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High-yield and high-throughput single-chirality enantiomer separation of single-wall carbon nanotubes

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ABSTRACT

Single crystals of single-wall carbon nanotubes are desired for precise analysis of the physical properties of carbon nanotubes, necessitating preparation of single-chirality enantiomers in large quantities. In this work, by investigating the effects of surfactant concentration and temperature on the enantiomer separation, we achieved large-scale single-chirality enantiomer separation for the first time using triple surfactant stepwise elution chromatography with a naturally produced dextran-based gel as the column medium. Through one-round programmed separation, milligram-scale of (11,−5) (equivalent to (5,6)) and (6,5) enantiomers were separated from CoMoCAT carbon nanotube soot. The separation yields estimated from the optical absorbance at 280 nm were 5.6% (11,−5) and 2.6% (6,5) per load of all SWCNTs, which correspond 28% and 13% per load of total (11,−5) and (6,5) enantiomers, respectively. This high yield is mainly attributed to the narrow chirality distribution and high concentrations of (11,−5) and (6,5) in CoMoCAT and the high-resolution selectivity of the triple surfactant system for two enantiomers. The high throughput is sufficient to prepare high-purity (11,−5) and (6,5) bucky papers.

1. Introduction

The atomic arrangement of single-wall carbon nanotubes (SWCNTs) is denoted by a pair of integers (n,m), the so-called chiral index, which determines its unique electrical, optical and physical properties [1]. Depending on the helical arrangement of the hexagonal network, SWCNTs are divided into achiral and chiral species. The latter have a mirror symmetric structure (different handedness) defined usually as (m,n), as an enantiomer. However, in this work, we use notation $(n + m,-m)$ instead of (m,n), where the indices of two enantiomers are defined to satisfy the condition of $0 \leq m \leq n$ [2,3], which is completely equivalent and is more convenient for theoretical calculation of SWCNT. Separation of single-chirality enantiomers is the final stage of structure-controlled SWCNTs separations and the separated enantiomers are very useful to clarify their intrinsic properties. For example, macroscopic ensembles of single-chirality enantiomers will enable fabrication of single crystals of SWCNTs, which can resolve many obscured features such as the three independent C–C bond lengths in chiral SWCNTs. Single-chirality enantiomers could have specific applications such as a chirality-selective column medium. Yoo et al. developed an SWCNT-coated silica gel column that can be used for the separation of organic molecules to reveal the interaction between SWCNTs and organic molecules, and the retention time was highly dependent on the molecules [4]. As an advanced application of SWCNT-coated silica gel columns, a single-chirality enantiomer-coated silica column could be used for chiral molecule separation, which is critical in biochemical and medical fields [5,6].

In the past decade, various separation methods have been developed to produce single-chirality enantiomers, including molecular recognition [7], density gradient ultracentrifugation [8,9], DNA-based aqueous two-phase extraction (ATP) [10], and gel column chromatography [11–13]. Compared with well-studied metallic/semiconducting [14–16] and single-chirality separation [17–27], single-chirality enantiomer separation requires more precise techniques to achieve chirality and handedness selectivity. Although these methods can achieve separation of single-chirality enantiomers, the throughput, an important issue for those who require bulk quantities of single-chirality enantiomers, was insufficient due to time-inefficient multiple-step processes and low separation yields. The reported throughputs of single-chirality enantiomer separation in previous studies were on the order of

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micrograms.

More recently, we reported large-scale single-chirality separation of (6,5) SWCNTs using stepwise elution chromatography [28]. However, enantiomer separation was not achieved. In the present study, gradient elution chromatography coupled with a circular dichroism (CD) detector revealed optimized separation conditions for enantiomers. Using the optimized parameters, we demonstrated single-chirality enantiomer separation of (6,5) and (11,−5) from CoMoCAT SWCNTs using triple surfactant stepwise elution gel column chromatography based on its high-resolution selectivity for the chiral angle, diameter, and handedness of SWCNTs, which is not available for the conventional single surfactant based gel chromatography [11]. The throughputs were 1.2 mg (11,−5) and 0.6 mg (6,5) enantiomers per one-round separation procedure. The estimated enantiomer separation yields were 28% (11,−5) and 13% (6,5) per load of total (11,−5) and (6,5) enantiomers. All these values were evaluated using the mass concentration, which was estimated from the optical absorbance at 280 nm.

2. Experimental

2.1. Preparation of the SWCNT dispersion

CoMoCAT SWCNTs (SG65, 0.7–0.9 nm in diameter, Sigma-Aldrich) were used as the starting material without additional treatment. SWCNT powder (100 mg) was dispersed in 100 ml of 0.5 wt% sodium cholate (SC, ultrapure ≥99.0%, Sigma-Aldrich) aqueous solution using a tip-type ultrasonic homogenizer (Sonifier 250D, Branson) at a power density of 30 W/cm^2 for 10 h. During this process, the glass bottle was placed in an 18 °C water bath to prevent thermal damage. The solution was ultracentrifuged for 2 h (S50A rotor, at 210,000 × *g*, CS150GX, Hitachi Koki), and the upper 80% of supernatant was recovered. Sodium dodecyl sulfate (SDS, ultrapure ≥99.0%, Sigma-Aldrich) was added to the recovered solution to create a 0.5% SC + 0.5% SDS mixed solution. Two bottles of SWCNT solution (160 ml total) were used in the separation procedure described in the main manuscript.

2.2. Optical characterization

Optical absorption spectra were measured from 1400 nm to 200 nm in 2 nm increments using an ultraviolet-visible-near-infrared spectrophotometer (UV-3600, Shimadzu). Excitation-emission mapping of the PL spectra were measured using a spectrofluorometer (Nanolog, HORIBA) equipped with a liquid nitrogen-cooled InGaAs near-infrared array detector. The excitation wavelength was varied from 400 nm to 800 nm in 5 nm steps, and the emission wavelength was varied from 791 nm to 1304 nm in 1 nm increments. The spectral slit widths were 7 nm for both the excitations and emissions. All raw intensities were corrected with the intensities of the lamp spectrum. The circular dichroism spectra of the sorted single-chirality enantiomers were measured from 900 nm to 200 nm in 1 nm increments using a CD spectropolarimeter (J-820, JASCO).

3. Results and discussion

3.1. Effect of surfactant concentration and temperature on the enantiomer separation

In the practical large-scale separation starting with the raw mixture, stepwise elution chromatography should be performed at optimal conditions. To achieve this goal, we determined the optimal surfactant concentrations and temperatures for the enantiomer separation of (6,5) and (11,−5) using gradient elution chromatography as described below.

High-performance liquid chromatography (HPLC, JASCO) coupled with ultraviolet (UV, MD-2018 Plus, JASCO) and CD (CD-2095 Plus, JASCO) detectors was used. The mixture of (11,−5) and (6,5) SWCNTs obtained from our recent chirality separation was used as the starting material [28]. In this method, the eluted mixture of (11,−5) and (6,5) was dissolved in an aqueous mixed surfactant solution of 0.5% SC, 0.5% SDS, and 0.03% sodium deoxycholate (DOC). However, (11,−5) or (6,5) SWCNTs dissolved in such solution cannot be adsorbed in gel column for further enantiomer separation due to high DOC concentration. To reduce the DOC concentration for re-adsorption of (11,−5) and (6,5) SWCNTs to the gel column, the mixed surfactant solution of 0.5% SC + 0.5% SDS + 0.03% DOC was diluted with 0.5% SC + 0.5% SDS aqueous solution to twice the volume and then loaded into a column (Tricorn 10/20, GE Healthcare) filled with 1 ml of dextran-based gel (Sephacryl S-200, GE Healthcare). After washing with the 0.5% SC + 0.5% SDS +0.02% DOC (purity ≥96.0%, Wako Pure Chemical Industries) solution, gradient elution chromatography was performed using an aqueous solution of 0.5% SC + 0.5% SDS + *x*% DOC, in which the DOC concentration was increased in a gradient from 0.02% with 0.0005% per minute increments (1-ml/min flow rate).

We performed the gradient elution chromatography at three column temperatures, 15, 20, and 25 °C. Fig. 1 shows the UV and CD chromatograms of the eluting solutions and the DOC concentration (*x*%) in the mixed surfactant of 0.5% SC + 0.5% SDS + *x*% DOC. Two optical absorption peaks were clearly observed in each UV chromatogram (e.g., two peaks at 0.028 and 0.030% DOC at 25 °C). At each DOC concentration, positive and negative CD peaks were observed. Here, the CD detector was set to 350 nm, corresponding to the E_{33} transition of (6,5), and the UV chromatogram was recorded using the optical absorption at 565 nm, corresponding to the E_{22} transition of (6,5) SWCNTs. The positive CD at the E_{33} transition is assigned to (11,−5), and the negative CD is assigned to (6,5) SWCNTs from theoretical calculations [13]. The opposite CD signs at different DOC concentrations demonstrated that gradient elution chromatography is effective for enantiomer separation. This can be understood as the handedness-dependent interactions with the optically active dextran-based gel, where the gel interacts more

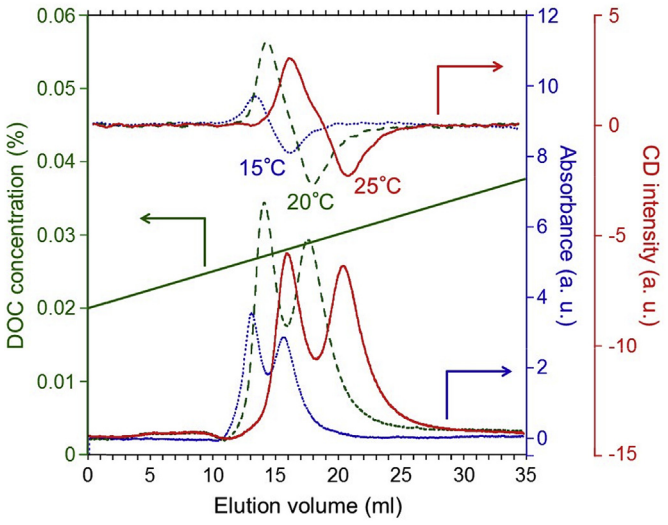

Fig. 1. UV and CD chromatograms of the eluting solutions at three column temperatures, 15 (blue, dotted curves), 20 (green, dashed curves), and 25 °C (red, solid curves), after smoothing and baseline correction processes, and the corresponding DOC concentration (green line) in the mixed surfactant of 0.5% SC + 0.5% SDS + *x*% DOC. (A colour version of this figure can be viewed online.)