Supporting Information of

Introduction of -$B(OH)_2$ group into graphene motif for pz orbital removal and ferromagnetic modulation

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1. Experimental

1.1 Materials.

Graphite was obtained from Thermo Fisher Scientific Co., LTD. Hydrogen peroxide (30%) and absolute ethyl alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Boric acid (H_3BO_3) was purchased from STREM CHEMICALS (Fluka, CAS Number: 10043-35-3) Polyvinylpyrrolidone (PVP) was purchased from STREM CHEMICALS. All other reagents were of analytical grade and used without further purification. CO_2 with a purity of 99.99%. was purchased from the Zhengzhou Shuangyang Gas Co. Deionized water were prepared with an ultrapure water apparatus.

1.2 Synthesis of graphene.

Typical experimental steps are as follows. Graphite (200 mg), boric acid (217 mg) and PVP (400 mg) were mixed in anhydrous ethanol (15 ml) and sonicated for 2 hours to form a homogeneous dispersion. After addition of hydrogen peroxide, the mixture was transferred to a supercritical CO_2 apparatus and heated to 80 °C. The mixture was then heated to 80 °C. Subsequently, carbon dioxide was injected into the autoclave under stirring at appropriate pressures (12, 14 and 16 MPa) for the reaction. After the mixture has reacted for 4 hours, the reaction unit is cooled to room temperature and the carbon dioxide is slowly released. After sonication for 30 minutes, the products were collected by centrifugation at 5000 rpm for 15 minutes at room temperature to remove aggregates. The precipitate was collected in a tube and centrifuged at 10,000 rpm for 20 minutes to remove the PVP and H_2O_2. After centrifugation at 10,000 rpm, the precipitates were combined and washed four times with ethanol before being dried in a vacuum oven at 60 °C overnight.

1.3 Characterization.

The morphology and structure of the sample were characterized by field emission SEM (JEORJSM-6700F), AFM (Nanoscope IIIA), TEM(JEOL JEM 2100) and HRTEM. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus

diffractometer (Bruker AXS, Germany) using Cu Kradiation. Raman spectra were recorded on a Renishaw microscope system RM2000 with laser wavelength of 532nm. X-ray absorption near edge structure (XANES) measurements were conducted at the insertion-device beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source located within the National Synchrotron Radiation Laboratory. The energy resolution for the absorption spectra is around 40 and 80 meV for the boron edges, respectively.

1.4 Computational methods.

All the calculations were based on Density Functional Theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) code utilizing the projector augmented wave method (PAW). The exchange-correlation energy of generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) was adopted. A vacuum of 20 Å perpendiculars to the sheets was applied to avoid the interaction between layers. A kinetic energy cut off of 450 eV was used for the plane-wave basis set. The sampling in the Brillouin zone was set with 5×5×1 by the Monkhorst-Pack method. Convergence criteria employed for both the electronic self-consistent relaxation and ionic relaxation were set to be 10^{-4} and 0.02 eV/Å for energy and force, respectively.

2. Supplementary Figures

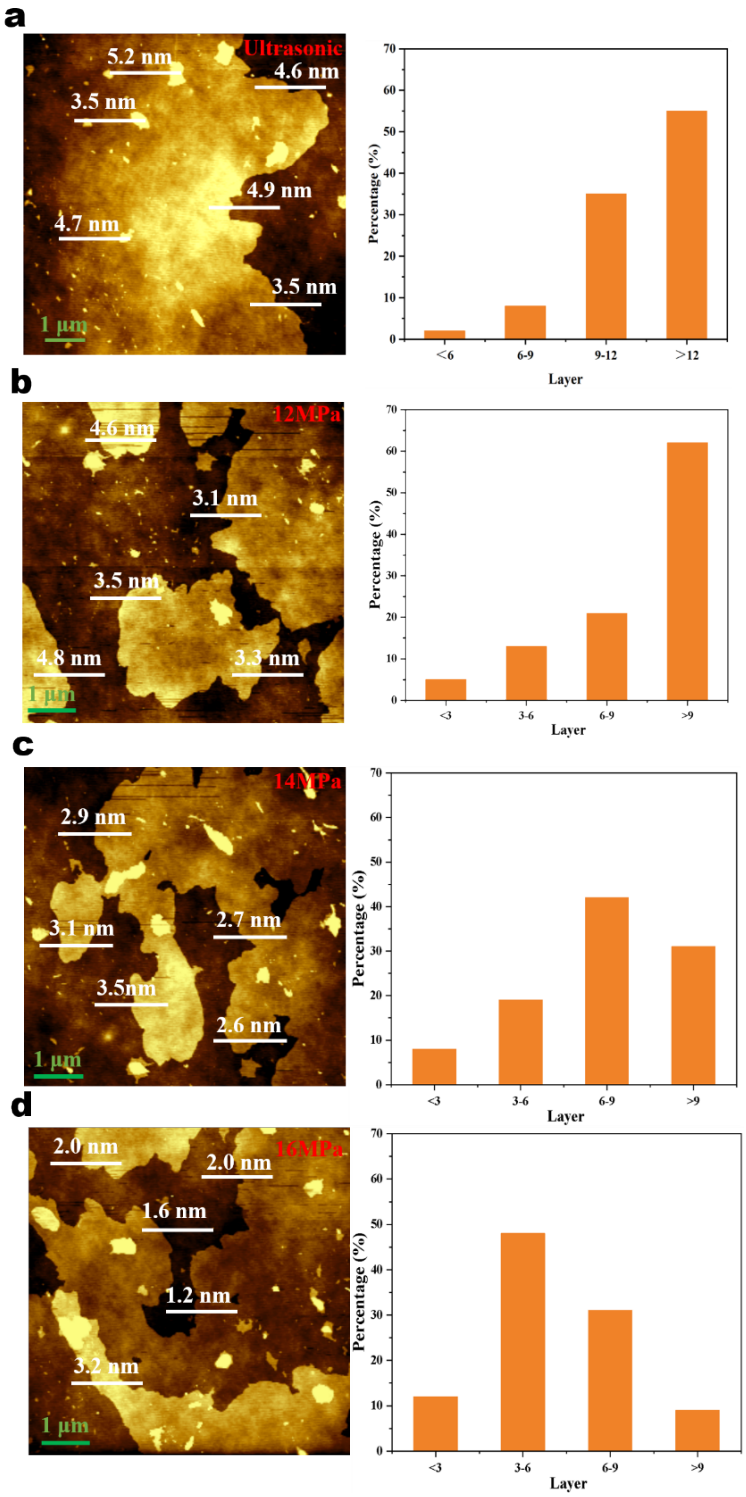

Fig. S1. AFM characterizations of samples (ultrasonicated graphite and B-GO-XMPa) and corresponding layer distributions derived from 50 nanosheets picked randomly from AMF images: (a) ultrasonicated graphite; (b) B-GO-12MPa; (c) B-GO-14MPa; (d) B-GO-16MPa.

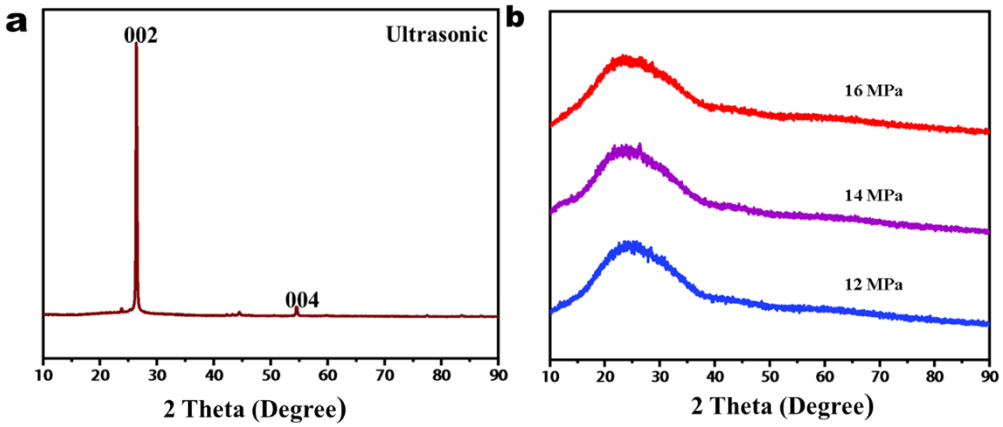

Fig. S2. (a) XRD characterizations of ultrasonicated graphite. (b) XRD patterns of B-GO-XMPa (X = 12, 14 and 16).

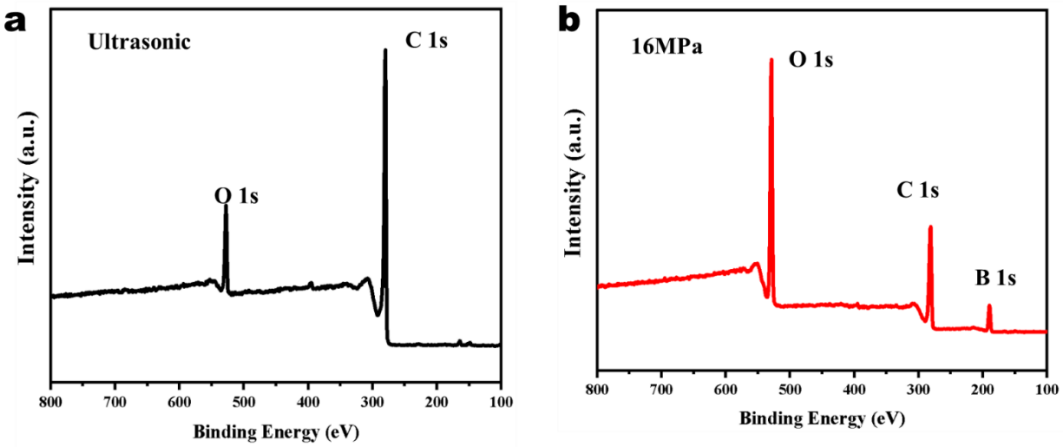

Fig. S3. (a) XPS survey scan of ultrasonicated graphite. (b) XPS survey scan of B-GO-16MPa.

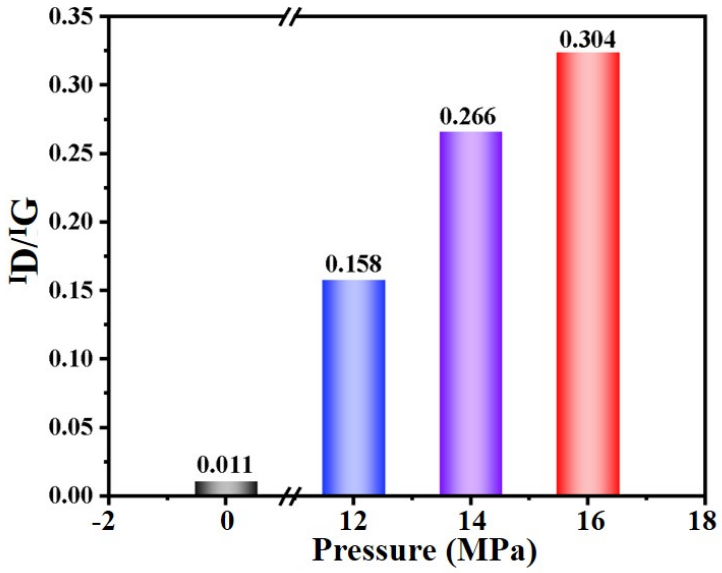

Fig. S4. I_D/I_G ratio derived from Raman characterizations in Fig. 4a.

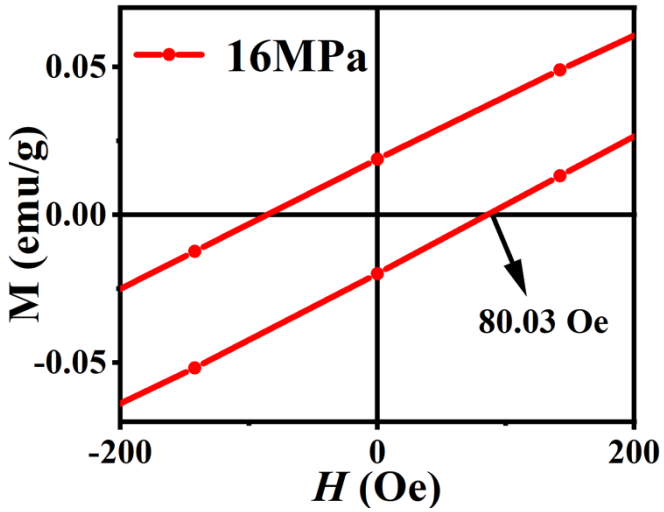

Fig. S5. M-H plot of B-GO-16MPa near H = 0 Oe, where the coercivity (Hc) is characterized to be 80.03 Oe.

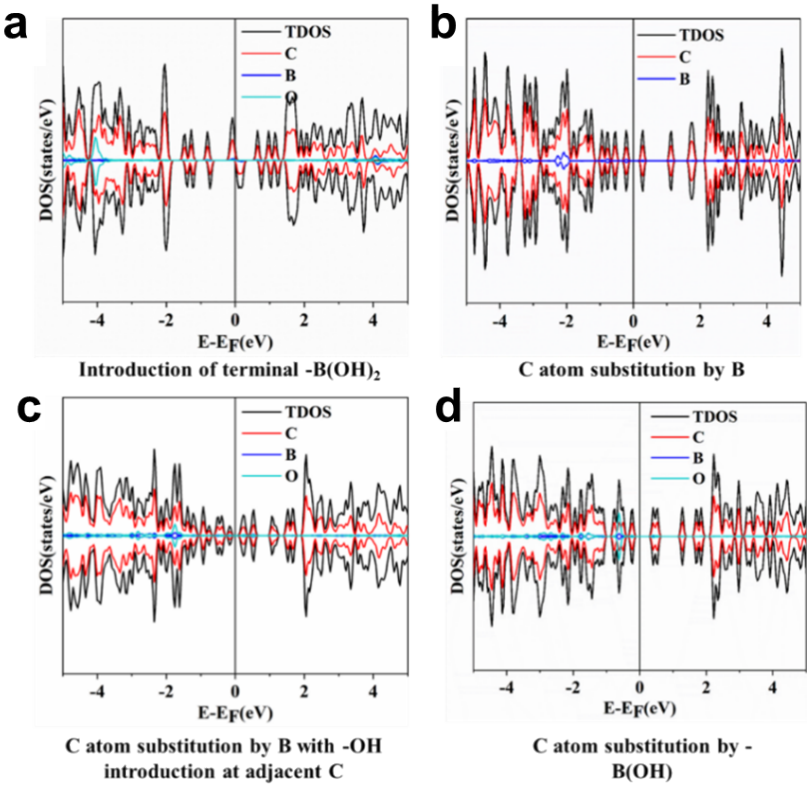

Fig. S6. Spin-resolved total density of states (DOS) and partial density of states (PDOS) of graphene-based structures with different functional groups or atoms introduced.

Table S1. Concentrations of different elements and functional groups of B-GO-XMPa and ultrasonicated sample based on XPS characterizations.

Sample	C%	O%	B%	C-C %	C-OH%	C-O%	O-C=O%	B-O%	B-C%
Ultrasonic	99.52	0.47	-	92.93	4.46	2.32	-	-	-
12MPa	93.91	4.52	2.23	79.21	12.67	5.76	2.28	5.35	1.36
14MPa	92.5	4.94	2.65	58.35	13.72	7.22	3.55	5.78	3.47
16MPa	90.6	5.32	3.12	45.88	15.33	8.75	3.87	8.23	4.26

Table S2. Summary of ferromagnetic properties of other metal-free graphene reported in the literature.

Material	Temperature(K)	Ms (emu/g)	Journal
Metal-free B-doped graphene quantum dots	6 K 300 K	2.935 emu/g 0.0398 emu/g	*Adv. Mater* **2017**, 29, 1605416[1]
B-doped g-C_3N_4 nanosheets	300 K	0.008 emu/g	*Sci. Rep.* **2016**, 6, 35768[2]
Strong ferromagnetism of g-C_3N_4 achieved by atomic manipulation	300 K	0.043 emu/g	*Nat. Commun.* **2023**, 14, 2278[3]
Tuned magnetic properties of Co-doped ZnO/B-doped graphene PN junction	300 K	0.02 emu/g	*Mater. Des.* **2018**, 149, 81[4]
This work	300 K	0.39 emu/g	

3. References

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2. D. Gao, Y. Liu, P. Liu, M. Si and D. Xue, *Sci. Rep.*, 2016, **6**, 35768.
3. L. Du, B. Gao, S. Xu and Q. Xu, *Nat. Commun.*, 2023, **14**, 2278.
4. Y. Xu, R. Zhang, J. Qian, H. Wang, P. Wang and S. Ye, *Mater. Des.*, 2018, **149**, 81-86.