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**ELECTRONIC SUPLEMENTARY INFORMATION (ESI)** 

## A tool box to ascertain the nature of doping and

## photoresponse in single-walled carbon nanotubes

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## Purification of SWCNTs

Pristine Single Walled Carbon Nanotubes produced by the HiPco® process, were acquired from Unidym<sup>™</sup> in raw form (Lot.# R1831). According to the manufacturer, the SWCNTs consist of bundled individuals in the range of 0.8-1.2 nm diameter and 100-1000 nm length, accompanied by residual metal (Fe) and carbonaceous particles (http://www.nanointegris.com/en/hipco). This raw material was purified in-house with organic solvents to eliminate moisture and part of their solid impurities. The process was done by dispersing SWCNTs in toluene (~35 g/L) through mild bath sonication (Cleanosonic® 40 kHz) followed by overnight magnetic stirring at room temperature. Then, some impurities segregated in the form of an orange oil, which was decanted off. The SWCNT paste was vacuum-filtrated (Omnipore® 0.45 µm pore size membrane) and the process was repeated with N,N-dimethylformamide (DMF) and methanol. Finally, SWCNTs were rinsed with diethyl ether, milled in mortar and dried under vacuum.

## **Reagents and solvents**

Sulfanilic acid (Fluka AG-Buchs SG, purity > 99%); 4-aminobenzylalcohol (Sigma-Aldrich, purity 99.8%); isopentyl nitrite (Alfa Aesar, purity 97%, stabilized with 0.2% of anhydrous sodium carbonate). Solvents were high purity grade (>98%) from Sigma-Aldrich or Alfa Aesar. All filtrations, unless otherwise stated, were performed through hydrophilic Teflon membranes (Omnipore<sup>®</sup> 0.45 µm pore size) assembled into a glass vacuum-filtration equipment.



Figure S1: Raman spectra in the D-band and the G-band region measured on SWCNTs and excited by a. 2.33 and b. 1.96 eV. The G-band is fitted by 2 Lorentzian and 1 BWF line-shape and 1 Lorentzian line-shape for the D-band component. The dotted grey curves correspond to the fitted components and to a sum of them.



Figure S2. DOS of the SWCNT (9,0) for the structure optimized with SIESTA (solid line) and CRYSTAL (dashed line).



Figure S3. UV-Vis spectra of SWCNTs (black line), A-SWCNTs (red dotted line) and B-SWCNTs (blue dashed line).



Figure S4: Raman spectra of the A-SWCNTs at different potentials in the RBM spectral region. The electrode potential range is from -1.5 to 1.5 V vs Ag pseudoreference electrode (from bottom to top). The spectra in black correspond to the 0 V potential. The electrochemical potential change between the curves is 0.1 V. The spectra were acquired using a. 2.33 and b. 1.96 eV laser excitation energy. The spectra are offset for clarity.



Figure S5: Raman spectra of the B-SWCNTs at different potentials in the RBM spectral region. The electrode potential range is from -1.5 to 1.5 V vs Ag pseudoreference electrode (from bottom to top). The spectra in black correspond to the 0 V potential. The electrochemical potential change between the curves is 0.1 V. The spectra were acquired using a. 2.33 and b. 1.96 eV laser excitation energy. The spectra are offset for clarity.



Figure S6.  $I_{RBM}$  vs  $E_{app}$  for SWCNTs in resonance at 2.33 eV. (a., b.) and 1.96 eV (c., d.) for: a. the band at 183 cm<sup>-1</sup> (semiconducting  $E_{33}^{S}$ ), b. the band at 268 cm<sup>-1</sup> (metallic  $E_{11}^{M}$ ) c. the band at 193 cm<sup>-1</sup> (metallic  $E_{11}^{M}$ ), and d. the band at 257 cm<sup>-1</sup> (semiconducting  $E_{22}^{S}$ ).



Figure S7: Cyclic voltammograms of SWCNTs (black line), A-SWCNTs (red line) and B- SWCNTs (blue line) films in 0.1 M  $\text{LiClO}_4/\text{acetonitrile}$ . Scan rate of 100 mV·s<sup>-1</sup>



Figure S8: Light-dark anodic scans for SWCNTs (black line), A-SWCNTs (red dotted line) and B- SWCNTs (blue dashed line) films in 0.1 M LiClO<sub>4</sub> acetonitrile. Scan rates of 2 mV·s<sup>-1</sup>.



Figure S9. Photoanodic current ( $I_{light}$ - $I_{dark}$ ) as a function of the  $E_{app}$  for SWCNTs (black circles), A-SWCNTs (empty red squares) and B- SWCNTs (empty blue triangles) films.