The Removal of Metallic Single-Walled using ATPS

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The Removal of Metallic Single-Walled Carbon Nanotubes Using an Aqueous Two-Phase System

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Here we report our findings on the removal of metallic single-walled carbon nanotubes using an aqueous two-phase system. The aqueous two-phase system contained as received carbon nanotubes, polyethylene glycol, dextran, N-methylpyrrolidone, cetyltrimethylammonium bromide, and water which phase separated into top and bottom phases. The top phase was dominated by polyethylene glycol whereas the bottom phase was dominated by dextran. The dextran-rich phase contained more semiconducting species while metallic species was more abundant in the polyethylene glycol rich-phase. It was found via Fourier-Transform Infrared Spectroscopy that cetyltrimethylammonium bromide only present in the dextran-rich phase. A selectivity mechanism is tentatively proposed and discussed.

Keywords: Carbon Nanotube, Aqueous Two Phase, Purification.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are rolled-up graphene sheets that possess exceptional mechanical and electrical properties.1 This makes carbon nanotubes the ideal material for making transistors2–5 and other electronic applications. The heterogeneity of as-produced SWCNTs limits its promising applications in fast nanoscale transistors and sensitive nanoscale sensors.6–7 Many efforts have been made to separate the metallic SWCNTs from the semiconducting SWCNTs including dielectrophoretic deposition,8 DNA-assisted separation,9 acid treatment,10 light-assisted oxidation,12 interaction with amine13 and column chromatography.14 These methods are promising. However, these physical and chemical methods such as microwave irradiation and acid treatments for example inevitably damage the SWCNTs. DNA-assisted separation has an added advantage as purification must be done gently. However, the scalability is a major concern. Industry demands fast, economic, high-yielding and efficient downstream processes for the partitioning and purification of SWCNTs. Aqueous two-phase system (ATPS) is an ideal technology to meet the above demands15 due to its low operational cost, non-toxic, fast and large scale purification.16 In view of these advantages, the main motivation of this paper is to develop a method of separating metallic SWCNTs from semiconducting SWCNTs by using an ATPS.

To purify carbon nanotubes using ATP separation technique, polyethylene glycol (PEG) and dextran are mixed together with organic solvent N-methylpyrrolidone (NMP), cetyltrimethylammonium bromide (CTAB) and water. PEG is dissolved in NMP while dextran is dissolved in water with 1% CTAB. The concept of the research is simple: when an ATPS partitions into two distinct phases, certain species of carbon nanotubes will be attracted to one of the components in an ATPS. In this report, the selective adsorption of amine onto semiconducting SWCNTs is applied.15,17 NMP and cationic surfactant CTAB are added to the system to disperse SWCNTs.18 Dextran has also been reported to wrap around a SWCNT.19,20 Using this system we found that metallic-SWCNT can be removed from dextran-rich phase. A selectivity mechanism is tentatively proposed and discussed.
2. EXPERIMENTAL DETAILS

2.1. Materials and Methods

PEG with average molecular weight \( M_w \) of 1,500 g/mol, anhydrous NMP with 99.5% assay, cationic surfactant CTAB and dextran with average \( M_w \) of 40,000 g/mol were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). SWCNTs with tube diameter 0.7~0.9 nm were sourced from Southwest Nanotechnologies. Deionised water with 1% w/w CTAB was used throughout the experiment. All experiments were conducted within a class 10 K clean room at temperature 19 °C.

2.2. Binodal Curves

A binodal curve is a curve plotted on a phase diagram to express the various phases of a system. The curve separates the two regions of bi-phase and homogeneous phase. This is the first step towards building an ATPS. The estimation of the binodal curve was done according to the method described by Albertsson.21 A few ATPSs were prepared by mixing stock solution of PEG in NMP and dextran in deionised water with 1% w/w CTAB. After mixing, the mixtures were sonicated using WiseClean Ultrasonic Cleaner (Daihan Scientific) at 50 W for 15 min. The cloudy mixture signified that two phases would eventually form. In order to approximate phase transition from two phases into homogeneous solution, deionised water was added slowly until the solution became clear. The binodal curve was plotted for various polymer, dextran and organic solvent concentrations.

2.3. Separation Experiment

To obtain the maximum dispersion of carbon nanotubes in the ATPS, the concentration of each phase forming components must be optimised. Hence, several points were identified from the phase diagram of PEG-NMP/dextran-water system for the separation experiment. A few vials containing different concentrations of PEG, dextran and NMP were prepared. 0.5 mg of pristine SWCNTs was then added into the mixtures and sonicated at 50 W for 20 min. The mixtures were allowed to incubate for 30 min. The volumes of the top and bottom phases were measured at the end of incubation. The results were tabulated to identify the concentrations that exhibit the best dispersibility of SWCNTs and visibility of phases.

2.4. Characterisation

The top and bottom phases were pipetted into two different vials and diluted with 2 ml of deionised water. The diluted solutions were taken for centrifugation at 4,000 rpm for 20 min. The supernatant was discarded. 2 ml of deionised water with 1% w/w CTAB was added to the precipitate. The dispersed SWCNT samples were characterised by using the Thermo Scientific Evolution 300 ultraviolet-visible-near infrared spectrophotometer (UV-Vis-NIR). The Raman signals were obtained using Renishaw Raman Microscope under excitation of 514 nm with power set at 50 mW. The X-ray Photoelectron Spectroscopy (XPS) beamline at the Synchrotron Light Research Institute (SLRI) in Thailand was used for XPS analysis. Furthermore, the contents of the ATPS were analysed using the Perkin Elmer Spectrum 400 Fourier transform infrared spectrometer (FTIR).

3. RESULTS AND DISCUSSION

Figure 1 shows the molecular structure of the different chemicals used in the experiment. Figure 2 shows the phase diagram of PEG-NMP/dextran-water system. It can be seen from the curve that the concentration of dextran-water required to form an ATPS can be as low as 1.25% w/w. The minimum concentration required for PEG-NMP to form two phases is 10% w/w. This could be due to the difference in the average \( M_w \) between PEG and dextran used. This phenomenon is consistent with previously published paper.22

Immediately after sonication, the mixture of the solution was dark as shown in Figure 3(a). It should be noted that the pristine ATPS without SWCNTs is transparent.
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In approximately 30 min, two distinct phases were formed as shown in Figure 3(b). It is worth noting that prior to two-phase partition; the dispersion of SWCNTs in the mixture does not exhibit SWCNT bundles. The formation of SWCNT bundles occurred after the two-phase partition.

The XPS spectrum is used to probe the presence of polymer in the sample. The sample has been washed with copious of water for at least three times to ensure virtually all polymers are removed. The bottom phase samples were illuminated with a 650 eV X-ray beamline from the SLRI, Thailand. Figure 4 shows the resultant XPS spectrum of the SWCNT extracted from the bottom phase. Fitting of the asymmetrical graph shows that there are two peaks; the peak at 285.0 eV and 286.2 eV originating from the C—C and C—O bonds, respectively. Since carbon nanotubes are made of carbon atoms, the C—C bond can be attributed to the carbon atoms. This is supported by an earlier results by Lee et al which shows that a typical XPS spectrum of the carbon 1S centres at 285.0 eV. Meanwhile, the peak centred at 286.2 eV is assigned to the C—O bond. The result is very close to the 286.4 eV published by the same group mentioned above. The high C—O content is most likely a contribution from polymer which suggest a possible wrapping of the polymer with SWCNTs.

UV-Vis-NIR spectroscopy is a widely utilized tool for the characterisation of SWCNTs. The reduction in the size of the peak signifies the reduction of a given species in a sample. Figure 5 shows the UV-Vis-NIR spectra for the SWCNTs absorbed in the top and bottom phases of the ATPS. The targeted area of investigation contains both metallic and semiconducting peaks. The peak at 475 nm represents the first Van Hove transition for the metallic species, denoted as $M_{11}$, while the second Van Hove transition for semiconducting species, denoted as $S_{22}$, falls between 480~750 nm. Within 480~750 nm region, the larger peak at 581 nm originates from the species with chirality (6,5), which is the dominant species in the as-received SWCNTs. The smaller peak at 670 nm comes from semiconducting species (7,6). To ease the discussion on the changes of metallic and semiconducting SWCNTs,
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Fig. 6. Raman spectra for top and bottom phases normalized at G+ peak (1581 cm⁻¹). The inset shows the RBM region of the Raman spectra. The RBM metallic peaks for the top phase are more intense compared to the bottom phase.

we focus on the region where M₁₁ and S₂₂ are located. The resultant curve is baseline-subtracted. The inset in Figure 6 shows the corresponding peaks at the dotted region normalized at S₂₂ peak at 581 nm. Despite the high absorbance for the bottom phase, the signal from the M₁₁ peak is undetected. It can be clearly seen that the M₁₁ peak at wavelength 471 nm has reduced in the bottom phase. The fluctuation seen at region 400~500 nm in the inset of Figure 5 is the result of the small background noise after baseline-subtraction. Raman spectroscopy can also be used to qualitative-evaluate the purity of SWCNTs.²⁸

Figure 6 shows the corresponding Raman spectra for the sample featured in Figure 5 normalized at 1581 cm⁻¹. Comparison with Kataura plot yielded RBM wavenumbers between 180~300 cm⁻¹ and 300~400 cm⁻¹ as metallic and semiconducting peaks respectively. By referring to the corresponding Raman curve in Figure 6, we can see that RBM metallic peaks for the top phase are more intense compared to the bottom phase. The broadening of G⁻ band in the top phase indicates the presence of metallic species.²⁹ Hence, both microRaman and UV-Vis-NIR results indicate that the metallic species are indeed more dominant in the top phase compared to the bottom phase.

By using FTIR spectroscopy, we investigated the contents of the two phases. From the FTIR results shown in Figures 7(a) and (b), we can see that the top phase is PEG-rich while the bottom phase is dextran-rich. Since PEG is more hydrophobic than dextran,²¹ water tends to aggregate in the bottom phase. However, NMP is equally distributed among the two phases. This means that the selective enrichment could not have been due to NMP. CTAB, an amine-bearing surfactant, is present in the bottom phase but not detected in the top phase. The signal of CTAB can be seen and compared clearly in Figure 7(b). Hence it is possible that the selective purification of SWCNTs is attributed to CTAB.

Fig. 7. (a) FTIR spectra of all the constituents of the ATPS from 1800 cm⁻¹ to 400 cm⁻¹ (b) of NMP 50% w/w, CTAB 1% w/w, bottom phase and top phase. There is a clear indication of CTAB in the bottom phase as shown in the dashed rectangle.

Fig. 8. An illustration of the reverse micellar effect. Note that the thin water layer is attracted close to the outer surface of a SWCNT.
The affinity of amine for semiconducting SWCNTs has been reported by numerous authors. The cationic surfactant CTAB has a polar head and a hydrophobic tail. Theoretical modelling suggested that the hydrophobic D-glucose units of dextran wrapped around the hydrophobic outer surface of a SWCNT with the hydroxyl group pointing away from the surface of the SWCNT. In our case, the hydroxyl groups attract a thin layer of water in close proximity to the SWCNT outer side-wall. CTAB does not dissolve in NMP. Hence, CTAB molecules selectively embed their polar heads into the thin water layer surrounding the semiconducting SWCNTs with their hydrophobic tails pointing towards NMP-rich environment. Such supramolecular self-organization of surfactant along a tube is called reverse micellar effect as illustrated in Figure 8. This is commonly applied in the biochemistry research to purify enzymes in organic solvents.

4. SUMMARY

An ATPS using a combination of dextran, PEG, NMP and water with 1% w/w CTAB is found to be effective in removing metallic SWCNTs from the semiconducting SWCNTs. The metallic species are significantly reduced in the bottom phase. The effect is driven by affinity of CTAB on semiconducting SWCNTs and reverse micellar effect. In short, we have developed a novel purification process which can be performed within a short timeframe relative to other methods at low cost and with potential for scalability and recycling of the polymer.

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References and Notes


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