Magnetic Fe nanoparticle functionalized water-soluble multi-walled carbon nanotubules towards the preparation of sorbent for aromatic compounds removal†

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Magnetic Fe nanoparticle functionalized water-soluble multi-walled carbon nanotubules (MWNTs) were prepared, characterized and used for the removal of aromatic compounds in water and re-use.

With the development of petroleum refining and chemical engineering, the release of various harmful organic chemicals into the environment has gained attention all over the world because of their toxicity and widespread use, especially aromatic compounds considered as carcinogens. Therefore, it is crucial to develop simple and efficient methods for getting rid of aromatic compounds in environmental water. The most widely used method for aromatic compounds elimination is to use activated carbons. However, activated carbons are notoriously difficult to separate from solutions, and thus magnetic separation[1,2] is an attractive alternative to filtration or centrifugation.

Carbon nanotubes (CNTs)-based materials have been the focus of intense research since their discovery,[3] due to their unique structure-dependent electrical, mechanical, and optical properties[4,5] which make them useful materials for a variety of applications, such as heterogeneous catalyst supports,[6] separation membranes,[7] field emission devices,[8] nano-composites,[9] gas storage materials[10] and chemical and biological sensors.[11,12] Recently, Long *et al.*[13] reported that the interaction of dioxin with CNTs was much stronger than that of dioxin with active carbon, and the removal efficiency for dioxin by MWNTs was much higher than other sorbents. Based on this finding, Cai *et al.*[14] prepared a MWNTs-packed cartridge for the solid-phase extraction of compounds such as bisphenol A and 4-*c*-nonylphenol in environmental water. Their results demonstrated that MWNTs should be powerful solid-phase extraction adsorbents for these compounds and that the analytes retained on the MWNTs can be easily desorbed. Thus, MWNTs may be great environmental water adsorbents for these compounds. However, the poor solubility of CNTs and the difficulty in collecting them from their dispersing medium can cause much inconvenience in their practical application. Deng *et al.*[15] reported that magnetic silica nanoparticle functionalized multi-walled carbon nanotubes met the two requirements simultaneously. However, it can be seen that there exists a small drawback in their practical application, due to their comparatively low water solubility. In addition, their preparation procedure is time-consuming. In order to take the best advantage of the CNTs to separate suitable compounds in environmental water, it is necessary to explore functionalized CNTs that are able to highly disperse in water and can easily be separated from their dispersion for re-use. On the basis of these considerations, we selected a simple route to fabricate functionalized magnetic MWNTs, which not only own efficient water solubility, but also can be easily separated from water.

We report here a simple method for fabricating magnetic Fe nanoparticle functionalized MWNTs and improving the water solublility of MWNTs. As a model, MWNTs were selected because benzene and related compounds had a higher bond energy with MWNTs than other sorbents, such as activated carbon, clays, pillared clays, γ-Al_2O_3 and zeolites.[15] With the in-depth research in the chemically modified CNTs, compared with other materials mentioned above, it is more facile to apply MWNTs to the removal of various harmful organic chemicals in environmental water. As a sorbent in water, it is very important to enhance its water solubility so as to improve its efficiency of adsorption.

For the synthesis of magnetic Fe nanoparticle functionalized and water-soluble MWNTs, a strategy was devised, as presented in Scheme 1. MWNTs were dispersed in $Fe(NO_3)_3{\cdot}9H_2O$ solution with the help of an ultrasonic bath. After draining excess water on a rotary evaporator with a vacuum pump and washing with distilled water, the resulting materials were reduced using H_2 at 560 °C and at 900 °C successively. The phenomenon of spontaneous penetration of fluids into wettable capillaries was taken as a guiding idea to load the nanotubes with magnetic nanoparticles.[16] In our experiment, when a capillary was set in contact with the $Fe(NO)_3$ solution, the fluid spontaneously penetrated inside with the help of an ultrasonic bath. Then, excess water was drained slowly on a rotary evaporator with a vacuum pump. In this process, due to adhesion forces inside nanotubes, the solvent outside the nanotubes evaporated more quickly than that inside, which led to a lower concentration inside the nanotubes. Because $Fe(NO)_3$ diffused easily from the high concentration to the low concentration area, a majority of $Fe(NO)_3$ deposited inside the nanotubes. The residue of $Fe(NO)_3$ outside nanotubes was almost removed in the washing of the process. Fe_2O_3 formed inside tube when heating temperature was higher than 500 °C. After reduction at 560 °C and 900 °C, respectively, only pure Fe was detected by XRD (ESI†). Thus, Fe nanoparticles were deposited inside the inner cavities of MWNTs. According to the literature,[15] Fe-MWNTs were attacked by carbon radicals generated by the thermal decomposition of azodiisobutyronitrile

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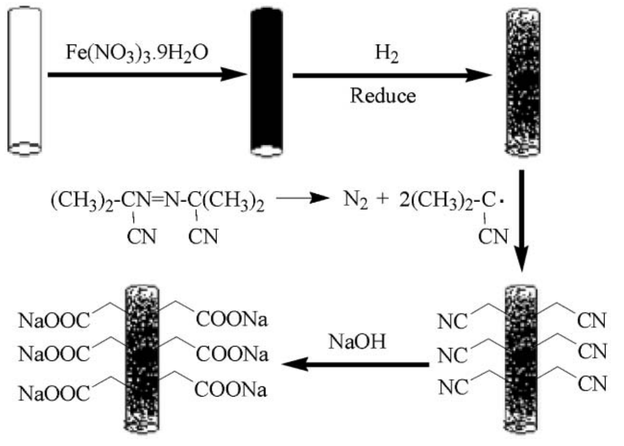
† Electronic supplementary information (ESI) available: experimental details for the preparation of Fe-MWNT-CH_2COONa, FT–IR and XRD characterization results. See DOI: 10.1039/b610842c



Scheme 1 Illustration of the preparation of magnetic Fe nanoparticle functionalized water-soluble multi-walled carbon nanotubules.

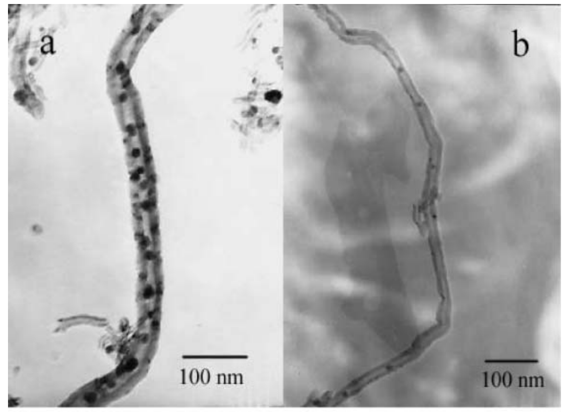
(AIBN), and Fe-MWNT-cyano (Fe-MWNT-CN) were produced. Subsequently, Fe-MWNT-CN was refluxed in sodium hydroxide aqueous solution–methanol mixture, resulting in the magnetic Fe (10.49 wt %) nanoparticle functionalized water-soluble MWNTs (Fe-MWNT-CH_2COONa).

As is shown from TEM micrographs in Fig. 1 (a, b), Fe nanoparticles are deposited inside the inner cavities of MWNTs. Before and after the addition of cyano radicals, MWNTs were characterized by Raman scattering. Fig. 1 (c) shows the Raman spectra (200–2000 cm^{-1}) of raw MWNTs and Fe-MWNT-CH_2COONa. Their spectra are normalized to the intensity of the D-band (1287 cm^{-1}). The effect of functionalization was a lower ratio of intensities of G- and D-bands in the spectra of Fe-MWNT-CH_2COONa compared with raw MWNTs. This lowered ratio of intensities between the two bands can be interpreted as an indication of an increased number of sp^3 hybridized carbon atoms in the Fe-MWNT-CH_2COONa.[17]

Further evidence for successful functionalization of Fe-MWNTs with organic groups was provided by thermogravimeric analysis (TGA) (Fig. 2a), photographs (Fig. 2b) and FT-IR spectra (ESI†). The quality of the carbon radicals attached to the Fe-MWNTs was determined from TGA of Fe-MWNT-CH_2COONa, which showed a weight loss about 29%. Fig. 2b displays the photographs of vials containing Fe-MWNTs in water, Fe-MWNT-CN in THF and Fe-MWNT-CH_2COONa in water, respectively. We found that Fe-MWNTs could well disperse in the corresponding solvent *via* modification of carbon radicals.

According to XRD data and the Scherrer equation (ESI†),[18] the grain size of an Fe nanoparticle inside the MWNTs is around 11.25 nm. Magnetic properties of Fe-MWNT-CH_2COONa were recorded in a Quantum Design vibrating sample magnetometer (VSM).

Fig. 3a showed hysteresis curves collected at 300 K. Fe-MWNT-CH_2COONa showed superparamagnetic behaviour and no remanence at room temperature. These data indicated one potential application of Fe-MWNT-CH_2COONa, that is, its use as an easily recoverable adsorbent. For example, after the addition of Fe-MWNT-CH_2COONa to water, there was a change from black to colorless within few minutes by placing a conventional laboratory magnet near the glass vial. As is shown in Fig. 3b, the black particles were attracted to the magnet, and the clear solution



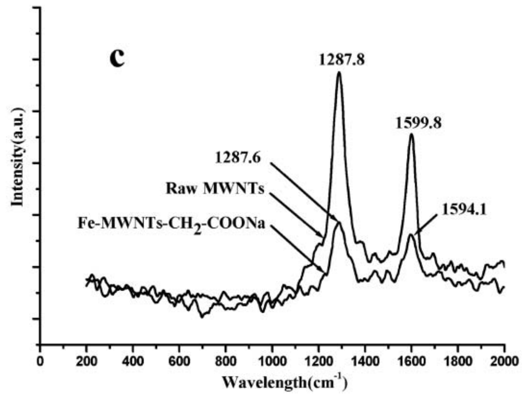


Fig. 1 TEM images of Fe-MWNT-CH_2COONa (a, b) and Raman spectra of raw MWMTs and Fe-MWNT-CH_2COONa (c).

could be easily decanted off or removed by pipette. This simple experiment proved that the Fe-MWNT-CH_2COONa possessed magnetism and could be potentially used as a magnetic adsorbent to remove aromatic compounds in liquid-phase processes.

The applicability of Fe-MWNT-CH_2COONa as a sorbent was investigated using four model aromatic compounds, *viz*., benzene, toluene, dimethylbenzene and styrene. Firstly, the four model aromatic compounds were dissolved in distilled water to get an aqueous solution, in which the concentration of each was 8.6 ppb. Then, after being washed by methanol and dried, 10 mg of Fe-MWNT-CH_2COONa was added to the aqueous solution of the corresponding model compound. The resulting mixture was

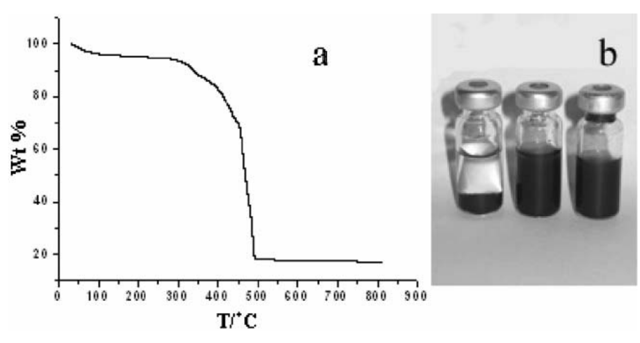


Fig. 2 TGA trace of Fe-MWNT-CH_2COONa measured in air flow with 5 °C min^{-1} (a); Fe-MWNTs in water (left), Fe-MWNT-CN in THF (middle), Fe-MWNT–CH_2COONa in water (right) (b).

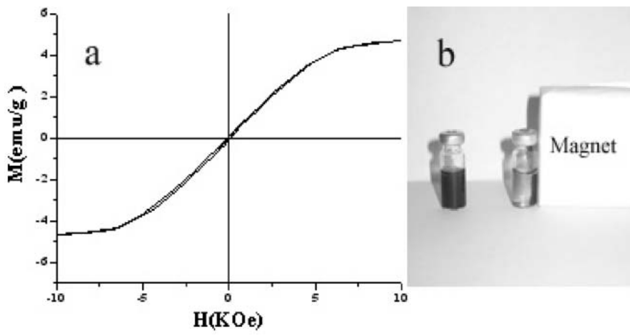


Fig. 3 Magnetic hysteresis cycles for Fe-MWNT-CH_2COONa (a); separation of Fe-MWNT-CH_2COONa by a magnet (b).

shaken at room temperature for a few minutes to form a homogeneous black dispersion. After standing for a few minutes, with the help of a magnet the Fe-MWNT-CH_2COONa was collected from the black dispersion by discarding supernatant liquid, due to the excellent magnetic separation ability of the tubules. Subsequently, the absorbed model compounds were eluted with 0.2 mL of methanol. Finally, 1.0 μL of the eluate was analyzed by gas chromatography (GC). According to the analytical data, the adsorbed percentages of benzene, toluene, dimethylbenzene and styrene are 79%, 81%, 83% and 88%, respectively, which showed that Fe-MWNT-CH_2COONa can be used as a potential sorbent in water. It is worth noting that after being washed several times by methanol and dried in vacuum, the Fe-MWNT-CH_2COONa can be re-used.

In conclusion, the Fe-MWNT-CH_2COONa can be used as a potential sorbent for removing benzene and related derivatives in water. Moreover, they can be re-used, due to their excellent magnetic separation ability. With the great progress in the methods of preparing carbon nanotubes, Fe-MWNT-CH_2COONa can be used as a tool for the purification of environmental contaminated water.

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