Characterization of Functionalized Single-Wall Carbon Nanotubes for Application to Dye-Sensitized Solar Cells

Song-Rim Jang, Jin Sup Hong, Kyoung-Hwa Jung, and Kang-Jin Kim
Division of Chemistry and Molecular Engineering, Korea University, Seoul, 136-701, Korea

Recently, it is reported that incorporation of single-wall carbon nanotubes (SWCNs) in TiO_2 electrodes enhances the short-circuit photocurrent of dye-sensitized solar cells (1). Interests in the dye-sensitized solar cells stem from their high solar conversion efficiency and potentially low-energy processing techniques. However, SEM analysis indicates that some portions of the SWCNs are poorly attached to nanocrystallineTiO$_2$ particles. To increase the interconnectivity between SWCNs and TiO_2 particles, it is worthwhile to shorten the chain length of the SWCNs by treating them with an acid-mixture of H_2SO_4 and HNO_3. The acid treatment is also known to terminate the ends of the shortened SWCNs with –COOH groups (2). As a result, the acid-treated SWCNs are expected to adsorb well to TiO_2 like Ru(II)-based dye molecules containing carboxylic acid groups. In this study, for the purpose of improving photovoltaic properties of dye-sensitized solar cells, we attempt to treat the SWCNs with an H_2SO_4-HNO_3 mixture and characterize the treated SWCNs by SEM, FT-IR, Raman, HRTEM, and XPS. Effects of the modification of TiO_2 films with the treated-SWNTs on the photocurrent-voltage (J-V) characteristics of the solar cells are investigated.

SWCNs were shortened upon treating with a 3:1 mixture of H_2SO_4 : HNO_3 for 24 h at 50 ºC with ultrasonication. A small amount of the treated-SWCNs was mixed with P25 in the preparation step of the TiO_2 colloidal solution. The resulting TiO_2 colloidal solution was spin-coated on FTO followed by annealing at 450 ^{o}C for 30 min in air. The film was coated with Ru(II)L_2(NCS)$_2$ in 3 x 10^{-4} M absolute ethanol for 24 h at room temperature. The redox electrolyte consisted of 50 mM I_2 and 0.8 M I^-. *J-V* curves were measured using a Keithley Model M236 source measure unit. Pt gauze was used as the counter electrode.

TEM images indicate that the SWCNs are shortened and swollen with having nodes along the shortened tubes. FT-IR spectra show that the treated SWCNs have an additional peak corresponding to the C=O stretching vibration at 1700 cm^{-1}, compared with non-treated SWCNs. Furthermore, a new peak at 289.6 eV appears in XPS (Fig. 1) together with the peak at 285.85 eV corresponding to the C1s binding energy, suggesting that the binding energy of C1s increases due to binding of the –COOH groups to the treated-SWCNs. The modification of SWCNs with –COOH groups is further evidenced by the weakening of the characteristic line at 1581 cm^{-1} of SWCNs in Raman spectra.

SEM data shown in Fig. 2 indicates that TiO_2 particles adhere well around the SWCNs, showing an image of the shortened-SWCNs entirely covered with TiO_2 particles. The J-V characteristics and stability of the DSSCs with the modified TiO2 film will be presented together with the detailed mechanism of variation of the J-V characteristics arising from the modification.

Acknowledgment
The Center for Electro- & Photoresponsive Molecules - KOSEF has financially supported this work.

References

1. K. –H. Jung, J. S. Hong, R. Vittal, K. –J. Kim, Chem. Lett., 864 (2000).
2. X. Nan, Z. Gu, Z. Liu, J. Colloid Interface Sci., 245, 311 (2002).

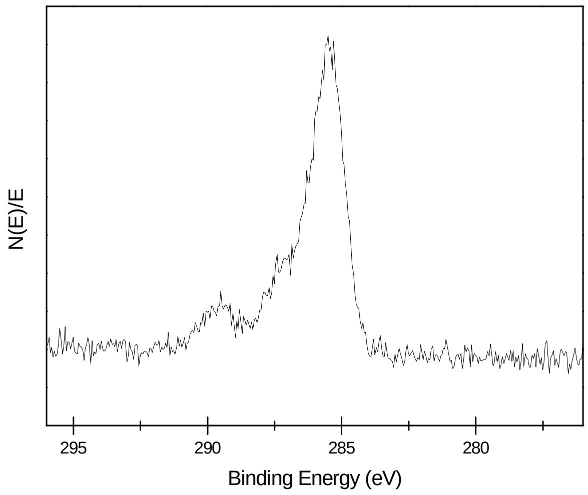

Fig. 1. XPS spectrum of C1s of TiO_2 film prepared with the shortened-SWNTs.

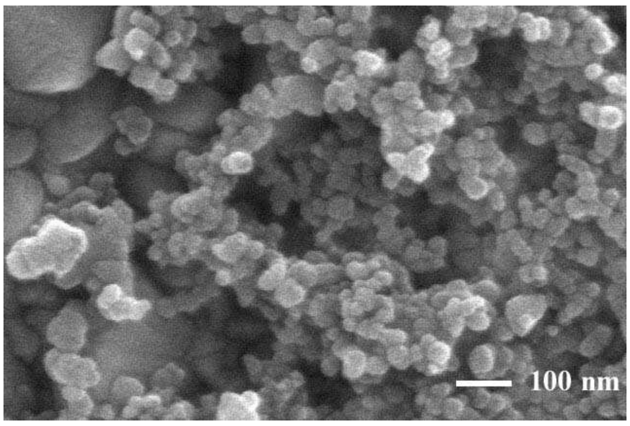

Fig. 2. Cross-sectional view of the SEM image of a TiO_2 film annealed at 450 ºC for 30 min, showing aggregates of SWNTs covered with TiO_2 particles.