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Contributed Paper

Morphology and Catalytic Activity of Gold Core-Platinum Shell Nanoparticles

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ABSTRACT

Morphologies, chemical compositions and optical properties of the hybrid gold core-platinum shell, Au@Pt, nanoparticles prepared by a simple reduction method were explored via a combination of transmission electron microscopy, energy dispersive X-ray spectroscopy and UV-visible spectrophotometry techniques. Various sizes of almost spherical and monodispersed Au@Pt core-shell nanoparticles were successfully achieved by changing of Au/Pt atomic ratios. The effect of Au/Pt atomic ratio on the electrocatalytic activities for these Au@Pt nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) is revealed by cyclic voltammetry in 1.0 M H_2SO_4 + 2.0 M methanol aqueous solution. The maximum activity is obtained by using atomic ratio of Au/Pt at ~1. Moreover, all Au@Pt/MWCNTs catalysts exhibited higher activities than that of Pt/MWCNTs catalysts.

Keywords: bimetallic nanoparticles, core-shell structure, morphology, catalyst, methanol oxidation

1. INTRODUCTION

As is well-documented, the important applications of the hybrid bimetallic nanoparticles depend on their morphology and catalytic activities, especially for the direct methanol fuel cells which is an energy-conversion device for the automotive and electrical applications [1-4]. So far, one of the interested hybrid metal structures is core-shell structure composed of low-cost core metal and platinum (Pt) shell [5,6]. For example, Ataee-Esfahani *et al.* reported that electrolytic activity of gold core-platinum shell, Au@Pt, is better than that of Pt nanoparticles for the oxygen reduction reaction [7]. Using gold as a core particles provide not only the lower cost but also improve the catalytic activity and overcome the CO poisoning problems [8]. Therefore, recently, a great deal of interest has focused on synthesis and investigation of the catalytic activity of the Au@Pt nanoparticles with the core-shell structure [9-11].

In 2006, Zeng *et al.* [9] reported a successful method to synthesize core-shell

Au-Pt nanoparticles by replacement reduction of Ag-Pt to form Au-Pt in the organic solvent. The phase transferring reagent is needed to transfer the Ag-Pt nanoparticles and gold salts from aqueous phase to toluene phase. However, many steps are involved in this method. Wang and co-workers [10] also used a reduction method to synthesize the Au-Pt core-shell nanoparticles. Unfortunately, the heat treatment is required in all reduction steps. Xu *et al.* [11] later used an alternative one-step ultraviolet irradiation method which need ultraviolet irradiation machine to generate the Au-Pt core-shell nanoparticles. In recent year, Feng's group [12] also used the successive reduction method to prepare Au@Pt nanoparticles with the core shell structure, however, this method need nitrogen purging and heating at 80 °C in the Pt reduction process.

Since, the ultimate goal of material processing is to obtain the desired products via simple steps and low-cost for further practical utilization. Thus, in this work, attempt has been made to synthesize various sizes of Au@Pt nanoparticles with core-shell structure by using a simple chemical reduction method (i.e. performed at room temperature and without nitrogen gas flow).

The obtained Au@Pt nanoparticles were carefully explored by UV-vis spectroscopy, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) techniques. Their potential uses as catalysts for methanol oxidation reaction were also investigated by cyclic voltammetry. Instead of using a typical Vulcan Xc-72 carbon [12], in this study, the MWCNTs are used as support materials due mainly to their excellent catalytic activity [13]. In addition, the effect of chemical composition and size of the Au@Pt nanoparticles on their catalytic activity was also investigated and discussed.

2. MATERIALS AND METHODS

In this work, $HAuCl_4$ (Merck) and H_2PtCl_6 (Merck) were used as metal sources, while ascorbic acid (Merck) and sodium citrate (Fluka) were used as reducing agents. For electrochemical measurement, methanol and H_2SO_4 were purchased from Baker analyzed, while multi-wall carbon nanotubes (MWCNTs) were obtained from Bayer. All chemicals were used without further purification. The employed successive reduction method was modified from those reported by Feng *et al.* [12]. All reduction processes were performed at room temperature and without nitrogen gas flow.

Gold nanoparticles, with an average diameter of 15 nm were prepared according to Frens's method [14]. Briefly, 100 ml solution containing 1 ml of 1% $HAuCl_4$ was brought to boil. While stirring, 2.50 mL of 0.0340 M sodium citrate was quickly filled into the solution. The color of the mixture turned to red wine within 5 min indicating of the formation of Au nanoparticles [12,14]. In order to eliminate the residual reducing agent, the obtained gold nanoparticles were then purified by centrifugation method. Second, 4.00 ml of the concentrated gold colloidal solution was brought into a cleaned flask. Instead of using the heating process required by previous work [12], certain volume of 0.0010 M H_2PtCl_6 and 0.1000 M ascorbic acid were added into the flask while stirring, the mixture was vigorously agitated at room temperature for 24 h under ambient condition. Within 4 h, the red color of the mixture turned into dark brown, indicating the formation of the Au@Pt nanoparticles [12,15]. The obtained Au@Pt nanoparticles were purified and concentrated using by centrifugation method. Various sizes and chemical compositions of the Au@Pt products (*i.e.* the Au/Pt atomic ratios ~ 1.0/

0.4, 1.0/1.0 and 1.0/1.6) were tailored by changing the volume of H_2PtCl_6 precursor.

In order to characterize the optical properties of these nanoparticles, the UV-vis spectra of the Au, Pt and Au@Pt nanoparticles in quartz cells were collected over the wavelength ranging from 200 to 800 nm using a Perkin Elmer instrument Lambda 25 spectrometer. The morphology and size distribution of Au and Au@Pt nanoparticles were examined by a JEM-2010 transmission electron microscope (TEM) operating at 200 kV. The elemental compositions and the formation of core-shell structure of Au@Pt nanoparticles were identified by energy dispersive spectrometer (EDS) which attached to a JEOL JSM-6335F field scanning electron microscope (FE-SEM) and TEM.

For the electrochemical measurements of Au@Pt/MWCNTs, a certain mass of dried multi-walled carbon nanotubes (MWCNTs) used as a supporter was added into the concentrated Au@Pt colloidal solution, keeping the total metal loading (Au and Pt) at 20% w/w. After stirring the mixture overnight, the resulting sols, black slurry of Au@Pt/MWCNTs catalysts composed with different Au/Pt atomic ratios, were dried at 90 °C in oven for 5 h. For Au/MWCNTs and Pt/MWCNTs, the same metal loading was prepared via similar conditions. A certain amount of 0.5% Nafion solution and phosphate buffer solution were mixed with the colloidal solution to form an ink. A measured volume of these inks were transferred onto a cleaned surface of glassy carbon electrode and dried by light from a 60-Watt light bulb. Three conventional electrode cells were used, the working electrode was a modified glassy carbon electrode (GCE) (3 mm in diameter), a Pt wire and Ag/AgCl were used as auxiliary and reference electrodes, respectively. The electrochemical properties of the Au/MWCNT, Pt/MWCNT and Au@Pt/MWCNT catalysts were investigated in 1.0 M H_2SO_4 + 2.0 M CH_3OH aqueous solution by cyclic voltammetry (CV) in the range of -0.15 V to +1.0 V at a scan rate of 50 mV/s. The electrolyte solution was flowed with N_2 gas before scanning.

3. RESULTS AND DISCUSSION

Figure 1 shows the UV-vis absorption spectra of Au, Pt and Au@Pt nanoparticles. Generally, an absorption peak around 520 nm (**b** curve) is detected indicating the surface plasmon resonance of the Au cores, which could be clearly observed without Pt coverage [16]. As expected, the absorption behavior of these Au@Pt particles slightly changes upon the formation of Pt shell on the surface of gold core (**c**-**e** curves). By increasing of the Au/Pt atomic ratios, the surface plasmon band of Au nanoparticles was gradually suppressed and shift to lower wavelength. This is probably due to the increase of Pt shell coverage, similar with other workers [10,12]. It should be noted that the Au plasmon absorption peak is absent when the atomic ratio of Au/Pt is ~ 1.0/1.6, This Uv-vis spectrum is similar to that observed in the pure Pt colloidal solution (**a**-curve) [17,18]. These UV-vis spectra (**c**-**e** curves) indicate a continuous increase of the Pt coverage on the gold surface, consistent with the literatures [10,11,19] and the increasing of nanoparticles sizes observed by TEM (Figure 2).

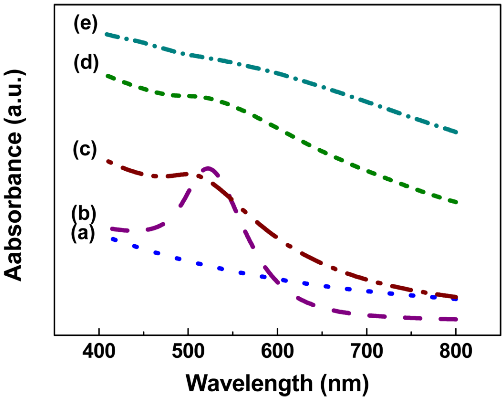

Figure 1. UV-Vis absorption spectra of Pt (a), Au (b) and Au@Pt colloidal solution which was obtained at different Au/Pt atomic ratios: (c) 1.0/0.4, (d) 1.0/1.0 and (e) 1.0/1.6.

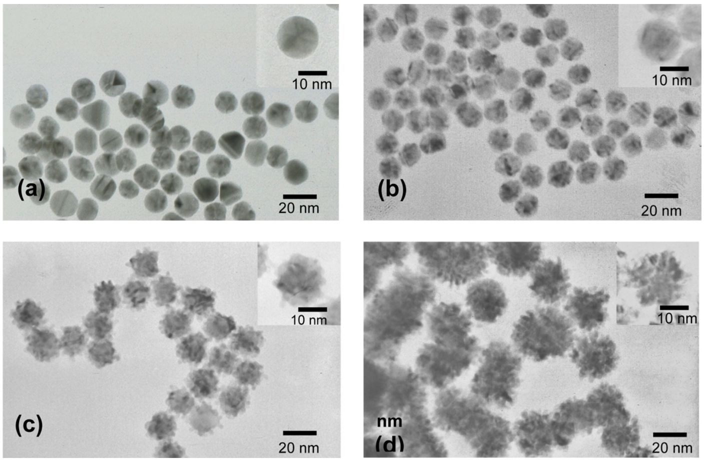

Figure 2. TEM images: Au (a) and Au@Pt with various atomic Au/Pt ratios: (b) 1.0/0.4, (c) 1.0/1.0 and (d) 1.0/1.6.

From Figure 2, it can be clearly seen that these nanoparticles exhibit almost spherical in shape, in good agreement with the previous studies [12,14]. More interestingly, the obtained particles also show narrow particle size distribution which is one of the advantages for the catalysis applications [1,7]. By measuring more than 70 nanoparticles from each TEM images, the average size is about 15 ± 1 nm for Au, 16 ± 1 nm for Au@Pt (1.0/0.4), 21 ± 1 nm for Au@Pt (1.0/1.0) and 30 ± 2 nm for Au@Pt (1.0/1.6), as listed in Table 1. It can be seen that, the mean size of the Au@Pt particles gradually increases with the reducing of Au/Pt molar ratios, indicating an increase of Pt coverage on the surface of gold core, consistent with the UV-vis analysis and also other works [7,12]. By comparison physical appearances of the gold nanoparticles (Figure 2(a)) to those of core-shell Au@Pt nanoparticles (Figure 2(b)-(d)), the gold nanoparticles appear as smooth surface whereas the Au@Pt nanoparticles with core-shell structure exhibit rough surface, indicate the coverage of Pt shell on the gold surface, similar with those observed in literature [12].

Table 1. Molar composition and estimated diameter of Au, Pt and Au@Pt nanoparticles.

Nanoparticles	Molar ratios (Au/Pt)		Diameters of nanoparticles (nm)*
	Precursor	Experimental	
Au	1.0/0.0	1.0/0.0	15 ± 1
$Au_1Pt_{0.4}$	1.0/0.5	1.0/0.4	16 ± 1
Au_1Pt_1	1.0/1.0	1.0/1.0	21 ± 1
$Au_1Pt_{1.6}$	1.0/2.0	1.0/1.6	30 ± 2
Pt	0.0/1.0	0.0/1.0	21 ± 5

*The data are obtained directly from TEM images

The elemental compositions of these Au@Pt catalysts were evaluated by EDS analysis, as listed in Table 1. The compositions of Au@Pt are similar to those calculated from the A/Pt ratio in the precursors. It is clearly seen that the particle size of Au@Pt increases with an increasing of Pt amount. This might be another evidence of increasing of Pt shell thickness, consistent with previous reports [8,12].

In the present study, EDS which is accessory of the JEM-2010 TEM was also employed to confirm the formation of core-shell structure in these Au@Pt nanoparticles by adjusting diameter of electron beam to ~ 4 nm and focus on two selected areas (*i.e.* the center and the edge of the particle). By illuminating electron beams on the center and the edge of the selected Au@Pt nanoparticles (Au/Pt ~ 1.0/1.0), Figure 3, it is seen that the central area of the Au@Pt nanoparticles contains both Au and Pt atoms, while Pt atoms are dominant in the edge. In addition, applying the selected area electron diffraction analysis to confirm the core-shell structure of Au@Pt nanoparticles was unsuccessfully in this study probably due to the overlapping of the diffraction patterns of Au and Pt.

Based upon these experimental results, it can be concluded that various sizes of spherical and well dispersed Au@Pt nanoparticles with core-shell structure can be successfully prepared at room temperature via a modified reduction method without nitrogen gas flow. Apart from achieving the desired products, the advantages of this modification also lie in the simple steps and instruments, low production cost and time-saving.

In order to explore the potential use of these nanoparticles as a catalyst for fuel cell applications, the influence of Au/Pt molar ratio on the electrocatalytic properties of Au@Pt/MWCNTs catalysts for methanol oxidation was investigated by cyclic voltammetry method in 1.0 M H_2SO_4 + 2.0 M methanol solution (Figure 4). For a comparison, electrocatalytic activities of each single constituent metal, Pt/MWCNTs and Au/MWCNTs were also investigated. When using the Pt/MWCNTs and Au@Pt/MWCNTs as catalysts, two oxidation peaks were observed at Pt/MWCNTs while the oxidation peaks at Au/MWCNTs are hardly observed. These two peaks are corresponded to the oxidation processes of methanol and intermediates produced in the methanol oxidation procedure [9,12].

High current density of the forward peak is the sign of achievement for catalyst development. It is clearly seen that all Au@Pt/MWCNT catalysts show higher current density of the forward peak than that of Pt/MWCNT catalyst indicating the superior catalytic activity, in agreement with other works [10,12]. Among all Au@Pt/MWCNT catalysts, the sample with Au/Pt molar ratio at ~ 1.0/1.0 (denoted as Au$_1$Pt$_1$) show higher current density and lower onset potential of the forward peak than those of other Au@Pt/MWCNT composition. The enhancement of CV signal of Au$_1$Pt$_1$ catalyst over that of Au$_1$Pt$_{0.4}$ is probably due to an increase of Pt content. It should be noted that even though the Pt content of Au$_1$Pt$_{1.6}$ increases, the current density of Au$_1$Pt$_{1.6}$ decreases. These might be due to the surface of Au core is fully covered by Pt, resulting in poisoning problem which usually found when using single Pt as a catalyst [8]. In addition, the decrease of current density of Au$_1$Pt$_{1.6}$ might be attributed to the increase of Au$_1$Pt$_{1.6}$ catalyst's size. Thus, it is likely that the chemical composition and particle size of catalyst might response to the change of catalytic activity. However, these parameters are not sometimes independent contribution factors and are interrelated [3].

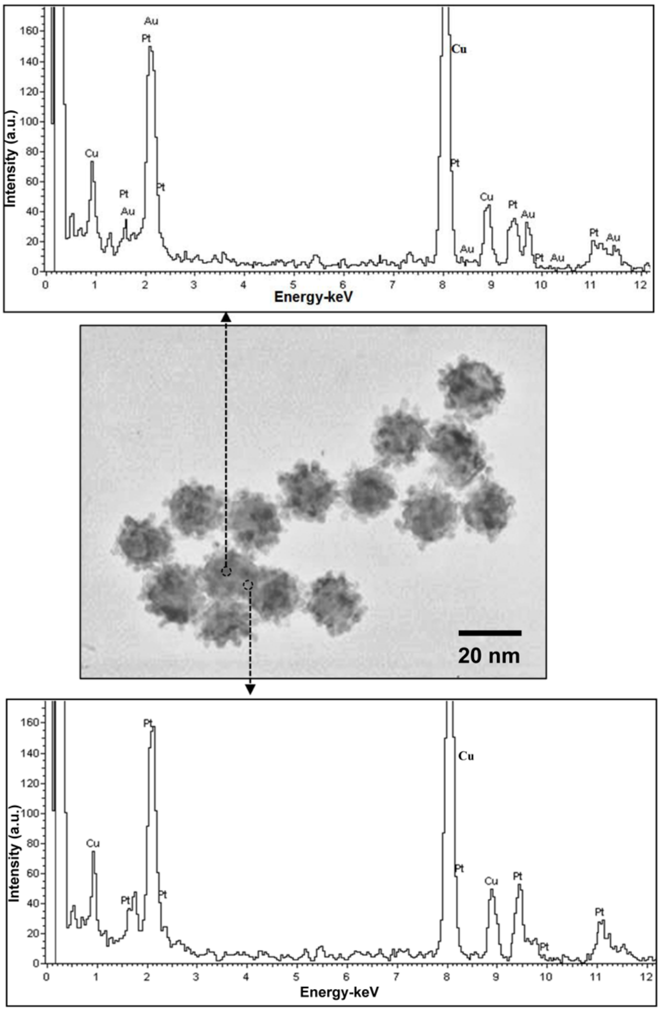

Figure 3. EDS analysis from the central (top) and the edge (bottom) areas of the Au@Pt (Au/Pt ~ 1.0/1.0) nanoparticles. (Cu signals corresponds to the copper grid used).

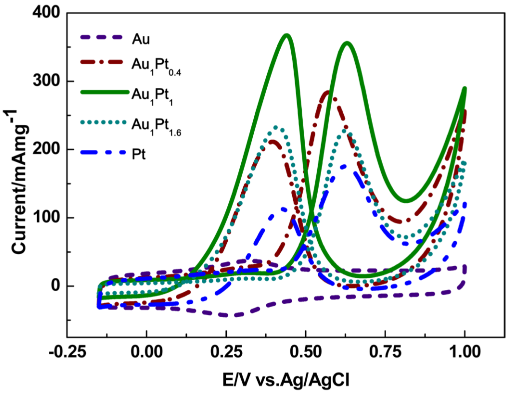

Figure 4. Cyclic voltammograms of Au@Pt/MWCNTs with various molar ratios in 1.0 M H_2SO_4 + 2.0 M methanol aqueous solutions at a scan rate of 50 mV/s.

Previous studies [20,21] reported that gold nanoparticles can enhance the electrolytic activity by catalyzing the poisonous intermediates such as CO which usually adsorb on the surface of Pt. In our work, the maximum current intensity can be obtained from Au/Pt at ~ 1.0/1.0 while Feng *et al.* [12] reported the maximum current intensity obtained from Au/Pt at ~ 1.0/2.0. The variation might be attributed to the effect of different supporting materials (MWCNTs or Vulcan carbon [13]). Therefore, using bimetallic catalyst can achieve oxidations of methanol due to an increase of electrochemical active surface area. Electronic effect of Au@Pt added metal as the hybrid metal could be able to modify the electronic structure of Pt valence band and weaken CO_{ad} adsorbtion. Moreover, this bimetallic metal CO adsorbed species is removed effortlessly. Platinum can adsorb methanol molecules on its surface while the second metal (Au) provides active surface oxides to oxidize adsorbed methanols at low potential. Still, there is a challenge to enhance the catalytic active of the Au@Pt nanoparticles for further study such as modification of particle morphology or adding another metal.

Finally, TEM images of Au@Pt (Au/Pt ~ 1.0/1.0)/MWCNTs catalyst before and after the catalytic property measurements are also show in Figure 5. It can be seen that the Au@Pt nanoparticles (dark spots) are uniformly dispersed within the multi-walled carbon nanotubes. In addition, it is clearly seen that the Au@Pt nanoparticles either before or after the catalytic measurements show similar morphologies *i.e.* size and shape. Thus, it can be stated that the morphology of these Au@Pt nanoparticles does not change significantly after performing as catalyst in methanol oxidation reaction.

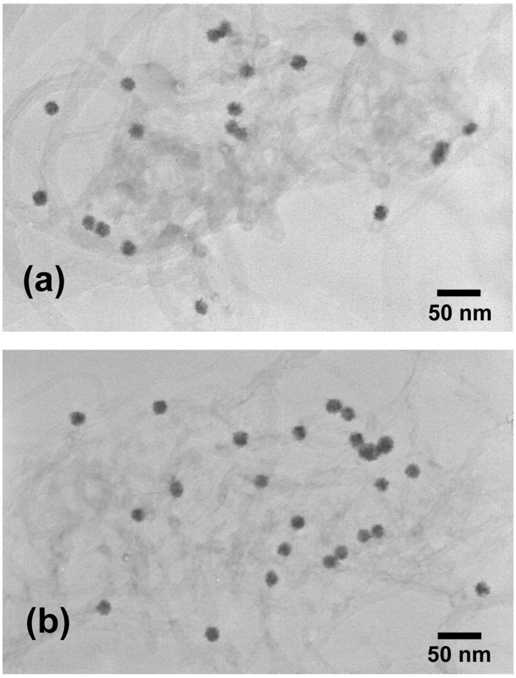

Figure 5. TEM images of the Au@Pt (Au/Pt ~ 1.0/1.0)/MWCNTs catalysts before (a) and after (b) catalytic property measurement by CV in 1.0 M H_2SO_4 + 2.0 M methanol aqueous solutions.

4. CONCLUSIONS

This study has demonstrated that various sizes of the bimetallic Au-core Pt-shell nanoparticles can be prepared at room temperature without nitrogen flow by changing Au/Pt molar ratio via a reduction method. It is seen that the change of size, morphology, chemical composition and optical property of the resulting from the Au core nanoparticles indicate the formation of Pt on the surface of Au core. Electrochemical catalysis for methanol oxidation shows the enhanced catalytic activity of Au@Pt/MWCNTs. In addition, Au@Pt/MWCNTs with molar ratio of Au/Pt at ~ 1.0/1.0 shows maximum catalytic activity. This might indicate the potential use of Au@Pt/MWCNTs (Au/Pt ~ 1.0/1.0) as a catalyst for further fuel cell applications.

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