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Graphene Oxide/Black Phosphorus Nanoflakes Aerogel with Robust Thermostability and Significantly Enhanced Photothermal Property in Air

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Experimental Section

1. Materials

Graphite powder (≥ 325 mesh) was purchased from purchased from Aladdin. Concentrated H_2SO_4, H_2O_2 (30 wt%), $K_2S_2O_8$, P_2O_5, $KMnO_4$, N-methyl-2-pyrrolidone (NMP) and ethanol were purchased from Sigma Aldrich. Black phosphorus crystals with high-purity were purchased from Smart Elements. Poly(oxypropylene) diamine (D_{400}, average M_n=400) was purchased from Aladdin and its detailed structural formula is $H_2N\text{-}[CH(CH_3)\text{-}CH_2\text{-}O\text{-}]_{6.1}\text{-}CH_2\text{-}CH(CH_3)\ \text{–}NH_2$. [1]

2. Preparations of graphene oxide nanosheet and BP nanoflakes

Preparation of graphene oxide (GO): Graphene oxide (GO) was prepared by a modified Hummers' method. [2] In brief, graphite powders (10 g) was carefully mixed with concentrated H_2SO_4 (45 mL) and $K_2S_2O_8$ (15 g) and P_2O_5 (15 g) were successively added into the above mixture with a continuous agitation. Then the mixture was kept at 80 ºC for 6 h to obtain pre-oxidized graphite. The pre-oxidized graphite solution was diluted by 1 L deionized water after cooled to room temperature and the corresponding precipitate was obtained by vacuum filtration using hydrophilic poly(tetrafluoroethylene) (PTFE) microporous membranes (0.20 µm) and repeatedly washed by deionized water until the pH=7 of filtrate was got. After drying at room temperature in air, the pre-oxidized graphite was thoroughly dried in vacuum oven at 50 ºC overnight.

The above pre-oxidized graphite (5 g) was added by concentrated H_2SO_4 (120 mL) at 0 ºC with ice bath and $KMnO_4$ (15 g) was then slowly added into the mixture under continuous agitation at a temperature below 10 ºC. Then, the mixture was kept at 35 ºC for 4 h. After cooled to room temperature, the mixture was diluted by 250 mL deionized water and stirred for 2 h. An addition of 700 mL deionized water was added, followed by dropping H_2O_2 (10 mL, 30 wt%) solution, which aimed at ending the oxidation of graphite. The precipitate was centrifuged and washed by water and HCl solution (1M) several time to fully remove the residual metal oxides and make sure the centrifugate was neutral. The final as-prepared GO precipitate was re-dispersed in deionized water and the approximate GO mass concentration was determined to be 0.485 wt%.

Preparation of BP nanoflakes (BPNFs): BP nanoflakes (BPNFs) were prepared by a liquid exfoliation method. In brief, 5 mg bulk BP was first grounded with N-methyl-2-pyrrolidone (NMP) in an agate mortar in air. The used NMP volume was 5 mL and the grounding time was about 40 min, respectively. It is noted that the grounding time of BP with NMP is of great importance for the final yield of BP. It is also noted that the coating of NMP for BP can protect BP from oxidation by oxygen in air for a short time. It is therefore that the grounding procedure can be performed just in air. After grounding, BP/NMP solutions with an original concentration of 1 mg/mL was sonicated by a tip probe with a power of 650 w for 3 hours, followed by a bath sonication with a power of 300 w for 6 hours. The temperatures in the both sonication procedures were kept with 0 to 10 ºC by ice-bath. The BPNFs/NMP solution was obtained by centrifugation with a speed of 7000 rpm for 20 min, and then the BPNFs precipitate were obtained by a 18000 rpm speed for 1h. To remove the residual NMP in BPNFs, the BPNFs were repeatedly resolved by ethanol and water for two times, then obtained by centrifugation. The as-prepared BPNFs were then re-dispersed in 1mL deionized water with a 5 min bath sonication with a power of 300 w to obtain a homogeneous BPNFs/water solution.

3. Preparation of GO/BPNFs and neat GO aerogel

According to Wang *et al*, [1] 4.86 µL D_{400} was first dissolved in the above 1mL BPNFs/water solution, then the homogeneous solution was thoroughly mixed with GO solution with 0.5 g. The vessel filled with the obtained GO/BPNFs/D_{400} solution was immersed into oil bath with 90 ºC for only 1 min. It is noted that in view of the degradation of BP induced by light [3] the vessel was first fully covered by aluminum foil before high temperature treatment. After ultrafast gelation of GO nanosheets, the formed GO/BPNFs hydrogel was then subjected by freeze-drying for 48 hours. As a control sample, neat GO aerogel without adding BPNFs was also prepared by a similar method.

4. Characterization

The morphologies of BPNFs was characterized by transmission electron microscopy (TEM). The typical image of BPNFs was obtained by performing TEM (JEM-1230) with at an accelerating voltage of 200 kV. The high-resolution image of BPNFs and selected-area electron diffraction (SAED) were performed by using a TEM instrument with a model type of FEI Tecnai G^2 F30 with an accelerating voltage of 300 kV.

The height-profiles of BPNFs and GO nanosheets were characterized by atomic force microscopy (AFM, Bruker). The BPNFs in ethanol solution and GO solution were spin-coating onto micas with a 3000 rpm speed for 30 s. Before measurement, the mica loaded with BPNFs was placed in vacuum oven at 75 ºC for overnight. And the mica with GO was dried in air for overnight.

The morphologies of GO/BPNFs and neat GO aerogel were obtained by using a field emission scanning electron microscopy (FESEM, SEM-Hitachi SU8010). The samples were coated with a thin layer of silver before characterization. An acceleration voltage of 5 kV was used for the samples. The work distances were 9.3 and 9.2 mm for GO/BPNFs aerogel and neat GO aerogel, respectively. The energy dispersive spectrometer (EDS) analysis was also performed at 20 kV. It is noted that the obtained both GO/BPNFs aerogel and neat GO aerogel are rather soft and that the SEM sample preparation should be careful to only press the margin of samples so as to maintain their original porous morphologies.

The BPNFs concentration in GO/BPNFs aerogel was determined by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA2100DV, PerkinElmer). In brief, the pre-weighted GO/BPNFs aerogel was first fully broken up in deionized water by bath sonication for 1h and then the mixture was added by HNO_3 solution for nitration for at least 3 days. After fully nitration, the sample mixture was diluted by deionized water and the precipitate was filtered by hydrophilic PTFE membrane (0.20 μm) to remove the residual aerogel sample. The filtrate was used to determine the P concentration in GO/BPNFs aerogel. Three samples were measured and the average value was reported.

X-ray photoelectron spectroscopy (XPS) was conducted by performing a PHI-5000 VersaProbe II (ULVAC-PHI) instrument using monochromatic Al Kα radiation. Wide scans of the samples were carried out in the range 1200−0 eV, and narrow scans were performed for the N1s, P2p and C1s regions. In particularly, when the sample's surface was sputtered, Ar-gun was used with a sputtering voltage of 4 kV and a sputtering area of 3 μm×3 μm. The sputtering depth was estimated to be 30 nm.

Fourier transform infrared spectroscopy (FTIR, PerkinElmer) was performed by using an ATR model with 64 scans. X-ray diffraction (XRD) patterns were obtained by using a Bruker-D8 instrument (λ=0.154 nm). The samples were pressed into a flat shape before measurement. The voltage and current used are 40 kV and 40 mA, respectively. The scanning speed used is 1º/min.

Photothermal properties of samples were characterized by using a 808 nm NIR laser instrument equipped with an infrared thermal imaging camera ((FLIR-160)) to measure the temperature change of samples. The used power density of light source in this study are 0.2 and 0.5 W/cm^2, respectively. In particularly, the sample of GO/BPNFs aerogel was first subjected by being applied 0.2 and 0.5 W/cm^2 power density, respectively, then repeatedly performed for other 7 cycles at 0.5 W/cm^2 power density. The photothermal behaviors of samples were characterized in air without any protection treatment.

The electrical properties were characterized by using a semiconductor parameter analyzer (Model: K14200 MPSMU with PreAmp) with a voltage sweep model under ambient conditions.

The rheological behaviors of samples were characterized by using an Anton Paar MCR 52 instrument. Dynamic frequency sweep experiments were measured from 1-100 rad/s at a fixed oscillatory strain of 0.2% at room temperature. Temperature sweep experiments were performed with a fixed angular frequency of 10 rad/s and a fixed oscillatory strain of 0.2 % in the range of 30-100 ºC at a heating rate of 5 ºC/min.

References:

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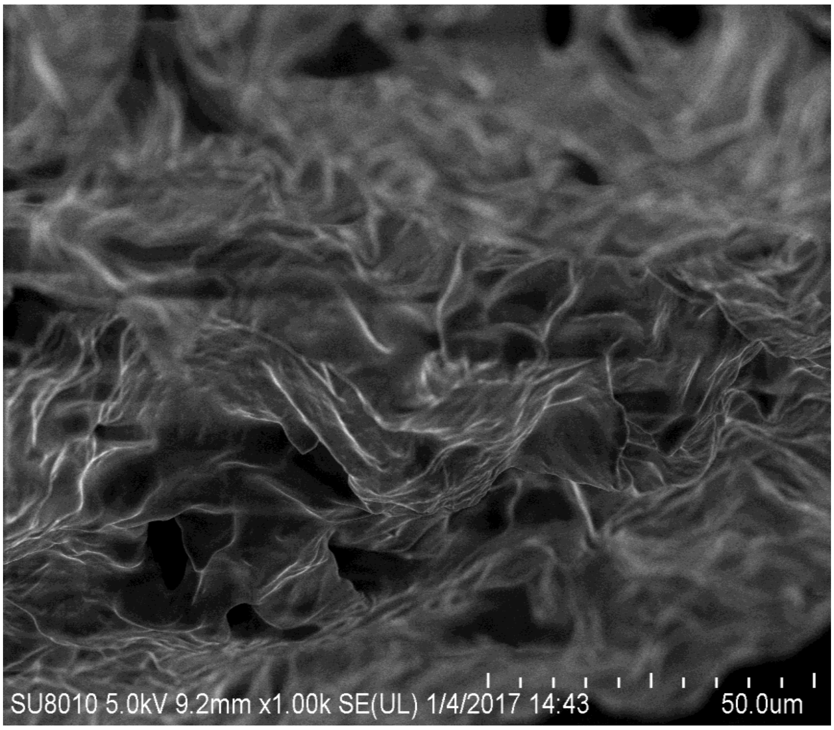

Fig. S1 SEM image of 3D GO/BPNFs aerogel at a low magnification (1k) showing the macroporous structures.

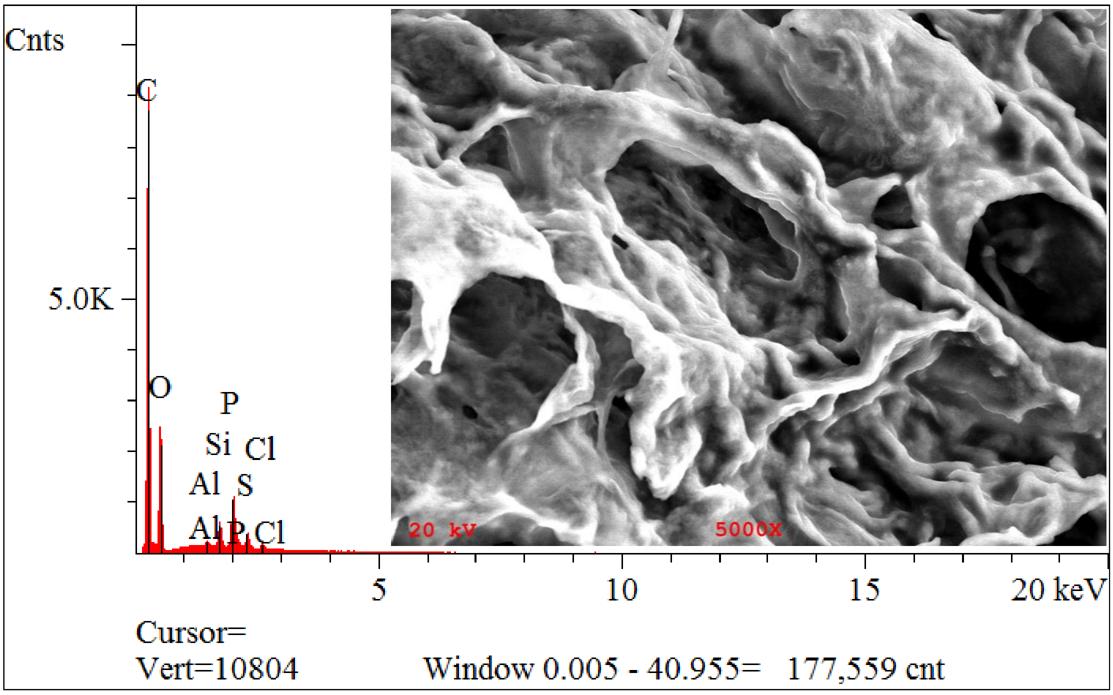

Fig. S2 Energy dispersive spectrometer (EDS) analysis of GO/BPNFs aerogel showing the presence of P element. The insert SEM image was the corresponding scanning area for EDS analysis.

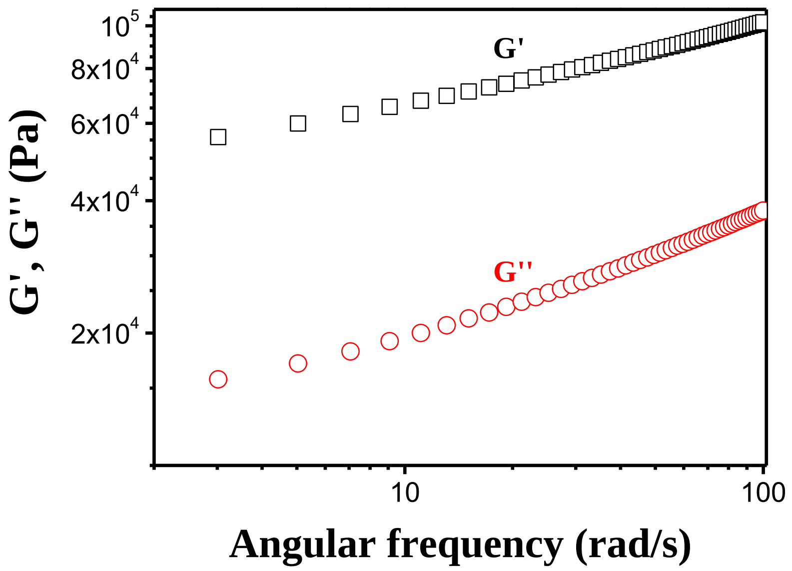

Fig. S3 Rheological behaviors of GO/BPNFs aerogel with 13.4 wt% BP loading: storage modulus (G’) as well as loss modulus (G’’) as a function of angular frequency with a fixed oscillatory strain of 0.2 % at room temperature.

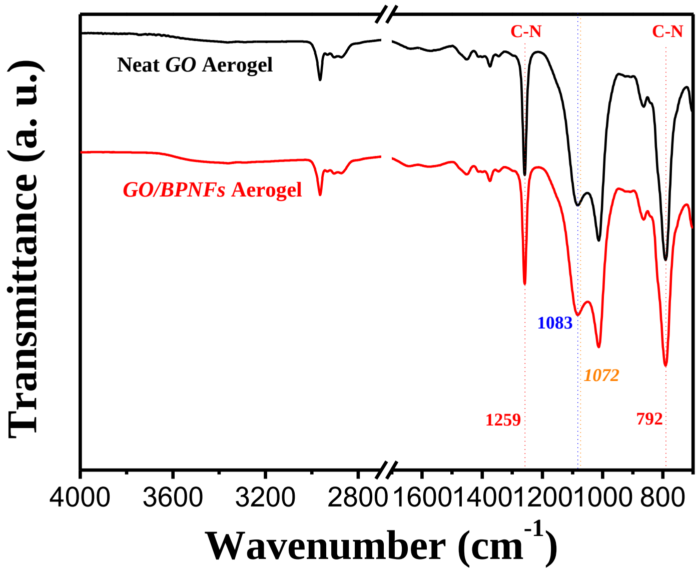

Fig. S4 Fourier transform infrared spectroscopy (FTIR) of neat GO aerogel and GO/BPNFs aerogel with 13.4 wt% BP content, respectively.

The peaks at 1259 and 792 cm^{-1} in both neat GO aerogel and GO/BPNFs aerogel are attributed to the formation of C-N bonds during the GO's gelation by interacting with D_{400} at 90 °C, which is absent in the GO and D_{400}, according to the report by Wang *et al.*[1] In addition, no peak was found at 1072 cm^{-1} in GO/BPNFs aerogel, compared with that of neat GO aerogel, suggesting that the BP is not oxidized by oxygen in the GO/BPNFs aerogel in our study. [2]

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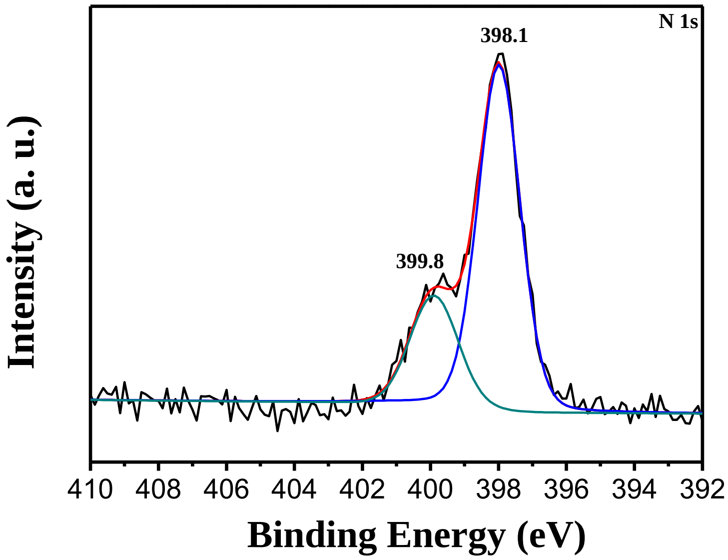

Fig. S5 XPS spectra of GO/BPNFs aerogel. The peaks at 398.1 and 399.8 eV in N 1s spectra suggesting the formation of C-N bond in the GO/BPNFs aerogel with 13.4 wt% BP content. [1, 2]

1. W. Wan, L. Li, Z. Zhao, H. Hu, X. Hao, D. A. Winkler, L. Xi, T. C. Hughes and J. Qiu, *Adv. Funct. Mater.*, 2014, **24**, 4915-4927.
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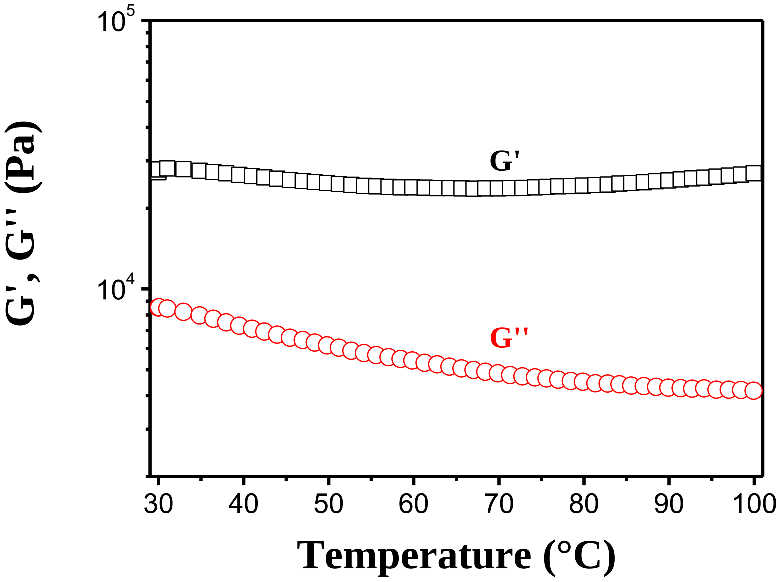

Fig. S6 Rheological behavior of GO/BPNFs aerogel with 13.4 wt% BP content: temperature sweep with a fixed angular frequency of 10 rad/s and a fixed oscillatory strain of 0.2 % in the range of 30-100 ºC at a heating rate of 5 ºC/min.