Lanthanide-Coordinated Black Phosphorus

Lie Wu, Jiahong Wang, Jiang Lu, Danni Liu, Na Yang, Hao Huang, Paul K. Chu, and Xue-Feng Yu*

Black phosphorus (BP) possesses unique physical properties and, owing to its intrinsic instability, the proper surface and chemical coordination is the key point in many applications. Herein, a facile and efficient surface lanthanide-coordination strategy based on lanthanide (Ln) sulfonate complexes is designed to passivate and functionalize different BP-based nanostructures including quantum dots, nanosheets, and microflakes. By means of Ln–P coordination, the lone-pair electrons of phosphorus are occupied, thus preventing oxidation of BP, and the LnL₃@BP exhibits excellent stability in both air and water. Furthermore, accompanied by the original photothermal performance of BP nanostructures, the Gd-coordinated BP has high R₁ relaxivities in magnetic resonance (MR) imaging, and other Ln (Tb, Eu, and Nd) coordinated BP structures exhibit fluorescence spanning the visible to near-infrared regions. Not only is LnL₃ surface passivation an efficient method to enhance the stability of BP, but also the MR or fluorescence derived from lanthanide ions extends the application of BP to optoelectronics and biomedical engineering.

Nanomaterials have attracted a lot of interest[1] because of the large number of surface atoms as well as specific surface area, but the performance and stability of nanomaterials are influenced by the environment.[2,4] Various surface modification strategies such as small molecular modification or inorganic packaging have been developed to prevent oxygen erosion or solvent induced quenching.[4,5] Much effort has also been devoted to setting up multifunctional on single-material platforms to achieve better practical performance. In this respect, surface functionalization is useful in the assembly of different functional modules and blocks,[6] and recent development of 2D materials has spurred research in this area.[7] Among the various types of 2D materials, black phosphorus (BP) is a shining star due to the distinctive properties[8,9] such as the layer-dependent bandgap,[10] active surface electronic states,[11] and broadband absorption spanning the ultraviolet (UV) and near-infrared (NIR) regions.[12,13] Particularly, BP-based nanostructures such as BP quantum dots (QDs) and nanosheets have good biocompatibility, large specific surface area, and excellent photothermal properties rendering them attractive in biomedical applications such as drug delivery, cancer therapy, tissue engineering, and biosensing,[14–16] However, because of the lone-pair electrons, BP is not stable in oxygen environment, especially under condition of water–oxygen coexistence.[17] Recently, various strategies such as self-assembled monolayers,[18–21] titanium ligand surface coordination,[22] covalent bonding,[23] and transition metal doping[24] have been developed to protect BP from the oxygen–water ambient condition. On the other hand, phosphorus is present in cells, tissues, and bones[25] and so specific detection of BP by conventional imaging techniques is difficult. As a result, it is difficult to trace the BP-based nanostructures[26] and conduct detailed biomedical studies in vivo.

Lanthanide-based composites constitute an important class of functional nanomaterials.[27] Benefiting from the inner-layer electron transition, many lanthanide (Ln) ions like Tb³⁺, Eu³⁺, and Nd³⁺ exhibit perform large Stokes shift and stable fluorescence,[28] and other Ln ions such as Gd³⁺ and Dy³⁺ yield magnetic resonance (MR) signals.[29] Lanthanides also have good biocompatibility[10] and can form covalent or other chemical bonds with many nonmetallic elements, for example, metal–phosphorus complexes,[31,32] In this work, lanthanide is utilized to modify BP using a lanthanide trifluoromethanesulfonates (Ln(Otf)₃; LnL₃ for short) based coordination strategy (Scheme 1a). Owing to the electrophilic effect of trifluoromethanesulfonate, the electron density of Ln³⁺ is reduced and the coordinating ability of Ln³⁺ is strengthened.[13] As shown in Scheme 1b, after modification with LnL₃ on different BP nanostructures (QDs and nanosheets), the empty orbital of the lanthanide ions is coordinated with the lone-pair electrons of phosphorus. The P–Ln coordination occupies the lone-pair electrons of phosphorus, prevents the oxidation, and makes the BP nanostructures to be stable in water and humid air. Modification with lanthanides also enables the BP to be fluorescence and MR response making it easier to trace BP-based biomaterials.

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The BPQDs are prepared by a two-step ultrasonic liquid exfoliation method. In brief, the bulk BP crystals were ground with N-methylpyrrolidone (NMP) for 30 min to get a coarse dispersions, then a 3 h probe sonication and a 10 h bath sonication were taken, the final dispersion were centrifuged for 20 min at 12,000 rpm, the final precipitation of BPQDs was collected and dispersed in NMP for the following surface modification. An excessive amount of GdL3 is added and the mixture is stirred for 20 h in darkness under Ar before the GdL3@BPQDs are collected by centrifugation. The transmission electron microscopy (TEM) image in Figure 1a shows that the GdL3@BPQDs have a diameter of about 3.7 nm and the inset high-resolution TEM (HR-TEM) image reveals lattice fringes of 2.3 Å corresponding to the (014) plane of BP. The energy-dispersive X-ray spectroscopy (EDS) spectra in Figure 1b exhibit characteristic peaks of P, Gd, F, S, C, and O. The Gd, F, and S peaks are assigned to the GdL3 and the atomic ratio of P to Gd is 1:6.5. After GdL3 modification, the Raman scattering peaks of

Scheme 1. a) Schematic diagram illustrates the synthesis of lanthanide-coordinated BP nanosheets/QDs; b) the formula of LnL3 and the atomistic model of the lanthanide ligand coordinated BP surface.

Figure 1. Characterization of GdL3@BPQDs: a) TEM and inset HR-TEM images; b) EDS spectra; c) Gd 4d XPS spectra of GdL3@BPQDs and GdL3; and d) P 2p XPS spectrum of GdL3@BPQDs.
BPQDs blueshift (Figure S1, Supporting Information) similar to previous observation of BP-based nanocomplexes. Moreover, the Zeta potential of BPQDs changes from $-32.5 \pm 1.4$ to $+28.6 \pm 1.6$ mV after GdL3 modification.

The X-ray photoelectron spectra (XPS) are acquired to confirm coordination between BP and GdL3 in GdL3@BPQDs. As shown in Figure 1c,d, compared with GdL3, the binding energies of Gd 4d$^{5/2}$ and Gd 4d$^{3/2}$ of GdL3@BPQDs shift negatively by 1.5 and 1.1 eV, respectively and the binding energy of P 2p of 132.9 eV suggests coordination between metal and phosphorus.[35] These results demonstrate that the electrons are transferred from P to Gd upon coordination.[36] The LnL3 (Ln(Otf)$_3$) is a sort of Lewis acid (electrophile) with lowest unoccupied molecular orbital energy level ranging from $-3$ to $-1$ eV, acting as effective acceptors of electrons.[37] As a result, the BPQDs, a Lewis base (nucleophile) is passivated by the LnL3 coordination. The P 2p$_{3/2}$ and P 2p$_{1/2}$ doublet peaks at 129.8 and 130.7 eV are in agreement with the reported value of crystalline BP[18–20] thus confirming that coordination occurs on the surface of BP and does not influence the BP structure substantially. The C 1s XPS spectrum and P 2s XPS spectrum in Figure S2 in the Supporting Information also corroborate surface coordination of GdL3 on BP.

To evaluate the effects of GdL3 coordination on the stability of BPQDs, the bare BPQDs and GdL3@BPQDs aqueous solution with the same concentration of 34 ppm were exposed to air for 8 d and the photos and optical absorption spectra were examined every other day. As shown in the white-light photos in Figure 2a, the dispersion of GdL3@BPQDs remains brown after 8 d but the bare BPQDs become transparent. The absorption spectra in Figure 2b display a similar trend and different from the GdL3@BPQDs, the absorbance intensity of the bare BPQDs decreases quickly. The GdL3@BPQDs are also stable in other solvents such as ethanol and N,N-dimethylformamide (DMF; Figure S3, Supporting Information). The P 2p XPS spectra of the bare BPQDs and GdL3@BPQDs during exposure are acquired and examined. With regard to the bare BPQDs (Figure 2c), the peak at 134.0 eV associated with P$_{\text{P}}$O$_{\text{y}}$[18–20] increases significantly, indicating serious oxidization of BP during exposure to humid air. In contrast, the P 2p XPS spectrum of GdL3@BPQDs (Figure 2d) is nearly unchanged under ambient conditions for 8 d providing evidence that surface coordination of GdL3 protects BP from degradation.

The surface modification strategy can be extended to BP with different sizes including nanosheets and microflakes. As a demonstration, BP nanosheets about 300 nm in size are obtained ultrasonically in an ultrasonic water bath and GdL3 coordination is performed as described earlier. After incubation in an aqueous solution for different periods of time, TEM images are acquired to monitor the morphological changes of the GdL3@BP nanosheets and bare BP nanosheets. As shown in Figure 3a, the GdL3@BP nanosheets are retained in the process but the bare BP nanosheets in Figure 3b are broken into fragments after 4 d and degrade after 8 d. The BP microflakes are mechanically exfoliated from the bulk crystal using scotch...
tape and transferred to a Si/SiO₂ substrate for GdL₃ passivation. As shown in Figure 3c,d, the lateral dimension of the green flat flake is about 5 µm. After exposure for 8 d, the GdL₃@BP flake on the substrate is unchanged but large and dense droplets are observed from the bare BP flake. The images of GdL₃@BP nanosheets and GdL₃@BP microflake suggest that the GdL₃-coordination can be employed for protecting the different BP structures from oxidation and degradation.

The versatility of the coordination strategy is assessed with other lanthanide elements including Y, La, Nd, Sm, Eu, Tb, and Er (Figure 4). The Ln loading masses are confirmed by EDS (Figure S4, Supporting Information) and elemental compositions are shown in Table S1 in the Supporting Information. To evaluate the stability of the different LnL₃@BP in water, LnL₃@BP and bare BP aqueous solution with the same concentration are exposed to air and the absorption intensity are recorded every other day. The ratios of the absorption intensity at 450 nm (A) to the original intensity (A₀) are shown in Figure 4. The ratio of the LnL₃@BP is maintained at over 90% after 8 d but that of the bare BP diminishes to 23% after 8 d. The results demonstrate that this modification strategy can be extended to other lanthanide elements to improve the stability of BP against oxidation and degradation. The trivalent lanthanides ions have a similar electronic configuration as [Xe]⁴f¹⁰ and the major contribution for chemical bonding comes from the 5d and 6s empty orbitals but the 4f electrons make no contributions. As a result, the trivalent lanthanides have similar chemical properties and can be used to occupy the lone pair of electrons of BP. The aforementioned results demonstrate the feasibility of the general surface coordination strategy based on lanthanides ligands (Lewis acids).

Figure 3. Stability evaluation of bare BP and GdL₃@BP with different sizes: TEM images of: a) GdL₃@BP nanosheets and b) bare BP nanosheets exposed to air for 0, 4, and 8 d; optical images of: c) GdL₃@BP flake and d) bare BP flake exposed to air for 0, 4, and 8 d.

Figure 4. Variation of the absorption ratios at 450 nm (A/A₀) of YL₃@BP, LaL₃@BP, NdL₃@BP, SmL₃@BP, EuL₃@BP, TbL₃@BP, ErL₃@BP, and bare BP with dispersion time in water.
to bind the lone-pair electrons of phosphorus (Lewis base), resulting in greatly enhanced stability of the BP-based nanostructures in air and water. Although other strategies have been suggested to protect BP, this strategy is still attractive due to the following points. First, compared to transition metal elements, Ln elements have bigger atomic radii and larger coordination numbers conducive to coordination of LnL₃ on BP. Secondly, since the 4f electrons do not contribute to bonding between lanthanide and phosphorus, the physical properties of the lanthanide ions are maintained. Thirdly, considering the multifunctionality of different lanthanide ions, the strategy may endow special functionalities as discussed in the following section.

Since BPQDs have been proposed as an efficient photothermal agent, the effect of the lanthanide coordination on the photothermal performance of BPQDs was examined. The aqueous solutions of bare BPQDs and GdL₃@BPQDs with the same concentration of 34 ppm were exposed to air for 8 d and the solution temperature were examined every other day by using an 808 nm NIR laser (1.0 W cm⁻²) as the light source. The photothermal heating curves in Figure 5 show that both the bare BPQDs and GdL₃@BPQDs induce much higher temperature rise than pure water under NIR irradiation at day 0. However, the BPQDs suffer from the stability problem, that the photothermal ability is decreased quickly after storing in water under ambient condition. In contrast, the NIR photothermal curve of GdL₃@BPQDs is well maintained in the day 8 test. Considering the little photothermal response capability of GdL₃ (Figure S5, Supporting Information), the photothermal-induced temperature raise of GdL₃@BPQDs is attributed to the BP. These results indicate that the stability of the BP’s photothermal performance is greatly improved by the GdL₃ coordination.

Functionalization of the lanthanide-coordinated BP is demonstrated with LnL₃@BPQDs (Ln: Gd, Eu, Tb, Nd). The MR performance of GdL₃@BPQDs is first examined. The in vitro spin-echo images of the GdL₃@BPQDs aqueous solutions with different concentrations are acquired with a 3.0 T clinical scanner (Figure 6a). As the concentrations of GdL₃@BPQDs
The fluorescence characteristics of TbL₃@BPQDs, EuL₃@BPQDs, and NdL₃@BPQDs are studied as shown in Figure 6c and Figures S6–S8 in the Supporting Information. Under UV illumination, the TbL₃@BPQDs emit green light and the emission peaks at 486, 540, and 583 nm are assigned to 5D₄→7F₅(5/2), 6, 4 transitions of Tb³⁺. The EuL₃@BPQDs emit red light at 590 nm (5D₀→7F₂ transitions), 613 nm (5D₁→7F₄ transitions), and 695 nm (5D₀→7F₁ transitions). Nd is a typical NIR emitter for sub-tissue imaging,[41] when excited by 730 nm lasers, the LnL₃@BP exhibits excellent stability in air and water. LnL₃-based surface passivation not only is an efficient way to protect BP but also can be extended to other 2D materials. Under UV illumination, the TbL₃@BPQDs emit green light and the emission peaks at 486, 540, and 583 nm are assigned to 5D₄→7F₅(5/2), 6, 4 transitions of Tb³⁺. The EuL₃@BPQDs emit red light at 590 nm (5D₀→7F₂ transitions), 613 nm (5D₁→7F₄ transitions), and 695 nm (5D₀→7F₁ transitions). Nd is a typical NIR emitter for sub-tissue imaging.[41] When excited by 730 nm lasers, the LnL₃@BP exhibits excellent stability in air and water. LnL₃-based surface passivation not only is an efficient way to protect BP but also can be extended to other 2D materials.

Mechanical Exfoliation of BP Microflakes: A Scotch tape-based mechanical exfoliation method was utilized to peel thin BP microflakes from the bulk crystal onto silicon (Si)/silicon dioxide (SiO₂) substrates that were sonicated in EtOH and blow dried with N₂.

**General Methods of Surface Coordination of BP:** The BPQDs or BP nanosheets were dispersed in NMP (1 mL, 5 µmol) and an excessive amount of LnL₃ was added. The mixture was stirred in darkness under Ar for 20 h. Afterward, the mixture was centrifuged at 12 000 rpm for 20 min and the precipitated LnL₃@BP was collected. The BP microflakes were processed by immersing the samples in the LnL₃ solutions for 10 h. After modification, the samples were rinsed with EtOH and stored for further use.

**NIR Laser-Induced Heat Conversion:** The photothermal conversion was measured on a continuous fiber-coupled semiconductor diode laser (808 nm, KS-810F-8000, Kai Site Electronic Technology Co., Ltd. Shaxi, China) with a power density of 1.0 W cm⁻² as the light source and an infrared thermal imaging camera (Fluke Ti27, USA) was used to monitor the temperature change. 1 mL of the bare BPQDs or GdL₃@BPQDs was added in a 1 cm path length quartz cuvette for investigation.

**Characterization:** The TEM and HR-TEM images and EDS spectra were acquired on the Tecnai G2 F20 S-twin transmission electron microscope at an acceleration voltage of 200 kV. The samples were dispersed in EtOH or ultrapure water and dropped 5 µL onto an ultrathin carbon support films for observation. Raman scattering was conducted on a Horiba Jobin-Yvon Lab Ram HR V150 high-resolution confocal Raman microscope equipped with a 633 nm laser. The samples were dispersed in EtOH and then dropped onto 300 nm SiO₂/Si substrates for investigation. XPS was carried out on the Thermo Fisher ESCALAB 250Xi XPS. The UV–vis–NIR absorption spectra were obtained at room temperature on the Lambda 25 spectrophotometer (PerkinElmer) with QSS-grade quartz cuvettes and fluorescence spectra were obtained at −20 °C on a fluorescence spectrometer (Edinburgh instruments P900, UK). The MR images were acquired on the 3.0 T clinical scanner (United Imaging 770). In brief, the solutions were pipetted in NMR tubes (2 mL in each tube) and placed in the clinical scanner at 3.0 T. T₁ spin-echo images of the solutions were performed. T₁ values were counted from the images.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the authors.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

black phosphorus, lanthanide, stability, surface modification, 2D materials

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Supporting Information for

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Keywords: Lanthanide, black phosphorus, surface modification, two-dimensional materials, stability.
**Figure S1.** Raman spectra of GdL₃@BPQDs and bare BPQDs.
Figure S2. (a) C 1s XPS spectra of GdL₃ and GdL₃@BPQDs; (b) P 2s XPS spectrum of GdL₃@BPQDs.
Figure S3. Absorption spectra of (a) bare BPQDs and (b) GdL₃@BPQDs after storing in water for different periods of time; (c) Variation of the absorption ratios at 450 nm ($A/A_0$) of GdL₃@BPQDs with dispersion time in DMF, EtOH and water.
Figure S4. EDS spectra of (a) YL$_3$@BP; (b) LaL$_3$@BP; (c) NdL$_3$@BP; (d) SmL$_3$@BP; (e) EuL$_3$@BP; (f) TbL$_3$@BP; (g) ErL$_3$@BP.
Figure S5. Photothermal heating curves of GdL₃ dispersed in water using the 808 nm laser as the irradiation source.
Table S1 Element composition of LnL₃@BP

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<th>Element At %</th>
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Figure S6. Excitation and emission spectrum of TbL₃@BPQDs.
Figure S7. Excitation and emission spectrum of EuL₃@BPQDs.

Figure S8. Excitation and emission spectrum of NdL₃@BPQDs.

Figure S9. Emission spectra of LnL₃ and LnL₃@BPQDs with same LnL₃ concentration. (a) TbL₃ and TbL₃@BPQDs with 375 nm excitation; (b) EuL₃ and EuL₃@BPQDs with 397 nm excitation; (c) NdL₃ and NdL₃@BPQDs with 730 nm excitation.