Sorting carbon nanotubes by electronic structure using density differentiation

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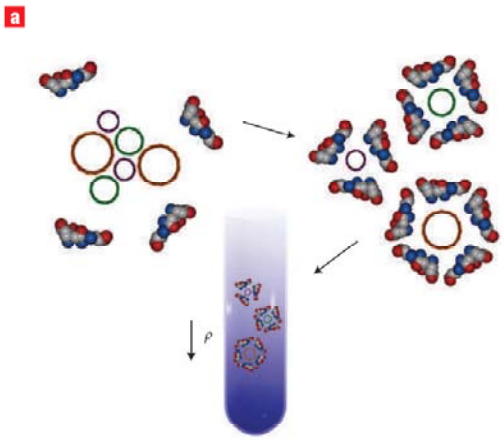
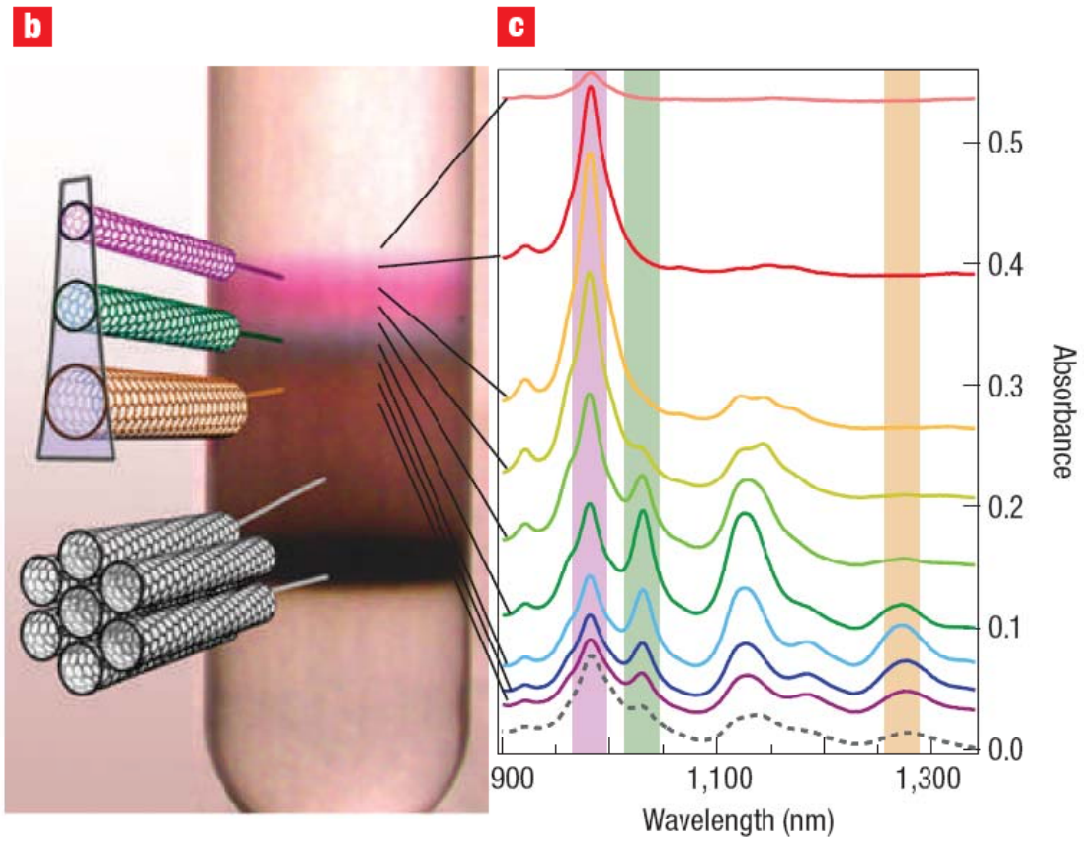
The heterogeneity of as-synthesized single-walled carbon nanotubes (SWNTs) precludes their widespread application in electronics, optics and sensing. We report on the sorting of carbon nanotubes by diameter, bandgap and electronic type using structure-discriminating surfactants to engineer subtle differences in their buoyant densities. Using the scalable technique of density-gradient ultracentrifugation, we have isolated narrow distributions of SWNTs in which >97% are within a 0.02-nmdiameter range. Furthermore, using competing mixtures of surfactants, we have produced bulk quantities of SWNTs of predominantly a single electronic type. These materials were used to fabricate thin-film electrical devices of networked SWNTs characterized by either metallic or semiconducting behaviour.





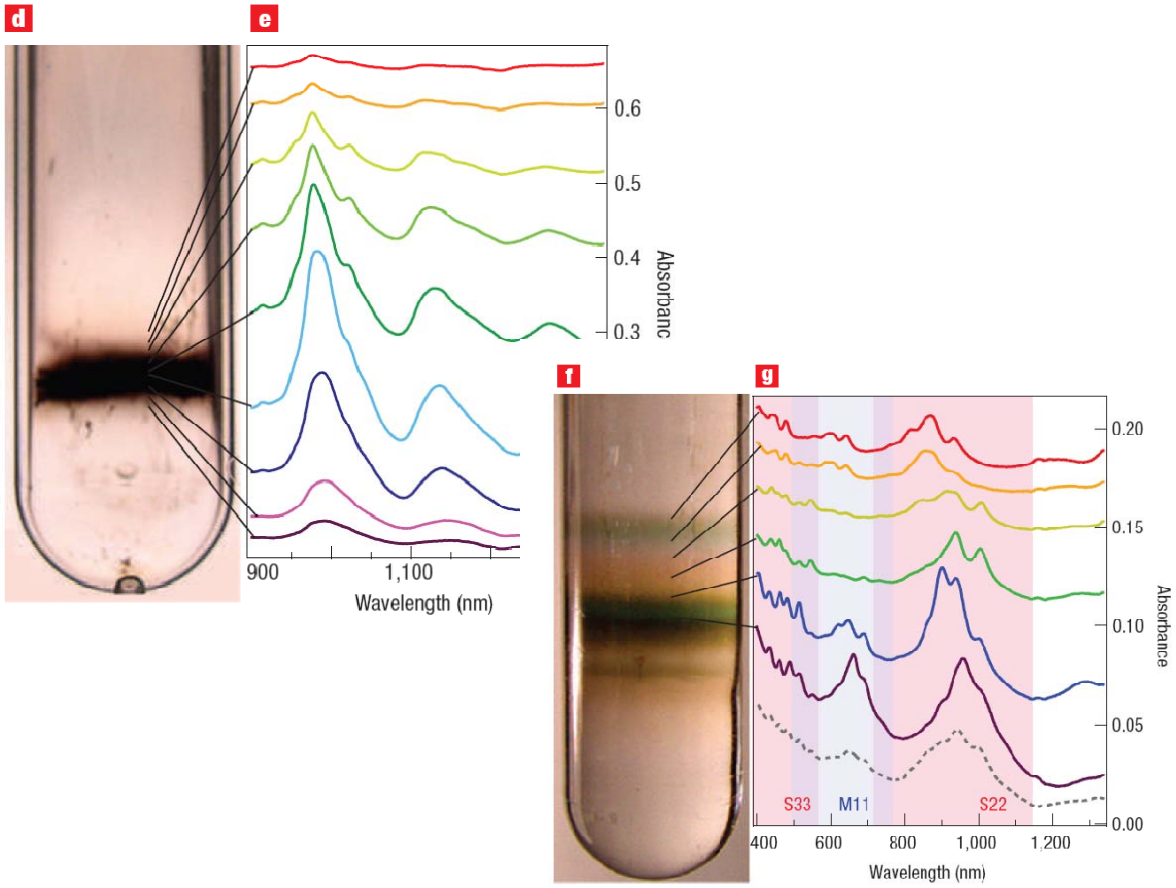


Figure 1 Sorting of SWNTs by diameter, bandgap and electronic type using density gradient ultracentrifugation.
a, Schematic of surfactant encapsulation and sorting, where r is density.
b–g, Photographs and optical absorbance (1 cm path length) spectra after separation using density gradient ultracentrifugation. A rich structure–density relationship is observed for SC-encapsulated SWNTs, enabling their separation by diameter, bandgap and electronic type. In contrast, no separation is observed for SDBS-encapsulated SWNTs. **b,c**, SC encapsulated, CoMoCAT-grown SWNTs (7–11 A°). Visually, the separation is made evident by the formation of coloured bands (b) of isolated SWNTs sorted by diameter and bandgap. Bundles, aggregates and insoluble material sediment to lower in the gradient. The spectra indicate SWNTs of increasing diameter are more concentrated at larger densities. Three diameter ranges of semiconducting SWNTs are maximized in the third, sixth and seventh fractions (highlighted by the pink, green and light brown bands). These have chiralities of (6,5), (7,5) and (9,5)/(8,7), and diameters of 7.6, 8.3 and 9.8/10.3 A° respectively. **d,e**, SDBS-encapsulated CoMoCAT-grown SWNTs (7–11 A°). In contrast, all of the SWNTs have converged to a narrow black band (d) and diameter or bandgap separation is not indicated (e). **f,g**, SC-encapsulated, laser-ablation-grown SWNTs (11–16 A°). Both enrichment by diameter and electronic type are observed. Visually, coloured bands of SWNTs (f) are apparent, suggesting separation by electronic structure. In the optical absorbance spectra, the second- and third-order semiconducting (highlighted pink) and first-order metallic (highlighted blue) optical transitions are labelled S22, S33 and M11, respectively5,22. The purple highlighted regions show where the semiconducting and metallic transitions overlap. The diameter separation is indicated by a red shift in the S22 band for fractions of increasing density. Additionally, the metallic SWNTs (M11) are depleted in the most buoyant fractions. Dr from top to bottom fraction, and r for the top fraction for c, e and g are 0.022, 0.096 and 0.026 g cm23 and 1.08, 1.11 and 1.08+0.02 g cm23, respectively. pH ¼ 7 for all parts. SWNTs before sorting are depicted as a dashed grey line in c and g.

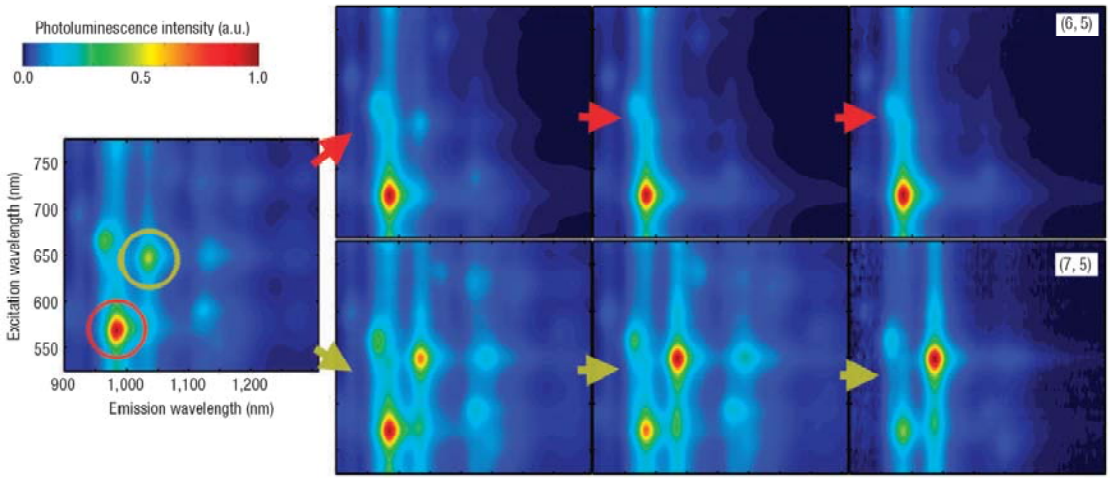
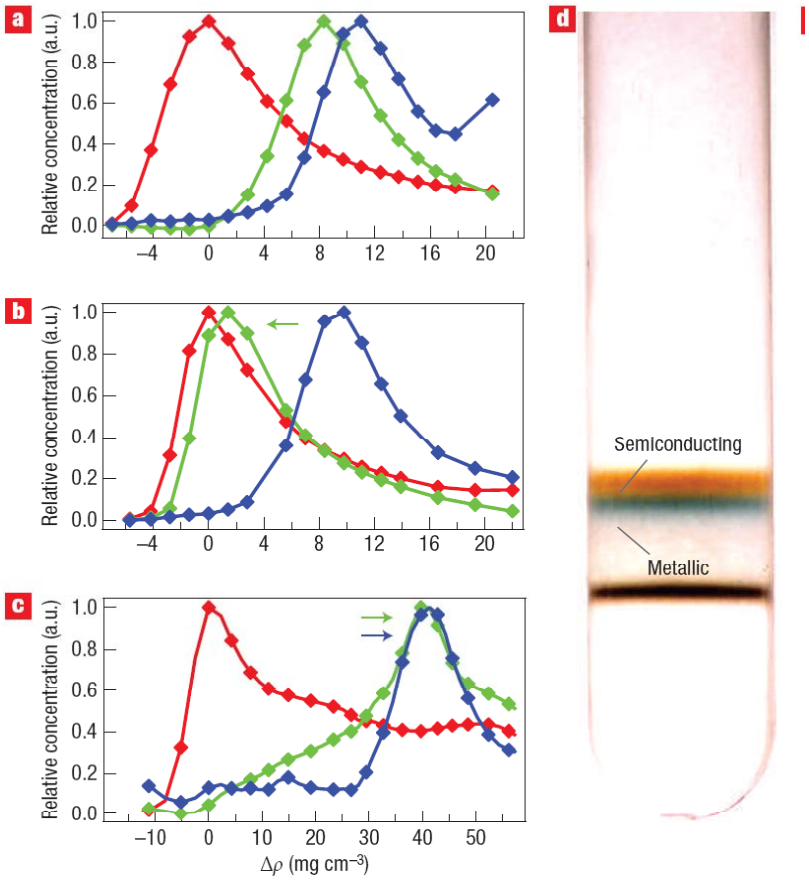
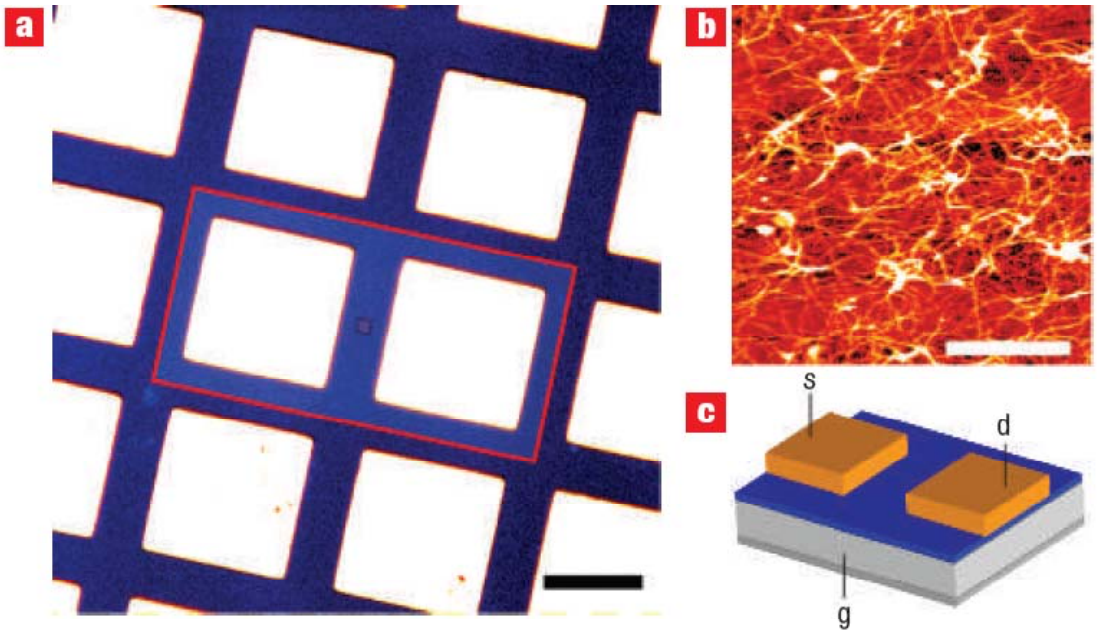


Figure 2 Refinement by repeated centrifugation in density gradients. By successively separating SC-encapsulated SWNTs, the isolation of specific, targeted chiralities improves. Plotted are photoluminescence intensities as a function of excitation and emission wavelengths. Here, the isolation of the (6,5) and (7,5) chiralities (circled red and green in the left-most plot) of SWNTs grown by the CoMoCAT-method before sorting, is improved (in the top and bottom panels, respectively) by successively repeating density gradient centrifugation for three iterations (from left to right). After three iterations of enriching the (6,5) chirality (7.6 Å), a narrow diameter distribution is achieved in which >97% of semiconducting SWNTs are within 0.2 Å of the mean diameter. Alternatively, refined isolation of the (7,5) chirality can be realized (bottom). In this case, after three iterations of sorting, the (7,5) chirality (8.3 Å), initially substantially less concentrated than the (6,5) chirality, becomes dominant. Further improvements may be possible with additional centrifugation cycles.

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