

## BANDGAP SELECTIVE CHEMICAL DOPING OF SEMICONDUCTING HIPCO SINGLE-WALLED CARBON NANOTUBES

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Bandgap modulation of single-walled carbon nanotubes (SWCNTs) can be achieved by encapsulation of metallofullerenes, covalent functionalization or changing the tube aggregation states. Another attractive idea is to dope SWCNTs by adding electron donors or acceptors since it allows us to control their electronic states without generating defects in the SWCNT bonding structures. Reversible doping in SWCNTs has been reported by utilizing either chemical dopants [1] or electrochemical methods [2]. A more recent paper reported a diameter selective charge transfer in a dopant-intercalated SWCNT system [3]. By adding a pH-sensitive dopant, ferricyanide, in an aqueous solution of SDS micelle-embedded individual SWCNTs, we show that we can reversibly control the electron Fermi level of isolated semiconducting SWCNTs and subsequently change their bandgap absorption.

Figure 1 shows the evolution of absorption spectra of SWCNT solutions with ferricyanide doping at various pH values. It is evident that the longer wavelength  $\nu_{11}$  absorptions, which belong to the first bandgap transition from larger diameter SWCNT, are sequentially suppressed with increasing acidity. The bandgap absorption characteristics, which are strongly dependent on the Fermi level of the electrons, can be reversibly adjusted by controlling the oxidation potential of the dopants via changing the pH value.

M.S. Strano et. al. reported that in the SDS-SWCNTs system, the absorption spectra of individual tubes show a bandgap selective protonation of the side walls of the tube between pH 6 and 2.5 [4]. To clarify the ferricyanide doping effect, a comparable experiment was also performed in an undoped SWCNT solution. In Figure 2, we compare the pH dependences of the chemical potential assumed to be the half bandgap energy ( $0.5 \cdot E_g$ ) for which absorption suppression has occurred for both the doped and undoped systems. It is evident that the chemical potential of the ferricyanide doped system shifts to higher pH range and shows a lower sensitivity to acidity compared to the undoped system. We believe that the origin of the selective modification of bandgap absorption for the ferricyanide-doped system is the electron-transfer between carbon nanotubes and ferricyanides. It is distinct from the selective protonation which forms a proton-SWCNT complex in an acidic environment ( $\text{pH} < 5$ ).

Figure 3 illustrates the energy band diagram of the dopant, metallic tubes and semiconducting tubes with different diameters. In the individual state all tubes can be accessed by the dopant and those SWCNTs whose valence bands lie above the reduction potential  $E$  of the ferricyanides would be doped. Consequently, the larger diameter semiconducting tubes are preferentially doped.

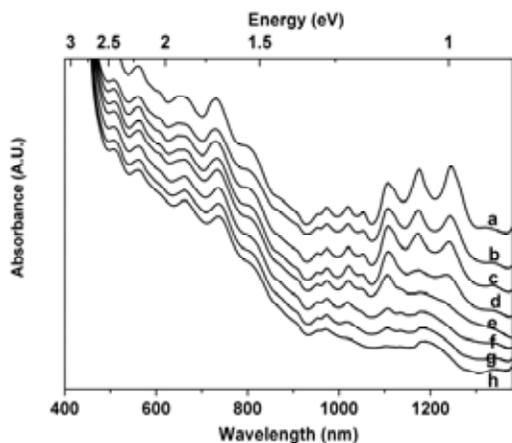
As our results demonstrate that diameter and hence bandgap selective doping of SWCNTs has been achieved, this means that the SWCNT should be positively charged to a greater or lesser extent as a function of diameter. It is well known that the charged and neutral molecules in solution respond differently to electrophoresis and dielectrophoresis respectively. The selective charging we present here may provide a possible route for bandgap-selective bulk separation of semiconducting SWCNTs. Also, the pH-sensitive selective doping phenomenon may have applications in biosensor or bio-detector research. Bandgap-selective chemical activity would be another potentially interesting application of selective doping because the electron Fermi level of SWCNTs, which relates to their reactivity, is adjusted by chemical potentials of dopants.

**References:**

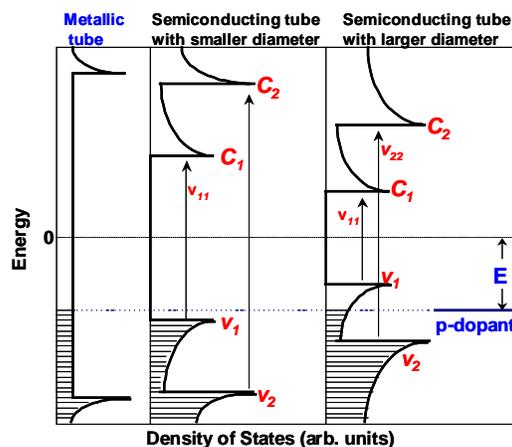
[1] P. Petit et al., Chem. Phys. Lett., **305** (1999) 370.  
 [2] S. Kazaoui et al., Appl. Phys. Lett., **78** (2001) 3433.  
 [3] A. Kukovec et al., Chem. Comm., (2000) 1730.  
 [4] M. S. Strano et al., J. Phys. Chem. **B107** (2003) 6979.

**Figures:**

**Fig. 1**



**Fig. 3**



**Fig. 2**

