様　式　Ｃ－１９、Ｆ－１９、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

平成　２８　年　１０　月　１９　日現在

機関番号：　８２１０８
研究種目：　若手研究(B)
研究期間：　2014～2015
課題番号：　２６８２０３２２

研究課題名（和文）Novel 3D Architectures of Carbon-Nitrogen Nanosheets for Energy Conversion

研究課題名（英文）Novel 3D Architectures of Carbon-Nitrogen Nanosheets for Energy Conversion

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交付決定額（研究期間全体）：（直接経費）　　3,100,000円

研究成果の概要（和文）：1. グラフェン3次元構造体を創製する新たな合成メソッドとして、ポリマー前身に基づいたアンモニウム塩補助のケミカル風船法が開発された。このメソッドは収率が高く(16 wt.%)、低コストである(0.25-0.75 US dollar per gram)。 2. このグラフェン3次元構造体を電気二重層キャパシタの電極として、高エネルギー密度を達成した。有機体システムで340 kW/kgの最大出力密度あり、50 Wh/kgのエネルギー密度を実現された。これは他の３Dグラフェン材料より優れています。この他にも、単結晶窒化ホウ素ナノシートはバイオマスに基づいた炭素熱還元法によって創製された。

研究成果の概要（英文）：1. A new synthesis method, i.e. ammonium-assistant chemical blowing based on a polymeric predecessor, was developed to produce 3D graphenes. The method had high yield (16 wt.%) and low cost (0.25-0.75 US dollar per gram).
2. Based on such 3D graphenes as electrodes of supercapacitors, the supercapacitors achieved high the energy density of 50 Wh/kg at the high maximum-power-density of 340 kW/kg in organic system, which is better than other 3D graphene materials in the same system. In addition, single-crystalline boron nitride nanosheets were produced via a biomass-based carbothermal reduction. They were used for highly thermal conductive insulating polymeric composites.

研究分野：　工学

キーワード：　グラフェン　３次元構造体　蓄電器　電気二重層　キャパシタ　ナノシート

１．研究開始当初の背景

Graphene-analogous nanosheets are rising material stars, yet usually-used graphene powders have high contact resistance, weak porosity structure, and low surface area. Three dimensional (3D) designed structures of graphenes are most desired to overcome such drawbacks and to deliver the unique properties of graphene-analogs to the macroscale; however current 3D graphenes suffer from poor electrical conductivity, and the interconnected self-supported reproducible 3D graphenes remain unavailable. This project aims to develop novel 3D structures of carbon-nitrogen nanosheets by effective production, and to study their applications in energy storage and conversion, *e.g.* supercapacitors.

２．研究の目的

This project aimed to develop a new synthesis method to realize the mass production of high-quality nanosheets of boron-carbon-nitrogen system, especially graphenes and 3D graphene bulk materials. The new materials would be applied as the electrodes of supercapacitors to realize high power density and high energy density.

３．研究の方法

The chemical vapor deposition process was used as the main synthesis route, in which the raw materials were heated to high temperature to produce the final graphene and graphene-analogous products. The materials were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), high resolution transmission electron microscope (HRTEM), electron energy loss spectroscopy (EELS) *etc.* The electrochemical workshop and methodology, *e.g.* cyclic voltammetry (CV), electrochemical impedance spectrometry, chronopotentiometry and so on, were applied to characterize the supercapacitors based on synthesized materials.

４．研究成果

The main achievements of this project included the novel synthesis of 3D strutted graphenes, and their applications to high-power high-energy supercapacitors.

(1) This project developed a new general synthesis method, *i.e.* ammonium-assistant chemical blowing, to produce 3D graphenes. The designed route, a facile one-pot heating of a sucrose-ammonium mixture, utilized chemically released NH_3 vapor to appropriately blow molten sugar-derived polymers into large polymeric bubbles. Ultra-thin walls of polymer bubbles were then graphitized into graphene membranes at 1350°C, which were supported by graphitic struts derived from previous polymer struts. This product was named as strutted-graphene, SG (Fig. 1).

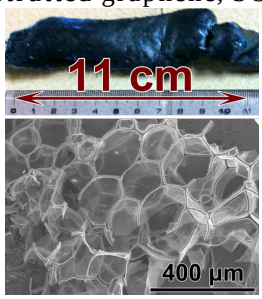

Fig. 1 (up) Photo of SG of *ca.* 100 mg; (down) SEM image of SG.

SG consisted of mono- or few-layered graphitic membranes that were tightly glued, rigidly fixed and spatially scaffolded by micron-scale graphitic struts (Fig. 2-3). Such a topological configuration provided intimate structural inter-connectivities, freeway for electron and phonon transports, huge accessible surface area, as well as robust mechanical properties. The graphene membranes had higher conductivity than the typical reduced graphene oxide. The overall route thus established a new protocol into the family of graphene syntheses, completely different from previous top-down exfoliations and bottom-up graphitizations. It had high yield (16 wt.%) and low cost (0.25-0.75 US dollar *per* gram). The self-supporting SG would open up a bright horizon and enable the “nano” potentials for the large scale applications of graphenes in material discipline.

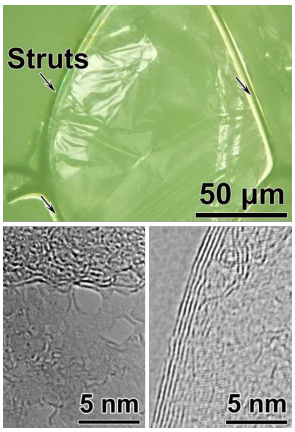

Fig. 2 (up) Optical image of a graphene membrane enclosed by 4 graphitic struts in the SG; (down-left) HRTEM image of a 2-4 layered graphene crossing over a 1-2 layered one with some concave and hole structures attached on the surface; (down-right) HRTEM image of a 5-layered

graphene membrane with the (002) plane spacing of 0.35 nm.

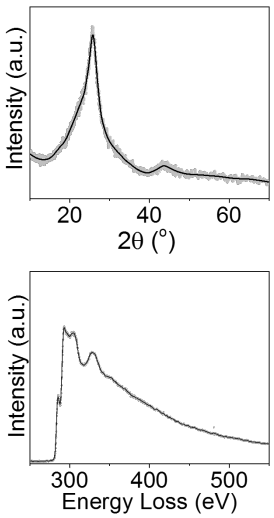

Fig. 3 (up) XRD, and (down) EELS profiles of SG, reflecting the dominant sp^2 hybridization and the high elemental purity.

(2) This project further realized the high energy density and high power density of SG-based supercapacitors. The interconnected networks of strutted graphenes prevented the restacking or agglomeration of graphenes membranes. SG thus fully exposed their huge surfaces and possess appropriate porosity in the large bubble cavities, which further ensured the high capacity and the small internal resistances of SG-based supercapacitors respectively. Their supercapacitors finally achieved the high maximum-power-density (10^6 W/kg), which was much better than previous 3D-graphene-based supercapacitors in electron double layer type in aqueous system. The additive/binder-free SG was also applied as electrodes in organic-system supercapacitors, which realized high energy density of 50 Wh/kg at the high maximum-power-density of 340 kW/kg (Fig. 4-5).

In addition, large quantities of boron nitride (BN) nanosheets were produced by a newly developed biomass-directed carbothermal reduction route. Single-crystalline and morphologically pure BN were obtained with a throughput of 20 gram *per* single production run. In the BN-reinforced polymeric composites, the 40 wt.% epoxy/BN-nanosheet composites demonstrated a 14-fold increase in thermal conductivity, which was envisaged to be particularly valuable for electronic packaging.

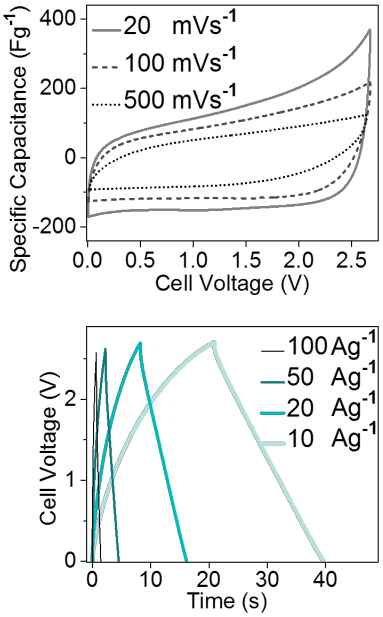

Fig. 4 Performances of SG-based supercapacitors: (up) CV curves under different scan rates; (down) Galvanostatic charging/discharging plots over designed currents.

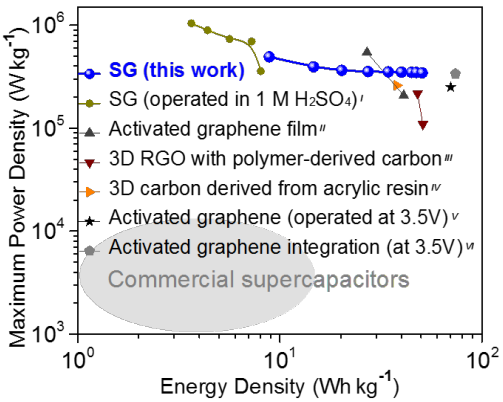

Fig. 5 Ragone plot of SG-based supercapacitors operated at 2.7 V comparing with other 3D graphene organic supercapacitors. *I*-*VI* were extracted from references ①-⑥.

＜引用文献＞

① X.B. Wang, Y.J. Zhang, C.Y. Zhi, X. Wang, D.M. Tang, Y.B. Xu, Q.H. Weng, X.F. Jiang, M. Mitome, D. Golberg, Y. Bando, *Nat. Commun.* 4 (2013) 2905.

② L.L. Zhang, X. Zhao, M.D. Stoller, Y.W. Zhu, H.X. Ji, S. Murali, Y.P. Wu, S. Perales, B. Clevenger, R.S. Ruoff, *Nano Lett.* 12 (2012) 1806-1812.

③ L. Zhang, F. Zhang, X. Yang, G.K. Long, Y.P. Wu, T.F. Zhang, K. Leng, Y. Huang, Y.F. Ma, A. Yu, Y.S. Chen, *Sci. Rep.* 3 (2013) 1408.

④ Y.Y. Li, Z.S. Li, P.K. Shen, *Adv. Mater.* 25 (2013) 2474-2480.

⑤ Y.W. Zhu, S. Murali, M.D. Stoller, K.J.

Ganesh, W.W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, *Science* 332 (2011) 1537-1541.
⑥ T. Kim, G. Jung, S. Yoo, K.S. Suh, R.S. Ruoff, *ACS Nano* 7 (2013) 6899-6905.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 4 件）

① Xiangfen Jiang, Xuebin Wang, Pengcheng Dai, Xia Li, Qunhong Weng, Xi Wang, Daiming Tang, Jie Tang, Yoshio Bando, Dmitri Golberg
High-Throughput Fabrication of Strutted Graphene by Ammonium-Assisted Chemical Blowing for High-Performance Supercapacitors,
Nano Energy, 16, 81, 2015.（査読有）

② Xiangfen Jiang, Qunhong Weng, Xuebin Wang, Xia Li, Jun Zhang, Dmitri Golberg, Yoshio Bando,
Recent Progress on Fabrications and Applications of Boron Nitride Nanomaterials,
Journal of Materials Science and Technology 31, 589, 2015.（査読有）

③ Qunhong Weng, Xi Wang, Xuebin Wang, Chao Zhang, Xiangfen Jiang, Yoshio Bando, Dmitri Golberg,
Supercapacitive Energy Storage Performance of Molybdenum Disulfide Nanosheets Wrapped with Microporous Carbons,
Journal of Materials Chemistry A 3, 3097, 2015.（査読有）

④ Xuebin Wang, Qunhong Weng, Xi Wang, Xia Li, Jun Zhang, Fei Liu, Xiangfen Jiang, Hongxuan Guo, Ningsheng Xu, Dmitri Golberg, Yoshio Bando,
Biomass-Directed Synthesis of 20 g High-Quality Boron Nitride Nanosheets for Thermoconductive Polymeric Composites,
ACS Nano 8, 9081, 2014.（査読有）

〔学会発表〕（計 5 件）

① Xuebin Wang, Xiangfen Jiang, Yoshio Bando, "3D Graphene and BN Nanosheets: Chemical-Blowing Synthesis and Applications for Composite and Energy Storage", Pacifichem 2015 Congress, December 15-20, 2015, Honolulu, Hawaii, USA.

② Xuebin Wang, Xiangfen Jiang, "Three-Dimensional Strutted-Graphene and its Supercapacitors", MRS Spring Meeting & Exhibit, April 6-10, 2015, San Francisco, USA.

③ Xuebin Wang, Xiangfen Jiang, "Syntheses and Composite Applications of Boron Nitride Nanosheets", MRS Spring Meeting & Exhibit, April 6-10, 2015, San Francisco, USA.

④ Xuebin Wang, "3D Graphene and Boron Nitride Nanosheets Grown by Chemical Blowing Route", The 4th Annual World Congress of Nano Science & Technology, October 29-31, 2014, Qingdao, China.

⑤ Xuebin Wang, "Recent Progress in 3D Graphene and Boron Nitride Grown by Novel Chemical Bubbling Route", The 15th IUMRS-International Conference in Asia, August 24-30, 2014, Fukuoka, Japan.

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