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# *Selective Separation of Carbon Nanotubes in Aqueous Two-Phase Systems: Partition Mechanisms, Parameter Optimization, and Scalability Challenges*

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***Abstract.*** Carbon nanotubes (CNTs) exhibit distinct types such as metallic and semiconducting properties due to their unique structures. However, these CNTs with similar characteristics are typically co-produced and mixed during synthesis, making their efficient separation and purification a major challenge that hinders high-end applications. As a green and mild liquid-phase separation technology, aqueous two-phase systems (ATPS) provide a novel approach for the highly selective separation of CNTs. This study aims to thoroughly investigate the separation efficiency and distribution mechanisms of different types of CNTs in ATPS, laying a solid foundation for promoting the widespread application of CNTs in fields such as electronics, energy, and composite materials.

***Keywords:*** aqueous two-phase systems, single-walled carbon nanotubes, chiral separation, surfactants

## 1. Introduction

### 1.1. Chirality of carbon nanotubes

The chiral structure of single-walled carbon nanotubes (SWCNTs) directly determines their electronic structure and physicochemical properties. This property-dependent characteristic makes the separation of specific chiralities of SWCNTs a critical challenge in the field of nanomaterials science [1]. Chirality can be described by a chiral vector, typically represented by a pair of integers (m, n) analogous to a spatial vector. The electronic properties vary with the chirality, which is determined by the direction of this roll-up vector. The chirality of carbon nanotubes is characterized by the chiral vector Ch= $m_{a1} + n_{a2}$ where m and n are non-negative integers. In applications such as high-speed, low-power nanoelectronic devices, the industrial-scale production of single-chirality carbon nanotubes holds significant technological value. However, conventional synthesis and separation methods struggle to meet the requirements for both purity and scalability [2]. Particularly in the separation of metallic single-walled carbon nanotubes (M-SWCNTs), existing techniques commonly face challenges such as insufficient selectivity and low yield [1]. The difficulty in chirality separation primarily stems from the strong van der Waals interactions between carbon nanotubes and the subtle differences in physicochemical properties among different chiral species

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[3]. While milligram-scale separation of single-chirality products has been achieved in recent years through methods such as gel chromatography, the separation efficiency remains constrained by factors including the diameter distribution of raw materials and surface treatment processes [4]. It is worth noting that research on enhancing the separation yield of high-purity (6,5) SWCNTs has demonstrated that optimizing separation conditions can significantly improve nanotube stability in solution and film-forming properties [5]. This provides a material foundation for developing high-performance nano-optoelectronic devices.

### 1.2. Advantages and challenges of aqueous two-phase systems for carbon nanotube separation

Apart from gel chromatography, another method that has gained significant attention in recent years is aqueous two-phase extraction (ATPE) technology, which was originally developed for the separation of biological particles [6]. Building on its mild separation conditions, excellent biocompatibility, and tunable interfacial properties, ATPE demonstrates unique advantages for SWCNT separation. Unlike conventional methods, PEG/dextran-based systems leverage interfacial tension-driven partitioning and surfactant-mediated chiral recognition to achieve selective distribution of specific chiral nanotubes [7,8]. However, this technology still faces multiple challenges. Primarily, the synergistic effects between surfactant chemistry and polymer chain length have not been fully elucidated [9]. Secondly, the separation efficiency of existing systems for specific nanotube structures, such as zigzag types, remains suboptimal [2]. Furthermore, during the transition from laboratory scale to industrial production, issues such as reagent costs, continuous operation, and product yield urgently need to be resolved.This review will systematically analyze the partitioning mechanisms of carbon nanotubes in aqueous two-phase systems, with a focus on the interfacial thermodynamic behavior of PEG/Dextran systems and surfactant-based regulatory strategies. By summarizing key influencing factors such as ultrasonic pretreatment [10], polymer composition [11], and environmental parameters, this review establishes optimization pathways for separation efficiency. Finally, addressing challenges in scalable production economics and engineering design, we prospect future development directions including AI-assisted optimization and microfluidic technology integration.

## 2. Research advances in the partitioning mechanisms of carbon nanotubes in PEG/Dextran systems

### 2.1. Chiral recognition mechanism of surfactants

The chemical properties of surfactants exert a decisive influence on the selective separation of single-walled carbon nanotubes (SWCNTs). Studies have shown that the selective extraction of specific SWCNT species can be achieved through the systematic regulation of polyethylene glycol (PEG) chain length, surfactant ratio, and structural variations [12]. Continuous titration experiments with cosurfactants have confirmed that when the surfactant concentration is below the critical micelle concentration (CMC), it can significantly alter the partitioning behavior of multi-walled carbon nanotubes (MWCNTs) [10,13]. Notably, the polymer-carbon nanotube complexation concentration (PCCC) directly reflects the surfactant-SWCNT interactions and can be used to guide the design of multi-step separation processes. As early as 2015, Jeffrey et al. [13] significantly expanded the diameter range for the separation of individual SWCNT species via aqueous two-phase extraction (ATPE) (Fig. 1a). Subsequently [9] , near-infrared fluorescence spectroscopy was employed to more rapidly and accurately determine the partitioning conditions of individual (n,m)-

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chiral SWCNTs, without considering the mass transfer limitations or interfacial adsorption issues encountered during ATPE separation. Meanwhile, Li et al. [1] demonstrated that the inflection concentration can be more intuitively observed from the sigmoidal curve fitted by the Hill equation: when the sodium dodecyl sulfate (SDS) concentration approaches the PCCC, the SWCNT partition coefficient (K) abruptly transitions from ≈0 (completely in the bottom phase) to ≈∞ (completely in the top phase). The host-guest switching from deoxycholic acid (DOC) to SDS induces a sudden change in the solvation energy on the SWCNT surface, thereby driving phase transfer. This provides theoretical guidance for predicting and designing surfactant concentrations (Fig. 1b,c).

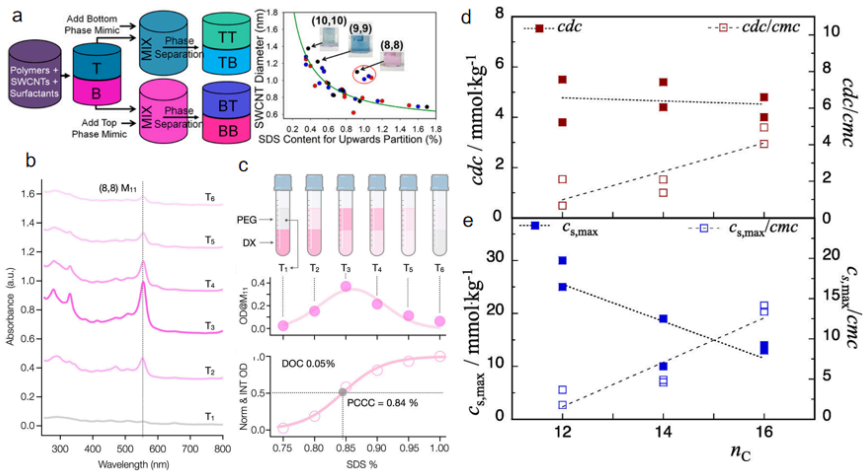


Figure 1. (a) Separation process and partitioning behavior of single-walled carbon nanotubes (SWCNTs). (b) UV-Vis absorption spectra of different samples. (c) Effect of SDS concentration on solution properties. (d) Relationship between the Zeeman effect and SWCNT concentration. (e) Relationship between the maximum SWCNT concentration and SWCNT chirality

## 2.2. The indirect regulation mechanism of PEG on the chiral selection of SWCNTs

In the PEG/Dextran system, the synergistic regulation of electrostatic interactions and hydrophobic effects is the key to achieving precise separation of carbon nanotubes. Meanwhile, the systematic design of polymer molecular weights (e.g., 40 kDa Dextran and 20 kDa PEG) can optimize the phase separation behavior [14]. Polyethylene glycol (PEG) indirectly influences chiral selection by regulating the microenvironment of surfactant competitive adsorption, providing an adjustable window for chiral selection, and ensuring phase separation stability: its molecular properties (molecular weight, concentration) alter the hydrophobicity of the PEG-enriched phase and surfactant adsorption kinetics, thereby amplifying the adsorption differences of surfactants onto single-walled carbon nanotubes (SWCNTs) with different chiralities [9]. Wim et al. [8] pointed out that the combined use of sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) can enhance chiral selectivity. PEG may indirectly affect the solubility and partitioning behavior of SWCNTs with different chiralities by regulating the adsorption conformation of SDS on the SWCNT surface. In summary, as an important component of the aqueous two-phase system, PEG indirectly achieves chiral selectivity for SWCNTs rather than directly recognizing the chiral structure.

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## 3. Optimization strategy for key parameters governing separation efficiency in the PEG/DX system

### 3.1. The key role and influence mechanism of ultrasonic dispersion pretreatment

Carbon nanotubes form bundles with highly complex morphologies stabilized by extensive van der Waals interactions, resulting in extremely poor solubility in both aqueous and organic solvents. To obtain stable colloidal suspensions essential for applications, three primary dispersion methods are employed: (i) utilization of organic solvents; (ii) covalent attachment of hydrophilic functional groups to nanotube surfaces; and (iii) physical adsorption of amphiphilic molecules (surfactants or polymers).

The effectiveness of ultrasonic dispersion is related to ultrasonic power/energy density, duration, and mode. For dispersants, it is associated with pH, temperature [15], total concentration, as well as the type and concentration of surfactants. Ionic surfactants (e.g., SDS, SDBS) stabilize the dispersion system through electrostatic repulsion generated by adsorption; among them, SDBS exhibits stronger adsorption capacity than SDS due to the π-π interactions between its benzene ring and the CNT surface, resulting in superior dispersion performance. Non-ionic surfactants stabilize the dispersion via steric hindrance effects and are less affected by solution pH and ionic strength. Polymer-based dispersants can provide stronger steric hindrance, leading to better dispersion outcomes, but may alter the intrinsic properties of CNTs. Marques et al. [16] found that anionic surfactants containing aromatic rings (e.g., SDBS, with a benzene ring in the hydrophobic moiety) and long alkyl chains (e.g., CTAB, with a C16 chain) exhibit superior dispersion performance. SDBS was the optimal dispersant among all tested surfactants, with the dispersion efficiency order being SDBS > CTAB ≈ CPyCl > STS > TTAB ≈ SDS > DTAB. Furthermore, as the alkyl chain length increases, the surfactant concentration required for saturated dispersion (cs,max) decreases linearly, which is significantly different from the hydrophobic interaction law in micellization (characterized by a decreasing cmc index). Studies have shown that the concentration of CNT solutions can be increased from 0.19 mg/mL to approximately 1 mg/mL through ultrasonic treatment combined with centrifugation and redispersion processes (Fig. 1d,e) [2]. However, ultrasonic parameters (e.g., power, duration) need to be precisely controlled to avoid structural damage to CNTs caused by over-treatment.

### 3.2. Systematic design of polymer composition and molecular weight

#### 3.2.1. Polymer type

Common aqueous two-phase systems (ATPS) consist of two incompatible polymers or a polymer and a salt. The polyethylene glycol (PEG)/Dextran dual-polymer system is currently the most extensively studied ATPS for separation applications. By precisely regulating the polymer molecular weights and composition ratio, this system enables highly selective separation of carbon nanotubes (CNTs) with different diameters and chiralities [11]. Studies have shown [9] that the synergistic effect of PEG chain length and surfactant ratio exerts a decisive influence on the separation performance.

The copolymer-salt ATPS has demonstrated unique advantages in CNT separation. By adjusting the type and concentration of salts, this system can precisely control the selective separation of single-walled carbon nanotubes (SWCNTs) with different chiralities. Lv et al. [17] constructed an ATPS using PEG and salts (e.g., phosphate, tartrate, etc.) (Fig. 2a), replacing the traditional

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polymer/polymer system (e.g., PEG/Dextran). This DNA-SWCNT separation technology achieves separation through the salting-out and electrostatic shielding effects of cations, the indirect regulation of the solution environment by anions, and a salt-switching strategy involving multi-step salt type alternation. It can obtain single-chiral CNTs with a purity exceeding 90% in a single step, and also realize gram-scale large-scale separation with a 200-fold increase in yield.

### 3.2.2. Fine-tuning of polymer molecular weight

Polymer molecular weight is another key variable besides the composition ratio in the design of aqueous two-phase systems (ATPS). It not only determines the basic phase behavior of the system but also profoundly regulates the partitioning selectivity and separation kinetics of carbon nanotubes (CNTs) by influencing interfacial tension and system viscosity. An increase in polymer molecular weight directly leads to a reduction in chain entanglement degree and conformational entropy, thereby enhancing the incompatibility between polymers. This enhanced incompatibility is intuitively reflected in the downward shift of the phase-forming critical point on the phase diagram. Meanwhile, molecular weight (especially that of PEG) also affects the partition coefficient of surfactants but does not significantly interfere with the surfactant competition mechanism. When the PEG molecular weight varies from 1.5 kDa to 20 kDa, the partition coefficient of SWCNTs changes slightly (Fig. 2e,f). For example, the polymer-carbon nanotube complexation concentration (PCCC) of (7,5) SWCNTs is 0.79% SDS in 6 kDa PEG, while it only slightly increases to 0.83% in 20 kDa PEG [9].

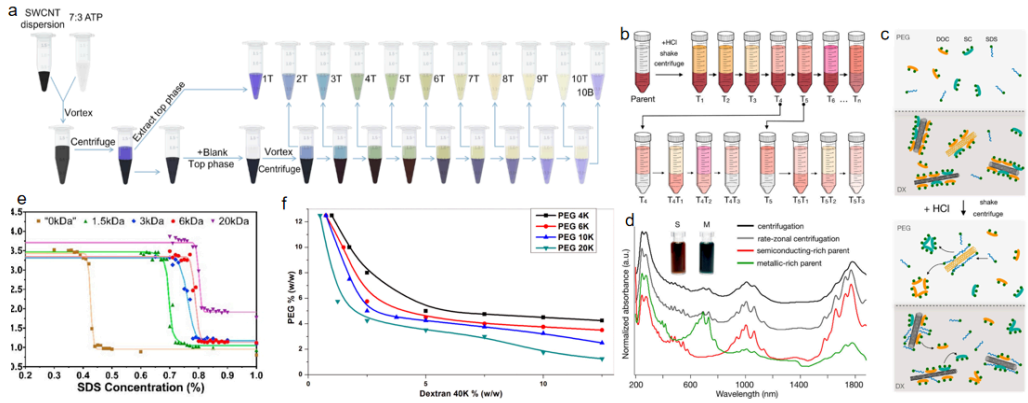


Figure 2. (a) Schematic of the single-walled carbon nanotube (SWCNT) separation process and partitioning behavior. (b) UV-Vis absorption spectra comparison of multiple samples (e.g., T1-T6) in the wavelength range of 300-800 nm. (c) Effect of SDS concentration on the relevant properties of the system. (d) Variation law of Zeeman effect-related spectral characteristics with SWCNT concentration. (e) Maximum concentration performance of different SWCNTs

Another direct consequence of molecular weight is a significant increase in system viscosity. High-molecular-weight polymer chains occupy a larger hydrodynamic volume in aqueous solutions and entangle with each other, which greatly enhances the viscosity of both phases under the same composition. The pursuit of thermodynamic stability (characterized by facile phase separation and high interfacial tension) typically requires a relatively high molecular weight. Studies have shown that [5] increasing the solvent viscosity can enhance the sorting yield of (6,5) SWCNTs by 11-fold. This is attributed to the reduced diffusion rate of SWCNTs, which prolongs the recognition and wrapping time of the (6,5) chiral structure by the polymer (PFO-BPy), thereby capturing more target

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SWCNTs. In contrast, the pursuit of rapid separation kinetics (high mass transfer rate) tends to favor the selection of lower molecular weights. Meanwhile, high-molecular-weight PEG (e.g., 20 kDa) provides a more favorable thermodynamic environment for achieving high-purity and high-selectivity separation of SWCNTs by forming a stable aqueous two-phase system (ATPS) with high interfacial tension.

### 3.3. Regulation mechanisms of pH value and ionic strength

pH value and ionic strength can alter the surface charge of carbon nanotubes, thereby regulating their partitioning in aqueous two-phase systems. pH serves as a crucial parameter, and the separation mechanisms of aqueous two-phase systems and gel permeation chromatography are interrelated, as both depend on intermolecular interactions including electrostatic and hydrophobic interactions. Under acidic conditions, the carboxyl groups of deoxycholic acid and sodium cholate undergo protonation to induce aggregation, and they are subsequently displaced by sodium dodecyl sulfate. This process facilitates the transfer of specific chiral single-walled carbon nanotubes from the dextran phase to the polyethylene glycol phase. Li et al. [18] achieved the separation of SWCNTs with different chiralities from the bottom phase to the top phase by stepwise addition of HCl, and obtained high-purity enantiomers after secondary purification. Additionally, pH can regulate the chiral separation of large-diameter SWCNTs (Fig. 2bcd).

## 4. Conclusion and prospects

Aqueous two-phase separation (ATPS) technology demonstrates broad application prospects in the separation and purification of carbon nanotubes (CNTs), exhibiting particular advantages in the chirality/optical activity-based separation of single-walled carbon nanotubes (SWCNTs). Its mild aqueous environment effectively preserves the intrinsic photoelectronic properties of CNTs [19], making it suitable for fabricating high-performance nanoelectronic devices [2] and biosensors [20] Compared with conventional methods, ATPS offers simplified operation, enhanced biocompatibility, and superior scalability, thereby establishing a critical foundation for practical applications of CNTs in materials science, biomedical engineering, and environmental engineering.

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