Characterization of Functionalized Single-Wall Carbon Nanotubes for Application to Dye-Sensitized Solar Cells
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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$_2$SO$_4$ 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$_2$SO$_4$–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$_2$SO$_4$ : HNO$_3$ for 24 h at 50 °C 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 °C for 30 min in air. The film was coated with Ru(II)$_2$(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 Cls binding energy, suggesting that the binding energy of Cls 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 TiO$_2$ film will be presented together with the detailed mechanism of variation of the J-V characteristics arising from the modification.

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References

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 °C for 30 min, showing aggregates of SWNTs covered with TiO$_2$ particles.