

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

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It was demonstrated that nanoprecise coatings of uniform and densely packed polymer layers on nanomaterials and uniform polymer coatings on individual nano-objects are formed using ultrasonic effects.

The development of surface nanostructure will be one of the key engines that drive our technological society in the 21st century. This rapidly growing area focuses on tailoring a nanomaterial surface structure for specific and unique properties.¹

Carbon nanofibers have one-dimensional structures that are chemically inert, and they possess mechanical strength, and high electrical and thermal conductivity. Therefore, they have been applied for various applications including bio-sensing technology² and energy conversion technology.³ However, the surface of the nanofiber is often not ideal for a particular application. Chemical and electrochemical coatings of the nanofiber substrates with conjugated polymers have long been investigated to modify their surface properties.^{4,5} However, the nanoprecise coatings on the surface of nanofibers were carried out with great difficulty due to their extremely small dimensions, high surface areas, and high surface energies, agglomeration of conjugated polymers before their deposition, and deposition as irregular nanoparticles or sediments (Fig. 1a). Hence, nanoprecise coating of the surface of nanofibers remained a challenging target.

On the other hand, ultrasonic irradiation in liquids induces transient cavitations: the formation, growth, and implosive collapse of bubbles.⁶ During the bubble collapse in the vicinity of solid materials suspended in liquid, a high-speed microjet and intense shockwave with high pressure are generated at their liquid–solid interface, and can lead to effective mass transfer toward the interface and increase in the reaction activity.⁷ Hence, it can be expected that such high-speed microjets (excess of 100 m s^{-1})⁸ with high pressure shock waves (up to several hundred MPa)⁹ would influence the overall surface of the nanomaterial suspended in liquid and control uniformly the mass transport of polymer sediments to the surface, and consequently a well-controlled nanoprecise coating of the polymer on the nanomaterials would be achieved (Fig. 1b). Herein, we wish to report a novel approach for the nanoprecise coating of the highly-regulated structure of polypyrrole (PPy) on a vapor-grown carbon fiber (VGCF) using

the physical effect of ultrasound. In addition, it was also found that the resulting nanocomposites exhibited unique electrical properties.

The nanocomposites were prepared by chemical deposition of PPy on VGCF with and without ultrasonic irradiation.† The mean diameter and length of VGCF was 150 nm and 10~20 μm , respectively (Fig. 2a). TEM analysis aids the determination of the polymer thickness and the visualization of the VGCF core (Fig. 2). The roughness of the coating was quite different in the absence and presence of ultrasound, and a highly uniform and dense nanoscale PPy film could be obtained in the presence of ultrasound (Fig. 2c). In addition, the chemical structure of PPy formed on VGCF was found not to be changed at all by ultrasonic irradiation.¹⁰ Such a drastic morphological change of a polymer material using ultrasonic irradiation could also be observed in the preparation of polyaniline colloids.¹¹

Nanoscale coating of PPy on VGCF strongly depends on the ultrasonic intensity. The variations of the roughness factor of PPy/VGCF composites prepared with different ultrasonic irradiation power at 20 kHz are demonstrated in Table 1. The most homogenous PPy film was obtained at the power density of 22.7 W cm^{-2} . However, the roughness of PPy film was increased at both lower and higher power densities, although the roughness was still less than that of PPy film obtained without ultrasonic irradiation (see S1 in ESI†). At a low power density of 7.5 W cm^{-2} , the roughness can be ascribed to ineffective mass transport of PPy sediments toward the VGCF surface. On the other hand, it is well

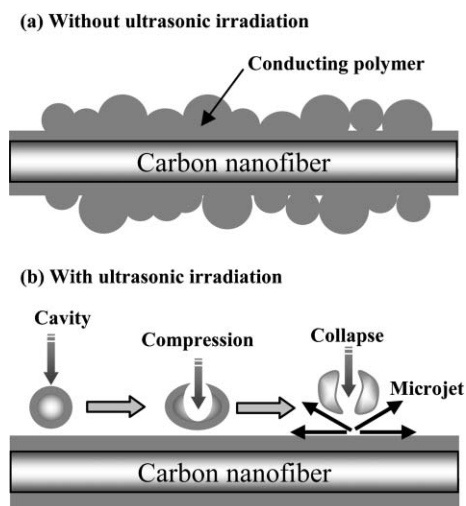


Fig. 1 Schematic illustration of the formation of a conducting polymer on carbon nanofibers (a) without and (b) with ultrasonic irradiation.

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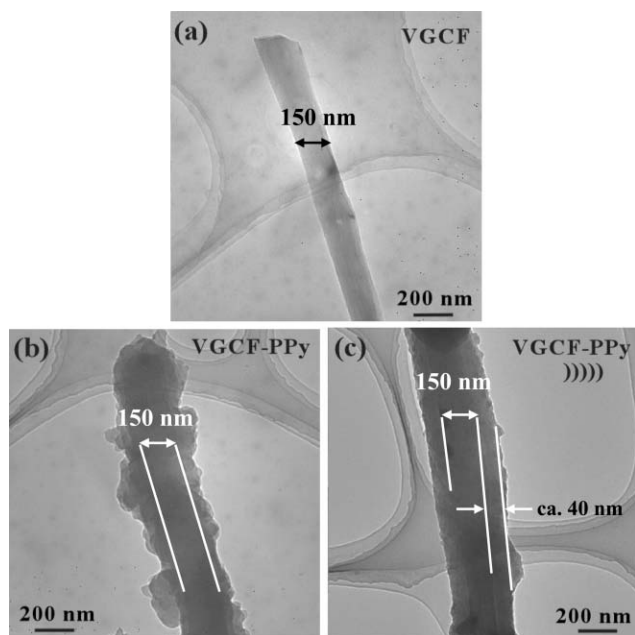


Fig. 2 TEM images of VGCF (a) and PPy/VGCF nanocomposite prepared in an aqueous solution containing Py monomer and VGCF (3 : 1 in w/w) without (b) and with (c) ultrasonic irradiation (20 kHz, 22.7 W cm^{-2} , 2 h).

known that ultrasonic irradiation of an aqueous solution results in the formation of hydrogen peroxide (H_2O_2) *via* the sonolysis of water.¹² Since the oxidation power of H_2O_2 is stronger than that of iron trichloride, the H_2O_2 formed, although the amount is minimal, would accelerate the polymerization of pyrrole¹³ and consequently larger polymer grains would deposit on the VGCF surface. In addition, damage to the PPy layer on VGCF by the cavitation microjet may be not negligible at higher power densities. These phenomena should lead to irregular coating. Thus, it is likely that ultrasonic intensity is an important factor for uniform nanoscale coating.

In order to investigate electrochemical properties of the PPy/VGCF nanocomposites, the composite samples were cast on ITO electrodes. By SEM observation of surface morphology of the composite electrodes (see S2 in ESI†), it was confirmed that the electrode modified with the nanocomposites prepared with ultrasonic irradiation had a smooth surface and uniform distribution of the composites compared to that prepared without the irradiation. Such a surface morphology can be ascribed to nanoprecise coating of the conducting polymer on individual nanofibers without their agglomeration.

Table 1 Effect of ultrasonic intensity on PPy coating on VGCF

Sample	Ultrasonic intensity/ W cm^{-2}	Average thickness of PPy coating/nm	Roughness ^b /nm
(1)	7.5	23.6	0.034
(2)	22.7	32.3	0.029
(3)	30.3	42.6	0.084
(4)	45.4	47.1	0.157
(5)	Without ultrasound	34.1	0.156

^a The composite samples were prepared in an aqueous solution containing Py monomer and VGCF (1 : 1 in w/w). ^b Roughness factor is standard deviation of the PPy film thickness.

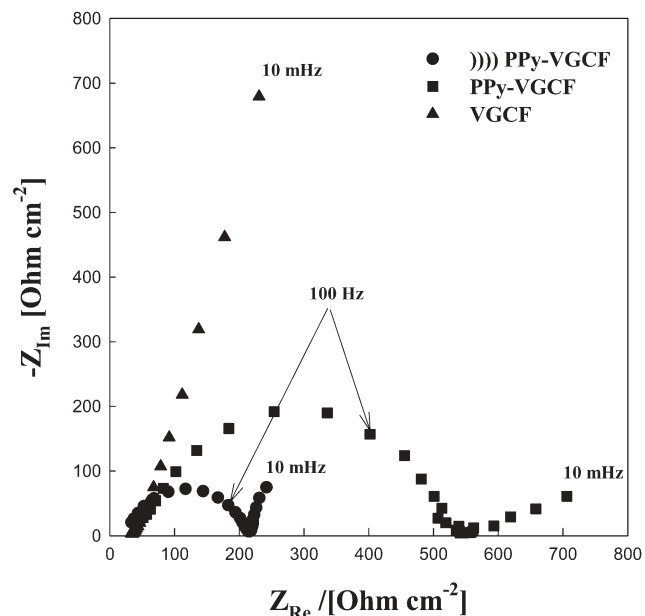


Fig. 3 Electrochemical impedance spectra of the ITO electrodes modified with VGCF and PPy/VGCF nanocomposites prepared with and without ultrasonic irradiation at open circuit potential in 0.5 M H_2SO_4 solution.

Fig. 3 shows the ac impedance results obtained for PPy/VGCF nanocomposite electrodes. Although the shapes of the plots for the nanocomposites were almost similar to each other, the charge transfer resistance of the composite prepared with the irradiation decreased by twice or more compared to that without the irradiation. This can be ascribed to results in the densely packaged polymer coating. Such a low charge transfer resistance is quite effective for fast electrical charge and discharge response of an electrochemical capacitor.

On the other hand, the capacitance of the composite prepared with ultrasonic irradiation (149 F g^{-1}) was higher than that without the irradiation (92.6 F g^{-1}). The capacitance of VGCF itself was 4.9 F g^{-1} and only capacitance current was observed without any peaks attributable to the presence of redox-active species in its cyclic voltammogram (see S3 & Table S1 in ESI†). The redox peak separation in the voltammogram of the composite synthesized with ultrasonic irradiation was narrow compared with that without the irradiation. Thus, the composite prepared with ultrasonic irradiation may be applied to high-performance electrochemical capacitor (see Table S2 in ESI†).

In summary, we have achieved highly-regulated nanocoating of a conducting polymer film on carbon nanofibers using ultrasonic irradiation. This new methodology using ultrasonic treatment has many practical advantages and characteristics: (a) The nanoprecise coating of a uniform polymer layer on nanomaterials; (b) The polymer coating on individual nano-objects; (c) The controlled modification of the outer surface of nanomaterials by varying the irradiation strength. It is hoped that the present methodology will make significant contributions to nanotechnology and open a new aspect of tailoring a nanomaterial surface structure.

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Notes and references

‡ Polypyrrole/VGCF nanocomposites were synthesized by a chemical method in the absence and presence of ultrasonic irradiation. 0.05 g of VGCF (average diameter: 150 nm, length: 10~20 μm) was dispersed in 100 ml of distilled water containing 0.35 mM SDS and 0.745 mM pyrrole, by vigorous stirring. The temperature of the solution was kept constant at 278 ± 0.5 K in a cooling bath. Ultrasonic irradiation was performed with a collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn (13 mm Φ , Branson Sonifier 450D) directly immersed in the solution and operated with an input power of 22.7 W cm^{-2} , unless otherwise stated. The horn was vertically positioned 5.0 cm above the cell bottom. FeCl_3 pre-dissolved in deionized water was added in several portions to the above solution with constant stirring. After 2 h, the resulting PPy/VGCF precipitate was vacuum-filtered and washed thoroughly with distilled water and methanol several times. Finally, it was dried under dynamic vacuum for at least 40 h at room-temperature. The initial weight ratio of PPy/VGCF was always kept at 1/1 or 3/1.

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- Fourier transform infrared (FTIR) spectroscopy was performed using a JASCO FTIR-8100A (Japan) FTIR instrument. A FTIR spectrum of the composite prepared with ultrasonic irradiation showed strong absorbance at 1535 cm^{-1} that is characteristic of the skeletal vibration of the pyrrole ring. Also, a strong band near 1041.7 and 1180.6 cm^{-1} is assigned to the in-plane vibration of the pyrrole ring. This spectrum was similar to that of polypyrrole formed in the absence of ultrasonic irradiation. Therefore, it was confirmed that the chemical structure of polypyrrole was not changed by ultrasonic irradiation.
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