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RAPID COMMUNICATION

Oxygen-doped boron nitride nanosheets with excellent performance in hydrogen storage

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Abstract
Hydrogen is considered one of the best energy sources. However, the lack of effective, stable, and safe storage materials has severely prevented its practical application. Strong effort has been made to try new nanostructured materials as new storage materials. In this study, oxygen-doped boron nitride (BN) nanosheets with 2–6 atomic layers, synthesized by a facile sol–gel method, show a storage capacity of 5.7 wt% under 5 MPa at room temperature, which is the highest hydrogen storage ever reported for any BN materials. Importantly, 89% of the stored hydrogen can be released when the hydrogen pressure is reduced to ambient conditions. Furthermore, the BN nanosheets exhibit an excellent storage cycling stability due to the stable two-dimensional nanostructure. The first principles calculations reveal that the high hydrogen storage mainly origins from the oxygen-doping of the BN nanosheets with increased adsorption energies of H_2 on BN by 20–80% over pure BN sheets at the different coverage.

Introduction

Two-dimensional (2D) nanomaterials are the most exciting nanomaterials since the discovery of graphene, because of many excellent quantum transport and mechanical properties [1]. Few-layered boron nitride (BN), an analog to

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graphene, is considered complementary to graphene for better heat but poor electron transport in 2D structures and many novel physical and mechanical properties [2], which cannot be observed in the highly conductive graphene. BN nanosheets have been synthesized by micro-mechanical cleavage [3], ultrasonication [4], high-energy electron beam irradiation of BN particles [5], wet ball milling [6], and chemical vapor deposition (CVD) [2b,7]. Among them, chemical processes seem to have some advantages in tuning their chemical composition and morphology [8]. On the other hand, low production quantity and/or the use of catalysts have made the testing of certain properties and potential applications difficult. Therefore, catalyst-free chemical processes for large-scale production of BN nanosheets have significant importance for any future application.

Hydrogen has been considered one of the most promising energy fuels for automobiles because it is a clean and environmental friendly energy with nearly zero emission of pollutants [9]. However, effective hydrogen storage is one of the biggest challenges which blocks the full utilization of hydrogen energy. Due to their good chemical and thermal stabilities, as well as low mass density, BN nanostructures including multiwall nanotubes [10], bamboo nanotubes [11], flower-like nanostructures [12], nanofibers [13], hollow spheres [14], and collapsed nanotubes [15], have been intensively studied and promoted as promising hydrogen storage materials. However, the most absorbed H_2 is found to be retained after removing the hydrogen pressure. More recently, porous BN microbelts show interesting hydrogen uptake [16]. Theoretical calculations have also been performed to investigate hydrogen adsorption on BN nanotstructures [17]. Recently, graphene has attracted a great deal of interest as a promising hydrogen storage medium due to its high specific surface and 2D structure [18]. Therefore, the combined advantages of the good chemical and thermal stability, light mass density as well as 2D structure make of the BN nanosheets are highly preferred for hydrogen absorbent materials.

Here, we report on the synthesis of oxygen-doped BN nanosheets via a sol–gel method, which has the advantages of a simple, catalyst-free and large-scale process. The as-grown BN nanosheets have 2–6 atomic layers and, more importantly, exhibit excellent performance and cycling stability in hydrogen storage. To better understand the absorption mechanisms on the BN nanosheets, first-principles calculations have been performed on the interaction of H_2 with BN nanosheets. The obtained results suggest that the unique 2D morphology of nanosheets and oxygen doping lead to the high hydrogen storage.

Experimental

Preparation of BN nanosheets

In a typical synthesis of few-layer BN nanosheets, B_2O_3 (0.28 g, Alfa-Aesar Chemical Co.) was dissolved in methanol (2 mL) at room temperature with fast stirring to form a clear, colorless solution, then solid urea (1.2 g, Alfa-Aesar Chemical Co.) was added into the solution. After 24 h of fast stirring, a white crystalline powder (a complex between the boron and the urea precursors) is formed. The resulting powders were put into a boat and then calcined at 5 °C/min to 1100 °C in a furnace under nitrogen/hydrogen (hydrogen: 5 vol%) flow for 1 h. The use of hydrogen gas can promote the nitriding reaction leading to faster nitridation of boron due to the more activity of hydrogen than nitrogen [19]. Finally, white oxygen doped BN nanosheets were produced with a yield of 70 mol% versus boron precursor.

Characterization

XRD measurements were carried out on a Panalytical X'Pert PRO diffraction system using Cu Kα radiation. TEM was performed on a JEOL 2100 (operating at 110 kV). HRTEM was carried out on a JEOL JEM-2200FS instrument working at 200 kV. AFM measurements were performed on a cypher atomic force microscope. XPS was performed using a Thermo Scientific K-Alpha ESCA instrument equipped with Al Kα monochromatized radiation at 1486.6 eV X-ray source. Nitrogen sorption isotherms were obtained using a Quadrasorb apparatus at 78 K. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

Hydrogen adsorption measurements

The hydrogen adsorption studies of the samples, with a typical amount of around 150 mg, were conducted in a conventional Sieverts-type apparatus (Suzuki, PCT-1SPWIN, Japan). Before measuring the hydrogen storage properties of the BN nanosheets, the samples were activated under vacuum at 350 °C for 10 h. The hydrogen adsorption rate measurements were performed at room temperature with a pressure of 5 MPa.

First-principle calculations

The calculations were performed with the Vienna Ab Initio simulation package (VASP) [20]. Projector-augmented-wave (PAW) potentials [21] were used to account electron–ion interactions, while the electron exchange correlation interactions were treated using the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [22]. To remove spurious interactions between neighboring structures due to periodic calculations, a vacuum layer of no less than 12 Å was taken in each nonperiodic direction. The energy cutoff was set to 400 eV and a Monkhorst–Pack scheme was used to sample the first Brillouin zone [23]. The adsorption energy calculated with energy cutoff of 500 eV changes less than 3 meV compared to that with 400 eV. Consequently, adsorption energy has converged with the energy cutoff of 400 eV. A spin-polarized calculation was used when necessary. The structures were full optimized with both the lattice vectors and atom coordinates with the criteria that the maximum force on each atom is less than 0.01 eV/Å. The Grimme parameterized DFT-D2 approach [24] was used to correct the van der Waals interaction between H_2 and BN layer. Quantitative desorption energies can be attained by high accuracy methods [25]. However, the purpose here is to better understand the hydrogen storage mechanism of BN nanosheets but not to obtain high accurate adsorption energy. As a result, the possible small error of adsorption