

## An easy and economically viable route for the decoration of carbon nanotubes by magnetite nanoparticles, and their orientation in a magnetic field

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### A simple, cheap and tunable approach for the decoration of carbon nanotubes by magnetite nanoparticles and their orientation in a magnetic field is reported.

Carbon nanotubes (CNTs) have unique electronic, mechanical, thermal and chemical properties that justify the steadily increasing attention paid to them.<sup>1</sup> Chemical functionalization of CNTs by non covalent and covalent bonding of organic molecules is extensively studied in order to improve dispersion in both liquid phases and polymer matrices. Insofar as they can be individualized, positioned and oriented onto surfaces, CNTs can find applications in nanoelectronics. For this purpose, multi-walled carbon nanotubes (MWNTs) have been grafted by preformed poly(2-vinylpyridine) (P2VP) chains by a covalent bonding technique.<sup>2</sup> In acidic water, the P2VP shell is protonated, which makes it easier to individualize and solubilize the MWNTs, to deposit them selectively onto an oppositely charged surface, and to use the polyelectrolyte shell as a template for the deposition of metal nanoclusters.<sup>2</sup> Although very efficient, this technique requires the synthesis of tailored P2VP prior to grafting onto the MWNTs. Recently, a new strategy has been reported for decorating CNTs with magnetic nanoparticles (Co, CoPt and Fe<sub>3</sub>O<sub>4</sub>).<sup>3</sup> CNTs have been modified by  $\pi$ - $\pi$  stacking with carboxylic acid containing pyrene, followed by the binding of the magnetic nanoparticles to the acid groups. However, the functional pyrene derivative has to be synthesized from expensive precursors, and decoration of the CNTs with the magnetic nanoparticles is uneven. Korneva *et al.* have proposed a new procedure to produce magnetic tubes by filling CNTs with paramagnetic iron oxide particles.<sup>4</sup> The advantage of these tubes is easy handling in a magnetic field. However, CNTs with a large outer diameter have to be used, and the magnetic nanoparticles are not located on the external surface, which makes them unavailable to further reactions (catalysis for instance).

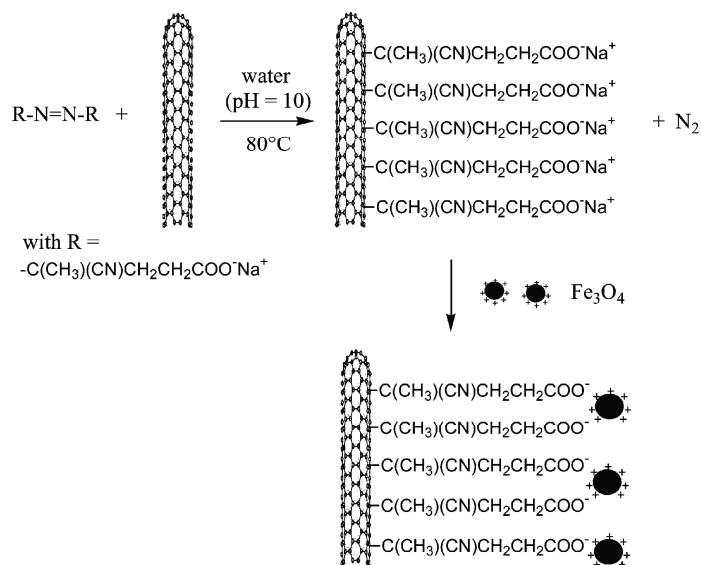
This communication aims at reporting a simple, cheap and tunable approach for the decoration of carbon nanotubes by magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) and their orientation in a magnetic field. In a first step, complexing groups for the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are grafted onto MWNTs by radical addition (Scheme 1). Actually, a commercially available radical polymerization initiator, 4,4'-azobis(4-cyanovaleric acid) (V501), is used, which, upon thermolysis, releases carboxylate (COO<sup>-</sup>) containing alkyl radicals. Complexing carboxylate groups for the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are therefore anchored to the MWNTs by a traditional radical addition mechanism. It must be remembered that the most common way to generate carboxylic acids at the surface of carbon nanotubes, CNTs-COOH, consists of refluxing the CNTs under strong oxidizing conditions (conc. HNO<sub>3</sub>), which results, however, in a severe reduction of the tube length. Moreover, the COOH groups are directly attached to the CNTs without any spacer.<sup>5</sup> More recently, an initiator for the nitroxide mediated polymerization has been used for the grafting of polyacrylic acid and amphiphilic diblock copolymers onto CNTs.<sup>10</sup> Nevertheless, the use of expensive alkoxyamines is required. In contrast, when MWNTs (MWNT THICK 95% purity, Nanocyl S.A.) are heated in the presence of the cheap and commercially available V501 (10 fold wt excess compared to MWNTs) in basic water at 80 °C overnight, C(CH<sub>3</sub>)(CN)CH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>, Na<sup>+</sup> radicals are directly grafted onto the MWNTs, without any substantial shortening of the tubes (as confirmed by TEM). The C3 aliphatic spacer between the carboxylate group and the CNT wall can impart mobility to the carboxylate groups, in favor of their access and further reaction.

The grafting ratio (GR), defined as the weight ratio of the grafted radicals to the nanotubes, has been determined by TGA after purification of the modified MWNTs (MWNTs-COONa) by repeated washing with basic water. The average GR is 6.5 wt%, which corresponds to a carboxylic group content of 0.44 mmol/g of MWNT. The MWNTs-COONa are easily dispersed in a stable manner in water (pH = 7) in contrast to neat CNTs. Fig. 1(a,b) compares the stability of 0.02 wt% dispersions of MWNTs-COONa and pristine MWNTs in water, 3 h after ultrasonication. The COONa groups of the modified nanotubes have been used as complexing groups for decoration with magnetite nanoparticles. Fe<sub>3</sub>O<sub>4</sub> nanoparticles with an average diameter of 5 nm were prepared by the modified Massart method by coprecipitation of a mixture of FeCl<sub>3</sub> (1 M) and FeCl<sub>2</sub> (2 M).<sup>6</sup> The nanoparticles were recovered by centrifugation and washed three times by a HNO<sub>3</sub> (1 M) solution which allows positive charges to be formed at the surface of the magnetite nanoparticles.<sup>7</sup> An aqueous dispersion of the positively charged magnetite nanoparticles was added to a stable aqueous dispersion of MWNT-COONa (0.02 wt%

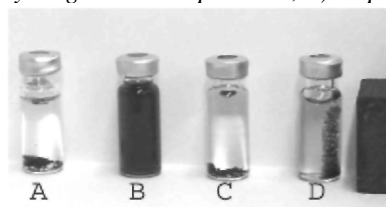
MWNT-g-COONa, pH = 7). A fast precipitation of the modified nanotubes is observed as the result of bonding of the magnetite nanoparticles to the MWNT-COO<sup>-</sup>Na<sup>+</sup> tubes (Fig. 1c). Formation of the MWNT-COO<sup>-</sup>Na<sup>+</sup>/Fe<sub>3</sub>O<sub>4</sub> nanohybrid is fast and takes place without heating or sonication. TEM and HRTEM images (Fig. 2) clearly show that the magnetite nanoparticles homogeneously and densely cover the MWNTs surface.

As shown in Fig. 2, the surface decoration is very homogeneous, no large aggregates or sporadic decoration being observed. The MWNT-COO<sup>-</sup>Na<sup>+</sup>/Fe<sub>3</sub>O<sub>4</sub> nanohybrids are easily recovered by filtration or with a magnet (Fig. 1d).

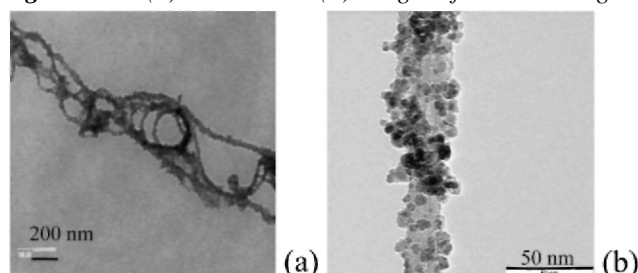
**Scheme 1** Schematic grafting of CNTs and decoration by Fe<sub>3</sub>O<sub>4</sub> nanoparticles.



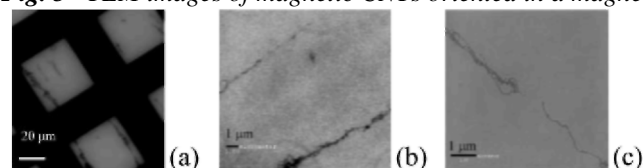
**Fig. 1** CNTs dispersions in aqueous solution: a) pristine CNTs; b) carboxylate grafted CNTs; c) CNTs decorated by magnetite nanoparticles; d) response of the CNTs to a magnet.



**Fig. 2** TEM (a) and HRTEM (b) images of the CNT/magnetite nanohybrids.



**Fig. 3** TEM images of magnetic CNTs oriented in a magnetic field (1 T).



These new MWNTs/Fe<sub>3</sub>O<sub>4</sub> nanohybrids have been oriented in a magnetic field by evaporating a drop of the MWNTs/Fe<sub>3</sub>O<sub>4</sub> nanohybrids dispersion on a 300-mesh copper grid placed in a magnetic field of 1 Tesla. TEM images (Fig. 3) confirm the remarkable orientation of the MWNTs in this field. Carbon nanotubes oriented and connected one to another over a large distance ( $\geq 10 \mu\text{m}$ ) are indeed observed. These magnetic nanotubes have great potential in several fields, such as biology<sup>8</sup> and electronics.<sup>9,11</sup> Magnetic coated CNTs have great potential as tips for high resolution Magnetic Force Microscopy (MFM).<sup>11</sup>

In conclusion, the surface of CNTs is easily modified by chemical grafting of traditional radical polymerization initiators of the azo type. Because a large range of reactive groups containing azo initiators are available, CNTs with a variety of organic functions (*e.g.*, amine, hydroxyl, carboxylic acid, amide,...) can be prepared by this grafting technique. Multi-walled carbon nanotubes have been accordingly grafted by carboxylate groups and homogeneously and densely decorated by magnetic nanoparticles by adding a solution of positively charged Fe<sub>3</sub>O<sub>4</sub> nanoparticles to the negatively charged MWNTs. Easy orientation in a magnetic field has been demonstrated. Due to high surface area, easy recovery and potential recycling, MWNTs densely decorated by metallic nanoparticles are of great interest for application in supported catalysis. Reduction reactions catalyzed by Pd nanoparticles immobilized onto MWNTs are under current investigation.

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