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Synthesis and characterization of FePt nanoparticle/ multi walled carbon nanotube composites

Yan Wang*, Lian Gao, Jing Sun and Yangqiao Liu
State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

This paper reports the synthesis of FePt nanoparticle (NPs)/multi walled carbon nanotube (FePt/MWNTs) nanocomposites, which have important potential implications to orient CNTs and the development of catalysts. FePt NPs have been synthesized by a chemical method, whose crystallite size is about 2.5-4 nm with a Fe content ranging from 50 to 65. MWNTs produced by chemical vapor deposition have been decorated with FePt nanoparticles under mild conditions without any pretreatment. When the diameter of MWNTs is about 20-30 nm, FePt NPs mostly attach onto the sidewalls of MWNTs. The amount of FePt NPs attached onto the MWNTs can be well controlled. Transmission electron microscope (TEM), high-resolution transmission electron micrograph (HRTEM) studies, and energy dispersive X-ray spectroscopy (EDS) spectra were performed to observe the nanostructure of these nanocomposites. The orientation in these nanocomposites has been studied initially.

Key words: FePt nanoparticles, MWNTs, Nanocomposite.

Introduction

Since carbon nanotubes (CNTs) were found in 1991 by Iijima, the remarkable mechanical, electronic, optical, and magnetic properties of carbon nanotubes have been intensively studied towards applications in many different fields [1-3]. Many of the potential applications of CNTs are based on their electronic properties, which could be controlled by their diameter, chirality, functional groups and orientation [4, 5]. However, misorientations of CNTs decrease sharply their performance in electrical applications more than expected, such as a lower electrical and thermal conductivities. Thus to overcome these limitation, it is urgent to study the orientation of CNTs. Several methods have been reported to orientate CNTs in a magnetic filed [6, 7]. For example, Correa-Duarte et al. used magnetic nanoparticles, such as Fe_3O_4 NPs, to attach onto CNTs to orient MWNTs in a magnetic field [8, 9]. However, the Fe_3O_4 NP size was usually 6-10 nm, which makes it difficult to directly synthesize magnetic NPs and CNTs nanocomposites under mild experimental conditions because of the high curvature. So it is critical to decrease the size of magnetic nanoparticles or find novel small size magnetic nanoparticles, from which one can synthesize a high atom ratio of metal NPs to CNTs nanocomposite to orient CNTs.

Here, we report a novel nanocomposite of FePt NPs and multi walled carbon nanotubes (MWNTs). FePt NPs, which were firstly synthesized by Sun et al. in 2000 [10], have attracted intensive studies for many applications such as high-density recording media and ferromagnetic nanocomposites [11-13]. Due to its high superparamagnetic property and the narrow size range, 2-10 nm, FePt NPs were chosen to synthesize the FePt/MWNTs nanocomposites in order to orient MWNTs in magnetic field [14]. Most of the CNT nanocomposites preparation need an initial chemical treatment of the CNTs before assembly, such as HNO_3 refluxing or mixing with a polymer [15]. As is known, the covalent functionalization has been found to deteriorate the intrinsic properties of CNTs [16]. Thus, in our studies, MWNTs have no any covalent functionalization pretreatment in order to keep their pristine properties. FePt NPs and MWNTs have been prepared separately. Then we can control the FePt NPs decoration density by adjusting the initial ratio of FePt NPs to MWNTs.

Experimental Procedure

FePt NPs with crystallite sizes of 2.5-4 nm were synthesized by following the procedure of Saita and maenosono [10]. FePt NPs were dried at 60 ^oC overnight. The CVD MWNTs were used directly without purification. Different ratios of FePt NPs to MWNTs were chosen to synthesize FePt/MWNTs nanocomposites. For example, 10 mg MWNTs and 10 mg FePt NPs were dispersed in 10 ml hexane by 30 minutes ultrasonication in a water bath, separately. Then the two reaction solutions were mixed and stirred at room temperature for 12 h. After centrifugation, some black powders were obtained. Then the nanocomposite was dispersed in $CHCl_3$ by horn ultrasonication for TEM examination.

*Corresponding author:
Tel : +86-21-52412720
Fax: +86-21-52413122
E-mail: wangyan@mail.sic.ac.cn

The MWNTs used in this study were synthesized by CVD at Chengdu Organic Institute, Chinese Academy of Sciences. Platinum (II) acetylacetonate [$Pt(acac)_2$, purity 97%], oleylamine, octyl ether and iron(III) ethoxide [$Fe(OEt)_3$, purity 95%] were purchased from Aldrich. All solvents were of reagent grade quality and were used without further purification. Nitrogen gas (> 99% purity) was purchased from Lixin Gas Corporation. A transmission electron microscope (TEM), a high-resolution transmission electron micrograph (HRTEM), and an energy dispersive X-ray spectroscopy (EDS) analysis were employed to study the MWNTs, FePt nanoparticles and the nanocomposites in a JEM 2100F JEOL with an accelerating voltage of 200 kV.

Results and Discussions

Fig. 1 shows that the TEM and HRTEM images of MWNTs, which were dispersed in $CHCl_3$. It is observed that the pristine MWNTs length ranges from several micrometers to 50 micrometers. According to the supplier, the content of MWNTs was about 95%. The inner diameter was in the range of 2-10 nm and the outer diameter was in the range of 10-30 nm. The thickness of MWNTs' sidewalls was about 3 nm, as seen from Fig. 1(b).

Fig. 2 shows that the TEM and HRTEM images of the prepared monodisperse FePt NPs, which was dispersed in hexane. The crystallite size of FePt NPs is uniform with a narrow diameter range from 2.5 to 4 nm, which are mostly 3.5 nm. EDS spectra show that the atomic content of Fe ranges from 50 to 65, which corresponds to an atom ratio of Fe to Pt ranging from 1 to 2.

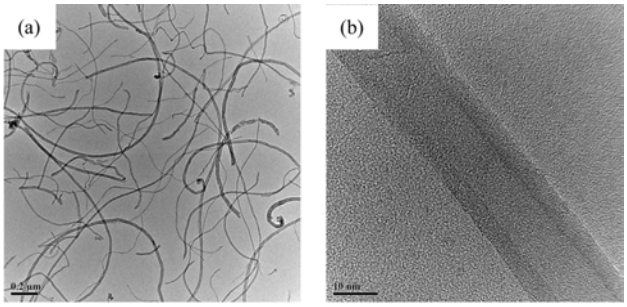

Fig. 1. TEM (a) and HRTEM images (b) of MWNTs dispersed in $CHCl_3$.

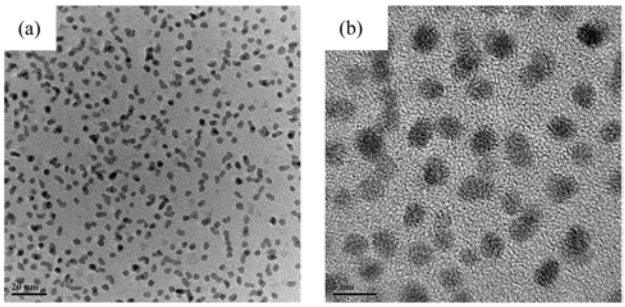

Fig. 2. TEM (a) and HRTEM images (b) of FePt NPs dispersed in hexane.

Fig. 3 shows the TEM and HRTEM images of a FePt/MWNTs nanocomposite, which was dispersed in $CHCl_3$. Fig. 3(a) shows that the FePt NPs are isolated from each other and uniformly attached to the sidewalls of MWNTs. When the diameter of MWNTs ranges from 20 to 30 nm, FePt mostly attach onto the sidewalls of MWNTs. However, when the diameter of MWNTs is about 15 nm, FePt hardly attach onto the sidewalls of MWNTs. Fig. 3(b) is a HRTEM image of the FePt/MWNTs nanocomposite, displaying a layer-by-layer morphology of the sidewall of the MWNTs and the crystalline facets of FePt NPs, which demonstrate the highly crystalline nature of metallic FePt NPs. This indicates that the diameter ratio of MWNTs to FePt NPs play a key role during the assembly procedure. When the ratio is higher than 7, MWNTs can be easily decorated with FePt NPs during the assembly under mild experimental conditions. When the ratio is lower than 5, only a few FePt NPs can attach on the sidewalls of MWNTs. In addition, the amount of FePt NPs attached on MWNTs can be controlled by the concentration of FePt NPs, which will be discussed in another report.

A possible formation mechanism of the FePt/MWNTs nanocomposite is schematically shown in Fig. 4. The literature suggests that FePt NPs are generally stabilized with alkyl carboxylic acid (ROOH) and alkyl amine (RNH_2) [17, 18]. –COOH can covalently link to Fe, forming iron carboxylate (–COO–Fe). The –COO– acts either as a chelate ligand, binding to Fe via two O atoms, or as a monodentate molecule, linking to Fe via only one O atom. On the other hand, $–NH_2$ prefers to bind to Pt via a coordination bond [17]. Also in our studies, the surfaces of FePt are stabilized by two single straight-chain hydrophobic groups ($–(CH_2)_{16}CH_3$ and $(–(CH_2)_{17}CH_3)$[17]. The surface

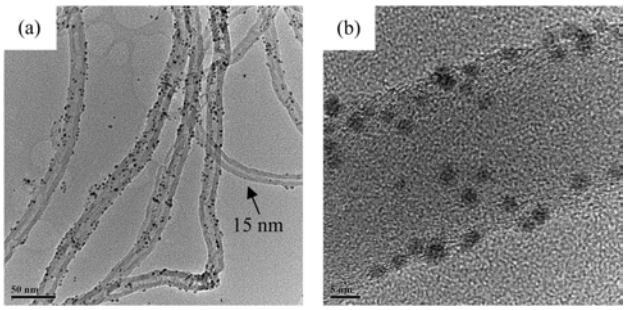

Fig. 3. TEM (a) and HRTEM images (b) of a FePt/MWNTs nanocomposite.

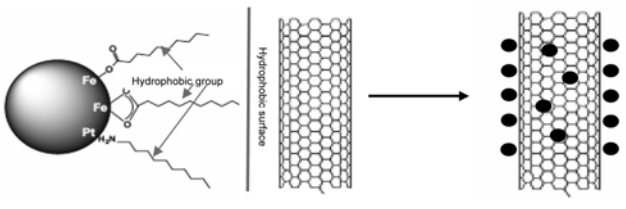

Fig. 4. Schematic illustrations of the assembly of FePt NPs [17] on MWNTs.

of MWNTs without a treatment is mainly graphite structure. In view of the inertness of MWNTs walls, we dispersed FePt NPs in $CHCl_3$, which is also an excellent solvent to wet MWNTs. And under stirring conditions, the alkene groups prefer to interact with the MWNTs surfaces, namely, FePt NPs attach onto MWNTs through the hydrophobic segment. The force between FePt NPs and MWNTs is a van der waals force. The magnetic separability of the nanocomposite was tested in $CHCl_3$ by placing a magnet near the glass bottle. The black sample was attracted toward the magnet in 30 minutes, demonstrating its magnetic sensitivity and potential implications to orient CNTs.

Summary

In summary, we report a novel synthesis of FePt/MWNTs nanocomposite assemblies. FePt NPs have been successfully loaded on the sidewalls of MWNTs under mild experimental conditions and a possible formation mechanism was discussed. The FePt NPs/MWNTs nanocomposite can not only make oriented CNTs possible but also may have potential applications in catalysis and for sensors.

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