



Full Length Article

Catalytically-etched hexagonal boron nitride flakes and their surface activity

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ABSTRACT

Hexagonal boron nitride (h-BN) is a ceramic compound which is thermally stable up to 1000 °C in air. Due to this, it is a very challenging task to etch h-BN under air atmosphere at low temperature. In this study, we report that h-BN flakes can be easily etched by oxidation at 350 °C under air atmosphere in the presence of transition metal (TM) oxide. After selecting Co, Cu, and Zn elements as TM precursors, we simply oxidized h-BN sheets impregnated with the TM precursors at 350 °C in air. As a result, microscopic analysis revealed that an etched structure was created on the surface of h-BN flakes regardless of catalyst type. And, X-ray diffraction patterns indicated that the air oxidation led to the formation of Co₃O₄, CuO, and ZnO from each precursor. Thermogravimetric analysis showed a gradual weight loss in the temperature range where the weight of h-BN flakes increased by air oxidation. As a result of etching, pore volume and pore area of h-BN flakes were increased after catalytic oxidation in all cases. In addition, the surface of h-BN flakes became highly active when the h-BN samples were etched by Co₃O₄ and CuO catalysts. Based on these results, we report that h-BN flakes can be easily oxidized in the presence of a catalyst, resulting in an etched structure in the layered structure.

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1. Introduction

Boron nitride (BN) is a ceramic material which has a high thermal stability and exists in diverse crystal structures such as hexagonal, sphalerite, and wurtzite structures [1,2]. Among them, hexagonal BN (h-BN) has attracted an attention as 2-dimensional (2-D) material due to its unique layered structure similar to graphite. The exfoliation of graphene from graphite [3] stimulated a study on 2-D layered materials such as h-BN [4–6] as well as MoS₂ [7–10], WS₂ [11–14] and WSe₂ [15–18]. And, h-BN also has a honeycomb lattice structure where B and N are arranged in an orderly way like MoS₂, WS₂, and WSe₂. These 2-D layered materials commonly have good thermal resistivity because of their high melting point. In general, BN has been known to melt at 2973 °C while the melting point of MoS₂, WS₂, and WSe₂ is around 1200 °C.

Due to these properties, it is difficult to modify the structure of those layered materials below 1000 °C under air atmosphere.

Etching is one of the ways to modify the structure or characteristics of a material for further application purpose. Recently, 2-D layered materials attracted an intensive interest, and diverse efforts have been made to etch the layered materials. Among them, extensive research was performed to investigate a way of etching graphene which has relatively a low thermal stability to be oxidized in air below 500 °C. Graphene was successfully etched by He ion beam [19], gas phase chemical approach using O₂ [20], and H₂ plasma [21]. Also, there was a study on etching graphene using catalytic reaction at 900 °C under H₂ atmosphere [22]. Even, MoS₂, which is thermally more stable than graphene, was etched by SF₆ + N₂ plasmas [23], cyclic process using chlorine radical and Ar ion-beam [24], and a chemical reaction by XeF₂ gas [25]. Furthermore, it was reported that WS₂ can be controllably etched by the treatment using an etchant [26].

Modifying the structure of BN is still challenging and significant work since BN has the highest melting point among the layered materials mentioned above. Nevertheless, several works reported successful results on etching BN. Plasma etching was

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used to achieve mono- or few-layers h-BN [27], or to fabricate BN nanoribbon from BN nanotube [28]. Also, it was reported that the exposure of h-BN on Ru at 700 °C under H₂ atmosphere led to an etched structure in h-BN [29]. However, these methods were conducted in a tiny sample of h-BN, or under flammable gas such as H₂ at high temperature. This stimulated us to etch h-BN under mild experimental conditions for mass-production of etched h-BN. Up to now, few efforts have been made to etch 2-D h-BN flakes at low temperature under air atmosphere. Considering that h-BN is thermally stable up to 2973 °C, it is significant work to etch h-BN flakes in air at low temperature. In addition, a method for etching in quantity is preferred to a technique treating a few flakes of h-BN.

In this study, we demonstrate an easy method to create an etched structure in h-BN layers at low temperature by using catalytic oxidation. The main idea of this work is to partially oxidize the surface of h-BN flakes in the presence of a catalyst at low temperature where h-BN has been known to be hardly oxidized. The oxidation finally generates an etched structure like a pit in the layered structure of h-BN. As a catalyst source, we chose Co, Cu, and Zn elements which exist in the form of nitrate complex. By impregnation method, the precursors of transition metal (TM) nitrate complex were deposited in h-BN powder, and the samples were oxidized at 350 °C for 2 hr in air. During the heat treatment, the precursors were decomposed into transition metal oxide (TMO) nanoparticles (NPs) in h-BN sheets and the formed NPs worked as a catalyst for the oxidation to create multivacancy in h-BN sheets. Especially, the multivacancy led to an etched structure like a pit in layered h-BN sheets with enhanced pore volume and pore area. Also, it was revealed that the etched surface by TMO was highly active due to the vacancies.

Till now, h-BN has been considered as a material which is not affected by air oxidation up to 1000 °C. In this work, we highlight that in the presence of a catalyst, h-BN can be easily etched below 1000 °C by losing its superior thermal stability, resulting in an active surface. Our method is very simple and proper to mass-production under atmospheric conditions. We think that etched h-BN flakes can be used in diverse fields such as energy storage, catalyst, gas adsorption, and water cleaning.

2. Experimental

2.1. Etched h-BN by catalytic oxidation

A powder sample of h-BN (purity: 98%) was shipped from Sigma-Aldrich and used as received. As precursors of TMOs, Co(NO₃)₂·6H₂O (Sigma-Aldrich, 98%), Zn(NO₃)₂·6H₂O (Sigma-Aldrich, 98%), and Cu(NO₃)₂·3H₂O (Sigma-Aldrich, 98%) were used. 0.06 g of each precursor was dissolved in 100 ml of ethanol, separately. Then, 0.2 g of h-BN powder was dispersed in each solution containing the precursor by sonication for 15 min. To obtain precursor-impregnated h-BN, the mixtures were heated under stirring at 80 °C till the ethanol was totally evaporated. After grinding to a fine powder, each sample was heated at 350 °C for 2 h under air atmosphere.

2.2. Characterization

Atomic force microscopy (AFM, Parks Systems, Park XE100) analysis was used to observe an etched structure created in h-BN layers. X-ray diffraction (XRD, Rigaku, Ultima4) analysis was conducted in order to confirm the crystal structure of TMOs. Thermogravimetric analysis (TGA, TA Instruments, Q500) was performed in the range from room temperature to 800 °C at a rate of 10 °C/min. By using Micromeritics ASAP 2020, N₂ adsorption-desorption measurement was performed at 77 K to examine pore

volume and area of h-BN powder. Barrett-Joyner-Halenda method was used to obtain pore volume and pore area versus pore diameter. Temperature programmed desorption (TPD, AutoChem II 2920, Micromeritics) analysis was carried out on etched h-BN powder by each catalyst as well as a pristine sample by using NH₃ (He + 10% NH₃) gas. For desorption analysis, the temperature was raised from 150 °C to 800 °C at the rate of 10 °C/min.

3. Results and discussion

The best way to confirm if an etched structure is created by catalytic oxidation is to directly observe the surface of h-BN flakes after the oxidation. Thus, we conducted AFM analysis on the h-BN samples oxidized with TM precursors. Before considering the effect of catalytic oxidation on a structural change in h-BN layers, we should investigate how oxidation itself influences a morphological change of h-BN layers in the absence of catalysts. Therefore, we oxidized pristine h-BN sample at 350 °C for 2 h and observed the morphology of the sample by AFM. Fig. 1(a) and (b) display the AFM images obtained from pristine h-BN layers and oxidized ones, respectively. Compared with pristine ones, the oxidized h-BN sheets in Fig. 1(b) do not represent any morphological change such as a crack or a pit in the flake. This means that oxidation itself does not affect the structural modification of h-BN flakes. Fig. 1(c) and (d) show the images of h-BN layers oxidized with Co precursor. In Fig. 1(c), we can surprisingly see cracks in the h-BN flakes which do not appear in pristine and the oxidized h-BN flakes. The cracks in the figure start from the edge and develop into the inside of the flakes. In addition, we can observe an uneven surface different from the surfaces shown in Fig. 1(a) and (b). To obtain detailed information on the superficial morphology, AFM image was taken at higher magnification as displayed in Fig. 1(d). We can notice that the surface of h-BN flakes oxidized with Co precursor is considerably etched. The diameter of an etched structure was measured to be ca. 70 nm as marked with an arrow in Fig. 1(d). When h-BN flakes were oxidized with Cu precursor, a similar superficial structure is obtained as presented in Fig. 1(e). A number of pits are present on the surface of the flake, and a crack is also observed in the flake as indicated with an arrow. The diameter of the etched structure was measured to be ca. 70 nm which is a similar value obtained from the case of Co catalyst. The same phenomenon is observed from h-BN layers oxidized with Zn precursor. In Fig. 1(f), we can see holes in several regions of h-BN flakes where an etched structure has a diameter of ca. 80 nm. From these results, we can infer that the presence of TM precursor contributes to the creation of an etched structure in h-BN layers by etching a layered structure.

To clarify that the surface of h-BN flakes was etched by the catalytic oxidation, we measured a height profile from the surface of all samples. Fig. 2 displays all the height profiles obtained along the dashed lines shown in Fig. 1. In the case of pristine h-BN, we can notice from Fig. 2(a) that the surface keeps a flat surface where the roughness deviation is less than 1 nm. No great difference is seen in the height profile measured from oxidized h-BN sheets at 350 °C which also have a surface roughness with a deviation of less than 1 nm. When h-BN was oxidized with Co precursor, a height profile with a large deviation was obtained as seen in Fig. 2(c). When considering that the interlayer distance of h-BN is 0.333 nm, this deviation is strong evidence that the surface was severely etched by catalytic oxidation. The same phenomenon happened in h-BN sheets oxidized with Cu precursor as seen in Fig. 2(d). A considerably large deviation was measured in the height profile after catalytic oxidation, compared with those obtained from pristine and oxidized h-BN flakes. This indicates that the superficial layers of h-BN were etched by the catalytic oxidation. Also, oxidizing h-BN with Zn precursor created a pit with a depth of about 2 nm

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