

LETTERS

Colloidal Palladium Nanoparticles: Reduction of Pd(II) by H₂; Pd_{Core}Au_{Shell}Ag_{Shell} Particles

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Palladium colloid with a narrow particle size distribution is formed in the reduction of PdCl₄²⁻ by hydrogen in aqueous solution, using sodium citrate as stabilizer. The absorption spectrum of the Pd particles depends on their content of chemisorbed hydrogen atoms. In the absence of hydrogen, the absorption maximum at 218 nm is present, which is expected from calculations. In the presence of hydrogen, the spectrum is flatter and peaks at 258 nm. Radiolytic methods are applied to prepare bimetallic Pd_{core}Au_{shell} and trimetallic Pd_{core}Au_{shell}Ag_{shell} particles, and the optical spectra of these structures are reported.

Introduction

Colloidal palladium nanoparticles, often in combination with another metal, have been prepared in various laboratories during the past few years, the main goal often being the investigation of their catalytic properties. Besides the pure metal particles,¹ Pd–Pt,² Au–Pd,³ Pd–Ag,⁴ and Pd–Cu⁵ particles have been made, often using boiling alcohol, hydroxylamine or formaldehyde as the reducing agent of the initial metal salts. Radiation has also been used to synthesize nanoalloys of Pd and Ag.⁶ The absorption spectrum of Pd-nanoparticles has been calculated by Creighton and Eadon,⁷ but it seems to have never been verified experimentally over the whole vis–UV range. The reason for this is the fact that all preparations involved substances (solvent or protecting polymer) which have strong UV absorptions that do not allow one to observe the predicted absorption maximum close to 225 nm. In the present work, PdCl₄²⁻ is reduced by hydrogen at ambient temperature in aqueous solution using citrate as stabilizer to obtain small Pd nanoparticles, and radiolytic methods are used to deposit Au or Au plus Ag shells around these particles. In both the radiolytic and H₂ reduction method no substances are introduced into the solution which hamper the determination of the UV absorption spectrum.

Experimental Section

Formation of Colloidal Pd. A 2.5×10^{-3} M Na₂PdCl₄ (Aldrich, 99.998%) stock solution was made and diluted to

obtain the desired concentration. The reduction occurred in a glass vessel, which had a sidearm carrying an optical cuvette (optical path is given on the ordinate axis of the spectra). The vessel was also equipped with a septum; substances could therefore be added via a syringe without bringing the solution into contact with air. The solution was first bubbled with argon to remove the air and then vigorously flushed with hydrogen for 90 s. The vessel was then closed and slightly shaken overnight. The volume of the vessel was 150 mL, and the volume of the solution was 20–50 mL. Considering the much higher H₂ concentration in the gas than in the liquid phase, there was always a vast excess of hydrogen in the reacting system. $(2-5) \times 10^{-4}$ M sodium citrate was used as stabilizer of the colloidal particles; within this concentration range, the particle size does practically not vary.

Deposition of Au. The principle of the method has previously been described.⁸ The desired amount of K₂Au(CN)₂ was added to the Pd colloid as well as 0.5 M methanol, and the solution flushed with nitrous oxide. The solution then was γ -irradiated in a commercial ⁶⁰Co source (dose rate: 9×10^2 Gy/h) until all Au–I in Au(CN)₂⁻ was reduced; this point was readily recognized by following the disappearance of the strong UV absorption bands of Au(CN)₂⁻. The reduced gold does not form pure gold particles, but all of it settles on the Pd particles to form a gold layer.

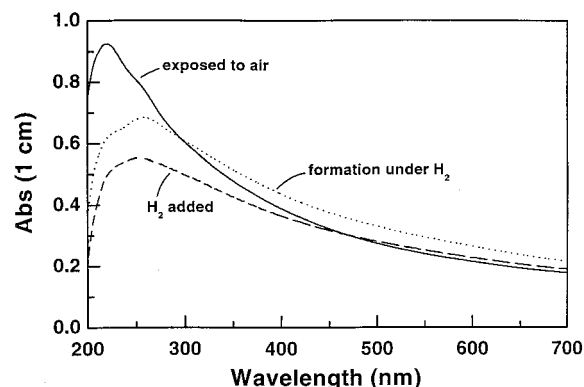


Figure 1. Absorption spectrum of a 2.5×10^{-4} M Pd colloid after its formation under hydrogen, after exposure to air for 20 min, and after reexposure to hydrogen. Citrate concentration: 5.0×10^{-4} M. (The blank also was 5.0×10^{-4} M citrate).

Deposition of Ag. The deposition of Ag on the $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$ particles to form concentric trimetallic particles followed the same principle. The desired amount of $\text{NaAg}(\text{CN})_2$ was added to the solution of the Pd–Au particles and the solution γ -irradiated until all the silver had been reduced. The deposition of silver was followed by the disappearance of the strong UV absorption of $\text{Ag}(\text{CN})_2^-$. All the reduced silver is used to form an outer shell around the particles.

The reduced solutions contained cyanide ions and were not stable when exposed to air. The CN^- ions were removed by adding ion-exchange resin (Amberlite, MB 150, Aldrich) under exclusion of air, shaking for 20 min, and decanting of the solution under air.

Electron microscopy was carried out with a 80 kV Hitachi 600 microscope.

Results and Discussion

Figure 1 shows the absorption spectrum of a completely reduced solution of 2.5×10^{-4} M Pd, which contained 5.0×10^{-4} M citrate and 2.5×10^{-4} M NaOH as stabilizer. The solution had a black color. The spectrum is rather broad, with a maximum at 258 nm and a shoulder at 218 nm. When this solution was exposed to air for about 20 min, it became more transparent and the color acquired a brownish tinge. As can be seen from Figure 1, the UV absorption below 300 nm strongly increased, and decreased at longer wavelengths. The former 218 nm shoulder is fully developed into a clear peak, whose position agrees fairly well with the calculated one (ca. 225 nm),⁷ and only a vestige of the 258 nm absorption is present. The first spectrum (under H_2) is attributed to Pd particles which are loaded with chemisorbed hydrogen atoms. The second spectrum (under air) is attributed to Pd particles essentially free from hydrogen. Figure 1 also shows the spectrum which was observed when hydrogen gas was reintroduced into the reaction vessel: the solution became darker and its spectrum broader, as the particles were re-loaded with H atoms. The effect is even stronger than in the original solution under hydrogen. The steps of removal of H atoms and loading with H_2 can be repeated several times, always with the corresponding optical changes.

Figure 2, left, shows an electron micrograph of the Pd particles. They have a narrow size distribution around 4 nm.

The gold–palladium combinations synthesized hitherto are of the $\text{Au}_{\text{core}}\text{Pd}_{\text{shell}}$ type. Figure 3 shows absorption spectra of $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$ type particles. The starting material was a 1.1×10^{-4} M Pd colloid (chemisorbed hydrogen removed). Various amounts of $\text{Au}(\text{CN})_2^-$ were reduced as described above. In

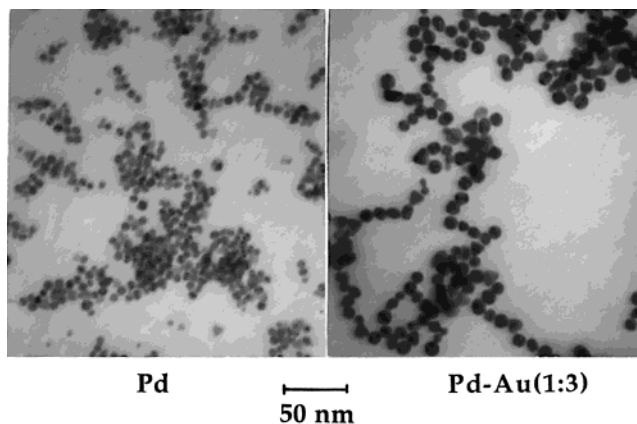


Figure 2. Electron micrographs of Pd (left) and Pd:Au = 1:3 (right) particles.

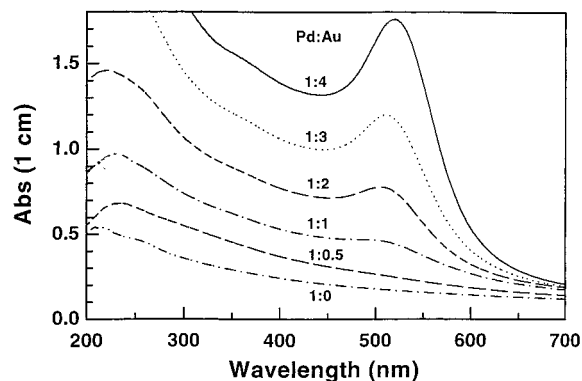
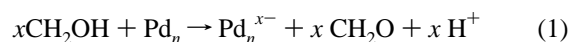


Figure 3. Absorption spectrum of Pd particles and Pd–Au particles of different composition. The molar Pd:Au ratio is given on the curves. Initial Pd concentration: 1.1×10^{-4} M. Citrate concentration: 2.0×10^{-4} M.

solutions, which contain methanol and nitrous oxide, γ -irradiation produces hydroxymethyl radicals as the only species that attacks solutes present in relatively low concentrations. The standard potential of the $\cdot\text{CH}_2\text{OH}$ radical (-1.1 V)⁹ is not negative enough to reduce $\text{Au}(\text{CN})_2^-$ in solution, as this would lead to a free Au atom, whose free enthalpy of formation is as high as 3.4 eV. In fact, the standard potential of the process $\text{e}^- + \text{Au}(\text{CN})_2^- (\text{aq}) \rightarrow \text{Au}_{(\text{aq})} + 2\text{CN}^- (\text{aq})$ amounts to -4.0 V. However, when the reduction takes place on the surface of a tiny “Pd nanoelectrode” in solution the potential for the reduction of $\text{Au}(\text{CN})_2^-$ is more positive: -0.6 V. This “electrode” reaction is believed to occur in 2 steps: electron deposition on the particles:



reaction of the deposited electrons:



At a molar Pd:Au ratio of 1:0.5 of the composite particles, the absorption is enhanced at all wavelengths without any sign of the plasmon absorption band of gold. At the ratio of 1:1, this band makes its first appearance at 504 nm. With increasing Au deposition, the wavelength of the peak is red-shifted (508 nm at 1:2; 513 nm at 1:3; 520 nm at 1:4). Pure gold particles (~ 10 nm) absorb at 520 nm.^{8b} Figure 2 (right) shows an electron micrograph of Pd–Au particles; note that they have a narrow size distribution, and that original Pd particles are no more

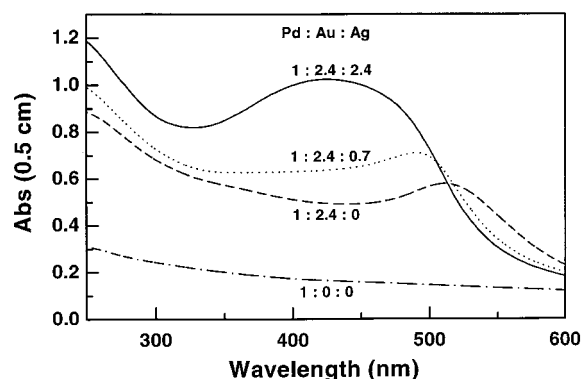


Figure 4. Absorption spectrum of particles containing different amounts of Pd, Au, and Ag. The molar composition is given on the curves. Initial Pd concentration: 1.1×10^{-4} M.

present. The pure Pd particles have a strong tendency to cluster; this tendency is less pronounced for the gold-covered ones.

The optical effects accompanying the deposition of silver on $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$ particles are shown in Figure 4. $\text{Ag}(\text{CN})_2^-$ is not reduced by hydroxymethyl radicals in solution, as the potential, at which the reaction $e^- + \text{Ag}(\text{CN})_2^- \rightarrow \text{Ag} + 2\text{CN}^-$ becomes possible, is too negative: -3.02 V.¹⁰ However, reduction can occur on the surface of the Pd–Au particles, the reason being that the conventional electrode potential of -0.31 V applies now. The reaction is believed to occur in two steps similar to eqs 1 and 2. As can be seen from Figure 4, deposition of Ag first leads to a blue-shift of the plasmon absorption band of the gold component in the particles, and later to the formation of a very broad plasmon band in the ~ 400 nm wavelength range where silver particles usually have a plasmon absorption band. In comparison, the plasmon band of pure silver particles is much more narrow and several times over exceeds the band of the trimetallic nanoparticles in Figure 4.

Final Remarks

Since the early investigations by Rampino and Nord about the reduction of the aqueous hydroxides of Pd and Pt by hydrogen,¹¹ little work has been done to study the optical properties of the nanoparticles formed; in fact, only experiments on Pt particles have been reported.¹² Colloid formation by reduction of PdCl_4^- by H_2 constitutes a convenient method for the preparation of palladium nanoparticles with a narrow size distribution. The reduction by citrate is more complicated, as it requires boiling under argon for a long time, if complete reduction has to be achieved.^{4c} Since the first observations on the cathodic charging of colloidal metal particles via free radical

attack and the use of the stored electrons to initiate unusual reductions in solution,¹³ many particle structures of preparative interest in colloid chemistry have been synthesized. Irradiation is a very useful and reproducible method to generate the initiating free radicals. The synthesis of bimetallic and trimetallic particles by the radiolytic method is demonstrated once more in the present work. These particles are of interest for the study of fast electronic processes in the femtosecond range;¹⁴ the results of those studies will be published elsewhere.

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