

Optically and catalytically functionalized multiple-cored magnetic nanoparticles

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Nanotechnology has reached the stage of development where the subject of most investigations is not individual nanoparticles but rather systems of much greater complexity. The diversity of the ultimate magnetic functionalities of these complex nanomaterials systems finds place in applications including such far-reaching challenges as bio-related sensors, [1] or catalysts. [2] This fascinating approach of artificial nanostructuring to create completely new ever-progressing magnetic materials and technologies was demonstrated to be directly dependent on the further improvement of the current materials used. The applications underlined will become feasible if previously one can exert control on the magnetism displayed.

With that in mind, two strategies were developed, focusing the synthetic efforts on the creation of multiple-cored magnetic nanoparticles, which tie together the intrinsic properties of the individual constituents (M_s , K_1 , etc.) and the collective properties of the final composites (dipolar interactions, grain-boundary or exchange-coupling effects between the subunits forming them).

The first strategy describes the synthesis of relatively large magnetic plasmonic composite particles. Their magnetic characteristics (M_s and H_c) reach sufficiently increased values if compared to other hybrid composites, owing to a compromise between size, percentage of the soft magnetic material, and to a remarkable morphology consisting of inner (smaller) cobalt boride clusters assembled as larger spheres (magnetic interactions) and stabilized with an outer shell of silica. These magnetically stable silica-coated cobalt boride spheres were optically functionalized, acquiring a characteristic SPB (surface plasmon band) (figure 1, left). Outstandingly, due to the silica formation procedure (acid- or acid- and base-catalyzed), silica shells between the optical and magnetic functionalities were proven to undergo chemical and morphological changes translated into an optical response. [1]

To check envisioned activities in fields, such as sensing, or for in vitro applications (in vivo applications are extremely hindered due to the high percent of cobalt in the magnetic core), the magnetic and optically active nanostructures were subjected to the following tests in which controlled fractions (1 and 10 vol %) of water were added to the ethanolic composite solutions, in restricted periods of time. In the presence of water in the solution, the composites with acid-catalyzed silica were subjected to characteristic morphological changes, for example, an increase in the typical thickness and roughness of the silica shell. These morphological changes were simultaneously reflected on the optical signal displayed, revealing dielectric changes near the gold nanoparticles' surface and electromagnetic coupling between them.

The same experiments were also carried out with composites built with silica deposited onto the magnetic cores using successive acid- and base-catalyzed silica condensation steps, but neither gelation nor dissolution of silica took place when the same amounts of water were added. The composites were, after that, transferred to aqueous and phosphate buffered saline (PBS) solutions, keeping the same morphology and optical properties. These results underline therefore these magnetic and optically active composites to be used in bio-related in vitro applications, taking advantage of their strong magnetic signal and SPB displayed.

The second strategy describes the synthesis of highly active and magnetically recoverable colloidal catalysts, synthesized assembling iron oxide and platinum nanoparticles with silica. Conveniently, these composites present multiple magnetic cores gaining special relevance in the catalysts recovery as responding to low magnetic fields. As a proof of concept, they were used to assess the retarded gold reduction in the cetyltrimethylammonium bromide (CTAB) micelles, permitting to tune the gold reduction rate and therefore the production of spherical or anisotropic gold nanostructures. [2]

The platinum-based catalytically active magnetic nanocomposite particles (Pt-MNC) were prepared by a successive combination of the base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) onto iron

oxide nanoparticles and the LbL self-assembly. The latter drives Pt nanoparticles onto the surface of the magnetic particles previously coated with silica (see scheme in figure 1, inset on the right). The Pt-MNC were investigated in terms of their catalytic activity and recyclability monitoring the Au^{3+} reduction in CTAB solution, reaction which is generally used for the synthesis of gold nanorods and becomes very appropriate for catalysis assessment because of its hindered reaction nature. Since the measurement of the SPB during the synthesis of Au nanostructures provides useful information in terms of the kinetics of the reactions, three typical sets of UV-vis spectra were used to monitor their formation (see figure 1b). Although the different experiments were accomplished under the same conditions of concentration of precursors and temperature, a faster reduction of Au^{3+} ions to give metallic gold was found as increasing the concentration of magnetic and catalyst nanocomposites.

The representative sets of data (displaying the exponential type of kinetics in which absorbance values approach a plateau) indicate that the reaction rate was clearly increased in the presence of the Pt-based nanocomposites. Because of the increasingly faster Au^{3+} reduction rate, the synthesis of different gold nanostructures was carried out, thermodynamically favoring the spherical shape. This increase in the reduction rate (from $2.4 \times 10^{-3} \text{ s}^{-1}$ to $7.36 \times 10^{-3} \text{ s}^{-1}$) leads to a decrease in nanorods yield and instead, the formation of some spherical particles is observed (much bigger proportion of particles compared to that appearing in a typical gold nanorods synthesis).

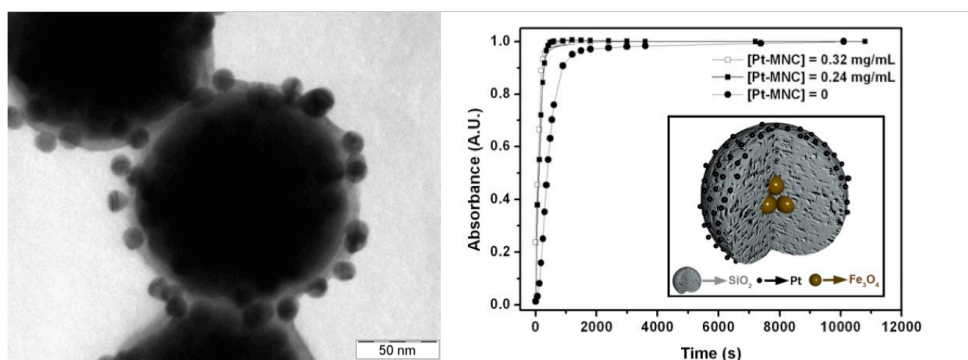
This tendency becomes raised as increasing the catalyst concentration in the reaction medium and ends up in the production of gold nanoparticles but no nanorods. Consequently, the UV-vis spectra shown have the SPB located around 520 nm and 800 nm for gold nanorods (for those structures synthesized without catalysts, $[\text{Pt-MNC}] = 0$), located around 520 and 740 nm (in the presence of the Pt-based nanocomposites ($[\text{Pt-MNC}] = 0.24 \text{ mg/mL}$) (spherical gold nanostructures were also formed so that an increase in the transversal SPB intensity is observed), and just around 540 nm for the highest catalyst concentration ($[\text{Pt-MNC}] = 0.32 \text{ mg/mL}$) which inhibits the anisotropic structures formation and forces the system to produce spherical nanoparticles instead.

In summary, magnetic composites optically or catalytically functionalized were synthesized and the assessment of their optical and catalytic activity was carried out in different experiments.

References

- [1] A. B. Dávila-Ibáñez, M. A. López-Quintela, J. Rivas, V. Salgueirino J. Phys. Chem. C (2010), 114, 7743-7750.
 [2] A. B. Dávila-Ibáñez, M. A. Correa-Duarte, V. Salgueirino J. Mater. Chem. (2010) 20, 326-330.

Figures



Optically (left) and catalytically (right) functionalized multiple-cored magnetic nanoparticles