Supporting Information

Rapid Synthesis of Ultrathin 2D Materials Through Liquid-Nitrogen

and Microwave Treatments

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S1. Materials and Methods: Materials

Commercially available *h*-BN (average 45 μ m, 99.5%) and flake graphite (~325 mesh, 99.999%) were purchased from Sigma-Aldrich. Tin powder, iodine, and red phosphorus were purchased from Sinopharm Chemical Reagent Co.,Ltd. All solvents were purchased from Aldrich and used as supplied without purification. All materials were used as supplied.

Bulk g-C₃N₄ powder was self-prepared by using a muffle furnace¹. A porcelain crucible containing 2 g melamine was calcined at 550 °C for 4 h with 2 °C/min heating rate in the center of the furnace. The obtained bulk g-C₃N₄ was brilliant yellow. Bulk black phosphorus (BP) was self-synthesized² *via* tin powder (1,000 mg), iodine (100 mg), and red phosphorus (500 mg) in a silica glass ampoule of 100 mm length, an inner diameter of 8 mm and a wall thickness of 1 mm. The mixture was heated from room temperature to 600°C in 7 h, and then kept for 5-10 h at 600°C. Finally, sub-4 millimeter-sized bulk BP single crystals were obtained.

S2. Materials and Methods: Methods

Microwave exfoliation process. The microwave exfoliation mainly includes the following two steps, first, soaking the raw materials (150 mg) in liquid nitrogen for an hour by cryo-pretreatment; second, transferring the bulk materials to a flask (100 ml) containing 50 ml of organic solvent with initial concentration of 3 mg/ml, followed by microwave circumfluence (Midea microwave oven, 1,000 W) for 15 min at the power of 700 W in condensed water. The organic solvents including N, N-Dimethyl Formamide (DMF), Methyl-2-Pyrrolidone (NMP), Diethyl Ether (DEE), 2-Propanol (IPA), CCl₄, Cyclohexane, Anisole, H₂O, IPA/H₂O=1:1 (the volume ratio of IPA to H₂O is 1:1) and so on.

The resultant dispersion was then purified by centrifugation. Briefly, the mixtures were centrifuged in 50-milliliter tapered plastic centrifuge tube at 3,500 r.p.m. for 10

min. The top two-thirds of the solution were extracted with a pipette for further use. The absorbance of exfoliated 2D g-C₃N₄, graphene, 2D BN and 2D BP was taken at 410 nm, 660 nm, 350 nm and 450 nm.

AFM samples were prepared on mica substrate. Free-standing film of dispersed exfoliated 2D materials was diluted and then spin coated onto the freshly cleaved mica wafer substrate. The as-centrifuged dispersions were dropcasted on holey carbon grids for TEM and HR-TEM characterization. The samples were prepared by drop-casting the dispersions onto Si substrate for SEM, XRD, Raman and contact angle experiments. And the above obtained substrates were treated in oven vacuum at 60 °C for 12 h to completely eliminate the effect of the solvent. For the SEM, AFM, TEM, XRD, Raman, the used solvent for 2D g-C₃N₄, graphene, 2D BN and 2D BP is water/IPA mixture (water: IPA=1:1).

S3 Materials and Methods: Equipment

The structure and morphology of the materials were performed by AFM (Digital Instrument Nanoscope IIIA), SEM (JEOL JSM-7001F), TEM and HR-TEM (FEI Tecnai F20), XRD (Bruker D8 X-ray scattering systems with Ni-filtered Cu K α radiation), Raman spectra (Thermo Fisher DXR, laser wavelength 532 nm), and UV-vis (Shimadzu UV-2450).

The photocatalytic hydrogen production was carried out in a 300 mL Pyrex reactor based on an online system (Labsolar-6A, PerfectLight, Beijing) as shown in **Figure S10**. The photocatalysts (0.01 g) were added into aqueous solution (90 mL water and 10 mL triethanolamine as hole sacrificial). Co-catalysts Pt were added by in-situ photodeposition method. A 3 wt % (respect to Pt) H₂PtCl₆· 6H₂O solution was added; the above system is first degased and then irradiated by a 300 W Xenon lamp (PLS-SXE 300C (BF), PerfectLight, Beijing). The photocatalytic H₂ evolution efficiency was calculated using an online gas chromatograph (GC D7900P, TCD detector). The oils absorption tests were as follows: Three different kinds of oils with different densities, including lubricating oil, crude oil and engine oil, were tested in this study. The capacity is assessed by measuring the mass of the dry obtained graphene and the mass oil contained, and then the ratio is obtained (W (wt/wt)%, the latter to the former). The samples were left in the oils for overnight to ensure full saturation before weighing. The weight measurements were performed quickly to avoid volatilization of the oils. The flake graphite was also tested in the same way to certify the excellent performance of graphene. The oil absorption ability of bulk BN and 2D BN can be also determined by the above process.



Figure S1. a) SEM images of bulk $g-C_3N_4$ before and b) after liquid nitrogen treatment for 1 h, N₂ adsorption-desorption isotherm and Brunauer-Emmett-Teller (BET) specific surface area of $g-C_3N_4$.



Figure S2. The yield of 2D g-C₃N₄ by (Condition 2) cryo-assisted microwave exfoliation, (Condition 1) microwave pulses treatment and (Condition 0) freezing treatment. The corresponding photographs of 2D g-C₃N₄ in the isopropanol/water (IPA/H₂O, volume ratio 1:1) solvent are provided.

2D materials	Methods	Processing time	Solvent	Yield	Ref. ^{1,} 3-7
g-C3N4, graphene, BN and BP	Microwave exfoliation	5~30 min	IPA etc.	3 wt%	This Work
Graphene	Sonication exfoliation	30 minutes	NMP	~1 wt%	[3]
MoS_2	Reflux pretreatment-mediated sonication approach	4 h	IPA, H ₂ O	1.5 wt%	[4]
MoS_2	Cryo-mediated sonication exfoliation	4 h	IPA/H2O =1:1	~1 wt %	[5]
Graphene	Evaporated exfoliation	~1 h	Tetrahydrofuran	4 wt%	[6]
Graphene	Shear exfoliation	20-75 min	NMP	<0.1 wt%	[7]
g-C ₃ N ₄	Thermal exfoliation	1 h	Air	~3 wt%	[1]

Fable S1.	Yield	of exfo	liation of	two-	dimensional	materials
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Figure S3. a) AFM images of the g-C₃N₄ by microwave pulses for 0 min, b) 5 min and c) 30 min after freezing treatment in the IPA/H₂O= 1:1 solvent, respectively. Insets are statistical analysis of the g-C₃N₄ thickness distribution by corresponding AFM image.



Figure S4. a) SEM images of 2D g-C₃N₄, b) graphene, c) 2D BN and d) 2D BP,

respectively.



Figure S5. a-b) XRD patterns of graphene and BP, c-d) Raman spectra of g-C₃N₄ and BN.



Figure S6. Typical contact angle images of bulk $g-C_3N_4$ with 7 different solvents. (a) H_2O , (b) IPA: $H_2O=1:1$, (c) IPA, (d) DMF, (e) NMP, (f) DEE, (g) CCl₄.



Figure S7. Typical contact angle images of flake graphite with 7 different solvents. (a) H₂O, (b) IPA: H₂O=1:1, (c) IPA, (d) DMF, (e) NMP, (f) DEE, (g) CCl₄.

Solvent	Surface tension	Polar component	Dispersive component	Polar/dispersive ratio
H ₂ O	72.75	50.65	22.10	2.29
IPA/H ₂ O=1:1	25.13	8.17	16.96	0.48
N,N-Dimethyl Formamide (DMF)	36.50	11.30	25.20	0.45
Methyl-2-Pyrrolidone (NMP)	40.79	11.58	29.21	0.40
Diethyl Ether (DEE)	18.92	2.90	16.02	0.18
2-Propanol (IPA)	23.00	3.50	19.50	0.18
CCl ₄	29.49	1.60	27.89	0.06
Cyclohexane	24.95	0.00	24.95	0.00
Anisole	33.97	/	/	/

Table S2. Total surface tension and surface tension components of the solvents



Figure S8. The average thickness of 2D g-C₃N₄ exfoliated in different solvents with varied (a) polar/dispersive ratio and (b) surface tension.



Figure S9. AFM images of graphene as-exfoliated in different solvents. (a) NMP, (b)

IPA.



Figure S10. Photo of photocatalytic reaction equipment.



Figure S11. Wavelength dependent quantum efficiency of 2D BP.



Figure S12. N₂ adsorption-desorption isotherm and Brunauer-Emmett-Teller (BET) specific surface area of (a) g-C₃N₄, (b) BN, (c)graphene and (d) BP. The 2D g-C₃N₄, 2D BN, graphene and 2D BP materials exhibit a BET specific surface area of 181.6, 211.4, 142.5 and 119.7 m²g⁻¹, which is larger than that of bulk g-C₃N₄, bulk BN, flake graphite and bulk BP (16.4, 23.5, 3.7 and 7.2 m²g⁻¹), respectively.

References

- 1. X. She, J. Wu, J. Zhong, H. Xu, Y. Yang, R. Vajtai, J. Lou, Y. Liu, D. Du, H. Li and P. M. Ajayan, *Nano Energy*, 2016, **27**, 138-146.
- 2. M. Köpf, N. Eckstein, D. Pfister, C. Grotz, I. Krüger, M. Greiwe, T. Hansen, H. Kohlmann and T. Nilges, *J. Cryst. Growth*, 2014, **405**, 6-10.
- Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, 3, 563-568.
- Y. Liu, C. Liang, J. Wu, S. J. Varma, Y. Nakanishi, A. Aliyan, A. A. Martí, Y. Wang, B. Xie, J. Kumar, K. Layne, N. Chopra, I. Odeh, R. Vajtai, J. Thomas, X. Peng, W. Yang and P. M. Ajayan, *Materials Today*, 2018, DOI: 10.1016/j.mattod.2018.06.007.
- 5. Y. Wang, Y. Liu, J. Zhang, J. Wu, H. Xu, X. Wen, X. Zhang, C. S. Tiwary, W. Yang, R. Vajtai, Y. Zhang, N. Chopra, I. N. Odeh, Y. Wu and P. M. Ajayan, *Sci. Adv.*, 2017, **3**, e1701500.
- 6. G. Bepete, E. Anglaret, L. Ortolani, V. Morandi, K. Huang, A. Penicaud and C. Drummond, *Nat. Chem.*, 2017, **9**, 347-352.
- K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O'Brien, E. K. McGuire, B. M. Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi and J. N. Coleman, *Nat. Mater.*, 2014, 13, 624-630.