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Attachment of Magnetic Nanoparticles on Carbon Nanotubes and Their Soluble Derivatives

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The magnetic modification of carbon nanotubes is described here. Pyrene can be noncovalently attached on the carbon nanotube surface. A carboxylic derivative of pyrene is used as interlinker for the binding of capped magnetic nanoparticles on the carbon nanotubes. The increased organophilic character of the capped nanoparticles induces high solubility in organic media for the modified carbon nanotubes.

Introduction

Currently, a large amount of research in carbon nanotube chemistry is directed to the synthesis of diverse organic derivatives with the aim to promote surface functionalization and simultaneously provide colloidal stability to the resulting modified carbon nanotubes (CN) in organic or aqueous media.[1−4] Such surface modification of CN through covalent bonding of functional organic molecules opens the way to structural materials of high technological importance.[5−9] However, a main disadvantage from covalent attachment is the uncontrollable reactions that take place over the surfaces and lead to a dramatic decrease in the challenging electronic properties of the nanotubes. On the other hand, the solubility of CN has been improved only in limited cases, usually in highly oxidized and thus shortened carbon nanotubes.[10,11]

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Another way to modify CN without covalent attachment involves polymer wrapping[12−14] or surfactant treatment,[15,16] both approaches ending in solubilized CN. Recently, a new class of CN products has been derived from the combination of CN with metal ions,[17−19] metals,[20−23] and semiconducting nanoparticles.[24−25] This class of CN derivatives shows promising features for nanoelectronics and other applications.

In this article a new strategy to derivatize CN with magnetic nanoparticles is described. In particular, capped iron oxide or cobalt and cobalt/platinum magnetic nanoparticles were attached to carbon nanotubes by means of an interlinker molecule, a carboxylic derivative of pyrene. The procedure relies on the known property of pyrene to interact with CN through $\pi-\pi$-stacking interactions resulting in its attachment to the nanotube surface.[26−29] The available carboxylic groups of pyrene derivative can be further linked to metal or metal oxide nanoparticles. Finally, the inorganic nanoclusters are well dispersed on the nanotube surface, while at the same time the organophilic sheath surrounding the inorganic partner offers the ensuing composites high solubility in organic solvents, such as chloroform, toluene, and hexane.[30−36] This method provides a direct route to synthesize CN−magnetic nanoparticles composites starting from preformed nanoparticles. This offers the possibility to predefine the size, shape, and amount of the nanoparticles attached on CNs, depending on the specific application. A further challenging goal is the ability to exchange the organophilic capping agents with hydrophilic ones (i.e., betaine affords very stable hydrosols[37]). Ferrofluids based on CN/magnetic oxides can find specific application in biology and biomedicine.[38,39]

Experimental Section

Synthesis and Characterization of Capped Iron Oxide Nanoparticles. To 2 g of ammonium iron sulfate $(NH_4)_2Fe(SO_4)_2$ in 50 mL of distilled water were added 1.14 g of KOH in 20 mL of water followed by 0.38 g of ammonium peroxodisulfate $(NH_4)_2S_2O_8$ in 10 mL of water and 1.5 mL of oleic acid in 30 mL of toluene. The mixture was heated at 80 °C for 30 min. The organic phase was separated, and the capped iron oxide nanoparticles were precipitated by ethanol. The XRD pattern in conjunction with Mössbauer results (not shown here) showed that iron oxide was magnetite. The average particle size calculated by Scherer's equation and the half-width of the intense (111) reflection was about 10 nm, comparable to the value obtained from TEM images. TG-DTA analysis showed that the organic part corresponded to nearly 25% of the total weight of the capped iron oxide nanoparticles.

Synthesis and Characterization of Capped Co and CoPt Nanoparticles. Capped Co and CoPt were prepared according to published methods.[40] The XRD pattern of Co nanoparticles showed the characteristic peaks at 44.5 and 51.8 of fcc Co phase. The average particle size, from Scherer's equation, and the (111) reflection was about 9.5 nm. The CoPt nanoparticles exhibited the characteristic reflections at 40.4, 46.9, and 68.3 2θ values of the fcc phase in the XRD pattern. The average particle size from Scherer's equation and the (111) reflection was about 4 nm.

Synthesis and Characterization of the Carboxylic Acid Pyrene Derivative (PyAH). A 1 mmol amount of pyrene aldehyde (Aldrich) and 1 mmol of amino undecanoic acid (Aldrich) were dispersed in 30 mL of absolute ethanol. The mixture was stirred at room temperature for 24 h, and the solution was separated from the unreacted pyrene aldehyde by filtration. After slow evaporation of ethanol the characteristic yellow Schiff base was precipitated. The FTIR spectrum of the product showed the characteristic peak of COOH at 1680 cm^{-1} and the absence of the aldehyde group at 1640 cm^{-1}.

Attachment of Capped Nanoparticles to Carbon Nanotubes. Single-walled carbon nanotubes (Aldrich) were purified by microwaves according to a published method[41] and further by refluxing in 2.5 M HNO_3 for 12 h and washed several times with water and dried. A 1 mg amount of SWNT was dispersed in a solution of 5 mg of PyAH in 50 mL of chloroform/ethanol (1:1). The mixture was stirred overnight, whereupon the yellow color of the supernatant disappeared. A solution of 5 mg of nanoparticle in 5 mL of chloroform was then added, and the mixture was stirred for 2 days. The solution was separated from the residue by filtration and washed with acetone. The yield of the reaction, based on the amount of carbon nanotubes that solubilized, was 90% for CN/magnetite, 70% for CN/CoPt, and 70% for CN/Co.

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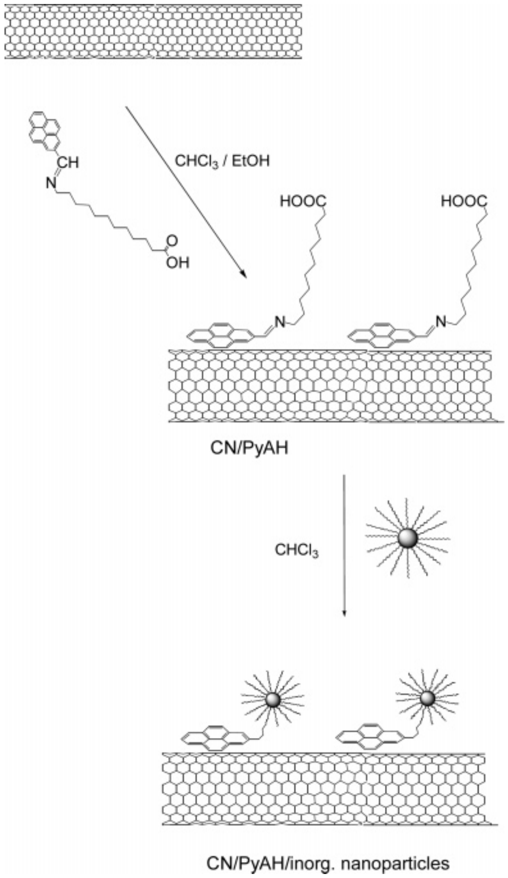
Scheme 1. A Schematic Representation of the Modification of Carbon Nanotubes by Capped Magnetic Nanoparticles



Results and Discussion

In the proposed approach the pyrene carboxylic derivative (PyAH, as shown in Scheme 1) was obtained from Schiff condensation of the commercially available pyrene carboxyaldehyde with an α,ω-amino acid. Amino undecanoic acid was employed here, but other similar amino acids could be similarly used. To remove metal impurities, pristine carbon nanotubes were primarily purified using microwaves[41] and soft acidic treatment. The total removal of metals was certified by XRD analysis. Then CN dispersed in chloroform was mixed with PyAH. After prolonged stirring the relative complex was formed as evidenced by loss of the yellow color of the Schiff base (PyAH) in the supernatant. In addition, the UV−vis spectrum of the CN−PyAH complex dispersed in chloroform showed the characteristic bands of PyAH slightly blue shifted due to interaction of the pyrene system with the nanotube surface (see Figure S1 in Supporting Information).

The sorption of PyAH by the nanotubes was not sufficient to increase their solubility in organic media. At this point a second stage of modification followed that involved interaction of the above CN−PyAH intermediate with preformed capped iron oxide (Fe_3O_4) nanoparticles.

The latter forms stable organic solutions when oleic acid is used as capping agent. After dispersion of a certain amount of CN−PyAH intermediate in solution and stirring, the major part of the solid was solubilized (70−90%). By removing the undissolved part product **1a**, CN−PyAH−Fe_30_4(oleate), was isolated by addition of alcohol to the solution and centrifugation and redissolved in toluene or chloroform, giving stable solutions for a long time. Similar solubilization was achieved when other capped magnetic nanoparticles such as CoPt or Co were mixed with CN−PyAH intermediate, resulting in formation of products **1b**, CN/PyAH/CoPt-(oleate), and **1c**, CN/PyAH/Co(oleate).

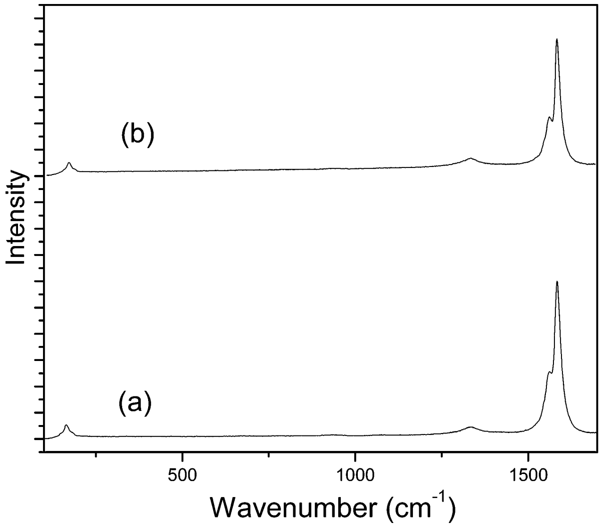


Figure 1. Raman spectra of carbon nanotubes (a) in the starting material and (b) after removal of iron oxide Fe_3O_4 and interlinker PyAH from the corresponding composites.

The stability of the magnetic organosols is attributed to linkage of the organophilic capped nanoparticles to the nanotubes. This is realized through the bonding of the carboxylate group of PyAH linker on the surface of the nanoparticles. This linkage formation took place by simply stirring the mixture without heating or sonication. It was signaled by a change in the color of the solution to dark brown and a gradual solubilization of the nanotubes. The high solubility of the capped nanoparticles in toluene, chloroform, or hexane (0.3−0.6 mg/mL) induced solubilization of the modified CN in these solvents. A schematic illustration of the modification procedure is shown in Scheme 1.

The interaction of capped iron oxide or metal nanoparticles with carbon nanotubes without the contribution of pyrene interlinker did not lead to the formation of similar soluble derivatives. To verify the presence of carbon nanotubes in the final products, samples of the latter were dissolved in toluene and treated with concentrated hydrochloric acid. Metal or metal oxide nanoparticles were converted to the chloride salts and dissolved into the water phase, whereas oleic acid and PyAH were dissolved in toluene. A black residue remained at the interface, and a typical analysis by Raman spectroscopy certified the presence of SWNT without any characteristic alteration in comparison with the spectrum of the starting material (Figure 1). However, this is an expected result since the modification was based on a noncovalent bonding to the nanotubes, which usually does not change the electronic properties and the structure of the nanotubes.

Products **1a**, **1b**, and **1c** were characterized by a number of techniques. The FT-IR spectra clearly showed the presence

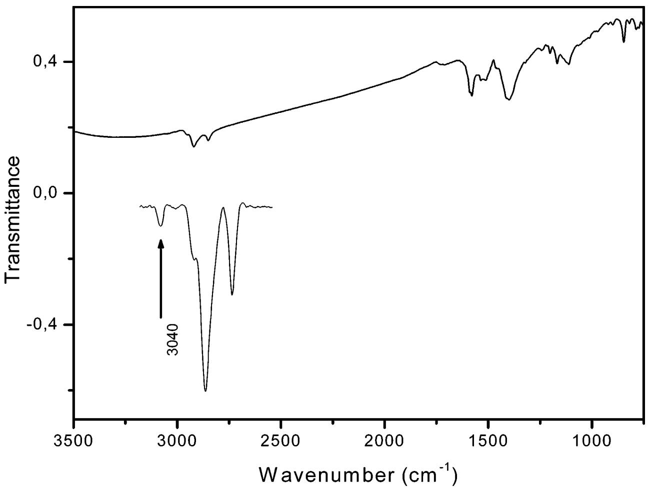


Figure 2. FT-IR spectrum of the product **1a** CN/PyAH/Fe_3O_4(oleate).

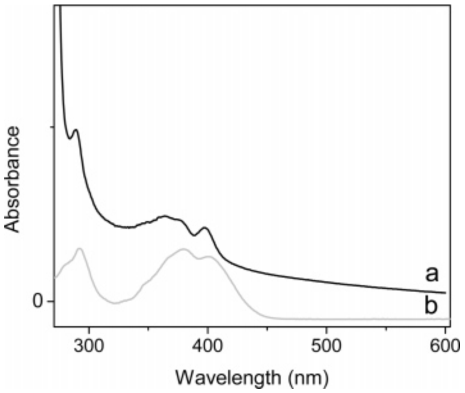


Figure 3. UV−Vis spectra of (a) the product **1a** CN/PyAH/Fe_3O_4(oleate) and (b) intermediate PyAH/Fe_3O_4 for comparison.

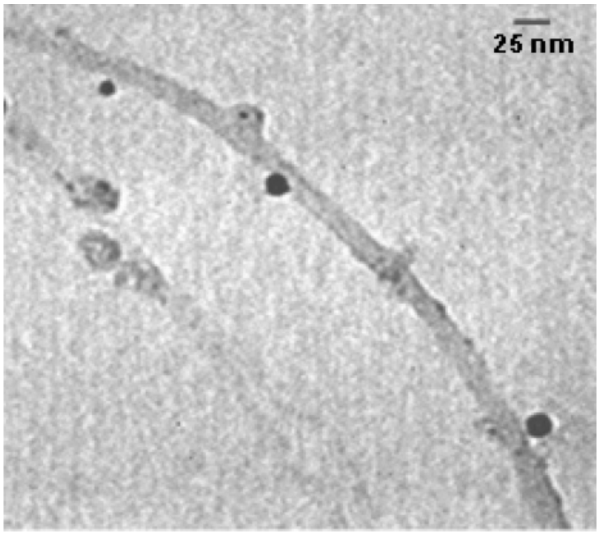


Figure 4. TEM image showing iron oxide nanoparticles bound on the carbon nanotubes surface.

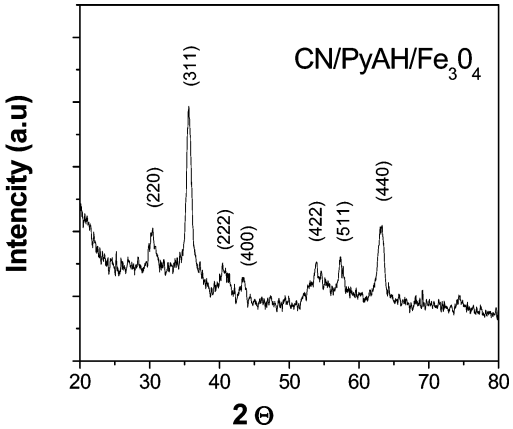


Figure 5. XRD patterns of CN composites with capped iron oxide nanoparticles.

of long aliphatic chains of oleic acid by the intense absorptions at 2920, 2851 cm^{-1} from the asymmetric and symmetric CH_2 stretching vibration and the absorptions at 1580 and 1400 cm^{-1} from the asymmetric and symmetric carboxylate units coordinated to the surface metal atoms. A characteristic peak of the pyrene group at 3040 cm^{-1} was also present (Figure 2).

The UV−vis spectra of the modified carbon nanotubes are useful not only for identification reasons but also for testing the stability of the resulting organosols. Thus, solutions of the CN derivatives in $CHCl_3$ (0.6 mg/mL) were stable for at least 3 weeks without changes in their UV−vis spectra. The known intense absorption bands of pyrene characterize the spectra from the derivatives' solutions (Figure 3 and S2 in Supporting Information). It is worth noting that in the spectra of the composites the pyrene absorptions are superimposed on a continuously rising background that originates from the presence of CNs. This background is not observed in the spectrum obtained from mixing the magnetic nanoparticles with PyAH (Figure 3, curve b).

TEM images from the magnetically modified carbon nanotubes were collected in order to confirm the linkage of the inorganic partners to the surface of CNs. A carefully selected micrograph in Figure 4 clearly shows a sporadic decoration of CN/PyAH with capped nanoparticles. In several other TEM images the magnetically modified nanotubes formed large aggregates which were not useful to provide any further information.

To characterize the presence of Fe_3O_4, Co, or CoPt nanoparticles in the final composite material, XRD patterns were also recorded. As presented in Figure 5, the XRD pattern of product **1a** consists of the characteristic peaks of iron oxide while in the case of products **1b** or **1c** with Co or CoPt nanoparticles, respectively, the related peaks also appeared (see Figure S3 in Supporting Infomation).

The two important goals of this procedure are the magnetic modification of carbon nanotubes and the enhanced solubility of the final products. Both characteristic properties are presented in the images of Figure 6. Photographs a and b show characteristic colored solutions from composite **1a** in chloroform in different concentrations. Photograph c presents composite **1a** dispersed in acetone and d the response of the acetone dispersion to a permanent magnet.

Another important issue, in this study, is that the nanoparticles are not directly attached on the nanotube surface. Due to the interlinker length, there is a controllable distance between the nanoparticles and the nanotube surface which could be interesting in the study of the electronic and magnetic properties of the modified carbon nanotubes.

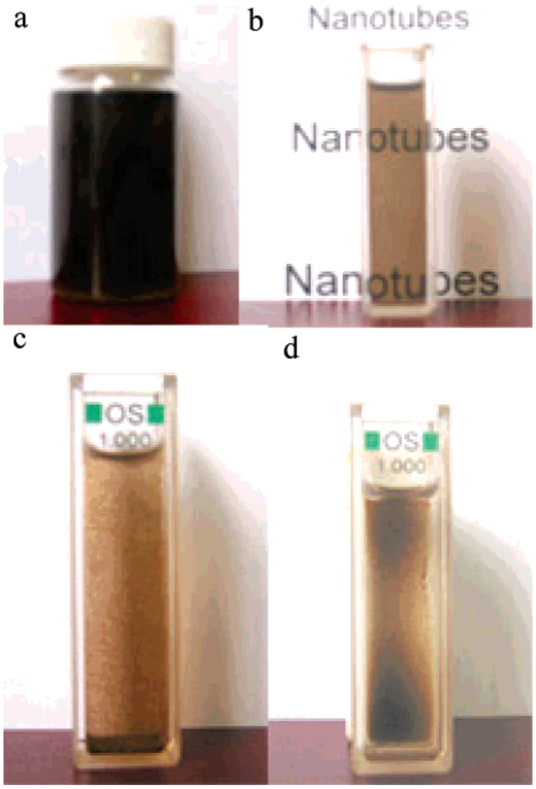


Figure 6. Photographs of (a,b) composites **1a** in chloroform in different concentration, (c) dispersion of composite **1a** in acetone, and (d) its response to a permanent magnet.

In conclusion, a simple and efficient method to attach magnetic nanoparticles to the surface of carbon nanotubes has been developed. The organophilic sheath surrounding the surface of the inorganic particles imparts to the CN enhanced solubility in organic solvents including chloroform, toluene, and hexane, and the resulting ferrofluids are stable for a long time. No significant changes in the properties of the composite materials were observed when the reactions were performed on a larger scale. There are few CN/metal derivatives reported in the literature without presenting remarkable solubility, unlike the composite described in this study. This is important since carbon nanotubes are practically insoluble in any solvent, and this is one of the main drawbacks in their applications. In addition, facile recovery of the starting CNs is successful because of the use of pyrene as interlinker. CNs in the magnetic composite materials remain intact since the nanoparticles are not directly attached to the tubes. This is important for the study of interactions between magnetic and electronic properties of the obtained composites. Finally, a serious problem in using CNs in nanoelectronics is handling them without destroying or altering their properties. On the contrary, the as-synthesized magnetically modified carbon nanotubes could be exploited in this way since they could be handled by magnetic forces without altering their electronic or mechanical properties.

Supporting Information Available: Additional figures for the characterization of the modified nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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