Preparation, characterization and application of magnetic silica nanoparticle functionalized multi-walled carbon nanotubes†

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Magnetic silica nanoparticle functionalized multi-walled carbon nanotubes (MS-MWNTs) were prepared, characterized and used for the convenient, rapid and efficient separation of trace aromatic compounds.

Since their discovery in 1991,[1] carbon nanotubes (CNTs) have attracted wide interest for their unique structural properties and outstanding physical properties.[2] With the great progress achieved in the field of CNTs, they have shown more and more potential applications in various fields such as hydrogen storage,[3] electonics,[4] optics,[5] structural materials,[6] chemical sensors[7] and as nanothermometers.[8] Moreover, due to their biocompatibility and low cytotoxicity, applications of CNTs have also been studied in the field of biological and medical study, particularly in the design of transporters or carriers of drug and molecular probes for protein and cell research.[9]

More recently, Long *et al.*[10] reported that the interaction of dioxin with CNTs is much stronger than the interaction of dioxin with activated carbon, and the removal efficiency for dioxin by MWNTs (multi-walled carbon nanotubes) was much higher than other sorbents. Based on this finding, Cai. *et al.*[11] prepared a MWNT-packed cartridge for the solid-phase extraction of compounds such as bisphenol A and 4-c-nonylphenol in environmental water samples. Their results demonstrated that MWNTs should be powerful solid-phase extraction adsorbents for these compounds, and the analytes retained on the MWNTs can be easily desorbed. These results suggest that CNTs maybe have great analytical potential as an effective absorbent for some compounds. However, the poor solubility of CNTs and the difficulty in collecting them from their dispersing media can cause much inconvenience in their practical application. Therefore, in order to make the best of the CNTs advantages (unique structure, high surface area, *etc.*) to separate suitable compounds in environmental water, it is necessary to explore functionalized CNTs that are able to fully disperse in aqueous media and can be easily separated from their dispersion for further determination. To the best of our knowledge, however, there have been few reports on the functionalization of CNTs to meet the two requirements simultaneously. In this communication, we reported a novel functionalized CNT, *i.e.* magnetic silica nanoparticle (magnetite nanoparticles coated with silica) functionalized multi-walled carbon nanotubes (MS-MWNTs). We further used these MS-MWNTs for the rapid separation of aromatic compounds in water. Our results suggested the possibility of wide applications for the MS-MWNTs for the rapid and efficient separation of various chemical compounds which could strongly interact with MWNTs.

Fig. 1 depicts the method used to prepare MS-MWNTs. The procedure consists of three main steps. First, MWNTs were attacked by carbon radicals generated by the thermal decomposition of azodiisobutyronitrile (AIBN), and cyano-MWNTs (c-MWNTs) were produced. Subsequently, c-MWNTs were refluxed in potassium hydroxide aqueous solution/methanol mixture, resulting in solubilized MWNTs (s-MWNTs). Then, silica coated magnetite nanoparticles (MS) were prepared by hydrolysis and condesation of tetraethylorthosilicate in the presence of magnetite nanoparticles as seeds, and the resulting MS nanoparticles were modified by a silane coupling agent, (3-aminopropyl) triethoxysilane (APS), leading to the formation of terminal amino groups on the surface of the MS nanoparticles. Finally, MS particle functionalized MWNTs (MS-MWNTs) were prepared by coupling APS-modified MS particles onto s-MWNTs *via* an amidation reaction between MS particles and s-MWNTs.

MWNTs (50 mg) were first treated in refluxing toluene solution containing 3.20 g AIBN at 75 °C for 4 h, then the product was washed with toluene repeatedly and cyano-MWNTs (c-MWNTs) was produced. The quality of the carbon radicals attached to the MWNTs was determined from thermogravimeric analysis (TGA) of the c-MWNTs, which shows a weight loss of about 40%

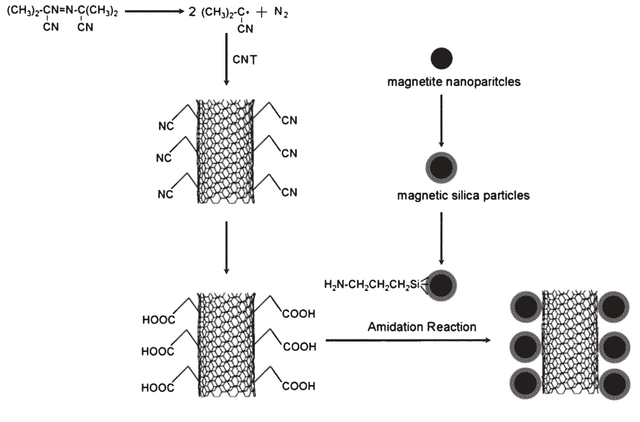

Fig. 1 The overall scheme for the preparation of magnetic silica particle functionalized multi-walled carbon nanotubes.

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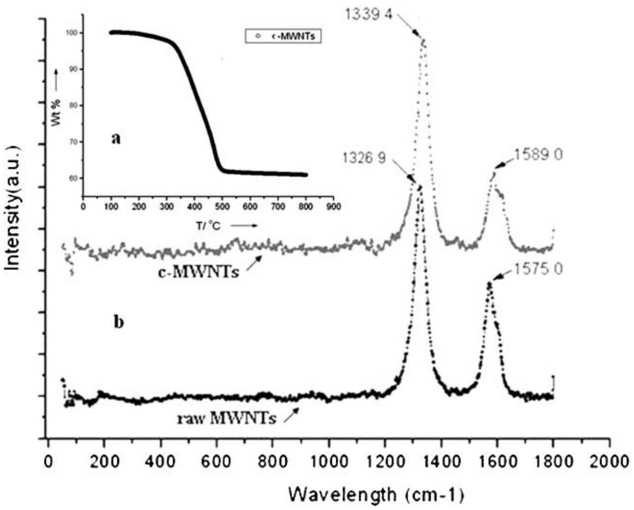

Fig. 2 (a) TGA trace of c-MWNTs measured in nitrogen flow with a heating rate of 5 °C min^{-1}. (b) Raman spectra (632.81 nm excitation line) of raw MWNTs and c-MWNTs.

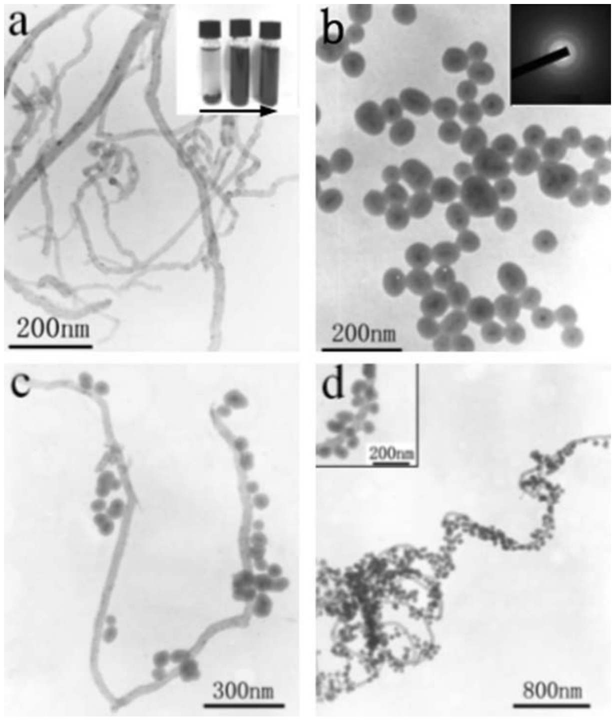

Fig. 3 (a) TEM image of s-MWNTs (the inset from left to right, shows the photographs of raw MWNTs in water, c-MWNTs in THF and s-MWNTs in water), (b) TEM image and electron diffraction pattern of APS-MS nanoparticles, (c) MS-MWNTs containing 15 wt% MS, and (d) MS-MWNTs containing 80 wt% MS.

(Fig. 2a). Raman spectroscopy has been used widely and successfully for characterization of carbon nanotubes. Fig. 2b is the normalized Raman spectra of the raw MWNTs and c-MWNTs, and both of them show a strong band at about 1580 cm^{-1} (G band), associated with the Raman-allowed phonon high-frequency E_{2g} first-order model, and a disorder-induced peak at about 1330 cm^{-1} (D band). The effect of functionalization is a lower ratio of intensities between the G- and D-bands in the spectra of c-MWNTs compared with raw MWNTs. By calculating the ratios, it was found that this ratio decreased from 0.537 to 0.376. This lowered ratio in intensities between the two bands can be interpreted as an indication of an increased number of sp^3 hybridized carbon atoms in the functionalized CNTs.[12,13]

Another very interesting feature is that the maxima of both the G- and D-bands shifted to higher frequencies for the c-MWNTs as marked in Fig. 2b. Moreover, the shoulder in the G-band at around 1617 cm^{-1} became more pronounced in the c-MWNTs. Owing to the high functionalization rate, the as-prepared c-MWNTs can easily and stably disperse in various organic solvents such as tetrahydrofuran (THF), acetone and toluene.

To prepare water dispersible MWNTs, the c-MWNTs (30 mg) were refluxed in a mixture of potassium hydroxide aqueous solution (10 M) and methanol, and solubilized MWNTs (s-MWNTs) with carboxylic groups were produced as a result of hydrolysis of the cyano groups on MWNTs. To prepare MS-MWNTs, magnetic silica nanoparticles with amino groups on their surfaces were first prepared following an analogous procedure as previously reported,[14] and MS-MWNTs were produced in THF by an amidation reaction between APS-magnetic silica particles (30 mg) and carboxylic MWNTs in the presence of 1-ethyl-3-(3-dimethyaminopropyl) carbodiimide (EDC). By changing the weight ratio of MS to s-MWNTs, MS-MWNTs with different amount of MS can be prepared. Fig. 3a shows a TEM image of the obtained s-MWNTs, showing a mixture of long MWNTs with different diameters. Compared with shorter CNTs produced by oxidative methods, the length of our s-MWNTs should remain unchanged, because they were modified in a relatively mild way. The inset in Fig. 3a, from left to right, shows the photographs of raw MWNTs in water, c-MWNTs in THF and s-MWNTs in water, which illustrates well dispersed MWNTs were obtained after modification with carbon radicals. Fig. 3b shows a TEM image and electron diffraction pattern of APS modified MS nanoparticles, indicating that the magnetite nanoparticles were fully encapsulated by silica and core-shell structured MS nanoparticles of about 60 nm were prepared. Fig. 3c and Fig. 3d show TEM images of the obtained MS-MWNTs bound by different amounts of MS nanoparticles, which clearly indicate that MS particles decorate the surface of MWNTs along their surface. It is worth noting that no MS-MWNTs were found in the case of samples prepared by simply mixing MS particles and s-MWNTs in THF. Therefore, the attachment of MS particles to the MWNTs is a result of chemical binding. The attachment of MS particles onto the side of MWNTs was also confirmed by SEM observation, which reveals that MS particles and MWNTs coexist in proximity of each other and indicates that they are bound to each other. Further evidence for the successful functionalization of MWNTS with magnetic silica nanoparticles was provided by FT-IR spectra (ESI†).

The results mentioned above demonstrate that silica-coated magnetite nanoparticles have been successfully bound to MWNTs. In order to characterize their magnetic properties, a vibrating sample magnetometer was used to record hysteresis loops of the prepared samples. Fig. 4a shows the magnetization curves of MS powder (the inset) and MS-MWNTs powder. Due to the existence of nanosized magnetite particles in the MS nanoparticles and MS-MWNTs, both of the magnetization curves exhibit superparamagnetic behavior, *i.e.* no remanence remained when the applied

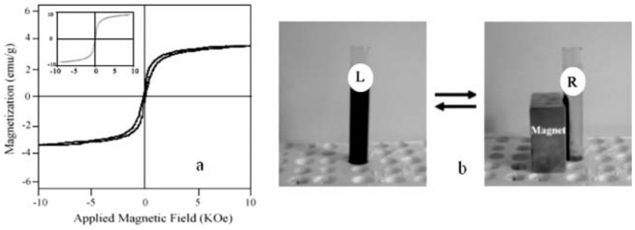

Fig. 4 (a) Magnetization curves of dried MS-MWNTs (contain 80 wt% MS) and MS nanoparticles (the inset); (b) the separation (R) and redispersion (L) process of MS-MWNTs containing 80 wt% MS.

magnetic field was removed. The prepared MS-MWNTs can be readily dispersed in water and form a stable dispersion, and the MS-MWNTs could be separated from their dispersion quickly once an external magnetic field of 2000 G was applied. This redispersion and separation process could be repeated readily as shown in Fig. 4b, which makes it possible to conveniently manipulate CNTs by the application of an external magnetic field.

Due to their unique structure and electronic properties, many new applications of CNTs have been explored in recent years, including protein immobilization and as a solid-phase extraction absorbent, *etc.* As reported previously, CNTs could be used as superior absorbents for some chemical compounds, particularly those with aromaticity. The strong absorption of CNTs towards aromatic compounds is probably due to the π–π-stacking interaction between the graphitic sidewalls of the CNTs and aromatic groups.[15] These reveal to us that our MS-MWNTs could be used for the separation of aromatic compounds in water. Because these MS-MWNTs can be easily dispersed in water, the separation process should be highly simplified with help of a magnetic field, and the separation efficiency should be greatly increased because the compounds have more chance to come into contact with these sorbents when they are fully dispersed in liquid media.

The applicability of MS-MWNTs as a separation tool was investigated using benzene, toluene, xylene and ethyl benzene as model compounds. In this procedure, MS-MWNTs were first washed with methanol and vacuum dried at 40 °C overnight. Then, 10 mg of the dried MS-MWNT was added to a 5 mL aqueous solution containing the four model compounds (concentration of 10 ppb for each compound). The mixture was sonicated at room temperature for 30 s to form a homogeneous black dispersion using a bath sonicator. After standing for 5 minutes, with the help of a magnet, the MS-MWNTs were collected from the black dispersion by discarding the supernatant liquid. 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–mass spectrometry (GC-MS). According the results of the GC-MS measurement, the recoveries of benzene, toluene, xylene and ethyl benzene are 84%, 87%, 88% and 91%, respectively, which suggests a good separation performance of MS-MWNTs.

In conclusion, we have described the preparation of magnetic silica functionalized MWNTs which have been demonstrated as powerful tools for the rapid, convenient and efficient separation of four aromatic compounds. The obtained magnetic MWNTs should be very helpful in analyzing trace aromatic contaminants in environmental water by using them as sorbents in the pre-treatment step prior to chromatographic analysis. Additionally, because CNT is a benign host to encapsulate protein molecules and the silica coatings on the surface of the magnetite nanoparticles are chemically inert materials, MS-MWNTs also offer high potential applications as separation. tools for the purification of protein, magnetically guided transporters for biologically active molecules or probe molecules.

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