Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Covalent functionalization of black phosphorus nanoflakes by carbon free radicals for durable air and water stability

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1) Preparation of Bulk Black Phosphorus

Bulk black phosphorus (BP) was prepared through a facile low-pressure transport route according to the literatures.[1] In detail, 500 mg of red phosphorus, 20 mg of tin, and 10 mg of SnI_4 were sealed in a quartz ampoule of 10 cm length, an inner diameter of 1.00 cm and a wall thickness of 0.25 cm. The tube was evacuated and placed horizontally, with the starting materials mixture located at the hot end and the empty ampoule side towards the colder middle section of a SA2-6-12TP muffle furnace. The tube was heated at 650 °C for 5 h with a heating ramp rate of about 1.35 °C per min and then the temperature was reduced to 500 °C with a cooling rate of 0.33 °C per min, followed with a natural cooling process. The product was collected and washed with hot toluene and acetone for several times to remove the residual mineralizer and then kept in a glovebox for further analysis.

2) Preparation of BP nanoflakes

BP nanoflakes (BPNFs) were prepared through a liquid phase exfoliation method according to the literature.[2] In a typical experiment for the synthesis of BPNFs, 40 mg of BP powder was added into 3 mL of isopropanol (IPA) in a mortar and then ground for 20 min. The mixture was transferred to a glass vial containing 77 mL of IPA. After it was sealed carefully, the vial was sonicated in an ice-bath for 16 h at the power of 490 W. The samples were subjected to thirty-two cycles of sonication, each maintains 30 minutes. Bath water was changed after each cycle to maintain a temperature below 30 °C. Afterward, the resultant brown suspension was centrifuged at 9000 rpm for 20 min to remove the residual unexfoliated particles and the supernatant containing BPNFs was collected for further use.

3) Functionalization of BPNFs

After 80 mL of BPNFs suspension in IPA was centrifuged at 12000 rpm for 20 min, the supernatant was removed and the precipitate was redispersed in 2 mL N-methyl-2-pyrrolidone (NMP). Then, 6 mL toluene solution containing 384 mg AIBN was added to the dispersion. Subsequently, in an Ar atmosphere, the resulting dispersion was heated at 75 °C for 4 h. After completion of the reaction, the product was separated from the mixture by centrifugation, washed with acetone and IPA repeatedly and then collected and dried in vacuum.

The physical mixture sample between BFNFs and AIBN (BFNFs + AIBN) were prepared in the same way except that the heating temperature was 20 °C.

Computational Methods

All our calculations were carried out using Cambridge Serial Total Energy Package (CASTEP)[3] based on the first-principle and plane-wave ultrasoft pseudopotential method within generalized gradient approximation (GGA) together with Perdew-Burke-Ernzerhof (GGA-PBE).[4] The cut-off energy of 400 eV was applied and a single molecule bonded to the single layer BP surface. The adsorption energy per AIBN is defined as $\Delta E = E(\mathrm{AIBN/BP}) - E(\mathrm{BP}) - E(\mathrm{AIBN})$. E(AIBN/BP) is the energy of covalently bound AIBN carbon free radicals to BP, and E(BP) and E(AIBN) are the initial energies of unassociated single layer BPNFs and AIBN carbon free radicals, respectively.

Characterization

X-ray diffraction (XRD) was recorded on a Rigaku D/max-2400 diffractometer at the wavelength of Cu Kα radiation. Transmission electron microscopy (TEM) images were taken on a Tecnai G^2 Tf20 electron microscope with an acceleration voltage of 200 kV. Atomic force microscope (AFM) images were obtained by a MFP-3D system. Raman spectroscopy was performed using a Lab RAM HR 800 with 532 nm excitation laser in the air under ambient conditions. Fourier transform infrared spectroscopy (FTIR) was recorded on a NEXUS-670 FTIR spectrometer. ^{31}P high power decoupling magic angle spinning nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance 400 MHz at room temperature. Besides, the samples for this characterization were prepared in the same method except that BFNFs were obtained by the centrifugal range between 3000 and 9000 rpm. X-ray photoelectron spectroscopy (XPS) analysis was carried on PHI-5702 X-ray photoelectron spectrometer. In a glove box, the obtained nanosheets were evenly redispersed in the IPA by ultrasound, and then dripped into silicon wafers and dried in vacuum for testing. After measuring the initial spectrum, the sample were placed into a glassware with temperature was 20-25 ℃ and the relative humidity was 50-54 % for

10 days. UV-vis-NIR diffuse reflectance spectra were obtained on a Lambda 950 UV-vis/NIR spectrophotometer. Moreover, the samples were evenly redispersed in the IPA, and then dripped on conductive glass and dried in vacuum for testing. ^{31}P liquid NMR spectroscopy was routinely recorded using a JNM-ESC 400M spectrometer. The prepared samples were dispersed in D_2O of a glass vial and continued to blow oxygen during the test. The measured supernatant was obtained by centrifugation in every time. After measuring the spectrum, the solution was recycled into the glass vial. Chemical shifts were calibrated using H_3PO_4 as a standard at 0 ppm.

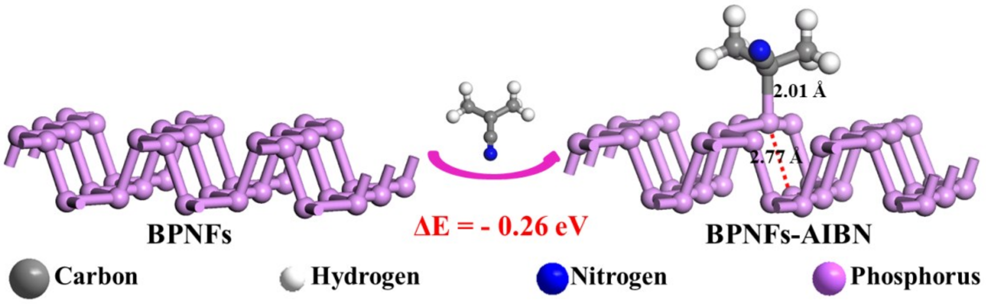

Fig. S1. The structures of single layer BPNFs and BPNFs-AIBN.

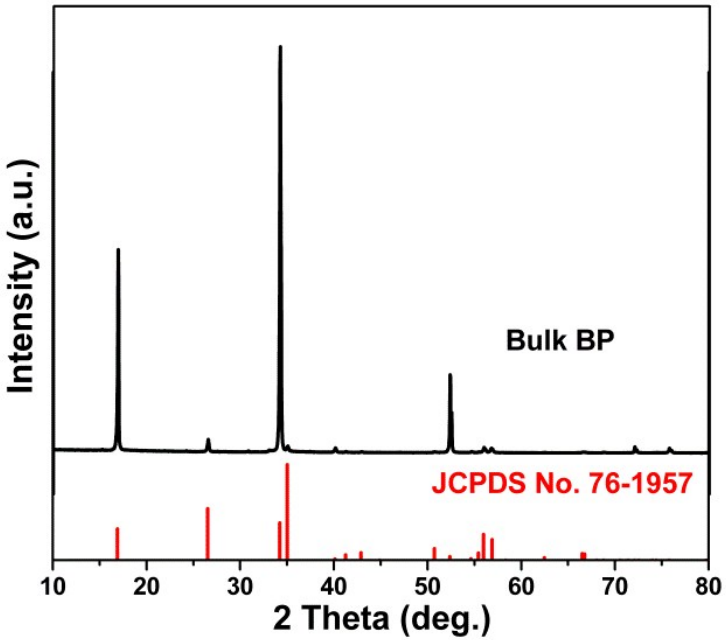

Fig. S2 XRD pattern of bulk black phosphorus.

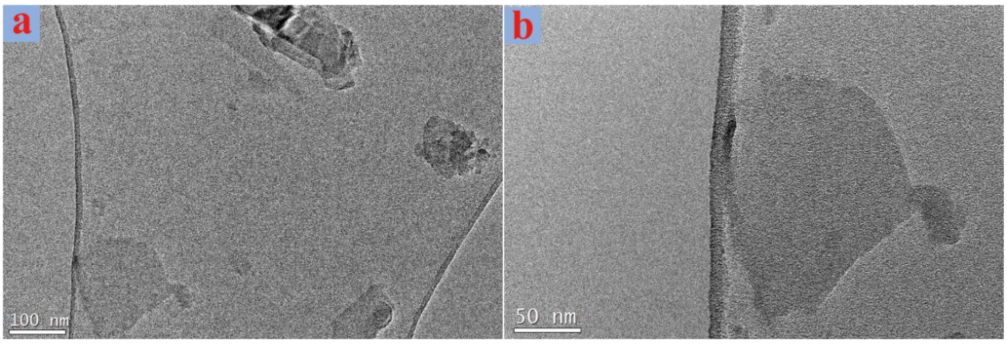

Fig. S3. TEM images of BPNFs.

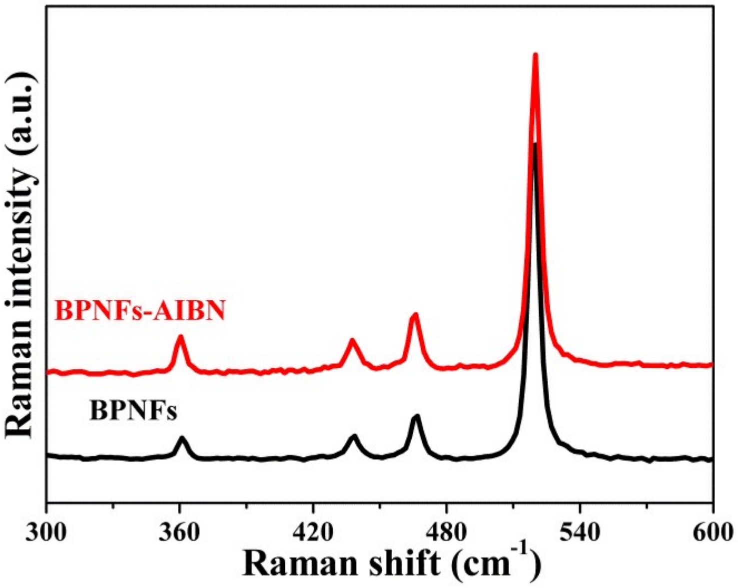

Fig. S4. Raman spectra of BPNFs and BPNFs-AIBN.

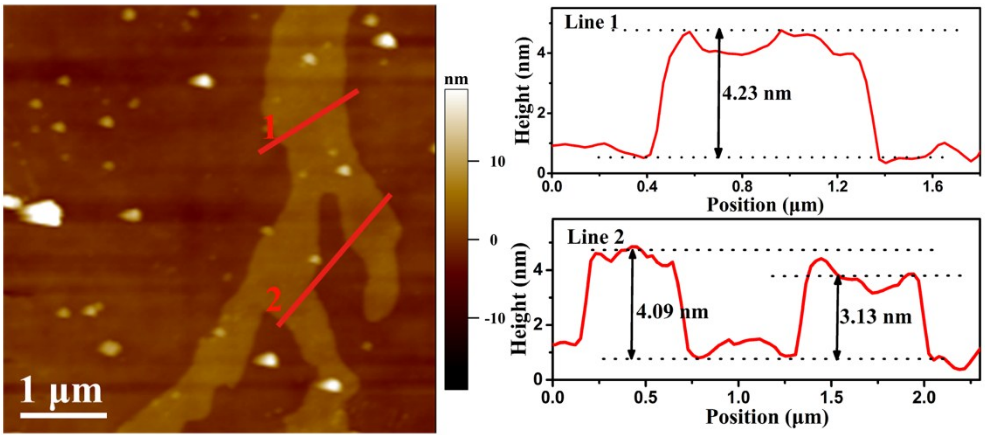

Fig. S5. AFM and corresponding height images of BPNFs

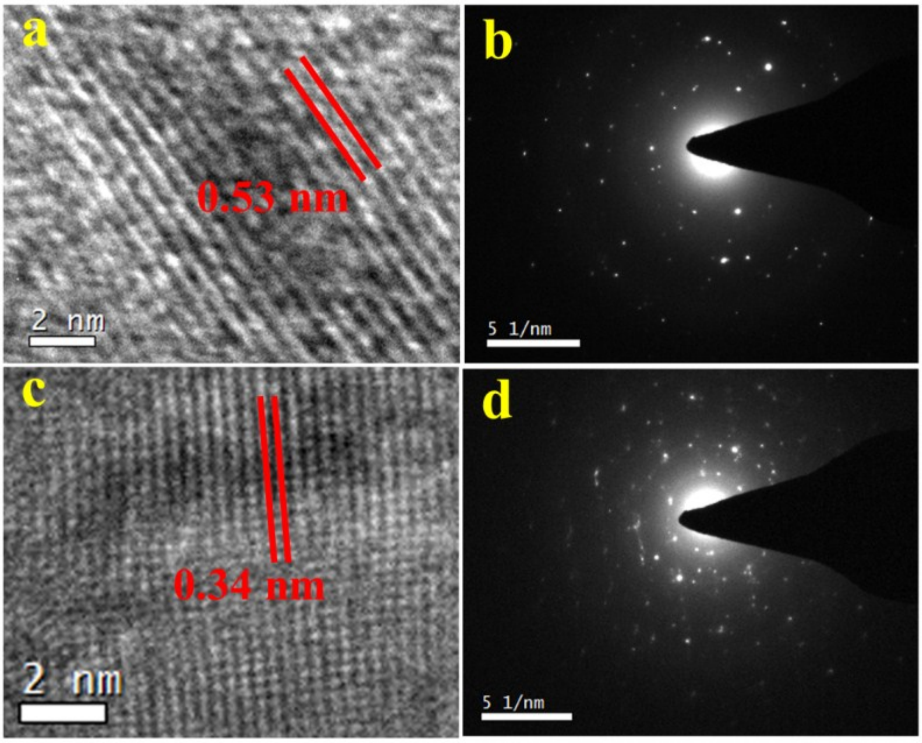

Fig. S6. (a, c) HRTEM images of BPNFs. (b, d) The corresponding SAED patterns of (a, c). The crystal plane spacing in (a, c) is 0.53 and 0.34nm corresponding to the (020) and (021) planes of the BP crystal, respectively. The HRTEM and SAED patterns revealed the single crystal structure of the BPNFs.

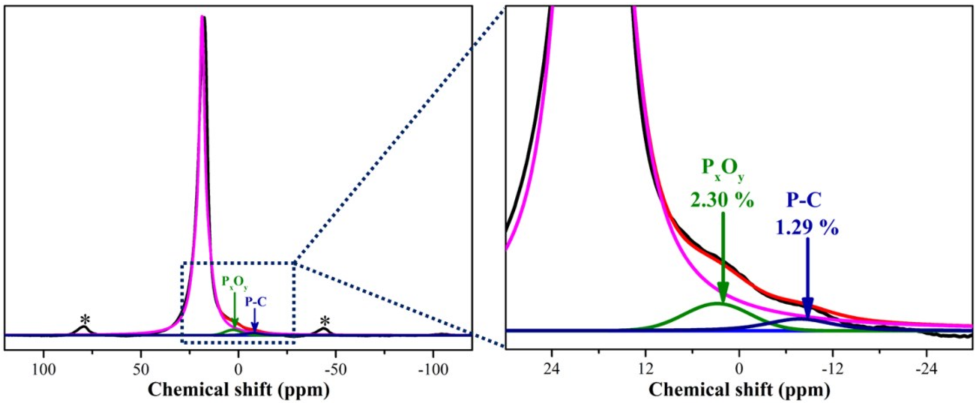

Fig. S7. ^{31}P solid-state NMR spectrum of BPNFs-AIBN. * deontes the peaks of spinning sideband.

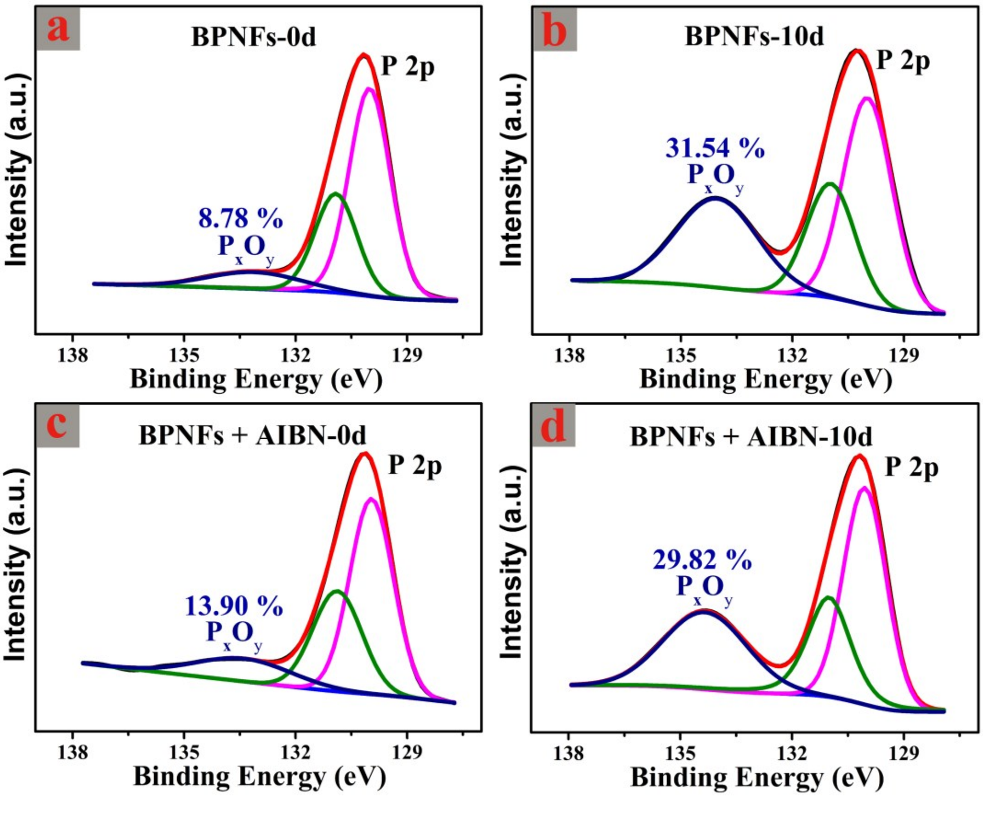

Fig. S8. XPS of BPNFs (a) freshly and (b) after 10 days, BPNFs + AIBN (c) newly and (d) after 10 days in the air.

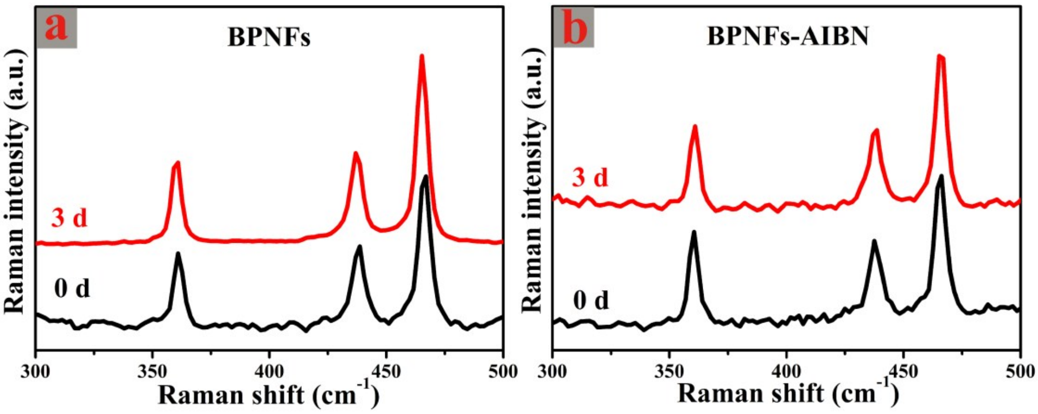

Fig. S9. Raman spectra of (a) BPNFs and (b) BPNFs-AIBN after 0 and 3 days in the air.

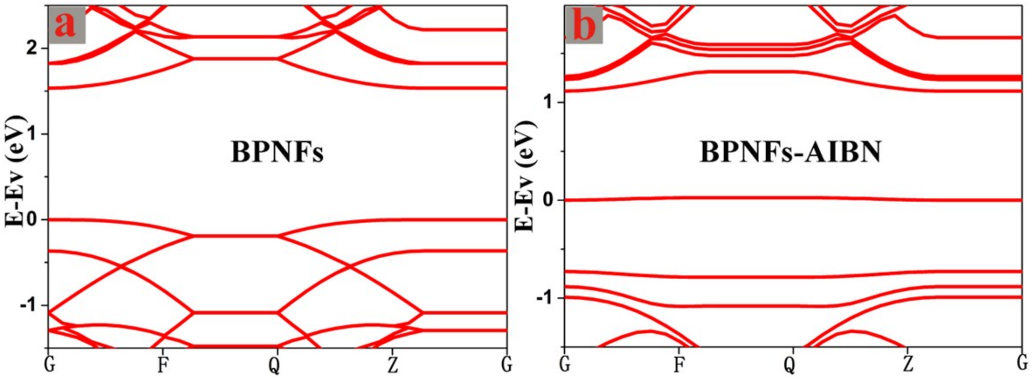

Fig. S10. Band structures of (a) BPNFs and (b) BPNFs-AIBN.

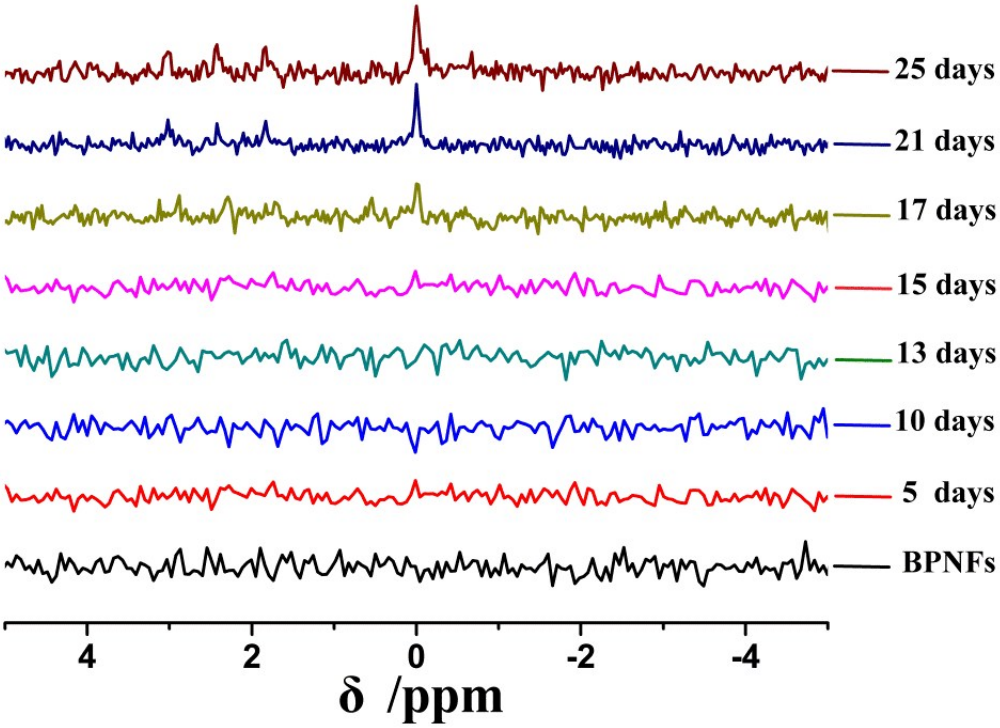

Fig. S11. Time dependence ^{31}P liquid NMR spectrum of the phosphorus species from degradation of exfoliated BPNFs in aqueous solution over a period of 25 days.

Reference:

1. (a) M. C. Stan, J. V. Zamory, S. Passerini, T. Nilges and M. Winter, *J. Mater. Chem. A*, 2013, **1**, 5293-5300; (b) 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.
2. A. H. Woomer, T. W. Farnsworth, J. Hu, R. A. Wells, C. L. Donley and S. C. Warren, *ACS Nano,* 2015, **9**, 8869-8884.
3. Clark S, Segall M D, Pickard C, Hasnip P, Probert M, Refson K and Payne M, *Z. Kristallorg.,* 2005, **220**, 567–570.
4. Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J, Payne M C, *J. Phys.: Condens. Mat.*, 2002, **14**, 2717–2744.