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Enhanced catalytic activity of solid and hollow platinum-cobalt nanoparticles towards reduction of 4-nitrophenol

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ABSTRACT

Previous investigations of hollow platinum nanoparticles have shown that such nanostructures are more active catalysts than their solid counterparts towards the following electrochemical reactions: reduction of oxygen, evolution of hydrogen, and oxidation of borohydride, methanol and formic acid. In this work we show that synthesised using standard galvanic replacement reaction (with Co templates) hollow platinum nanoparticles exhibit enhanced catalytic activity also towards reduction of 4-nitrophenol by sodium borohydride in water. Unlike in the case of procedures involving hollow platinum catalysts employed so far to carry out this reaction it is not necessary to couple analysed platinum nanoparticles to the surface of an electrode. Simplification of the analyzed reaction may eliminate same experimental errors. We found that the enhanced catalytic activity of hollow Pt nanoparticles is not only connected with generally observed larger surface area of hollow nanostructures, but is also due to the contamination of formed hollow nanostructures with cobalt, from which sacrificial templates used in the synthesis of hollow Pt nanostrustures have been formed. Because using sacrificial templates is a typical method of synthesis of hollow metal nanostructures, formed hollow nanoparticles are probably often contaminated, which may significantly influence their catalytic activity.

1. Introduction

Nanoparticles of noble metals are widely used as catalysts in many important fields [1–3]. High price of noble metals significantly limits, however, their practical applications. To decrease the consumption of expensive noble metals in practical commercial catalysts the following approaches have been applied: (i) alloying of noble metal with non-noble metals [4,5], (ii) formation of core-shell nanoparticles with noble metal shell and non-noble metal core [6,7], and (iii) formation of noble metal hollow nanostructures [8–12]. The last approach is especially interesting. Therefore, many groups synthesised hollow nanostructures and compared their catalytic activity with analogous solid objects [8–29]. In many works higher catalytic activity of hollow nanoparticles is explained by the fact that hollow metallic structures have lower density and hence higher surface area than analogous solid nanoparticles.

In the field of catalysis, platinum has attracted particular attention. Therefore, we decided to investigate platinum hollow nanoparticles. Previous comparative studies of solid and hollow platinum nanoparticles have revealed that hollow platinum nanoparticles are catalytically more active than their solid counterparts in the following electrochemical reactions: oxidation of methanol [13–24], oxidation of formic acid [25,26], oxidation of borohydride [27], reduction of oxygen [8–12] and evolution of hydrogen [28,29]. Hollow Pt nanostructures are often synthesised by the galvanic replacement reaction using sacrificial templates from a less active metal [11–18,26–28], especially cobalt [13–15,26–28]. Therefore, hollow Pt nanoparticles may be contaminated by the material from which sacrificial template was created. This may significantly influence their catalytic activity. In this work we decided to verify whether contamination by the other metal typically used for the synthesis of the sacrificial templates may, in some cases, significantly influence the catalytic activity of platinum nanostructures.

As mentioned above all works showing enhanced catalytic activity of hollow platinum nanostructures have been carried out using electrochemical setups and platinum nanoparticles were deposited on the surface of an electrode (in comparative experiments the same mass of nanospheres and solid Pt nanoclusters had to be deposited). Differences in the sticking of various platinum nanoparticles to the surface of an electrode (and hence differences in the efficiency of the electron transfer between nanoparticles and an electrode) may, however, introduce significant errors in these measurements. Therefore, it would be very useful to find a model

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heterogeneous catalytic reaction carried out using standard sols of platinum nanostructures – this should allow for simpler quantitative comparison of catalytic activity of hollow and solid platinum nanoparticles. We found that as such model reaction one can use reduction of 4-nitrophenol by sodium borohydride in water. 4-Nitrophenol is a common byproduct from the production of synthetic dyes, pesticides, and herbicides [30]. 4-Nitrophenol is easily reduced by sodium borohydride in the presence of metals nanoparticles [31,32]. In particular nanoparticles of coinage metals are excellent catalysts for this reduction [33]. The catalytic properties of various metal nanoparticles strongly depend on their electronic structure and their adsorption properties, and hence, for example, some bimetallic metal nanoparticles catalyse reduction of 4-nitrophenol with rates that strongly differ from a simple linear interpolation between the rates of the two pure metals [34,35]. Moreover, the progress of the reduction of 4-nitrophenol by sodium borohydride may be easily determined from a simple spectroscopic UV–vis measurement (from the temporal disappearance of the strong adsorption band due to the nitrophenolate). Therefore, reduction of 4-nitrophenol is one of the model catalytic reactions studied by many groups. Recently Xia et al. reported that under the similar catalysis conditions hollow gold nanospheres showed a higher activity than other gold nanocatalysts towards this reduction [36].

2. Experimental

2.1. Materials

$H_2PtCl_6{\cdot}6H_2O$, K_2PtCl_4, $PtCl_2$, and $CoCl_2{\cdot}6H_2O$ were purchased from Sigma-Aldrich. A 30% $HAuCl_4$ solution (99.99% trace metals basis) in dilute HCl was acquired from Mennica Panstwowa (Poland). Sodium borohydride and polyvinylpyrrolidone (PVP) with the average molar mass ~40,000 g mol^{-1} were purchased from Fluka Analytical. Ethylene glycol, 4-nitrophenol, sodium citrate (Na_3Cit) and NaOH were acquired from POCH S.A. (Poland). Nitrogen (≥99.999%) were purchased from Air Products. All chemicals were used without further purification or treatment. Water used for all experiments was purified by Millipore Milli-Q system and has the resistivity of *ca.* 18 MΩ cm.

2.2. Synthesis of nanoparticles

Pt nanoparticles were synthesised using slightly modified procedure proposed by Baranova et al. [37]. Briefly speaking $H_2PtCl_6{\cdot}6H_2O$ was dissolved in 20 ml of 0.15 M NaOH solution in ethylene glycol to obtain final concentration of H_2PtCl_6 equal to 0.03 M. The solution was rigorously stirred for 30 min. Then the solution was heated and refluxed for 3 h at 160 °C. The finally produced suspension of Pt nanoparticles was black. Solid Pt nanoparticles doped by cobalt were synthesised by the addition of $CoCl_2$ to the solution of Pt nanoparticles (the number of moles of introduces $CoCl_2$ was equal to the number of moles of platinum). Subsequently, the solution of sodium borohydride (n_{NaBH4}:n_{CoCl2} = 2.5) has been added to reduce cobalt cations. Then the reaction mixture was kept under air to oxidise deposited metallic cobalt layer.

Platinum hollow nanoparticles were synthesised using procedure similar to those reported by Liang et al. [13]. Briefly, 100 ml of water was placed in a three-neck bottle. Then 0.1 ml of 0.4 M $CoCl_2$ and 0.4 ml of 0.1 M Na_3Cit solutions were added. Subsequently, the flask was sealed and solution was deoxygenated by nitrogen influx for 30 min. After this time 0.1 ml of freshly prepared 1 M sodium borohydride solution was rapidly injected. The reaction mixture adopted dark brown colour which indicated formation of cobalt nanoparticles. An anaerobic environment is vital for this reaction because cobalt nanoparticles are unstable in the presence of oxygen. Solution of Co nanoparticles was kept under nitrogen influx for 1 h. In this time solutions containing 10 ml of water and various amounts (15–35 μl) of 0.1 M K_2PtCl_4 were prepared (for example, when using 15 μl of 0.1 M K_2PtCl_4 solution the ratio of numbers of moles of Pt and Co in the final reaction mixture was equal to 0.13:1). Finally, samples of 30 ml of prepared cobalt nanoparticles were added to the prepared K_2PtCl_4 solutions and kept under air. Obtained sol of hollow platinum nanoparticles was colourless. Schematic diagram of the synthesis procedure is shown in Fig. 1.

For comparison experiments Au@Pt nanostructures were also produced. These nanoparticles were synthesised using procedure developed by Nilekar et al. for the deposition of platinum layers on noble metals nanoparticles [38]. In the first step 0.2 mmol of $HAuCl_4$ and 54 mg of PVP were dissolved in 60 ml of ethylene glycol. The solution was heated to 60 °C. Then freshly prepared solution of $NaBH_4$ in ethylene glycol (160 mg of $NaBH_4$ was dissolved in 20 ml of ethylene glycol) was added dropwise to the $HAuCl_4$ solution. Colour of the reaction mixture became purple. In the next step 40 ml of obtained gold colloid was injected into the $PtCl_2$ suspension (0.068 mmol of $PtCl_2$ was added to 20 ml of ethylene glycol). The temperature of the reaction mixture was quickly ramped to 60 °C and then slowly brought to 100 °C and held in this temperature for 3 h.

2.3. Decomposition of 4-nitrophenol

The catalytic properties of metal nanoparticles were examined by the analysis of the kinetic of the reduction of 4-nitrophenol by sodium borohydride. Typically, 2 ml of water, 20 μl of 0.01 M aqueous solution of 4-nitrophenol and *ca.* 40 μl of suspension of metal nanoparticles (the actually added volume was corrected in such a way that the same mass of platinum was introduced into the cuvette) were placed into a 10 mm quartz cuvette (with nominal volume of 3.5 ml) from Starna Cells, Inc. In the next step 0.3 ml of 0.1 M freshly prepared solution of sodium borohydride were added. After this the colour of the solution suddenly changed from pale yellow to tight yellow, due to formation of 4-nitrophenolate ions. To investigate the decomposition of nitro-aromatic compounds UV–vis absorption spectra were recorded in the spectral range between 250 and 500 nm every 30 s.

2.4. Experimental techniques

UV–vis absorption spectra were collected using a Thermo Scientific Evolution 201 spectrophotometer. The transmission electron microscopy (TEM) analysis were carried out using LIBRA 120 (Zeiss, Germany) electron microscope working at an accelerating voltage of 120 kV and equipped with the In-column OMEGA filter. The samples of obtained suspensions of different platinum nanoparticles for TEM measurements were dropped onto Formvar-coated 400-mesh nickel grids (Agar Scientific) and allowed to dry. To determine the chemical composition of hollow Pt nanoparticles the samples of such nanostructures have been deposited on surface of the graphite substrate and studied with a Merlin field emission scanning electron microscope (Zeiss, Germany). The elemental analysis was performed with an energy-dispersive X-ray microanalysis (EDS) probe (Bruker).

3. Results and discussion

3.1. TEM analysis of obtained metal nanoparticles

Fig. 2 shows TEM micrographs of the obtained Pt and Au@Pt nanoparticles. As can be seen from images presented in Fig. 2a

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