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Control of amine density onto SPION by the use of different alkoxysilanes

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Abstract –Superparamagnetic iron oxide nanoparticles (SPION) was synthesized via the coprecipitation of ferrous and ferric salts in an alkaline medium assisted by ultrasonic. The magnetite obtained was functionalized with different alkoxysilanes to verify the influence of the alkoxides groups. The method used in this study allowed the synthesis of magnetite with narrow distribution and uniform size. The colorimetric assay showed that the amine density decreases with the decrease of hydrolysable alkoxides groups (APTES>APDES>APES). In FTIR spectra, this fact can be observed by increase of the band (3000-2800 cm^{-1}) regarding the C-H stretching, which it is provide of the ethyl groups of APDES and APES.

Superparamagnetic iron oxide nanoparticles (SPION), such as Fe_3O_4 and γ-Fe_2O_3, have unique properties that qualify them in various applications. Most of these applications require the nanoparticles to be chemically stable, uniform in size, and well dispersed in liquid media. The hydrolysis of organosilanes and surface modification by sol-gel method onto SPION surface is one way to improve chemical stability and also it possibilities provides the surface modification for biomedical applications[1,2]. This functionalization is provided by functional groups (–COOH, $–NH_2$, –SH, etc.). The amino group is chosen to be immobilized on the surface of SPION, because it can be easily conjugated with the carboxyl group of antibody or antigen. Therefore, the control of amine density on SPION surface is an important step in this process [1,2].

In this work, the SPION synthesis was carry out via the coprecipitation of ferrous and ferric salts in an alkaline medium assisted by ultrasonic. Magnetite particles were collected by a permanent magnet and it was washed out with ethanol before to be drying under air at room temperature. The SPION functionalization was carry out with 3-aminopropiltriethoxisilano (APTES), 3-aminopropil-ethyl-diethoxisilano (APDES) and 3-aminopropil-diethyl-ethoxisilano (APES) in aqueous solution, which the alkoxysilanes concentration was kept at 0.25 %(v/v). The average size, morphology and the crystalline structure of the SPIONS functionalized were characterized by the techniques of X-ray diffraction (XRD), transmission electron microscopy (TEM), magnetic hysteresis measurements and Fourier transformed infrared spectroscopy (FTIR). The amine density was taken place by the colorimetric assay using 4-nitrobenzaldehyde [3].

The method used in this study allowed the synthesis of SPION with narrow distribution and uniform size. The diffraction peaks in the X-ray diffraction spectra of the samples are characteristic for a spinel structure of magnetite similar to that of bulk magnetite (Figure 1a). The Figure 1b shows typical magnetization loops for uncoated and APTES-coated Fe_3O_4 at 300 K, where no reduced remanence and coercivity were observed. All samples show typical superparamagnetic behaviors. To sample ATPES-coated observed that the value of magnetization decreased due to the presence of the diamagnetic component. The APTS condensation onto SPION surface was verified by the Si-O-Si stretching, the C-N stretching and the N-H deformation in the FTIR spectra. The colorimetric assay showed that the amine density decreases with the decrease of hydrolysable alkoxides groups (APTES>APDES>APES) (Table 1). In FTIR spectra, this fact can be observed by increase of the band (3000-2800 cm^{-1}) regarding the C-H stretching, which it is provide of the ethyl groups of APDES and APES. A shift of absorption characteristic band of Fe–O(583 cm^{-1}) stretching vibration frequency also was observed. The shifts were 598.6, 595.1 and 586.6 for samples APES, APDES and APTES respectively. This shifts can be explained according to the formation of Fe–O–Si bonds on SIPION surface, which the larger electronegativity of the $–Si(O-)_x$, in relation to the Fe-O-H it causes one increase of bond force constant of Fe-O bonds[4]. Therefore, (APTES, APDES and APES)-coated magnetite nanoparticles were prepared, which verified that a decrease of amine density was in agreement with the hydrolysable alkoxides groups.

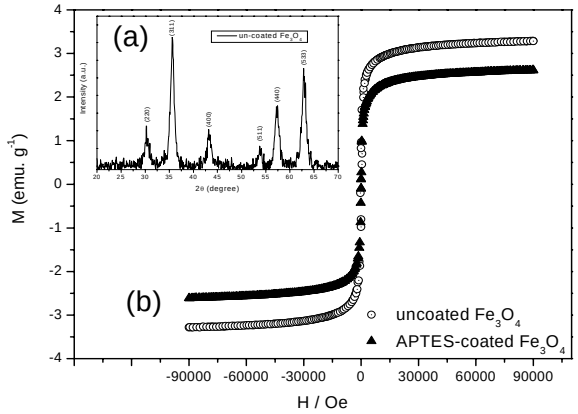

Table 1: Amine density of samples by the colorimetric assay using 4-nitrobenzaldehyde

Sample	d_{NH2} (nmol.mg^{-1})
APTES	8.70
APDES	3.20
APES	2.28

Figure 1. (a) X-ray powder diffraction patterns of uncoated Fe3O4;
(b) Magnetization vs. applied magnetic field for uncoated and APTES-coated Fe3O4 at 300 K.

References

[1] T. Gong, D. Yang, J. Hu, W. Yang, C. Wang and J.Q. Lu, Colloids and Surfaces A: Physicochem. Eng. Aspects 339 (2009) 232–239.
[2] A. K. Gupta and M. Gupta. Biomaterials 2005, 26, 3995.
[3] I.J. Bruce and T. Sen, Langmuir 21(2005) 7029-7035.
[4] M. Ma, Y. Zhang, W. Yu, H. Shen, H. Zhang and N. Gu, Colloids and Surfaces A: Physicochem. Eng. Aspects 212 (2003) 219-/226.