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Supporting Information

New Solvent-Stabilized Few-Layer Black Phosphorus for Antibacterial Applications

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Experimental

Materials

All chemicals used in this work were of analytical grade and used as supplied. All solvents were purchased from Aladdin Reagents unless otherwise specified. *N*,*N*′-dimethylpropyleneurea (DMPU, Energy Chemical, product number: W610006), *N*-cyclohexyl-2-pyrrolidone (CHP, Sigma Aldrich, product number: 232254), N-methyl-2-pyrrolidone (NMP, product number: M100588), isopropanol (IPA, product number: I112012), dimethylformamide (DMF, product number: D111999), 1,3-dimethyl-2-imidazolidinone (DMI, product number: D109179), levulinic acid (LA, product number: L104281), propylene carbonate (PC, product number: P105723), dimethylsulfoxide (DMSO, product number: D103273), ethanol (product number: E130059), tetrahydrofuran (THF, product number: T103260), acetone (product number: A112150), toluene (product number: T112180), hexane (product number: H109654). All solvents were degassed under high-purity nitrogen prior to use, and then transferred to the glovebox. BP crystal (> 99.998%) was obtained from Nanjing MKNANO Tech Co., Ltd. (www.mukenanao.com), People's Republic of China.

Exfoliation and dispersion of BP nanosheets in DMPU, propylene carbonate (PC), levulinic acid (LA) and other best reported solvents

Typically, phosphorene dispersions were prepared by adding bulk BP to a solvent (5 mL in a 50 mL round-bottom flask) in a glove box. The dispersions were subjected to ultrasonication using a bath sonicator (KQ-400KDE, Kunshan Ultrasonic instrument Co., Ltd., Jiangsu, China; 400 W, 40 kHz). The samples were subsequently centrifuged in a glove box to remove any poorly dispersed BP material. The top two-thirds of the dispersions were gently extracted by pipetting after centrifugation. For better reproducibility, the water level, the exact position of flasks, the bath temperature, and the volume of dispersions were ensured to be similar as possible during each preparation. UV-vis absorbance spectroscopy was employed to determine the concentration after CF, C_{BP}. For kinetic experiments, phosphorene dispersions were prepared by adding bulk BP to 60 mL of DMPU at $C_{\mathrm{I}} = 1$ mg mL^{-1} in a 100 mL round-bottom flask in a glove box.

Antibacterial test in LB-agar coated plates

We tested the antibacterial activities of BP and other two-dimension materials by using a LB-agar coated plate counting method. One mL of *E. coli* (or *S. aureas*) with OD value of 0.8~1.0 was added into a 2 mL sterile centrifuge tube. The supernatant was separated from the tube by centrifugation at 8000 rpm for 3 min. One mL of a candidate material (160 μg mL^{-1}) was added into the supernatant, which was then subjected to submerged cultivation at 37 °C, 200 rpm, 30 min. The resulting bacteria samples were diluted to 10^{-5} level, which were then used to coat LB-agar plate, and subjected to cultivation at 37 °C for 16 h. The number of colonies was determined by using a cell counter. *E. coli* (or *S. aureas*) was treated with two-dimension materials (160 μg mL^{-1}) at 37 °C for 4 h on a shaking bed (200 rpm). These materials-treated bacterial samples were fixed with 2.5% glutaraldehyde and 30, 50, 70, 80, 90, 95, and 100% (v1/v2, in water) ethanol dehydration for SEM observation.

In vitro cytotoxicity assay

The cytotoxicity of BP nanosheets was evaluated by MTT cytotoxicity assays with HeLa cells. HeLa cells were seeded in 96-well plates at a density of 1×10^4 cells/well for 24 h (37 °C, 5% CO_2) to allow cells attachment. And the cells were incubated with different concentrations of BP in standard cell media. The cell viability of HeLa was analyzed using MTT cytotoxicity assays and read at OD 490 nm with a spectramax microwell plate reader.

Characterization

Scanning electron microscopy (SEM) was performed using a field emission microscope (FEI Quanta 600 FEG) operated at 20 kV and equipped with an energy-dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) was conducted using an aberration corrected transmission electron microscope (JEOL 2200) with 80 kV accelerating voltage. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were obtained by a JEOL JEM-ARM 200F microscope incorporated with a spherical aberration correction system for STEM. Energy-dispersive X-ray spectroscopy (EDX) mapping was performed using a 100 mm2 JEOL Centurio SDD EDX detector. (S)TEM samples were prepared by depositing a droplet of suspension onto a Cu grid coated with a lacey carbon film. Atomic force microscopy (AFM) images were obtained on a system (NT-MDT) in tapping mode at room temperature. To alleviate the problems associated with deposition of nanosheets onto substrates from high-boiling point solvents, the BP in DMPU was transferred to ethanol before drop casting the samples. Optical absorption spectra were measured using a PERSEE UV-vis spectrophotometer. X-ray photoelectron spectra (XPS) were carried out on a K-Alpha spectrometer (Thermo Fisher Scientific Inc., Switzerland) equipped with a monochromatic Al Kα source operated at 150 W. Raman spectroscopy was used to assess possible oxidation of BP nanosheets. Raman spectra of BP samples deposited on 300 nm thick SiO_2/Si substrates were collected with a Renishaw in Via Raman microscope with a He/Ne Laser excitation at 532 nm.

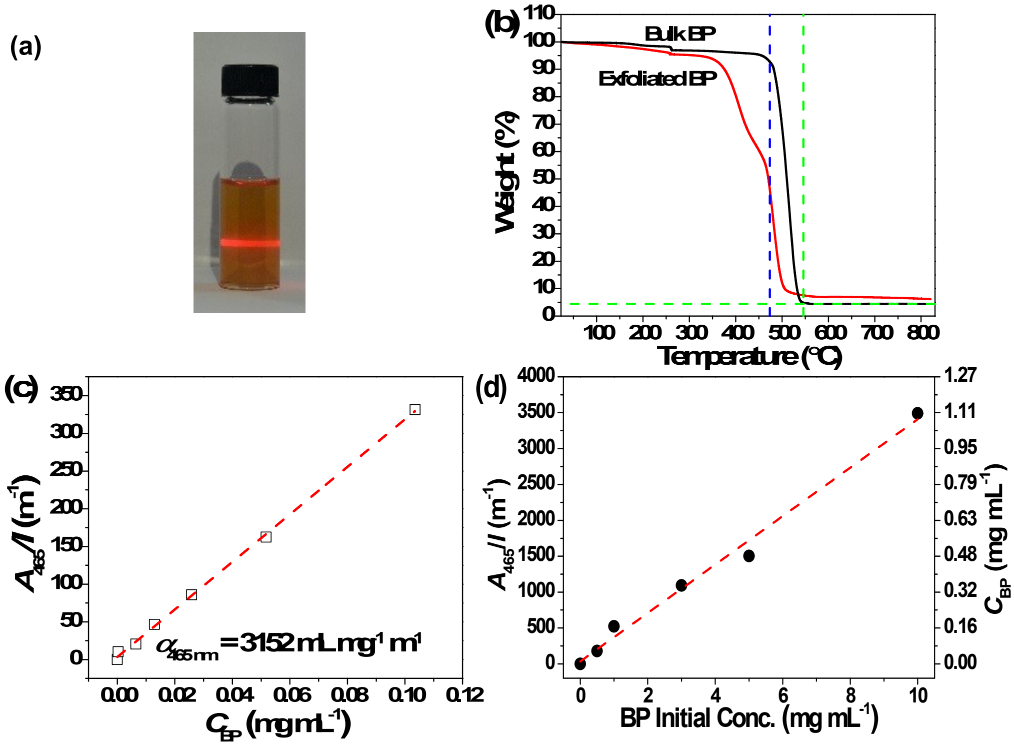

Figure S1. (a) Photograph of a phosphorene dispersion in DMPU. The Tyndall effect of the dispersion confirms its colloidal nature. (b) TGA thermograms for bulk and exfoliated BP obtained with a ramp rate of 10 °C min^{-1} in N_2 in both cases. (c) A_{465}/l versus C_{BP}. A straight line fit through the points gave the absorption coefficient at 465 nm of α = 3152 mL mg^{-1} m^{-1} (31.52 cm^2 mg^{-1}). (d) A_{465}/l and C_{BP} versus BP initial concentration.

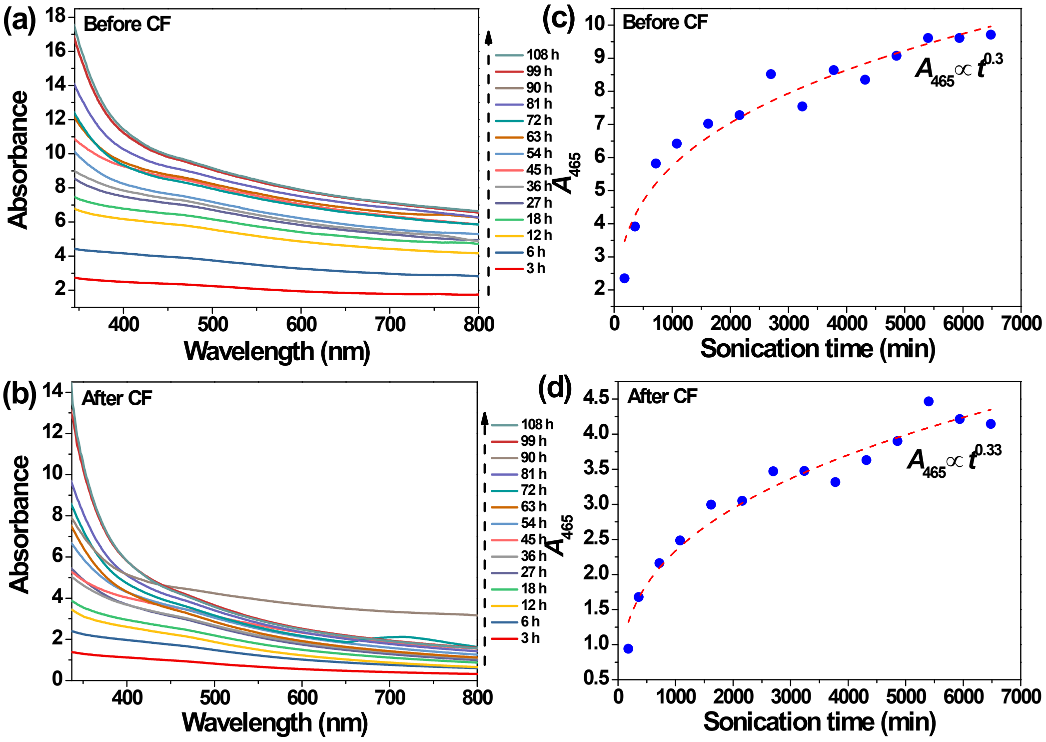

Figure S2. UV/visible spectra of phosphorene dispersions in DMPU as a function of sonication time: (a) before CF and (b) after CF. OD_{eff} values are apparent optical densities obtained by measuring dilutions of dispersions (so that) and then multiplying measured spectra by dilution factor. Optical densities at 465 nm measured as a function of sonication time: (c) before CF and (d) after CF. Dispersions had a total phosphorene concentration $C_I = 1$ mg mL^{-1}. The dashed lines in graphs a and b are the fitting results, which show power law behaviours.

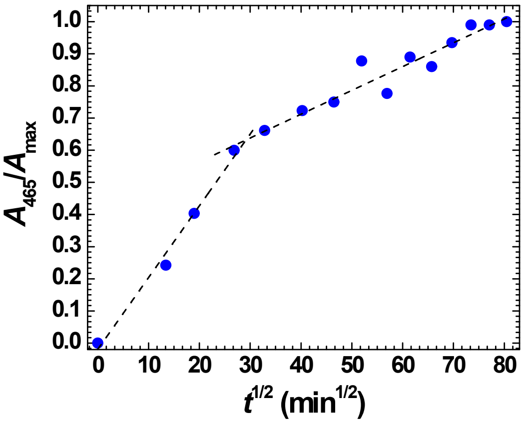

Figure S3. Diffusion scaling analysis of experimental absorbance data.

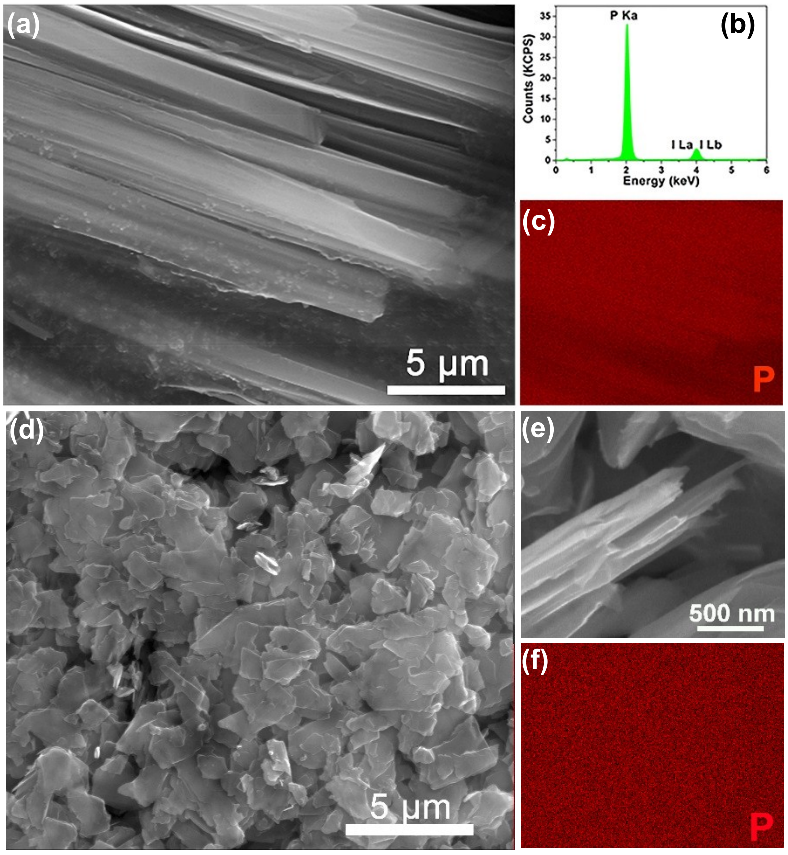

Figure S4. (a) SEM image and (b) EDX pattern of bulk BP crystals, the element I is from raw materials introduced during preparation. (c) EDX mapping image of P taken from the region shown in (a). (d) Low- and (e) high-magnification SEM images of exfoliated BP nanosheets in DMPU. (f) EDX mapping image of P taken from the area shown in (d).

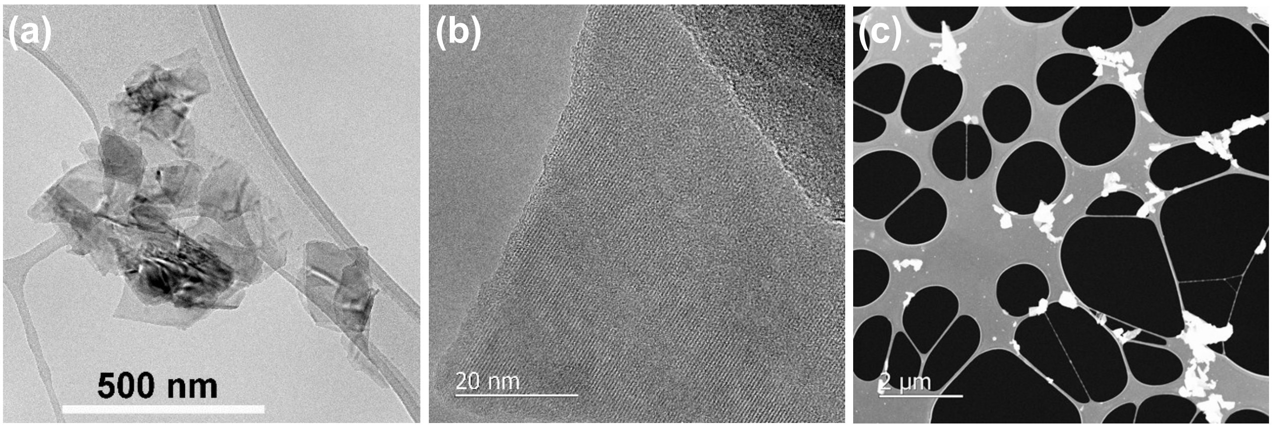

Figure S5. (a) Typical low- and (b) high-magnification TEM, and (c) HAADF-STEM images of exfoliated BP nanosheets in DMPU.

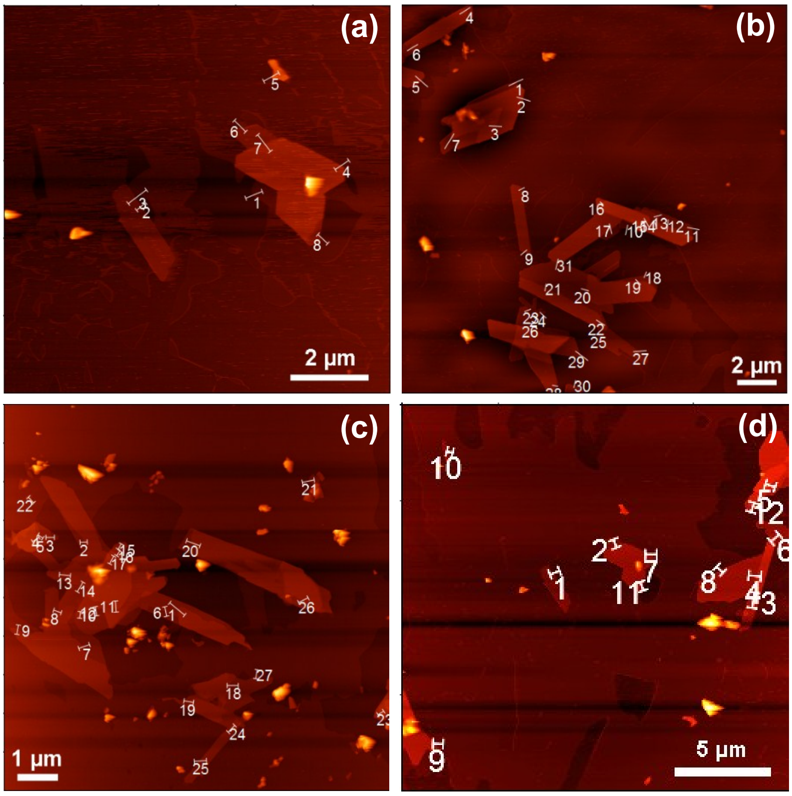

Figure S6. (a)-(d) Tapping mode AFM images of phosphorene dispersions (initial BP concentration C_I = 1 mg mL^{-1}; t_{sonic} = 3 h; CF: 3000 rpm, 30 min) deposited on 300 nm thick SiO$_2$/Si wafers. Thickness distribution was derived from AFM counting of 122 different flakes shown in (a)-(d), using a Gwyddion software.

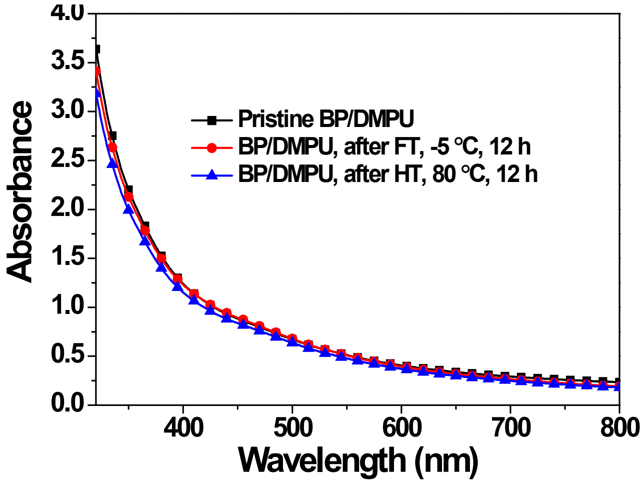

Figure S7. Absorbance spectra of phosphorene dispersions before and after freezing

(-5 °C) and heat treatment (80 °C) for 12 h.

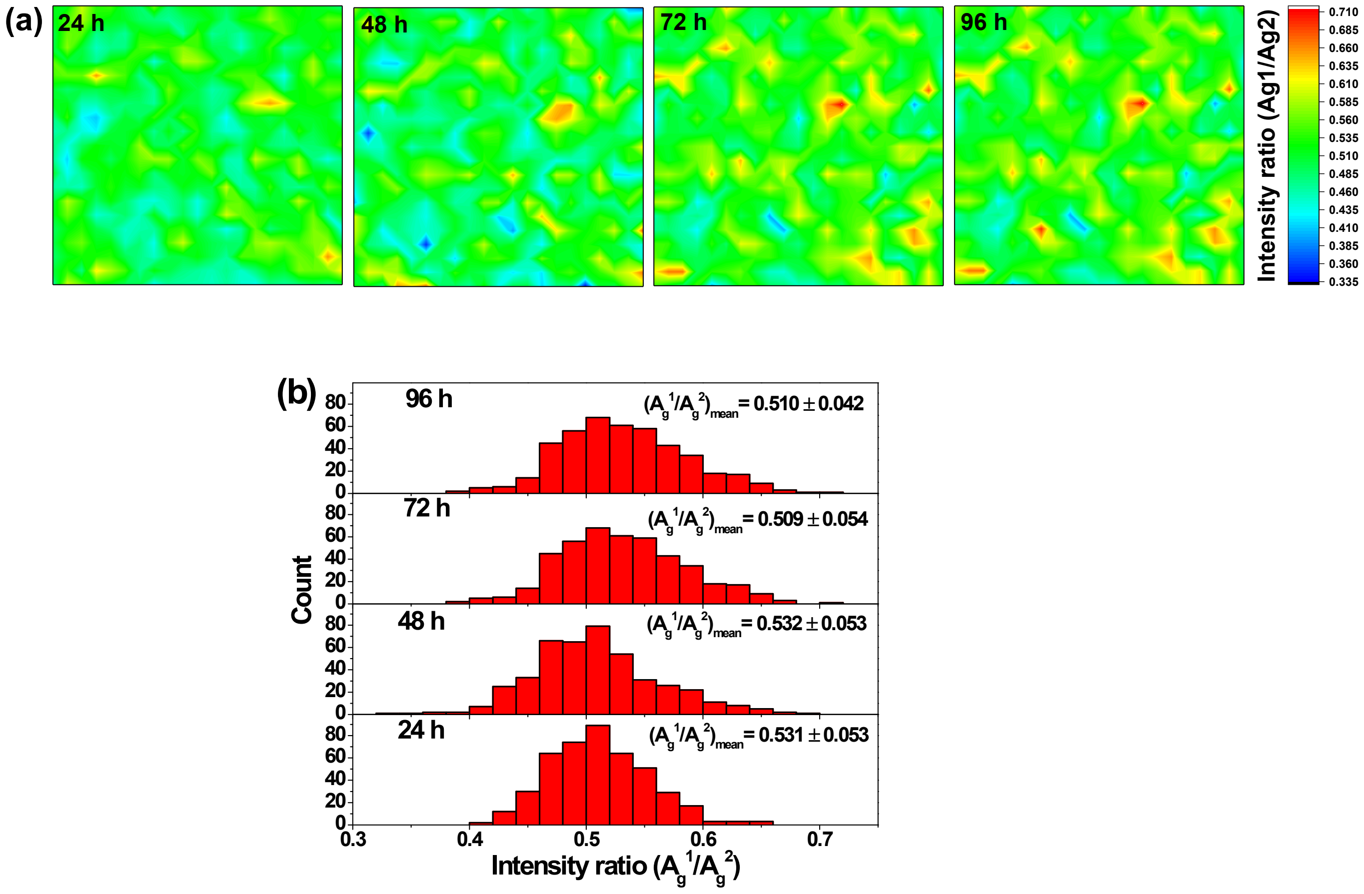

Figure S8. (a) Raman maps and (b) histograms of A_g^1/A_g^2 intensity ratios for DMPU exfoliated BP nanosheets after exposure to air for 24, 48, 72, and 96 h.

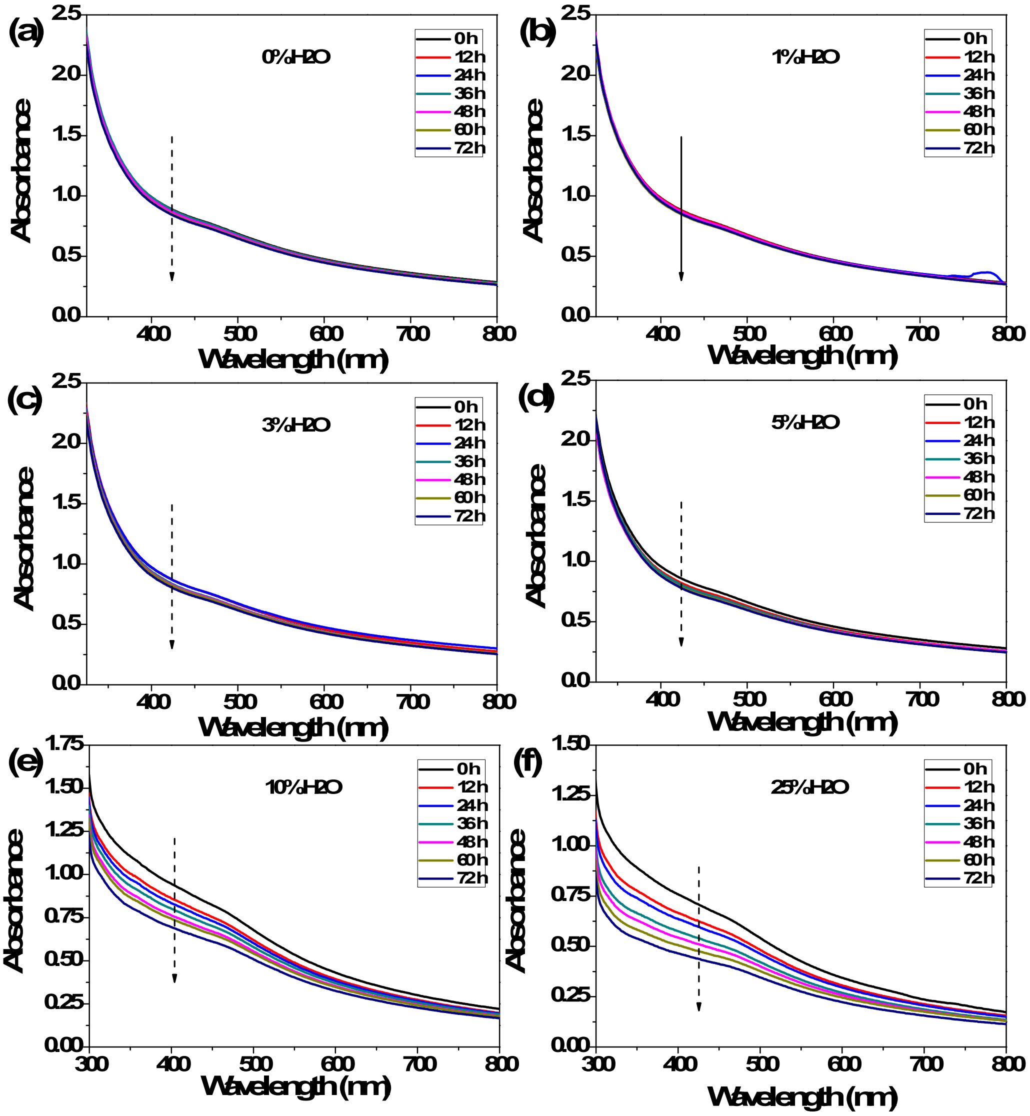

Figure S9. UV-vis optical absorption spectra of phosphorene dispersions in DMPU (C_I = 1 mg mL^{-1}; t_{sonic} = 3 h; CF: 3000 rpm, 30 min) as a function of time with addition of 0 vol.%, 1 vol.%, 3 vol.%, 5 vol.%, 10 vol.%, and 25 vol.% H_2O.

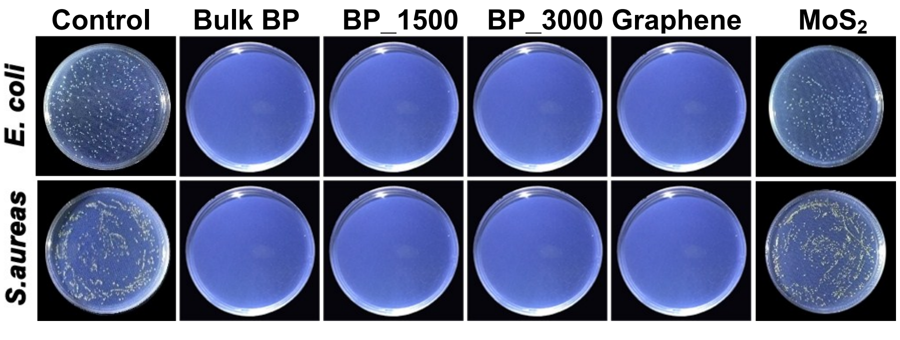

Figure S10. Photographs of bacterial colonies of *E. coli* (top panel) and *S. aureas* (bottom panel) on the agar plates with bulk BP, BP_1500 and BP_3000 nanosheets, graphene, and 2D MoS_2 after irradiation for 10 min.

Table S1. Comparison of BP dispersions stabilized by solvents, surfactants, polymer, ionic liquids and other additives.

Dispersion		Exfoliation condition	Concentration (mg mL^{-1})	Dimension	Chemical stability	Ref.
Solvent	*N*-methyl-2-pyrrolidone (NMP)	C_I: 5 mg mL^{-1}; bath ultrasonication: 820 W, 37 kHz, 24 h; CF: 1500 rpm, 45 min	N/A	Thickness: 3.5-5 nm Lateral size: ~100 nm	N/A	[1]
		C_I: 5 mg mL^{-1}; bath ultrasonication: 400 W, 48 h; CF: 1000-4000 rpm, 60 min	N/A	N/A	N/A	[2]
		C_I: 1 mg mL^{-1}; tip ultrasonication: 30 W, 1 h; CF: 500-15000 rpm, 10 min	~0.4	Thickness: 16-128 nm	Relatively stable after 7 d of ambient exposure	[3]
		C_I: 1 mg mL^{-1}; bath	N/A	Thickness: ~82 nm (3000 rpm); ~44 nm	N/A	[4]

		ultrasonication: 110 W, 40 kHz, 8 h; CF: 3000 rpm, 10 min, then 5000 rpm, 10000 rpm, 15 min		(3000-5000 rpm); ~3 nm (10000 rpm) Lateral size: few micrometers (3000 rpm); ~500 nm (3000-5000 rpm); ~200 nm (10000 rpm)		
		C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h;CF: 3000 g, 30 min	~0.044 ± 0.011	N/A		
	Cyclopentanone	C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.037 ± 0.017	N/A	N/A	
	1-Cyclohexyl-2-pyrrolidone (CHP)	C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g,	~0.025 ± 0.007	N/A	N/A	

		30 min				
		C_{I}: 2 mg mL^{-1}; tip ultrasonication: 750 W, 60% amplitude, 5 h; CF: 1000 rpm, 30 min	1	Thickness: ≤10 layers (~70%) Lateral size: 100 nm–3 mm	Partial degradation (<15%)	[5]
	1-Dodecyl-2-pyrrolidinone (N12P)	C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.022 ± 0.006	N/A	N/A	[6]
	Benzyl benzoate	C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.032 ± 0.017	N/A	N/A	[6]
	1-Octyl-2-pyrrolidone (N8P)	C_{I}: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g,	~0.037 ± 0.015	N/A	N/A	[6]

		30 min				
	1-Vinyl-2-pyrrolidinone (NVP)	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.062 ± 0.021	N/A	N/A	[6]
	Benzyl ether	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.003 ± 0.004	N/A	N/A	[6]
	1,3-Dimethyl-2-imidazolidinone	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.066 ± 0.01	N/A	N/A	[6]
	Cyclohexanone	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.003 ± 0.002	N/A	N/A	[6]

	Chlorobenzene	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.0008 ± 0.001	N/A	N/A	[6]
	Dimethylsulfoxide (DMSO)	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.029 ± 0.002	N/A	N/A	[6]
		C_I: 0.2 mg mL^{-1}; bath ultrasonication: 130 W, 15 h; CF: 200 rpm, 30 min	~0.01	Thickness: 15-20 nm Lateral size: ~532 nm	N/A	[7]
	Benzonitrile	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.11 ± 0.017	N/A	N/A	[6]
	N-methylformamide	C_I: 0.5 mg mL^{-1}; bath	~0.051 ± 0.018	N/A	N/A	[6]

		ultrasonication: 13 h; CF: 3000 g, 30 min				
	Dimethylformamide (DMF)	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.041 ± 0.005	N/A	N/A	[6]
		C_I: 0.2 mg mL^{-1}; bath ultrasonication: 130 W, 15 h; CF: 200 rpm, 30 min	~0.01	Thickness: < 5 nm (>20%) Lateral size: ~190 nm	N/A	[7]
	Benzaldehyde	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g, 30 min	~0.016 ± 0.014	N/A	N/A	[6]
	Isopropanol (IPA)	C_I: 0.5 mg mL^{-1}; bath ultrasonication: 13 h; CF: 3000 g,	~0.039 ± 0.008	Thickness: monolayers (~45%) Lateral size: 0.05-3 μm	~5% of the phosphorus was oxidized by exposure to light	[6]

		30 min			(λ = 460 nm) and oxygen with some water	
		C_I: 5 mg mL^{-1}; bath ultrasonication: 400 W, 48 h; CF: 1000-4000 rpm, 60 min	N/A	Thickness: 1-21 nm Lateral size: 50-200 nm	N/A	[2]
		C_I: 1 mg mL^{-1}; bath ultrasonication: 300 W, 10 h; CF: 2000 rpm, 60 min	0.034	Thickness: ~3 nm Lateral size: < 1 μm	Relatively stable after 3 months of ambient exposure	[8]
	Acetone	C_I: 5 mg mL^{-1}; bath ultrasonication: 400 W, 48 h; CF: 1000-4000 rpm, 60 min	N/A	N/A	N/A	[2]
		C_I: 1 mg mL^{-1}; ultrasonication:	N/A	Thickness: < 100 nm	N/A	[9]

		300 W, 10 h; CF: 2000 rpm, 60 min				
	Ethanol	C_I: 2.5 mg mL^{-1}; bath ultrasonication: 400 W, 48 h; CF: 1000-4000 rpm, 60 min	N/A	Thickness: 1-21 nm Lateral size: 50-200 nm	N/A	[2]
	γ-butyrolactone(GBL)	C_I: 1 mg mL^{-1}; bath ultrasonication: 300 W, 10 h; CF: 2000 rpm, 60 min	~0.1	Thickness: ~3 nm Lateral size: < 1 μm	Relatively stable after 3 months of ambient exposure	[8]
	Water	C_I: 1-10 mg mL^{-1}; tip ultrasonication: 95-475 W, 30-300 min; CF: 1500-5000 rpm, 30 min	~0.4	Thickness: ~9.4 nm (2500 rpm); ~5.2 nm (5000 rpm) Lateral size: ~200 nm	Weak oxidation of the BP surface in the presence of oxygen	[10]
Surfactants	SDS/water	C_I: 1 mg mL^{-1}; bath ultrasonication:	~0.4	Thickness: 4.5 nm	N/A	[12]

		70 W, 1 h; CF: 500-15000 rpm, 2 h				
Polymers	PVP/ethanol	C_{I}: 0.5-10 mg mL^{-1}; bath ultrasonication: 400 W, 40 kHz, 3 h; CF: 3000 rpm, 30 min	~0.66	Thickness: monolayer (~51%) Lateral size: 200 nm-4 μm	Relatively stable after 7 d of ambient exposure（3.9 atom%）	[13]
Ionic liquids	[BMIM][BF$_4$]	Grinding for 20 min; C_{I}: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.29	N/A	N/A	[11]
	[BMIM] [TfO]	Grinding for 20 min; C_{I}: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.22	N/A	N/A	[11]
	[BMIM] [Tf$_2$N]	Grinding for 20	0.17	N/A	N/A	[11]

		min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.				
	[EMIM] [Tf_2N]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.1	N/A	N/A	[11]
	[EMIM][BF_4]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.75	N/A	N/A	[11]
	[HMIM]) [BF_4]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF:	0.73	N/A	N/A	[11]

		4000 rpm, 45 min.				
	[OMIM] [BF_4]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.14	N/A	N/A	[11]
	[HOEMIM] [TfO]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.95	Thickness: 8-8.9 nm	N/A	[11]
	[HOEMIM] [BF_4]	Grinding for 20 min; C_I: 3 mg mL^{-1}; ice-bath ultrasonication: 100 W, 24 h; CF: 4000 rpm, 45 min.	0.91	N/A	N/A	[11]
Others	Phytic acid/DMF	C_I: 1 mg mL^{-1}; bath ultrasonication:	N/A	Thickness: ~3-4 nm Lateral size: ~4-28 μm	N/A	[14]

		50 kHz, 8 h; CF: 2000 rpm, 5 min				
	NaOH/NMP	C_{I}: 0.5 mg mL^{-1}; ultrasonication: 40 kHz, 4 h; CF: 3000 rpm, 10 min; 12000 rpm, 20 min; 18000 rpm, 20 min	N/A	Thicknesses: 5.3 ± 2.0 nm (3000 rpm); 2.8 ± 1.5 nm (18000 rpm) Lateral size: 670 nm (12000 rpm); 210 nm (18000 rpm)	N/A	[15]

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