

Composite Ag-Pt Nanoparticles in Aqueous Solution

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It is shown that the saturation of an aqueous solution containing K_2PtCl_4 with hydrogen in the presence of 6.3 nm silver nanoparticles leads to the reduction of platinum on the silver surface and the formation of Ag/Pt core-shell nanoparticles. The Ag:Pt molar ratio is varied from 9:1 to 1:9 for synthesizing Pt shell layer of different thickness. An apparent shift of Ag surface plasmon band from 405 nm to 230 nm and broadening of one with decrease of Ag:Pt ratio was observed. The TEM images and SAED pattern of Pt@Ag nanoparticles has been obtained. The UV-Vis and TEM data confirms a formation of Ag/Pt core-shell nanoparticles.

Keywords: Nanoparticles, Platinum, Pulse radiolysis, Silver, Optical spectra, Synthesis, hydrogen.

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1. INTRODUCTION

Studying the properties of bimetallic nanoparticle core-shell type, which contain the noble metals [1, 2] causes a great interest. This applies in particular to Pt and Pd, due to their exhibited high catalytic activity [3]. However, the high cost of these metals makes researchers look for ways to reduce their content in the catalyst without loss of catalytic activity. Previous studies have shown that the number of shell layers may have a significant effect on the properties of the synthesized composite. In work [4], the catalytic activity of bimetallic nanoparticles of Ag@Pt has been controlled by changing the thickness of silver shell. Coating of nanoparticles of titanium oxide with a thin layer of gold has led to the appearance of the photo-catalytic activity of the synthesized particles [5].

In the present paper, the preparation particles is described, which contain a silver nucleus and platinum shell of different thicknesses. The particles are made by reducing Pt(II) in an aqueous solution of the “radiolysis” silver nanoparticles on their surface by hydrogen. The pulse radiolysis technique [6] and the hydrogen reducing method [7] to synthesize bimetallic nanoparticles are used. It's allowed to obtain colloidal solutions without co-products of reducing formed in the case of other methods, which could have a significant effect on the process of formation of bimetallic nanoparticles and their properties. The effect of the composition of bimetallic Pt@Ag nanoparticles on their optical and catalytic properties is studied.

2. MATERIALS AND METHODS

2.1 Materials

Potassium tetrachloroplatinate (II) (K_2PtCl_4 , 99.99%), silver perchlorate hydrate ($AgClO_4 \cdot H_2O$, 99.999%) from Aldrich, methylviologen dichloride hydrate (MV, 98%), sodium polyacrylic acid 2100 sodium salt (PANa) from Fluka, sodium formiate ($HCOONa$, 99.99%) by Reachim, sodium hydroxide ($NaOH$, 99.0%) from Chimmed, pure hydrogen (H_2 , 99,999%) were

used. All glassware and Teflon-coated magnetic stirrer bar were cleaned with aqua regia, followed by copious rinsing with purified water. Solutions were prepared in distilled water, which was additionally deionized with a “Vodoley” water system and had a conductivity of no higher than 0.056 $\mu S/cm$.

2.2 Characterization

A Carl Zeiss LEO912 AB OMEGA microscope was used to obtain transmission electron microscope (TEM) images and the selected area electron diffraction pattern (SAED) of the nanoparticles. UV-vis absorption spectra were recorded on Varian Cary 100 spectrophotometer with water-cooled Peltier accessory.

2.3. Synthesis procedure

2.3.1. Ag nanoparticle

An Ag hydrosol with diameter of about 6 nm was prepared by the pulse radiolysis technique [6]. A 2 ml of 10 mM sodium polyacrylate solution was mixed with the 20 ml of 1 mM aqueous solution of $AgClO_4$, then 68 ml 0.29 mM aqueous solution of sodium formiate was added. The deaerated solutions were irradiated on the electron beam accelerator U-2 with electron's energy equal 7 MeV.

2.3.2. Pt nanoparticle

A Pt hydrosol was obtained by hydrogen method [7]. A 20 ml 1 mM aqueous K_2PtCl_4 was mixed with 80 ml of 0.25 mM sodium polyacrylate solution, then the solution was saturated by hydrogen with stirring at 1 atm and 20 °C and stored for 1 day for complete Pt(II) reduction and form Pt hydrosol. The size of the spherical particles that formed ranges from 5-8 nm.

2.3.3. Pt@Ag nanoparticle

A sample of the Ag nanoparticle prepared as mentioned above was used as a source of particle cores for preparation of a series of Ag/Pt bimetallic nanoparti-

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cles with the expected core-shell structure and varying thicknesses of Pt shells. A preparation of core-shell Ag/Pt bimetallic nanoparticles was prepared as follows: 5 ml of 0.2 mM fresh aqueous K_2PtCl_4 solution and 5 ml of 0.4 mM PANa solution was mixed, and then it was added to 10 ml of 0.1 mM Ag hydrosol. The resulting solution was stirred with a magnetic stirrer for one hour, and then it was deaerated and saturated with hydrogen to form the core-shell particles. Analogously, Ag-Pt core-shell nanoparticles with a calculated quantity of Ag:Pt molar ratio of $Ag_{90}Pt_{10}$, $Ag_{80}Pt_{20}$, $Ag_{60}Pt_{40}$, $Ag_{40}Pt_{60}$, $Ag_{20}Pt_{80}$ and $Ag_{10}Pt_{90}$ were prepared.

3. RESULTS AND DISCUSSION

Absorption spectra of colloidal solution of Ag/Pt core-shell nanoparticles with different composition, Ag and Pt colloids are shown in Fig. 1. Typical absorption spectra of colloidal silver and platinum are characterized by an absorption band with maximum at 400-410 nm for silver, due to the absorption of surface plasmons, and the faint maximum at 215 nm with a smooth

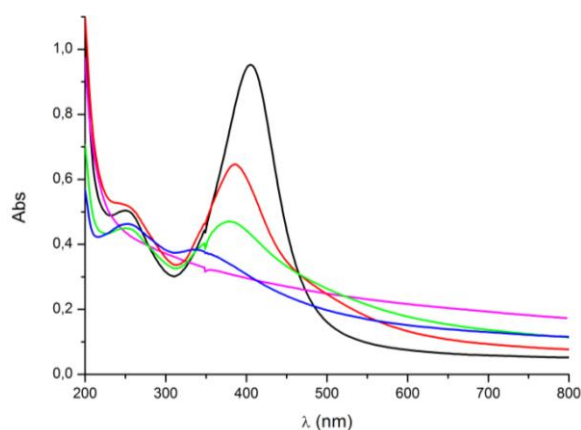


Fig. 1 – UV-vis absorption spectra of the Ag, Pt and bimetallic Pt@Ag nanoparticles with various ratio (black) $Ag_{80}Pt_{20}$; (red) $Ag_{60}Pt_{40}$; (green) $Ag_{40}Pt_{60}$; (blue) $Ag_{20}Pt_{80}$; (magenta) Pt

drop-down absorption at longer wavelengths, caused by the conversion of d-electrons for platinum. Fig. 2 shows the optical absorption spectrum of nanoparticles of Ag, Pt, and a mixture of nanoparticles of Pt and Ag with different molar ratio. The 410 nm surface plasmon peak is due to Ag plasmon band and it gradually decreases with the reduction of Ag:Pt molar ratio. Comparing of absorption spectra of Pt@Ag nanoparticles (Fig. 1) with those physical mixtures of monometallic (Fig. 2) have shown that the bimetallic particles had a different spectral profile both from the monometallic particles and from their physical mixture.

The standard potential of the pair $E^0(Pt^{2+}/Pt) = 1.188$ V [8] is lower than the potential of a pair of $E^0(Ag^+/Ag) = 0.799$ V in [9], which should lead to recovery of platinum and oxidized silver. Thus, the mixing of colloidal silver with an aqueous solution should occur the reaction (1), but in this case platinum in the solution is in the form of ions $PtCl_4^{2-}$, and the standard potential of the pair $E^0(PtCl_4^{2-}/Pt) = 0.758$ V [8] which is less than a pair of potential Ag^+/Ag , and thus the reaction (1) can't occur,

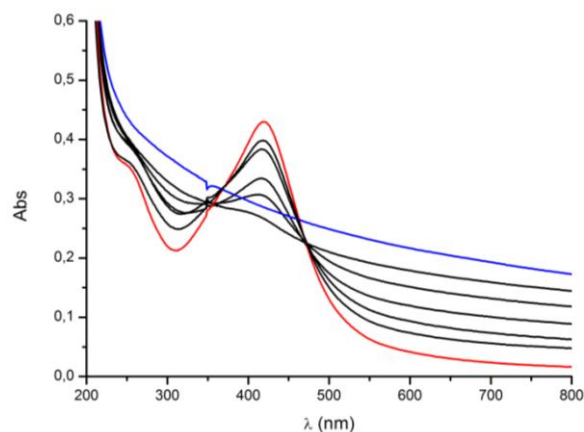
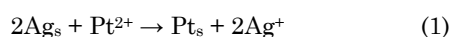


Fig. 2 – UV-vis absorption spectra of the both Ag and Pt nanoparticles and the various molar ratios physical mixtures of individual Ag and Pt nanoparticles (red) Ag; $Ag_{80}Pt_{20}$; $Ag_{75}Pt_{25}$; $Ag_{50}Pt_{50}$; $Ag_{25}Pt_{75}$; (blue) Pt

as evidenced by the absence of any change in the optical spectrum of the solution within a few hours of observations, would indicate the flow of the reaction (1). The reduction process begins only after saturation of the reaction mixture with hydrogen. In this case there was a slight induction period and a rapid reducing of platinum in a few seconds. Previous studies have shown that full reduction of platinum with hydrogen continued for quite a long time [17]. Because of this we can conclude that the reduction of platinum in the presence of silver nanoparticles is catalytic.

Fig. 3 and fig. 4 shows TEM micrographs and histograms of size distributions of silver nanoparticles and bimetallic Pt@Ag nanoparticles with different molar ratio of metals. Silver nanoparticles obtained by radiolysis have nearly spherical shape and size distribution is well described by the lognormal law. The average size of the received NP was 6.3 nm. On the images are

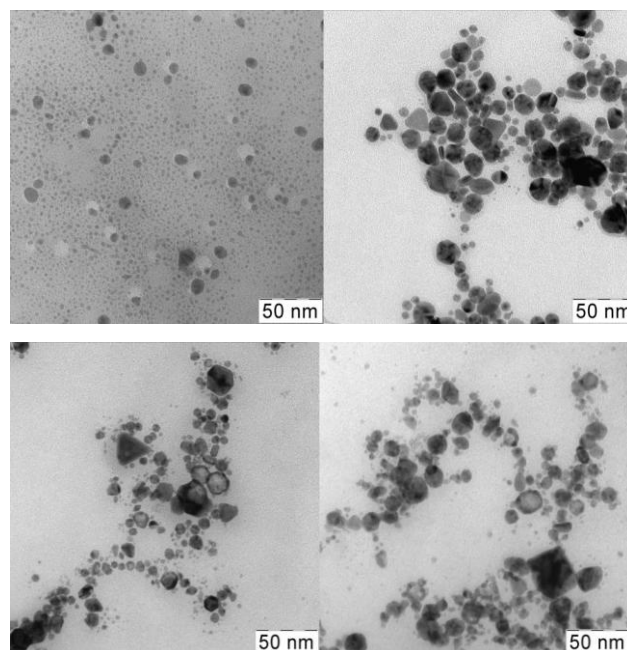


Fig. 3 – TEM images of an Ag and a Pt@Ag various ratio nanoparticles (Ag, $Ag_{80}Pt_{20}$, $Ag_{60}Pt_{40}$, $Ag_{40}Pt_{60}$)

readily identified the components of bimetallic nanoparticles (core-shell). TEM images of core-shell nanoparticles display an unusual “core-shell” contrast and

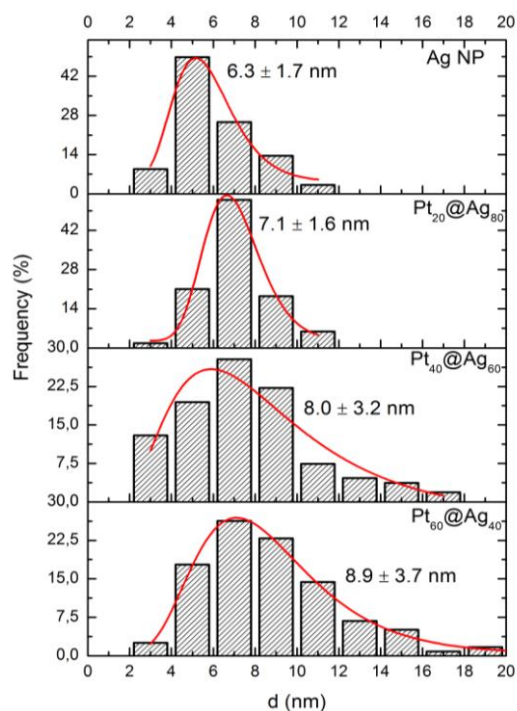


Fig. 4 – The size distribution histograms of an Ag and a Pt@Ag various molar ratio nanoparticles. (Ag, Ag₈₀Pt₂₀, Ag₆₀Pt₄₀, Ag₄₀Pt₆₀)

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have a bright central part and dark out part indicating the formation of core-shell nanostructure, where the bright central part correspond to the expected Ag core and the dark out part to the Pt shell. The difference in brightness due to the difference in the densities of the core and shell materials of Ag and Pt, respectively. The reduced on the silver nanoparticles surface platinum forms the shell, which leads to an increase in average particle size that can be clearly seen from the sequence of histograms of size distributions shown in Fig. 4, as well as the previously approved increase in absorption at long wavelengths.

4. CONCLUSION

The synthesis and characterization of core-shell type nanoparticles Pt@Ag with different thicknesses of platinum shell was described. The reduction of platinum in the presence of silver nanoparticles is catalytic. The UV-Vis and TEM data confirms a formation of Ag/Pt core-shell nanoparticles. An apparent shift of Ag surface plasmon band from 405 nm to 230 nm and broadening of one with decrease of Ag:Pt ratio was observed. The TEM images and SAED pattern of Pt@Ag nanoparticles has been obtained.

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