Thin $h$-BN nanosheets synthesized using probe ultrasonication for dual functional applications

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Abstract

Synthesis of hexagonal boron nitride ($h$-BN) nanosheets has attracted intensive attention due to their promising applications in pollutant adsorptions and optical sensors. Bath sonication is known as a traditional method for synthesizing nanosheets. However, the challenge remains in obtaining ultrathin $h$-BN nanosheets. Here, much thinner $h$-BN nanosheets are achieved using the probe ultrasonication technique, which produces much high shear forces as an efficient liquid exfoliation strategy. The as-prepared $h$-BN nanosheets show better performances in both dyes adsorption and Raman enhancement than the samples synthesized using the bath sonication. More importantly, the relatively stronger Raman enhancement can be adopted to evaluate the adsorption ability of the $h$-BN nanosheets. Hence, the current work demonstrates the new synthesis method of ultrathin $h$-BN nanosheets and their potential application to monitor the adsorption performance using Raman enhancement.

Introduction

Boron nitride (BN) is a chemical compound consisting of equal numbers of boron (B) and nitrogen (N) atoms [1]. The $h$-BN is a white slippery BN polymorph with a layered structure analogous to graphite [2]. The layered structure can also be stacked in the rhombohedral structure. It is a wide band gap ceramic with remarkable properties including high thermal conductivity and stability, strong resistance to oxidation, and chemical inertness [3–6]. Properties of the few-layer BN sheets have been attracting steady interest over the last several years [3,7], and many applications based on these properties can perform in various fields [8–16].

Recently, it has been reported that $h$-BN shows excellent optical properties. It is highly polar and insulating with a large band gap of 5.9 eV [2,17], and the interface dipole interaction...
is strong and dominant [18]. Compared to graphene plasmon polaritons, the phonon polaritons in $h$-BN possess extremely high confinement and even lower loss [19,20]. In addition, $h$-BN shows a natural hyperbolicity [21,22], which can potentially be used to explore exotic optical properties such as Raman enhancements [18] and biosensors [23].

In addition, $h$-BN can also be used as an ideal adsorber for removing pollutant dyes because of its high specific surface area [24]. Technically, absorption performance could be evaluated by measuring ultraviolet (UV)-visible absorption spectra. However, due to a relatively low sensitivity of UV-visible spectra [25], detecting trace analytes is still challenging. Here, considering that the Raman enhancement technique is a powerful vibrational spectroscopy that allows highly sensitive detection of low concentration analytes [26,27], we strategically adopt the Raman spectra to monitor the adsorption performance, replacing the UV-visible spectra, by taking advantage of the Raman enhancement function of the $h$-BN nanosheets.

Various methods have been reported to isolate few-layer $h$-BN nanosheet materials in multimilligram quantities using dispersion-based approaches [28–33]. One route is to use the bath sonication technique simply under the assistance of solvent, such as H$_2$O and N,N-dimethylformamide [34], that exhibits polar-polar interactions with the $h$-BN surface to separate the layered structure effectively. However, to obtain few-layer nanosheets, some extra treatments are needed. For example, amine molecules are added to complex with boron atoms on the $h$-BN surface to trigger exfoliation and solubilization of the nanosheets [35]. In addition, it is also popular to get the $h$-BN nanosheets in aqueous solutions with a surfactant [36]. However, impurities are easily brought using these methods and their applications in related fields will be inevitably affected. Therefore, it is important to find a more efficient way to synthesize aqueous dispersions of ultrathin $h$-BN nanosheets without the use of surfactants or organic functionalization.

Recently, probe ultrasonication technique is reported for exfoliating bulk materials [37–39]. There are several advantages of the probe ultrasonication, including higher dispersibility, construction flexibility [40], and a higher exfoliation power [39,41], which enable this technique more suitable for the synthesis of nanosheets. In this work, we report the synthesis of few-layer $h$-BN nanosheets using a liquid exfoliation method in H$_2$O through the probe ultrasonication. Our result demonstrates that the technique is a facile and efficient route to obtaining few-layers $h$-BN nanosheets. Furthermore, its dual functional applications including the Raman enhancement and the dye adsorption have also been discussed.

Experimental section

Materials preparation

The probe ultrasonication technique to synthesize thin $h$-BN nanosheets is as follows: 300 mg $h$-BN powder (Aladdin Chemistry Co. Ltd) was exfoliated in a deionized water solution (400 ml) for 8 h with an aid of a probe ultrasonication cleaner (200 W, UP400S) and the dispersion was left to stand overnight. Then, the upper part of the dispersion was centrifuged at 5500 rpm for 20 min (Anke TGL-15B Centrifuge) to obtain a homogeneous dispersion of the $h$-BN nanosheets. For comparison, the bath ultrasonication with an ultrasonic bath cleaner (200 W, KQ 5200DE) was also employed to synthesize $h$-BN nanosheets using the exactly same amount of materials and under the same experimental conditions.

Characterizations

The morphology of the $h$-BN nanosheets was characterized using a scanning electron microscope (SEM) (Quanta 600 FEG), transmission electron microscope (TEM) (FEI Tecnai F30G2), and atomic force microscope (AFM) (SPM5500). The X-ray diffraction patterns (XRD) were collected using an Empyrean PA Analytical XRD system with reference X-ray illumination as Cu KR radiation at 0.154 nm.
Nitrogen adsorption-desorption measurements were carried out on an ASAP 2020 volumetric adsorption analyzer. Before the measurements, the h-BN nanosheet samples were outgassed in the degas port of the adsorption apparatus. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method, which has become a standard tool for surface area estimation. The adsorption equilibrium is:

$$\frac{P}{V(P_0-P)} = \frac{1}{CVm} + \frac{C-1}{CVm} \cdot \frac{P}{P_0}$$

(1)

where $P$ is nitrogen partial pressure; $P_0$ is saturated vapor pressure of nitrogen; $Vm$ is monolayer nitrogen saturated adsorption capacity; $V$ is adsorption capacity, and $C$ is the constant of adsorption equilibrium. The parameters, including $P$, $P_0$, $V$, can be directly measured by the analyzer. $Vm$ can then be calculated based on the equation (1). Then the further calculation was carried out through the equilibrium:

$$S_g = 4.325Vm$$

(2)

where $S_g$ is the data of the specific surface area.

For the dye adsorption measurements, UV-visible absorption spectra were collected using a Shimadzu Lambda 35 UV-visible spectrophotometer. The spectrum range was typically from 200 to 700 nm. The rhodamine B (RhB) aqueous solution with the initial concentration of $10^{-3}$ M and the h-BN nanosheets (20 mg) were added to a cuvette for the adsorption measurement. For the Raman measurements, a Lab RAM HR Raman spectrometer (Horiba Jobin Yvon) was employed. The wavelength of the excitation laser is 633 nm; a power of the excitation laser is approximately 5 mW, and the laser beam is around 1 μm. Regarding the CuPc Raman measurements, the thickness of CuPc on the silicon-based substrate and the h-BN nanosheet-based substrate was both about 1 nm. Regarding the RhB Raman measurements, the solution with RhB and h-BN nanosheets was directly obtained from the cuvette. Both the UV-visible and the Raman spectra were obtained with the corresponding time, e.g. 5, 10, 15, and 20 min.

Results and discussion

Structural analysis of h-BN nanosheets

The h-BN nanosheets were obtained by peeling off from the raw h-BN powder. The SEM and TEM images of the raw h-BN particles have been provided for comparison. As shown in Figure S1 in the supporting information, relatively large and thick h-BN particles aggregate together. The high-resolution TEM (HRTEM) image at the edge of a raw h-BN particle clearly shows that the thickness is nearly 30 nm and about 85 layers (Figure S1d). The photographs of the as-prepared h-BN nanosheets using the bath sonication and probe ultrasonication are shown in Figure S2. The suspension solution of the h-BN nanosheets obtained by the probe ultrasonication shows the white color, while the suspension solution of the h-BN nanosheets achieved by the bath sonication exhibits a milky and light yellow appearance. Furthermore, the SEM, TEM and AFM images of the h-BN nanosheets synthesized by the bath sonication and probe ultrasonication are showed in Figure 1. Compared to the nanosheets using the former, the nanosheets manufactured using the latter exhibit a thinner thickness. Multilayer nanosheets have been observed when the bath sonication is used, as shown in Figure 1a and b. In contrast, the thinner structures have been seen, which are nearly transparent to the electron beam and show a low contrast (Figure 1d and e). Figure 1 is the HRTEM image of the h-BN nanosheets synthesized using the probe ultrasonication. Although the layer number is not obviously confirmed, the BN lattice illustrated in Figure 1 shows a hexagonal pattern with a lattice parameter of 0.25 nm, indicating that the h-BN structure has a hexagonal layered structure. The electron diffraction of the TEM image is also shown in Figure 1 displaying a hexagonal symmetry. To carefully examine the thickness of the exfoliated h-BN nanosheets, AFM is further employed. Figure 1c and f show the AFM images of the exfoliated h-BN nanosheets from the bath sonication and probe ultrasonication, respectively. The corresponding height profiles indicate that the thickness of the h-BN nanosheets from bath sonication and probe ultrasonication is about 1.44–0.7 nm, which implies that the
as-prepared $h$-BN nanosheets are about 5 and 2 layers, respectively. Thus, our experiment demonstrates that the $h$-BN powders can be efficiently broken up and separated into few-layer sheets using the probe ultrasonication method. The previous study shows that the sonication-assisted water polarity effect plays a significant role in producing $h$-BN nanosheets through using bath sonication [39]. In addition, the hydrolysis of $h$-BN under the probe ultrasonication condition also participates in the exfoliation process [42–44]. The shear forces in the probe ultrasonication process are the key factors that will influence the nanostructures of the final products [42], which are helpful for the hydrolysis of more OH free radical and H atoms than the bath sonication process [43]. This free radical could alternately compress and stretch to form vibration so as to peel off the nanosheets [44].

Figure 1. Morphological and structural characterizations of the $h$-BN nanosheets.

(a) SEM images of the $h$-BN nanosheets synthesized using bath sonication, (b) TEM images of the $h$-BN nanosheets synthesized using bath sonication, (c) AFM images of the $h$-BN nanosheets synthesized using bath sonication (the inset images are the height profile plots corresponding to the marked white lines), (d) SEM images of the $h$-BN nanosheets synthesized using probe ultrasonication, (e) TEM images of the $h$-BN nanosheets synthesized using probe ultrasonication, (f) AFM images of the $h$-BN nanosheets synthesized using probe ultrasonication (the inset images are the height profile plots corresponding to the marked white lines), (g) high-magnification image of the $h$-BN nanosheet synthesized using the probe ultrasonication, (h) high-magnification image of the $h$-BN nanosheet synthesized using the probe ultrasonication, (i) electron diffraction of the as-prepared $h$-BN nanosheets obtained using the probe ultrasonication.
The UV-visible spectra of the h-BN nanosheets are taken at room temperature to reveal the difference between the two samples synthesized by bath sonication and probe ultrasonication. As shown in Figure 2, the absorption peak of the h-BN nanosheets synthesized through the bath sonication is 260 nm. Interestingly, the absorption peak is blue-shifted from 260 to 222 nm when the probe ultrasonication is applied. The blueshift of absorption peak can be attributed to the size and thickness reduction of the nanosheets [45]. On the basis of Tauc’s formulation [46]:

$$\omega^2 \varepsilon = (h\omega - E_g)^2$$  (3)

where \(\varepsilon\) is the optical absorbance, \(h\) is Planck constant \(4.13567 \times 10^{-15}\) eV, \(E_g\) is the band gap, and \(\omega = 2 \pi / \lambda\). \(\omega\) is the angular frequency of the incident radiation (\(\lambda\) is the wavelength). Herein, the band gap \(E_g\) reduces along with an increase of the nanosheet layers because the layer-layer interaction increases the dispersion of the electronic bands and tends to reduce the band gap [41]. The expansion and simplifying treatment of the Tauc’s formulation lead to:

$$E_g = 1465 \varepsilon^2 / \lambda.$$  

Thus, it is easily understandable of the blue-shift of the absorption peak along with the layer reduction of the h-BN nanosheets.

X-ray diffraction is used to investigate the crystal structure and phase components of the products. The XRD profile of the raw h-BN materials is also provided for comparison. As shown in Figure 2, all of the diffraction peaks are corresponding to the (002), (100), (101), (102), (004), (110), and (112) planes of h-BN with a lattice constant of \(a = 0.25\) nm [47,48], which is similar to that in the HRTEM image. In addition, both the intensity and the half-peak width of the (002) peak are gradually increased from the raw h-BN materials, the h-BN nanosheets obtained from the bath sonication, to the h-BN nanosheets achieved from the probe ultrasonication. The (002) peak of the h-BN achieved by the probe ultrasonication becomes stronger relative to other diffraction peaks than that of the other two samples, which leads one to speculate that the (002) crystal faces of the h-BN nanosheets are exposed more compared with the other samples. The h-BN nanosheets may be exfoliated from the precursor BN powder along the (002) plane without destroying its crystalline structure, and our result is consistent with the previous reports [47,49,50]. The thickness of the h-BN plane can be calculated by the Scherrer equation:

$$L_c = \frac{K \lambda}{\beta \cos \theta}$$  (4)

where \(L_c\) is the mean thickness of the h-BN plane, \(K\) is a dimensionless shape factor (about 0.9), \(\lambda\) is the X-ray wavelength, \(\beta\) is the half-peak width, and \(\theta\) is the Bragg angle. In our current work, the half-peak width becomes gradually wider from the raw h-BN powder, the h-BN nanosheets obtained by the bath sonication, to the h-BN nanosheets achieved by the probe ultrasonication, the thickness of the h-BN plane, in turn, will decrease. Therefore, both the intensity and the half-peak width of the (002)
peak changes reflect that the as-prepared $h$-BN obtained by the probe ultrasonication is relatively thin nanosheets. Besides, the samples from the probe ultrasonication display a slightly low angle shift, which can be contributed by the polar solvent molecules inserted into the stratified structure interlayer and then enlargement of the diffraction spacing distance. According to the equation:

$$2d \sin \theta = \lambda$$

where $d$ is the diffraction spacing distance, $\theta$ is the diffraction angle, and $\lambda$ is excitation wavelength, which is fixed. When the diffraction spacing distance is increased, the diffraction angle becomes decreased.

**Multifunctional properties and applications of $h$-BN nanosheets**

The potential applications of the $h$-BN nanosheets obtained using the probe ultrasonication technique including adsorbing dyes and Raman measurement have been evaluated. Firstly, the specific surface area has been assessed by measuring the N$_2$-sorption isotherms. As shown in Figure 3a and b, the N$_2$-sorption isotherms can be categorized as type IV and an H3 hysteresis loop [51]. For the two samples, a significant increase of the adsorption branch between 0.3$P_0$ and 0.8$P_0$ and a pronounced hysteresis demonstrate the existence of mesoporous structure. The samples acquired from the probe ultrasonication have a higher surface area ($41 \text{ m}^2/\text{g}$) than the samples from the bath sonication ($23 \text{ m}^2/\text{g}$), which is mainly attributed to the thinner and fewer layer nanosheets. The large surface area will be more efficient in adsorbing and removing dyes.

The adsorption kinetic test of the $h$-BN nanosheets was conducted to evaluate its adsorption rate of an organic dye. Herein, RhB is chosen as the indicant agent for examining the adsorption performance. The characteristic peak at about 554 nm can be ascribed to RhB [52]. As shown in Figure 4a and c, the RhB concentration declines when the absorption time increases. Along with the RhB adsorption in the presence of the $h$-BN nanosheets synthesized through the bath sonication, the RhB characteristic peak become nearly invisible after about 35 min. In contrast, the RhB characteristic peak becomes too weak to be observed in 20 min after the $h$-BN nanosheets obtained from the probe ultrasonication, suggesting that the RhB removal is more efficient for the $h$-BN synthesized using the probe ultrasonication. Furthermore, the corresponding kinetic adsorption points of the RhB solution for a different time in the presence of the $h$-BN nanosheets have been plotted. As shown in Figure 4b and d, the obtained experimental data are found to fit approximately a pseudo-first-order kinetic model by the linear transforms $\ln (C_t/C_0) = -kt$ ($k$ is the kinetic constant). The rate constants calculated from the slopes of the straight lines are 0.06 and 0.12 for $h$-BN from the bath sonication and the probe ultrasonication, respectively. Obviously, the adsorption rate of the sample from the probe ultrasonication is two times of that from the bath sonication, which further confirms that the samples with

![Figure 3. N2 adsorption–desorption characterization of the $h$-BN nanosheets.](image-url)

(a) N2 adsorption–desorption of the $h$-BN samples synthesized using bath sonication, (b) N2 adsorption–desorption of the $h$-BN samples synthesized using probe ultrasonication.
the thinner thickness obtained from the probe ultrasonication process exhibit a higher adsorption efficiency.

One the other hand, the Raman enhancement of the as-prepared \( h \)-BN nanosheets has been performed. As shown in Figure 5a and b, the Raman spectra are obtained from the samples treated with the same concentration of CuPc and excited with the 633 nm laser. The Raman bands at about 682, 749, 958, 1457, and 1534 cm\(^{-1}\) can be attributed to CuPc and agree well with literature data [53]. According to the enhancement factor (EF) formulation:

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{ref}}} \times \frac{N_{\text{ref}}}{N_{\text{SERS}}} \tag{6}
\]

where \( I_{\text{SERS}} \) is the enhanced intensity of CuPc probe molecules on the \( h \)-BN nanosheet substrate, \( N_{\text{SERS}} \) is the number of single layer molecules covering on the \( h \)-BN nanosheet substrate under the laser spot, \( I_{\text{ref}} \) is the spontaneous Raman scattering intensity from the probe molecules under the laser spot on a blank Si substrate, and \( N_{\text{ref}} \) is the number of single layer molecules covering on the blank Si substrate under the laser spot. The relative intensity of the characteristic band at 682 cm\(^{-1}\) is 1462 in the Raman spectrum from the \( h \)-BN nanosheets after the bath sonication, while it is 4221 in the Raman spectrum from the \( h \)-BN nanosheets after the probe ultrasonication. The thickness of CuPc on the silicon and the \( h \)-BN nanosheet-based substrate is both about 1 nm. As a result, the EF based on the \( h \)-BN nanosheets from the bath sonication is calculated to be about 10, while the EF based on the \( h \)-BN nanosheets from the probe ultrasonication is about 38. This result is comparable to the previous report about graphene-like nanosheets, such as the CVD grown MoS\(_2\) (EF: 10–20), CVD grown

Figure 4. Adsorption evaluation of the \( h \)-BN nanosheets with UV-visible absorption spectra.

(a) UV-visible absorption spectra of the RhB solution for different time in the presence of the \( h \)-BN nanosheets synthesized using bath sonication, (b) the corresponding kinetic adsorption plots of the RhB solution for different time in the presence of the \( h \)-BN nanosheets synthesized using bath sonication, (c) UV-visible absorption spectra of the RhB solution for different time in the presence of the \( h \)-BN nanosheets synthesized using probe ultrasonication, (d) the corresponding kinetic adsorption plots of the RhB solution for different time in the presence of the \( h \)-BN nanosheets synthesized using probe ultrasonication.
$h$-BN (EF: 10–30) depending on the particular Raman peaks [18]. This enhancement is due to a strong dipole−dipole coupling from the $h$-BN nanosheets, and the $h$-BN nanosheets have a polar structure, which can induce an interfacial dipole interaction with the CuPc molecules. In addition, the fewer-layer nanosheets show 3.8 times stronger Raman enhancement than the samples from the bath sonication. The main reason is the change of the matching degree between the energy band of $h$-BN and the energy band of probe molecules, which will influence the strength of the chemical enhancement [54]. Besides, the $h$-BN with gradually increased layers absorbs more light from the irradiation laser and thus slightly decreases the Raman enhancement [55]. Therefore, the thinner $h$-BN nanosheets are more suitable for the Raman enhancement application.

Considering the relatively weak detection sensitivity and insufficient “fingerprint information” of UV-visible spectra in monitoring dye adsorption process [25], the Raman measurements of RhB dyes based on the $h$-BN have been performed to monitor the adsorption process. As shown in Figure 6a and c, the Raman spectra of RhB molecules are obtained from the $h$-BN and RhB solution in the cuvette collected during the different reaction time. The Raman bands at about 1200, 1279, 1357, 1507, 1529, and 1648 cm$^{-1}$ can be attributed to RhB [56–58]. It is observed that the primary Raman bands gradually enlarge their intensities with an increase of time without the emergence of new bands. Taking a Raman spectrum obtained from the sample collected after adsorbing for 10 min as an example (Figure 6a and c), the peaks from the probe ultrasonication process exhibit higher intensities than that of the bath sonication process. It is easily understood that the higher adsorption capacity and the stronger Raman enhancement are the main reasons for the stronger Raman intensity of RhB in the presence of the $h$-BN synthesized using the probe ultrasonication. In order to investigate whether the SERS (Surface Enhanced Raman Scattering) signals are related to the dye concentration, it is necessary to plot ln($C_t/C_0$) against time, where $C_0$ is the initial intensity of the Raman peak at the time of 5 min, and $C_t$ is the intensity of the corresponding Raman peak at 5, 10, 15, and 20 min. As shown in Figure 6b and d, the plots of ln($C_t/C_0$) versus time for the Raman peaks give straight lines similar to that obtained from the UV-visible spectra. These results indicate that the Raman spectra can also reflect the pseudo-first-order kinetics of the adsorption process. The rate constants calculated from the slopes of the straight lines are 0.11 and 0.18 for $h$-BN from the bath sonication and the probe ultrasonication, respectively. These molecules in the aqueous solution diffuse and are simultaneously adsorbed onto the surface of the nanosheets, which ensure the continuous adsorption of the dye molecules. Therefore, it is not surprising to observe that the adsorption rate on the surface of the $h$-BN nanosheets synthesized using the probe ultrasonication is higher than that synthesized using the bath sonication. It is evident that a UV-visible absorption spectroscopy only provides information of the adsorption process in solution, rather than on the surface of the nanosheets where an adsorption proceeds. In contrast, the Raman enhancement technology provides an excellent alternative to monitoring the adsorption process on the surfaces of the $h$-BN nanosheets. These thinner $h$-BN nanosheets exhibit a high adsorption activity and good Raman enhancement performance, which provides an excellent platform.
for monitoring the adsorption process of dye molecules. Compared with UV-visible spectroscopy often used to monitor adsorption processes, Raman enhancement technology can reflect more the adsorption process occurring on the surfaces of the h-BN nanosheets.

**Conclusion**

In conclusion, we have demonstrated a facile technique to fabricate thinner nanostructures of h-BN nanosheets using the probe ultrasonication as a liquid phase exfoliation method. Such nanostructures show a better adsorption activity than the samples obtained from the bath sonication. Moreover, the Raman enhancement of these samples demonstrates that the thinner nanosheets exhibit excellent capability than the samples from the bath sonication. More importantly, these thinner h-BN nanosheets provide an excellent platform for monitoring the adsorption process of dye molecules by the Raman enhancement technology.

**Supporting material**

S1. **Morphology characterization of the raw BN materials.** (a) SEM image of the raw h-BN power materials, (b) TEM image of the raw h-BN power materials, (c) TEM image of the raw h-BN power materials, (d) HRTEM image of the raw h-BN power materials. (PNG)
S2. Photographs of the \( h\)-BN nanosheets. (a) The dried powder of the \( h\)-BN nanosheets prepared using probe ultrasonication, (b) suspension solution of the \( h\)-BN nanosheets prepared using probe ultrasonication, (c) the dried powder of the \( h\)-BN nanosheets prepared using bath sonication, (d) suspension solution of the \( h\)-BN nanosheets prepared using bath sonication. (PNG)

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Competing interests

The authors declare that they have no conflict of interest.

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