



Methylviologen mediated electrochemical synthesis of catalytically active ultrasmall bimetallic PdAg nanoparticles stabilized by CTAC

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ABSTRACT

Efficient electro-synthesis of the monodisperse ultrasmall spherical mono- and bimetallic nanoparticles (NP) of Ag and Pd stabilized in the CTAC shell in solution bulk was carried out by methylviologen mediated reduction of equimolar amounts of Pd(II) and Ag(I) (1.5 mM) in the presence of CTAC (75 mM) at controlled potentials of the MV²⁺/MV^{•+} redox couple in water/0.1 M NaCl medium at room temperature. Metal ions are quantitatively converted to NP upon consumption of the theoretical amount of electricity. Sizes of isolated PdNP and AgNP are 5 ± 1 nm and 18 ± 5 nm, respectively. Bimetallic PdAgNP were obtained in three ways: (i) by preliminary synthesis of PdNP and subsequent reduction of AgCl (Pd/AgNP); (ii) by preliminary synthesis of AgNP and subsequent reduction of PdCl₂ (Ag/PdNP); (iii) by joint reduction of PdCl₂ and AgCl (Ag-PdNP). In all cases, a solid-solution alloy PdAgNP is obtained. The driving force for the alloy formation is the energy gain of ~33 kJ/mol of an alloy. In the first way, the NP size (8 ± 2 nm) and the Pd content in the alloy (76%) are slightly higher than in the other two methods (6 ± 1 nm, 50 and 68%), but the alloy crystallite size (2–5 nm) in NP is the same. PdNP and alloys NP exhibit a high catalytic activity toward the *p*-nitrophenol reduction and the Suzuki-Miyaura cross-coupling reactions. In the reduction reaction, an addition of silver to palladium decreases the catalytic activity of NP. The catalytic activity of alloys in the coupling reaction correlates with the Pd content in an alloy. And the catalytic activity of the alloy Pd/AgNP obtained in the first method of the NP preparation is higher than that of PdNP.

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1. Introduction

In recent years, metal nanoparticles (MNP) have attracted increasing attention due to their unique properties and diverse potential uses in catalysis, electronics, biomedicine, optics, analysis, etc. [1–7]. From the catalysis point of view, bimetallic (poly-metallic) NP are of no less interest. Bimetallic nanocatalysts are extensively studied in catalytic reactions for the preparation of various substrates and in energy conversion processes in fuel cells [8–16]. Certain successes have been achieved in the synthesis of different types of monodisperse bimetallic NP (solid solutions; intermetallics; composites, in particular core/shell type) as well as in the catalysis of chemical and electrochemical reactions by them [8–17]. In summary, it can be said that the catalytic properties of

bimetallic NP depend on the composition, structure, size and shape of NP. The catalytic characteristics (activity, selectivity, durability) can be tuned by the addition of the second metal to the first one due to fine modification of electronic properties and/or through structural factors. This can also lead to a decrease in cost of catalyst, the synergistic effect of two metals or the bifunctionality of the catalyst.

Palladium and silver containing bimetallic nanocatalysts (PdAgNP) catalyze a wide range of reactions: hydrogenation, coupling (Suzuki-Miyaura, Sonogashira, Heck reactions), hydrogen production by the decomposition of formic acid, selective and deep oxidation of organic substances, oxygen oxidation of CO, etc. [18–30]. For this purpose, NP of different architectures are used: alloys and nanocomposites of the Ag core/Pd shell type. The main method of their synthesis in solution bulk is a joint or stepwise chemical reduction of metal salts and metal complexes [18–22,31–34]. The physical [35–38] and biochemical [39]

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