

Supporting information

Fully Solution-Processed Transparent Conducting Oxide-Free Counter Electrodes for Dye-sensitized Solar Cells: Spray-Coated Single-Wall Carbon Nanotube Thin Films Loaded with Chemically-Reduced Platinum Nanoparticles

Sang Yong Kim,[†] Yesel Kim,[†] Kyung Moon Lee,[†] Woo Sug Yoon,[‡] Ho Seok Lee,[‡] Jong Tae Lee,[‡] Seung-Joo Kim,[†] Yeong Hwan Ahn,[†] Ji-Yong Park,[†] Tai Kyu Lee,[‡] and Soonil Lee^{†}*

[†]Department of Physics and Division of Energy Systems Research, Ajou University, Suwon 443-749, Korea

[‡]NANOPAC, Yongin, 449-832, Korea

E-mail: soonil@ajou.ac.kr

Figures S1 and S2 are direct evidences for anodic doping and de-doping of SWCNT CEs after nitric- and formic-acid treatments, respectively. In Figure S1, transmittance of an as-deposited SWCNT film clearly shows three absorption bands that correspond to E_{11} and E_{22} transitions of semiconducting SWCNTs and E_{11} transition of metallic SWCNTs, respectively. After nitric acid treatment, the semiconducting E_{11} absorption band disappears almost completely, and the semiconducting E_{22} -band absorption is substantially reduced. Such bleaching of the semiconducting absorption bands is a direct evidence of anodic doping.^{1,2} However, the two semiconducting absorption bands are fully recovered after formic acid treatment. Reappearance of the disappeared semiconducting absorption bands is a direct evidence for de-doping. On the contrary to the semiconducting absorption bands there is no discernable change in the metallic absorption band. Inset of Figure S1 is a landscape photo taken through the semi-transparent SWCNT CE decorated with Pt NPs. It is interesting to note that 30~40% transmittance in long visible wavelength range is sufficient to see through such a SWCNT CE.

Figure S2 shows changes in Raman spectra taken at the excitation wavelength of 532 nm. Blue-shifts of G and G' peaks following the nitric acid treatment are the result of anodic doping.¹⁻³ On the contrary, formic acid treatment has resulted in red-shifts of G and G' peaks. The downshifted positions of G and G' peaks coincide with those of as-deposited SWCNT films. Such identical G- and G'-peak positions are another direct evidence for de-doping.

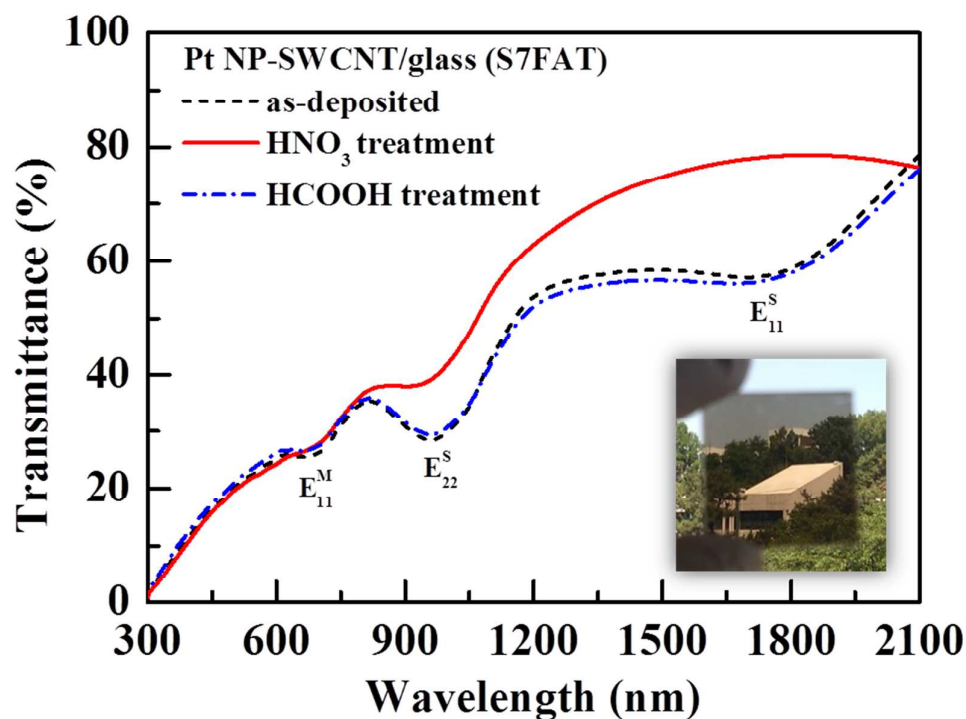


Figure S1. Change in transmittance following nitric- and formic-acid treatments. Three absorption bands that correspond to E_{11} and E_{22} transitions of semiconducting SWCNTs and E_{11} transition of metallic SWCNTs, respectively, are apparent in the transmittance of as-deposited SWCNT films. However, E_{11} and E_{22} absorption bands of semiconducting SWCNTs almost disappear after nitric acid treatment, whereas there is no discernable change in the metallic absorption band. Such bleaching of the semiconducting absorption bands is a direct evidence of anodic doping. Similarly, reappearance of the two semiconducting absorption bands after formic acid treatment is a direct evidence of de-doping. Inset shows a landscape seen through the semi-transparent Pt NP-loaded SWCNT CE.

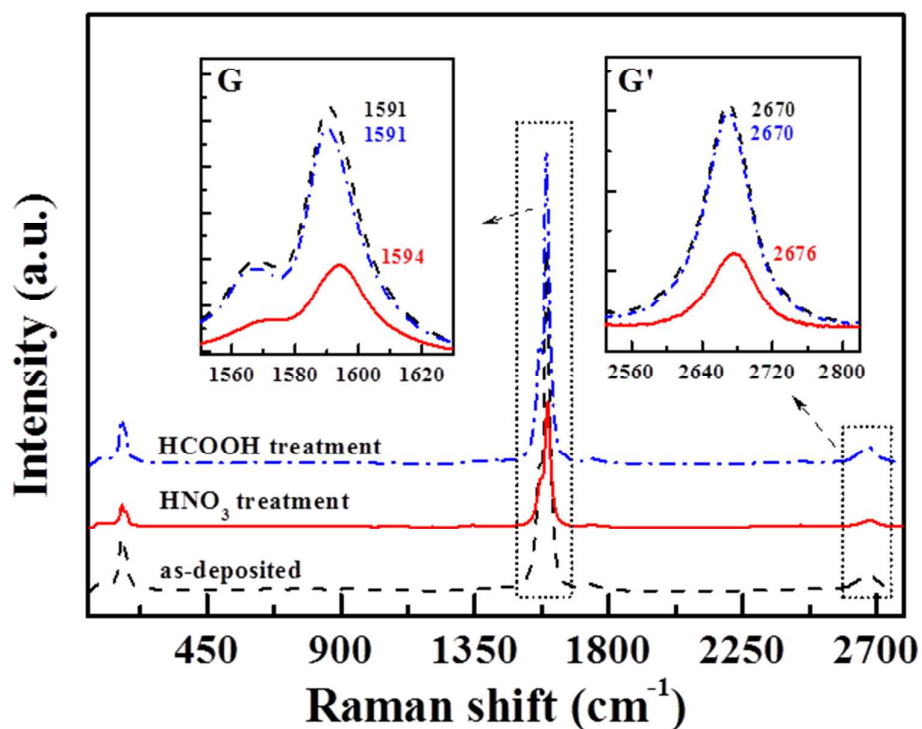


Figure S2. Change in Raman spectra following nitric- and formic-acid treatments. The excitation wavelength is 532 nm. Nitric acid treatment has induced upshifts of G and G' peaks due to anodic doping. On the contrary, formic acid treatment has resulted in downshifts of G and G' peaks to the positions that coincide with those of as-deposited SWCNT films. Such identical G- and G'-peak positions are direct evidence for de-doping.

REFERENCES

1. Shin, D.-W.; Lee, J. H.; Kim, Y.-H.; Yu, S. M.; Park, S.-Y.; Yoo, J.-B. A Role of HNO_3 on Transparent Conducting Film with Single-Walled Carbon Nanotubes. *Nanotechnology* **2009**, *20*, 475703-475708
2. Miyata, Y.; Yanagi, K.; Maniwa, Y.; Kataura, H. Highly Stabilized Conductivity of Metallic Single Wall Carbon Nanotube Thin Films. *J. Phys. Chem. C* **2008**, *112*, 3591–3596.
3. Geng, H.-Z.; Kim, K. K.; So, K. P.; Lee, Y. S.; Chang, Y.; Lee, Y. H. Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films. *J. Am. Chem. Soc.* **2007**, *129*, 7758–7759.