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Electronic Supplementary Information

Preparation, Characterization and Application of Magnetic Silica Nanoparticles Functionalized Multi-walled Carbon Nanotubes

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Experimental Section

Materials:

MWNTs generated via chemical vapor deposition (CVD) method were purchased from Shenzhen nanoport (Shenzhen, China), and the purity is over 90%. Other reagents including AIBN, toluene, sodium hydroxide, hydrochloric acid, methanol, (3-aminopropyl) triethoxysilane and four model aromatic compounds are A.R. grade and were used as supplied.

Preparation of solubilized multi-walled carbon nanotubes (s-MWNTs)

50mg MWNTs were dispersed in 50mL of toluene by sonication for 10min. Then, under continuous stirring, 10mL of toluene solution containing 3.20g AIBN was added to the dispersion. Then, in a N_2 atmosphere, the resulting dispersion was heated at 75 ^oC for 4h. The product was repeatedly washed with toluene and vacuum dried at 40^oC overnight, and cyano-MWNTs (c-MWNTs) were produced. To prepare s-MWNTs, 30mg c-MWNTs were dispersed in a mixture of methanol and sodium hydroxide (10M), the resultant dispersion was allowed to reflux at 60 ^oC for 48h. Then, the product was precipitated with hydrochloric acid and washed with deioned water for four times and. Finally, the purified product, i.e. s-MWNT was vacuum dried at 40 ^oC overnight.

Preparation of APS modified magnetic silica nanoparticles

The synthesis procedure for APS modified magnetic silica nanoparticles is similar to our previous report. Specifically, 2.0g magnetic nanoparticle colloidal dispersion (2.0wt %) synthesized by chemical co-precipitation method was diluted with 40mL water and 160mL ethanol, under continuous mechanical stirring, 5.0mL ammonia solution (30wt%) was added. In order to obtain silica-coated magnetic nanoparticles of narrow size distribution, the precursor of tetraethyl orthosilicate (2.0mL) was consecutively added to the reaction mixture, the reaction was allowed to proceed at 40 ^oC for 24h. Then, (3-aminopropyl) triethoxysilane (APS) was added to the reaction

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mixture and the mixture was stirred for another 24h at 40 ^{o}C. The silica-coated magnetic nanoparticles grafted with APS were collected by magnetic separation followed by washing with ethanol for 4 times and with water for 4 times. Then, water was added to achieve a suspension of the obtained colloidal particles of 2.0wt%.

Preparation of MS-MWNTs

Typically, for preparation of MS-MWNTs with larger amount of MS loaded, 10mg s-MWNTs, together with 1.00g suspension of APS modified magnetic silica nanoparticles were dispersed in 60mL of deioned water. The mixture was sonicated for 10min. Then, under continuous mechanically stirring, 5mL aqueous solution containing 5mg 1-ethyl-3-(3-dimethyaminopropyl) carbodiimide (EDC) was added, and this resulting dispersion was heated at 80 ^{o}C for 24h. Finally, the MS-MWNTs were collected from the raw product and washed with deioned water by magnetic isolation. To calculate the MS content in MS-MWNTs, 5% HF aqueous was used to etch the MS particles from MS-MWNTs powder, and the amount of MS could be attained by calculation of the weight of remained MWNTs. The content of MS particles in the prepared MS-MWNTs by this typical recipe was about 80wt%.

Application of MS-MWNTs for separation of four model aromatic compounds

Four model aromatic compounds including benzene, toluene, xylene and ethyl benzene were dissolved in deioned water to get an aqueous solution in which the concentrate of each of them is l.0 ppb. Then, 10mg MS-MWNTs which was previously washed by methanol and vacuum dried was added to the aqueous solution of model compounds. The resulting mixture was sonicated at room temperature for 30s 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 supernatant liquid. Subsequently, the absorbed model compounds were eluted with 0.2mL of methanol. Finally, 1.0μL of the eluate was analyzed by gas chromatography-mass spectrometry (GC-MS).

FT-IR Characterization

Further evidence for the successful functionalization of MWNTs with magnetic silica nanoparticles was provided by FT-IR spectra. The FTIR spectra of raw MWNTs, c-MWNTs, s-MWNTs, APS modified MS nanoparticles and MS-MWNTs are shown in Figure 1. Compared with the spectrum of raw MWNTs (Figure 1a), c-MWNTs (Figure 1b) present at ca. 2890cm^{-1}corresponding to the stretch model of C-H bonds and the characteristic peak of cyano groups at ca. 2160cm^{-1}, which implies that carbon radicals originated from AIBN were efficiently grafted onto MWNTs. In the spectrum of s-MWNTs (Figure 1c), the disappearance of the peak of -CN groups and the appearance of peak at ca. 1725cm^{-1} confirms that carboxylic groups were produced via hydrolysis of –CN groups on MWNTs. In the spectrum of APS-MS (Figure 1d), peak at ca.1625 cm^{-1} is assigned to the N-H bending vibration resulted from APS molecules grafted on MS surface. Additionally, bands corresponding to Si-O-Si symmetric and asymmetric vibrations are located at 1100cm^{-1}and 795cm^{-1}, respectively.[17] In the spectrum of MS-MWNTs (Figure 1e), the peaks at around 2800-300cm^{-1} are associated with the C-H stretch mode. The amide carbonyl group of MS-MWNTs appears at 1655cm^{-1}, and the peak at ca.1570cm-1(Amide II) is associated with the N-H bending vibration in the second amide. Moreover, several peaks including the typical peak of MWNTs at around 1100cm^{-1} were overlapped by bands corresponding to Si-O-Si symmetric vibrations.

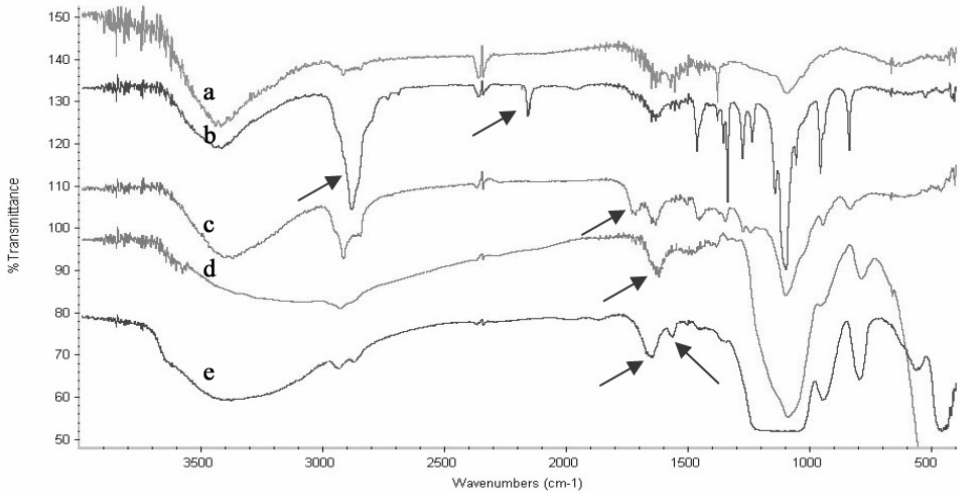

Figure 1 FT-IR spectra of (a) raw MWNTs, (b) c-MWNTs, (c) s-MWNTs, (d) APS modified MS nanoparticles and (e) MS-MWNTs containing 80wt% MS.