

Notes

Synthesis of Au Nanoparticles Supported on Metal Oxides ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and TiO_2) by PS-PVP Block Copolymer Encapsulation Method

Gil-Pyo Kim, Young-Soo Jung, Seung-Bum Yoon, Dong-Woo Kim, and Sung-Hyeon Baek*

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea

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Introduction

In the past, nanoparticles are of great interest as a new class of materials in electronics, optics, catalysis, ceramics, and magnetic storages. Specially highly dispersed nanoparticles have demonstrated high catalytic activities in many reactions. For example, bulk gold doesn't show any catalytic activity, however, isolated nanoparticles (< 10 nm) have demonstrated high catalytic activity and selectivity in a number of reactions.^{1,2} Nanoparticulate gold supported on various metal oxides has been reported as a promising catalyst in low-temperature oxidation of CO, catalytic combustion, epoxidation and partial oxidation of hydrocarbon, water-gas shift reaction.³⁻⁶ The catalytic properties are influenced by the dispersion, structure and interaction of gold nanoparticles with the support as well as by the support type.⁷⁻¹¹

Lots of methods, including impregnation, precipitation, electrodeposition and block copolymer encapsulation method have been proposed for the synthesis of Au nanoparticles.¹²⁻¹⁶ Among these methods, PS-PVP block copolymer micelle can be widely used for the synthesis of nanoparticles because it is easy to control particle size and density by changing the molecular weight of each block.¹⁷ Monometallic and bimetallic colloids stabilized in the micellar core of PS-PVP in toluene for hydrogenations.¹⁸ But these works on this method almost have been done for the synthesis of monolayer thin films by means of self-assembly.¹⁹

In this study, Au nanoparticles were synthesized by PS-

PVP block copolymer encapsulation method and impregnated on two different metal oxides, hetero polyacid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and TiO_2 (P-25). The influence of calcination conditions (temperature and time) on Au particle size was studied for Au/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. And, photocatalytic activity of Au/ TiO_2 for the decomposition of acetaldehyde was investigated.

TiO_2 has been widely applied in decomposition of undesired chemical substances in air and water. Although TiO_2 has been known as a very effective photocatalyst, it is photochemically activated only by UV light due to a wide band-gap (3.2 eV). From economical point of view, solar energy is the most desired light source for photocatalysis. For utilizing the solar energy efficiently, synthesis of materials with visible-light-driven photocatalysis is very important.²⁰⁻²² Several approaches based on TiO_2 modification have been reported for achieving the visible-light-driven photocatalysis.

In this work, Au nanoparticles supported on P-25 was used as a photocatalyst for the decomposition of acetaldehyde under visible light illumination.

Experimental

Synthesis of Au nanoparticles stabilized in the core of PS-PVP micelles was performed in toluene medium. Three different kinds of polymers (PS-bP2VP; 54300-8800, 81000-14200, 53000-43800) were purchased from Polymer Source, Inc.. Proper amount of PS-PVP was dissolved in toluene (5 mg/mL) and stirred for 5 h at room temperature to form inverted micelles. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich) was then added into the solution in a dry box. The resultant solution was stirred for 2 days at room temperature to allow metal precursor to diffuse into the core of inverted micelles. After diffusion, metal diffused micelle solution was filtered using the syringe filter and impregnated on the surface of metal oxides (P-25, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) at 40 °C in rotary evaporator. After evaporation of toluene, the dried powder was calcined at various temperatures.

Synthesized sample underwent more detailed analyses. The average size of Au nanoparticles was determined using transmission electron microscopy (TEM, Philips CM200) and the valence of metal was investigated by X-ray photon spectroscopy (XPS, Kratos Axis Ultra) after calcination at 350 °C. Optical property of Au doped P-25 was examined by UV-Vis spectroscopy (SHIMADZU Solid Spec 3700).

The decomposition of acetaldehyde was carried out in a closed borosilicate reactor. Proper amount of Au/ TiO_2 was put in reactor and the reactor was purged with N_2 containing 1,000 ppm acetaldehyde for 15 min. Proper amount of air was then injected into reactor for the oxidation of acetaldehyde. The reactor was illuminated from a light source through optical fiber (Series 2000, LUMATEC), which cuts

*Corresponding Authors. E-mail: shbaeck@inha.ac.kr

off UV light and transmits only visible light ($\lambda > 420$ nm). Xenon-arc lamp (201-1k, SCIENCETECH) was used as a light source. After photocatalytic reaction, the conversion of acetaldehyde was determined by a gas chromatograph equipped with flame ionization detector (FID).

Results and Discussion

The influence of calcination conditions on particle size of metal cluster was investigated. Figure 1 shows several TEM images of Au nanoparticles supported on $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ after calcination at various temperatures (250, 300, 350, 420 °C) for 1 h. PS(81000)-PVP(14200) was used as a templating agent.

When the as-synthesized powder was thermally treated at 250 °C (Figure 1(a)), fine grain substructure was observed, corresponding to gold particles located at the core of PS-PVP micelle. This image shows that PS-PVP block copolymer was not removed completely at 250 °C.

When the sample was calcined at above 300 °C, polymer removal and the formation of nano clusters were observed, as shown in Figure 1(b), 1(c), 1(d). After calcination at 300 °C or 350 °C, the particle size of gold was 7-9 nm. In the case of sample calcined at 420 °C, however, agglomeration of Au particles was observed as shown in Figure 1(d). From the results of TEM analyses, it was confirmed that block copolymer was decomposed above 300 °C. However, at higher temperature than 400 °C, migration and agglomeration of gold particles occurred.

The effect of calcination time was investigated. Figure 2(a) and 2(b) show TEM images of Au nanoparticles on $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ synthesized using PS(53000)-PVP(43800) as a templating agent after calcination at 350 °C for 1 and 2 h,

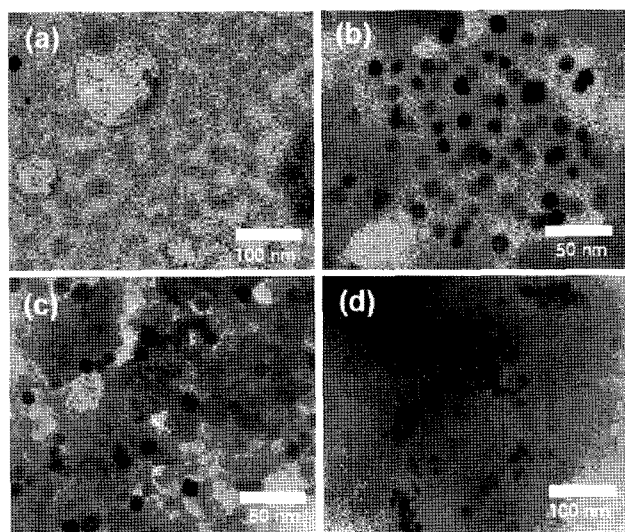


Figure 1. TEM images of Au/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPA) calcined at different temperatures (a) 250 °C, (b) 300 °C, (c) 350 °C, and (d) 420 °C. PS(81000)-PVP(14200) was used as a templating agent.

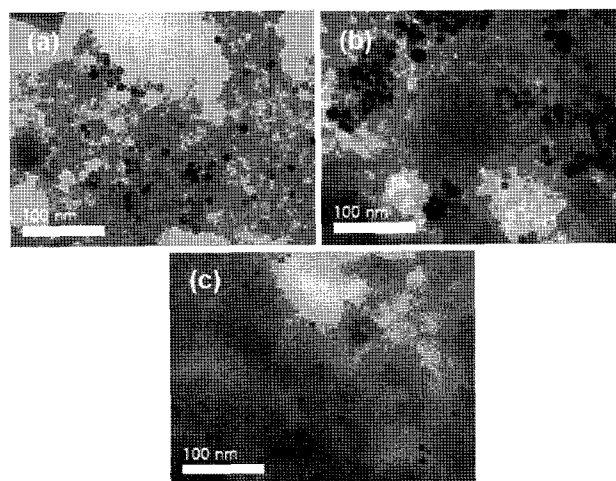


Figure 2. TEM images of Au/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPA) (a) calcined for 1 h at 350 °C, (b) calcined for 2 h, and (c) prepared using PS(54300)-PVP(8800) as a templating agent after calcination for 1 h at 350 °C. (a) and (b) were prepared from PS(53000)-PVP(43800) micelles.

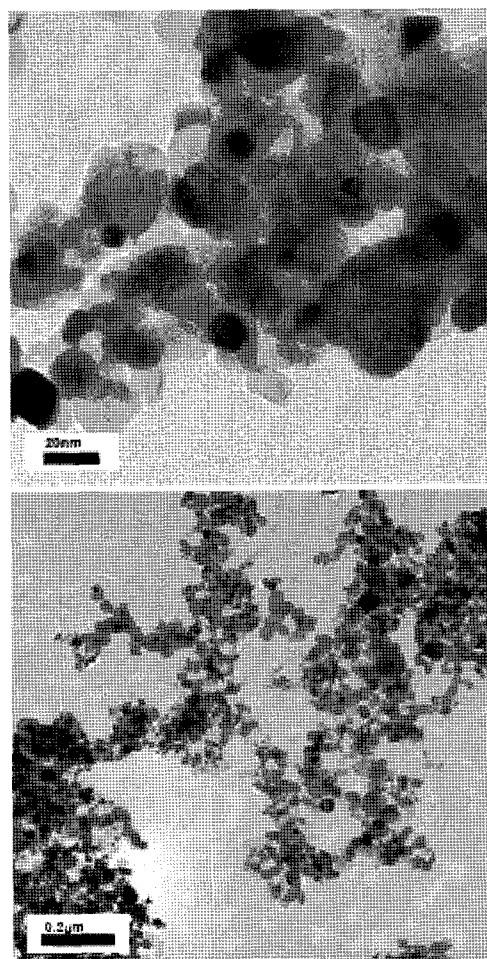


Figure 3. TEM images of Au/ TiO_2 (P-25) after calcination at 350 °C.

respectively. The increase of particle size and sintering were observed with increasing calcination time. The particle size of gold after calcination for 1 h at 350°C was about 8-9 nm. After calcinations for 2 h, however, it was about 11-12 nm, probably due to the sintering of gold particles and agglomeration. It was reported that the particle size of gold nanoparticles on support is strongly dependent on calcination conditions and the interaction with support.²² It was concluded from the above results that the particle size of gold was dependent on calcination temperature and time.

Au supported on HPA was also prepared using different polymer, PS(54300)-PVP(8800) (Figure 2(c)). The size of gold (Figure 2(c)) on HPA prepared from PS(54300)-PVP(8800) was about 4-5 nm after calcinations for 1 h at 350°C , and it was much smaller than that prepared from PS(53000)-PVP(43800) (Figure 2(a)). These results can be explained by the difference of PVP molecular weight. PS(54300)-PVP(8800) has much smaller core space in inverted micelle than PS(53000)-PVP(43800) because it has lower molecular weight of PVP, resulting in smaller particle size of gold.

Nanoparticulate Au/ TiO_2 was also prepared using PS(81000)-PVP(14200) as a templating agent. Figure 3 shows TEM images of Au nanoparticles supported on TiO_2 (P-25) after calcination at 350°C . Due to the contrast difference between TiO_2 and nanoparticulate Au, Au nanoparticles were clearly observed. Although most of Au nanoparticles are located irregularly on the surface of TiO_2 , the particle size of gold was shown to be about 9-11 nm and they were well dispersed on the surface of TiO_2 .

XPS analysis was performed to investigate the valence state of Au. Figure 4 shows the XPS spectra of Au 4f photoelectron of the Au supported on TiO_2 . The raw data was corrected using binding energy of C-1s peak at 285 eV. The emission of 4-f photoelectron from Au was identified in two peaks at 87.0 and 83.4 eV of binding energy, both of which are assigned to metallic gold (Au^0). The gold diffused into the core of inverted micelle is known to be stabilized as

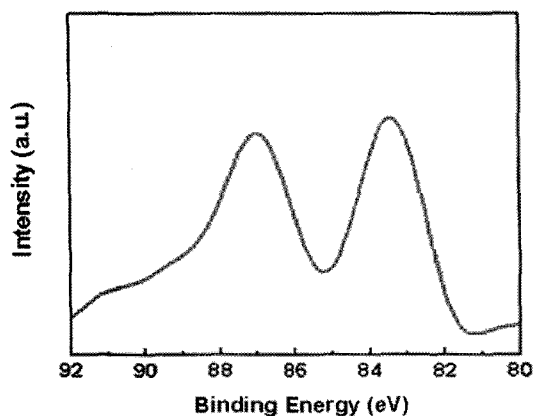


Figure 4. XPS of Au-4f after calcination at 350°C for 1 h.

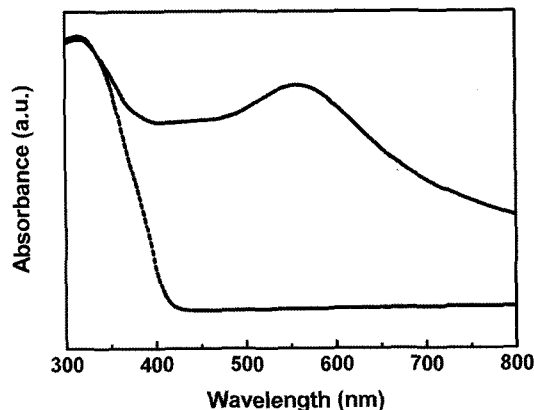


Figure 5. UV-VIS spectroscopy of (a) Au doped TiO_2 (Solid Line) and (b) pure TiO_2 (Dashed Line).

Au^{3+} in AuCl_4^- complex ion, but after removal of polymer by calcination at above 300°C , it was reduced to Au^0 from Au^{3+} .¹⁷

Optical properties of Au supported on TiO_2 were investigated by UV-Vis spectroscopy. The optical properties of photocatalysts are very important because it represents the number of photons absorbed. The UV-Vis spectroscopy of TiO_2 (P-25) and Au supported on TiO_2 (P-25) are compared in Figure 5 after calcination at 350°C for 1 h. P-25 showed the rapid increase of absorbance at around 410 nm wavelength, but no absorption band was found above 410 nm. In the case of Au supported on P-25, the increased absorption at visible region was remarkably observed at around 560 nm due to the plasma resonance of nanoparticulate gold. This means Au nanoparticles are well dispersed on the surface of P-25.

Photocatalytic activities of Au supported on TiO_2 (P-25) were investigated using acetaldehyde decomposition reaction under visible light illumination.²³⁻²⁶ Acetaldehyde has been known as one of the typical bad odor-causing gases in

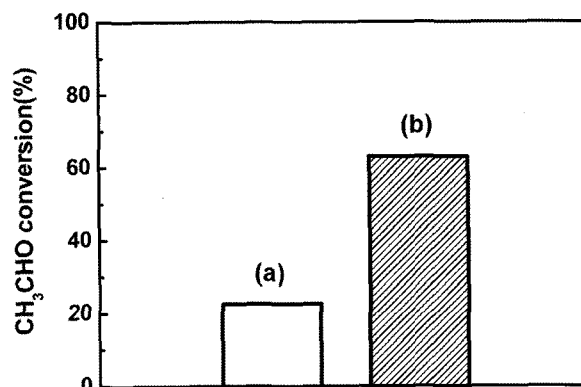


Figure 6. Acetaldehyde conversion after 3 h-reaction under visible light illumination; (a) pure TiO_2 (P-25) and (b) Au doped TiO_2 .

indoor air, which result in sick house syndrome.²⁷

Figure 6 compares the conversions of acetaldehyde after 3 h illumination of visible light ($\lambda > 420$ nm) over pure TiO₂ and Au doped TiO₂ prepared by PS-PVP block copolymer encapsulation method. The conversion of acetaldehyde over pure TiO₂ was observed to be about 22.5%, but Au/TiO₂ showed about 3 times higher activity after 3 h visible light illumination. It has been well known that the surface morphology and composition significantly affect photocatalytic activity and doping has been widely used for the improvement photocatalytic activity.

From the results in Figure 6, it could be concluded that nanoparticulate Au on the surface of TiO₂ remarkably improved the photocatalytic activity for decomposition of acetaldehyde under visible light illumination. The enhanced catalytic activity of Au/TiO₂ can be attributed to the significant increase of visible light absorption which was confirmed by UV-Vis spectroscopy (Figure 5). Au/TiO₂ prepared by PS-PVP block copolymer encapsulation method looks promising for environmental applications and the effect of doping amount and the effect of Au particle size on the photocatalytic activity are under investigation.

Conclusions

Au supported on metal oxides (P-25, HPA) was successfully synthesized by PS-PVP block copolymer encapsulation method. The size of nanoparticles was strongly dependent on calcination conditions (time and temperature). The particle size was also controlled by selection of the appropriate length of PVP part in block copolymer. When particulate gold was doped on the surface of P-25, it strongly improved visible light absorption by plasma resonance. Compared with pure TiO₂, Au supported on P-25 demonstrated much higher photocatalytic activity for acetaldehyde decomposition under visible light illumination. The enhanced photocatalytic activity could be attributed to the increase of visible light absorption and catalytic activity of nanoparticulate Au.

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