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PALLADIUM NANOPARTICLES SYNTHESIS WITH CONTROLLED MORPHOLOGY OBTAINED BY POLYOL METHOD

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În această lucrare se prezintă sinteza nanoparticulelor de Pd cu morfologie controlată prin metoda poliol la 140°C, folosind diferiţi precursori de paladiu ($PdCl_2$ and K_2PdCl_4) şi stabilizatori (polivinil pirolidonă, PVP şi bromură de cetil trimetil amoniu, CTAB). Nanoparticulele de Pd obţinute din $PdCl_2$ prin reducere cu etilenglicol, în prezenţă de PVP sunt sferice, cu un diametru mediu de 7.5 nm. Prin utilizarea unui amestec de surfactanţi, PVP şi CTAB, au rezultat particule de Pd poliedrale cu dimensiuni medii de 8.4 nm în cazul reducerii în aer şi respectiv de 6.3 nm când sinteza s-a realizat în condiţii similare, dar în atmosferă de argon.

The paper deals with the synthesis of Pd nanoparticles with controlled morphology by polyol method at 140 °C, using different palladium precursors ($PdCl_2$ and K_2PdCl_4) and stabilizers (polyvinylpyrrolidone, PVP, and cetyl trimethyl ammonium bromide, CTAB). Pd nanoparticles synthesized from $PdCl_2$ in the presence of PVP by reduction reaction with ethylene glycol in argon atmosphere have spherical shape and 7.5 nm average size. By using a mixture of surfactants, PVP and CTAB, Pd nanoparticles resulted in polyhedral shapes with the average size of 8.4 nm (for those obtained in air), and 6.3 nm (for those synthesized in argon atmosphere), respectively.

Keywords: Pd nanoparticles, polyol method, controlled morphology

1. Introduction

Noble metal nanocrystals play an important role in different fields of science, such as catalysis, medicine, electronics, etc. For most of these applications, the size, shape and size distribution of metal nanoparticles constitute the key factors. As a consequence, efforts have been focused on the synthesis of noble metal nanoparticles (NP) with well-controlled morphology [1, 2]. Several synthesis strategies are applied to achieve the morphology control. Among these,

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the polyol method consists in using ethylene glycol as reducing agent for metallic cations that are reduced to metallic colloids by receiving electrons from the oxidation of ethylene glycol to glycol acid, which is present in its deprotonated form as glycolate anions in alkaline solution [3]. The use of polyalcohols, like ethylene glycol, as reducing agents for obtaining metallic nanoparticles has some advantages, due to the formation of ketones or carboxylic acids as by-products, which can be easily removed from the reaction mixture – unlike the residues of other reducing agents such as sodium borohydride or other boranes.

The morphology of palladium nanoparticles strongly depends on the reaction conditions like temperature, duration, pH, and the type of metallic precursor and stabilizer. *Thiébaut* [4] has reported that the palladium particle size distribution of the colloidal solution decreased with increasing pH. Adding a certain amount of base in the reaction mixture leads to an increase of the reduction rate, thus determining smaller particle size formation. The paper presents our results on the synthesis of Pd nanoparticles by polyol method by using different palladium precursors and stabilizers.

2. Experimental

The palladium nanoparticles were synthesized by the polyol method. The function of the stabilizer was fulfilled by polyvinylpyrrolidone (Fig. 1), a non-ionic polymer (Sigma Aldrich, M=10000) and a mixture of PVP and cetyl trimethyl ammonium bromide, $C_{16}H_{29}N^+(CH_3)_3Br$ (Sigma Aldrich, ≥ 98%), a cationic surfactant, respectively.

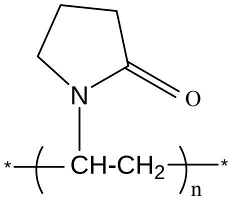

Fig. 1. Structure of polyvinylpyrrolidone

In a typical synthesis, in a three-neck flask equipped with a reflux condenser, a corresponding amount of surfactant was dissolved in ethylene glycol. Separately, Pd precursor was solubilised in ethylene glycol. The reduction reaction of Pd(II) ions for all the samples was performed at 140 °C, 90 minutes under magnetic stirring in an oil bath. The introduction of Pd(II) solution in ethylene glycol was done by hot injection at 140 °C.

For the Pd sample named **Pd1**, the raw compounds are palladium (II) chloride (that is not soluble in ethylene glycol), and PVP. Firstly, $PdCl_2$ was dissolved in concentrated ammonia according to the chemical reaction (1), and then ethylene glycol was added. The solution of Pd(II) ions in ethylene glycol was added next, by hot injection to the reaction mixture. The PVP concentration in ethylene glycol was of 30 mM and the molar ratio, Pd^{2+} : PVP (the repeating unit), was of 1:10. The reduction reaction was performed in a protecting argon atmosphere in closed system, at 140 °C, for 90 minutes.

$$PdCl_2 + 4NH_3 \rightarrow [Pd(NH_3)_4]Cl_2 \qquad (1)$$

For the synthesis of the sample named **Pd2**, potassium tetrachloro palladate, K_2PdCl_4, and a mixture of PVP and CTAB, in a molar ratio, K_2PdCl_4 : PVP : CTAB, 1:20:15, were used. Both stabilizers were dissolved in ethylene glycol and their solution was heated under magnetic stirring in argon atmosphere at 140 °C. Then, K_2PdCl_4 solution in ethylene glycol was added; the concentration of Pd^{2+} ions in the reaction mixture was of 5 mM. The reduction reaction was performed under continuous argon bubbling. The sample named **Pd3** was synthesized in the same conditions as for Pd2 sample, but in air. Pd colloids are stable several weeks.

The Pd samples were washed with acetone and then with ethanol several times to remove the organic compounds and most of the stabilizers by centrifugation. The reduction reaction was controlled by UV-vis spectroscopy on an Able Jasco V560 spectrophotometer. A drop of alcoholic suspension of separated Pd nanoparticles was placed on a carbon film coated copper grid and investigated by transmission electron microscopy and selected area electron diffraction (SAED), by using a high resolution transmission electron microscope (HRTEM) TECNAI F30 G^2 with linear resolution of 1Å.

3. Results and discussions

Pd(II) ions forms stable complex as compounds with nitrogen containing organic compounds. So, palladium precursors coordinate to PVP before the reduction reaction. During and after the reducing process, Pd colloids are stabilized by hydrophobic interactions between the hydrophobic part of the stabilizer and the metallic surface. The reducing process was monitorized by performing Uv-vis spectra. In figure 2 it can be observed the UV-vis spectra of Pd(II) – PVP in ethylene glycol. The peak at 294 nm can be assigned to $[Pd(NH_3)_4]^{2+}$, while the peak at 212 nm corresponds to PVP. A clear shift of the baseline absorbance is observed indicating the light scattering effects due to Pd colloid formed in the solution. The solution color changed from yellow to brown. By the reducing process, the peak from 294 nm shifts towards lower wavelengths (262 nm) and another peak at 314 nm appears, that could be assigned to the presence of $[PdCl_4]^{2-}$, which could be formed as intermediary product besides Pd colloids.

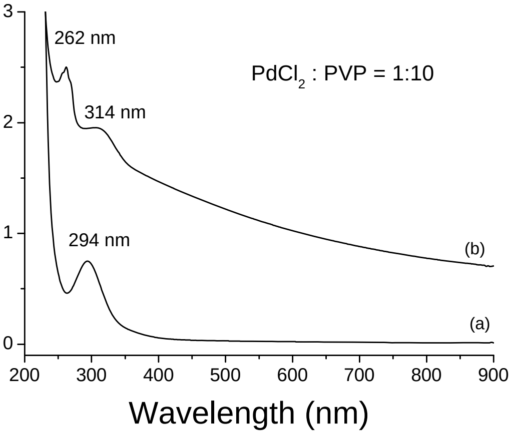

Fig.2. UV-vis spectra of $PdCl_2$ – PVP reaction mixture before the reducing process *(a)* and after 1 h *(b)*

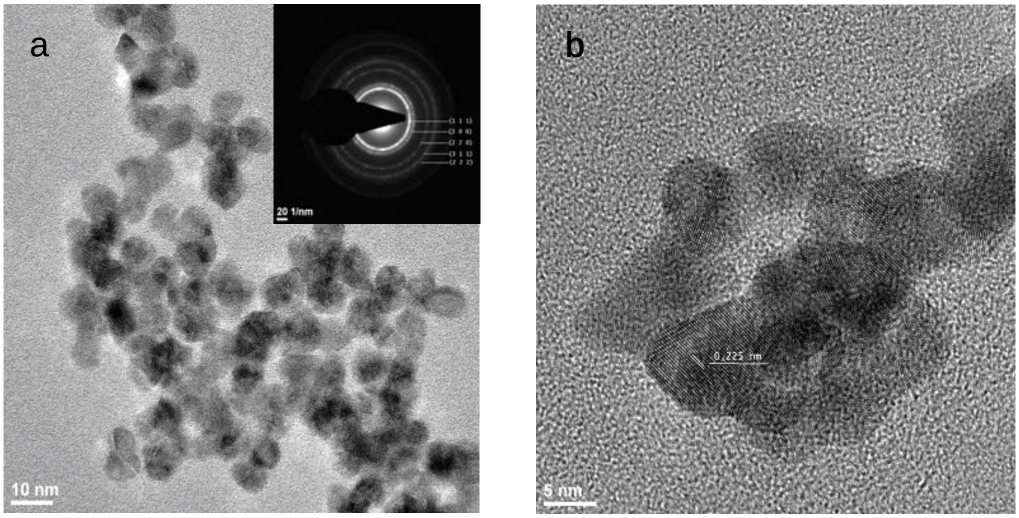

Fig. 3. TEM image of the **Pd1** sample; the SAED pattern (inset) taken from an assembly of Pd nanoparticles indicating that these are highly crystalline *(a)*. HRTEM image of the Pd1 sample *(b)*

Pd nanoparticles synthesized in the presence of PVP as stabilizer (Pd1 sample) are spherical with 7.5 nm average size, determined by measuring approximately 100 particles by using ImageTool software. The TEM analysis has shown the formation of metallic Pd nanoparticles with narrow size distribution, in the range of 5-10 nm. Mainly, the spherical nanoparticles are monodisperse, but some Pd polyhedral clusters consisting in two crystallites can be observed (Fig. 3a). In the HRTEM image (Fig. 3b), one can notice the fringes separated by 2.25 Å, which agrees with the {111} lattice spacing of cubic metallic palladium nanoparticles, Fm3m symmetry group (ICDD 05-0681). The selected area electron diffraction analysis demonstrates the face-centered cubic Pd nanoparticles formation (Fig. 3a inset).

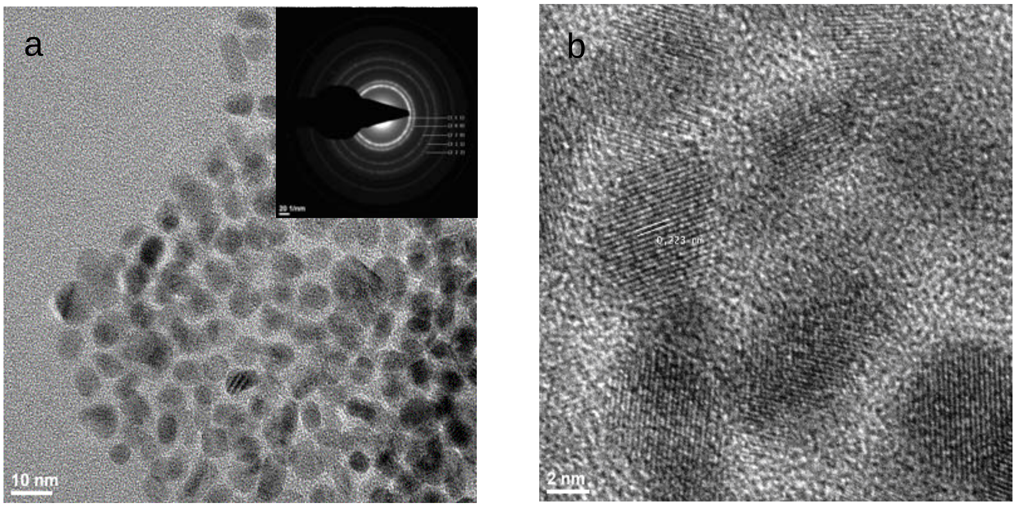

Fig. 4. TEM image of the **Pd2** sample (inset, the SAED pattern of Pd nanoparticles) *(a)*;. HRTEM image of the **Pd2** sample *(b)*

Using a mixture of surfactants, PVP and CTAB has led to the obtaining of metallic crystalline Pd nanoparticles (**Pd2** and **Pd3** samples) with polyhedral shape (Fig. 4a inset). TEM analysis of **Pd2** sample synthesized in argon protecting atmosphere shows the polyhedral Pd nanoparticles formation with 6.3 nm average size, statiscally calculated by measuring around 100 particles. The Bragg lattice spacing is 2.23 Å according to metallic palladium ICDD 87-0645, as HRTEM investigation has proved (Fig. 4b). The relative low contrast of Pd nanoparticles could be explained by the presence of some polymeric species on the surface of metallic particles that could not be removed in the wahing step. *Zhang, Y et al.* [5] have reported the obtaining of cubic Rh nanoparticles with 6.4 nm average size by using a mixture of surfactants, PVP and tetradecyl trimethylammonium bromide. These authors have reported the synthesis of Pd nanoparticles from ammonium hexachloropalladate, in the presence of the same mixture of surfactants as in the case of the formation of Rh nanoparticles. They have obtained Pd nanoparticles by the reduction of the ammonium hexachloropalladate at 140 °C, 1h with diameter in the range of 10-26 nm and 17.4 nm average size.

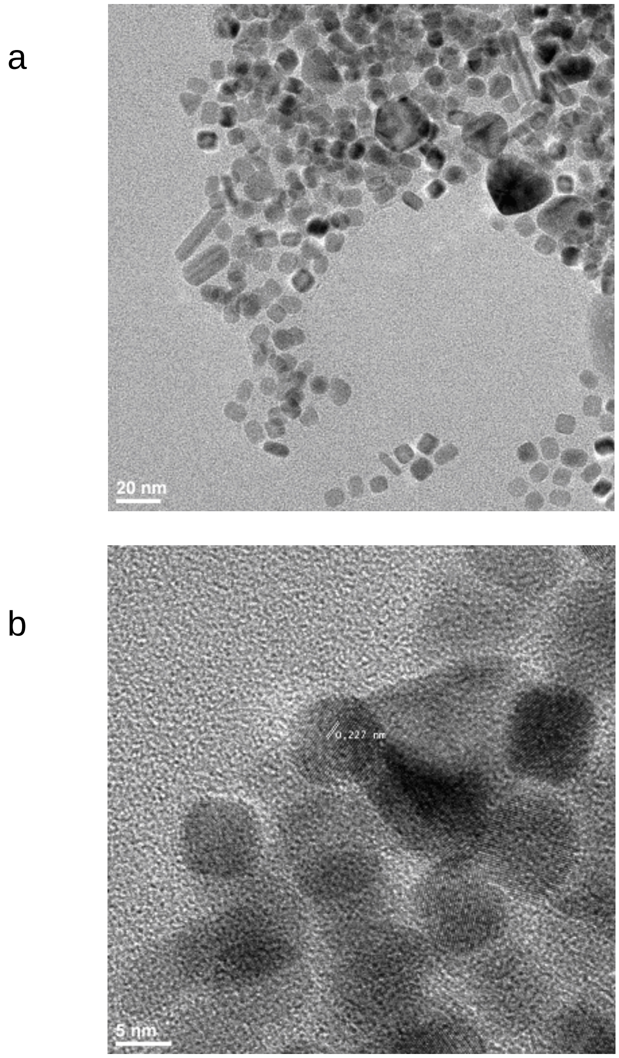

Fig. 5. TEM image of the **Pd3** sample *(a)*; HRTEM image of the **Pd3** sample *(b)*

The synthesis of **Pd3** sample was performed in the same conditions as for the **Pd2** sample, but in air. The TEM analysis has shown the formation of polyhedral Pd nanoparticles with 8.4 nm average size. Generally, Pd nanoparticles are monodisperse, but some clusters consisting of few crystallites can be noticed (Fig. 5a). In Fig. 5b, one can observe the lattice spacing of 2.27 Å characteristic to metallic Pd nanoparticles with cubic symmetry (ICDD 01-1310). The TEM investigation has also shown the formation of some species of 20-60 nm length and 5-11 nm, that could be some carbon nanotubes resulted by ketones decomposition (the by products of the reducing reaction). *Xiong, Y.,* [6], has found that the oxygen could be responsible to the selective removal of initial formed twinned Pd particles by dissolution with $[PdCl_4]^{2-}$ formation. Thus, after initial dissolution stage, $[PdCl_4]^{2-}$ are reduced with an increased reduction rate. Therefore, uniform single crystal cubooctahedra of Pd with 8 nm average size could be synthesized by polyol method at 110 °C by controlled oxidative etching process.

6. Conclusions

Pd nanoparticles with uniform size and shape by polyol process at 140 °C were synthesized. It is possible to control the morphology of Pd nanoparticles by choosing the suitable stabilizer and synthesis atmosphere. This is important for the future catalytic application. Using PVP as stabilizer, spherical Pd nanoparticles were obtained with 7.5 nm average size. In the case of the syntheses performed in the presence of a mixture of surfactants, PVP and CTAB, polyhedral Pd nanoparticles were obtained, larger for the reduction process in air than those prepared in argon protective atmosphere.

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