also seen in the high catalytic performance of Au(III) species for the PROX of CO in the presence of excess H$_2$. The reason for the higher reactivity of Au(III) with CO than with H$_2$ might be lower adsorption energy of CO on Au(III) species in comparison with adsorption of H$_2$.

The chemical state and the structure of Au/TiO$_2$-CO and Au/TiO$_2$-H were analyzed by X-ray absorption fine structure (XAFS) spectroscopy and Cs-corrected scanning transmission electron microscopy (STEM). The STEM measurement was performed on B01B1 at SPring-8, and the STEM on a JEOL-ARM200F operated at 200 kV.

Fig. 2(a) shows the Au L$_3$ edge XANES spectra of Au/TiO$_2$-CO and Au/TiO$_2$-H, together with that of the as-prepared Au/TiO$_2$. The clear and large peak of the as-prepared Au/TiO$_2$ at 11922 eV, which is so-called white line, is derived from the electronic transition from 2p$_3/2$ to the holes in 5d$_{3/2}$, 3/2. The large peak of the as-prepared Au/TiO$_2$ is due to Au(III) having 5d holes. On the other hand, the spectra of Au/TiO$_2$-CO and Au/TiO$_2$-H did not present such a peak at 11922 eV, indicating that they are in metallic state. The absorbance of Au/TiO$_2$-CO at 11922 eV was almost identical to that of Au/TiO$_2$-H. Thus, Au/TiO$_2$-CO has no significant difference in chemical state from Au/TiO$_2$-H.

Fig. 2(b) exhibits the FT of extended XAFS (EXAFS) spectra of Au/TiO$_2$-CO and Au/TiO$_2$-H, together with Au foil as a reference. Both of the catalysts showed two peaks at 2-3 Å due to Au-Au scattering. The two peaks of the catalysts were much smaller than Au foil, indicating that both of the catalysts are composed of AuNPs. The peak intensity of Au/TiO$_2$-CO and Au/TiO$_2$-H did not present such a peak at 11922 eV, indicating that they are in metallic state. The absorbance of Au/TiO$_2$-CO was almost identical to that of Au/TiO$_2$-H. Thus, Au/TiO$_2$-CO has no significant difference in chemical state from Au/TiO$_2$-H.

Typical high angle annular dark field (HAADF) STEM images of Au/TiO$_2$-CO and Au/TiO$_2$-H are presented in Fig. 3. The electron dose of our STEM observation was $9.9 \times 10^1$ e$^{-}$ Å$^{-2}$, which is smaller than the previous literatures that deal with structural analysis of metal nanoparticles in atomic scale by STEM. Thus, AuNPs would maintain their structures when taking the STEM images in our observation conditions. The particle size of Au/TiO$_2$-CO and Au/TiO$_2$-H was analyzed to obtain the particle size distributions (Fig. 3). The average particle size of Au/TiO$_2$-CO (1.6 ± 0.6 nm) was larger than Au/TiO$_2$-H (1.5 ± 0.4 nm). This result is consistent with that of the EXAFS analysis.

We deeply investigated the structure of AuNPs based on the atomic resolution HAADF STEM as shown in Fig. 4. Interestingly, Au/TiO$_2$-CO showed twinned AuNPs (T-AuNPs) at high probability.
Au/TiO₂ has much larger catalytic activity than Au/TiO₂-H. In addition, by using the STEM, we also confirmed that AuNPs of both of the catalysts have the same facetted (hemispherical-like) structure on TiO₂ (Fig. S7). These results indicate that Au/TiO₂-CO has smaller perimeter of AuNPs on interface with TiO₂ in comparison with Au/TiO₂-H. Usually, the catalytic activity of AuNPs increases with an increase of the perimeter. However, Au/TiO₂-CO with smaller perimeter showed higher catalytic activity than Au/TiO₂-H. Namely, the enhanced catalytic activity of Au/TiO₂-CO cannot be explained by the perimeter. In addition, both of the catalysts showed facetted structures (Fig. S8). It is considered that the difference of their catalytic activities is not derived from the morphology (facetted or rounded). The enhanced catalytic activity of Au/TiO₂-CO also cannot be explained by the chemical state of AuNPs, because the chemical state of Au/TiO₂-CO was almost the same as Au/TiO₂-H. On the other hand, Au/TiO₂-CO showed 6 times higher percentage of T-AuNPs than Au/TiO₂-H. The high percentage of T-AuNPs on Au/TiO₂-CO may be the reason for the high catalytic activity, because T-AuNPs have unique structure as follows: T-AuNPs have local hcp stacking of close packed planes (The fcc structure has an ABCABCABCABCABCBA arrangement of close packed planes. On the other hand, the hcp structure has an ABABAB arrangement. The twinned fcc structure has a ABCABCABACBACBA arrangement, and locally has hcp stacking on twinning boundary as indicated by the underline); in addition, if T-AuNPs have five folded multiple twinned structure, e.g., decahedral structure, they inherently have strained structure. Such unique structures of T-AuNPs would affect the catalytic activity. Actually, as described above, some previous studies have demonstrated that twin boundary in AuNPs enhances their catalytic activity for CO oxidation reaction. Therefore, we concluded that the high catalytic activity of Au/TiO₂-CO is derived from the high probability of T-AuNPs.

In summary, we prepared Au/TiO₂ by CO treatment at r.t. and investigated its chemical state, particle size, and crystal structure by comparing Au/TiO₂ prepared by the conventional H₂ reduction at 200°C. The major difference between the two samples was in the crystal structure: the percentage of T-AuNPs on Au/TiO₂-CO (> 50%) was ca. 6 times higher than that on Au/TiO₂-H. We applied Au/TiO₂-CO to the CO oxidation reaction, and showed its higher catalytic activity than Au/TiO₂-H. It is concluded that the high catalytic activity of Au/TiO₂-CO is derived from its high percentage of T-AuNPs. The finding in this study would contribute to design of crystal structure of supported MNPs and development of their catalytic performance.

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Fig. 4. Atomic resolution HAADF STEM images: (a) twinned AuNPs (T-AuNPs) and (b) single AuNPs (S-AuNPs). (c) Crystal-structure distributions of Au/TiO₂-CO (red) and Au/TiO₂-H (blue) after the CO oxidation reaction for 0.5 h.

Fig. 5. CO conversion as a function of temperature for Au/TiO₂-CO (red circle) and Au/TiO₂-H (blue triangle).
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References