Synthesis and Characterization of Pd /Ag Nanomaterial

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Synthesis of a Pd/Ag nanopowder was achieved by reduction of tetraaminopalladium(II) sulphate with formic acid in the presence of macroporous granular silver support. The product was characterized by chemical and structural analyses as: inductively coupled plasma-mass spectroscopy (ICP-MS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM). The nanomaterial may have potential electrochemical and/or catalytic applications, being a more economical alternative to pure palladium nanoparticles due to high silver content.

Keywords: nanomaterial, Pd/Ag, tetraaminopalladium(II).

Synthesis of a nanomaterial by depositing palladium on silver support aims to achieve a product which meet the properties of the substrate and of deposited metal too; such material with high specific surface has potential electrochemical and/or catalytic applications.

Metallic silver has specific applications based on some remarkable properties, being the metal with the highest electrical and thermal conductivity. Palladium has outstanding catalytic properties being used along with platinum for flue gas catalytic converters. Finely divided palladium is used in hydrogenation and dehydrogenation reactions, usually deposited on activated charcoal, various other catalytic applications involving its use [1]. Palladium membranes are used to achieve high purity hydrogen [2]. Palladium is used as electrode for electrochemical applications and sensors. Potentially hydrogen storage applications should be based on large hydrogen amounts absorption [3].

Various routes have been used to obtain palladium nanostructures. Being a noble metal, Pd(II) precursors can be easily reduced with weak reducers reagents. Reduction of some palladium precursors was achieved in aqueous solution with formate using sodium polyacrylate as stabilizer [4] by sonochemical methods [5], by substitution of Co [6] or by exogene biosynthesis [7]. Usually, various palladium nanostructures were obtained in alcohols as solvents and reducers, or ethylene glycol with PVP as stabilizer [8-10]. Reduction of some palladium precursors was achieved with thioethers in toluene [11], with $NaBH_4$ in the presence of phosphines [12], with superhydride in THF in the presence of thiols [13, 14], or with $NaBH_4$ in inverse emulsions with toluene, tetraoctylammonium bromide (TOAB) and octadecyl mercaptan [15]. A high specific surface catalyst has been synthesized by thermal decomposition of $[Pd(NH_3)_4][Pd(N_3)_4]$ complex mixed with Al_2O_3 [16].

The synthesis procedure of Pd/Ag nanomaterial presented in this study aims to be feasible and to achieve a high silver percent and also a high degree of support coverage.

Experimental part

Materials and devices and methods

Pd/Ag nanomaterial synthesis was achieved by reduction of $[Pd(NH_3)_4]SO_4$ solution with formic acid in the presence of macroporous silver previously synthesized.

Granular macroporous silver (support) was obtained by reducing silver sulphate with ascorbic acid in aqueous heterogeneous phase [17]. An ammonia solution of tetraamminopalladium(II) sulphate, *p*H 9.5-10 (Wieland) with 5g/L Pd(II) was used as palladium precursor. Formic acid (85%) was used as reducing agent. Double demineralized water and 95% ethanol were used for washing.

Preliminary tests were carried out in test tubes. For preparative synthesis, reagents were added into 1 liter flask with three necks provided with a magnet (5cm). The flask was put on a magnetic stirrer provided with heating (AG-2). A reflux condenser and a temperature sensor (Fluke 80PK-22) connected to a Fluke 289 multimeter in data logger mode were fitted.

A Jasco V-560 apparatus was used to control the Pd(II) reduction by UV-Vis spectra. A Thermo X series device was used to determine Pd percent of the product by ICP-MS. Images were performed on an MC5A optical microscope and on a Philips CM 20 TEM. A Rigaku Miniflex 2 apparatus was used for registration of X-ray diffraction using Cu-Kα_1 line between 2θ angles 30 - 70°. FTIR spectroscopy investigations were done on a Perkin Elmer TWO Standard apparatus. Electrical conductive properties were evaluated using a Fluke 289 multimeter by measurement of the resistance of a cylindrical column sunk material placed in a glass tube with 23 cm length and 8.1 mm internal diameter, tube ends being connected to multimeter by silver disks.

Some preliminary tests preceded Pd/Ag nanomaterial synthesis.

Preliminary tests

Testing method of reducing metallic precursor without support

To test the reducing of $[Pd(NH_3)_4]^{2+}$ precursor in solution with formic acid (without porous silver support), 5 mL Pd

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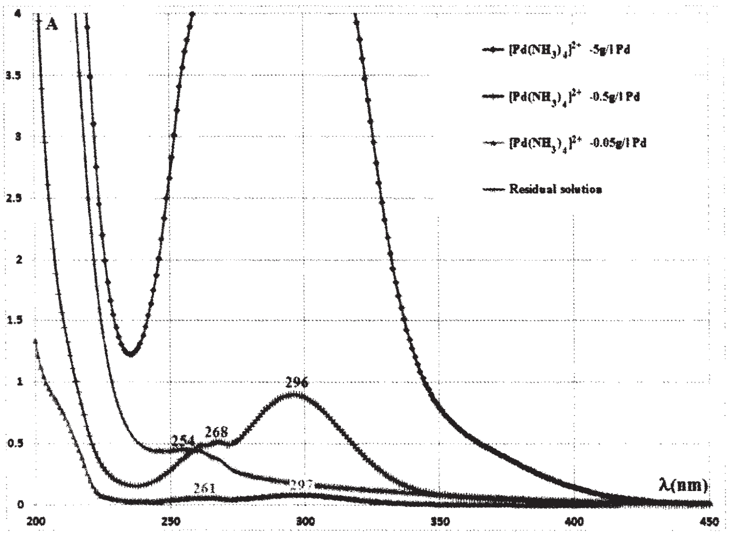


Fig. 1. UV-Vis spectra of solutions containing $[Pd(NH_3)_4]^{2+}$ ions and of the residual solution

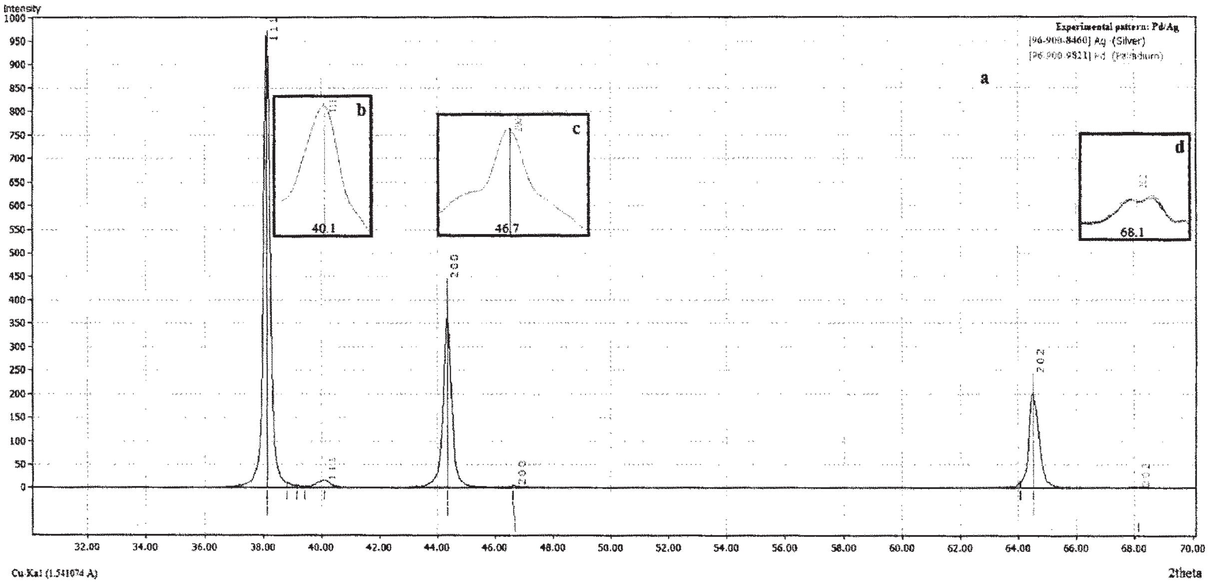


Fig. 2. XRD graph of Pd/Ag nanomaterial (a); zoom on Pd peaks (b,c,d).

precursor was put in a test tube and 0.05 mL formic acid was added, mixture being slowly heated. It was noted that a layer of metallic palladium (mirror) is readily obtained on the tube walls.

Testing synthesis route of Pd/Ag nanomaterial

10 mL Pd precursor (equivalent to 50 mg Pd), 0.1 mL formic acid and 0.950 g macroporous granular silver were put in a tube. The tube was heated until boiling, noting the selective deposition of palladium only on macroporous silver. The product was filtered and washed repeatedly with water. A relatively homogeneous gray deposition was observed using an optical microscope. The control of Pd(II) reduction reaction was obtained using UV-Vis spectra: the initial solution containing $[Pd(NH_3)_4]SO_4$ with 5 g/L Pd(II) has a very strong absorbance at ~ 290 nm, the peak exceeding the measuring range of the device. The main peak was observed with reasonably intensities on aqueous dilutions containing 0.5 g/L Pd(II) (at 296 nm) or 0.05 g / L Pd(II) (at 297 nm), but in these cases a secondary peak at 268/261 nm was also observed. The residual solution separated after filtration has one single weak peak at 254 nm (fig. 1). The low absorbance of residual solution with the absence of ~ 296 nm characteristic peak for $[Pd(NH_3)_4]^{2+}$ confirm completion of reaction.

Pd/Ag nanomaterial synthesis

Same proportions of reagents as in the preliminary stage of testing method for depositing palladium on macroporous silver support have been used. A mixture of 200 mL Pd precursor solution (equivalent to 1 g Pd), 2 mL formic acid and 19 g macroporous granular silver was heated under stirring in a flask up to boiling point.Solution was maintained at boiling under reflux for 20 min, then heating was turned off and the flask was cooling in water, the condenser and the magnetic stirrer being removed. Reaction started above 40°C, being notified the deposition of Pd on Ag by darkening of the suspension. The product was separated by vacuum filtration, it was washed repeatedly with water and finally with ethanol. The product was dried in an oven at 110°C for 30 min. A quantity of 19.768 g material was obtained.

Results and discussions

Chemical and structural characterization of Pd/Ag nanomaterial

The ICP-MS assay has shown 4.5% Pd.

XRD diagram (fig. 2) shows three intense peaks at 38.1°, 44.3°, 64.5° corresponding to (111), (200), (202) crystalline planes of fcc-Ag and three weak peaks at 40.1, 46.7 and 68.1° corresponding to (100), (200) and (202) Miller indices of fcc-Pd, in agreement with the composition determined by ICP-MS. The Pd/Ag nanomaterial has gray appearance

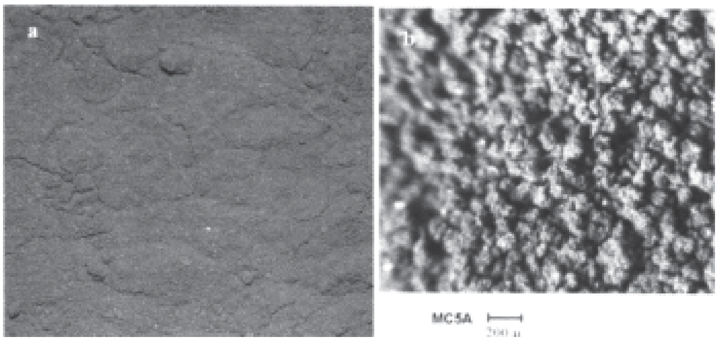
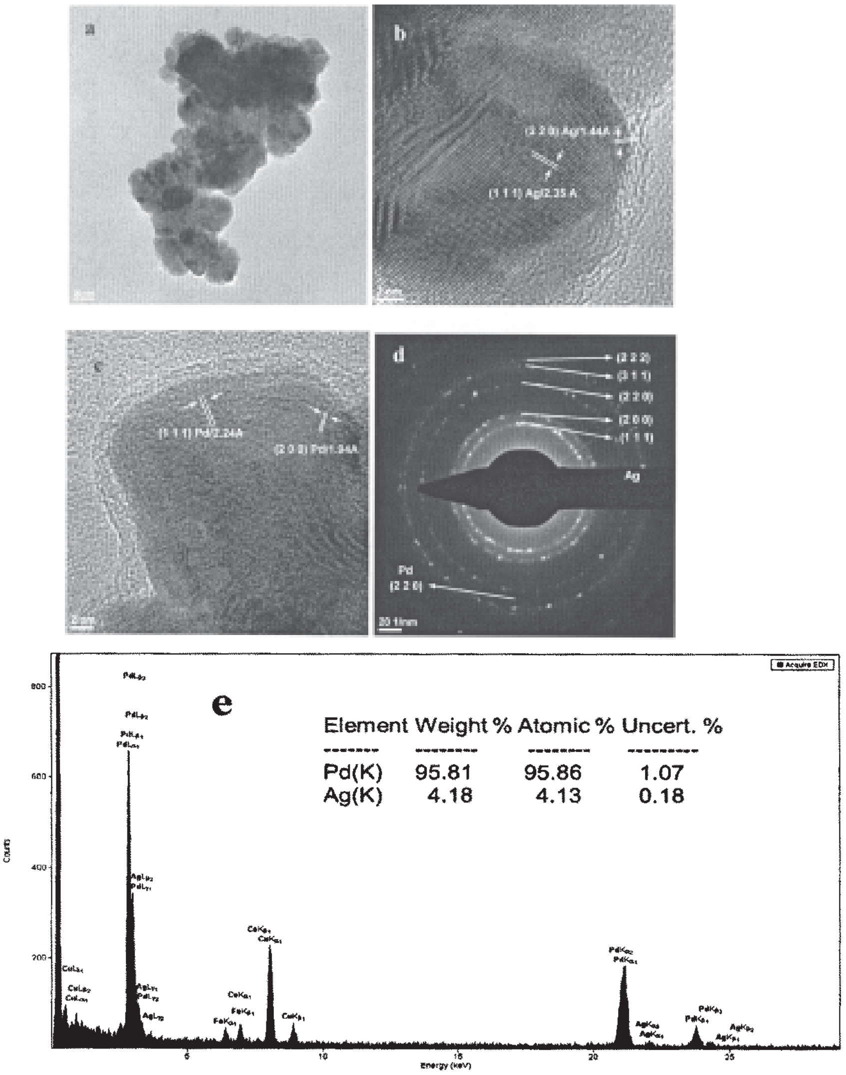


Fig. 3. Pd/Ag nanomaterial image (a). Detail under the optical microscope (b)



Element	Weight %	Atomic %	Uncert. %
Pd(K)	95.81	95.86	1.07
Ag(K)	4.18	4.13	0.18

Fig. 4. TEM (a), HRTEM (b, c), SAED (d) iages, EDX graph and surface composition (e) of Pd/Ag nanomaterial

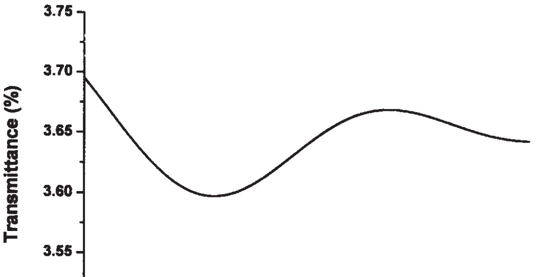


Fig. 5. FTIR spectrum of prepared Pd/Ag nanomaterial

(fig. 3a), more fine compared to the support which is silvery and composed of irregular sized granules [17]. Relatively homogeneous granules of about 100 μm were observed using an optical microscope (fig. 3b). TEM images (fig. 4a) show aggregates of particles. HRTEM images (fig. 4 b, c) put in evidence details of the Ag and Pd crystallites. SAED pattern (fig. 4d) show frequently points of crystalline planes of Ag and rare points of Pd in agreement with the composition. From EDX graph (fig. 4e) it could be observed the dominant presence of Pd lines, Ag lines having small amplitudes. This result, apparently contrary with the Pd content and the small values of XRD Pd peaks might be due to the continuity of palladium layer deposited on the support, EDX being a surface analysis.

The FTIR spectrum of Pd/Ag powder shows the absence of bands characteristic to unreacted starting materials or other impurities. A band at 3350 cm^{-1} may be assigned to the hydroxyl groups (fig.5).

The main characteristics of Pd/Ag nanomaterial compared with those of macroporous silver substrate are shown in table 1. The nanomaterial electrical resistivity is

Table 1
COMPARATIVE CHARACTERISTICS OF MACROPOROUS SILVER SUPPORT, RESPECTIVELY OF Pd/Ag NANOMATERIAL

Characteristics	Ag-macro.	Pd/Ag	Remarks
Pd (% *weight*)	-	4.5	ICP-MS
Crystallites medium size (nm)	39.29	-	XRD
Pd coverage (%)	0	95.86	EDX
Reaction yield (%)	-	90	ICP-MS
Apparent density (g/cm^3)	1.397	1.62	Gravimetry
Porosity (%)	86.7	84.7	
Resistivity (Ωm)	2.02×10^{-5}	6.98×10^{-4}	Electrical resistance

greater than support due to its discontinuity, contact between particles being achieved via palladium, surface layer having a resistivity greater than of pure silver (10.56 μΩ cm electrical resistivity for bulk palladium [18, 19], compared with 1.59 μΩ cm electrical resistivity for bulk silver [19]). Electrical resistivity for silver nanostructures have values larger then bulk silver (4.6- 44.3 μΩ m resistivity for silver depositions obtained by ink-jet method [20]).

Conclusions

Synthesis of Pd/Ag nanomaterial was achieved with high yield by reducing tetraaminopalladium(II) ion with formic acid in the presence of macroporous granular silver support. The process is easily accessible, allowing obtaining a nanomaterial with high contain palladium coating. The nanomaterial may have potentially electrochemical and/or catalytic applications, being a more economical alternative to palladium nanoparticles due to high percentage of silver, cheaper than palladium.

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