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A green approach to magnetically-hard electrically-conducting polyaniline/$CoFe_2O_4$ nanocomposites

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ABSTRACT

Magnetically-hard, electrically-conducting polyaniline/$CoFe_2O_4$ nanocomposites were prepared by oxidative polymerization of *N*-(4-aminophenyl)aniline using molecular oxygen or hydrogen peroxide as the oxidants and magnetic $CoFe_2O_4$ nanoparticles, both uncoated and oleic acid-coated, with the double role of polymerization catalyst and magnetic filler. Oleic acid-coated nanoparticles showed higher catalytic activity than uncoated ones, especially under aerobic conditions. The size of the nanoparticles did not undergo significant changes during the polymerization process. The nanocomposites are magnetically hard with large remanence/saturation ratio, very large coercivity (8–15 kOe at 5 K) and do not display superparamagnetic effects even at RT. The addition of Fe^{3+} as a further oxidant allowed to tune the electroconductive properties of the materials, with conductivity ranging from $7.3 \cdot 10^{-5}$ S/cm to $5.5 \cdot 10^{-3}$ S/cm.

1. Introduction

Nanocomposite materials combining an electrically conducting polymer (ECP) and magnetic nanoparticles (NPs) have been intensively investigated for their fascinating application as electrochromic devices [1,2], electromagnetic interference shields [3,4], non-linear optical systems [5], and microwave absorbers [6]. Among ECPs, polyaniline (PANI) is particularly interesting for its high conductivity, easy synthesis, low cost, and good environmental stability, which make it a promising candidate for many applications. PANI is unique for its tunable electrical conductivity. Among the forms that PANI can assume (reduced leucoemeraldine, half-oxidized emeraldine and oxidized pernigraniline), only the half-oxidized, half-protonated emeraldine salt is electrically conductive. In general, PANI/magnetic-NP composites are prepared by multi-step approaches involving separate NP synthesis and aniline polymerization. The latter requires strong stoichiometric oxidants, such as $(NH_4)_2S_2O_8$ or metal ions in high oxidation state [7], and the resulting inorganic by-products represent a serious drawback related to waste management [8]. Up to now, PANI/$CoFe_2O_4$ nanocomposites were prepared by these approaches [9–19]. They comprised PANI in the conductive form and were only moderately hard [9–13] despite $CoFe_2O_4$ is the magnetically hardest cubic ferrite. Applications as EMI shielding materials [10,11,13], photocatalysts [14,16], bactericides [17,18], and supercapacitors [19] were demonstrated.

Recently, we reported on the use of eco-friendly oxidants, such as O_2 and H_2O_2, with the aid of suitable catalysts as a "green" alternative to produce ECPs [20–24]. In particular, Fe_3O_4 NPs resulted to be active catalysts in the oxidative polymerization of N-(4-aminophenyl)aniline (aniline dimer, AD), leading to electrically conductive, superparamagnetic PANI/Fe_3O_4 nanocomposites [24]. We herein report on the behavior of $CoFe_2O_4$ NPs as a polymerization catalyst and magnetic nano-filler for the preparation of PANI/$CoFe_2O_4$ nanocomposites. $CoFe_2O_4$ NPs were proven to be an effective catalyst allowing to achieve magnetically hard nanocomposites with high magnetization and coercivity. The electrical conductivity of the nanocomposites could be tuned by adding a further environmentally-friendly oxidant.

2. Material and methods

2.1. Reagents and instruments

All chemicals were used as received without any purification. FT-IR spectra (400–4000 cm^{-1}) were recorded by a JASCO

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FT/IR-410 spectrophotometer using pellets of samples dispersed 1:100 w/w in KBr. UV–Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer using 0.087–0.353 mM solutions in *N*,*N*-dimethylformamide. For transmission electron microscopy (TEM, Zeiss LIBRA-200FE), a drop of NP dispersion (toluene) or nanocomposite suspension (acetonitrile) was evaporated on a carbon-film grid. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D IIIMAX horizontal-scan powder diffractometer with Cu Kα radiation. The metal content of the NPs and nanocomposites was determined by atomic absorption spectroscopy (AAS) on a AAS 3100 PerkinElmer spectrophotometer after sample mineralization in aqua regia. EDS (Energy Dispersive X-ray Spectroscopy) characterization was carried out on a Hitachi TM1000 SEM microscope. The electrical conductivity was measured by an AMEL 338 multimeter as detailed in Section 2.5. A Quantum Design MPMS XL-5 SQUID magnetometer was used to measure the magnetic properties of NPs and nanocomposites as detailed below (Section 2.6).

2.2. Preparation of $CoFe_2O_4$ NPs

2.2.1. Preparation of uncoated $CoFe_2O_4$ NPs

According to the method of Kang et al. [25], aqueous solutions of $FeCl_3{\cdot}6H_2O$ (0.30 M, solution A) and $CoCl_2{\cdot}6H_2O$ (0.15 M, solution B) were prepared dissolving the appropriate amount of salts in 0.4 M aq. HCl. 10 mL of each solution (Fe/Co = 2, atomic ratio) were mixed and stirred for 20 min at 80 °C under nitrogen. Then, 1.5 M aq. NaOH was quickly added until reaching pH 13 under vigorous stirring. After 2 h the product was magnetically decanted, washed repeatedly with distilled water until neutral pH and dried at 70 °C in oven (yield 91%).

2.2.2. Preparation of oleic acid-coated (OAC) $CoFe_2O_4$ NPs

Oleic acid (0.2 g) was added to dried uncoated $CoFe_2O_4$ NPs (0.75 g) and stirred in 63 mL of toluene to obtain a uniform suspension. The concentration of $CoFe_2O_4$ in the suspension was measured by AAS (11.9 $mg_{CoFe_2O_4}$/ml).

2.3. Synthesis of PANI/$CoFe_2O_4$ nanocomposites

2.3.1. Oxidative polymerization reaction by molecular oxygen

460 mg (2.5 mmol) of *N*-(4-aminophenyl)aniline (AD) were dissolved in 40 mL of 0.03 M aq. HCl. Different amounts of uncoated or OAC $CoFe_2O_4$ NPs were added (AD/$CoFe_2O_4$ = 5, 10, 50 M ratio). The suspension was stirred under molecular oxygen ($p_{O_2} = 2$ bar) for 72 h at 80 °C. The resulting dark solid was collected by filtration, washed with water and acetone and dried at 383 K overnight. A blank test was repeated in the absence of $CoFe_2O_4$ NPs and no solid product was obtained.

2.3.2. Oxidative polymerization reaction by hydrogen peroxide

460 mg of AD (2.5 mmol) were dissolved in 40 mL 0.03 M aq. HCl. Different amounts of uncoated or OAC $CoFe_2O_4$ NPs (AD/$CoFe_2O_4$ = 5, 10, 50 M ratio) and 0.77 mL of aq. H_2O_2 (30%, w/w) were added (H_2O_2/AD = 3, molar ratio). The reaction mixture was stirred at RT for 24 h. The product was collected by filtration and treated as above (Section 2.3.1). The reaction was repeated in the absence of $CoFe_2O_4$ NPs and, as previously reported [21,24], a green solid material, identified as emeraldine salt (ES), was obtained (sample 1).

2.3.3. Oxidative polymerization reaction by hydrogen peroxide and Fe^{3+}

The reactions were carried out as described in Section 2.3.2 in the presence of $CoFe_2O_4$ NPs and adding $FeCl_3$ (AD/Fe = 1000, molar ratio) into the mixture (sample 11).

2.4. Synthesis of leucoemeraldine

Leucoemeraldine was prepared as described in Ref. [26]. 1 g of sample 1 was de-doped with 20 mL of 1.5 M aq. NaOH, obtaining emeraldine base (EB). The latter was filtered and washed with water until neutrality of the mother liquors. 300 mg of EB were dispersed in 5 mL of aq. hydrazine (35%). After 5 h the product was filtered, washed with acetone, dried under vacuum and stored under nitrogen (sample 2).

2.5. Conductivity measurements

For conductivity measurement, 200 mg of finely powdered sample (ES (sample 1), leucoemeraldine (sample 2), and PANI/$CoFe_2O_4$ nanocomposites) were pressed between 13 mm anvils with force 10 ton for 30 min. The resulting disk was next pressed with force 2 kg for 30 min. Resistance R was measured by an AMEL 338 multimetre and conductivity σ was obtained as

$$\sigma = (1/R)(\ell/A) \tag{1}$$

where ℓ is the thickness of the disk, R is the resistance and A is the area of the disk base.

2.6. Magnetic measurements

Weighted amounts of powdered samples were packed in Teflon ribbon and set in the magnetometer sample space. Magnetization isotherms $M(H)$ were measured between +50 and −50 kOe at 5 K after field cooling (FC, H_{cool} = +50 kOe) from 295 K. The temperature dependence of the magnetization $M(T)$ was measured between 5 and 300 K using a measuring field H_{meas} = 10 Oe in both zero-field cooling (ZFC) and FC (H_{cool} = 10 Oe) modes. The raw data were corrected for diamagnetic contributions.

3. Results and discussion

3.1. Catalytic polymerization of AD

As demonstrated by Wei et al. [27], owing to the higher oxidation potential of aniline with respect to AD, the slowest step of polyaniline synthesis consists in the aniline monomer oxidation into AD. Recently, we demonstrated that this kinetic bottleneck can be overcome by using AD as reagent since it can be easily polymerized by mild oxidants (H_2O_2 or O_2) in the presence of suitable catalysts [23,24]. As previously observed by us for Fe_3O_4 NPs [24], both uncoated and OAC $CoFe_2O_4$ NPs exhibited catalytic activity (Table 1). The reaction yield was calculated according to Eq. (2):

$$\text{Yield\%} = \left(\sum_{\text{mass insoluble materials}} \Big/ \sum_{\text{mass reagent}} \right) \times 100 \tag{2}$$

where $\Sigma_{\text{mass reagent}}$ = AD + HCl + $CoFe_2O_4$ + oleic acid. To compare the NP activity between reactions involving O_2 or H_2O_2, it is useful to subtract from the yield of the reaction carried out in the presence of H_2O_2 the yield observed in the same conditions but in the absence of NPs, as the latter arises from NP-independent polymerization. Considering the yield values in brackets in Table 1, it is clear that the NPs resulted to be more active under aerobic conditions than in the presence of H_2O_2, in agreement with literature [8]. Furthermore, whereas similar catalytic activity was observed for both $CoFe_2O_4$ NPs types using O_2, in the presence of H_2O_2 OAC NPs exhibited higher catalytic performances than uncoated NPs. This behavior could be ascribed to the ability of cubic ferrites (in particular, $MnFe_2O_4$ and $CoFe_2O_4$) to decompose H_2O_2 [28], decreasing the oxidant concentration in the reaction mixture and thus producing polymer in lower yield. The coating of OAC NPs probably reduces