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The goal of this research project is to develop highly conductive graphene composite carbon nanofiber (CNF) webs with an electrical conductivity larger than 1×103 S/cm. In addition, metal-oxide-nanostructures on the surface of CNF webs will also be developed. These highly conductive and surface-modified CNF webs will be utilized for high-performance electrodes of energy storage devices including flexible ones.

15. SUBJECT TERMS

Conductors, Composite Materials, Graphene, nano-fibers

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Final Report of "Graphene-Composite Carbon Nanofiber-Based Electrodes for Energy Storage Devices" (Grant No. FA2386-12-1-4094)

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Department of Organic and Polymeric Materials, Tokyo Institute of Technology

Carbon nanomaterials, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphenes, have attracted a considerable amount of attention in energy conversion and storage fields such as electrodes, conductive additives, and capacitors because of their high surface area, good electrical conductivities, and chemical stability. The goal of this research project is to develop highly conductive graphene composite CNF webs with an electrical conductivity larger than 1000 S/cm. In addition, metal-oxide-nanostructures on the surface of CNF webs were developed. The developed CNF webs were utilized for electrodes of electrochemical supercapacitors.

1. Development of highly conductive graphene composite CNF webs

Graphene, a single-atom-thick sheet of sp^2 bonded carbon atoms, have received considerable interest due to their extraordinary electronic properties. Herein we used graphene nanoribbon (GNR), thin elongated stripes of graphene, as a conductive filler of CNFs. The GNR/carbon composite nanofibers were prepared by electrospinning from poly(acrylonitrile) (PAN) containing graphene oxide nanoribbons (GONRs), and successive twisting and carbonization.The electrospinning process can exert directional shear force coupling with the external electric field to the flow of the spinning solution. During electrospinning, the well-dispersed GONRs were highly oriented along the fiber axis in an electrified thin liquid jet (**Figure 1**). The addition of GONRs at a low weight fraction significantly improved the mechanical properties of the composite nanofibers. In addition, the carbonization of the matrix polymer enhanced not only the mechanical but also the electrical properties of the composites (the more detailed data are included in the attached PDF file). The oriented GONRs contained in the PAN nanofibers effectively functioned as not only the one-dimensional nanofiller but also the nanoplatelet promoter of stabilization and template agent for the carbonization and enhanced the electrical conductivity of the GNR/carbon composite nanofiber webs (up to more than 150 S/cm for apparent surface conductivity of the webs) and yarns (up to more than 500 S/cm). At present, the optimization of graphitization process at higher than 1500 °C are now in progress to improve the electrical conductivity

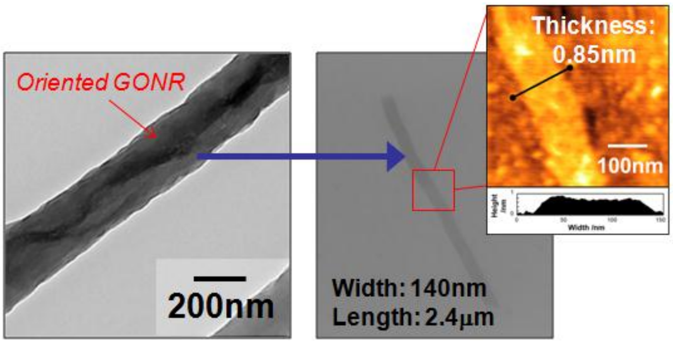

Figure 1 Scanning electron micrograph of the electrospun PAN composite nanofibes containing oriented graphene oxide nanoribbons prepared by unzipping of multi-walled carbon nanotubes.

2. Surface modification of highly conductive CNF webs with metal-oxide nanostructures

We prepared hierarchy-structured CNF webs by electrodeposition of nanostructured manganese oxide (MnO_x) on CNFs. The electrodeposition were conducted in a standard three-electrode cell (CNF webs were used as the substrate of the deposition). The surface of the CNFs was covered with the needle-like MnO_x nanowires (MnO_x NWs) after the deposition (**Figure 2**). The X-ray diffraction analysis also revealed that the nanowires have a γ-MnO_2 crystalline phase.

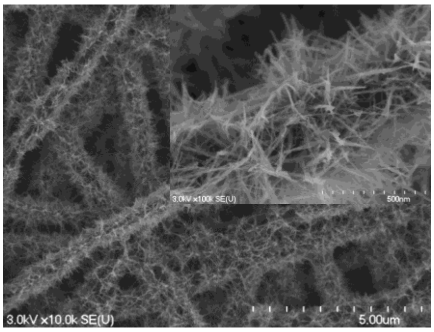

Figure 2 Typical scanning electron micrograph of CNF webs after electrodeposition. (Inset) a micrograph with large magnification.

3. Performance evaluation of energy storage devices with CNF web electrodes

To estimate the potentiality of the developed CNF webs, we fabricated CNF/MnO_2-based electrochemical supercapacitors and evaluated their performance. The capacitance increased with an increase in the amount of MnO_2 NWs (duration of the deposition) (**Figure 3**). This indicates that the hierarchy-structured CNF electrode facilitates the electrochemical reaction at the surface of MnO_2 NWs due to their large surface area and the charge transportation by their CNF network structure.

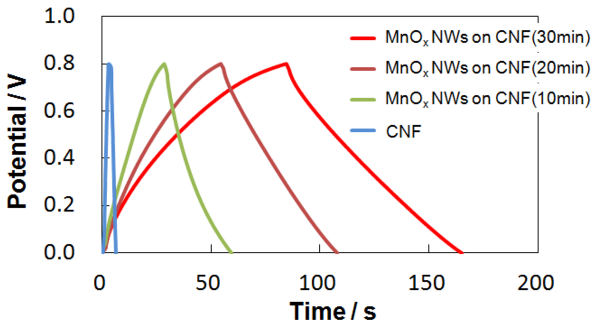

Figure 3 Charge/discharge curves of CNF webs after electrodeposition with various duration.

Researchers

Name	Organization, Division	Title	Degree	Specialty
Hidetoshi Matsumoto	Tokyo Institute of Technology, Graduate School of Science and Engineering	Associate Professor	Dr. Eng.	Nanomaterials Energy Conversion
Akihiko Tanioka	Tokyo Institute of Technology, Graduate School of Science and Engineering	Professor Emirates	Dr. Eng.	Polymer Structure & Property
Mamoru Meguro	Tokyo Institute of Technology, Graduate School of Science and Engineering	Graduate student	B.Eng.	Nanofibers Electrochemistry

Publications

1. “Electrospun composite nanofiber yarns containing oriented graphene nanoribbons” H. Matsumoto*, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka, W. Lu, J. M. Tour
ACS Applied Materials & Interfaces, **5(13)**, 6225-6231, July 2013. (Please see attached PDF file)

Presentations

International

1. “Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons
H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka, W. Lu, J. M. Tour

Electrospinning and Nanofibers: Symposium in Honor of the 85th Birthday of Darrell Reneker, Meeting: 247th ACS National Meeting, Dallas, TX, USA March 16-20, 2014. *Abstract accepted*. (**Oral & Slected Poster at Sci-Mix Interdivisonal Poster Session**)

2. "Preparation of hierarchical structured carbon nanofiber electrodes"
   Y. Saito, M. Meguro, M. Ashizawa, H. Matsumoto
   The 2013 Tsinghua Univ.-Tokyo Tech.-Kunming U. of Sci. & Tech. Workshops on Nanomaterials, Kunming, China, November 14-17, 2013. (**Poster**)

Domestic

1. "Preparation of hierarchical structured carbon nanofibers by electrospinning and electrodeposition"
   H. Matsumoto, Y. Saito, M. Meguro, M. Ashizawa
   51th Symposium on Polymer and Water, Society of Polymer Science, Japan, Tokyo, December 7, 2013. (**Oral**)
2. "Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons"
   H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka,
   2013 The Society of Fiber Science and Technology, Japan Autumn Meeting, Nagoya, Japan, September 5-6, 2013. (**Oral**)
3. "Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons"
   H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka,
   The 4th Annual Meeting of the Nanofiber Society, Tsukuba, July 5, 2013. (**Poster**)
4. "Preparation of hierarchical structured carbon nanofibers by electrospinning and electrodeposition"
   H. Matsumoto, M. Meguro, S. Imaizumi, M. Ashizawa, A. Tanioka,
   The 4th Annual Meeting of the Nanofiber Society, Tsukuba, July 5, 2013 (**Poster**).
5. "Preparation of hierarchical structured carbon nanofiber electrodes"
   H. Matsumoto, M. Meguro, S. Imaizumi, M. Ashizawa, A. Tanioka,
   2013 The Society of Fiber Science and Technology, Japan Annual Meeting, Tokyo June 12-14, 2013. (**Oral**)
6. "Preparation of hierarchical structured carbon nanofiber electrodes"
   M. Meguro, S. Imaizumi, M. Ashizawa, H. Matsumoto, A. Tanioka,
   62nd Society of Polymer Science, Japan Annual Meeting, Kyoto, May 29-31, 2013. (**Poster**)