

All the Dope on Nanotube Films

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Ideas for the use of carbon nanotube thin films as flexible, transparent, conducting electrodes germinated seemingly independently in several laboratories in the early part of the past decade. Notable early publications came from Siegmund Roth's group at the Max Planck Institute for Solid State Research in Stuttgart,¹ from Sanjeev Manohar and co-workers, then at the University of Texas, Dallas,² from George Gruner's lab at UCLA,³ and from our laboratory at the University of Florida,⁴ where our demonstration of unanticipated performance sparked much further interest. It was clear from the outset that, for the highest conductance at high transmittance, the nanotubes would have to be charge-transfer-doped. Early understanding of charge transfer doping in the nanotubes came from the pioneering studies of Jack Fischer⁵ and the late Peter Eklund,⁶ who had cut their research teeth in the field of graphite intercalation complexes. As in graphite, the π and π^* bands of the graphene-like nanotube sidewalls exchange charge with either acceptor or donor chemical species, lowering the overall free energy of the complex, and in either case increasing the carrier density (holes or electrons) on the nanotubes.

The resistance across such films is, however, still much larger than the near-ballistic on-tube transport would suggest. The behavior of graphite again provides critical clues to the dominant source of this impedance. In graphite, the c -axis conductivity—where the carriers must traverse the 3.4 Å intersheet gap—is 3–4 orders of magnitude lower than the on-sheet, a - b -axis conductivity. Given a comparable intertube distance in nanotube films (known from Jack Fischer's early X-ray diffraction studies in ropes of single-wall nanotubes⁷), it stood to reason that the impedance in the films is dominated by the tube–tube contacts.

What does charge transfer doping imply for the tube–tube contacts? If the impedance is dominated by tube–tube contacts and the doping affects only the on-tube conductance, then a series resistance model

ABSTRACT Transparent, conducting, nanotube thin films have shown promise in a number of applications, the range of which has just been increased significantly. Scientists at the National Renewable Energy Laboratory have done much in recent years to advance the understanding and application of these films. In this issue of *ACS Nano*, Blackburn and colleagues report their study of the doping power of n-type charge transfer donor dopants, finding that hydrazine effects n-type doping approximately comparable in strength to the p-type doping induced by nitric acid. This expands the potential range of applications for such films to electron injection and collection.

would imply only a small, fractional change in the overall film conductivity rather than the factor of 5–10 times change that is often observed. So doping, it would seem, principally affects the tube–tube contacts. But hold on, not so fast: in typical nanotube samples, we have 1/3 metallic and 2/3 semiconducting nanotubes. Hence, if the doping turns on the semiconducting nanotubes, then within a parallel resistance model we would expect a factor of 3 effect. So does the doping have a major effect at the contacts or not? Bear in mind that for graphite the c -axis conductivity generally *decreases* with increasing intercalation, so graphite, at least in this case, would suggest the opposite of what seems to occur in nanotubes (but for two-dimensional graphite, the intercalant must push apart adjacent graphene sheets, increasing the gap that carriers must traverse, while for tube–tube contacts, the dopant species can simply slide around to the side without necessarily changing the tube–tube spacing).

The quality of the metallic/semiconducting nanotube separations made available by density gradient ultracentrifugation (pioneered by Hersam and colleagues in 2006⁸) made such questions experimentally accessible, and that is just what a group from the National Renewable Energy Laboratory (NREL), led by Jeffrey Blackburn⁹ and Teresa Barnes,¹⁰ sought to discover in 2008. Turning what was then merely speculative inference into beautiful science, the NREL team performed doping experiments on type-separated samples that addressed this important question. They concluded

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that (1) indeed, doping has a major impact at the tube–tube junctions, improving the transport across them; and (2) doped semiconducting nanotubes provide more conductive films than metallic nanotube films, whether the latter are doped or not. These follow from the fact that conductivity scales with the carrier density, which depends in turn on the integrated product of the Fermi function and the density of electronic states (DOS), the result of which falls away for all but a narrow range within kT of the Fermi level. For the metallic nanotubes that have a flat DOS over the doping range employed, the on-tube conductance should not have changed at all, so the observed change, by a factor of 4, in the conductivity of the predominantly metallic nanotube film upon doping leads to the first finding. The second finding follows (in our view) based simply on the observation that a doped semiconducting nanotube whose Fermi level is pushed to underlie a van Hove singularity has a much higher DOS coming into the integral than does a comparably doped metallic nanotube. The NREL group suggested that more is at work, but for that, you will have to read their papers.

More recently, Blackburn and NREL colleagues have worked on a related topic even closer to our hearts. In 2004, as our lab contemplated potential applications for the films as electrodes, the aspect that most captured our imagination was something never before seen in conventional metal electrodes: the low density of electronic states of the nanotubes in the vicinity of the Fermi level, derived from the reduced dimensionality, implies a metallic electrode having a Fermi level that can be modulated by well over an electronvolt. This feature was exploited previously to modulate the carrier density of semiconducting nanotubes used as the active channel in field effect transistors, but here we were instead contemplating the nanotubes as injection

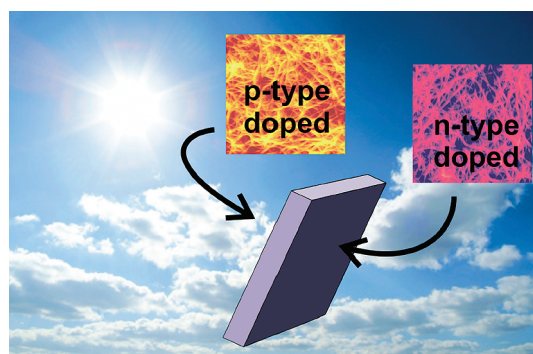


Figure 1. Solar cell concept exploiting p- and n-type nanotube films as the charge collection electrodes in a p-i-n type device.

electrodes. Since the Fermi level line-up across a material interface dictates the transport across the junction, the ability to tune the Fermi level (*i.e.*, work function) of both the metallic and semiconducting nanotubes provided a new degree of freedom, enabling a facile junction engineering. What most intrigued us was the idea of active electronic control over the nanotube electrode side of the junction, so that is the direction our work has taken over the past few years,^{11,12} but the nanotube Fermi level is of course also readily modulated by chemical charge transfer doping. p-Type acceptor dopants are far more air-stable than n-type donor dopants, so, apart from early work done with alkali-metal donor dopants under highly controlled conditions, comparatively little work has been done with n-type dopants. Obtaining the full benefit of a junction engineering that exploits nanotubes, however, requires both p- and n-types, and that is where Blackburn and colleagues have most recently made headway.

Studying a range of known amine n-type dopants and applying a broad range of analysis techniques, Blackburn and colleagues have found that hydrazine (first used as a donor dopant in single nanotube devices by Avouris and colleagues at IBM¹³) is about as good at n-type doping the nanotube films as nitric acid is at p-type doping them. Transparent conducting p-doped nanotube films have been exploited

as the hole injection electrodes in light-emitting devices since 2004¹⁴ and as the hole collection electrodes in photovoltaic devices since 2005.¹⁵ As discussed by Blackburn and colleagues in this issue of *ACS Nano*, the well-characterized hydrazine n-type-doped films can now begin to be contemplated as transparent electron-injecting and electron-collecting electrodes in devices. For example, one can envision a slab of intrinsic silicon (Figure 1) coated on one side with a thin transparent p-doped nanotube film, while the other side is coated with a hydrazine n-doped film creating a p-i-n type solar cell. Hydrazine-doped nanotube films could also be considered as replacements for the PCBM (phenyl C₆₁ butyric acid methyl ester) network in bulk heterojunction organic solar cells. The graphene community at work on transparent conducting graphene film electrodes will, no doubt, also take notice.

The hydrazine doping is sensitive to air exposure but so are the low

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work function metals that are used in many high-tech devices. Work must be done in an inert atmosphere glovebox, but encapsulation must generally be done there anyway, so this is not an especially onerous requirement. Questions to be addressed as such devices are developed will be the stability of the dopants against migration or electromigration with long-term operation and the potential for chemical reaction of the hydrazine with adjacent layers, but the potential pitfalls will only be discerned by trying, and the benefits could be great. Kudos to the research team at NREL for continuing to push the boundaries.

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