

## Synthesis of core–shell silver–platinum nanoparticles, improving shell integrity



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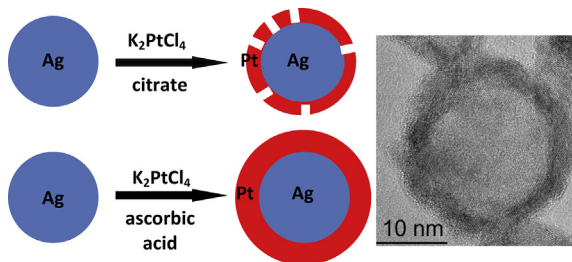
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### HIGHLIGHTS

- Properties of differently synthesized Ag@Pt nanoparticles have been compared.
- A procedure of preparation of pinhole-free Ag@Pt and Au@Pt nanoparticles is proposed.
- Surface of Ag@Pt nanoparticles is reconstructed after CO desorption.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Silver–platinum core–shell (Ag@Pt) nanoparticles have been synthesized using various methods. In the case of Ag@Pt nanoparticles synthesized by the standard method based on the galvanic replacement reaction between Ag seeds and  $\text{PtCl}_4^{2-}$ , transmission electron microscopy micrographs revealed well visible core–shell structure. However, electrochemical experiments showed that relatively large amount of silver can be easily stripped off from such nanoparticles. Significant improvement on the integrity of the deposited platinum shell can be achieved when nanoparticles are synthesized by the seeded growth reaction including reduction of  $\text{PtCl}_4^{2-}$  with ascorbic acid at room temperature. To obtain pinhole-free platinum layers (where Ag oxidation is not observed) relatively large amount of platinum must be deposited. For example, to cover 11 nm Ag seeds, the number of moles of platinum in the formed Ag@Pt nanoparticles must be at least equal to the number of moles of Ag. It was also found that a similar seeded growth reaction may be used to form pinhole-free Au@Pt nanoparticles. The electrochemical behaviour of those two systems (Ag@Pt and Au@Pt nanoparticles) towards CO stripping was rather different. While the CO-stripping on Au@Pt occurred at typical potentials and without a significant reconstruction of the original surface, CO stripping voltammograms on Ag@Pt were very unusual and exhibited both exceptionally strong binding of CO to the surface, and such a reconstruction of the surface that silver atoms were no longer compactly covered by platinum.

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## 1. Introduction

Recently, there is a significant interest in bimetallic metal nanoparticles since they exhibit optical, electronic, magnetic and

catalytic properties that are distinct not only from the bulk metals, but also from the properties of corresponding monometallic nanoparticles [1–5]. Among many kinds of bimetallic nanoparticles synthesized and investigated so far, very interesting are those obtained from silver and platinum. Although in bulk it is very difficult to prepare AgPt alloys due to a broad miscibility gap below 900 K [6] (even when melted together, it is impossible to form below ca. 400 °C silver–platinum binary alloys with compositions

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between about  $\text{Ag}_2\text{Pt}_{98}$  and  $\text{Ag}_{95}\text{Pt}_5$  [7]), many different kinds of silver–platinum bimetallic nanoparticles have been already synthesized. In general, AgPt nanoclusters may be obtained as relatively homogeneous alloy nanoparticles [8–12] or as core–shell nanostructures (both as platinum-covered silver cores [13–18] and as silver-covered platinum cores [19]). In addition, for core–shell nanostructures both the core and the shell may be also formed from an alloy.

Platinum and many of its alloys revealed very interesting catalytic properties. For example, AgPt alloy nanostructures exhibited enhanced catalytic activity for methanol electrooxidation [10,20], catalytic oxidation of *o*-phenylenediamine by hydrogen peroxide [10], and higher activity towards hydrogen evolution reaction [21]. Schaal et al. showed that the efficiency of the catalytic hydrogenation of 3,4-epoxy-1-butene increases significantly (by a factor of 3) when the surface of the Pt catalyst is covered with sub-monolayer of Ag [19]. Yu et al. showed that Ag@Pt core–shell nanoparticles deposited on multi walled carbon nanotubes exhibited attractive electrocatalytic activity for oxygen reduction [13]. High activity for oxygen electro-reduction was also reported by Lee et al. for AgPt nanoshells [22].

In many cases AgPt nanoparticles are synthesized by the galvanic replacement reaction between the “seed” Ag nanoparticles and  $\text{K}_2\text{PtCl}_4$  [14,21,23,24] or  $\text{H}_2\text{PtCl}_6$  [25,26] being the reactions between Ag and  $\text{K}_2\text{PtCl}_4$  or  $\text{H}_2\text{PtCl}_6$  as follows:  $2\text{Ag} + \text{PtCl}_4^{2-} \rightarrow \text{Pt} + 2\text{AgCl} + 2\text{Cl}^-$  [23,24] and  $4\text{Ag} + \text{PtCl}_6^{2-} \rightarrow \text{Pt} + 4\text{AgCl} + 2\text{Cl}^-$  [25,26], respectively. With the reduction of  $\text{PtCl}_4^{2-}/\text{PtCl}_6^{2-}$ , platinum is formed and deposited onto the surface of the nanoparticle and the silver “seed” is (partially) dissolved. According to previous investigations, platinum layer formed by such galvanic replacement is porous (discontinuous) [15,25] or/and silver–platinum alloy is formed [21]. The electrochemical experiments reported in this contribution will show that relatively large amount of silver can be easily stripped from such Ag@Pt nanoparticles, thus supporting previous assumptions about the poor quality of the platinum layer formed during simple galvanic replacement. Consequently, an improvement of the integrity of the platinum layer in Ag@Pt nanoparticles would be desirable. We will show that a significant improvement of the shell integrity can be achieved when Ag@Pt nanoparticles are synthesized by the seeded growth reaction including reduction of  $\text{PtCl}_4^{2-}$  with ascorbic acid at room temperature. A similar approach was also used to deposit platinum layers on gold cores. In both cases, the integrity of the formed platinum layers was verified by the electrochemical measurements.

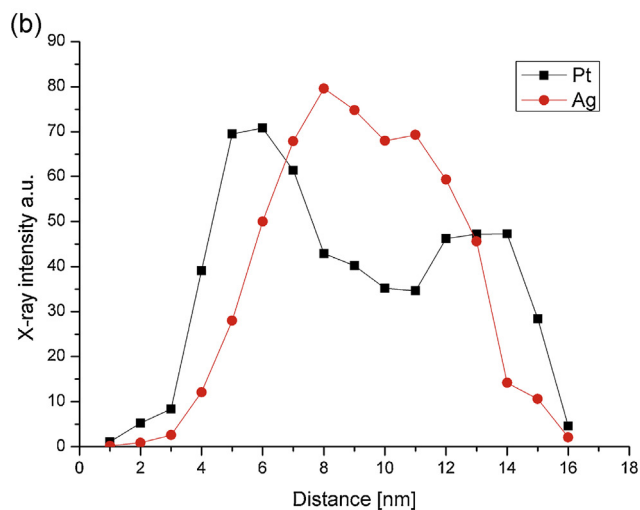
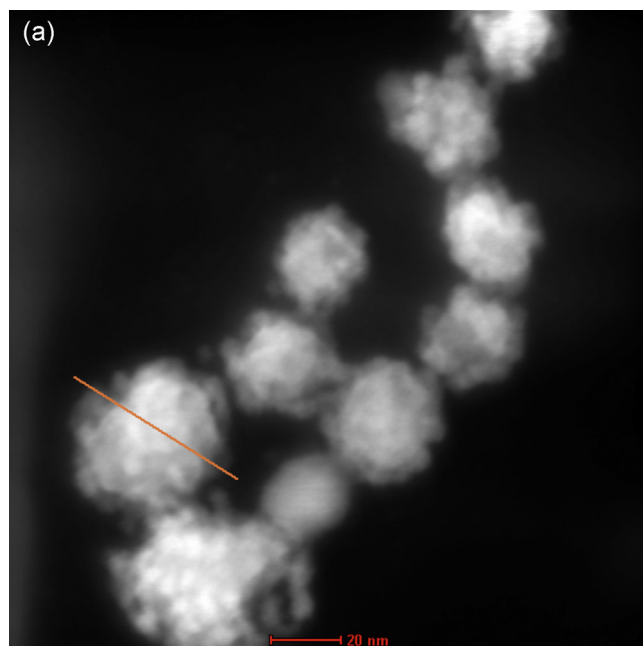
## 2. Experimental

### 2.1. Materials

Trisodium citrate dihydrate, ascorbic acid and silver nitrate were obtained from POCH SA. Potassium tetrachloroplatinate (II)  $\geq 99.9\%$  was purchased from Sigma–Aldrich. A 30 wt.%  $\text{HAuCl}_4$  solution in dilute HCl (99.99% trace metals basis) was acquired from Mennica Panstwowa. Sodium borohydride  $\geq 99\%$  was purchased from Fluka. All of the chemicals were of analytical reagent grade and were used without further purification. Water used for all experiments was purified in Millipore Milli-Q manner. All glass used was cleaned by washing in aqua regia and then very carefully rinsed with water.

### 2.2. Synthesis of Ag@Pt and Au@Pt nanoparticles

Ag@Pt core–shell nanoparticles were prepared using three different approaches: citrate method (CM), ascorbic method (AM) and microemulsion method (MM). The Ag seeds used in the CM and AM



**Fig. 1.** (a) TEM image of Ag@Pt nanoparticles (CM). (b) Intensity of characteristic X-ray radiation of Pt and Ag along the Ag@Pt (CM) nanoparticle. The drawn on the TEM image line (see (a)) represents the path where the beam was scanned to obtain the elemental composition analysis.

were obtained in the same way. In detail, 20 ml of water solution containing 20  $\mu\text{mol}$  of  $\text{AgNO}_3$  and 62  $\mu\text{mol}$  sodium citrate was prepared under constant stirring. Total amount of 10  $\mu\text{mol}$  of fresh sodium borohydride cold water (4 °C) solution was added quickly in 20 droplets of 20  $\mu\text{l}$  each. The final solution of Ag seeds was left for at least 24 h. The second step of CM consisted of addition of Ag seeds to boiling water solution of  $\text{K}_2\text{PtCl}_4$  followed by addition of sodium citrate. The mixture was boiled for 1 h. The second step of AM consisted of addition of ascorbic acid and  $\text{K}_2\text{PtCl}_4$ . In MM 0.1 M  $\text{AgNO}_3$  water solution was added to the mixture of *n*-heptane and surfactant polyethylene glycol dodecyl ether (BRIJ®30). The proportions water:oil:surfactant were such that microdroplets of water were formed and acted as microreactors. Upon addition of  $\text{NaBH}_4$  ( $n_{\text{NaBH}_4}:n_{\text{Ag}^+} = 2:1$ ) seeds of Ag, whose size was restricted by the size of a microdroplet, formed. The solution was left for at least 30 min. Then, a determined amount of  $\text{K}_2\text{PtCl}_4$  was added to the microemulsion and the mixture was left for at least 1 h. After

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