Quick and easy enrichment of metallic carbon nanotubes

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Enrichments of up to 80% can be achieved quickly and simply through the preferential oxidation of semiconducting nanotubes.

A carbon nanotube (CNT) can exhibit either metal or semiconductor electronic behavior, depending on the molecule’s chirality. The metallic variety is used in conductive films and transparent electrodes, while the semiconducting type is in great demand for high-performance field effect transistors (FET). Unfortunately, current synthesis methods can’t produce pure batches of either type, probably because of structural similarities, and instead generally produce twice as many semiconducting nanotubes as metallic nanotubes. This mixture can degrade application performances. For example, metallic CNTs reduce an FET’s on/off current ratio, while semiconducting CNTs lower a thin film’s overall conductivity. Thus, it is essential to have an effective way to separate the two types in order to better realize CNT potential.

There are several separation methods, but all have shortcomings. For example, both electrophoresis and ion chromatography combined with DNA wrapping are effective, but require large carbon nanotube quantities that are difficult to obtain. Bulk separation methods based on the slightly higher chemical reactivity of metallic nanotubes have been reported. These use $N_2^+$ (the nitronium ion) and amines, but because the reactivity contrast is so slight the treatments tend to be complicated and time consuming. Recently, we have overcome these problems with a method that enriches the metallic nanotubes simply by heating with hydrogen peroxide. Just keeping CNTs in a hydrogen peroxide water solution can increase the metallic nanotube concentration as high as 80%.

Most chemical methods of carbon nanotube separation are based on a metal’s higher reactivity due to the finite electronic density of states (DOS) at the Fermi level. However, because the nanotube’s one-dimensional electronic band structure yields a small DOS, the reactivity difference is small, as was noted above. Our method increases this difference by controlling the state density with chemical doping.

As a starting material, we used the high-purity, single-wall CNTs produced by the high pressure catalytic decomposition of carbon monoxide (HiPCO) process. The sample was dispersed in a 30% hydrogen peroxide water solution, and kept at 90°C for 47 minutes. The solvent bubbled during the reaction, indicating the decomposition of hydrogen peroxide and the production of reactive oxygen. The reaction greatly reduces the number of carbon nanotubes, probably through the conversion of carbon into CO or CO2 during the oxidation. The optical absorption spectrum of the remaining nanotubes showed a strong band indicative of metallic CNTs with an estimated concentration of 80%. The efficacy of this method is demonstrated by the low resistance of thin films with a 60% metal nanotube concentration, measuring less than half the resistance of films using unprocessed CNTs.

Based on reaction rates and concentrations determined from rate equations, 10% of the semiconducting nanotubes are oxi-
dized per minute, while only 7% of the metallic variety are. The large difference in oxidation speeds accounts for our method’s relative enrichment of metallic CNTs. This situation is a reversal of the usual one where the metallic nanotubes are more reactive, and has never been observed when the reaction has been conducted in air.

A possible explanation for the rate reversal may be that hydrogen peroxide, a known weak-hole dopant, can slightly lower a nanotube’s Fermi level. This could lead to a charge transfer from the nanotubes to the hydrogen peroxide that would change the semiconductors into metals with higher state density and reaction rates than the original metallic nanotubes.

In CNTs, the coexistence of metal and semiconductor varieties has degraded applications that rely on nanotube electronic properties. Our quick and easy hydrogen-peroxide based enrichment process addresses this shortcoming, and allows, for example, the higher thin-film conductivity that is important for transparent electrodes. We have also demonstrated that doping can control CNT chemical reactivity, a finding that can be applied for more efficient selective purification and, perhaps, to a more-precise CNT separation.

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