

Preparation of Nitrogen-doped Carbon Nanowire Arrays by Carbonization of Mussel-inspired Polydopamine

Youngseok Oh^{*‡}, Jea Uk Lee^{**‡}, Wonoh Lee^{***†}

ABSTRACT: Based on mussel-inspired polydopamine (PDA), a novel technique to fabricate carbon nanowire (CNW) arrays is presented for a possible use of porous carbon electrode in electrochemical energy storage applications. PDA can give more porosity and nitrogen-doping effect to carbon electrodes, since it has high graphitic carbon yield characteristic and rich amine functionalities. Using such outstanding properties, the applicability of PDA for electrochemical energy storage devices was investigated. To achieve this, the decoration of the CNW arrays on carbon fiber surface was performed to increase the surface area for storage of electrical charge and the chemical active sites. Here, zinc oxide (ZnO) nanowire (NW) arrays were hydrothermally grown on the carbon fiber surface and then, PDA was coated on ZnO NWs. Finally, high temperature annealing was performed to carbonize PDA coating layers. For higher energy density, manganese oxide (MnO_x) nanoparticles (NPs), were deposited on the carbonized PDA NW arrays. The enlarged surface area induced by carbon nanowire arrays led to a 4.7-fold enhancement in areal capacitance compared to that of bare carbon fibers. The capacitance of nanowire-decorated electrodes reached up to 105.7 mF/cm^2 , which is 59 times higher than that of pristine carbon fibers.

Key Words: Polydopamine, Zinc oxide, Carbon nanowire, Carbonization, Nitrogen-doping, Electrochemical capacitance

1. INTRODUCTION

Dopamine mimics the repetitive catechol-amine structure of the 3,4-dihydroxy-L-phenylamine found in the mussel's foot protein, *mytilus edulis*, which has the excellent adhesion with virtually all organic and inorganic surfaces [1-3]. Furthermore, polydopamine (PDA), a polymeric form of dopamine, has high thermal stability and can give high yield of graphitic carbon due to the structural similarity with the phenolic resin [4]. Also, the abundant amount of amine functional groups in PDA can lead nitrogen (N)-doping effect when applying high temperature treatment, so that PDA can give better electrical properties [5]. Therefore, carbonized PDA coating may offer a great potential to fabricate high performance carbon-based electrodes from the simultaneous advantages of graphitic carbon provision and N-doping effect.

The array of zinc oxide (ZnO) nanowires (NWs) has been

extensively employed as promising electricity nano-generators based on the piezo-resistive effect [6]. Owing to the piezo-electric and semiconductor properties, ZnO NWs are suitable for gas sensors, solar cells, light emitting diodes, and energy harvesting materials [7]. Additionally, ZnO NWs can increase the interfacial strength between the fiber and matrix from their rigidity and strong affinity, where they can provide a better mechanism to transfer load from matrix to fiber by effective mechanical interlocking [8,9]. Here, ZnO NWs are used as nano-sized templates for constructing carbon nanowire (CNW) arrays.

Three-dimensionally porous carbon electrodes have received great attention for next-generation energy and a semi-permanent storage device because they can be used as a secondary battery, battery replacement, and supercapacitors with a high charge-discharge efficiency and cycle life characteristics [10]. The mechanism of electrochemical electrodes is generally

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*Composites Research Division, Korea Institute of Materials Science, Changwon 51508, Korea

**C-industry Incubation Research Center, Korea Research Institute of Chemical Technology, Daejeon 34114, Korea

***†School of Mechanical Engineering, Chonnam National University, Gwangju 61186, Korea, Corresponding author (E-mail: wonohlee@jnu.ac.kr)

‡These authors are equally contributed.

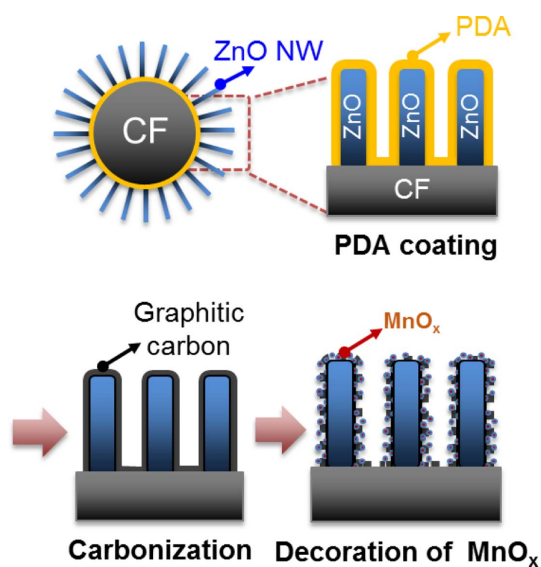


Fig. 1. Schematic illustration to prepare CNW arrays using ZnO NWs and PDA with MnO_x

described with the concept of electrical double layer capacitors (EDLCs) based on the electrostatic movement of the ions at the electrode-electrolyte interface. EDLCs have advantages over batteries such as fast charge/discharge rate (high power density), long life cycles and simple and stable structure. Nevertheless, their low energy density far below that of the secondary batteries is regarded as a main short coming. To overcome such disadvantages, pseudo-capacitors have been designed by including reversible faradaic electrochemical reaction of functionalized materials such as metal oxide and conducting polymer, which can produce large energy density [11].

In this study, we suggest a facile fabrication of porous carbon-nano electrodes, which is consisted of uniform CNW arrays on carbon fibers (CF) serving as an effective large area for storage of electrical charge and the chemical active sites for the pseudo-capacitive reactions. The CNW arrays were achieved by coating carbonized PDA on the hydrothermally grown ZnO NW arrays. In order to obtain higher energy density, MnO_x which is considered to be the most attractive oxide material by adding pseudo-capacitance. Sequential scheme was schematically shown in Fig. 1.

2. EXPERIMENTAL

2.1 Growth of ZnO NWs

For the synthesis of ZnO NW growth, 40 mL of 1 mM of zinc acetate solution (Sigma-Aldrich) was added to 320 mL of ethanol, and 40 mL of 2 mM sodium hydroxide solution was added to 100 mL of ethanol. The solutions were heated separately to 65°C then mixed together under vigorous stirring for 30 min. The ZnO nanoparticle seeds were coated on the carbon fibers by dipping into the solution and then annealing the

fibers at 150°C for 10 min for a total of three times. And then 3.71 g of zinc nitrate hexahydrate (Sigma-Aldrich) and 1.75 g of hexamethylenetetramine (Sigma-Aldrich) were dissolved in 500 mL of distilled (DI) water and heated to 90°C. The fibers were dipped into the beaker containing the growth solution while maintaining the temperature at 90°C for 2.5 h. The fibers were rinsed with DI water to remove precipitates [9].

2.2 Coating and Carbonization of PDA

Before coating PDA, ZnO NW-coated carbon fibers were rinsed with ethanol and fully dried. For the polymerization of dopamine, 100 mg of dopamine hydrochloride (Sigma-Aldrich) was added into a pH 8.5 Tris-buffer solution (10 mM, 100 mL). PDA coating process was performed by dipping the fibers into the solution for 24 h [12,13]. Since the dopamine is self-polymerized under the weak basic condition, the polymerization occurs during the coating time. Finally, the carbonization was performed at 600°C in Ar gas for 2 h.

2.3 Coating of MnO_x NPs

Manganese oxide, which are considered to be the most attractive oxide material owing to high abundance, low cost, and environment-friendliness, was introduced for further increase of electrochemical capacitance [14]. For the MnO_x NPs coating process, potassium permanganate (KMnO_4 , 0.5 M) and sodium sulfate (Na_2SO_4 , 0.5 M) were mixed with equal volume. The fibers were immersed in the solution for 8 h and then the fibers were cleaned several times using DI water.

2.4 Characterization

Chemical structure analysis was studied by the X-ray photoelectron spectroscopy (XPS) analysis using a Theta Probe AR-XPS System (VG ESCALAB MKII spectrometer) equipped with a monochromatic Mg $K\alpha$ ($h\nu = 1486.6$ eV) source at a power of 150 W (15 kV \times 10 mA). The surface morphologies of the coated-fiber were investigated by a scanning electron microscope (SEM, JEOL JSM-5800) observation. A three-electrode cell consists of an Ag/AgCl (3 M KCl) electrode as the reference electrode, a platinum mesh as the counter electrode and the fibers as the working electrode in 0.5 M Na_2SO_4 electrolyte. The electrochemical behaviors were measured with an electrochemical potentiostat (VersaSTAT 3, Princeton Applied Research)

3. RESULTS AND DISCUSSION

First, vertically aligned and ordered ZnO NW were coated on PDA-coated CFs using a hydrothermal method. Since CFs are too stable and inert to be modified in both physical and chemical ways, PDA is pre-coated on the CF surface in order to facilitate the deposition of ZnO seeds. Furthermore, such pre-coated PDA can induce strong interfacial adhesion

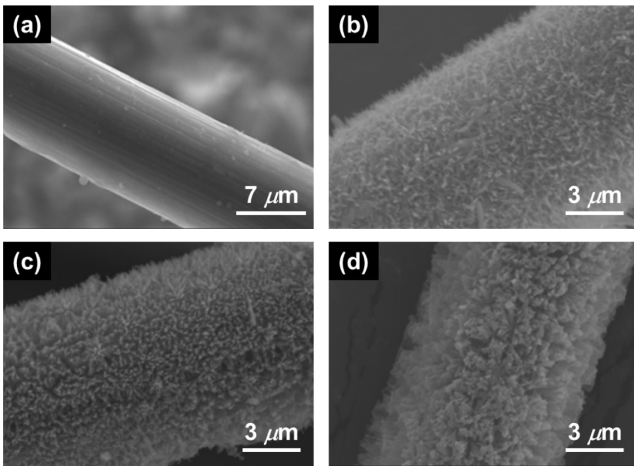


Fig. 2. SEM images of (a) a pure CF, (b) ZnO NWs grown on a CF, (c) CNW by carbonization of PDA, and (d) MnO_x NPs decorated on CNW-coated CF

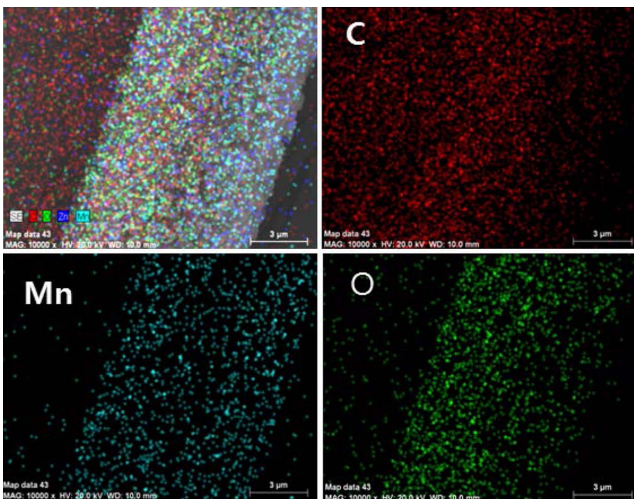


Fig. 3. EDS mapping images of MnO_x NPs-decorated CNW arrays

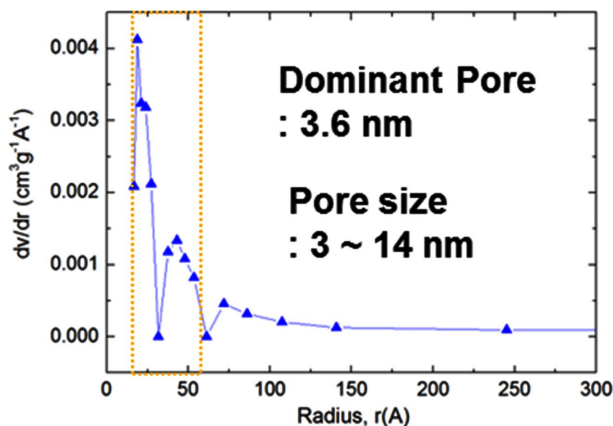


Fig. 4. Pore distribution in CNWs

between ZnO NWs and CF, and therefore prevent ZnO NWs from being detached and exfoliated [13].

The ZnO nanowire arrays serve as templates for generating CNW arrays. The ZnO NWs were grown uniformly on the CF surface (Fig. 2(a)) as shown in Fig. 2(b) with a length of 1.1 μm and a diameter of 50 nm. Fig. 2(c) reveals the morphology of CNW arrays after coating carbonized PDA layers on the ZnO NW arrays. The obtained CNWs have about 80~100 nm in diameter and 1.3~1.5 μm in length. After deposition of MnO_x nanoparticles (NPs), the CNWs became slightly longer in length and larger in diameter (Fig. 2(d)).

Energy-dispersive X-ray spectrometry (EDS) mapping analysis of elements is shown in Fig. 3. Uniformly dispersed blue and green dots along the CNW-coated CF indicates that KMnO₄ and carbonized PDA layers were fully reacted each other, and MnO_x NPs were homogeneously grown on the CNW templates. Therefore, a carbon layer and pseudo-capacitive MnO_x NPs were successfully constructed on the CF.

The specific surface area (SSA) was also measured using the Brunauer-Emmett-Teller (BET) method and we found that SSA increased from 5.0 m²/g to 63.8 m²/g by introducing

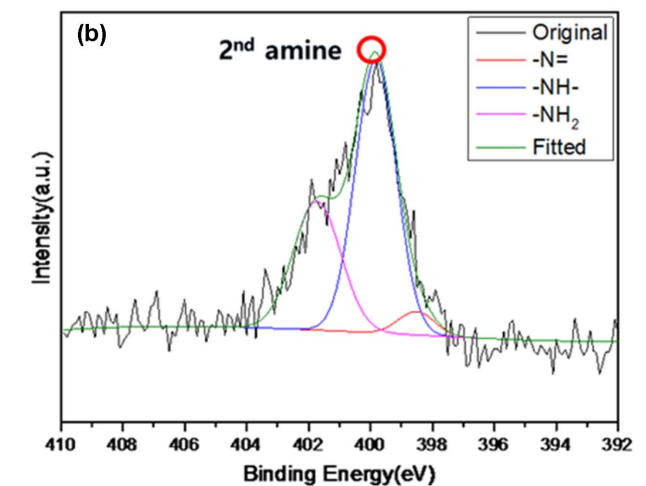
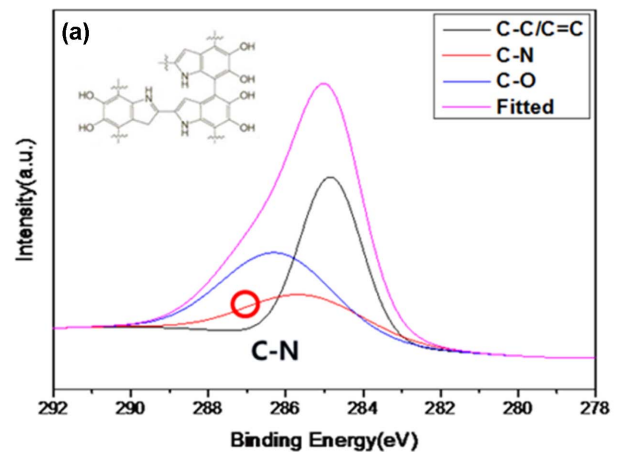


Fig. 5. XPS spectra of PDA-coated NWs before graphitization: (a) C 1s and (b) N 1s

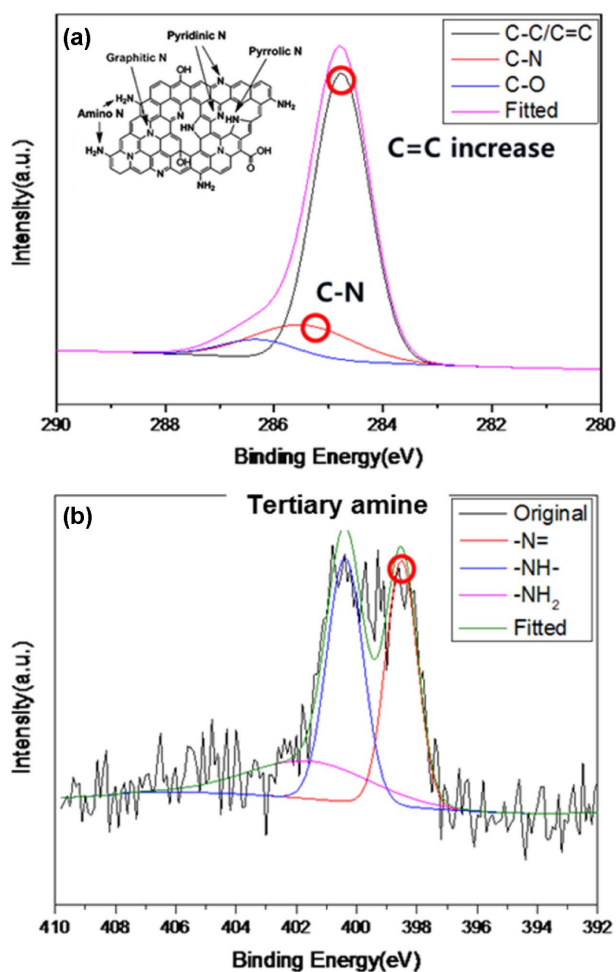


Fig. 6. XPS spectra of PDA-coated NWs after graphitization: (a) C 1s and (b) N 1s

CNWs using PDA graphitization. Also, as shown in Fig. 4, the dominant pore size in CNWs was 3.6 nm and the distribution was 3~14 nm, which represents meso-pores, which are beneficial to high capacitance.

Identification of PDA can be examined by XPS analyses before carbonization treatment as shown in Fig. 5. The existence of a peak of N 1s represents the nitrogen component in PDA. Fig. 5(a) shows three species of C 1s peaks corresponding to C-C/C=C (284.8), C-O (286.2), and C-N (285.5 eV) components, respectively [13]. Such a C-N component is another fingerprint of the PDA coating. In Fig. 5(b), N 1s XPS spectra of PDA-coating were deconvoluted into three peaks with binding energies at 398.5, 399.8, and 401.7 eV corresponding to -N=, -NH-, and -NH₂ components, respectively [13]. The dominant secondary amine peak suggests an indolic structure representing the polymerized dopamine on ZnO NWs. Therefore, it can be confirmed that PDA was successfully coated on ZnO NWs.

The successful graphitization and N-doping can be examined by investigating XPS analyses for after carbonization of

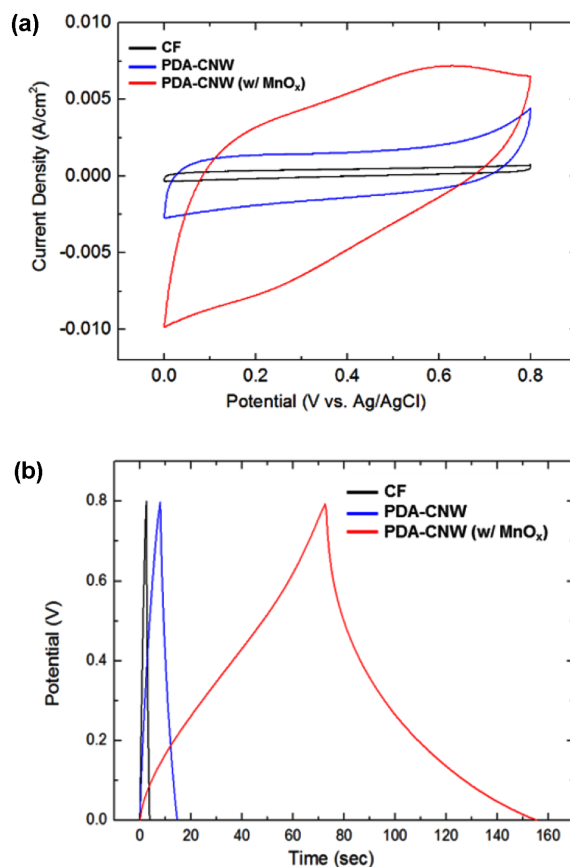


Fig. 7. (a) CV and (b) CCD curves of CFs, PDA-CNW, and MnO_x NPs-decorated PDA-CNW

PDA-coated NW arrays. Fig. 6(a) shows the increase of a C=C component in deconvoluted C 1s peaks, which represents the increase of graphitic carbon species after thermal annealing treatment. Also a C-N component was well observed in the C 1s XPS spectra, which is originated from the chemical structure of PDA. Most interestingly, it can be found that the amount of tertiary amines increased after carbonization process. Such increase indicates pyridinic or graphitic nitrogens in graphitic carbon structures, which was illustrated as an inset in Fig. 6(a). These tertiary amines are originated from rich amine functionalities of PDA and are strong evidence for N-doping in CNW arrays.

Electrochemical measurements were conducted in a three-electrode electrochemical cell with a Pt mesh counter electrode, an Ag/AgCl reference electrode, and a 0.5 M Na₂SO₄ aqueous electrolyte. Fig. 7(a) shows the cyclic voltammetry (CV) curves of pure CFs, PDA-CNW, and MnO_x-decorated PDA-CNW electrodes which were collected at the scan rate of 100 mV/s.

A nearly rectangular shaped curve obtained from a PDA-CNW electrode suggested that CNW arrays worked as active sites for efficient EDLC. Also, the addition of MnO_x NPs exhibited highly increased capacitance induced by the faradaic reaction. The improved electrochemical performance was also

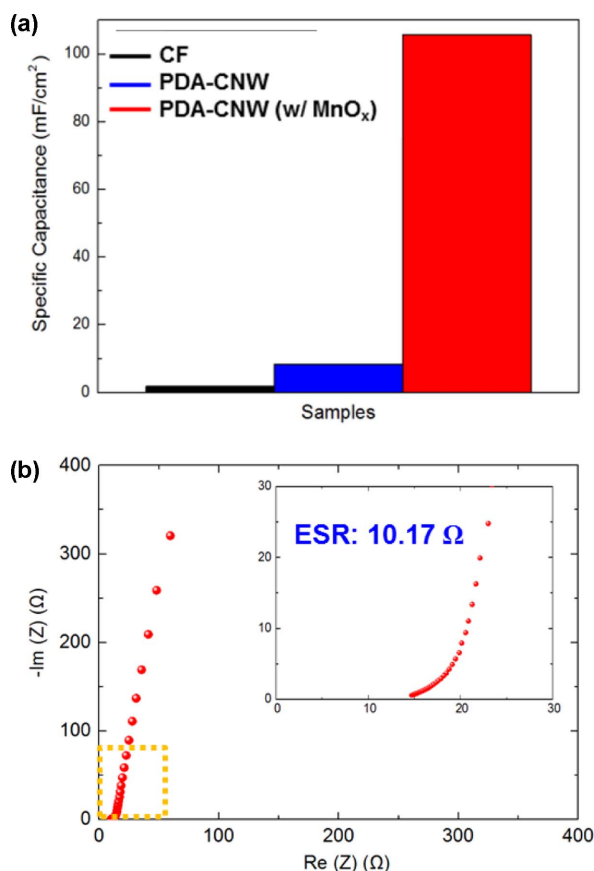


Fig. 8. (a) Comparison of specific capacitance and (b) a Nyquist plot of PDA-CNW electrodes

confirmed by galvanostatic charge-discharge tests performed under different current densities. Fig. 7(b) shows the galvanostatic cyclic charge-discharge (CCD) curves at current density of 1.0 mA/cm². The charge-discharge time for MnO_x-decorated electrodes was remarkably prolonged over PDA-CNW as well as pure CFs.

Fig. 8(a) shows the comparison of specific capacitance values obtained from the galvanostatic CCD curves. The areal capacitance of PDA-CNW achieved 8.4 mF/cm² at a current density of 1.0 mA/cm², which was approximately 4.7 times increased of the areal capacitance compared to that of pure CFs (1.8 mF/cm²). Furthermore, the areal capacitance of MnO_x-decorated PDA-CNW (105.7 mF/cm²) was 59 times higher than that of the PDA-CNW without MnO_x NPs. In the Nyquist plot as shown in Fig. 8(b), the value of equivalent series resistance (ESR) was measured as 10.17 Ω, which is very low compared to conventional carbon-based electrodes. Furthermore, low Warburg impedance in the plot indicates negligible interfacial resistance between CNW electrode surface and electrolyte, and the nearly parallel line to *y*-axis represents good EDLC characteristic of the developed CNW electrodes.

4. CONCLUSIONS

In this study, we presented a novel fabrication of CNW arrays using carbonization of PDA in ZnO NWs and their electrochemical performance for use as electrochemical energy storage applications. The CNW arrays on CFs were successfully constructed by sequential process including ZnO NW growth, PDA coating, and graphitization of PDA. The prepared PDA-CNWs, which have N-doped graphitic carbon layers, were contributed to increase of the surface area, resulting in enhanced EDLC and specific capacitance. And the uniformly coated CNW arrays were effective in increasing the loading of the pseudo-capacitive MnO_x NPs. This PDA-based carbon-nano electrodes offers a great potential for the development of the portable and miniaturized electrochemical energy storage system.

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REFERENCES

1. Waite, J.H., and Tanzer, M.L., "Polyphenolic Substance of Mytilus Edulis: Novel Adhesive Containing L-dopa and Hydroxyproline," *Science*, Vol. 212, No. 4498, 1981, pp. 1038-1040.
2. Lee, H., Scherer, N.F., and Messersmith, P.B., "Single-molecule Mechanics of Mussel Adhesion," *Proceedings of the National Academy of Sciences*, Vol. 103, No. 35, 2006, pp. 12999-13003.
3. Lee, H., Dellatore, S.M., Miller, W.M., and Messersmith, P.B., "Mussel-inspired Surface Chemistry for Multifunctional Coatings," *Science*, Vol. 318, No. 5849, 2007, pp. 426-430.
4. Liu, R., Mahurin, S.M., Li, C., Unocic, R.R., Idrobo, J.C., Gao, H., Pennycook, S.J., and Dai, S., "Dopamine as a Carbon Source: the Controlled Synthesis of Hollow Carbon Spheres and Yolk-structured Carbon Nanocomposites," *Angewandte Chemie International Edition*, Vol. 50, No. 30, 2011, pp. 6799-6802.
5. Ryu, S., Chou, J.B., Lee, K., Lee, D., Hong, S.H., Zhao, R., Lee, H., Kim, S.-G., "Direct Insulation-to-conduction Transformation of Adhesive Catecholamine for Simultaneous Increases of Electrical Conductivity and Mechanical Strength of CNT Fiber," *Advanced Materials*, Vol. 27, No. 21, 2015, pp. 3250-3255.
6. Wang, Z.L., and Song, J., "Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays," *Science*, Vol. 312, No. 5771, 2006, pp. 242-246.
7. Xiao, X., Yuan, L., Zhong, J., Ding, T., Liu, Y., Cai, Z., Rong, Y., Han, H., Zhou, J., and Wang, Z.L., "High-strain Sensors Based on ZnO Nanowire/polystyrene Hybridized Flexible Films," *Advanced Materials*, Vol. 23, No. 45, 2011, pp. 5440-5444.
8. Lin, Y., Ehlert, G.J., and Sodano, H.A., "Increased Interface

- Strength in Carbon Fiber Composites Through a ZnO Nanowire Interphase," *Advanced Functional Materials*, Vol. 19, No. 16, 2009, pp. 2654-2660.
9. Galan, U., Lin, Y., Ehlert, G.J., and Sodano, H.A., "Effect of ZnO Nanowire Morphology on the Interfacial Strength of Nanowire Coated Carbon Fibers," *Composites Science and Technology*, Vol. 71, No. 7, 2011, pp. 946-954.
 10. Simon, P., and Gottsi, Y., "Materials for Electrochemical Capacitors," *Nature Materials*, Vol. 7, No. 11, 2008, pp. 845-854.
 11. Yang, P., Xiao, X., Li, Y., Ding, Y., Qiang, P., Tan, X., Mai, W., Lin, Z., Wu, W., Li, T., Jin, H., Liu, P., Zhou, J., Wong, C.P., and Wang, Z.L., "Hydrogenated ZnO Core-Shell Nanocables for Flexible Supercapacitors and Self-Powered Systems," *ACS Nano*, Vol. 7, No. 3, 2013, pp. 2617-2626.
 12. Lee, W., Lee, J.U., Jung, B.M., Byun, J.-H., Yi, J.-W., Lee, S.-B., Kim, B.-S., "Simultaneous Enhancement of Mechanical, Electrical and Thermal Properties of Graphene Oxide Paper by Embedding Dopamine," *Carbon*, Vol. 65, 2013, pp. 296-304.
 13. Lee, W., Lee, J.U., Byun, J.-H., "Catecholamine Polymers as Surface Modifiers for Enhancing Interfacial Strength of Fiber-reinforced Composites," *Composites Science and Technology*, Vol. 110, 2015, pp. 53-61.
 14. Yu, G., Hu, L., Liu, N., Wang, H., Vosgueritchian, M., Yang, Y., Cui, Y., and Bao, Z., "Enhancing the Supercapacitor Performance of Graphene/MnO₂ Nanostructured Electrodes by Conductive Wrapping," *Nano Letters*, Vol. 11, No. 10, 2011, pp. 4438-4442.