Sonochemically Prepared Platinum−Ruthenium Bimetallic Nanoparticles

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Colloidal bimetallic nanoparticles of Pt−Ru have been synthesized by sonochemical reduction of Pt(II) and Ru(III) in aqueous solutions. Transmission electron microscope (TEM) images indicate that sequential reduction of the Pt(II) followed by the Ru(III) produces particles with a core shell (Pt@Ru) morphology. In the presence of sodium dodecyl sulfate, SDS, as a stabilizer, the particles have diameters between 5 and 10 nm. When polyvinyl-2-pyrrolidone, PVP, is used as the stabilizer, the rate of reduction is much faster, giving ultrasmall bimetallic particles of ∼5 nm diameter.

Introduction

Colloidal dispersions of bimetallic nanoparticles have garnered a lot of attention in recent years, particularly in the areas of optoelectronic applications and catalysis. In the realm of optoelectronic applications, metal nanoparticles have interesting size- and shape-dependent optical and electronic properties that can be suitably modulated by the addition of another metal.[1] For catalytic applications, the expectation is that they will have better catalytic properties than the component metals alone or even have new properties. Chemical preparation of these colloidal bimetallic systems usually involves one of two methods: (i) simultaneous reduction of the precursor metal ions and (ii) sequential reduction of the precursor ions. The latter usually gives rise to core−shell structures. In both cases, polymers or ligands are added during the reduction process to prevent aggregation of the formed colloidal nanoparticles. For catalytic applications, it is desired to have well-dispersed particles of uniform shape and size.

Sonochemical reduction methods have an advantage in this regard. Suslick et al. were among the first to use ultrasound to synthesize bimetallic particles.[2] They used a 20 kHz transducer to synthesize Fe−Co alloys from nonaqueous solutions containing $Fe(CO)_5$ and $Co(CO)_3(NO)$ complexes. Shafi et al. have used a similar procedure to prepare Co−Ni alloys.[3] However, the particle sizes in these cases are quite large. Okitsu et al. have shown recently that, in the case of ultrasound-initiated reduction of metal ions in aqueous solution, particle sizes and distribution are governed by the reduction rate, with faster rates leading to smaller and more uniform particles.[4] Mizukoshi et al. have synthesized bimetallic particles of gold and palladium with a narrow size distribution by sonochemical reduction of an aqueous solution containing both Au(III) and Pd(II) ions.[5,6] They reported core−shell morphology for the resulting nanoparticles with a Pd shell over the Au core. Bimetallic nanoparticles with Au core and Pd shell have also been synthesized by Kan et. al. using successive sonochemical reduction of the precursors $Pd(NO_3)_2$ and $HAuCl_4$ in ethylene glycol.[7] Takatani et al. have also reported the sonochemical synthesis of bimetallic nanoparticles of Au/Pt and Au/Pd in the presence of different surfactants.[8]

A bimetallic system of great interest is Pt−Ru, because of its usefulness as a methanol oxidation catalyst in direct methanol fuel cells (DMFC). We present here the sonochemical synthesis of platinum−ruthenium bimetallic nanoparticles by ultrasonic irradiation of an aqueous solution of Pt(II) and Ru(III) at a frequency of 213 kHz. We are able to synthesize Pt−Ru nanoparticles with a core−shell geometry by successive reduction of Pt(II) and Ru(III).

Experimental Details

A solution containing 1 mM ruthenium chloride, $RuCl_3$, 1 mM potassium tetrachloroplatinate, K_2PtCl_4 (both from Aldrich), 0.2 M propanol, and either 8 mM sodium dodecyl sulfate (SDS) or 1 mg/mL of polyvinyl-2-pyrrolidone (PVP, MW = 55 000) in 0.1 M perchloric acid was used as the initial solution for sonication. Perchloric acid is necessary to dissolve the $RuCl_3$. The solutions were sonicated using an ultrasound transducer (L-3 Communications, ELAC Nautik GMBH) operating at a frequency of 213 kHz. The sonication cell has a volume capacity of 200 mL, in which a 15 mL vial containing 10 mL of the platinum (II) solution was placed. An argon atmosphere was maintained above the solution throughout the experiment. Sonication was carried out in continuous wave mode. A constant temperature of 20 °C was maintained during the sonication by circulating water through a jacket around the sonication cell. All sonication experiments were carried out at ultrasonic power between $110-125$ mW mL^{-1} measured by calorimetry. This power was determined to be the optimum power setting based on the efficiency of sonochemical reduction. The sonication was stopped at various times, and absorption spectra were obtained using a 1 mm quartz cell on a Varian spectrophotometer (Cary Bio50).

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Transmission electron microscope (TEM) images of the sonochemically prepared metal colloids were obtained on a transmission electron microscope (Philips CM-10) at a voltage of 100 kV. To obtain the TEM images, a single drop of the colloidal platinum was deposited on 3 mm carbon supported Cu grids. Higher-resolution TEM images were obtained on a JEOL transmission electron microscope (JEM 2010) operating at 200 kV. Energy-dispersive X-ray analysis was used to determine the elemental composition of the colloidal particles.

Results and Discussion

Acoustic cavitation leads to the formation of highly reactive H• and •OH radical species in aqueous solutions. These species (H•) may react directly with metal ions in bulk solution or be scavenged by added organic solutes.[4] In the latter case, the organic radicals that are produced may subsequently reduce the metal ions in solution.[9] The exact mechanism after the homolysis of water leading to the sonochemical reduction of metal ions in aqueous solution is discussed in previous reports.[9] In a recent paper, we reported the sonochemical synthesis of ruthenium nanoparticles from a solution of $RuCl_3$.[10] The reaction is slow, and reduction of a 1 mM Ru(III) solution to Ru(0) takes almost 13 h. Hence, the particles obtained are relatively large with an average diameter between 15 and 20 nm. However, it could be anticipated that the reduction of ruthenium (III) should be significantly enhanced in the presence of an electron scavenger such as platinum.

Noble metal colloids such as silver and platinum act as a sink for excess electrons, and these electrons can initiate reduction of other solutes. Henglein and Mulvaney have used this principle to achieve the reduction of Cd^{2+} adsorbed onto colloidal silver by 1-hydroxyethylmethyl radicals.[11] The 1-hydroxyethylmethyl radicals are generated when a colloidal silver solution containing Cd^{2+} ions and acetone and 2-propanol is exposed to γ irradiation. The colloidal silver particles act as "nanoparticles−electrodes" and store the excess electrons generated by the 1-hydroxyethylmethyl radicals. These stored electrons can then reduce the adsorbed Cd^{2+} ions to generate a layer of cadmium around the silver metal. The results presented below show that the presence of platinum ions can enhance the reduction rate of Ru(III) and at the same time produce bimetallic nanosized particles of platinum and ruthenium.

Figure 1a shows the absorption spectra of an aqueous solution containing 1 mM Pt^{2+} and Ru^{3+} along with 8 mM SDS (stabilizer), 200 mM propanol (the reaction of alcohols with the primary radicals generate secondary reducing radicals,[9] which enhance the metal ion reduction process), and 0.1 M $HClO_4$ as a function of sonication time. The initial spectrum at time $t = 0$ shows prominent absorption bands centered at 560, 450, and 400 nm in the visible region of the spectrum arising from Ru(III). Commercial $RuCl_3$ contains a variety of oxochloro and hydroxochloro species of variable oxidation states, and the difficulties associated with ruthenium reduction stem from impure starting material.[12] However, when sonicated simultaneously with Pt(II), the reduction rate for the ruthenium ions is quite fast. Within 4 h, nearly all of the above-mentioned absorption bands have disappeared, and a clear brown solution is obtained. Just as Henglein et al. have shown in the case of the Cd^{2+} reduction on silver colloids in the presence of reducing radicals, the platinum colloids can act as nanoelectrodes, and electrons are transferred to the platinum surface from the reducing radicals produced by the propanol and surfactant during sonication. The accelerated reduction rate for Ru(III) is most likely due to these excess electrons on the platinum surface
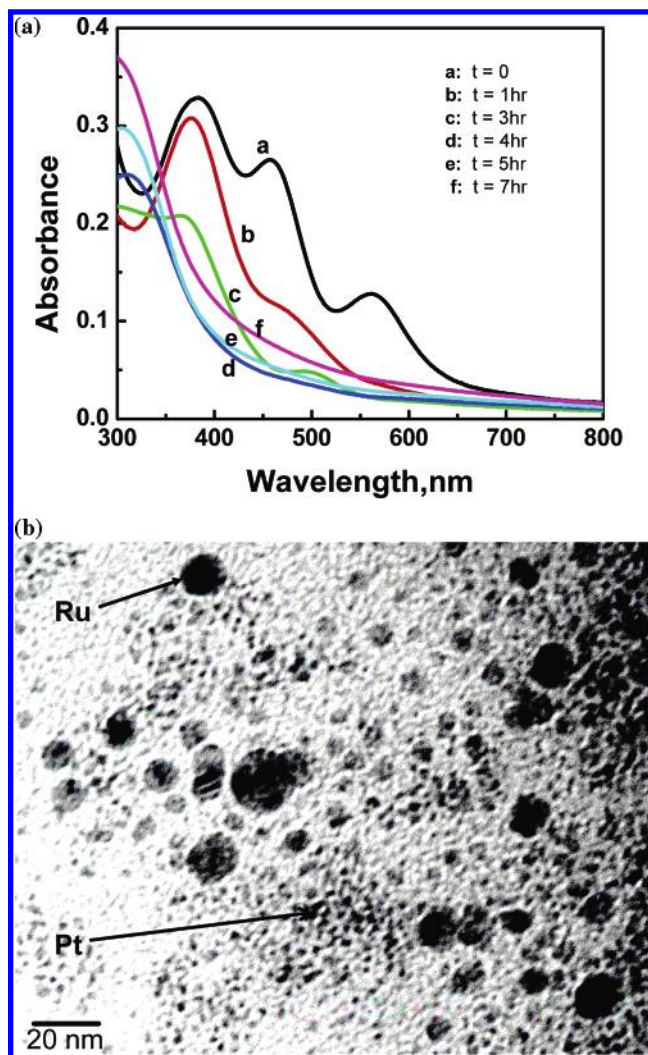
Figure 1. (a) Absorption spectra showing the simultaneous sonochemical reduction of an aqueous solution of 1 mM $RuCl_3$ and 1 mM K_2-$PtCl_4$ containing 0.1 M HClO4, 8 mM SDS, and 0.2 M propanol under argon atmosphere. **a:** $t = 0$. **b:** $t = 1$ h. **c:** $t = 3$ h. **d:** $t = 4$ h. **e:** $t = 5$ h. **f:** $t = 7$ h. The ultrasound frequency used was 213 kHz. (b) TEM image of Pt−Ru nanoparticles synthesized following 7 h of simultaneous sonication of 1 mM Pt(II) and 1 mM Ru(III) at 213 kHz. The accelerating TEM voltage was 100 kV.

donated by the reducing radicals produced by sonolysis. The changes in the absorption spectrum also indicate that reduction of the Ru(III) occurs simultaneously with the reduction of the Pt(II). The faster reduction rate for Pt(II) relative to Ru(III) means that colloidal platinum nanoparticles are preferentially produced which eventually accelerate the formation of Ru(0). The overall accelerated reduction rate of Ru(III) can be attributed to the existence of excess electrons on the surface of the Pt nanoparticles donated by the reducing alcohol radicals produced by sonolysis. Figure 1b shows the TEM image obtained at an accelerating voltage of 100 kV of the particles obtained from this simultaneous sonication. It mostly contains a mixture of particle sizes with the larger ones presumably ruthenium particles and the ultrasmall ones platinum. This is consistent with our experimental observations that sonochemical reduction of platinum (II) to produce platinum colloids is substantially faster than similar reduction of ruthenium (III) and that faster reduction rates result in smaller particle sizes. We have done control experiments to determine the size of pure platinum and pure ruthenium particles when produced individually by sonochemical reduction. Sonochemical reduction of Pt(II) under
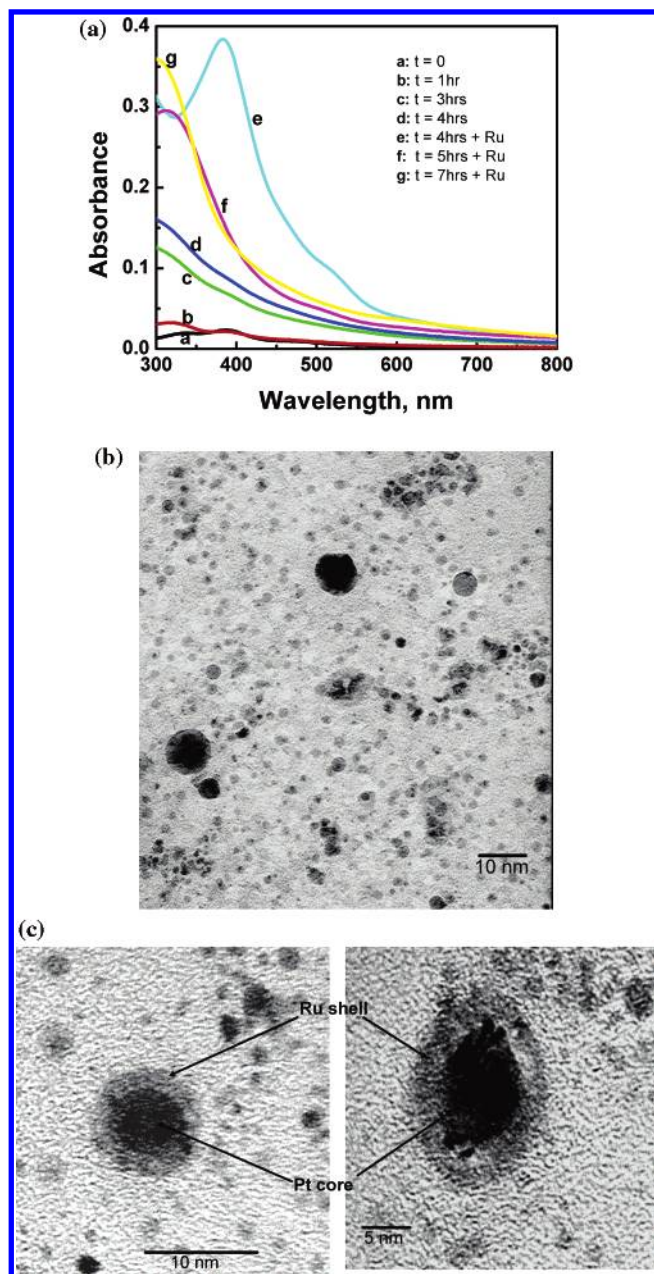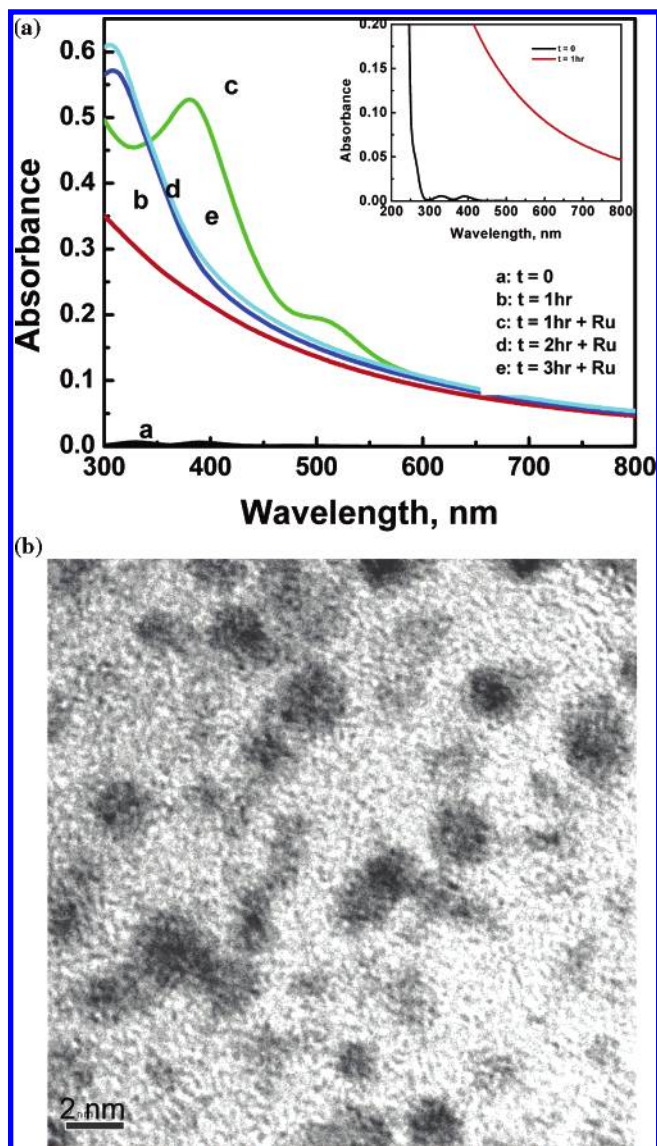
Figure 2. (a) Absorption spectra showing the sequential sonochemical reduction of 1 mM $PtCl_4^{2-}$ solution in 200 mM propanol, 0.1 M $HClO_4$, and 8 mM SDS followed by the reduction of 1 mM $RuCl_3$ under argon atmosphere. The $RuCl_3$ solution was added after the $PtCl_4^{2-}$ solution was sonicated for 4 h. **a**: $t = 0$. **b**: $t = 1$ h. **c**: $t = 3$ h. **d**: $t = 4$ h. **e**: $t = 4$ h + Ru(III). **f**: $t = 5$ h. **g**: $t = 7$ h. The ultrasound frequency used was 213 kHz. (b) TEM image of Pt−Ru nanoparticles synthesized following 7 h of sequential sonication of 1 mM Pt(II) and 1 mM Ru-(III) at 213 kHz. The accelerating TEM voltage was 100 kV. (c) TEM images obtained at an accelerating voltage of 200 kV of Pt−Ru nanoparticles synthesized following sequential sonication of 1 mM Pt-(II) and 1 mM Ru(III) at 213 kHz. Two representative particles are shown at different magnifications. The same copper grid sample used to obtain the image in Figure 1 was used in this case.

identical conditions produces platinum colloids with particle sizes of ∼5 nm, while similar sonochemical reduction of Ru-(III) produces particles that average well over 15 nm in size. These images are included in the Supporting Information (Figures S1 and S2).

We have also carried out sequential sonolysis where we initially apply ultrasound to the tetrachloroplatinate solution containing 8 mM SDS, 200 mM propanol, and 0.1 M $HClO_4$

Figure 3. (a) Absorption spectra showing the sequential sonochemical reduction of 1 mM $PtCl_4^{2-}$ solution in 200 mM propanol, and 1 mg/mL PVP (MW: 50 000) followed by the reduction of 1 mM $RuCl_3$ under argon atmosphere. The $RuCl_3$ solution was added after the $PtCl_4^{2-}$ solution was sonicated for 4 h. **a**: $t = 0$. **b**: $t = 1$ h. **c**: $t = 1$ h + Ru(III). **d**: $t = 2$ h. **e**: $t = 3$ h. Inset shows the reduction of the $PtCl_4^{2-}$ solution prior to the addition of $RuCl_3$. The ultrasound frequency used was 213 kHz. (b) TEM image of Pt−Ru nanoparticles synthesized in PVP following sequential sonication of 1 mM Pt(II) and 1 mM Ru-(III) at 213 kHz. The accelerating TEM voltage was 200 kV.

to produce colloidal platinum. When all of the Pt(II) has been reduced, the $RuCl_3$ solution was added to the Pt colloidal solution and sonication continued. Figure 2a shows the absorption spectra of the colloidal solutions beginning with the tetrachloroplatinate solution at time $t = 0$ and continuing through the addition of the $RuCl_3$ and its reduction. Curve e shows the absorption spectrum immediately upon addition of the ruthenium chloride. Only one prominent feature at 400 nm remains in the absorption spectrum indicating an instantaneous partial reduction of Ru(III) upon addition to the colloidal platinum solution. Reduction to Ru(0) is complete at the end of 3 h. Figure 2b shows the TEM image of the nanoparticles produced from this sequential sonochemical reduction obtained at an accelerating voltage of 100 kV. At this resolution, we observe a mixture of particle sizes. The ultrasmall ones are most likely platinum particles based on our control experiments, but the larger ones

(5−10 nm) appear to be core−shell structure, i.e., a platinum core with a ruthenium shell around it. To confirm these core−shell structures, we have examined the same sample on the same copper grid at higher resolution at 200 kV, and the resulting TEM images are shown in Figure 2c. All the larger particles (>5 nm diameter) do indeed show clearly defined core−shell bimetallic structures with the ruthenium forming a layer around the platinum particles. We have chosen two representative particles to illustrate this geometry in Figure 2c. The platinum particle sizes are ∼7 nm, while we estimate the thickness of the ruthenium shell to be between 2 and 3 nm.

The effect of the stabilizer on the reduction rate was also examined by using PVP, a common colloid stabilizer, instead of SDS. As with the SDS systems, a sequential reduction process where ultrasound was initially applied to an aqueous solution containing 1 mM Pt^{2+} along with 1 mg/mL of PVP and 200 mM propanol. The formation of colloidal platinum is very rapid and is complete within 1 h of sonication. The change in the absorption spectrum following sonication of the Pt(II) solution in PVP is shown as an inset in Figure 3a. At the end of 1 h, when all of the Pt(II) was reduced, the $RuCl_3$ solution was added to the Pt colloidal solution and sonication continued. Figure 3a shows the absorption spectra of the colloidal solutions beginning with the tetrachloroplatinate solution at time $t = 0$ and continuing through the addition of the $RuCl_3$ and its reduction. The reduction rate is clearly faster in PVP as compared to SDS. It is difficult to adequately explain the difference in the rate of reduction observed with the two different stabilizers. The primary function of both PVP and SDS is to stabilize the metal particles. They do not influence the sound field (supported by hydrophone measurements of the acoustic field) and do not affect the bubble dynamics.[13] On the basis of these observations, we are confident that both SDS and PVP do not affect the cavitation bubbles or the bubble field or the sound field. It must be remembered that SDS is a negatively charged solute and can complex with some of the positive metal ion complexes in solution and conversely repel the negatively charged species, which is particularly relevant when considering reactions on the surface of the colloid particles in the system. Also, the degree of adsorption of the stabilizer on the colloid particles can be expected to be quite different, and this too will affect the size of the colloid particles formed. How all these effects contribute to the rate of reduction in the complex system remains to be understood. The TEM images of the particles obtained following sonication in the presence of PVP (Figure 3b) show ultrasmall 2 nm sized particles. While the TEM images of these ultrasmall particles do not conclusively indicate a core−shell structure, energy-dispersive X-ray analysis of the TEM sample confirms the presence of ruthenium and platinum.

It is clear that the reduction of ruthenium proceeds faster in the presence of platinum. We are currently investigating the electrocatalytic activity in methanol oxidation of these bimetallic colloids and comparing this with a mixture of pure Pt and Ru colloids to determine if the geometry of the structures determines their catalytic activity.

Supporting Information Available: Figures S1 and S2 showing the TEM images of pure Pt and Ru colloids prepared using ultrasound. This material is available free of charge via the Internet at http://pubs.acs.org.

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