様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

平成 ２９ 年　 ６ 月　 ７ 日現在

機関番号：８２１０８
研究種目：若手研究(B)
研究期間：2015～2016
課題番号：１５Ｋ１８２１６
研究課題名（和文）Highly Porous BN-nanomembrane Foam for Water Cleaning and Gas Storage

研究課題名（英文）Highly Porous BN-nanomembrane Foam for Water Cleaning and Gas Storage

研究代表者
蒋　湘芬（JIANG, XIANGFEN）

国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・NIMSポスドク研究員

研究者番号：５０７５０６６８

交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：この研究では、安価なホウ酸原料を使用し、窒化ホウ素の相分離という炭素発泡の手法を駆使し、新しい多孔性窒化ホウ素を合成した。この多孔性窒化ホウ素材料は、1400m2/gという高い表面積を実現した。
この多孔性窒化ホウ素材料は、表面増強ラマン分光法の支持体として機能し、高容量で安定した水浄化用吸着剤および水素吸収が可能な高効率吸着剤として利用されることが期待されている。

研究成果の概要（英文）：1. A new porous boron nitride material is synthesized via using boric acid as a cheap raw material and via the mechanisms of blowing and carbon - boron nitride phase separations. The porous boron nitride material has high specific surface area around 1400 square meter per gram.
2. The porous boron nitride materials are used as good supports in surface enhanced Raman spectroscopy, as high-capacity stable sorbents for water cleaning, and as highly efficient reservoirs for hydrogen absorption.

研究分野：工学

キーワード：無機材料創成　合成プロセス　三次元の多孔性ナノシート

１．研究開始当初の背景

Boron nitride (BN), an isoelectronic structure to carbon, has unique properties and functions sometimes complementary to carbon, *e.g.* high insulation and anti-oxidation properties. Advanced BN nanomaterials were developed in past decades of years, *e.g.* fullerenes in 1990s (Appl. Phys. Lett. 1998, 73, 2441), nanotubes in 1990s (Chem. Commun. 2002, 1290), and nanosheets or white graphenes in 2010s (Adv. Mater. 2011, 23, 4072), along with their carbon counterparts in history. Activated carbon, a functional material widely used today, can easily reach a specific surface area (SSA) of 2000-3000 m^2/g. However, its similar sister system, porous BN material, is still suffering from the low SSA due to the difficulty of controlling binary boron and nitrogen systems. For instance, the BN foam synthesized *via* a chemical blowing method has the SSA of 140 m^2/g, much lower than that of activated carbon (Adv. Mater. 2011, 23, 4072).

２．研究の目的

This project aimed to develop a high-SSA porous BN monolith-like material, and to study its novel applications in pollution detection, water cleaning, as well as hydrogen adsorption.

３．研究の方法

The synthesis routes were carried out using solution-based chemistry and high-temperature annealing. The BN materials were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and Raman spectroscopy. The SSA was measured using nitrogen physisorption system. Hydrogen uptake was tested in hydrogen adsorption system.

４．研究成果

(1) We synthesized a new porous BN-nanomembrane foam with high SSA up to 1400 m^2/g *via* combining the mechanisms of chemical blowing and carbon-BN phase separation.

At the first step, we selected cheap materials of boric acid and polyethylene glycol (PEG) to replace the expensive feedstock such as ammonia borane. The synthesis route is to heat the waxy mixture of boric acid and PEG in a tube furnace at 1000^oC in ammonia atmosphere. The decomposition of PEG blew the system into a foam. At the same time, the newly formed boron nitride was well spread in PEG matrices, because PEG inhibited the in-plane growth of BN. After removing the carbon parts, the porous network of a BN foam was obtained (Fig. 1). The porous BN foam has low cost, but its SSA is 127 m^2/g which is not high enough.

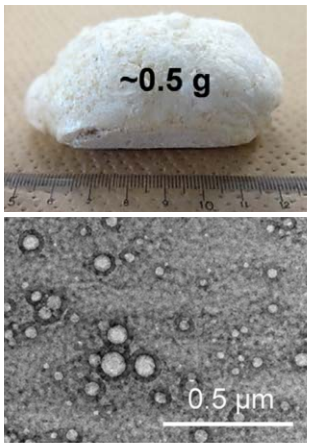

Fig. 1 (top) Photo of porous BN foam synthesized from boric acid and PEG. (bottom) TEM image of the porous structure of the membrane in the BN foam.

To achieve the high SSA of BN, we used another system of formaldehyde solution, dicyandiamide, and boric acid. The raw materials were mixed and reacted into a transparent viscous precursor liquid: boric acid dissolved formaldehyde dicyandiamide resin. When heating the liquid resin at 180^oC, a porous monolith was obtained due to the self-released gas to blow the gradually curing polymers. After pyrolysis at 1100^oC in ammonia atmosphere, the nitridation occurred and carbon was removed. Finally a porous BN monolith was obtained (Fig. 2). The high SSA is achieved up to 1400 m^2/g. Hence, a high-throughput low-cost high-SSA porous BN monolith is realized.

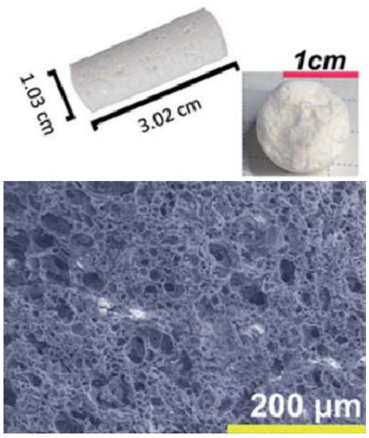

Fig. 2. (top) Photo of the porous BN monolith. (bottom) SEM of porous structures of the BN monolith.

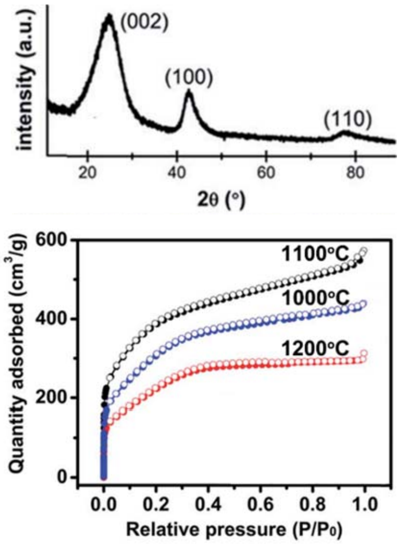

Fig. 3. (top) Representative XRD pattern of the porous BN monolith. (bottom) Nitrogen adsorption-desorption isotherms of the porous BN monolith pyrolyzed at the marked temperatures.

(2) We explored and studied the high-performance applications for water purification and hydrogen storage based on the developed porous BN materials.

Water pollution is a problem for global environments. An in-advance emphasis when treating water is to identify the pollutants. We designed a pollutant capturing surface enhanced Raman spectroscopy (SERS) substrate, namely porous BN decorated with Ag nanoparticles, in which the BN adsorbed and accumulated pollutants while the Ag nanoparticles provided SERS activity. The SERS detection limit is enhanced to be 10^{-9} M to a dye Rhodamine B. Besides, the pores of BN protected the silver particles from aggregation which makes BN/Ag a stable and recyclable SERS substrate.

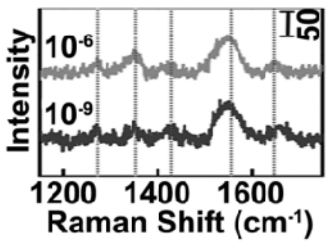

Fig. 4 Raman spectra of the solutions with the same amount of Rhodamine B but at different concentration on our BN/silver substrates.

The 1400 m^2/g porous BN monolith shows spacious hydrophobic surfaces with hierarchical pore structures. It was applied for the highly efficient separation and adsorption purification of oil/water systems. The BN materials demonstrated the excellent adsorption capacity up to 71-98 vol.% toward a wide selection of oil contaminants as well as Rhodamine B. It exhibited stable adsorption performance and reliable recovery by burning oil-saturated matter in air followed by annealing in ammonia atmosphere at 900°C with no damage to its monolithic shape, and no weakening of its adsorption ability over many cycles.

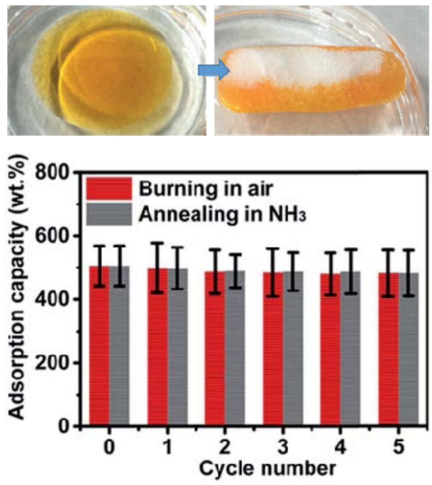

Fig. 5 (top) Photo of the adsorption process of a salad oil in water before and after putting in porous BN monolith. (bottom) Recyclability of the porous BN monolith for oil adsorption.

In addition, we investigated the hydrogen absorption property of the porous BN materials. A decent and reversible hydrogen uptake of 2.14 wt.% at 77 K and 1 MPa was demonstrated due to the high surface area, which is better than that of previous BN nanotubes.

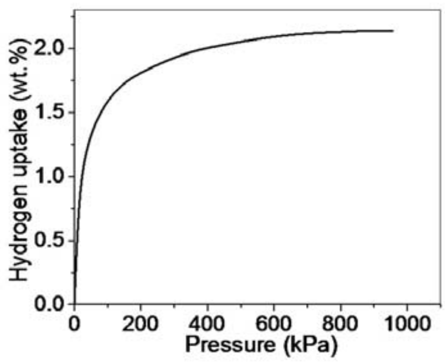

Fig. 6 Hydrogen adsorption isotherms of the porous BN materials recorded at 77 K.

In summary, this project developed a new high-SSA porous BN material using cheap feedstock, and it indicated that the porous BN materials have a great potential for high-end applications in water purification and treatment, as well as in gas adsorption and storage.

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　5　件）

① Yanming Xue, Pengcheng Dai, Xiangfen Jiang, Xuebin Wang, Chao Zhang, Daiming Tang, Qunhong Weng, Xi Wang, Amir Pakdel, Chengchun Tang, Yoshio Bando, Dmitri Golberg
Template-free Synthesis of Boron Nitride Foam-like Porous Monoliths and Their High-end Applications in Water Purification,
J. Mater. Chem. A, 4, 1469, 2016.（査読有）
http://dx.doi.org/10.1039/C5TA08134C

② 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）
http://dx.doi.org/10.1016/j.nanoen.2015.06.008

③ Qunhong Weng, Yusuke Ide, Xuebin Wang, Xi Wang, Chao Zhang, Xiangfen Jiang, Yanming Xue, Pengcheng Dai, Kenji Komaguchi, Yoshio Bando, Dmitri Golberg
Design of BN Porous Sheets with Richly Exposed (002) Plane Edges and Their Application as TiO_2 Visible Light Sensitizer,
Nano Energy, 16, 19-27, 2015.（査読有）
http://dx.doi.org/10.1016/j.nanoen.2015.06.004

④ Pengcheng Dai, Yanming Xue, Xuebin Wang, Qunhong Weng, Chao Zhang, Xiangfen Jiang, Daiming Tang, Xi Wang, Naoyuki Kawamoto, Yusuke Ide, Masanori Mitome, Dmitri Golberg, Yoshio Bando
Pollutant Capturing SERS Substrate: Porous Boron Nitride Microfibers with Uniform Silver Nanoparticle Decoration,
Nanoscale, 7, 18992, 2015.（査読有）
http://dx.doi.org/10.1039/C5NR05625J

⑤ Xiangfen Jiang, Qunhong Weng, Xuebin Wang, Xia Li, Jun Zhang, Dmitri Golberg, Yoshio Bando
Recent Progress on Fabrications and Applications of Boron Nitride Nanomaterials: A Review,
J Mater. Sci. Technol., 31, 589, 2015.（査読有）
http://dx.doi.org/10.1016/j.jmst.2014.12.008

〔学会発表〕（計　1　件）

① Xiangfen Jiang, Xuebin Wang, Dmitri Golberg, Yoshio Bando, Mass Production of 3D Strutted Graphene by Ammonium-assisted Chemical Blowing for High-performance Supercapacitors in Organic Electrolytes, The 2016 International Conference on Advanced Capacitors, May 23-27, 2016, Otsu, Shiga, Japan.

６．研究組織

(1)研究代表者

蒋　湘芬（JIANG, XIANGFEN)
国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・NIMS ポスドク研究員
研究者番号：50750668

(2)連携研究者

板東　義雄（BANDO, YOSHIO)
国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・最高運営責任者
研究者番号：10344433

王　学斌（WANG, XUEBIN)
国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・NIMS ポスドク研究員
研究者番号：20724628

翁　群紅（WENG, QUNHONG)
国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・NIMS ポスドク研究員
研究者番号：70771210