

Separate deposition of two types of metal nanoparticles on support material for enhancing catalytic activity

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ABSTRACT

The separate deposition of Au and other metal nanoparticles (NPs), such as Pt and Pd NPs, on various support materials was developed as an effective method for enhancing the visible photo- and thermal catalysis of these materials. The type of support material is also important for both types of catalytic activities. However, the methods are limited to mesoporous-induced separate deposition and colloid photodeposition with a hole scavenger (CPH), and there may be a limited number of applicable support materials.

We established the separate deposition of Au and Pt NPs on TiO_2 by the regioselective chemisorption and subsequent in situ NaBH_4 reduction of Au(III) complex ions. The application of the chemisorption of Au(III) complex ions to such supports as SrTiO_3 , ZnO , In_2O_3 , Al_2O_3 , has been reported, and future application of the regioselective chemisorption-induced separate deposition of Au and other metal NPs on various support materials may enable the development of new photo- and thermal catalysts.

Key words: Nanocomposite, Separate deposition, Metal complex, Regioselective chemisorption

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INTRODUCTION

Discovery of the excellent thermal catalytic activity of Au nanoparticles (NPs) for CO oxidation has triggered intensive research on thermal catalysis by Au NPs for other reactions [1]. Au NPs also possess unique absorption in the entire visible-light region as a result of localized surface plasmon resonance (LSPR) [2]. This unique light absorption suggested Au NPs have the potential to be used as visible-light photocatalysts as well as thermal catalysts. The development of highly active photocatalysts that effectively use sunlight as the energy source is a key element for realizing a sustainable society. Visible-light photocatalysts are important because UV light accounts for only ~5% of total solar energy, whereas visible light accounts for ~50% of total solar energy [3]. Au NP-loaded metal oxides (Au/MOs) have emerged as a new type of visible-light photocatalyst driven by excitation of the LSPR [4].

The LSPR excitation of Au/MOs normally induces oxidation ability on the Au surface by the interfacial electron transfer from the Au NP to the conduction band of the MO. In the visible-light irradiation of TiO_2 -supported Au NPs with a bimodal size distribution (BM-Au/ TiO_2), however, LSPR excitation-induced electron transfer between larger Au NPs

and smaller Au NPs occurs through the conduction band of TiO_2 , resulting in charge separation [5]. As a result of this charge separation, the surfaces of the smaller and larger Au NPs efficiently operate as the oxidation and reduction sites, respectively, and the BM-Au/ TiO_2 exhibits significantly enhanced visible-light photocatalytic activity. However, Au NPs are not necessarily better than other metal NPs as cocatalysts for reduction sites. The catalysts show high activities if efficient cocatalyst particles such as optimal metal NPs are loaded as reduction sites. Additionally, the poor visible-light response of the cocatalyst probably leads to the enhancement of the photocatalytic activity by the unidirectional electron transfer from Au NPs to the cocatalyst, and the surfaces of the Au NPs and the cocatalyst efficiently operate as the oxidation and reduction sites, respectively.

The separate deposition of Au and other metal NPs on support materials was recently developed as an effective method for enhancing the visible photo- and thermal catalytic activities of these metals [3, 6-7]. The type of support material is also important for the visible photo- and thermal catalytic activities, which were enhanced by an increase of the permittivity and a negative shift of the

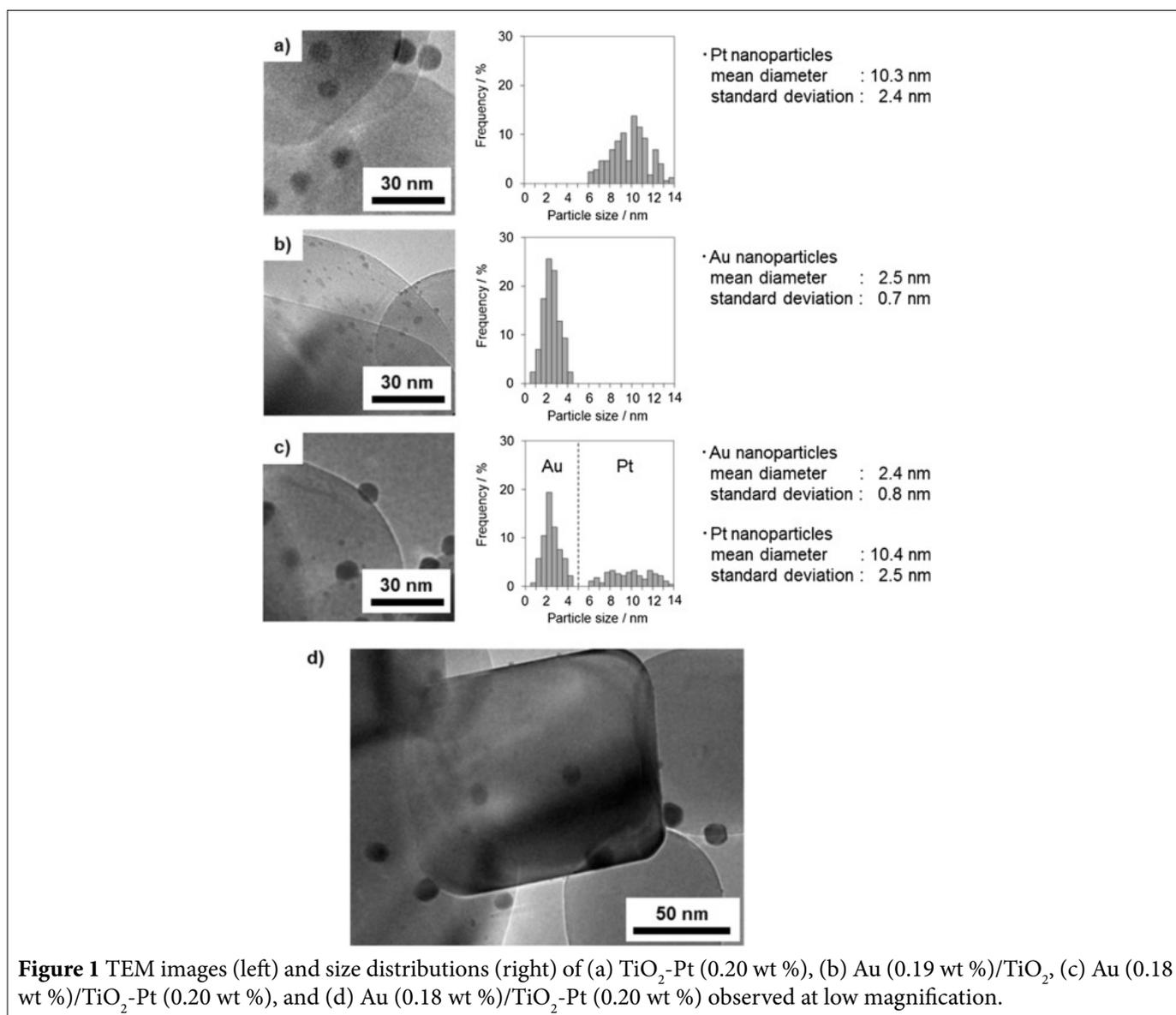
conduction band edge, respectively, of the support [5, 8-9]. However, the methods have previously been limited to colloid photodeposition with a hole scavenger (CPH) [3, 6] and mesoporous-induced separate deposition [7], and there may be a limited number of applicable support materials for these methods. Recently, we have established a new method for the separate deposition of Au and Pt NPs on TiO_2 [10]. This article describes the new method for the separate deposition of two types of metal NPs on TiO_2 .

REGIOSELECTIVE CHEMISORPTION-INDUCED SEPARATE DEPOSITION

In the first step, Pt NPs were loaded onto TiO_2 (TiO_2 -Pt) by photodeposition [11] using an ultraviolet light-emitting diode (NCSU033B, Nichia). After washing and centrifuging the TiO_2 -Pt particles three times, they were vacuum dried, then heated at 600 °C for 20 h in an Ar atmosphere. In

the second step, Au NPs were loaded onto the prepared TiO_2 -Pt by chemisorption [12] followed by subsequent NaBH_4 reduction of the Au(III) complex ions (CR method) as follows: TiO_2 -Pt was added to an aqueous solution of HAuCl_4 that had been adjusted to pH 6.0 with NaOH. The suspension was stirred and heated at 70 °C for 1 h. The particles were washed three times with distilled water, and then dried under vacuum. The particles were redispersed in a NaBH_4 solution in ethanol and the suspension was stirred at 25 °C for 60 min. The resultant particles were washed repeatedly with distilled water, then dried under vacuum to obtain Au/ TiO_2 -Pt. The second step was also applied to unmodified TiO_2 to prepare TiO_2 loaded with Au NPs (Au/ TiO_2) as a comparative sample.

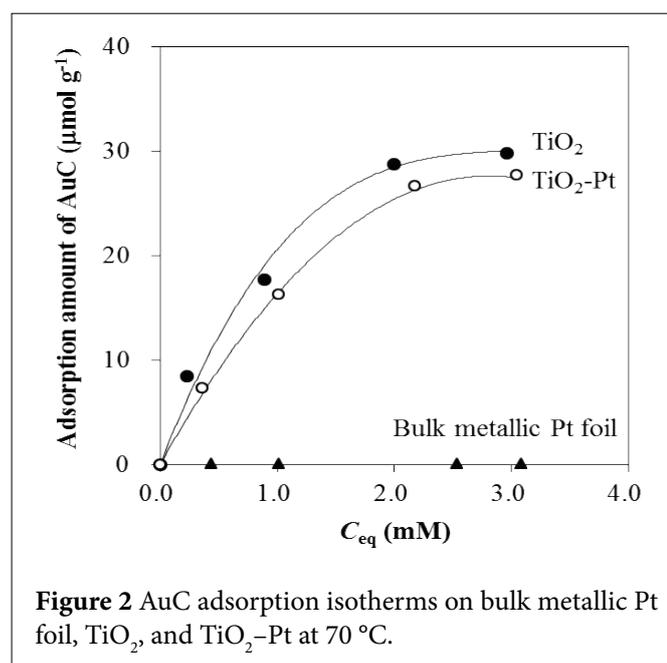
Figure 1a shows a transmission electron microscopy (TEM) image of TiO_2 -Pt containing 0.20 wt % Pt. Pt NPs with a



mean diameter of 10 nm can be seen on the TiO₂ surface. The TEM image of Au (0.19 wt %)/TiO₂ (Figure 1b) shows a mean Au NP diameter of 2.5 nm and a relatively narrow size distribution. In the TEM image of Au (0.18 wt %)/TiO₂-Pt (0.20 wt %) (Figure 1c and 1d), both smaller and larger particles, with mean diameters of 2.4 and 10 nm, respectively, are highly dispersed on the TiO₂ surface. The smaller and larger NPs in Au/TiO₂-Pt were assigned to Au and Pt, respectively, based on the TEM images of the Au/TiO₂ and TiO₂-Pt particles. This indicates that the small Au and large Pt NPs were each loaded onto the TiO₂ surface.

Additionally, X-ray photoelectron spectroscopy was carried out to provide strong evidence for the separate deposition of the Au and Pt NPs [10]. The Pt 4f_{7/2} and Pt 4f_{5/2} binding energies of Au/TiO₂-Pt (70.6 and 73.9 eV, respectively) agreed well with those of TiO₂-Pt. The Pt4f binding energy of Au(core)-Pt(shell)/TiO₂ was reported to be lower than that of TiO₂-Pt because of partial electron transfer from Au to Pt [13]. Therefore, the similar binding energies of Au/TiO₂-Pt and TiO₂-Pt indicate that the Au and Pt NPs were individually located on the TiO₂ surface rather than bound together. Thus, a new method for the separate deposition of small Au and Pt NPs on TiO₂ has been established.

The adsorption isotherms of the Au(III) complex ions in the TiO₂ and TiO₂-Pt samples were then measured to explain the separate deposition of the Au and Pt NPs. Under the experimental conditions, the Au(III) complex ions existed primarily as [Au(OH)₃Cl]⁻ (AuC) [12,14], and the chemisorption of AuC on the surface of TiO₂ resulted in the formation of Au(OTi)₃ monolayer via the following reaction [12]:



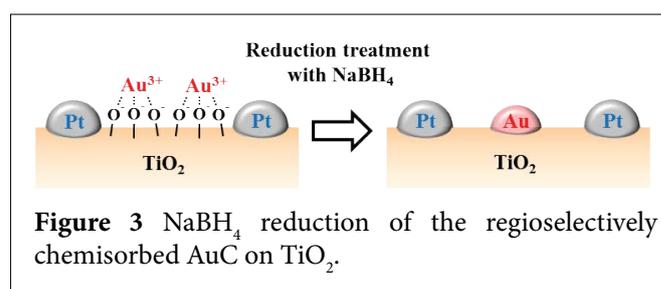
Although approximate saturation was reached on TiO₂ and TiO₂-Pt at a high concentration of AuC, the amount of AuC adsorbed on TiO₂-Pt was lower than that on TiO₂ (Figure 2). This result could probably be attributed to a decrease in the available TiO₂ surface area after loading with Pt NPs. The amount of AuC adsorbed for the unsupported Pt NPs should be measured for comparison. It was difficult to recover the unsupported Pt NPs after the adsorption isotherm experiments, however; therefore, bulk metallic Pt foil consisting of all Pt planes [15] was used instead of the unsupported Pt NPs, in which the (111) planes are mainly exposed [16]. No adsorption was observed on the surface of the bulk metallic Pt foil, and indicating that AuC was regioselectively chemisorbed on the TiO₂ surface.

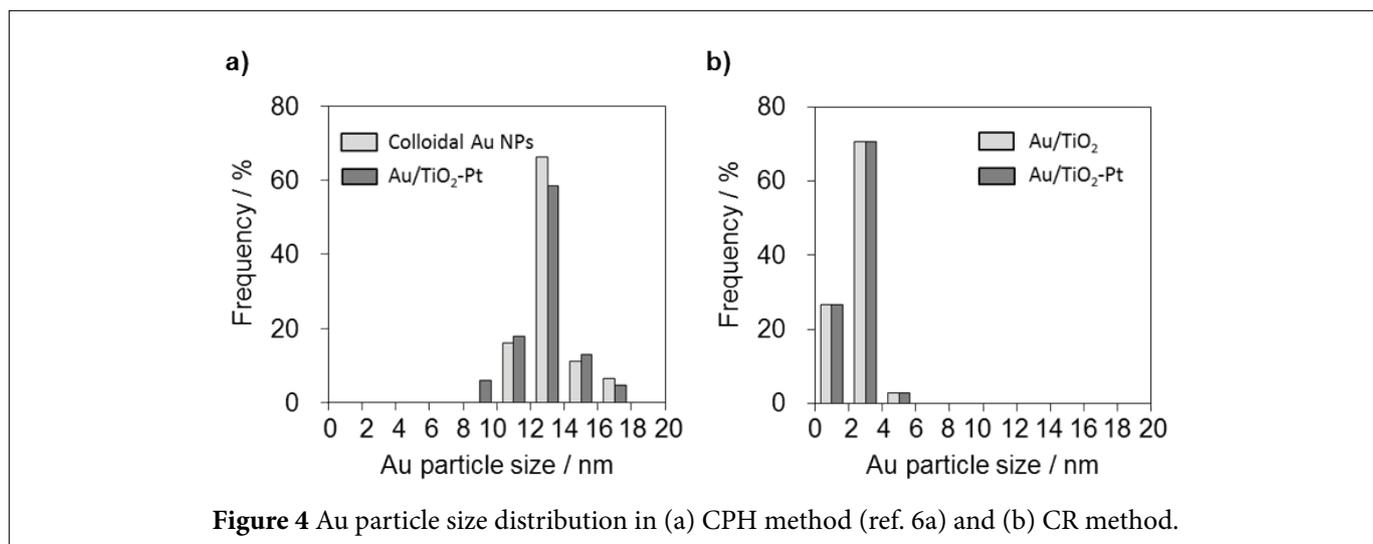
The subsequent in situ NaBH₄ reduction of the regioselectively chemisorbed AuC probably led to the separate deposition of the Au and Pt NPs (Figure 3). Thus, the chemisorption patterns of AuC revealed a mechanism whereby Au and Pt NPs were separately deposited on the surface of TiO₂. Chemisorption of AuC to supports such as SrTiO₃, ZnO, In₂O₃, and Al₂O₃ has previously been reported [9, 17]. Therefore, this method could be used in designing the deposition locations of small Au NPs and other NPs of various metals such as Pt on various support materials.

SEPARATE DEPOSITION METHOD COMPARISON

The size distributions of the Au NPs prepared by different separate deposition methods were compared. The CPH method caused the particle size of the deposited colloidal Au NPs (average particle size: 13 nm) to decrease compared with the undeposited colloidal Au NPs, probably because of TiO₂ photocatalyzed dissolution of the Au NPs [18] (Figure 4a). In contrast, the CR method provided small Au NPs within a narrow and similar size distribution on both Au/TiO₂-Pt and Au/TiO₂ (Figure 4b). The deposition of small Au NPs within a narrow size range was probably caused by the in situ NaBH₄ reduction of the regioselectively chemisorbed AuC.

The thermal catalytic activity of Au NPs has been shown to reach a maximum at a diameter of approximately 3 nm [1c, 17]. In addition, it has been reported that the visible photocatalytic activity of Au NPs increases as the size of the NPs decreases [19]. Therefore, the deposition of small Au





NPs with a narrow size distribution should increase both visible photo- and thermal catalytic activities.

CONCLUSIONS

The separate deposition of Au and Pt NPs on TiO_2 was established by the regioselective chemisorption and subsequent in situ NaBH_4 reduction of AuC on TiO_2 . This method is expected to be useful in designing the deposition locations for small Au NPs and various other metal NPs on various support materials. Furthermore, this process may enable the development of new thermal catalysts and photocatalysts.

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