Supplementary Material (ESI) for Chemical Communications

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Electronic Supplementary Information

Surfactant and polymer-free electrochemical micropatterning of carboxylated multi-walled carbon nanotubes on indium tin oxide electrodes

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Chemicals and reagents. ITO electrode was obtained from Geomate (www.geomatec.co.jp), and micropatterned ITO electrode was obtained from Freemtec (www.freemteck.com). Multi-walled CNT (produced by CVD method, catalog number = 636487), catechol, hydroquinone, acetic acid, and sodium acetate were received from Sigma-Aldrich. KNO_3 was obtained from Fluka. Acetate buffer consisted of 65 mM acetic acid and 35 mM sodium acetate (pH 4.5). Doubly distilled water was used for preparing aqueous solutions, and all chemicals were used without further purification.

Carboxylation of multi-walled CNT. 0.1 g multi-walled CNT was added in a 100 mL of mixed solution of concentrated H_2SO_4 and HNO_3 (3:1 by volume), and then the solution was sonicated for 8 h to generate carboxylic groups. Afterward, the mixture was diluted with water, hold still for 8 h, and then upper part of the diluted solution was decanted. The dilution and decantation procedure was repeated six times. The resulting mixture was filtered and washed with water. Finally, CMWCNTs were dried at 60 °C for 24 h.

Electrochemistry. The electrochemical experiment was performed using a CHI 617 and CHI 708 (CH Instruments). The electrochemical cell consisted of an ITO working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode.

Transmission electron microscope (TEM) images. Figure S1 shows TEM images of CMWCNTs before and after electrochemical deposition. There is no significant change in TEM images, which confirms that electrochemically deposited CMWCNTs do not have any type of coating on their surface after electrochemical deposition.

Raman spectra. Raman spectra were obtained using a Jobin Yvon/HORIBA LabRAM spectrometer equipped with 514.5 nm laser source and an integral microscope (Olympus BX 41). Figure S2 shows Raman spectra of purchased multi-walled CNTs, CMWCNTs, and electrochemically deposited CMWCNTs. The spectra show that three kinds of CNTs have similar intensity ratio of D band (disorder) over G band (Graphite) (I_D/I_G). The multi-walled CNTs that we used in our experiment was produced by CVD method and purified. By this reason, graphitic quality of multi-walled CNTs was not good. As a result, the I_D/I_G ratio of purchased multi-walled CNTs is high and there is no significant change in the ratio after the acid treatment for carboxylation.

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X-ray photoelectron spectra (XPS). From XPS data of C1s (Figure S3), we can clearly see that a significant amount of carboxylic groups are generated after acid treatment and that these carboxylic groups remain after electrochemical deposition. This is in agreement with the increased solubility of multi-walled CNTs after acid treatment. XPS data of N1s (Figure S4) show that three samples contain a small amount of nitrogen.

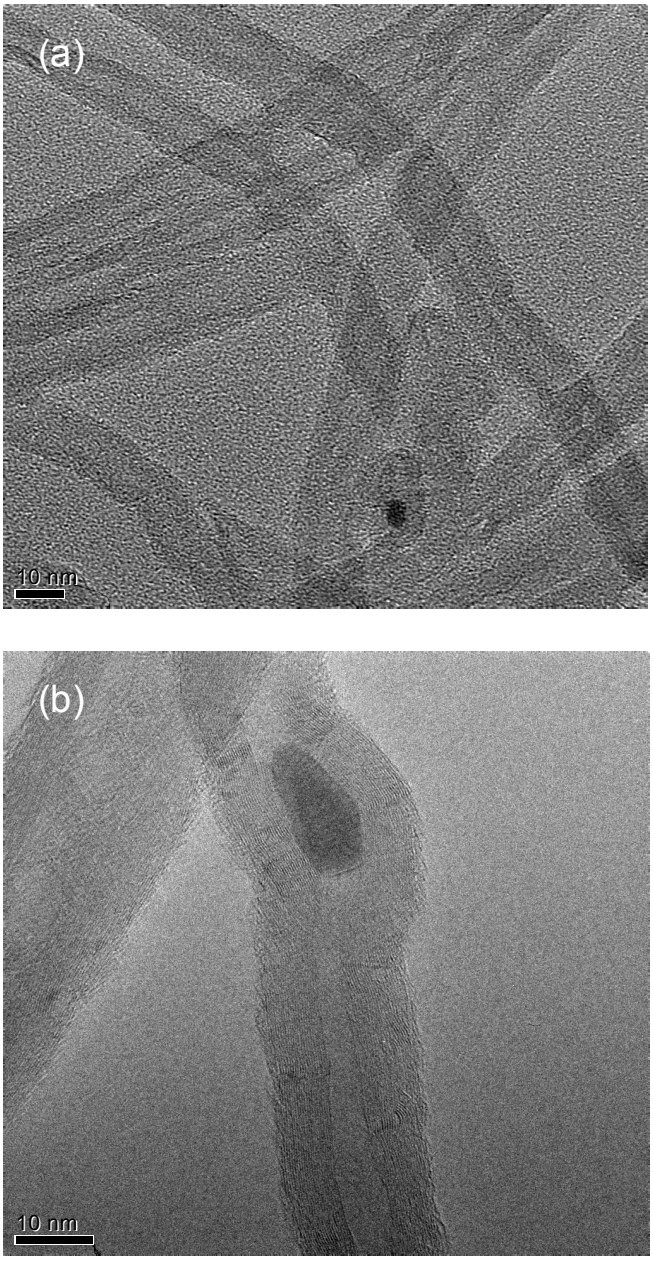

Figure S1. TEM images of CMWCNTs (a) before and (b) after electrochemical deposition.

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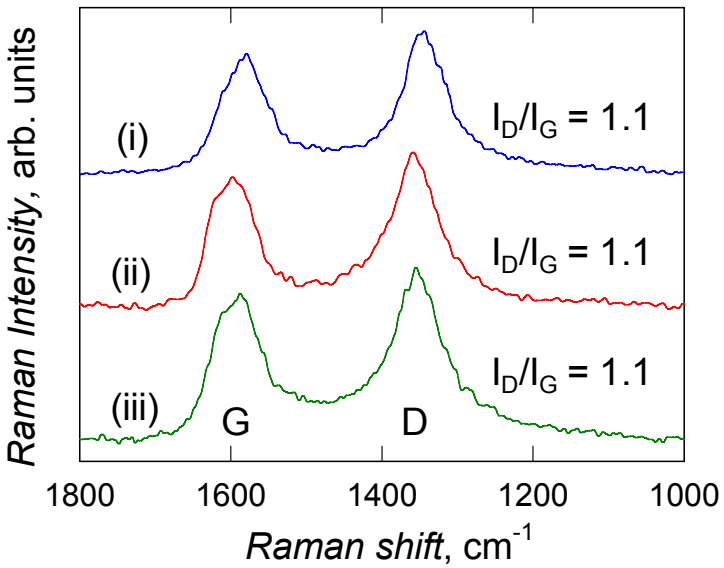

Figure S2. Raman spectra of (i) purchased multi-walled CNTs, (ii) CMWCNTs, and (iii) electrochemically deposited CMWCNTs

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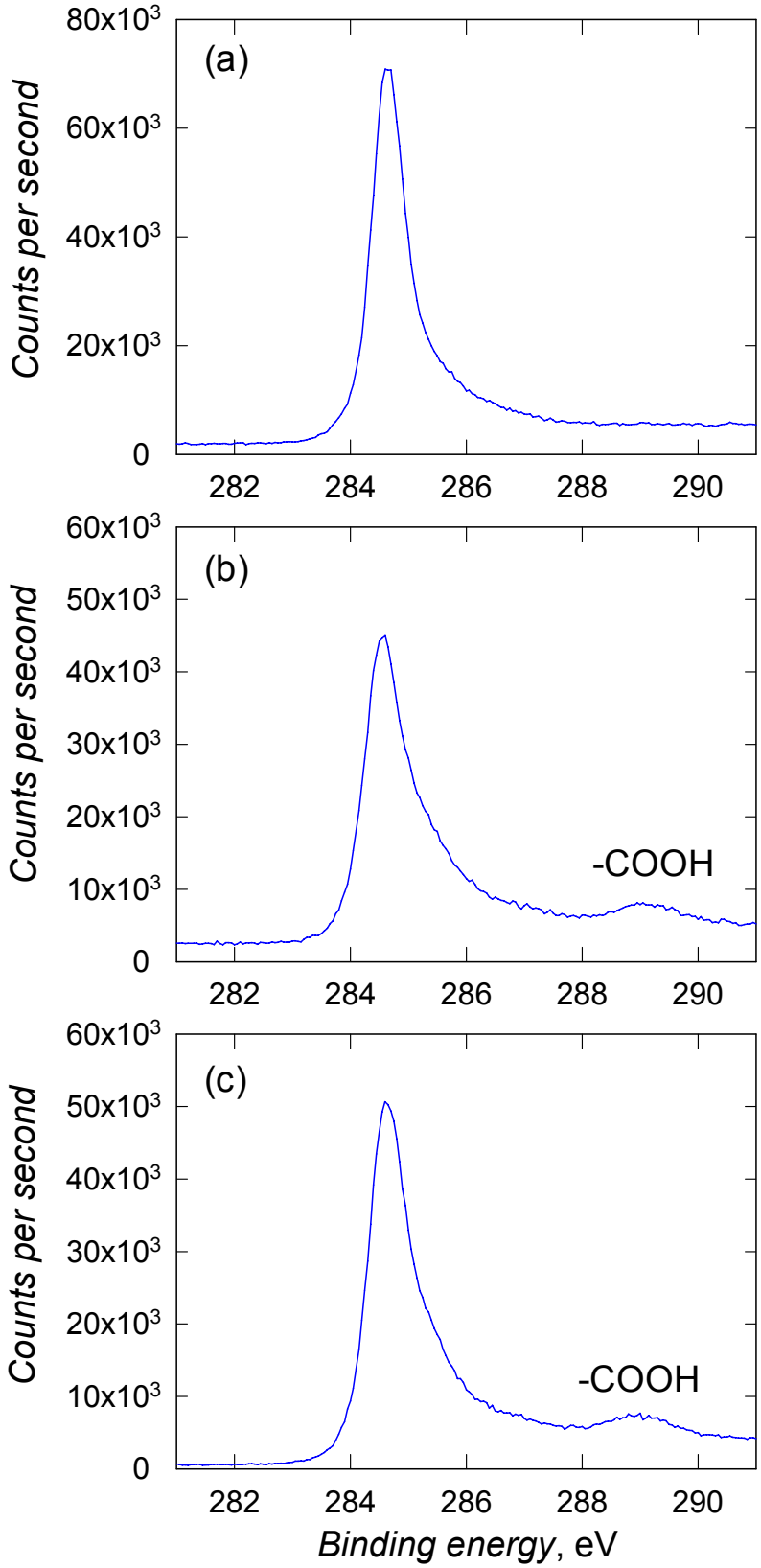

Figure S3. XPS data of C1s for (a) purchased multi-walled CNTs, (b) CMWCNTs, and (c) electrochemically deposited CMWCNTs.

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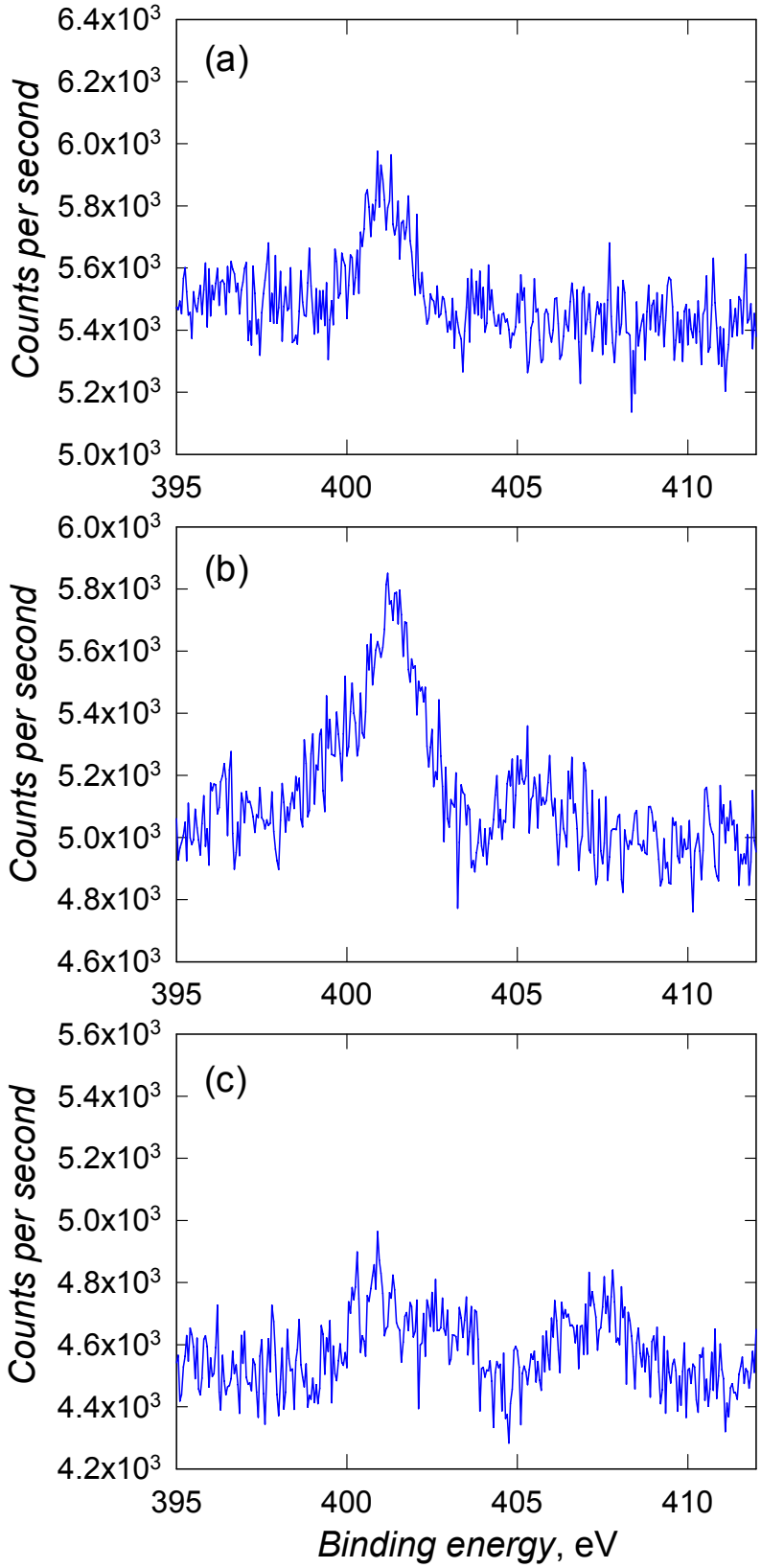

Figure S4. XPS data of N1s for (a) purchased multi-walled CNTs, (b) CMWCNTs, and (c) electrochemically deposited CMWCNTs.