Recovery of high-purity Pt from Pt-Au bimetallic nanoparticles using organic aqua regia

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Abstract

Using organic aqua regia, a recently discovered powerful organic leaching agent, an effective process of recovering Pt directly from Pt-Au bimetallic nanoparticles was demonstrated. The purities of the Pt recovered from a mixture of Au and Pt nanoparticles and from Pt-Au core-shell nanoparticle catalyst are as high as (99.49±0.22) %, and (95.02±0.08) %, respectively. The novel recovery process promises applications in catalysis industry.

Keywords: organic aqua regia; bimetallic; platinum; gold; nanoparticle; recovery

1 Introduction

Bimetallic nanoparticles (NPs) of noble metal elements represent a new class of functional materials and have been investigated intensively in the past fifteen years [1–2]. Among the various combinations of bimetallic NPs, Au-Pt core-shell NPs (sometimes called Pt-decorated Au NPs, Pt-layered Au NPs, or Au-Pt dendritic hetero-aggregate NPs to account for the morphology of the non-uniform and porous Pt shell) is an important category that has demonstrated improved catalytic activities [3–6] and multifunctionality [7–8]. The importance of Au-Pt bimetallic NPs is more than their intriguing properties and potential applications. Pt is becoming increasingly important because of growth in environmentally-friendly applications such as fuel cells and pollution-control catalysts. However, Pt is scarce on the earth. Researchers, especially materials chemists, have been trying to push Pt utilization to its theoretical maximum; this accounts significantly for the broad interest in Pt-M (M=Au, Pd, Ni, etc.) bimetallic NPs [9–12]. Actually, no matter how efficient Pt utilization is, efficient recovery of Pt elements from catalyst NPs is highly desired from the viewpoint of sustainable growth. Current recovery process of Pt relies solely on the oxidative dissolution of Pt in strong inorganic acids, e.g., aqua regia, and subsequent precipitation or absorption of the dissolved Pt out of the solution [13–14]. The non-selectivity of the inorganic acids results in the dissolu-

tion of other noble metal elements at the same time with Pt, and it is still a great challenge to extract high-purity Pt via the precipitation or absorption processes. A further purification process is feasible but very complex and costly. It is reasonable to predict that the very small amount of Pt used in the Pt-M catalyst NPs makes the recovery process even more challenging.

Recently, Lin *et al.* [13] reported our discovery of organic aqua regia ("organicus liquor regius"—to be accurate in Latin), which is simply composed of thionyl chloride ($SOCl_2$) and an organic solvent like pyridine (py). Organic aqua regia shows an interesting dissolution selectivity toward noble metals and may find various important applications in the near future, especially for the recovery of Pt from spent catalysts [13,15]. In the present letter, the author demonstrates that organic aqua regia can recover high-purity Pt efficiently from Au-Pt core-shell NPs as well as from mixtures of Au and Pt NPs.

2 Experimental

Au NPs were synthesized by reducing 12 mg $HAuCl_4·3H_2O$ in 10 ml oleylamine at 105 °C for 2 h under an Ar blanket, collected by precipitation with ethanol and centrifugation, and washed with mixtures of acetone and hexane [16]. Pt NPs were synthesized by reducing 30 mg $H_2PtCl_6·6H_2O$ in 20 ml ethylene glycol (containing 35 mg

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polyvinylpyrrolidone, M_w=29000) at 165 °C for 2 h under an Ar blanket, collected by precipitation with acetone and centrifugation, and washed with mixtures of acetone and ethanol [17]. 20 mg dried Au NPs and 5 mg dried Pt NPs were mixed (XRD pattern shown in Fig. 1(c) and then added into 10 ml SOCl$_2$ to form a dark brown mixture. A certain amount of py was added at room temperature, changing the colour of the mixture to light brown. The solution was diluted into 200 ml acetonitrile. The dissolved Au went into the solution; the non-dissolved NPs were precipitated out of the solution, washed, and collected. The yield was calculated by dividing the weight of the collected recovered Pt NPs by the starting weight of the Pt NPs in the mixture, i.e., 5 mg.

Au-Pt core-shell NPs were synthesized by a sequential reduction reaction in oleylamine [3,16,18]. Au core was formed by reducing 24 mg HAuCl$_4$·3H$_2$O in 10 ml oleylamine at 120 °C for 3 h under an Ar blanket. 25 mg platinum acetylacetonate was dissolved in 10 ml oleylamine at 70 °C, and then added into the dark purple Au colloidal solution at 120 °C under vigorous stirring. The solution was fast heated up to 235 °C, and kept for 3 h. The whole synthesis process was under Ar protection. The core-shell NPs were collected by precipitation with ethanol and centrifugation, and washed

with mixtures of acetone and hexane. 10 mg of the dark brown core-shell NPs were added into organic aqua regia composed of SOCl$_2$ and py (3:1 in volume) at room temperature, and then diluted into 400 ml acetonitrile. The acetonitrile solution was then mixed with 50 ml hexane under vigorous stirring. After the mixing, the mixture went through a fast phase separation (Fig. 2) at room temperature. The dissolved Au went into the bottom acetonitrile phase (shallow). Pt NPs were extracted out of the acetonitrile solution, and re-dispersed in the upper hexane phase (dark). It is surprising that the oleylamine capping agent is so strongly coordinated to the surface of the Pt NPs that it results in the easy extraction of the capped Pt NPs by hexane. After the acetonitrile was recycled by distillation and condensation (>95% of the acetonitrile was recovered). Au was recovered simply by calcination (Fig. 3 and Fig. 4(b) [13]. The Pt NPs/hexane dispersion was washed several times by mixing with deionized water to remove the ionic residuals. The Pt NPs was recovered after distillation of the hexane.

All the chemicals above were used as purchased from Sigma-Aldrich. UV spectra were measured by UV-2450 (Shimadzu Co.). X-ray diffraction (XRD) was performed in a Panalytical X'Pert Pro diffractometer system, with theta-2theta scan mode, using Cu X-ray source. The follow-
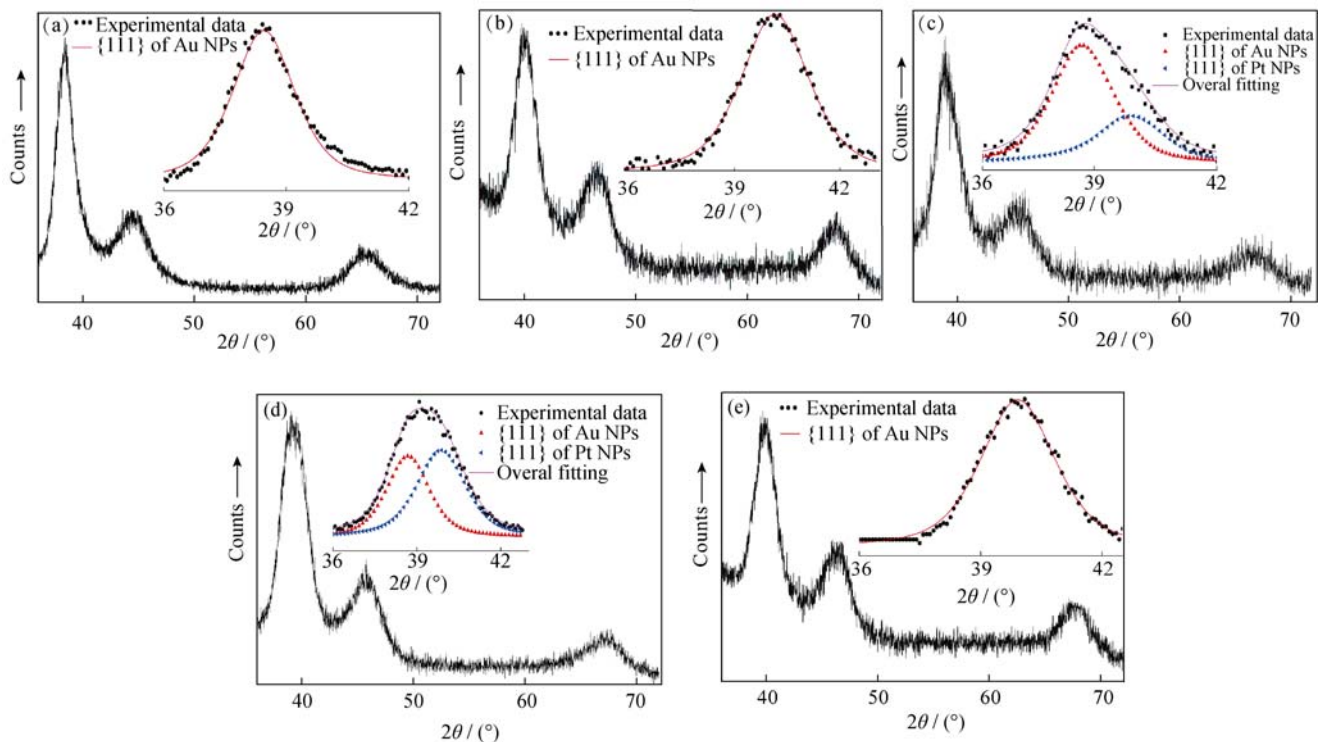

Fig. 1   XRD patterns of the synthesized Au NPs (a), Pt NPs (b), mixture of the NPs (c), collected precipitate powders after 1 min leaching in organic aqua regia composed of 10 ml SOCl$_2$ and 0.5 ml py (d), and collected precipitate powders after 10-min leaching in organic aqua regia composed of 10 ml SOCl$_2$ and 3 ml py (e)
(The insets being the high-resolution {111} diffraction peaks of the powders, and the results of peak fitting)

Fig. 2   **Photograph showing the extraction result of Pt NPs from the dissolved Au after the leaching process: the bottom phase being the acetonitrile solution with dissolved Au; the upper phase is the extracted Pt NPs dispersed in hexane. (The two layers can be easily separated (inset))**
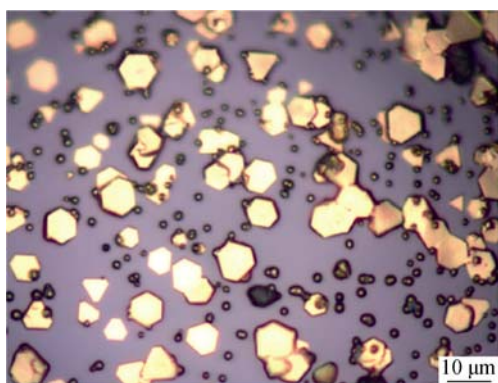
Fig. 3   **Photograph showing the recovered Au particles after the calcination process**

ing parameters were used for collecting the patterns: 200 s/step, 0.02 °/step. Peak positions were calibrated systematically. For peak fitting, slow (300 s/step) and finer-step (0.01 °/step) scans were adopted. Each of the fitting curves is a combination of a Gaussian function and a Lorentzian function to account for the data distribution and the equipment shape, respectively. Au and Pt concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS, Elan DRC II, PerkinElmer, USA). Sample digestion was performed according to the method previously described in the Ref. [16]. The digested solutions were diluted with 18 MΩ DI water and analyzed by ICP-MS. Indium was used as the internal standard.

3   Results and discussion

XRD patterns of the synthesized Au and Pt NPs are shown in Figs. 1(a) and 1(b), respectively. The average sizes of the Au and Pt NPs are approximately 4.8 and 4.3 nm, respectively, based on calculation according to Scherrer's

equation (using {111} peaks only, so are the calculations from here after).

The leaching process of the NPs mixture is monitored by XRD characterizations of the collected precipitate powders (comparing Figs. 1(c) and 1(d)): with leaching of the Au NPs from the mixture, the relative intensity of the Pt {111} peak with regard to the Au {111} peak increases. Pt NPs are recovered after a thorough leaching of the Au NPs (Fig. 1(e)). Comparing Figs. 1(b) and 1(e), no distinct broadening of the Pt {111} peak after the leaching process is observed, which indicates that the recovered Pt NPs may remain intact during the leaching. The purity of the recovered Pt is (99.49±0.22)%, determined by ICP-MS. The yield of the recovered Pt is 80%~86% (3.9~4.3 out of the 5 mg). With optimization of the recovery process, and a more accurate yield evaluation process, the yield would probably be improved in the future.

UV-vis spectrum and XRD pattern of the synthesized Au-Pt core-shell NPs are shown in Fig. 4(a) and Fig. 5, respectively, which are consistent with those reported in literature about Au-Pt core-shell NPs.[1,4,6,9,11,12,16]. The average diameter of the Au core (by fitting the XRD pattern and calculation based on Scherrer's equation) is 5.8 nm. A very broad Pt {111} peak is evident, corresponding to 3.2 nm in size. The XRD pattern of the recovered Pt NPs is shown in Fig. 4(c). The poor signal-to-noise ratio, the weak {200} and {220} peaks, and the broad {111} peak (corresponding to an average size of 3.2 nm) are all characteristic of the poor crystallinity and small size of the Pt NPs initially in the form of shells in the Au-Pt core-shell NPs.[12,16] The purity of the recovered Pt is (95.02±0.08) %. The purity is
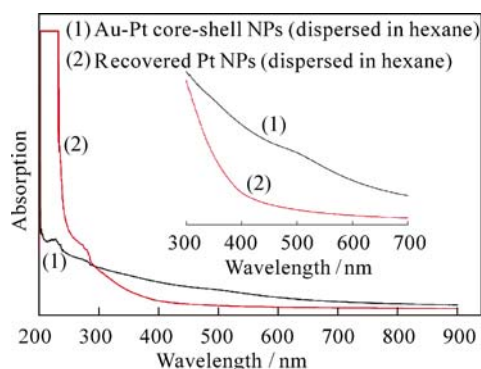
Fig. 4   **UV-vis spectra of the synthesized Au-Pt core-shell NPs (1), and the recovered Pt NPs after the leaching process (2). A weak surface plasmon resonance (SPR) peaked at around 510 nm being observed of the core-shell NPs; in contrast, SPR disappears after the Au NPs being leached thoroughly (The inset being the enlargement of the SPR regime)**
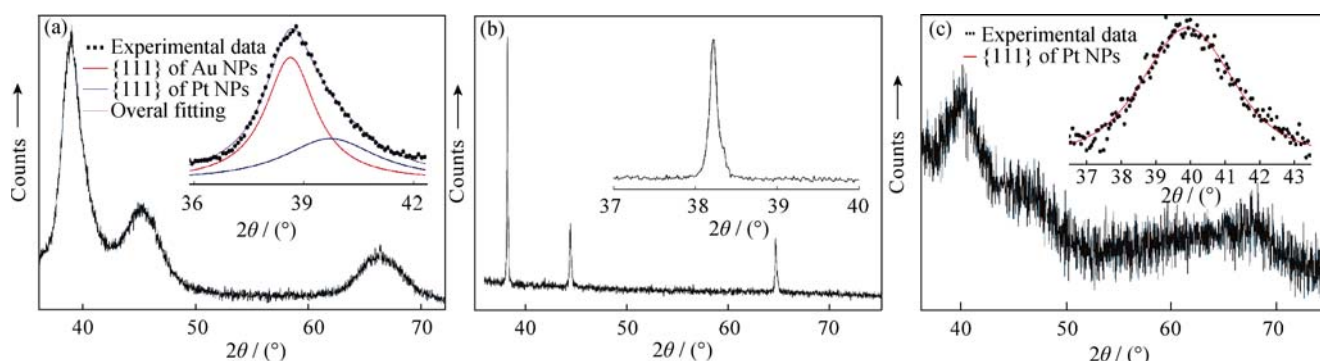
Fig. 5 **XRD patterns of the synthesized Au-Pt core-shell NPs (a), the recovered Au by dissolution and calcination (b), and the recovered Pt NPs (c) (The insets being high-resolution {111} diffraction peaks of the powders, and the results of peak fitting)**

relatively low, in comparison with the recovered Pt from the mixture of Pt and Au NPs. A possible reason is that a small amount of Au atoms are mixed indistinguishably into the lattice of the Pt shell during the sequential synthesis process of the Au-Pt core-shell NPs. The recovered Pt and Au are around 2.1 and 6.7 mg, respectively.

4 Conclusion

The author demonstrates a novel process to recover Pt from Pt/Au bimetallic nanoparticles. The preliminary results show that the purities of the Pt recovered from the mixture of Au and Pt nanoparticles, and from the Pt/Au core-shell nanoparticle catalyst are as high as (99.49±0.22)%, and (95.02±0.08)%, respectively, with acceptable yields. Optimization of the recovery process is needed to further improve the purity and the yield of the recovery process.

Acknowledgements

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