Influence of n-alkylamine ligands in properties of magnetic palladium nanoparticles

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Size confinement to a nanometer scale has induced effects not observed in macroscale. That is the case of magnetic properties, which are often remarkably different from those of their bulk counterparts, in particular in the case of materials that are known to have nonmagnetic or antiferromangetic ground states in bulk [1]. A candidate material for controllable magnetism could be palladium because this metal is nearly ferromagnetic, lying close to a ferromagnetic instability [2]. Consequently, Pd magnetic nanoparticles could play an important role not only in the understanding magnetism at nanoscale, but also in the applications to magnetic devices and especially in biomedical fields because of its good biocompatibility.

In this sense, monodispersed magnetic palladium nanoparticles, between 2 and 4 nm, surrounded by amine ligands have been successfully synthesized and characterized by infrared spectroscopy (IR), X-Ray Diffraction (DRX), thermogravimetry (TG) and Transmission Electron Microscopy (TEM). Finally, the magnetic behaviour has been studied by magnetization measurements. Additionally, the effect of ligand chain length on the particles properties has been analyzed.

Palladium nanoparticles were synthesized following the Brust method [3], which is based on the transfer of $NaPdCl_4$ from an aqueous solution to toluene, using tetraoctylammonium bromide (TOAB) as the phase-transfer reagent. The reduction of the solution, with $NaBH_4$ aqueous solution, in the presence of $CH_3(CH_2)_nNH_2$ (n = 3, 5, 7, 9) ligands yields four kinds of Pd-NR nanoparticles with different chain length. To confirm the attachment of the n-alkylamine ligands to Pd IR spectroscopy was used.

In order to know the stability of the samples and the quantity of organic matter, thermogravimetric measurements were performed. A first mass loss (4-8 %), related to the absorbed solvent, takes place at temperature around 100 ºC. Subsequently, a loss corresponding to the capping agent, above 200 ºC, was observed in the 11% to 28% range depending on the sample.

Size distributions of the nanoparticles are very homegeneous. TEM measurements also indicate that the particle size of each of the four studied systems fluctuate in a specific size range. Furthermore, the particle size decreased with the increase of the carbon chain length of the $CH_3(CH_2)_nNH_2$ ligand. From these measurements together with TG analysis, Pd:N relation on nanoparticle surfaces have been estimated ranging from 6:1 to 1:1, depending on the sample.

The ferromagnetic character of the nanoparticles has been proved by the presence of hysteresis loops in M vs H measurements at 293 K and 5 K. The samples present saturation at low field, around 10 kOe, and coercive fields between 60 and 100 Oe. However, the obtained magnetization values are notoriously variable from one sample to another. Electron magnetic resonance measurements corroborate these results.

References

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