A simple *in-situ* synthesis of carbon nanotubes embedded with magnetic nanoparticles by thermolysis of the organic-inorganic hybrid perovskite [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺)

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In this work, the incorporation of dicyanamide building blocks in organic-inorganic hybrid compounds is found to be a promising strategy for the synthesis of multiwall carbon nanotubes embedded with magnetic nanoparticles (M@CNTs). Following a novel one-step, scalable and fast synthetic route, M@CNTs are obtained by simple calcination of the organic-inorganic hybrid perovskite [TPrA][M(dca)₃] (TPrA = tetrapropylammonium, M = Ni²⁺ and Co²⁺, dca = dicyanamide). The resulting M@CNTs (M = Ni and Co) display a regular morphology, and an essentially mesoporous network of ~250 m² g⁻¹. Whereas the Co@CNTs composite displays a broad pore size distribution (PSD) up to 6 nm, Ni@CNTs show a strictly controlled unimodal PSD, centered at around 5 nm. The monitoring of their thermal decomposition by X-ray diffraction, electron microscopy, thermogravimetric and spectroscopic analysis allows proposing a calcination mechanism and establishing the conditions to obtain optimal materials. Moreover, magnetization studies reveal a ferromagnetic behaviour of the obtained M@CNTs, with small coercive fields due to the size of the magnetic nanoparticles. In addition, preliminary essays of oil adsorption-desorption capacity reveal a promising potential for spilled oil recovery using this easily-synthesized materials. All these physicochemical properties render these composites good candidates for other nitrogen-rich CNT common applications.

1. Introduction

Hybrid nanocomposites of carbon nanotubes with encapsulated magnetic nanoparticles (M@CNTs) are emerging materials with an enormous technological interest related to their multifunctional properties.^{1,2} Since their discovering in the early 90s,³ carbon nanotubes (CNTs) have shown to exhibit unique mechanical, thermal and chemical stabilities together with a tunable electric conductivity, among other functional properties.⁴ Thus, these materials find applications in a wide range of fields such as micro- and nanoelectronic (flat panel displays,⁵ sub-22 nm node technologies,⁶ flash memories,⁷ spintronics,⁸ etc.), energy storage systems (supercapacitors,⁹ batteries,¹⁰ etc.), and even biomedical and pharmacological applications^{11,12} due to their chemical inertness and biocompatibility.

Moreover, combining CNTs with magnetic nanoparticles (NPs) can lead to novel and enhanced multifunctional properties, as demonstrated in several areas. For instance, the porous surface of CNTs in combination with the magnetic behaviour of the NPs allow removing pollutants from water and recovering of the material by an external magnet.¹³ In another context, magnetic nanoparticles embedded in carbon nanotubes can induce magneto-conductance for spintronic applications.¹⁴ The electromagnetic behaviour of these materials can also enhance optical properties, which are interesting to develop very sensitive spectroscopic techniques, such as surface-enhanced Raman scattering.¹⁵ Moreover, such composite materials can be used as probes in characterization ferromagnetic resonance imaging¹⁶ and even contrast agents for medical magnetic resonance imaging (MRI).¹⁷ In addition, the chemical inertness, biocompatibility and water solubility of these materials, render these electromagnetic compounds great candidates for bio- and nanomedical applications, such as nanocarriers for targeted drug delivery,¹⁸ “nano-syringes” for metal transport¹⁹ or hyperthermia for cancer treatment.²⁰

Generally speaking, it is preferable to use nanoparticle-filled nanotubes, instead of CNTs decorated with external nanoparticles. For instance, in the filled systems the external surface of the CNTs is more accessible to the adsorption or to an additional functionalization. Moreover, when using metals as magnetic nanoparticles, the encapsulation protects the metals against their oxidation.

In the case of the nanoparticle-filled CNTs, it is further desirable to control the nanoparticle filling. Thus, for example, a partial filling allows a channel-like structure for accessible adsorption and transporting sites.

In this context, the synthesis of hybrid carbon nanotubes heterostructures with encapsulated magnetic nanoparticles can be developed by two main strategies: *in-situ* and *ex-situ* methods.¹ *In-situ* processes involve the filling of the tube during the synthetic route and include mainly chemical vapor deposition (CVD) and arc discharge methods, where a metal catalyst controls the kinetic growing. Conversely, the *ex-situ* techniques consist of filling the carbon nanotubes after their synthesis by means of wet chemistry, electrochemistry and gas or evaporation techniques.

Unluckily, most of these procedures involve several-step reactions, relatively complex operational conditions, high cost, low reproducibility or difficulties in terms of practical applications. Therefore, it is highly desirable to find simple, reproducible, scalable and low-cost methods to synthesize M@CNTs, with a good control in terms of type, diameter, length, morphology and orientation of the nanoparticles and the CNTs.

Recent studies have highlighted the potential of some relatively new families of compounds such as organic-inorganic hybrid materials as precursors and templates for the preparation of nanoporous carbon structures, by means of direct carbonization.²¹⁻²⁶ This is the case of some metal-organic frameworks (MOFs) and porous coordination polymers (PCPs) such as Al-PCPs,^{27,28} MOF-5 and isorecticular compounds (IRMOF),^{29,30} ZIF-8,³¹ ZIF-67,³² and related materials. Nevertheless, there are only very few studies on obtaining carbon nanotubes by direct calcination of organic-inorganic hybrid materials.^{33,34}

To fill this gap we have carried out the present study. The starting research hypothesis relies on the idea that the inclusion of dicyanamide anions and magnetic metal cations within organic-inorganic hybrid structures could be a promising strategy to obtain nitrogen-enriched carbon nanotubes with embedded magnetic nanoparticles by simple calcination.

In that context, dicyanamide ligands (dca) are known to be useful precursors for obtaining N-rich carbons. For example, it has been reported that molecular dicyanamide salts trimerize heated above 300 °C, forming triazine units³⁵⁻³⁸ that can be used as precursors for nitrogen-rich graphite sheets.³⁹ More recently, dicyanamide-containing ionic liquids⁴⁰⁻⁴² and molecular salts⁴³⁻⁴⁷ have been used to obtain N-graphite materials. Nevertheless, there are very scarce studies about carbon nanotubes and “nanoworms” with embedded magnetic nanoparticles derived from direct calcination of dicyanamide related-salts or ionic liquids.^{40,48}

In this work, we use the new multisensitive organic-inorganic hybrids of formula [TPrA][M(dca)₃] (TPrA: tetrapropylammonium, (CH₃CH₂CH₂)₄N⁺; dca: dicyanamide, (N(CN)₂)⁻; M = Ni²⁺ and Co²⁺) and perovskite-like structure⁴⁹⁻⁵¹ as precursors, as they can provide both nitrogen-rich carbon sources and metal catalysts for the formation of CNTs during their calcination.

In order to get reliable insights into the calcination mechanism, the thermal evolution of the samples has been monitored by means of thermogravimetric analysis (TGA), elemental analysis, Fourier transform infrared (FT-IR) and Raman spectroscopies, powder X-ray diffraction (PXRD) and scanning and transmission electron microscopy (SEM and TEM). The combination of these diverse techniques, as well as nitrogen adsorption and magnetization studies, has led to a complete characterization of the resulting materials.

As shown below, this has led us to one of the first successful synthesis of carbon nanotubes with embedded Ni and Co nanoparticles, M@CNTs, achieved by direct calcination of an organic-inorganic hybrid compound with perovskite-like structure.

Additionally, preliminary studies reveal promising oil adsorption capacity of the obtained samples, oil which can be subsequently thermally desorbed at 450 °C with recovery of the M@CNTs materials.

2. Experimental

2.1. Synthesis of the [TPrA][M(dca)₃] hybrid precursors

The [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) compounds were prepared from commercially available reagents without further purification, namely Co(NO₃)₂·6H₂O (98%, Sigma-Aldrich), Ni(NO₃)₂·6H₂O (≥98.5%, Sigma-Aldrich), [TPrA]Br (98%, Aldrich), Na(dca) (96%, Aldrich) and absolute ethanol (Panreac). A reagent amount of deionised water was also used in the synthesis.

The synthetic method used is a variation of that previously reported for obtaining [TPrA][M(dca)₃] (M = Mn²⁺, Fe²⁺, Co²⁺ and Ni²⁺) hybrids.⁵¹ The procedure was as follows (see Fig. S1a of ESI): a mixture of a solution of [TPrA]Br in ethanol and a solution of Na(dca) in water was mixed with another solution of M(NO₃)₂·6H₂O in water, where M = Ni²⁺ and Co²⁺. After stirring at 30 °C, the solvent was evaporated in a rotary evaporator and a polycrystalline powder was obtained (green for the Ni-compound and pink for the Co-compound) with a yield of ~95% in both cases. The precipitate was collected by filtration and washed with ethanol. This variation of

the synthesis considerably shortens the previously reported 1-week method⁵¹ and highly enlarge the amount of organic-inorganic hybrid compounds that can be obtained, see Fig. S1b of ESI.

2.2. Synthesis of the M@CNTs

M@CNTs (M = Ni and Co) were synthesized in a relative large scale (see Fig. S1c of ESI) by thermolysis of the precursor compounds inside a conventional tubular furnace, equipped with a quartz tube and under a nitrogen flux of 350 ml min⁻¹. The thermal treatment used was heating from room temperature to 900 °C at 5 °C min⁻¹ and cooling back to room temperature during 10 hours.

2.3. Powder X-ray Diffraction

The formation of the precursor compounds, of the final M@CNTs and the evolution of the intermediate samples (at room temperature, 25 °C, and annealed at 305 °C, 390 °C, 440 °C, 470 °C, 600 °C, 900 °C and 1300 °C) were followed by powder X-ray diffraction (PXRD) using a Siemens D-5000 diffractometer, with CuK α radiation ($\lambda=1.5418$ Å) working at room temperature. The PXRD patterns of the [TPrA][M(dca)₃] M = Ni²⁺ and Co²⁺ hybrids were compared with the profiles obtained from their single crystal structure, which were generated by the Mercury 3.5.1 software.⁵² The obtained patterns had enough quality to allow their Le Bail analysis using the GSAS+EXPGUI software.^{53,54} The PXRD patterns of the samples annealed at different temperatures were compared with the PXRD patterns of M(dca)₂,⁵⁵ Ni (JCPDS No.00-004-0850), NiO (JCPDS No.00-073-1523), Co (JCPDS No.00-015-0806), CoO (JCPDS No.00-065-2902) and C-graphite (JCPDS No.00-001-0640), respectively. The average crystallite size of the M particles in the M@CNTs was estimated from X-ray diffraction line broadening by using the Debye-Scherrer equation;⁵⁶ the instrumental broadening was determined using a LaB₆ powders (NIST SRM660a).

2.4. Elemental analysis

Elemental analyses for C, N, and H content in the precursor [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) compounds and in the final M@CNTs were carried out using a FLASHEA1112 (Thermo-Finnigan) Analyzer.

2.5. Thermal characterization

Thermogravimetric analysis (TGA) were carried out in a TGA-DTA Thermal Analysis SDT2960 equipment. For these experiments, approximately 25 mg of sample were heated at a rate of 5 °C min⁻¹ from 25 °C to 1300 °C using corundum crucibles under a flow of dry nitrogen.

2.6. FT Infrared and Raman spectroscopies

Fourier transform infrared spectra of the solid products, and of the gases released during the TGA analysis, were analyzed on a Bruker vector FT-IR spectrometer TGA, in the range of 400 to 4000 cm⁻¹.

The Raman spectra of the products were recorded using a T64000 Jobin-Yvon spectrometer, with a charge coupled device (CCD) camera (40-4000 cm⁻¹) and a photocounting device (10-200 cm⁻¹). The 514.5 nm linear polarized line of Ar⁺ laser was chosen for excitation. The effect on the laser power on the Raman spectra was previously studied in order to prevent the self-heating of the sample.

2.7. Scanning and transmission electron microscopy

The morphology of the samples obtained after calcination was studied by scanning and transmission electron microscopy (SEM and TEM). SEM analysis was performed by means of a JEOL JSM 6400 microscope. TEM analysis was performed using a JEOL 1010 microscope operating at 100 kV. For that purpose, the samples were suspended in isopropanol, and deposited onto copper grids.

2.8. Assessment of the porous structure

Textural characterization was carried out by N₂ physisorption at 77 K on a Micromeritics ASAP 2010 volumetric adsorption system. The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.99 whereas the specific surface area was estimated by using the Brunauer-Emmett-Teller (BET) equation. The pore size distributions (PSD) were obtained by applying the Quenched Solid State Functional Theory (QSDFT) method assuming pores of cylindrical shape.⁵⁷

2.9. Magnetic studies

The magnetization of the M@CNTs (M = Ni and Co) samples as a function of the applied magnetic field, $M(H)$, was studied at room temperature using a vibrating sample magnetometer (VSM), model DMS-1660. For that purpose, a magnetic field was applied from -10kOe to +10kOe and the data were registered in steps of 200 Oe in the range of 0 to 2500 Oe, and in steps of 1500 Oe in the range of 2500 to 10000 Oe.

On the other hand, the temperature dependence of the Zero-field-cooled (ZFC) and field-cooled (FC) magnetization of the samples was studied in a Quantum Design PPMS SQUID magnetometer in the temperature range 5-400 K, using a magnetic field of 100 Oe.

2.10. Oil adsorption-desorption essays

A commercial motor lubricant based on ester, 100% synthetic ($\rho = 0.862 \text{ g cm}^{-3}$ at 20 °C and $\mu = 46.4 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C) was used for the adsorption tests. For each test, an aliquot of 50 mg of M@CNTs was spilled on top of the oil-water mixture up to saturation of the materials (2 minutes). The desorption of oil from the M@CNTs materials was induced by heating from room temperature to 600 °C with a ramp of 5 °C min⁻¹ in a TGA-DTA Thermal Analysis SDT2960 instrument equipped with a Bruker vector FT-IR spectrometer to monitoring the released gases.

3. Results and discussion

Carbon nanotubes with embedded Ni and Co nanoparticles, M@CNTs (M = Ni and Co), were synthesized in a relative large scale by thermolysis of the corresponding [TPrA][M(dca)₃] precursor compounds at 900 °C under nitrogen atmosphere. Those [TPrA][M(dca)₃] precursors were, in turn, synthesized by mixing three solutions of [TPrA]Br/ethanol, Na(dca)/water and M(NO₃)₂·6H₂O/water at 30 °C.

Table 1. Results of elemental analysis for the [TPrA][M(dca)₃] samples (Obs.) compared with the theoretical values (Calc.) and with reported data (Ref. 49).

		C (%)	H (%)	N (%)
	Ref. 49	48.62	6.41	31.41
[TPrA][Ni(dca) ₃]	Calc.	48.78	6.37	31.61
	Obs.	49.24	6.22	31.08
	Calc.	48.76	6.36	31.59
[TPrA][Co(dca) ₃]	Obs.	49.01	6.18	31.10

3.1. Characterization of the [TPrA][M(dca)₃] precursors

Le Bail refinement of the PXRD patterns confirm the formation of the [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) as both samples exhibit the orthorhombic *Pnna* crystalline structure described in the literature for these compounds at room temperature,⁵¹ (Fig.S2 of ESI).

Moreover, these samples are single-phase materials without associated secondary phases. The elemental analysis data, summarized in Table 1, are also in agreement with those reported for these compounds.⁴⁹

The results of the FT-IR spectra for both compounds (shown in Fig. S3 and Table S1 of ESI) are also in fully agreement with the literature data.^{38,49}

3.2. Thermal decomposition of the [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) precursors

The thermal decomposition of the [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) compounds was monitored by TGA. As it can be seen in Fig. 1 both the Ni- and Co-precursors exhibit a quite similar thermal evolution, with four weight losses as a function of temperature: (i) a first abrupt weight loss in the interval [250-300] °C, (ii) a second weight loss at [300-500] °C, (iii) a third progressive weight loss at [500-650] °C, (iv) a last and smaller weight loss that continues up-to 1300 °C.

The FT-IR spectra of the gases released during the TGA experiment help understanding the decomposition mechanism see Fig. S4 of ESI. In that context, during the first and second weight losses IR bands around [1000-1500] cm⁻¹ and [2800-3200] cm⁻¹ are observed, which can be assigned to $\nu(\text{C-C})$ and $\nu(\text{C-H})$, and attributed to

the TPrA cations, as well as bands around $[2000-2360] \text{ cm}^{-1}$ can be assigned to $\nu(\text{C-N})$ and $\nu(\text{C}\equiv\text{N})$ vibrations of the dca ligands. Meanwhile, during the third weight loss the first ones are no longer detected while those of the dca ligands are still present and can also be observed up-to 1300°C , even if its intensity decreases as temperature increases.

On the basis of these TGA and FT-IR results we have estimated the nature and amount (per formula unit) of the species released during the thermal treatment as follows (see Fig. 1): (a) the two first weight losses ($\sim 50\%$) correspond to ~ 1 dca anions and ~ 1 TPrA cations; (b) the third weight loss ($\sim 20\%$) is equivalent to ~ 1.5 dca anions and (c) the fourth weight loss ($\sim 10\%$) is assigned to ~ 0.4 dca anions.

This thermal decomposition has also been followed by analysing the PXRD patterns of the $[\text{TPrA}][\text{M}(\text{dca})_3]$ samples annealed at $300 < T(^{\circ}\text{C}) \leq 1300$.

Figure 1. TGA decomposition curve for the precursor $[\text{TPrA}][\text{M}(\text{dca})_3]$ materials, where $\text{M} = \text{Ni}^{2+}$ (green) and Co^{2+} (pink).

In that context, it should be indicated that both the Ni- and Co-samples exhibit the same behaviour illustrated in Fig. 2 for the Ni-one. As it can be seen there, the room temperature $[\text{TPrA}][\text{M}(\text{dca})_3]$ ($\text{M} = \text{Ni}^{2+}$ and Co^{2+}) structure has transformed into $\text{M}(\text{dca})_2$ [Ref. 55] in the interval $[305-440]^\circ\text{C}$, with coexistence of amorphous material, evidenced by the hump-shape of the PXRD pattern (Fig. S5 of ESI). After the second weight loss, and from 470°C to 1300°C , peaks at around 44.5 (44.2), 51.9 (51.6) and 76.4 (75.8) $^\circ 2\theta$ are observed in the patterns and assigned to metallic $\text{M} = \text{Ni}$ and Co , respectively, with cubic symmetry (space group $Fm-3m$), and a weak peak around $26.3^\circ 2\theta$ attributed to the characteristic (002) graphite crystallographic plane (Fig. S6a of S.I.). At 1300°C peaks 37.3 (36.5), 43.3 (42.4), and 63.0 (61.6) $^\circ 2\theta$ are also identified, corresponding to a metal oxide impurity (NiO and CoO , respectively, cubic, S.G.: $Fm-3m$), negligible for lower temperatures. It is worth noting that in the temperature range $[470-900]^\circ\text{C}$ only the coexistence of graphite and metallic Ni or Co, are observed. Meanwhile at higher temperatures (1300°C), the PXRD reveal that part of the metals have oxidized to the corresponding oxides NiO and CoO , respectively. Another interesting remark is that as temperature increases, the peak at $26.3^\circ 2\theta$ becomes narrower and the signal to noise ratio increases (Fig. S6a of ESI), indicating the improvement of the graphite crystallinity. Moreover, the diffraction peaks corresponding to metallic Ni and Co also become narrower (Fig. S6b of ESI), pointing to an increase of the crystal size of the metallic particles with temperature. The average diameter of the metal particles in the samples treated at 900°C , estimated by the Debye-Scherrer equation from the width of the characteristic diffraction peaks, is around 27 and 23 nm , for Ni and Co samples respectively.

Summarizing, during thermal heating the precursor compounds $[\text{TPrA}][\text{M}(\text{dca})_3]$ ($\text{M} = \text{Ni}^{2+}$ and Co^{2+}), transform into $\text{M}(\text{dca})_2$ and an amorphous material in the temperature interval $\sim [250-450]^\circ\text{C}$, releasing up-to ~ 1 dca ligand and ~ 1 TPrA cation per formula unit.

Figure 2. Structural evolution of the precursor Ni-compound as a function of temperature. For a better view, the obtained PXRD patterns have been normalized and displaced along the *Intensity*-axis (o = graphite; * = Ni; + = NiO).

Subsequently, in the interval $\sim[450-900]$ °C the as-obtained $M(dca)_2$ compound continues releasing dca ligands, and the M^{2+} cations ($M = Ni^{2+}$ and Co^{2+}) get reduced to M^0 metals.

In addition, the remaining dca ligands seem to transform into a graphite-like material. Finally, when continuing heating at increasingly higher temperatures, the metallic M^0 particles increase their size while the carbon material improves its crystallinity. Nevertheless, at 1300 °C part of these M^0 particles reoxidize to M^{2+} forming metal oxides (MO).

3.3. Morphology, crystallinity and composition of the M@CNTs

The morphology of the Ni and Co samples at different annealing temperatures (600, 900 and 1300 °C) was studied by scanning and transmission electron microscopy (SEM, TEM) and is shown in Fig. 3 and Fig. S7 of ESI. Fig. S7a y Fig. S7b show that these materials after calcination at 900 °C exhibit micropores. A detailed view of the previous figures is shown in Fig. S7c y Fig. S7d, revealing a submicrometric structure of the Ni and Co samples, respectively. For obtaining further information, TEM studies were performed. TEM micrographs (see images of Fig. 3) prove that both samples are formed by nanotubes. In the samples annealed at 600 °C metallic nanoparticles covered by amorphous carbon shells are observed together with a few multiwall carbon nanotubes, also embedded with metallic nanoparticles. More interestingly, in the samples annealed at 900 °C only well-formed multiwall carbon nanotubes covering the metallic nanoparticles are observed. Most of such CNTs have a diameter of around 24 nm and 20 nm in the case of Ni@CNTs and Co@CNTs, respectively.

Meanwhile, the length of most of the CNTs is higher for the Co sample, up-to 1 μm , compared to 300 nm for the Ni@CNTs. Another interesting remark is that the average size of the metal nanoparticles is around 17 nm, with a size distribution in the range 2-45 nm for Ni and 5-35 nm for Co (Fig. 4), similar to carbon-coated nanoparticles obtained by other high precision techniques, such as pressure chemical vapour deposition (~ 20 nm).⁵⁸ These results show a reasonable agreement with those obtained by the Debye-Scherrer analysis of the PXRD data (diameters of 27 and 23 nm for Ni and Co, respectively)

Ni@CNTs

Co@CNTs

Figure 3. TEM micrographs of the samples obtained after annealing at different temperatures: 600 °C, 900 °C and 1300 °C.

Figure 4. Size distribution of the M nanoparticles in the M@CNTs obtained at 900 °C, estimated by measuring the diameter of 100 nanoparticles from TEM micrographs: (a) Ni; (b)Co.

However, both results cannot be straightforwardly compared, since TEM analysis provides local information, obtained on a finite number of particles, while PXRD measures the average particle size of the bulk of the sample.

In the case of the 1300 °C-annealed samples larger agglomerated metallic particles surrounded by a non-so well defined carbon material are identified, indicating the destruction of the CNTs as also observed in the literature.⁵⁹ This observation suggests that the partial loss of the protection-carbon coat at temperatures as high as 1300 °C allows the partial oxidation of the M^0 to MO , as detected by PXRD patterns, once the samples are exposed to the air atmosphere.

The crystallinity of the M@CNTs obtained at 900 °C was also checked by Raman spectroscopy. A typical Raman spectrum, as that shown in Fig. S8 of ESI, consists of a strong band at $\sim 1580\text{ cm}^{-1}$ (G band), assigned to the E_{2g} first-order mode of the graphite plane, another strong band at $\sim 1350\text{ cm}^{-1}$, assigned to the D band that is related to the presence of defects and impurities in the carbon nanotubes, and a weaker band at $\sim 2570\text{ cm}^{-1}$ (2D band or the second-order harmonic of the D band) in full agreement with the literature for highly graphitized nanostructures.^{33,34,60} Nevertheless, the calculated values for the intensity ratio I_D/I_G of 0.95 and 0.70 for Ni@CNTs and Co@CNTs, respectively, reveal the presence of defects in our samples (in higher number in the Ni- than in the Co-one) due to disruptions of the perfect graphitic lattice of the sp^2 -hybridized carbon.⁶⁰ Those defects can be probably caused by the incorporation of nitrogen to the carbon nanotubes,⁴⁸ result which points to the idea that this technique allows the obtention of nitrogen-rich CNTs.

Moreover, the chemical composition of the well-formed M@CNTs at 900 °C was estimated by elemental analysis of C, N and H. Table S2 of ESI summarizes and compares the chemical composition of the [TPrA][M(dca)₃] precursors —calculated from the nominal formula— with the chemical composition of the M@CNTs —found by elemental analysis and deduced from TGA (% relative to the precursor initial mass and % normalized per final M@CNTs mass)—.

As it can be seen there, the elemental analysis of Ni@CNTs leads to C (19.83%), N (1.09%) and H (<0.1%); thus, the rest (~78.98%) can only be reasonably attributable to Ni. This result is in full agreement with the estimations from TGA: around 20.10% of the weight corresponds to the carbon part and the rest (around 79.90%) corresponds to Ni.

In the case of Co@CNTs, the elemental analysis evidences C (38.93%), N (1.26%), H (<0.1%), being 59.71% attributable to Co; meanwhile from TGA we estimate around 55.08% of Co. It is noteworthy that this higher proportion of M in Ni@CNTs (79.90%) compared to Co@CNTs (55.08%) agrees with the results observed by TEM

Another very interesting result is the content of N found in both Ni@CNTs (1.09%) and Co@CNTs (1.26%) samples, resulting in N/C ratios of 5.5:100 and 3.2:100, respectively comparable to those previously reported in nitrogen-rich carbon nanotubes (i. e. 5.2:100).⁴⁸

3.4. Comparison of [TPrA][M(dca)₃] versus M(dca)₂ as precursors of M@CNTs

As thermal monitoring could suggest that the M(dca)₂ species are good starting materials to obtain M@CNTs, we have synthesized the Ni(dca)₂ as reported⁵⁵ (from now on Ni(dca)₂-pure), and we have annealed this sample under similar conditions to those used for [TPrA][Ni(dca)₃]. Nevertheless, after the annealing at 900 °C significant different morphologies are observed by TEM (Fig. S9 of ESI): the sample from Ni(dca)₂-pure results to be much less ordered, and presents higher size and shape dispersion of the NPs and CNTs. Significantly, the colours of the samples before this annealing at 900 °C were already quite different (as shown in Fig. S9 of ESI): Ni(dca)₂-pure was green, while the sample derived from [TPrA][Ni(dca)₃] annealing was brown (light-brown at 305 °C and dark brown at 440 °C), even if PXRD shows the same Ni(dca)₂ crystalline structure for the three samples, but with a hump-shape for the [TPrA][Ni(dca)₃]-derived due to the co-existence of some amorphous material (Fig. S5 of ESI), as previously commented.

In addition, the FT-IR spectra are different (Fig. S10 of ESI): the annealed [TPrA][Ni(dca)₃] exhibits a broader band in the ~[830-1750] cm⁻¹-region, which is attributed to the overlapping of the bands associated with new C-C, C=C and C-N bonds formed during the thermal treatment and related to the amorphization. Moreover, the elemental analysis of the [TPrA][Ni(dca)₃] annealed at 305 °C exhibits a higher percentage of organic material (% CNH) than the sample coming from Ni(dca)₂-pure (Table S3 of ESI).

Based on these findings, we conclude that the organic TPrA building blocks of the [TPrA][M(dca)₃] precursors contribute to the formation of amorphous material which, in turn, play a key role in the morphology of the final M@CNTs.

3.5. Porous structure of M@CNTs

The shape of the N₂ isotherms (Fig. 5a) is typical type IV characterized by the presence of a hysteresis loop due to the capillary condensation. It reflects that both samples display a nanostructured porosity with a wide proportion of mesopores.

Figure 5. (a) N_2 adsorption/desorption isotherms and (b) pore size distribution (PSD) versus pore-diameter for the M@CNTs (M = Ni and Co). Ni@CNTs achieves a total pore volume of $0.29 cm^3 g^{-1}$ and an equivalent BET-surface area of $235 m^2 g^{-1}$. Its isotherm shows a well-defined capillary condensation above 0.4 P/P_0 which corresponds to the presence of interconnected pores network. Fig. 5b shows a quite controlled pore size distribution with a marked unimodal contribution from pores of around 5 nm. On the contrary, this feature is hardly observed in Co@CNTs. This material displays a significant lower pore volume ($0.19 cm^3 g^{-1}$) and a broad PSD up to 6 nm. Nevertheless, the slightly more significant presence of smaller pores in Co@CNTs allows reaching a BET-surface area of $277 m^2 g^{-1}$. The analysis of the isotherms for both materials by the D-R equation reports a characteristic energy E_0 of around $16-17 kJ mol^{-1}$, which indicates somewhat supermicroporosity of about 1.8-2 nm.⁶¹

3.6. Magnetic characterization of M@CNTs

The room temperature magnetization versus magnetic field curves of the M@CNTs annealed at 900 °C are shown in Fig. 6. As it can be seen there, both samples seem to exhibit ferromagnetic behaviour at room temperature as indicated by the open hysteresis loops with remnant magnetization M_R of $1.79 emu g^{-1}$ (Ni@CNTs) and $2.01 emu g^{-1}$ (Co@CNTs), saturation magnetization M_s reached at rather small magnetic fields (10000 Oe or 1 T), and finite coercive fields H_c (67 Oe and 282 Oe, for Ni@CNTs and Co@CNTs samples, respectively). The low values of M_s (around $12.85 emu g^{-1}$ for Ni@CNTs and $12.38 emu g^{-1}$ for Co@CNTs) in comparison to the bulk materials ($\sim 54 emu/g$ for Ni bulk and $\sim 160 emu g^{-1}$ for Co bulk)⁶² are due to the mass ratio of the magnetic material and the non-magnetic carbon in the M@CNTs. This magnetic behaviour of these M@CNTs, with particularly small hysteresis and low critical fields H_c at room temperature, is related with the small diameter of the M nanoparticles, whose average particle size is in fact around the predicted⁶³ critical diameter (D_{cr}) for the Ni and Co single domain particles ($D_{cr-Ni} = 55 nm$; $D_{cr-Co} = 15 nm$)⁶³.

Figure 6. Magnetization (emu g^{-1}) versus Magnetic Field (Oe) of M@CNTs obtained at 900 °C, (M = Ni and Co). Inset: enlarged view of the low field region.

To make sure that the observed behavior corresponds to the particle blocked state, we have measured the temperature dependence of the magnetization (see the ZFC and FC curves of the Fig. S11 in ESI) and estimated their blocking temperature.

As it can be seen there, the ZFC magnetization increases upon heating in the whole temperature range studied and remains lower than the FC magnetization at least up to 400 K.

In this scenario, we expect a superparamagnetic behaviour of the particles with a blocking temperature T_B higher than 400 K.

On the other hand and by looking carefully at the hysteresis loops, we also observe that they are not symmetric in coercive field. This could be a sign of partial oxidation of the NPs,^{64,65} as the presence of antiferromagnetic (AF) MO in contact with the M is reported to lead the exchange bias phenomena in those type of nanoparticulated systems.^{66,67} Such result corroborates the presence of traces of metal oxide in our samples, that can be only hardly detected by XRD as explained above.

With all those results in mind, we can conclude that the here proposed synthetic method is a good approximation to obtain M@CNTs with magnetic NPs near the size region of magnetic single domain.

3.7. Oil adsorption and desorption

We have performed preliminary essays of the capability of the obtained M@CNTs samples for selective oil adsorption in an oil-water mixture. As the behavior for both Ni- and Co-samples is similar, we show here only the results for the Ni@CNTs sample. As shown in Fig. S12a of ESI, the Ni@CNTs sample floated on the oil film, which shrinks toward the sample until saturation of the Ni@CNTs. After 2 minutes, the oil-saturated Ni@CNTs material could be easily collected using a magnet (see Fig. S12b of ESI). After the oil adsorption, the Ni@CNTs was heated in the TGA equipment from room temperature to 600 °C in order to thermally desorb the oil pollutant. In these conditions, the oil desorption started at ~70 °C, process which was completed at ~450 °C (Fig. 7a), that is, in the temperature range in which the Ni@CNTs are still thermally stable.

As evidenced in Fig. 7b, FT-IR spectra of the gas released indicated only oil desorption in the whole temperature range, therefore confirming selective adsorption of the oil in the Ni@CNTs while water was not adsorbed. From weight measurements and TGA analysis we found a selectively oil adsorption capacity ($m_{(\text{Oil}+\text{M@CNTs})}-m_{(\text{M@CNTs})}/m_{\text{M@CNTs}}$) of 2.2 g g^{-1} , for both Ni@CNTs and Co@CNTs samples.

This oil adsorption capacity, which is comparable to values described in the literature for other carbon-coated magnetic nanoparticles,⁶⁸ reveal a promising potential for spilled oil recovery using this easily-synthesized material.

4. Conclusions

This work shows that the incorporation of dicyanamide building blocks in organic-inorganic hybrid compounds is a promising strategy to use such materials as precursors for the synthesis of multiwall carbon nanotubes

with embedded magnetic nanoparticles (M@CNTs). Herein, it is described a novel one-step, scalable and fast synthetic route that, at difference with other complex CVD or arc-discharge methods, just by direct calcination of the organic-inorganic hybrid perovskite [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺), allows to obtain M@CNTs (M = Ni and Co) with regular morphology and essentially mesoporous structure. Their specific surface-area is around 250 m² g⁻¹ but whereas Co@CNTs display a broad pore size distribution up to 6 nm, Ni@CNTs show a strictly controlled unimodal PSD, centered at around 5 nm.

Figure 7. (a) TGA graph for the thermal oil desorption from the M@CNTs materials, measured from room temperature to 600 °C, with a ramp of 5 °C min⁻¹; and (b) FT-IR spectra of the gas released at 95 °C and 325 °C.

The monitoring techniques for the calcination evolution (TGA, FT-IR and Raman spectroscopies, elemental analysis and PXRD) suggest that the precursors [TPrA][M(dca)₃] (M = Ni²⁺ and Co²⁺) evolve towards a coexistence of crystalline M(dca)₂ (M = Ni²⁺ and Co²⁺) with amorphous material, which under further heating transform into M@CNTs (M = Ni and Co). The calcination temperature is critical to obtain homogeneous well-defined M@CNTs, being ~900 °C the optimal temperature.

Meanwhile, at 600 °C the formation of CNTs is not completed and at 1300 °C these CNTs are unstable and the magnetic NPs become less homogeneous, more agglomerated and some of them get oxidized.

Magnetization studies as a function of magnetic field reveal a ferromagnetic behaviour of the obtained M@CNTs, with the magnetic NPs exhibiting particle sizes near the region of magnetic single domain.

Interestingly, preliminary essays have shown that these M@CNTs can selectively adsorb oil from an oil-water mixture with a capacity of 2.2 g g⁻¹ ($m_{\text{Oil+M@CNTs}} - m_{\text{M@CNTs}} / m_{\text{M@CNTs}}$), and that the oil can be subsequently thermally desorbed at 450 °C, with recovery of the M@CNTs materials.

These physicochemical properties of the obtained M@CNTs, combined with the large N/C ratio (up to 5.5:100), rend the materials good candidates for other nitrogen-rich CNT common applications.

Therefore, this work can encourage further research on the applications and development of M@CNTs by this route with improved properties.

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