



Separation of single-walled carbon nanotubes using aqueous two-phase system



Malcolm S.Y. Tang^a, Pau Loke Show^b, Yu Kiat Lin^c, Kai Lin Woon^a, Chin Ping Tan^d, Tau Chuan Ling^{c,*}

^aLow Dimensional Material Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

^bManufacturing and Industrial Processes Division, Faculty of Engineering, Centre for Food and Bioproduct Processing, University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Ehsan, Malaysia

^cInstitute of Biological Sciences, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

^dDepartment of Food Technology, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

ARTICLE INFO

Article history:

Received 13 March 2013

Received in revised form 22 January 2014

Accepted 26 January 2014

Available online 6 February 2014

Keywords:

Aqueous two-phase system

Polyethylene glycol

Dextran

Carbon nanotubes

Purification

ABSTRACT

The separation of metallic single-walled carbon nanotubes (M-SWCNTs) from semiconducting single-walled carbon nanotubes (S-SWCNTs) in as-received SWCNTs is an important step to integrate carbon nanotubes into electronic applications. In this study, the effect of molecular weight (M_w) of polyethylene glycol (PEG) on the separation of M-SWCNTs from as-received SWCNTs using aqueous two-phase system (ATPS) consist of PEG, dextran, organic solvent N-methylpyrrolidone (NMP) and water has been investigated. PEG with M_w 6000 and 10,000 showed higher partition coefficient (K) and yield (Y). The semiconducting single-walled carbon nanotube (S-SWCNT) was attracted to the bottom phase. Varying the concentration of PEG 6000 and dextran could enrich the purity of M-SWCNT in the top phase to 0.2574 compared to the pristine value of 0.1506. The volume ratio (V_R) that gave the highest enrichment of M-SWCNT is found to be 1.5. However, there was no significant changes in purification factor (PF) and purity when the concentration of NMP and water were manipulated. This finding provides a solid foundation for the studies of ATPS to separate different species of SWCNTs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Aqueous two-phase system (ATPS) is a very useful technique for proteins purification and recovery [1,2]. It is a benign and nontoxic separation technique that uses water-soluble, phase separating polymer/polymer or salt/polymer system [3,4]. One example of a polymer/salt system is polyethylene glycol (PEG)/potassium phosphate, and an example for polymer/polymer system is the PEG/dextran [5]. In recent years, ATPS has evolved into more than just polymer/polymer and polymer/salt system. One example is the alcohol/salt-based ATPS [1]. Creative manipulation of ATPS such as multiple-step purification, recycling of phase components [6,7], and the introduction of aqueous two-phase flotation (ATPF) [8,9] method have made ATPS an even more attractive separation method. ATPS has a few advantages over other purification methods such as low cost, short processing time and the potential for large scale purification [10]. The factors that influence the outcome of separation includes: type of polymer used; molecular weight

(M_w) of the polymer involved [11]; temperature of system [11,12]; pH of system [12]; and also the addition of salt [13].

Single-walled carbon nanotubes (SWCNTs) are rolled-up sheets of graphene [14]. It possesses excellent electrical properties and thus has a huge potential in the electronics industry [15]. As-prepared SWCNTs, however, naturally contain two different species of tubes namely the semiconducting SWCNT (S-SWCNT) and metallic SWCNT (M-SWCNT) [16]. Different species of carbon nanotubes are used for different applications. M-SWCNT is used for interconnect applications or making electronic sensors [17,18] while the S-SWCNT is used to form the semiconducting channel of a field effect transistor (FET) [19–21]. It is therefore imperative to separate the two species of nanotubes before integrating it in electronics. Many purification methods have been proposed for SWCNT over the years, for example dielectrophoretic deposition [22,23], DNA-assisted separation [24], acid treatment [25], light-assisted oxidation [26], amine interaction [27], trapping of semiconducting SWCNTs using agarose gel [28], and microwave irradiation [29,30]. Acid treatment, unfortunately, results in unwanted carboxylic functionalities [31]. The DNA-assisted separation is economically impractical for large scale purification. A highly efficient and cost effective purification of M-SWCNTs is

* Corresponding author. Tel.: +60 3 79674104; fax: +60 3 79674178.

E-mail address: tcling@um.edu.my (T.C. Ling).

the method using microwave oven. However, the thermal destruction of M-SWCNTs using microwave induces uncontrollable damages to neighbouring S-SWCNTs [32]. Therefore ATPS may become a cost-efficient, scalable, time-saving and simple SWCNT separation protocol. To separate SWCNTs using an ATPS, a new ATPS has been developed using PEG, dextran, N-methylpyrrolidone (NMP), cetyltrimethylammonium bromide (CTAB) and water. The PEG/dextran system is chosen for this study because it is the most widely used ATPS system with rich reservoir of literature [33,34]. Moreover, dextran has been reported to wrap around SWCNT [35]. PEG is selected for its ability to solubilise in water as well as many types of organic solvents [36]. Organic solvent NMP and cationic surfactant CTAB are known to disperse both multi [37] and single-walled carbon nanotubes [38] effectively. The separation of metallic and semiconducting species is due to the attraction between amine and semiconducting species [27]. This affinity is expected to cause the S-SWCNT to move towards amine-rich bottom phase while leaving the metallic species in the amine-poor phase. In this report, the effects of different M_w of PEG on the purification factor, yield and partition coefficient of nanotubes species were studied. In the process of separating the different species of SWCNTs, the parameters can be varied to maximize the yield and purity of SWCNTs.

2. Materials and methods

2.1. Materials

PEG with average M_w of 4000, 6000, 10,000 and 20,000 g/mol, anhydrous N-methylpyrrolidone (NMP) with 99.5% assay, cationic surfactant cetyltrimethylammonium bromide (CTAB), and dextran with average M_w of 40,000 g/mol were sourced from Sigma–Aldrich Co. (St. Louis, MO, USA). SWCNTs with tube diameter 0.7–0.9 nm were sourced from Southwest Nanotechnologies [39]. All chemicals used in this study were of analytical grade. Deionized water with 1% (w/w) CTAB was used throughout the experiment.

2.2. Phase diagram

The phase diagram was constructed using the cloud-point technique as reported by Albertsson [40]. First, PEG was dissolved in organic solvent NMP to create a PEG stock solution, while dextran was dissolved in deionized water with 1% (w/w) CTAB to create a dextran stock solution. Then, a few ATPSs were formed by mixing the PEG and dextran stock solution together. The mixtures were next sonicated using WiseClean Ultrasonic Cleaner (Daihan Scientific) for 15 min. The resulting turbid mixture indicated that two-phase could form. Deionized water was then added slowly until the turbidity disappeared. The phase-transition points were estimated by weighing the mass of deionized water added into the system. The binodial curves were plotted at different PEG and dextran concentrations.

2.3. Partition experiments

In this experiment, the systems were constructed in 7 ml vials by adding a certain quantity of PEG and dextran stock solution of 50% (w/w), 0.5 mg of SWCNTs, appropriate amount of deionized water and NMP in order to obtain 4.0 g final mass. The concentration of PEG, dextran, water and NMP were manipulated to observe the effect on the SWCNTs. The content was mixed thoroughly by gentle agitation, followed by ultrasonication for 15 min. The mixture was then left to incubate for 30 min. The volumes of top and bottom phases were measured and recorded as volume ratio (V_R).

The samples from the two phases were then withdrawn for analysis.

2.4. Analysis

The top and bottom phases were isolated into two different vials. Each was then diluted with 2.0 ml of deionized water. The resultant solutions were centrifuged for 20 min at 4000 rpm. The supernatant was discarded. 2.0 ml of deionized water with 1% (w/w) CTAB was later added to the precipitate, followed by ultrasonication for 15 min. The dispersed SWCNT samples were analyzed using the Thermo Scientific Evolution 300 ultraviolet–visible–near infrared spectrophotometer (UV–Vis–NIR).

Due to the large percentage (up to 42.5% (w/w)) of organic solvent in the system, this ATPS is very different compared to conventional ATPS. We observed throughout our experiment that the system could not maintain the two phases over a long period of time. The bottom phase would often salt-out if left to incubate for more than 4 h, whereby the bottom phase would harden into solid that could not be re-solubilised in water or organic solvent. The nature of the solid has yet to be determined because of its inability to solubilise in water or organic solvent. Therefore it is important to pipette out the top and bottom phase for analysis as soon as two phases are formed.

We also observed throughout our experiment that temperature has a strong influence on the formation of the two phases. It took a longer time for the two phases to form if the ATPS were left to incubate in an oven (45 °C), and relatively shorter time if left to incubate in the clean room where the temperature is maintained at 19 °C. The reason for this is because the energy supplied to the polymer molecules by the heat is stronger than the intermolecular attraction between polymer molecules. The molecules are able to move freely, and thus exhibit fluid-like characteristics. As temperature drops, the energy individual polymer molecule decreases. Therefore the intermolecular attraction becomes dominant and causes the polymer molecules to form long polymer chains.

Nevertheless, it took about 30 min for the two phases to form at room temperature. At higher temperature, the viscosity of the ATPS is much lower. At low temperature, the viscosity increased and the ATPS exhibited gel-like characteristics. The viscosity of both phases under the influence of temperature has not been quantified in our experiment.

2.5. Partition coefficient (K), volume ratio (V_R), purification factor (PF), purity and yield

According to the Beer–Lambert’s law, absorption is proportional to the concentration of the absorbing species in a given material.

$$A = \epsilon bc \quad (1)$$

where A represents the absorbance, ϵ and b represents the molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$) and the path length of the experimental sample, respectively. Here, the c represents the concentration of the composite in the solution (mol L^{-1}).

Therefore, it is possible to sum up the absorbances for the metallic species and semiconducting species to obtain the total absorbance of the sample.

Using the definition of absorbance stated in Eq. (1), the partition coefficient (K) for different species of nanotubes is calculated according to Eq. (2):

$$K = \frac{A_T}{A_B} \quad (2)$$

where A_T and A_B being the absorbance of metallic or semiconducting species in the top and bottom phases, respectively.

The specific activity, SA of sample is described by Eq. (3):

Download English Version:

<https://daneshyari.com/en/article/641320>

Download Persian Version:

<https://daneshyari.com/article/641320>

[Daneshyari.com](https://daneshyari.com)