Supplementary Material for Chemical Communications

Supplementary data

Highly-regulated nanocoatings of polymer films on carbon nanofibers using ultrasonic irradiation

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1. Materials

All chemicals were used without further purification. Pyrrole (Py) was purchased from Tokyo Kasei Co.. Anhydrous iron (III) trichloride ($FeCl_3$) and sodium dodecyl sulfate (SDS) were purchased from Wako Co.. Vapor- grown carbon fiber (VGCF) was received from Showa Denko Co.. Distilled and deionized water was used as a solvent for chemical synthesis.

2. TEM measurement

Transmission electron microscopy (TEM) images were recorded with a Hitachi H-8100 Electron Microscope, operating at 200 kV. Samples were prepared by placing a drop of the VGCF and PPy/VGCF solution, prepared in the absence and presence of ultrasound, onto a carbon-coated copper grid on an underlying tissue paper and then dried in desiccator for 48 h.

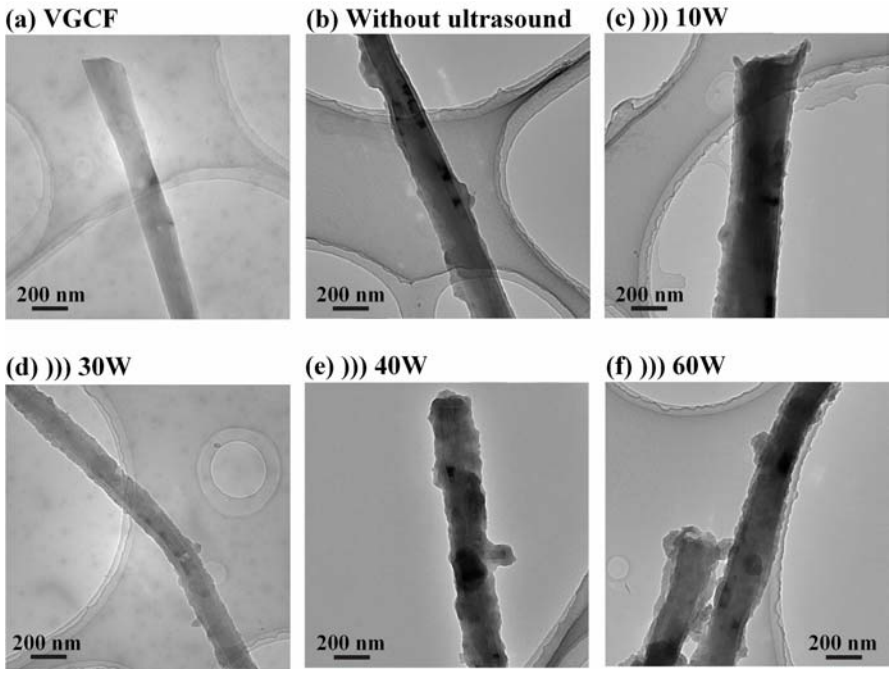

Figure S1. TEM images of PPy/VGCF composites prepared in an aqueous solution containing Py monomer and VGCF (1:1 in w/w) with ultrasonic irradiation at various intensities.

3. Preparation of Composite Electrode and SEM measurement

Procedures for electrode preparation are as follows: the PPy/VGCF nanocomposites and polyvinilidenchloride (PVdF as a binder) were mixed in a mass ratio of 80:20 and dispersed in N-methyl-2-pyrrolidine (NMP). The slurry was cast on an ITO electrode with an applicator and then dried under vacuum at 70 °C for ca. 2h. The thickness of the

electrode was about 20 μm. After preparation of PPy/VGCF composite electrodes, surface morphology of the composites electrodes was observed by SEM (VE-7800, Keyence Co.), operating at 2 kV.

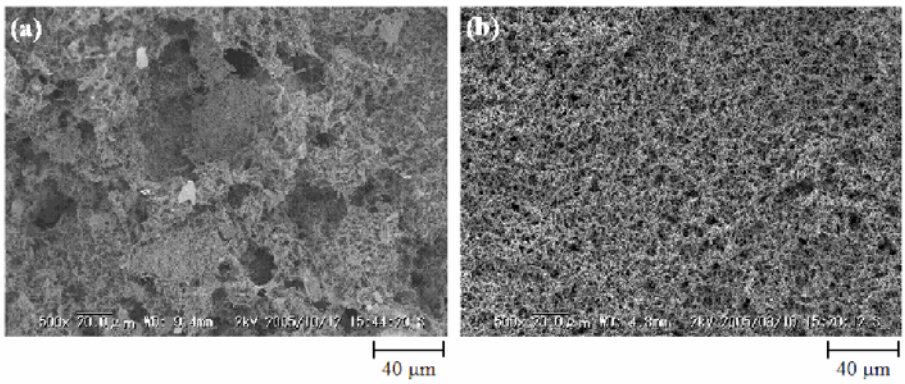

Figure S2. Scanning electron micrographs of the ITO electrodes modified with PPy/VGCF composites prepared without (a) and with (b) ultrasonic irradiation.

4. Measurement of Electrochemical Impedance Spectroscopy and Cyclic Voltammetry

Electrochemical measurements were conducted using a conventional three-electrode configuration. Indium-thin oxide (ITO) electrodes coated with PPy/VGCF nanocomposites were used as the working electrode. A Pt coil and SCE were used as the counter and reference electrodes, respectively. The resistance of the nanocomposites was measured with ac impedance on Solartron SI 1260 impedance/gain-phase analyzer within a frequency sweep from 10 kHz to 10 mHz at open circuit voltage with 10 mV amplitude. The composite films exhibited only diffusive (high frequency) and capacitive (low frequency) behavior.

Figure S3 shows the cyclic voltammograms (CVs) obtained for the PPy/VGCF composite prepared with and without ultrasonic irradiation. The CVs characteristics of the PPy/VGCF composites were recorded at the scan rates of 50 mV s^{-1}. The capacitance was calculated by $C = (It)/\Delta V$, where I is the current, t is time, andΔV is voltage range. The capacitance of polypyrrole/VGCF prepared with and without ultrasonic irradiation was shown in Table S1.

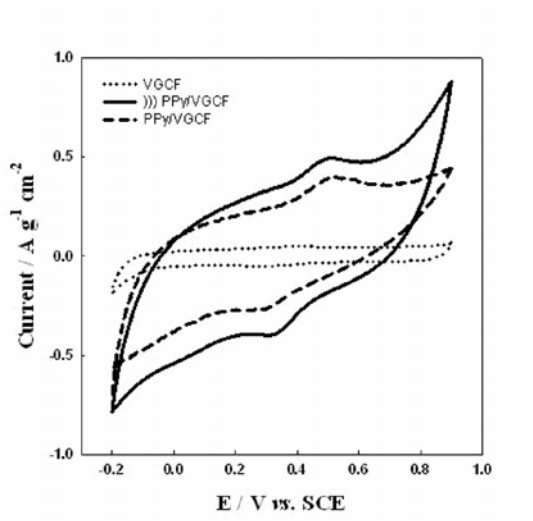

Figure S3. Cyclic voltammograms of PPy/VGCF nanocomposite prepared in an aqueous solution containing Py monomer and VGCF (3:1 in w/w) with and without ultrasonic irradiation in 0.5 M H_2SO_4 solution at a scan rate of 10 mV s^{-1}.

Table S1. Capacitance of PPy/VGCF prepared with and without ultrasonic irradiation

Sample	*Py:VGCF	**Discharge capacitance / F g^{-1}	***Roughness factor / nm
(a)	0:1	4.9	-
(b)	1:1	36.0	0.084
(c)	)))) 1:1	63.0	0.156
(d)	3:1	92.6	0.353
(e)	)))) 3:1	149	0.168

* The composite samples were prepared in an aqueous solution containing Py monomer and VGCF (1:1 or 3:1 in w/w).
** Discharge capacitance of the composite electrodes was estimated by voltammerty (0.5 M H_2SO_4 solution, scan rate: 50 mV s^{-1}).
*** Roughness factor is standard deviation of the polypyrrole thickness.

5. Capacitance of polypyrrole composite with various carbon materials

This new methodology using ultrasonic treatment has many practical advantages for energy storage devices based on various carbon materials such as active carbon (AC) and multi-wall carbon nanofiber (MWNT). Each composite prepared with ultrasonic irradiation shows higher discharge capacitance compared with that without the irradiation. It is hoped that the present methodology will make significant contributions to nanocomposite materials and open a new aspect of tailoring a nanomaterial surface structure.

The synthesis of the PPy/(AC or MWNT) nanocomposites followed the method of synthesizing the PPy/VGCF nanocomposite. The initial weight ratio of Py/(AC or MWNT) was always kept at 1/1. Procedures for electrode preparation are as follows: the PPy/(AC or MWNT) nanocomposites and polyvinilidenchloride (PVdF as a binder) were mixed in a mass ratio of 80:20 and dispersed in N-methyl-2-pyrrolidine (NMP) solution. The slurry was cast on an ITO electrode with an applicator and then dried under vacuum at 70 □ for ca. 2h. The capacitance of PPy/(AC or MWNT) prepared with and without ultrasonic irradiation was shown in Table S2.

Table S2. Capacitance of polypyrrole/various carbon composites prepared with and without ultrasonic irradiation

Sample	Py:AC[(a)]	*Discharge capacitance / F g^{-1}	
(a)	0:1	0.235	
(b)	1:1	26.8	
(c)	)))) 1:1	49.5	
Sample	Py:MWNT[(b)]	*Discharge capacitance / F g^{-1}	**Roughness factor / nm
(d)	0:1	13.1	-
(e)	1:1	36.0	0.089
(f)	)))) 1:1	63.0	0.055

[(a)] Activated carbon, [(b)] Multi-wall carbon nanotube.
* Discharge capacitance of the composite electrodes was estimated by voltammetry (0.5 M H_2SO_4 solution, scan rate: 50 mV s^{-1}).
** Roughness factor is standard deviation of the polypyrrole thickness.