

Synthesis, characterization and functionalization of magnetic nanoflowers

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Abstract: Core-shell magnetic flower-like gold nanoparticles were synthesized. The particles have diameters in the 100-500 nm range and were superparamagnetic. Surface chemistry was used to chemically modify the nano-flowers. Attached enzymes showed good activity after several stages magnetic collection, drying and redispersion steps.

Flowerlike nanoparticles (FNP) show potential applications in fields like sensors, biology, catalysis and optics. In particular gold FNP are promising in chemical and biochemical sensing. So far, gold FNP have been obtained mainly deposited onto substrates [1,2]. However, the synthesis of such nanostructures in solution has proved to be a difficult task. In this work we present the synthesis, characterization and chemical modification of magnetic core-shell FNP, consisting of a gold flower-like shell grown onto a magnetic core.

Magnetite nanoparticles were synthesized by co-precipitation of ferric and ferrous ions. In a lapse of 10 minutes, 25 ml de 25 % NH₃ were added at room temperature to 100 ml of a solution containing 12 g de FeCl₃ and 6 g de FeCl₂ in 0.1 % HCl. The precipitate, composed by Fe₃O₄, was collected with the aid of a magnet, washed with distilled water to eliminate the excess of ferric ion (characterized by its orange color) and dried at 60°C during an hour. Then, 30 mg of Fe₃O₄ were added to a solution 80 ml of toluene containing 0.25 ml of oleic acid (OAc) and 0.25 ml of oleilamine (OAm), and dispersed by means of ultrasonic agitation during 15 minutes. A solution of gold in toluene was obtained by a two-phase extraction between a solution of tetraoctilammonium bromide in of toluene and an aqueous solution containing of KAuCl₄, the aqueous phase being discarded. Then, the magnetite dispersion was added to the organic phase obtained from the extraction and 100 mg of hydroquinone dissolved in 20 ml of 2-propanol were added. After three hours, nanoparticles were collected with a magnet, washed twice with toluene under ultrasonic agitation, and re-dispersed in a solution of OAc and OAm. By varying the ratio OAc/OAm FNP in the range 100-500 nm were obtained.

In figure 1 SEM and HRTEM of the FNP are shown. The flower-like structure can be appreciated, where the “petals” are formed by (111) planes of gold. VSM measurements showed that the FNP are superparamagnetic.

The FNP can be easily functionalized. In a typical experiment the particles were suspended in a solution of p-mercaptobenzoic acid (PMB) by 30 minutes, magnetically collected, washed and dried. In figure 2, vibrational spectra of the functionalized particles is shown. The bands due to the vibrational modes of the PMB bounded to the FNP are clearly depicted. In further experiments horseradish peroxidase (HRP) was attached to the PMB-modified FNP through the carbodiimide reaction. The FNP-HRP were collected and transferred to an electrochemical cell, where the enzymatic activity of the enzyme was measured (figure 3). The experiments show that the magnetic FNP can be a powerful tool in biochemical sensing.

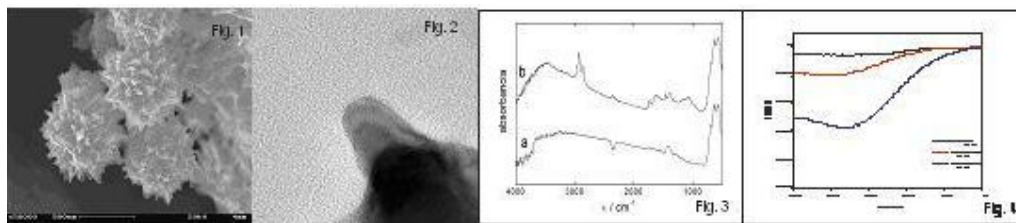


Fig.1: SEM image of nanoparticles. **Fig.2:** HR-TEM image of a petal. **Fig.3:** IR spectrum of a functionalized particle with cysteine. **Fig.4:** Electrochemical measure of HRP activity.

1.- G. Duan, W. Cai, Y. Luo, Z. Li and Y. Li; Appl. Physics Lett. **89** (2006) 211905.

2.- J-H Kim, T. Kang, S.M. Yoo, S.Y. Lee, B. Kim and Y-K. Choi, Nanotechnology **20** (2009) 235302.