Electronic Supplementary Information

Negatively Charged 2D Black Phosphorus for Highly Efficient Covalent Functionalization

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1. Spectroscopic characterization



Figure S1. (a) UV-vis-NIR absorption and representative Tauc plot from the absorption curve (b) of the BP-Li nanosheets. The inset in (a) is the fitted material extinction coefficient.



Figure S2. Raman spectra of BP-Li and bulk crystalline BP. According to previous reports,¹ the thinner the BP layers, the smaller hindrance of oscillation, which can be reflected by the blue shift of Raman signal position from bulk materials to few layer 2D structure.



Figure S3. Raman and FT-IR spectra of BP-Li and BP-NO₂ (the ratios of BP and 4-NBD are 1:0.25, 1:1, 1:2 and 1:4, respectively). The peaks appearing in the 1500-1400 cm⁻¹ result from the deformation of aryl ring, while the deformation vibration of the C-H appears at 1155 cm⁻¹. The 1110 cm⁻¹ peak is attributed to the C-N vibration of the phenyl-NO₂ bond coupled with a C-H wag motion in FT-IR spectra.



Figure S4. XPS spectra of BP-NO₂ (a) and high resolution C ls spectra (b). XPS survey spectra show signals representing elements O, N, C and P in BP-NO₂ in (a). C-O, C=O and C-P peaks can be assigned in the high resolution XPS spectra of C ls in (b).



Figure S5. High resolution P 2p XPS spectra of BP-Li (a) and BP-NO₂ in different ratios (the mole ratios of BP and 4-NBD are 1:0 (a), 1:0.25 (b), 1:1 (c), 1:2 (d) and 1:4 (e), respectively).

Table S1. Summary of the percent composition of the different bonds in the samplesshown in Figure S5.

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Sample	P-P (%)	P-C (%)	P-O (%)
BP-NO ₂ (1: 0.25)	95.54	4.46	0
BP-NO ₂ (1: 1)	91.35	8.47	0.18
BP-NO ₂ (1: 2)	78.37	15.25	6.38
BP-NO ₂ (1: 4)	32.38	48.20	19.42
BP-Li	100	-	-

2. Control experiments of diazonium functionalization

The controlled experiments are described as follow: (1) Under argon atmosphere, 2.0 mL of *n*-BuLi (2.0 M) in hexane was added to 31 mg (1.0 mmol) BP powder, which had been pre-dried in a glove box at 100 °C for ca. 30 minutes. After the addition of 5 mL of dry *n*-hexane, the dispersion was heated to 75 °C overnight in a 10 mL two-neck round-bottom flask equipped with one condenser under argon atmosphere. After intercalation, a certain amount of water (~3-4 mL) was carefully added to the cooled brown suspension (Caution: hydrogen released during the process). 950 mg 4-NBD (4 mmol) was then added to the mixture. The reaction mixture was stirred for 5 h and filtered through a 0.1 µm reinforced membrane filter. Purification of the sample was performed by washing in *n*-hexane, deionized water (until pH=7), isopropanol and acetone serval times until the solvent turned into colorless. (2) BP powder was added to NMP and the sample was sonicated of 24 h in order to obtain BP nanosheets. The brown suspension was centrifuged at a rate of 2000 rpm for 10 min to remove the remaining bulk material and 15000 rpm for 20 min to collect the precipitate. Under argon atmosphere, 145 mg 4-NBD (1 mmol) was added to 8 mg (~0.25 mmol) as-prepared liquid exfoliated nanosheets suspension. The same after treatment as described in control experiment (1) was carried out. The sample is abbreviated as BP+4-NBD. (3) First, BP nanosheets sonicated from NMP was centrifuged at a rate of 2000 rpm for 10 min to remove the remaining bulk material and 15000 rpm for 20 min to collect the precipitate. Second, 8 mg (~0.25 mmol) BP nanosheets was redispersed in 5 mL acetonitrile and followed by the addition of CuI (36mg, 0.25mmol) and 4-NBD (36mg, 0.25mmol). After stirring for 5h, the mixture was filtered through a 0.1 µm membrane filter and washed with deionized water, isopropanol, and acetone for serval times. The sample is abbreviated as BP-CuI. To compare, the BP-NO₂ was synthesized and was abbreviated as control experiment (4) (n_P: n_{4-NBD}=1:1, 1:4, respectively). The reaction conditions are summarized in Table S2.

No. Producti	Production of DD nonochoots	Reaction time(h)	BP:4-NBD	Catalyst	
	Production of BP nanosneets		(in mmol)	Catalyst.	
1	Li ⁺ intercalation with water	5	1:4	no	
2	NMP sonification	5	1:4	no	
3	NMP sonification	5	1:1	CuI	
4	Li ⁺ intercalation	5	1:1/1:4	no	

Table S2. Summary of the conditions in three different control experiments and BP-NO₂



Figure S6. (a) High resolution XPS spectra of P 2p of control experiment (1) prepared by the addition of deionized water after lithium ion intercalation; (b) XPS spectra of control experiment (2) BP +4-NBD; (c) XPS spectra of control experiment (4). Notes the ratio of BP and 4-NBD are controlled the same (BP: 4-NBD=1: 4).



Figure S7. FT-IR spectra of BP+4-NBD (red line), BP-CuI (blue line) and BP-Li reacted with 4-NBD (BP-NO₂, green line and black line). The signals of the nitro group at \sim 1520cm⁻¹ and \sim 1350cm⁻¹ (grey regions) can be easily detected in BP-NO₂ while no signal appears in BP+4-NBD or BP-CuI at the same regions.

The products from these control experiments were carefully characterized by XPS (Figure S6) and FT-IR spectroscopies (Figure S7). The XPS data of control experiment (1) is presented in Figure S6a. The sample added water did not display any signal belong to phosphorus. While the XPS data of the sample produced without the involvement of water exhibits an obvious signal in binding energy between 135 eV to 128 eV, which can be ascribed to phosphorus element (Figure S6c). Therefore, no-water involving method turned out to be more viable. The absence of water was not only decisive for the subsequent reaction but also much more effective. This observation also confirmed our hypothesis that the negatively charged BP nanosheets are much easier to react with diazonium salt and the presence of water may quench the negative charges that are crucial for the diazonium addition reactions.

In the XPS spectra, the product of control experiment (2) shows two peaks around 130 eV but without the typical C-P bond at around 133 eV (Figure S6b). In addition, neither the band at ~1520cm⁻¹ nor the one at ~1350 cm⁻¹ were observed in the FT-IR spectrum, indicative of the absence of nitro groups (Figure S7). In control experiment (3), the addition of CuI is designed for a signal electron transfer (SET) to 4-NBD and might improve the reactivity of 4-NBD by forming nitro phenyl radicals. However, further FT-IR spectra (Figure S7) analysis still proved that the desired reaction failed to induce the covalent functionalization. Comparison between the results from the different reaction conditions (Table S2) indicates that all the neutral BP samples exhibited much lower reactivity to the addition of 4-NBD than that of the negatively charged BP-Li. Even in the third control reaction, which involved CuI as the catalyst to promote the radical addition reaction, the FT-IR spectra of the product showed weak signal corresponding to the attached nitrophenyl moiety on BP surface. Hence, the neutral BP nanosheets prepared by long-time sonication showed much lower reactivity in comparison with that obtained by lithium ion exfoliation, corroborating the essential role of lithium ion intercalation on the formation of negatively charged BP substrate for further reaction.

Two crucial conclusions can be drawn from the above facts. First, lithium ion exfoliation can provide negatively charged nanosheets, which improve the reactivity

of BP nanosheets compared with simply exfoliated ones. Second, the after treatment should not involve water, in order to avoid quenching of the negative charges. Therefore, the results from different reactions confirm that negatively charged BP nanosheets are essential for diazonium functionalization.

3. Material characterization



Figure S8. High resolution XPS spectra of P 2p of BP prepared via lithium ion intercalation before the processing wash (a) and after wash (b). The pink region can be ascribed to the P-O-P bonds signals.² After wash for serval times with different reagents (*n*-hexane, deionized water, isopropanol and acetone), the BP-Li only maintained the original P-P bonds in BP (pale blue regions). After washing, the P-P bonds show a slight shift (~0.14 eV) to high binding energy.^{3, 4} Moreover, the double peaks (pale yellow region) located around 129 eV appeared before washing with deionized water.

Sample	Component	Region Peak position/eV		Area/%
BP before wash (Figure S8a)	P (pale yellow)	P _{1/2 p}	129.57	3.61
		P _{3/2 p}	128.72	7.22
	P (pale blue)	P _{1/2 p}	130.17	16.92
		P 3/2 p	129.30	33.83
	P (pink)	P _{1/2 p}	131.13	12.84
		P 3/2 p	130.30	25.58
BP after wash	D (noto blue)	P 1/2 p	130.31	33.84
(Figure S8b)	r (pale blue)	P _{3/2 p}	129.44	66.16

Table S3. Summary of the binding energies of the different regions in Figure S8.



Figure S9. Raman (a) and FT-IR (b) spectra of BP-NH₂.



Figure S10. TEM images of BP-NO₂ after 200 days.

4. Z-scan test

Table S4. Comparison of the fitted nonlinear optical parameters for the BP-Li, BP-

Samples	<i>E</i> (µJ)	Т	β (m/W)	$I_S(W/m^2)$
BP-Li		0.77	-1.4×10 ⁻¹⁰	1.49×10 ¹²
BP-NO ₂	4.2	0.77	-6.9×10 ⁻¹¹	3.04×10 ¹²
BP-NH ₂		0.77	-1.9×10 ⁻¹⁰	1.00×10^{12}

 NO_2 and BP-NH₂.

The Z-scan data were fitted to the nonlinear transmission equation using a sum of two nonlinear absorptions with opposite signs:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_S} + \beta I$$
 (eq. S1)

where $\alpha(I)$ is the total nonlinear absorption coefficient, α_0 the linear absorption coefficient, β the negative nonlinear absorption coefficient, I the incident laser intensity and I_S the saturation intensity, defined as the laser intensity at which α_0 drops to 50% of its initial value. All of the samples gave large nonlinear absorption coefficient, with the numerically estimated values of β for BP-Li, BP-NO₂ and BP-NH₂ are -1.4×10⁻¹⁰, -6.9×10⁻¹¹ and -1.9×10⁻¹⁰ m/W, respectively (**Table S4**). BP-NH₂ exhibited the highest β absolute value.



Figure S11. Decay curves of BP-Li (a), BP-NO₂ (b) and BP-NH₂ (c) at 542 nm. The pump excitation is at 532 nm.

We previously proposed induced exciton bleaching led to saturable absorption of 2D BP upon laser excitation, as the material absorbed strongly at both 532 nm (2.33 eV) and 1064 nm (1.17 eV) under the long ns pulse width.⁵ The other two BP samples (BP-NO₂ and BP-NH₂) also exhibit long lifetime components on millisecond (ms), indicating that the photo-induced long-lived electron-hole pairs are delocalized within the sample domains. Such a long lifetime exciton bleaching of the three samples may contribute to their saturable absorption behavior. Interestingly, when BP was modified by either aminophenyl (-NH₂) or nitorphenyl (-NO₂), additional much shorter lifetime components (BP-NO₂: 372 µs; BP-NH₂: 396 µs) on the microsecond (µs) time scale appeared as a result of introduction of functional groups on the surface.

5. Photoluminescence lifetimes



Figure S12. Fluorescence decay of BP-Li (black) and BP-NO₂ (blue) and the exponential fits (red). The λ_{ex} of BP-Li is 330 nm, and the λ_{em} is 402 nm. The λ_{ex} of BP-NH₂ is 300 nm, and the λ_{em} is 450 nm. The λ_{ex} of BP-NO₂ is 300 nm, and the λ_{em} is 450 nm. The lifetime of BP-NH₂ (τ_1 =6.54 ns, 14.7%; τ_2 =1.49 ns, 85.3%) is longer than that of BP-Li (τ_1 =4.23 ns, 25.1%; τ_2 =1.23 ns, 74.9%), whereas the signal intensity of BP-NO₂ is too low to be recorded.

The photoluminescence (PL) lifetimes of the three samples are quite different. The BP-NH₂ (τ =2.23 ns) has a longer lifetime than BP-Li (τ =1.98 ns), whereas the signal intensity of BP-NO₂ is too low to be recorded (**Figure S12**). The presence of electron-donating or accepting groups shows great influence on their PL lifetime. Modified with electron-donating aminophenyl groups, the lifetime of BP-NH₂ is significantly lengthened compared with the unmodified nanosheets (BP-Li). Meanwhile, the aminophenyl modified BP also displayed the optimal saturable performance in the Z-scan tests. In contrast, the BP-NO₂ showing the lowest PL intensity displays the lowest saturable absorption performance among the three samples.

6. Reduction of 4-nitrophenol



Figure S13. UV–vis absorption spectra of 4-nitrophenol reduced by NaBH₄ in the presence of BP-NH₂-Au (a), BP-Au (b), and Au NPs (c) as the catalyst and no catalyst (d). (e-h) are the corresponding plots of $-\ln (A_t/A_0)$ as a function of time obtained from (a-d), respectively.

After the addition of NaBH₄, the yellow solution exhibited a clear UV–vis absorption peak at 400 nm, as the deprotonated 4-nitrophenol generated 4-nitrophenolate anion. As exhibited in **Figure S13a**, after the addition of BP-NH₂-Au, a decrease of absorption at 400 nm can be clearly observed, attributed to the reduced 4-nitrophenolate concentration. Meanwhile, a new peak at 300 nm appeared, corresponding to the formation of 4-aminophenol. As a control experiment, the time-dependent UV-vis absorption spectra were also collected without the addition of BP-NH₂-Au, shown in **Figure S13d**. In the absence of BP-NH₂-Au, the absorption of 4-nitrophenol remained unchanged and no new peak was observed. Moreover, the physical mixture of BP nanosheets with Au NPs (with the same concentration of P and Au as in BP-NH₂-Au, abbreviated as BP-Au) and Au NPs were also tested for comparison (**Figure S13b** and **S13c**). BP-NH₂-Au exhibits the optimal catalytic activity than BP-Au and Au NPs.

Taking into account that the concentration of NaBH₄ is practically a constant throughout the reaction, (in large excess high molar ratio with respect to 4-nitrophenol, 800:1; see **Synthetic Procedures**), this reaction rate (r) obeys an apparent first-order S12

reaction kinetic behavior with respect to the 4-nitrophenol concentration, which can be described by the following equation:

$$r = -\frac{dC}{dt} = kC \tag{eq. S2}$$

where C represents the concentration of the 4-nitrophenol and the coefficient k is the apparent reaction rate constant. The integrated form of the above kinetic equation is as the following:

$$-\ln\left[\frac{C}{C_0}\right] = kt$$
 (eq. S3)

where C_0 is the initial concentration of 4-nitrophenol (at t = 0 min). Based on this function, we calculated the *k* via linear fitting (**Figure S13e-f**). The apparent rate constant of BP-NH₂-Au is approximately 1.10 min⁻¹.



Figure S14. TEM images of the Au NPs (a-b), BP-Au (c-d), and BP-NH₂-Au (e-f)

before (left) and after (right) the catalytic reactions.



Figure S15. The UV-vis spectrum of BP-Au.

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