

# Preparation and Optical Absorption Spectra of Au<sub>core</sub>Pt<sub>shell</sub> and Pt<sub>core</sub>Au<sub>shell</sub> Colloidal Nanoparticles in Aqueous Solution

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Bimetallic gold and platinum particles of the Pt–Au and Au–Pt core–shell type are prepared using hydrogen reduction and radiolysis techniques. The optical absorption spectra are recorded and compared to various Au–Pt particles described in the literature. Au<sub>core</sub>Pt<sub>shell</sub> particles catalyze the hydrogen reduction of silver ions to yield trimetallic particles.

## Introduction

Bimetallic gold and platinum nanoparticles in colloidal solution have been described at various occasions; they are of interest because of their catalytic properties. Miner et al.<sup>1</sup> synthesized gold–platinum alloys by simultaneously reducing chloroplatinic and chloroauric acid in aqueous solution with citrate, and they found that the absorption spectra of the alloy particles were not additive of those of the pure components. Yonezawa and Toshima<sup>2</sup> refluxed ethanol/water solutions of the two materials in the presence of poly(vinylpyrrolidone) and obtained particles that they interpreted as being of the Au<sub>core</sub>–Pt<sub>shell</sub> type. Rémita et al.<sup>3</sup> used ionizing radiation to simultaneously reduce HAuCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> in an aqueous solution containing poly(acrylic acid) as stabilizer.

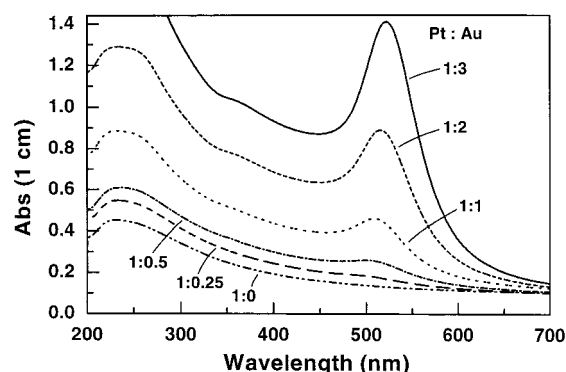
Schmid et al.<sup>4</sup> reduced PtCl<sub>6</sub><sup>2−</sup> in an aqueous gold sol by hydroxylamine; they obtained particles consisting of a 18 nm gold core surrounded by platinum crystals of about 5 nm. Similar enlargement techniques are applied in the present work to prepare both Au<sub>core</sub>Pt<sub>shell</sub> and Pt<sub>core</sub>Au<sub>shell</sub> particles. In both cases, the core particles were first prepared, and the shell of the second metal was subsequently deposited.

## Experimental Section

A 20 nm gold sol was prepared by citrate reduction of NaAuCl<sub>4</sub> as described by Turkevich.<sup>5</sup> A 12 nm platinum sol was prepared by hydrogen reduction of aged PtCl<sub>4</sub><sup>2−</sup> in an aqueous solution containing sodium polyacrylate.<sup>6</sup> To age PtCl<sub>4</sub><sup>2−</sup>, a 10<sup>−2</sup> M solution of the potassium salt was made and diluted as desired after standing for at least 2 days; the aged salt contains mainly Pt(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>.<sup>6</sup>

The platinum layer around the gold particles was deposited by adding aged PtCl<sub>4</sub><sup>2−</sup> to the gold sol and slightly shaking the mixture under hydrogen overnight. The rate of PtCl<sub>4</sub><sup>2−</sup> reduction is more than 10 times faster under these conditions than in the absence of the gold particles. The gold layer around the platinum particles was produced radiolytically.<sup>7,8</sup> The desired amount of K<sub>2</sub>Au(CN)<sub>2</sub> and 0.2 M methanol were added to the Pt sol, and the deaerated mixture was exposed to the  $\gamma$ -rays of a <sup>60</sup>Co source until all the Au(CN)<sub>2</sub><sup>−</sup> was reduced. The dose rate was 9 × 10<sup>2</sup> Gy/h.

Before recording the spectra, the solutions were treated with ion-exchange resin, Amberlite M 150, to remove ions that absorb in the UV, such as Cl<sup>−</sup> and CN<sup>−</sup>. The particles were observed



**Figure 1.** Absorption spectra of Pt particles before and after deposition of various amounts of gold. Overall Pt concentration:  $1.0 \times 10^{-4}$  M. Polyacrylate stabilizer:  $5.0 \times 10^{-5}$  M. The molar Pt:Au ratio is given on the curves.

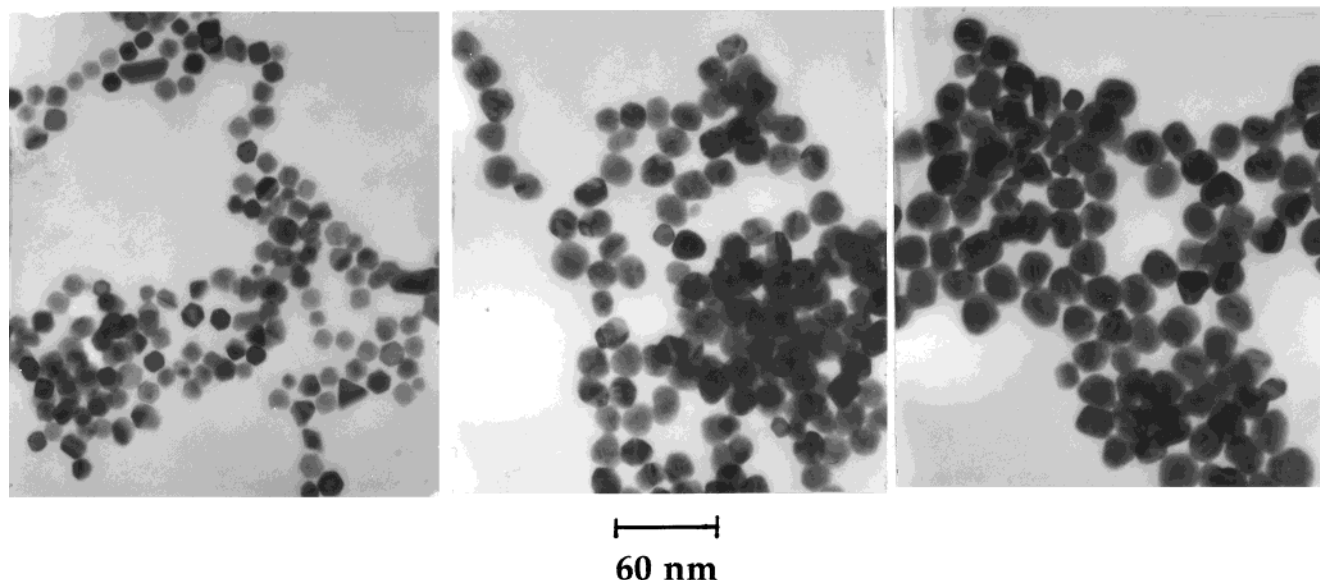
in an electron microscope, Hitachi 600, operating at 80 kV; samples were prepared by putting a copper–carbon grid on a drop of the solution on oil paper and letting the drop dry almost completely.

## Results

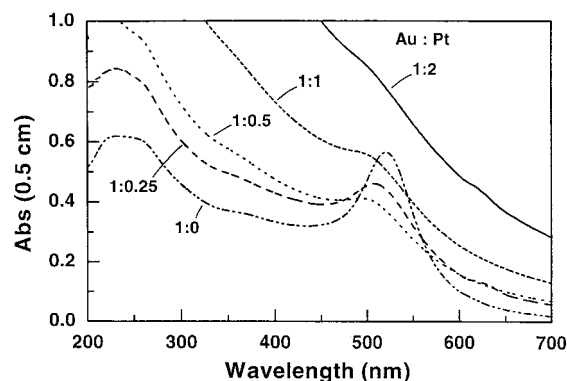
Absorption spectra of colloidal solutions of Pt<sub>core</sub>Au<sub>shell</sub> particles are shown in Figure 1. The concentration of Pt was  $1.0 \times 10^{-4}$  M in all the cases. The core particles have a narrow size distribution around 12 nm, as can be seen from the electron micrograph in Figure 2. The spectrum of the Pt particles exhibits an increasing absorption toward shorter wavelengths until a maximum is reached at about 215 nm. This maximum has also shown up in calculations of the Pt spectrum<sup>9</sup> and has been described in an earlier study.<sup>6</sup> With growing Au deposition, the plasmon absorption band of gold appears with increasing intensity. It peaks at 504 nm at a molar Pt:Au ratio of 1: 0.25 and moves toward longer wavelengths with increasing gold content: 506 nm at a ratio of 1:0.5; 510 nm at 1:1; 516 nm at 1:2; 522 nm at 1:3. Figure 2 also shows the electron micrographs of two examples of Au-coated particles. The increase in size with increasing Au deposition can clearly be seen. It is in agreement with the increase expected from the relation

$$D = D_{\text{core}}(1 + V_m(\text{Au})[\text{Au}]/V_m(\text{Pt})[\text{Pt}])^{1/3} \quad (1)$$

where the  $V_m$ 's are the mole volumes and the [ ]'s are the overall



**Figure 2.** Electron micrographs of the Pt particles before and after deposition of gold: (left) Pt core particles; (middle) Pt:Au = 1:1; (right) Pt:Au = 1:2.



**Figure 3.** Absorption spectra of Au particles before and after deposition of various amounts of platinum. Overall gold concentration:  $3.0 \times 10^{-4}$  M. The particles were stabilized by  $2.0 \times 10^{-4}$  M poly(vinyl sulfate). The molar Au:Pt ratio is given on the curves.

concentrations of the two metals involved ( $D$ : diameter). This indicates that the additional growth occurs on top of the existing platinum seeds.

The spectra of  $\text{Au}_{\text{core}}\text{Pt}_{\text{shell}}$  particles are shown in Figure 3. The gold concentration was  $3.0 \times 10^{-4}$  M in all cases. With increasing Pt deposition, the plasmon band of gold is damped and moves toward shorter wavelengths until it is positioned at 510 nm at an Au:Pt ratio of 1:0.5. When still more Pt is deposited, the intensity around 500 nm increases rapidly and the gold plasmon absorption vanishes; i.e., the unstructured behavior of the Pt absorption prevails. Figure 4 shows electron micrographs of the gold particles before and after deposition of Pt.

The  $\text{Au}_{\text{core}}\text{Pt}_{\text{shell}}$  particles catalyze the reduction of silver ions by hydrogen; this reduction does not take place in the absence of the particles. A typical experiment is illustrated by Figure 5. The spectrum of the 20 nm gold particles is shown and that of the Au–Pt particles after Pt deposition in the ratio 1:0.5 as described above. The overall gold concentration was  $3.0 \times 10^{-4}$  M and that of platinum  $1.5 \times 10^{-4}$  M at this point. Then  $1.0 \times 10^{-4}$  M  $\text{AgClO}_4$  was added and the solution kept under hydrogen for 2 h. The absorption increased at all wavelengths, the gold plasmon band being further flattened, and a vestige of

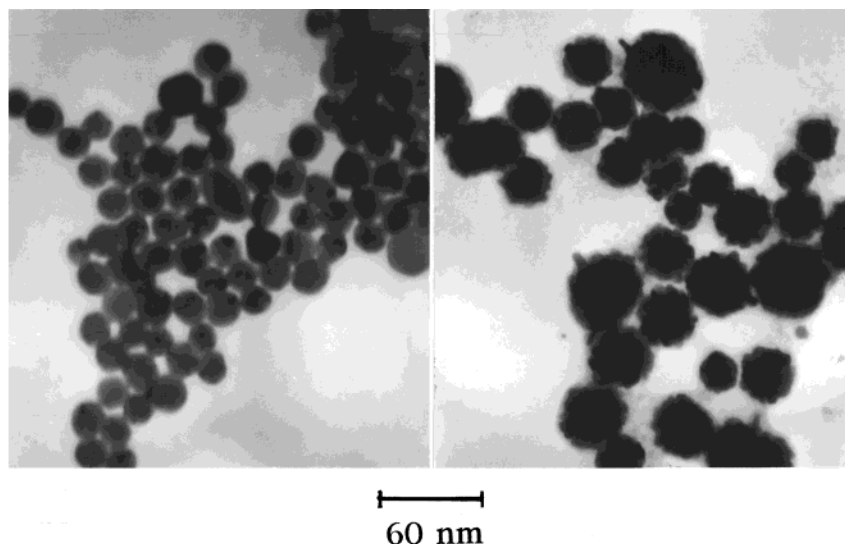
the 380 nm plasmon absorption band of silver can be seen. To check whether all the silver ions had been reduced, 0.2 M methanol was added and the solution exposed to  $\gamma$ -radiation, which is known to reduce  $\text{Ag}^+$  efficiently;<sup>10</sup> no increase in the 380 nm band was observed. It is concluded that the treatment with hydrogen led to complete  $\text{Ag}^+$  reduction.

## Discussion

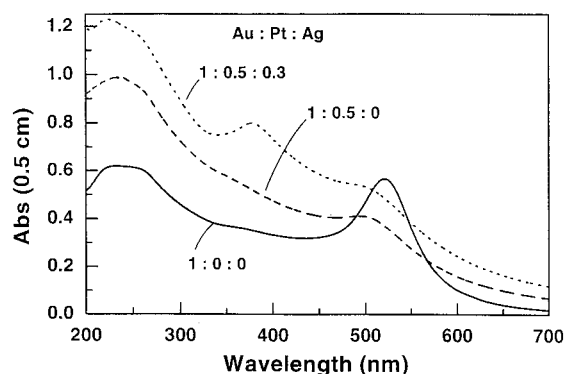
The particles are clearly separated in the electron micrographs; i.e., their spectra can be attributed to truly single particles in solution without any disturbances by agglomeration. The Pt particles in Figure 2 are nicely faceted polyhedra, as has earlier been found.<sup>6,11</sup> When gold is deposited, the shape of the particles appears to round off. The absorption spectra of the Au-coated Pt particles hardly concur with the spectra of bimetallic particles published hitherto;<sup>1,2,4</sup> in those cases the particles were either alloys (as postulated in ref 1) or of the  $\text{Au}_{\text{core}}\text{Pt}_{\text{shell}}$  type (as postulated in refs 2 and 4).

The electron micrographs of Figure 4 show the increase in size of the gold particles upon Pt deposition. The deposited Pt shell, however, is ragged, similar to the shell reported in the Pt deposition by hydroxylamine.<sup>4</sup> This is understood in terms of the initial formation of Pt islands on the gold particle surface, which then grow in preference to the further reduction on gold. Thus, the catalytic action of a Pt surface for the chemical reduction of aged  $\text{PtCl}_4^{2-}$  seems to be stronger than that of a Au surface. The spectra in Figure 3 bear some similarity to the spectra reported in ref 2, where it was postulated that gold is reduced first in a mixture of gold and platinum acids. However, the very strong increase in absorption at the higher Pt contents of the particles was not observed in ref 2; this may be taken as an indication for the formation of some pure Pt particles besides the bimetallic particles in ref 2.

The observations made in the experiment of Figure 5 are interpreted as the formation of a concentric trimetallic particle, the deposited silver being present in a thin outer layer, in which the plasmon oscillation is strongly damped. One could argue that separated silver particles were formed. However, a pure  $1.0 \times 10^{-4}$  M silver colloid has a very much stronger plasmon band (absorbance at 380 nm about 1.0) and practically does not absorb above 500 nm.<sup>10</sup>



**Figure 4.** Electron micrographs of Au core particles before (left) and after (right) deposition of platinum in the ratio 1:2.



**Figure 5.** Absorption spectra of Au particles before and after deposition of one or two layers of Pt and Ag. The overall gold concentration was  $3.0 \times 10^{-4}$  M in all cases. The molar ratios of the metals involved are given on the curves.

The bimetallic particles reported here are also being investigated in femtosecond laser experiments with respect to electron–phonon dynamics; such experiments have recently been carried out on gold particles over a wide size range.<sup>12,13</sup> It turns out that  $\text{Pt}_{\text{core}}\text{Au}_{\text{shell}}$  particles exhibit an extraordinarily large electron–phonon coupling constant. The details of these findings will be published elsewhere.<sup>14</sup>

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