Hydrogen Storage in Carbon and Oxygen Co-Doped Porous Boron Nitrides

Qunhong Weng,* Lula Zeng, Zhiwei Chen, Yuxin Han, Kang Jiang, Yoshio Bando, and Dmitri Golberg*

Fuel cell vehicles powered by hydrogen are particularly attractive and competitive among rapidly developing new energy-driven automobiles. One critical problem for this type of vehicles is the high cost for hydrogen storage due to the lack of efficient and low-pressure hydrogen storage technologies. In the frame of development of hydrogen physisorption-relied materials, attention has mostly been paid to the textural designs of porous materials, including specific surface area, pore volume, and pore size. However, based on the hydrogen physisorption mechanism, hydrogen adsorption energy on a material surface is another key factor with regard to hydrogen uptake capacity. Herein, solid experimental evidences are provided and it is also proven that the chemical states of porous boron nitride (BN) materials remarkably affect their hydrogen adsorption performances. The developed carbon and oxygen co-doped BN microsponges exhibit the hydrogen uptake capacity per specific surface area of 2.5–4.7 times larger than those of undoped BN structures. These results show the importance of chemical state modulations on the future designs of high-performance hydrogen adsorbents based on physisorption approaches.

1. Introduction

Hydrogen provides a form of energy that features pollutant free nature and high energy density. Hydrogen can be massively produced from a variety of resources or by sustainable electrolysis/photo-splitting of water using renewable energies.[1,2] Vehicles powered by H2 fuel cells (FCVs) not only avoid the environmental pollution problems and CO2 emissions caused by fossil fuel consumptions in traditional cars, but also effectively rival the electric vehicles (EVs) that work based on rechargeable lithium ion batteries. On some key performances, FCVs exhibit notable advantages, for example, the refueling time for FCVs is only a few minutes, much quicker than the typical hours needed in EV recharges. Importantly, FCVs are also considered to have better safety.[3,4] However, the present solutions with respect to H2 storage for FCVs mainly rely on the development of high-pressure light H2 containers to achieve high-density storage which themselves create another safety risk for FCVs because of high pressures involved. In addition, such techniques add additional energy cost to refuel H2 and create the needs for high-strength containers. Thus, realizing high-density and low-pressure H2 storage becomes a critical problem for further FCV development and popularization.

Hydrogen can be stored or accumulated in materials by the mechanisms of physisorption, chemisorption, and/or chemical reactions. Compared with chemisorption and chemical reactions, physisorption has numerous peculiar advantages such as quick adsorbing and releasing speeds, excellent reversibility, and high cycling stability, but it usually faces the problems of relatively low uptake capacities.[5] The advantageous features make the design of H2 adsorbents based on the physisorption mechanism very attractive and challenging. It is known that material textural properties, such as specific surface area (SSA), pore volume and H2 adsorption energy, are the critical factors governing the H2 uptake capacity for any physisorption adsorbent.[6] Higher SSA provides more available material surfaces for H2 molecule adsorptions, whereas the larger H2 adsorption energy suggests enhanced H2 adsorption interactions and higher uptake capability for a given surface area.

To date, H2 physisorption-type materials based on metal-organic frameworks (MOFs) and porous carbons[5,7–9] have

DOI: 10.1002/adfm.202007381

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202007381.

Prof. Q. Weng, L. Zeng, Z. Chen, Y. Han, K. Jiang
School of Materials Science and Engineering
Hunan University
Changsha 110016, P. R. China
E-mail: wengqh@hnu.edu.cn
Prof. Y. Bando, Prof. D. Golberg
International Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)
Namiki 1, Tsukuba, Ibaraki 3050044, Japan
E-mail: dmitry.golberg@qut.edu.au
Prof. Y. Bando
Institute of Molecular Plus
Tianjin University
No. 11 Building, No. 92 Weijin Road, Nankai District
Tianjin 300072, P. R. China
Prof. Y. Bando
Australian Institute for Innovative Materials
University of Wollongong
Squires Way, North Wollongong, NSW 2500, Australia
Prof. D. Golberg
Centre for Materials Science and School of Chemistry and Physics
Queensland University of Technology (QUT)
Brisbane, QLD 4000, Australia

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202007381.
widely been reported. Both the structures could reach very high SSAs, but the interactions of H2 molecules and the adsorbing surfaces are fairly weak and need to be further enhanced; the reported H2 adsorption energies for MOFs and C materials are usually lower than 10 kJ mol−1.[10,11] Although being much less explored, porous boron nitrides (BNs) are a type of interesting H2 storage materials which deserve more attentions. First, numerous high-SSA porous BN materials have been developed in recent years.[12–14] For example, the present authors reported the synthesis of porous BN microbelts and BN microsponges with the SSA values of up to 1488 and 1900 m2 g−1, respectively. These porous BN structures showed a reversible H2 storage capacity of up to 2.6 wt% at −196 °C and at a low pressure of 1 MPa.[15,16] Employing a strategy to prepare the porous BN materials with a large excess of N-precursors,[17,18] Wu et al. fabricated BN nanosheets with the SSAs of up to 1900 m2 g−1, which were found to depend on the solvents used to dissolve the precursors.[19] Marchesini et al. developed the porous BN structures using mixed N precursors and boosted the material SSAs to 1924 m2 g−1. They found that the prepared porous BN materials had outstanding CO2 uptake performances.[20] Besides, many other porous BN materials had also been developed and proposed as efficient adsorption materials for various compounds.[21–26] In theory, BN can form stable porous structures with the SSAs of up to 4800 m2 g−1 and enhanced H2 adsorption energy of up to 173 kJ mol−1, suggesting its great potentials in further development of porous BN H2 accumulators.[27,28]

On the other hand, the interactions between BN surface and H2 molecules are readily strong and modulable. Theoretical calculations have predicted quite high adsorption energy of H2 on the BN surfaces, which is 40% higher than those on the carbon analogues. Further chemical modifications of the BN surfaces would enhance their affinities of H2,[29] for example, substituting one B atom by one C atom in BNNTs, or one N atom with a O atom in BN nanosheets, leads to higher adsorption energy for the H2 molecules.[30] Lei et al. experimentally found that 4 at% oxygen doping of BN nanosheets with the SSA of 536 m2 g−1 had boosted the H2 uptake to 5.7 wt% under 5 MPa at room temperature.[31] Theoretical simulations confirmed the higher H2 adsorption energy at the O-dopant sites compared with the solo BN structures because of an enhanced polarization effect.[31–33] Meanwhile, C and O co-doping of BN reported by Kumar et al. using the first principle calculations showed much more efficient adsorption of H2 (adsorption energy = 0.28 eV or 27 kJ mol−1) as compared with the C- (0.16 eV), O- (0.18 eV) and 2C-doped (0.17 eV) counterparts.[34] These progresses suggest a promising route to design efficient H2 adsorbents based on co-doped BN structures.

In this work, we report on the controlled fabrications of porous BN materials with different textural properties and chemical states, and demonstrate the importance of chemical states for their H2 adsorption performances in experiment. We first synthesized the microsponge-like porous BN materials, and systematically investigated the effects of nitrogen-/boron-precursor mole ratios and reaction temperatures on their structural and textural parameters. Various microscopic and spectroscopic techniques, including high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy were employed to analyze the structures of the BN materials. N2 adsorption-desorption isotherms measured at −196 °C were applied for SSA, pore volume, and pore size distribution (PSD) calculations, while H2 adsorption performances were evaluated via recording material H2 sorption isotherms at −196 °C and 0–1 MPa. We found that the H2 uptake capacity of the BN microsponges (BNMSs) does not follow the changing trend of the SSA or total pore volume of the materials, particularly for the samples synthesized at relatively low temperatures of 700–900 °C. Then, chemical compositions and states of the materials were studied by comprehensive elemental analysis, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), verifying unneglectable carbon and oxygen doping in the BN structures synthesized at relatively low temperatures. The H2 uptake capacity per SSA for the co-doped BNMS prepared at 800 °C had reached up to 5.5 × 10−3 wt% g−1, that is, 2.5–4.7 times of those values for undoped BN materials. This work provides a solid experimental evidence of the remarkably enhanced H2 affinities of the C and O co-doped BN surfaces and stresses on the importance of surface chemistry on designing advanced H2 adsorbents for high-density and low-pressure H2 storage.

2. Results and Discussion

The BN microsponges were prepared using the precursors of boric acid (BA) and guanidine carbonate (GC) adducts, which respectively provided boron and nitrogen sources. The synthesized powders show porous structures with the sizes over the micrometer scale (Figure S1 and S2, Supporting Information). The nomination of the BNMS samples follows BNMS-m-T abbreviations in which the m and T represent the GC/BA mole ratio and synthesis temperature, respectively. With the variation of GC/BA mole ratio from 1:1 to 6:1, the structures of the obtained BNMSs change remarkably, as shown in Figure 1. The BNMS-1-1100 sample prepared with the GC/BA ratio of 1:1 and the synthetic temperature of 1100 °C has a uniform TEM contrast under low magnifications; the high-magnification HRTEM image reveals an amorphous structure as shown in Figure 1a. With the increase of the GC/BA ratio the pore structures develop accordingly. Particularly, the pore size becomes too expanded and the pore walls are composed of only a few interconnected ribbon-like BN nanosheets, as seen in the BNMS-3-1100 sample (Figure 1c). This is because the excess GC component in the precursor would finally decompose and leave void structure in the product. With the increase of the GC ratio, meso- and macropores appear in the BNMSs. The pore structures may be over-expanded and lead to the formation of the peculiar interconnected ribbon-like BN nanosheets. Further increasing in the GC/BA ratio to 6:1 results in the formation of nanosphere-like structures (Figure 1d).

We then investigated the effect of reaction temperature on the formation of BNMS structures by setting the GC/BA ratio to 1.5:1. Figure 2 shows the structure evolutions of the samples prepared at temperatures from 700 to 1200 °C. Unlike the change in GC/BA ratio, the BNMS materials obtained under different temperatures have similar morphologies. One noticeable feature is the growth of BN layers with the increase of the temperature; the BN layered structures become much clearer
and the length of the layers becomes much longer, as revealed by the HRTEM images. This indicates the possible presence of rich chemical and structural variations of the BNMSs prepared at relatively low temperatures.

XRD and Raman characterizations were then performed. The broaden and weak (002) and (100) XRD diffraction peaks at $2\theta = 24.01-25.06^\circ$ and $42.60-42.86^\circ$, shown in Figure 3a, confirm the presence of disordered BN phases. The calculated (002) interlayer distance $d_{002}$ is 0.353-0.370 nm, which is clearly larger than that of the crystalline h-BN $d_{002}$, that is 0.333 nm.$^{[35]}$ With an increase in GC/BA ratio the $d_{002}$ value slightly decreases, from 0.362 to 0.353 nm, as derived from the downshifting BN(002) peaks (Figure 3c). However, the $d_{002}$ value reveals a slight increase and then quick shrink with increase in temperature from 700 to 1200 °C (see Figure 3c). Raman spectroscopy was also adopted to evaluate the crystallinity and ordering of the BN structures. The $E_{2g}$ vibration mode of h-BN single crystals is at 1367 cm$^{-1}$ with the FWHM value of 9.1 cm$^{-1}$. With decrease of BN crystalline domain sizes, the $E_{2g}$ mode shifts toward higher frequencies accompanied with the increased FWHM values.$^{[37]}$ Figure 3b shows the $E_{2g}$ peaks of the BNMSs prepared at different GC/BA ratios and temperatures. These are located at 1373–1380 cm$^{-1}$, which are 6–13 cm$^{-1}$ shifting to a higher frequency. The FWHM value ranges from 37 to 72 cm$^{-1}$ (Figure S3, Supporting Information). These results imply the reduction of domain sizes compared with highly crystalline h-BN materials. Furthermore, increase of the GC/BA ratio or the reaction temperatures leads to the overall downshifts of the $E_{2g}$ peaks and reductions of the FWHM values, indicating the improvement of the ordering for the BN phases.

N$_2$ adsorption and desorption isotherms were measured at −196 °C to determine the BET SSAs and other textural properties of BNMS samples, as shown in Figure 4. Based on the IUPAC classification, the recorded isotherms belong to the typical type I and type H4 loops, indicating the presence of micropores and slit-shaped mesopores that cause capillary condensations. For the BNMSs prepared at 1100 °C with the GC/BA ratio changed from 1:1 to 3:1, the BNMS-1.5-1100 displays the highest BET SSA of 1080 m$^2$ g$^{-1}$ and total pore volume of 1.01 cm$^3$ g$^{-1}$ at P/P$_0 = 0.995$ (Figure 4b). The optimal pore size distribution profiles derived from the Quenched Solid Density Functional Theory (QSDFT) indicate the dominated slit-shaped micropores with the width of 0.8–1.0 nm. Larger pores with the sizes of 4.1 and 6.9 nm become more prominent with increase.

Figure 1. HRTEM images of BNMS samples prepared at 1100 °C with different GC/BA ratios. a) 1:1; b) 1.5:1; c) 3:1; d) 6:1. The insets are the illustrative structural models of the synthesized BNMSs. The scale bars of the top- and bottom-row images are 0.2 µm and 5 nm, respectively.

Figure 2. HRTEM images of BNMS samples prepared at different temperatures with a constant GC/BA ratio of 1.5:1. a) 700 °C; b) 800 °C; c) 900 °C; d) 1000 °C; e) 1200 °C. The scale bars of the top- and bottom-row images are 0.2 µm and 5 nm, respectively.
in GC/BA ratio (Figure S4, Supporting Information). The SSAs and total pore volumes of the BNMSs prepared at different reaction temperatures and at the fixed GC/BA ratio of 1.5:1 are summarized in Figure 4d. It is seen that from 700 to 1000 °C, both the SSA and total pore volume evolve a valley at 800 °C, which may be caused by the structural reorganizations led by the reactions between guanidine and BA, and thereafter, pore development. The SSA and total pore volume for BNMS-1.5-800 are 397 m² g⁻¹ and 0.45 cm³ g⁻¹, respectively. When the temperature is over 1000 °C, the SSA and total pore volume decrease along with the rise of synthesis temperatures. This trend is likely caused by an ordering of the BN phase, as also indicated by the XRD and Raman data. The BNMS-1.5-1000 sample shows the highest SSA of 1290 m² g⁻¹ and total pore volume of 1.04 cm³ g⁻¹ among the BNMSs.

H₂ adsorption performances were studied using isothermal adsorption and desorption at −196 °C at a pressure range of 0–1 MPa. As shown in Figure 5a,b, all the materials display totally reversible adsorption-desorption behaviors, which are typical for the H₂ physisorption. Figure 5a illustrates the H₂ excess uptakes of the BNMSs prepared as a function of GC/BA ratio at the constant synthesis temperature, while Figure 5b summarizes the H₂ adsorption-desorption isotherms of the BNMS samples obtained under different synthesis temperatures but at the fixed GC/BA ratio of 1.5:1. Among BNMSs with different GC/BA ratios, the sample prepared at the GC/BA ratio of 1.5:1 has the highest H₂ uptake of 2.11 wt% at a relatively low pressure of 1 MPa, in accordance with the SSA changes of the materials. Surprisingly, the H₂ uptake capacity decreases monotonously (from 2.33 to 2.10 wt% at 1 MPa, or from 1.35 to 1.17 wt% at 0.1 MPa) for the samples synthesized at the temperatures from 700 to 1200 °C and at the optimized GC/BA ratio of 1.5:1. Such a trend doesn’t follow either SSA or total pore volume changes of the materials (Figure 5d and Figure S5, Supporting Information). The detailed H₂ uptake capacities of the BNMSs prepared at different conditions are summarized in Figure 5c. Figure 5d plots the H₂ uptake capacities at 1 and 0.1 MPa versus the SSA values of the materials; it can be seen that the BNMS samples prepared at temperatures over 1000 °C generally keep the linear correlations between the H₂ uptake and SSA values, no matter what the GC/BA ratio is used, while the BNMSs prepared at 700–900 °C deviate remarkably.
from such linear range. The calculated H₂ uptake capacity per SSA for BNMS-1.5-800 reaches 5.5 × 10⁻³ wt% g⁻¹ m⁻², which is 2.5–3.5 times of those values for materials synthesized over 1000 °C, and 3.1–4.7 times of the BNMS samples prepared using BA and dicyandiamide,[16] or 2.7–4.1 times of the reported BN porous microbelts[15] at the same testing conditions, as well as 3.3 times of the porous turbostratic BN materials if compared at 0.1 MPa.[38]

It is known that both textural properties, such as SSA and total pore volume, and H₂ adsorption energy on a material surface play important roles for H₂ physisorption. The higher SSA and H₂ adsorption energy favor boosting H₂ uptakes. Thus, considering the SSAs it is reasonable to attribute the unusual high H₂ uptake capacities of BNMS-1.5-700, BNMS-1.5-800 and BNMS-1.5-900 samples to their higher affinities to H₂ molecules. To understand the chemical structures of these BNMS materials in depth, we then performed detailed bonding and chemical state analysis, including elemental analysis, XPS, IR, etc.

We first performed comprehensive elemental analysis for the BNMS materials. The contents of B, C, N and O were independently determined by different analytical methods (See Experimental Section for details). The results show that the BNMS samples are mainly composed of B and N with the B/N ratios close to the stoichiometric 1:1 value. Carbon contents are at a very low level of ≤0.1 at% for the samples prepared at the temperatures over 1000 °C, which are also qualitatively suggested by the EDX spectra (Figure S6, Supporting Information). But for the BNMSs prepared at 700–900 °C, there are minor C contents, up to 2.2 at%, detected (BNMS-1.5-700) (see Figure 6b and Table S1, Supporting Information, for details). Furthermore, the materials contain a certain amount of oxygen. As seen in Figure 6b, the O content generally tends to decrease along with the rise of synthesis temperatures. The BNMS samples prepared at the lower temperatures have the higher O contents—for example, 10.0 at% for BNMS-1.5-700—likely due to the incomplete reaction between guanidine and BA. It is noted that the O contents in the samples are unavoidably overestimated because of the porosity nature of the materials and the difficulty in complete removals of adsorbed moisture and oxygen. The C and O contents given by XPS analysis are also shown in Figure 6b; both the element contents are obviously overestimated due to the XPS analysis features, but the method still gives the similar carbon and oxygen content changing trends for the BNMS materials prepared at different temperatures.

XPS survey and IR spectroscopic analysis give further structural information on the bonding/chemical states. The results confirm the presence of oxygen in the materials synthesized at different temperatures. The BIs can be fitted by two peaks at the binding energies of 190.6 and 192.0 eV, which should be ascribed to B–N and B–O units in the materials.[39] As for Cls...
peaks, they can be fitted by the main C–C bonding at 284.8 eV and additionally with the presence of clear C–N and C–O components at 288.7 and 286.4 eV (Figure S7, Supporting Information), respectively. It is noted that C–N bonding decreases along with increase in the synthesis temperature. The IR spectra shown in Figure 6d also confirm the existence of B–O and C–N bonds in the products besides the dominated B–N vibration in the BNMS samples prepared at low temperatures.[39–41] These results clearly demonstrate the chemical state deviations of the BNMS samples prepared at 700–900 °C compared with others.

The C and O dopants in the BN structures are considered as the origin of the higher affinity for H₂, as illustrated in Figure 6a. There have been several theoretical works stressing the importance of structural modifications with regard to H₂ adsorption, for example, Jhi et al. used pseudopotential density functional methods to study the adsorption behaviors of H₂ on BN nanotubes with different doping and structural defects. They not only found that the binding energy of H₂ molecule on BNNTs had increased by 40% compared to that on CNTs, but also predicted that the binding energy had remarkably increased by ~50% via substituting one B atom with a C dopant in the BNNTs.[29] Besides, Lei and coworkers performed the first principle calculations and found that oxygen-doping of the BN nanosheets on the N sites favored the H₂ adsorption due to the enhanced H₂ adsorption energies by 20–80% compared with those of pure BN sheets based on different coverage.[31] Similar conclusions were also drawn in other theoretical reports regarding the H₂ adsorption on the O-doped BN nanostructures.[32,33] Furthermore, C and O co-doping of the BN was predicted to have stronger H₂ adsorption energy up to 0.28 eV or 27 kJ mol⁻¹; the value is remarkably higher than those for materials solely doped by C (0.16 eV) and O (0.18 eV) atoms, as calculated by first principle calculations.[34] In the present work, the C and O co-doped BNMS materials have been successfully prepared. These BN structures possess higher H₂ adsorption energies and deliver much enhanced H₂ storage capacity per SSA. From these results, one may conclude that the linear correlations between H₂ uptake capacity and SSA or other textural parameters that observed in porous BNs and many other materials can only be established if the same or close surface chemical states for the materials are given.[42,43]

3. Conclusion

In addition to controllable textural engineering, our work proves the importance of chemical state designs for porous BN structures in H₂ adsorptions. We have synthesized the sponge-like porous BN materials through one-step and template-free reactions between GC and BA under various conditions and systematically studied their structures, textural properties, chemical states and H₂ adsorption performances. The typical carbon and oxygen co-doped BN microsponges prepared at the GC/BA ratio of 1.5:1 and at 800 °C have a relatively modest SSA of 397 m² g⁻¹ but exhibit the H₂ uptake capacity of 2.19 wt% at 1 MPa and −196 °C, which is higher than those of undoped BN samples having notably higher SSAs of up to 1290 m² g⁻¹.
The resultant $\text{H}_2$ uptake capacity per SSA for the BN samples reaches up to $5.5 \times 10^{-3}$ wt% g$^{-2}$, which is 2.5–4.7 times of those figures for the undoped BN structures. These results suggest that the linear correlations between $\text{H}_2$ uptake capacity and SSA observed in porous BNs and many other materials can be only established on the conditions of the same or close surface bonding/chemical states. Our work not only provides solid experimental evidence on the significantly enhanced $\text{H}_2$ affinities of the BN surfaces through C and O co-doping, but also stresses the importance of chemical modifications for future designs of high-performance $\text{H}_2$ adsorbents.

4. Experimental Section

**Synthesis of BN Microsponges:** GC and BA at different ratios were dissolved in hot deionized water. After evaporation of water at $\approx 90$ °C, the solids were precipitated and collected. Then, the prepared GC-BA powders were loaded into a tube furnace and calcined at NH$\text{}_3$ flows at preset temperatures for 3 h with a heating rate of 10 °C min$^{-1}$. Different calcination temperatures, from 700 to 1200 °C, were used for the synthesis of the BN materials.

**Structure and Composition Characterization:** The morphology and structure observations were carried out by using a Hitachi S-4800 SEM and JEM-3000F HRTEM operated at 300 kV. XRD data were collected on a Rigaku Ultima III (Cu Kα); Raman data were recorded on a Horiba Scientific LabRAM HR Evolution with a 514.5 nm excitation laser; XPS spectra were taken on an EscaLab Xi+ (ThermoFischer) using pollutant C for binding energy calibrations (C1s = 284.80 eV); infrared spectroscopies were performed on a Bruker Vertex 70 FTIR spectrophotometer.

For the comprehensive elemental analysis, different elements were measured independently. The content of boron (B) was determined by ICP-OES method (IRIS advantage, Nippon Jarrell-Ash Co.). Carbon (C) content was measured on a carbon/sulfur determinator (CS-444LS, LECO Co.), based on an infrared absorption (IRA) method after induction combustion and using CaCO$_3$ as the standard substance, while nitrogen (N) and oxygen (O) contents were measured by an oxygen/nitrogen determinator (TC-436AR, LECO Co.) using Si$_3$N$_4$ and Y$_2$O$_3$ as the N and O standard substances, respectively. The N contents were determined based on the thermal conductivity changes, and O contents were measured based on the IRA after fusion the samples under He gas.

SSA Measurements and $\text{H}_2$ Uptake Capacity Evaluations: N$_2$ adsorption-desorption isotherms were recorded at $-196$ °C on a Quantachrome Autosorb iQ analyzer after outgassing of samples at 150 °C for 12 h. SSAAs were calculated by the Brunauer-Emmett-Teller (BET) equation. The pore size distributions were calculated based on the QSDFT theory. The hydrogen uptake performances were evaluated by measuring their adsorption and desorption isotherms on a Belsorp-HP-30 system (BEL Japan, Inc.) at $-196$ °C and 0–1 MPa. Before the measurements, all samples were outgassed at 150 °C for 12 h.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (NSFC; no. 21903021), the Innovation Platform and Talent Plan of Hunan Province (2019RS1027), and the Fundamental Research Funds for the Central Universities.

Figure 6. a) Schematic illustration of the enhanced $\text{H}_2$ affinity on C- and O-co-doped BN surface. b) Plots of carbon and oxygen contents in the BNMS samples prepared at different temperatures. Carbon and oxygen contents were derived from XPS analysis or determined independently by an infrared absorption (IRA) method after induction combustion or fusion under inert gas (see Experimental Section for details). c) XPS B1s surveys and d) IR spectra of the samples prepared at the GC/BA ratio of 1.5 and at different temperatures.
for the Central Universities ( Hunan University: 531119200114). D.G. is grateful to the Australian Research Council (ARC) for granting a Laureate Fellowship, No. FL160100089.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
boron nitride, doping, hydrogen storage, porous

Received: August 29, 2020
Revised: September 30, 2020
Published online: October 16, 2020

[1] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Norskov, T. F. Jaramillo, Science 2017, 355, eaad4998.
[2] D. Yan, Y. Li, J. Huo, R. Chen, L. Dai, S. Wang, Adv. Mater. 2017, 29, 1606459.
[3] Z. P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. W. Chen, Nat. Energy 2018, 3, 279.
[4] I. Staffell, D. Scamman, A. V. Abad, P. Balcombe, P. E. Dodds, P. Ekins, N. Shah, K. R. Ward, Energy Environ. Sci. 2019, 12, 463.
[5] T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen, Nat. Rev. Mater. 2016, 1, 16059.
[6] F. Zhang, P. C. Zhao, M. Niu, J. Maddy, Int. J. Hydrg. Energy 2016, 41, 14535.
[7] S. Li, Q. Xu, Energy Environ. Sci. 2013, 6, 1656.
[8] M. P. Suh, J. P. Hye, T. K. Prasad, D. W. Lim, Chem. Rev. 2012, 112, 782.
[9] Y. D. Xia, Z. X. Yang, Y. Q. Zhu, J. Mater. Chem. A 2013, 1, 9365.
[10] L. J. Murray, M. Dinc, J. R. Long, Chem. Soc. Rev. 2009, 38, 1294.
[11] G. Yushin, R. Dash, J. Jagiello, J. E. Fischer, Y. Gogotsi, Adv. Funct. Mater. 2006, 16, 2288.
[12] Q. H. Weng, X. Wang, X. Wang, Y. Bando, D. Golberg, Chem. Soc. Rev. 2016, 45, 3959.
[13] J. Xiong, J. Ji, W. S. Zhu, H. M. Li, J. Energy Chem. 2020, 40, 99.
[14] R. Han, F. Liu, X. Wang, M. Huang, W. Li, Y. Yamauchi, X. Sun, Z. Huang, J. Mater. Chem. A 2020, 8, 14834.
[15] Q. H. Weng, X. B. Wang, C. Y. Zhi, Y. Bando, D. Golberg, ACS Nano 2013, 7, 1558.
[16] Q. H. Weng, X. Wang, Y. Bando, D. Golberg, Adv. Energy Mater. 2014, 4, 1301525.
[17] A. Nag, K. Raidongia, K. P. S. S. Hembram, R. Datta, U. V. Waghmare, C. N. R. Rao, ACS Nano 2010, 4, 1539.
[18] W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, Nat. Commun. 2013, 4, 1777.
[19] P. Wu, W. Zhu, Y. Chao, J. Zhang, P. Zhang, H. Zhu, C. Li, Z. Chen, H. S. Dai, Chem. Commun. 2016, 52, 144.
[20] S. Marchesini, C. M. McGilvery, J. Bailey, C. Petit, ACS Nano 2017, 11, 10003.
[21] H. Jiang, L. Ma, Q. Yang, Z. Tang, X. Song, H. Zeng, C. Zhi, Solid State Commun. 2019, 294, 1.
[22] F. Liu, S. Li, D. Yu, Y. Su, N. Shao, Z. Zhang, ACS Sustainable Chem. Eng. 2018, 6, 16011.
[23] R. Shankar, M. Sachs, L. Franças, D. Lubert-Perquel, G. Kerherve, A. Regoutz, C. Petit, J. Mater. Chem. A 2019, 7, 23931.
[24] M. Wang, Y. Bai, B. Zhang, B. Zhong, Y. Yu, J. Zhang, X. Huang, G. Wen, Ceram. Int. 2019, 45, 6684.
[25] J. Wang, K. Ai, L. Ju, J. Mater. Chem. A 2019, 7, 16850.
[26] J. Liang, Q. Song, J. Lin, Y. Huang, Y. Fang, C. Yu, X. Xue, Z. Liu, C. Tang, Chem. Eng. J. 2019, 373, 616.
[27] J. Dai, X. Wu, J. Yang, X. C. Zeng, J. Phys. Chem. Lett. 2014, 5, 393.
[28] J. Dai, X. Wu, J. Yang, X. C. Zeng, J. Phys. Chem. Lett. 2013, 4, 3484.
[29] S. H. Jhi, Y. K. Kwon, Phys. Rev. B 2004, 69, 245407.
[30] A. Lale, S. Bernard, U. B. Demirci, ChemPlusChem 2018, 83, 893.
[31] W. Lei, H. Zhang, Y. Wu, B. Zhang, D. Liu, S. Qin, Z. Liu, Y. Ma, Y. Chen, Nano Energy 2014, 6, 219.
[32] A. Tokarev, E. Kjeang, M. Cannon, D. Bessabarov, Int. J. Hydrogen Energy 2016, 41, 16984.
[33] F. Shayanfar, R. Shahsavari, Langmuir 2016, 32, 13313.
[34] E. M. Kumar, S. Sinthika, R. Thapa, J. Mater. Chem. 2015, 3, 304.
[35] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. C. Tang, C. Y. Zhi, ACS Nano 2010, 4, 2979.
[36] Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, Science 2007, 317, 932.
[37] R. J. Nemanich, S. A Solin, R. M. Martin, Phys. Rev. B 1981, 23, 6348.
[38] J. Kim, J. Han, M. Seo, S. Kang, D. Kim, J. Ihm, J. Mater. Chem. A 2013, 1, 1014.
[39] Q. Weng, D. G. Kvashnin, X. Wang, O. Cretu, Y. Yang, M. Zhou, C. Zhang, D. M. Tang, P. B. Sorokin, Y. Bando, D. Golberg, Adv. Mater. 2017, 29, 1700695.
[40] Q. Weng, Y. Ide, X. Wang, X. Wang, C. Zhang, X. Jiang, Y. Xue, P. Dai, K. Komaguchi, Y. Bando, D. Golberg, Nano Energy 2015, 16, 19.
[41] G. Feng, M. Guan, Q. Lai, H. Mi, G. Li, Q. Ma, Q. Fei, Y. Huan, Z. Song, New J. Chem. 2016, 40, 8444.
[42] Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J. E. Fischer, J. Am. Chem. Soc. 2005, 127, 16006.
[43] G. Yushin, R. Dash, J. Jagiello, J. E. Fischer, Y. Gogotsi, Adv. Funct. Mater. 2006, 16, 2288.