NICKEL NANOPARTICLES DEPOSITED INTO AN ACTIVATED POROUS CARBON: SYNTHESIS, MICROSTRUCTURE AND MAGNETIC PROPERTIES

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Activated carbons (AC) are being extensively used for adsorption and catalytic purposes, mainly due to their outstanding efficiency together with a wide availability and low cost [1]. Frequently, they are exploited in liquid phase for a number of applications, such as, catalyst or catalytic supports, to remove contaminants or for recovering specific products. On the other hand, if the selective manipulation of valuable substances associated with AC is pursued, magnetic separation could be the most effective strategy for achieving this task. However, the commonly used magnetic adsorbents have poor porous characteristics, and the conventional synthesis procedures are too complex and expensive for large production compared with those of AC porous materials [2].

In this contribution, we present a new and easy-to-follow synthesis procedure to prepare magnetically separable porous carbons [3,4]. The starting material is a commercial and low-cost AC with a high pore volume ($1.47 \ cm^3 g^{-1}$), which after being impregnated with an aqueous solution containing sucrose and nickel nitrate, and a subsequent heat-treatment, results in the formation of Nickel nanoparticles dispersed along the porous AC. The addition of sucrose favours protection against acid corrosion. The final amount of Ni in the sample is around 12 wt. %. We will also present and discuss the correlation between microstructure, morphology and magnetic response of these Ni-AC nanoparticles.

The room temperature x-ray powder diffraction pattern can be indexed using the Bragg reflections of a face centred cubic crystal structure with a lattice parameter close to that of bulk Nickel. Transmission electronic microscopy (TEM) shows that the Nickel nanoparticles are quasi-spherical in shape and uniformly dispersed throughout the carbon matrix, with a rather broad crystalline size distribution (diameter values in the range 7 to 25 nm, see fig. 1) and a mean diameter of 16(1) nm.

The magnetic properties of the Ni-AC sample have been investigated using a Vibrating Sample Magnetometer, through the measure of both the temperature (from 2 K to 300 K) and applied magnetic field (up to 1.5 T) dependence of magnetization. The saturation magnetization at room temperature is around 4 $Am^2 kg^{-1}$, high enough to manipulate the sample using conventional magnets. Magnetization vs. applied magnetic field cycles, M(H), show hysteresis for temperatures below 150 K, with a coercive field $H_c \approx 40$ mT at T = 2 K, while the reversible M(H) behaviour at 300 K suggests that the nanoparticles are in superparamagnetic (SPM) regime (see fig. 2). From the measured M(H) cycles at different temperatures, we have obtained the temperature evolution of H_c (see fig. 3). The inset of figure 3 shows the almost linear H_c vs $T^{1/2}$ behaviour, which allows us to estimate a value of the blocking temperature, $T_B \approx 62$ K, which can be associated with the nanoparticles of 16 nm in diameter.

On the other hand, zero-field-cooling magnetization vs. temperature, $M_{ZFC}(T)$, curve, measured under a low applied magnetic field ($\mu_0 H = 1$ mT), shows a broad maximum around 100 K, with a rapid increase of the magnetization from nearly vanishing values at 10 K. Besides that, the $M_{FC}(T)$ (field cooling) and $M_{ZFC}(T)$ curves does not overlap up to temperatures above 200 K.

These experimental findings suggest that the blocking temperature is not unique for the whole system, as it can be expected due to the broad crystalline particle-size distribution. In other words, the smaller particles (7 nm) become superparamagnetic at temperatures slightly above 10 K, while the largest ones (25 nm) have T_B values close to room temperature. The fit of the $M_{ZFC}(T)$ curves using the Stoner-Wohlfarth model allows us to estimate a value for the effective magnetic anisotropy constant, which is double to that of the Ni bulk, in good agreement with previously reported data in other Ni-nanoparticle systems [5]. Finally, this easy-synthesis route for preparing Ni-AC nanoparticles with the possibility of controlling the nanoparticle size seems to be the most challenging issue for tailoring intrinsic properties such as the effective magnetic anisotropy.

References:

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Figures:
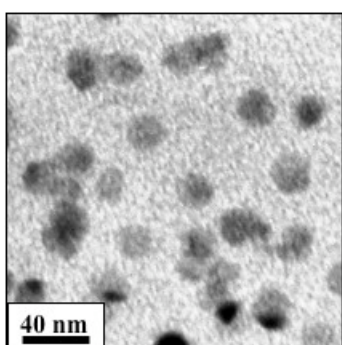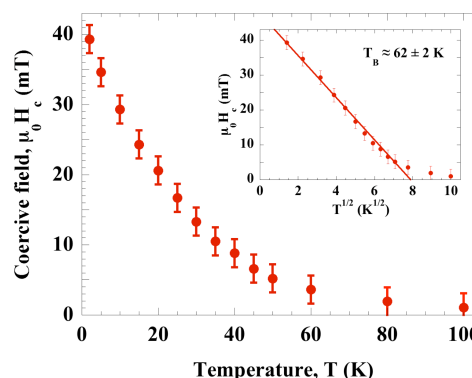

Figure 1. TEM image of the Ni-AC sample

Figure 3. Hc vs. T and $T^{1/2}$ (inset) behaviours of the Ni-AC sample.
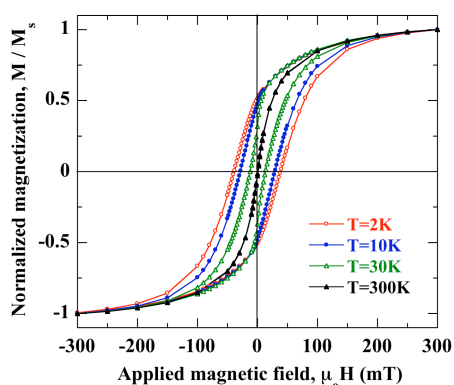
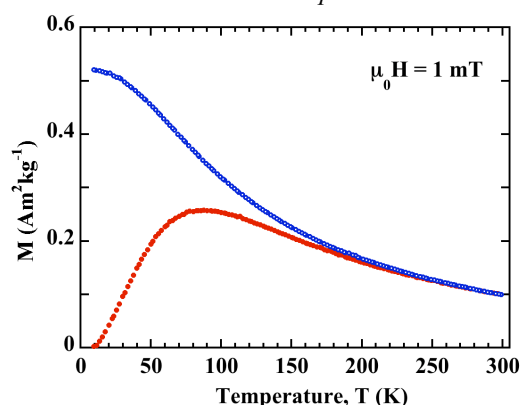

Figure 2. M(H) cycles measured at four selected temperatures

Figure 4. ZFC and FC magnetization vs. temperature curves.