# Ultracentrifugation of single-walled nanotubes

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**Single-walled carbon nanotubes (SWNTs) are high aspect ratio cylinders of carbon (~1 nm in diameter) whose walls are one atomic layer thick and have an atomic arrangement analogous to graphite. The SWNT atomic structure is defined by a two-dimensional chiral vector whose components are specified by a pair of positive integers: (*n*,*m*). This chirality of the SWNT dictates its properties. Unfortunately, current methods for producing SWNTs lack control over chirality, leading to significant polydispersity in the properties of as-synthesized SWNTs. Consequently, the widespread use of SWNTs in electronics, photonics, and sensors has been limited by their inhomogeneity.**

In an effort to realize the technological promise of SWNTs, many techniques have been developed to sort SWNTs by their physical and electronic structure. Examples include dielectrophoresis[1], chemical functionalization[2], selective etching[3], controlled electrical breakdown[4], anion exchange chromatography[5], and size exclusion chromatography[6]. While these approaches have been implemented for small-scale use, none have yet been adopted for industrial-scale separation of SWNTs.

We describe an alternative strategy for sorting SWNTs called density gradient ultracentrifugation (DGU). It combines several desirable attributes for large-scale production, including scalability, compatibility with a diverse range of raw materials, noncovalent and reversible functionalization chemistry, and iterative repeatability[7,8].

Historically, DGU has been widely used in biochemistry and the pharmaceutical industry for separating subcellular components[9]. DGU works by exploiting subtle differences in buoyant density. The species of interest are loaded into an aqueous solution with a known density gradient. Under the centripetal force of an ultracentrifuge, the species sediment toward their respective isopycnic points (i.e. the position where their density matches that of the gradient). With suitable choice of the initial gradient, the species spatially separate by density at which point they can be removed by a process known as fractionation.

For DGU to be successful, the buoyant density of a SWNT must be directly related to its physical and electronic structure. Since a SWNT is a hollow cylinder, all of its mass is located on its surface. The buoyant density (mass-to-volume ratio) of a SWNT will be proportional to the surface-to-volume ratio for a cylinder, which is inversely proportional to the diameter. If DGU occurred in vacuum, then the SWNT buoyant density would follow this simple inverse relationship with its diameter. However, since DGU occurs in aqueous solution and SWNTs are strongly hydrophobic, amphiphilic surfactants must be used to disperse the SWNTs. Consequently, the actual buoyant density of an SWNT in a DGU experiment will be a function both of the geometry of the SWNT and the thickness and hydration of the amphiphilic surfactant coating.

When a surfactant is chosen that uniformly and identically encapsulates all of the SWNTs in solution, then the buoyant density is only a function of the SWNT diameter. On the other hand, if a surfactant or combination of surfactants are chosen that encapsulate SWNTs as a function of their electronic structure (e.g. metallic versus semiconducting), then DGU can sort SWNTs by properties beyond simple geometrical parameters. Ultimately, the combination of clever surfactant chemistry and DGU enables tunability in sorting SWNTs.

Fig. 1 outlines the DGU process for SWNTs produced by the CoMoCAT growth strategy[10]. This method produces SWNTs by carbon monoxide disproportionation using a proprietary Co/Mo catalyst. Even though CoMoCAT SWNTs possess a relatively narrow diameter distribution (0.7–1.1 nm), a number of distinct chiralities can be identified from optical absorption spectra. The first step is to disperse the SWNTs in aqueous solution using an amphiphilic surfactant such as sodium cholate. Although ultrasonication leads to a high yield of individually encapsulated SWNTs, some small bundles of SWNTs remain (Fig. 1a). Since these bundles possess a higher density than individually encapsulated SWNTs, they will simply sediment to the bottom of the density gradient during ultracentrifugation.

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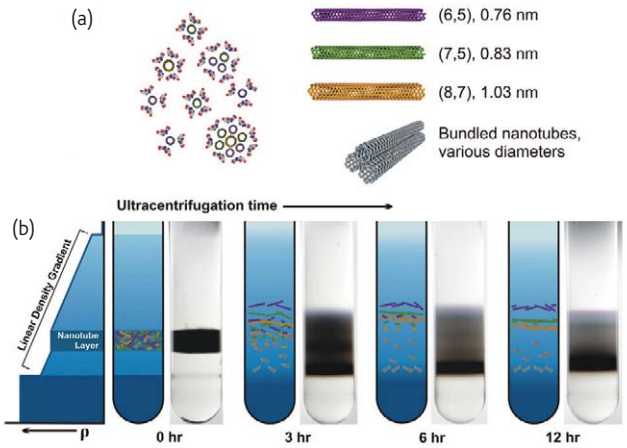


*Fig. 1 (a) Schematic of surfactant-encapsulated SWNTs. The chiral vectors and diameters of three specific SWNTs are identified. (b) Schematics and photographs of an ultracentrifuge tube at four points in the DGU process.*

The dispersed SWNT solution is then injected into a linear density gradient that is formed from a solution of water and iodixanol ($C_{35}H_{44}I_6N_6O_5$). By varying the concentration of iodixanol, which has a higher density than water, a density gradient can be formed (Fig. 1b). By injecting the SWNTs near their isopycnic point in the gradient, the distance that they need to travel and thus the ultracentrifugation time are minimized. Fig. 1b also shows the ultracentrifuge tube at different points in the DGU process. After 3 hrs at a centripetal acceleration of 288 000 g, the SWNTs begin to sediment but have not yet reached their equilibrium position. After 6 hrs, layering of the SWNTs by their physical and electronic structure is apparent. Finally, after 12 hrs, the SWNTs are clearly layered to the point where fractionation can commence. Evidence for a successful DGU run includes the formation of visibly colored bands (Fig. 1b). Using one of several fractionation methods, the colored bands are removed from the centrifuge tube and collected sequentially in optical cuvettes. Optical purity of the resulting solutions is a direct indicator of monodispersity in the SWNT physical structure and electronic properties. Fig. 2 shows five distinct, monodisperse SWNT fractions from one DGU run.

The positive attributes of DGU are many. Easily controlled parameters, such as surfactant chemistry, initial density gradient profile, and ultracentrifugation acceleration and time provide flexibility for a broad range of raw SWNT materials. The use of noncovalent and reversible surfactant chemistry implies that the encapsulating molecules can be easily removed via dialysis or copious rinsing. The ability to remove the surfactants is particularly important for electronic applications where functionalization chemistry can compromise electrical contacts. DGU can be repeated iteratively. Following the first DGU round, the best fraction can be placed into a second gradient and the process repeated. In this manner, nearly arbitrary levels of purity can be achieved through multiple iterations. Finally, through the widespread use of DGU in the pharmaceutical industry, the scalability and economic viability of DGU have already been demonstrated.

*Fig. 2 Following DGU and fractionation, optically pure SWNT samples are isolated into distinct cuvettes. The color differences between the vials provide evidence for successful sorting of SWNTs by physical and electronic structure.*

The prospects are promising for DGU-prepared SWNTs and commercialization of this approach has already been initiated[11]. DGU-prepared SWNTs have been exploited in transistors and metallic coatings[8]. The optical purity of the SWNTs has been exploited in time-resolved, pump-probe laser spectroscopy studies of ultrafast carrier dynamics[12,13]. Additional applications that are likely to benefit from monodisperse SWNTs include transparent conductors, high-speed integrated circuits, and nanocomposite materials. With further progress, homogeneous SWNT materials have the potential to realize many of the objectives outlined in the National Nanotechnology Initiative[14]. mt

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*Conflict of interest statement: Mark C. Hersam is a cofounder of NanoIntegris, a start-up company that is commercializing DGU of SWNTs.*

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