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Magnetic nanoparticle-based separation of metallic and semiconducting carbon nanotubes

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Abstract

We report a simple and scalable method for the separation of semiconducting single-walled carbon nanotubes (SWNTs) from metallic SWNTs using magnetic nanoparticles (MNPs) functionalized with polycationic tri-aminated polysorbate 80 (TP80). MNPs–TP80 are selectively adsorbed on acid-treated semiconducting SWNTs, which makes the semiconducting SWNTs be highly concentrated to over 95\% under a magnetic field. Almost all the field effect transistor network devices, which were fabricated using separated semiconducting SWNTs, exhibited a p-type semiconducting behavior with an on/off ratio of higher than 10\textsuperscript{4}.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have received considerable attention because of their excellent electrical and mechanical properties that have led to a wide range of potential applications, such as flexible electronics, sensors, and solar cell technology [1–4]. However, since SWNTs are always grown as bundles of metallic and semiconducting tubes, for practical applications it is necessary to have a high-volume method of separating metallic and semiconducting SWNTs [5]. Various methods have been reported for separating metallic and semiconducting SWNTs, including dielectrophoresis [6–8], selective oxidation [9], amine extraction [10–12], aromatics extraction [13, 14], polymer wrapping [15, 16], and density-gradient ultracentrifugation [17]. Among them, non-covalent functionalization of nanotube sidewalls is of particular interest since it can easily perform large-scale separation. With an octadecylamine (ODA) or porphyrin-assisted method, the semiconducting SWNTs are more strongly adsorbed by ODA or derivatized porphyrin than are the metallic SWNTs [10, 13]. These functionalized SWNTs are stably suspended in organic solvents, whereas the unfunctionalized SWNTs are precipitated. As a result, semiconducting SWNTs are enriched in the supernatant and metallic SWNTs are predominant in the precipitate. However, this process is limited by the tendency of SWNTs to agglomerate into mixed bundles, since both types of SWNTs are co-adsorbed.

To overcome this tendency, we developed a separation method using magnetic nanoparticles (MNPs) functionalized with polycationic tri-aminated polysorbate 80 (TP80) (figure 1). MNPs–TP80, which have superparamagnetic properties, are selectively adsorbed on acid-treated semiconducting SWNTs due to the selective interaction of the amine group toward acid-treated SWNTs [10], and these semiconducting SWNTs are then easily collected by applying a magnetic field. Since MNPs–TP80 disperse well in water, a surfactant such as sodium dodecyl sulfate (SDS) can be added to isolate the SWNT bundles. The resulting semiconducting SWNTs have high concentrations of over 95\%.
2. Experimental section

2.1. Preparation of dispersed SWNT solution

SWNT powders produced by arc-discharge (Hanwha Nanotech, Grade ASP-100F) were carboxyl-functionalized through sonication in a mixture of H2SO4 (120 ml), and HNO3 (40 ml), and DI water (50 ml) for 24 h [18]. The solution was filtered through a Millipore filter, followed by vacuum-drying for 12 h. Subsequently, acid-treated SWNTs (150 mg) were added to 0.01 M SDS dissolved in deionized water (500 ml), and sonicated for 10 h at room temperature to obtain a well-dispersed SWNT solution. The dispersed SWNT solution was centrifuged at 30 000 rpm for 3 h at 4°C to remove the nondispersible SWNTs, and the resulting supernatant solution was carefully decanted.

2.2. Synthesis of MnFe2O4–TP80

MnFe2O4–TP80 were prepared as reported previously [19]. First, MnFe2O4 nanoparticles (MNPs) with a diameter of approximately 12 nm were synthesized using the seed-mediated growth method. Then, to modify the surface of MNPs with amine groups, tri-aminated polysorbate 80 (TP80) was synthesized using 1,1′-carbonyldiimidazole (CDI) as a zero-length cross linker. Finally, MNPs–TP80 were prepared by a nanoemulsion method. 50 mg of MnFe2O4 nanoparticles were dissolved in 4 ml of hexane (as the organic phase), and this phase was mixed with 20 ml of phosphate buffer saline (as the aqueous phase) containing 100 mg of TP80. After mutual saturation of the organic and aqueous phases, the emulsion was ultra-sonicated in an ice-cooled bath for 10 min at 450 W. The organic solvent was evaporated overnight at room temperature, and the products were purified by a centrifugal filter with two cycles at 30000 rpm for 1 h. The size distribution and zeta-potential of MNPs–TP80 measured by laser scattering (ELS-Z, Otsuka electronics) were 40.73 ± 4.63 nm and 25.36 ± 1.87 mV, respectively.

2.3. Separation of semiconducting and metallic SWNTs using MNPs–TP80

MNPs–TP80 suspended in DI water were added to the dispersed SWNT solution (1:10, v/v), and then sonicated for 20 min at room temperature. Then, a permanent magnet was placed at the bottom of a vial containing a mixture of the SWNT solution and the MNPs–TP80 solution to collect the SWNTs functionalized with MNPs–TP80. As shown in figure 2(a), the color of the mixture in the bottom of the vial became dark brown, changing to light brown in the upper part of the vial. This indicated that the SWNTs adsorbed with MNPs–TP80 had concentrated in the bottom of the vial due to the magnet. After one day, the upper mixture was carefully decanted with the magnet remaining at the bottom of the vial. Field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images for SWNTs from the bottom of the vial (SWNTs-bm) and from the upper part of the vial (SWNTs-up) are presented in figures 2(b) and (c), respectively. As expected, MNPs–TP80 were observed along SWNTs-bm (figure 2(b)), with few MNPs–TP80 found along SWNTs-up (figure 2(c)). In addition, we also measured the magnetization curves for SWNTs-bm and SWNTs-up using a vibrating sample magnetometer (VSM; Model 7407, Lakeshore). As shown in figure 3, SWNTs-bm exhibited a superparamagnetic property, whereas SWNTs-up did not, showing that SWNTs adsorbed with MNPs–TP80 were collected into SWNTs-bm.

2.4. Measurements of Raman, photoluminescence (PL), and ultraviolet–visible–near-infrared (UV–vis–NIR) absorbance spectra

Raman analysis was carried out using a micro-Raman spectrometer (LabRam HR, Jobin-Yvon) at 1.96 eV (632.8 nm, He–Ne laser) and 2.41 eV (514.5 nm, Ar⁺ ion laser) excitation at 100× magnification and 1 µm spot size. PL spectra were obtained using an Applied NanoFluorescence NS2 NanoSpectralyzer®. The PL was detected using a TE-cooled InGaAs array and a 786 nm fluorescence excitation laser was used. The UV–vis–NIR absorption spectra were measured using a spectrophotometer (Varian Cary 5000).

2.5. Fabrication of field effect transistor (FET) network devices

FET network devices, whose channel length and width were 5 and 30 µm, respectively, were fabricated on SiO2 (300 nm)/Si substrates. The SWNT solution was dropped on the substrate, followed by heating at 80°C to evaporate the solvent. Then, metal electrodes were made by depositing Cr/Au (3 nm/50 nm) and using a lift-off technique. The electrical transport measurements were conducted in air at room temperature using a semiconductor parameter analyzer (4200-SCS, Keithley).

2.6. Removal of MNPs–TP80

To remove MNPs–TP80 from the carbon nanotubes’ surface, acid treatment was performed after separation of SWNTs. The
Figure 2. (a) Photographs of the experimental process. FESEM and TEM images of SWNTs-bm (b) and SWNTs-up (c). The scale bar of the TEM images is 20 nm.

Figure 3. Magnetization ($M$–$H$) curves measured for SWNTs-up and SWNTs-bm. The inset is the magnetization curve of MNPs–TP80.

SiO$_2$ (300 nm)/Si substrate, which the SWNT solution was dropped on, was immersed in hydrochloric acid for 30 min at 200 $^\circ$C.

3. Results and discussion

To characterize the separated SWNTs, we investigated the Raman spectra. Figures 4(a)–(c) show the radial breathing modes (RBM) measured at 1.96 eV excitation for pristine SWNTs, SWNTs-bm, and SWNTs-up, respectively. The diameter of the SWNTs was estimated to be approximately 1.23–1.41 nm [20–23]; this is comparable to the diameter of arc-discharged nanotubes (1.4 ± 0.4 nm) reported by others [20]. For the pristine SWNTs, containing both semiconducting and metallic SWNTs, two peaks at 170 and 190 cm$^{-1}$ were observed. In contrast, the SWNTs-bm exhibited a nearly complete suppression of the 190 cm$^{-1}$ peak, whereas the SWNTs-up had an enhanced 190 cm$^{-1}$ peak. According to the RBM analysis [20], the peaks at 170 and 190 cm$^{-1}$ are ascribed to semiconducting and metallic SWNTs, respectively. Therefore, these results indicate the selective adsorption of MNPs–TP80 on semiconducting SWNTs, leading to the increased concentrations of semiconducting and metallic SWNTs in SWNTs-bm and SWNTs-up, respectively. We also measured Raman spectra at 2.41 eV excitation (see supporting figures, figure S1, available at stacks.iop.org/Nano/22/045703/mmedia) and similar results were obtained. In figures 4(d)–(f), the G-band Raman spectra measured at 1.96 eV excitation are shown for pristine SWNTs, SWNTs-bm, and SWNTs-up, respectively, which are used to distinguish between metallic and semiconducting SWNTs through differences in their Raman lineshapes at about 1560 nm$^{-1}$($G^-$) [5]. Indeed, different lineshapes of $G^-$ were observed for SWNTs-bm and SWNTs-up, supporting the selective adsorption of MNPs–TP80 on semiconducting SWNTs.

In addition to Raman analysis, we also measured NIR PL spectra for SWNTs-bm, pristine SWNTs, and SWNTs-up solutions, as shown in figure 5. Compared with the
Figure 4. Raman spectra measured at 1.96 eV excitation showing RBM for pristine SWNTs (a), SWNTs-bm (b), and SWNTs-up (c). Corresponding G-band measured at 1.96 eV excitation for pristine SWNTs (d), SWNTs-bm (e), and SWNTs-up (f).

Figure 5. NIR photoluminescence (PL) spectra measured for SWNTs-bm, pristine SWNTs, and SWNTs-up at an excitation of 786 nm. PL of pristine SWNTs, a significant enhancement of PL at about 990 nm was noted for SWNTs-bm, whereas this peak was considerably suppressed for SWNTs-up. These findings confirmed that semiconducting SWNTs were predominant in SWNTs-bm and metallic SWNTs were abundant in SWNTs-up [17].

To estimate the ratio of metallic to semiconducting SWNTs, we measured the UV–vis–NIR absorption spectra for pristine SWNTs, SWNTs-bm, and SWNTs-up, as shown in figures 6(a)–(c), respectively. For SWNTs-bm and SWNTs-up, the spectrum measured for the MNPs–TP80 solution (see supporting figures, figure S2, available at stacks.iop.org/Nano/22/045703/mmedia) was subtracted from the measured spectra to minimize the influence of MNPs–TP80. As with the Raman spectra, the pristine SWNTs and SWNTs-up showed two absorption peaks, at ~1.2 and 1.7 eV, that correspond to $S_{22}$ interband transitions in the semiconducting SWNTs, and $M_{11}$ transitions in the metallic SWNTs, respectively [24–26]. The areas of the $S_{22}$ and $M_{11}$ bands were calculated using a linear fitting method [27], allowing the proportion of semiconducting and metallic SWNTs to be estimated at 67% and 33% for the pristine SWNTs, and 51% and 49% for SWNTs-up. Compared with the pristine SWNTs, the metallic content was somewhat enhanced in SWNTs-up. The proportion of metallic SWNTs could be increased even more if a higher magnetic field was applied or if the magnetic field was applied for a longer time, since all the semiconducting SWNTs adsorbed with the MNPs–TP80 might not have been fully pulled down. The SWNTs-bm showed only the absorption peak at 1.2 eV, which is consistent with the Raman data (figures 4(b) and (e)); the proportions of semiconducting and metallic SWNTs were estimated to be approximately 95% and 5%, respectively. These results clearly show that semiconducting SWNTs can be effectively separated from metallic SWNTs, using the MNPs–TP80-based separation method.

For comparison, we carried out similar separation experiments using ODA, as described in [10]. Approximately 80% of the semiconducting SWNTs were retained in the tetrahydrofuran supernatant (inset of figure 6(b)). This lower purity was possibly attributed to the presence of bundles, since the surfactant that isolates the SWNT bundles could not be used for the ODA-based separation method. These results show that the MNPs-based separation method produces a
higher purity of semiconducting SWNTs than the ODA-based separation method.

The electrical transport properties of separated SWNTs were confirmed through the characterization of FET network devices fabricated on Si substrates with a thermally grown 300 nm thick SiO₂ layer. As shown in figure 7(a), the SWNTs-bm device exhibited a p-type semiconducting behavior with an on/off ratio of $10^4$. In contrast, the SWNTs-up device was much less sensitive to $V_G$, indicating that its composition was predominantly metallic SWNTs.

To determine the uniformity of FET network devices, we fabricated 54 SWNTs-bm devices by dropping the SWNTs-bm solution onto the channel area without intentionally controlling for thickness. Almost all devices showed the p-type semiconducting behavior. A histogram of the on/off ratio for these 54 devices is presented in figure 7(b). Three devices yielded an on/off ratio of $10^6$, and 44 devices exhibited an on/off ratio $\geq 10^4$. These results demonstrate that the performance of SWNT network devices can be significantly improved by using SWNTs-bm.

4. Summary

We have developed a method for separating metallic and semiconducting SWNTs using MNPs–TP80. MNPs–TP80 selectively attach to acid-treated semiconducting SWNTs due to the selective interaction of amine groups with acid-treated semiconducting SWNTs, allowing their collection using a magnetic field. This MNPs–TP80-based separation method has two advantages. First, it yields a high purity of semiconducting SWNTs because the dispersion of MNPs–TP80 in water enables a surfactant to help to isolate SWNT bundles. Indeed, Raman, PL, UV–vis–NIR absorption spectra, and electrical measurements all revealed that the collected SWNTs (SWNTs-bm) contained over 95% semiconducting SWNTs. This purity might be further increased by repeating the separation procedure. The second advantage is that the method is very simple and inexpensive, so it should be applicable within industrial production.

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