

Supporting Information

A Single-Step, Electrochemical Synthesis of Nitrogen doped Blue Luminescent Phosphorene

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1. Experimental methods

Synthesis of NPQDs-1

2 mg/mL dispersion of black phosphorus (ACS materials) is prepared in de-aerated ethanol. 30 μ L of the dispersion is physisorbed onto a 3 mm glassy carbon working electrode (GCE) and dried. The room-temperature electrochemical exfoliation is performed in a three-electrode cell where the black phosphorus coated GCE is employed as a working electrode, Pt wire as quasi reference electrode and Pt mesh as the counter electrode. 0.1 wt% of Tetraethylammonium tetrafluoroborate (TEATFB or NEt₄BF₄) in Ar-saturated acetonitrile is used as the electrolyte. An electric field of -2.0 V is applied for 2 h. The electrolyte is collected and centrifuged at 5000 rpm for 15 minutes to remove larger fragments (bottom part). The top portion (Supernatant) is again centrifuged at 9000 rpm for 45 minutes and the collected material is washed with acetonitrile and further used for characterization.

Synthesis of NPQDs-2: Synthesis of NPQDs-2 is carried out by following the same protocol as that of NPQDs-1 except that the supporting electrolyte is changed to 0.1 wt % lithium perchlorate (LiClO₄).

1.1 Materials Characterization

The as synthesized PQDs-1 and PQDs-2 are characterized by multiple materials Characterisation techniques. X-ray photoelectron spectroscopy measurements are carried out using a ThermoScientific Multilab 2000 Base system with a Twin Anode Mg/Al(300/400 W) X-Ray Source. The diffraction patterns are recorded using a PANalytical PW3040/60 X'pert PRO system using an X-ray tube with Cu target (Radiation at 0.154 nm). Transmission Electron Microscopy (TEM) imaging is carried out using an FEI, Tecnai 20 G2 electron microscope. Absorption spectra are collected using a VARIAN Cary 500 scan UV-Vs-NIR double beam spectrophotometer. Fluorescence measurements are carried out using a VARIAN Cary Eclipse Fluorescence Spectrophotometer with a Xenon Pulse lamp as the source. The slit width was maintained at 5 nm for all measurements. Electrochemical synthesis is carried using a BioLogic SP-150 model potentiostat. Raman spectra is recorded in Horiba, LabRAM HR Evolution Raman spectrometer.

2. PLE spectra of PQDS and emission mechanism

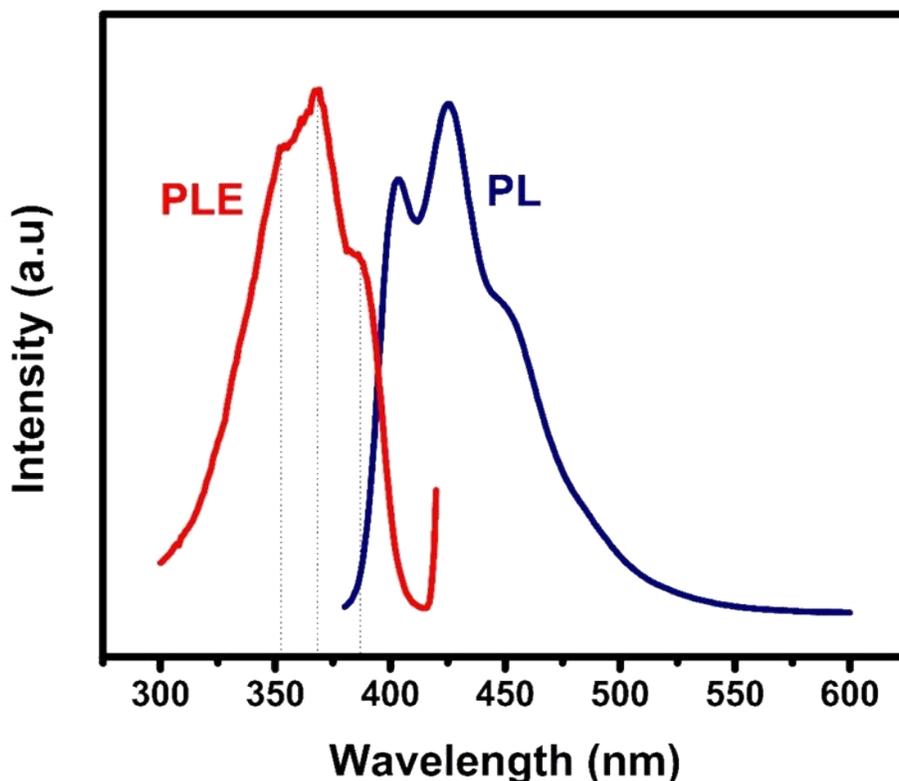


Figure S1. PLE spectrum of NPQDs-1 monitored at 424 nm emission wavelength

The energy difference between the two PLE peaks (Figure 3c) at 353 nm (ca. 3.51 eV) and 367 nm (ca. 3.38 eV) is ~ 0.13 eV. Interestingly, the energy difference between the two PL emission peaks at 403 nm (ca. 3.08 eV) and 424 nm (ca. 2.92 eV) is very close to this value (0.16 eV). Also, the energy difference between the two PLE peaks at 367 nm (ca. 3.38 eV) and 387 nm (ca. 3.20 eV) matches with the two PL peaks at 424 nm (~ 2.92 eV) and 450 nm (~ 2.76 eV). Therefore, it can be inferred that the PL mechanism of the blue luminescent NPQDs-1 involves three emission transitions: one from the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO) and the other two from LUMO to occupied molecular orbitals (OMO-I and OMO-II) which are below the HOMO. It is very likely that the ground state consists of three different energy states. Nevertheless, these are a function of size of QDs, edge configuration (arm chair or zig zag) and surface passivation.[1] Notably, the electron donating functional groups on PQDs as evident from FT-IR spectrum create a larger electron density on the

phosphorene moieties due to the electron transfer from functional groups to the quantum confined phosphorene nanostructures. This enhances overall electron energy of the ground state HOMO and the two OMO levels and shortens the bandgap. Due to the upliftment of the ground state energy level, the NPQDs-1 exhibit relatively less quantum size effect. Therefore the excitation wavelength-independent nature of PL of NPQDs-1 presumably arise from the effect of functional groups.

2.1 Calculation of PL Quantum yield

In principle, the relative photoluminescence (PL) quantum yield (QY) is determined based on absorption-emission spectroscopy. As a first step, the UV-Visible spectrum of the sample and the standard (reference) is recorded and the wavelength of the absorbance is noted. This is noted as the excitation wavelength for recording fluorescence (360 nm) and the fluorescence spectra of the same solutions (sample and reference) are recorded. Following this, the integrated PL intensity of the sample is compared with the same quantity of a standard whose QY is known. QY can be calculated according to the following equation:

$$\Phi_S = \Phi_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{n_S^2}{n_R^2}$$

where Φ_S and Φ_R are the photoluminescence QY of the sample and that of the reference, respectively; I_S and I_R are the integrated intensities (areas) of sample and reference spectra, respectively; A_S and A_R are the absorbance of the sample and the reference respectively and n_S and n_R are the refractive indices of the sample and reference solution respectively. For the QY calculation, quinine sulfate was taken as standard (PLQY=0.54).

3. FT-IR Spectra of NPQDs-1 and BP

The strong peak noticed for both bulk black phosphorous and NPQDs-1 at 1099 cm^{-1} and 1400 cm^{-1} corresponds to P-O bond and P=O bond stretching vibrations respectively.[2,3] A P-OH stretching at 2380 cm^{-1} is observed for black phosphorous. On the contrary, strong stretching vibrations for nitrogen containing functional groups are noticed for NPQDs-1. A strong peak appeared at 3439 cm^{-1} indicates P-NH₂ stretching mode and P-NH bending mode is noticed at 1637 cm^{-1} . A weak P-N bond stretching vibration is also noticed at 736 cm^{-1} .

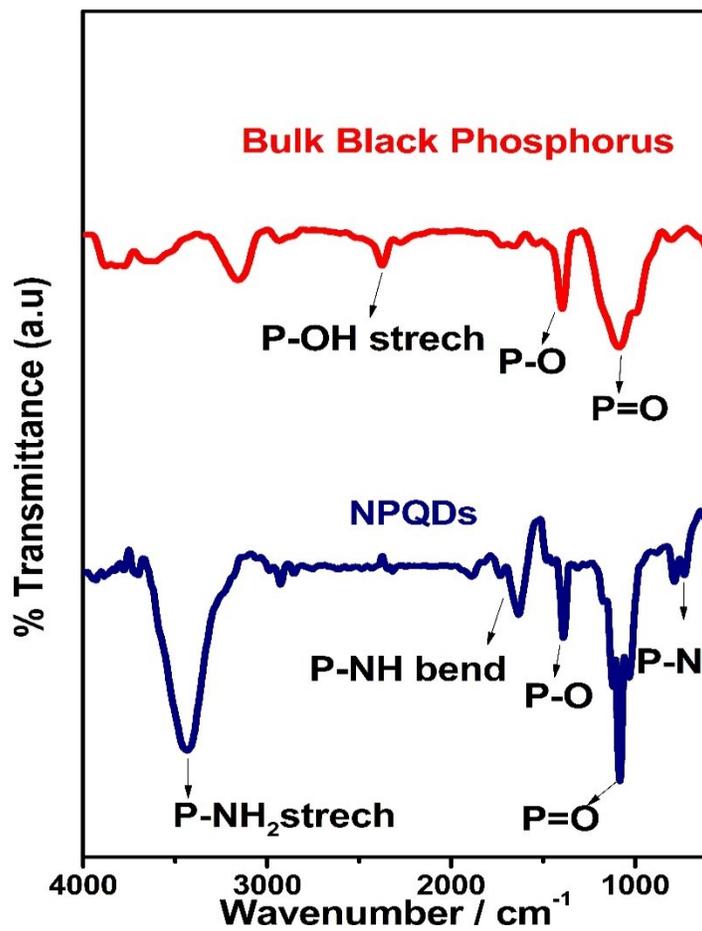


Figure S2. FT-IR spectra of black phosphorus and NPQDs-1

3.XP survey spectrum and O1s spectrum of NPQDs-1

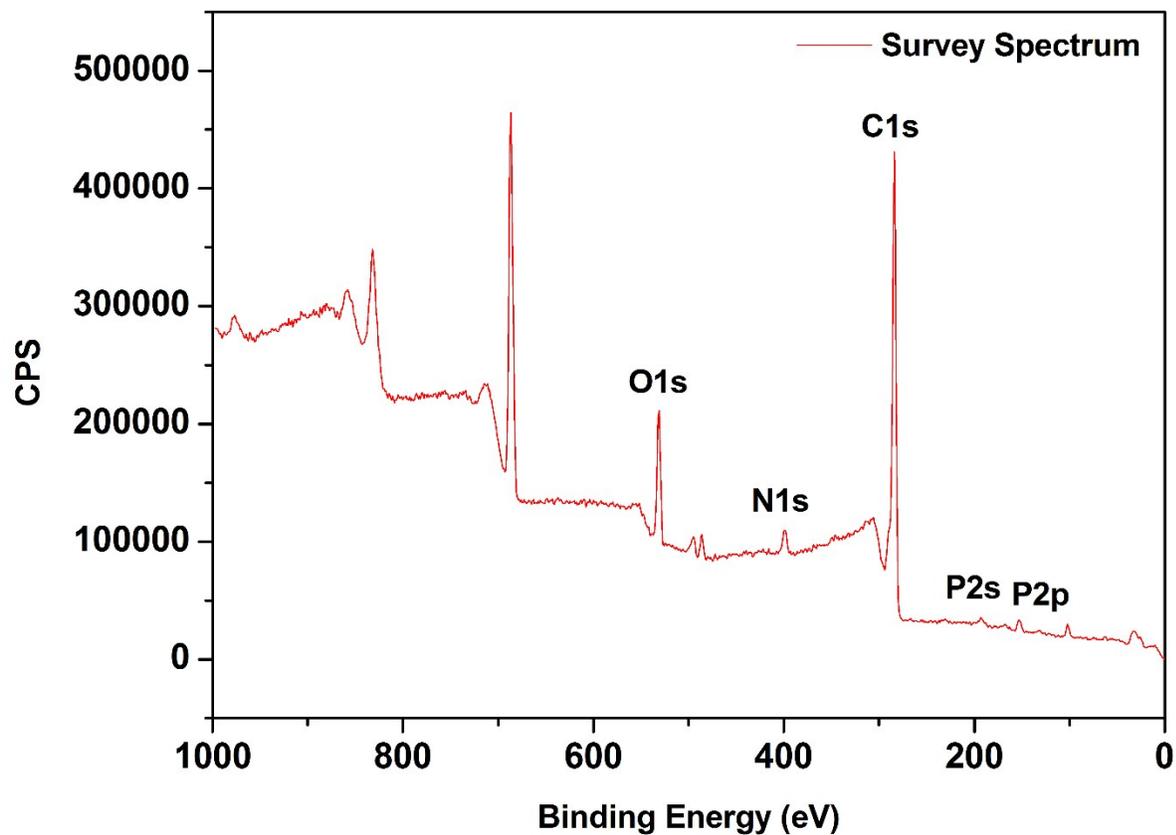


Figure S3.XP survey spectrum of NPQDs-1

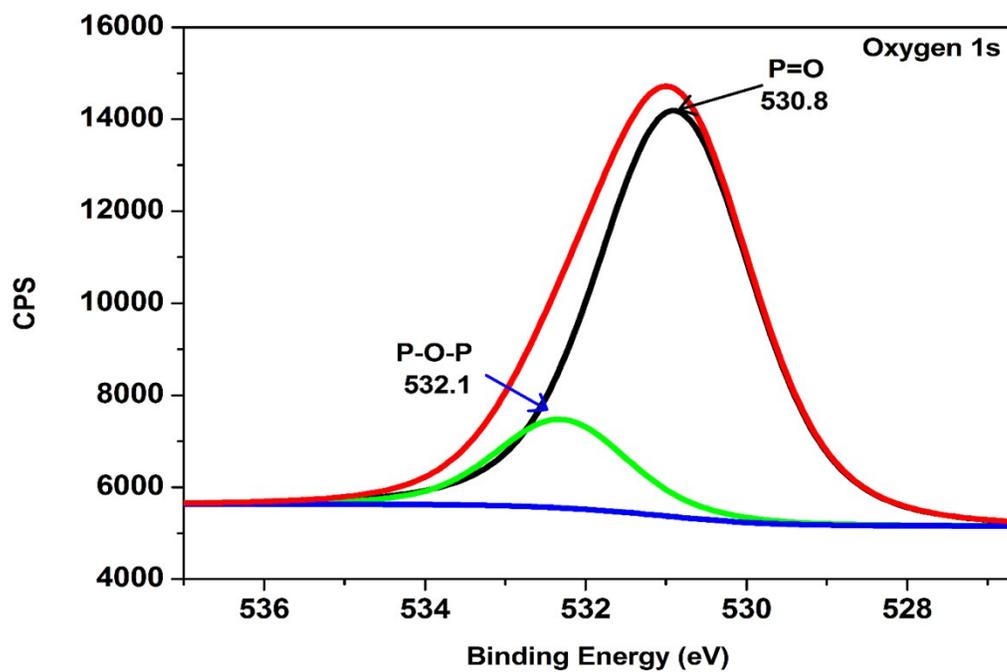


Figure S4. O 1s XPS spectrum of NPQDs-1

5. Transmission electron microscopy images of NPQDs-2

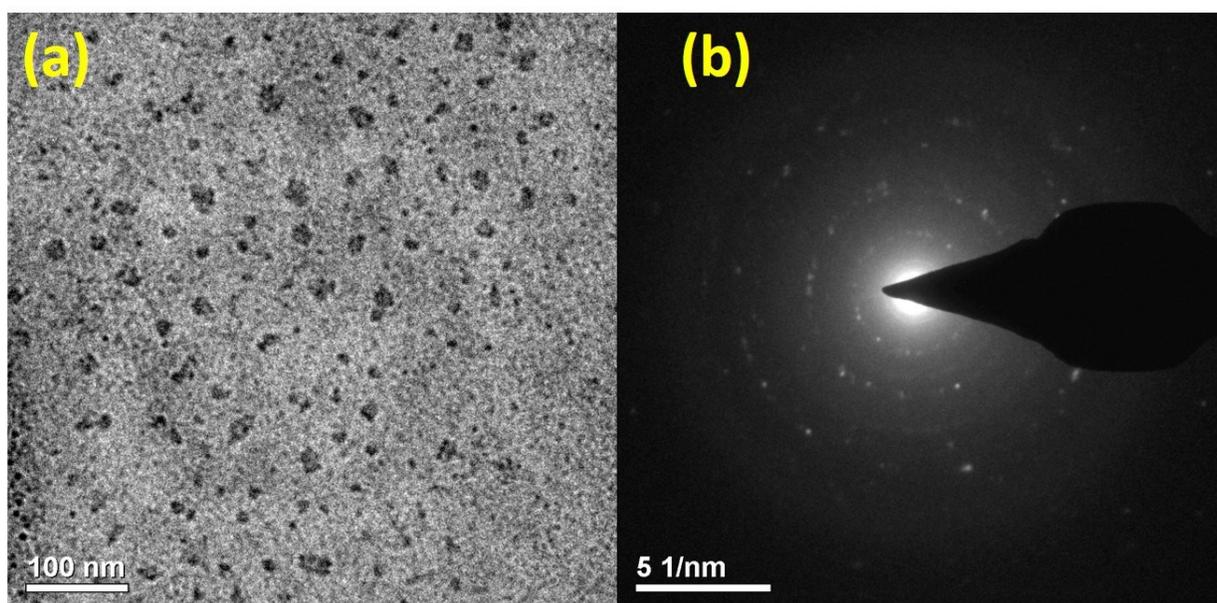


Figure S5.(a) TEM image of NPQDs-2 (b) SAED pattern of NPQDs-2

6. FTIR spectrum of NPQDS-2

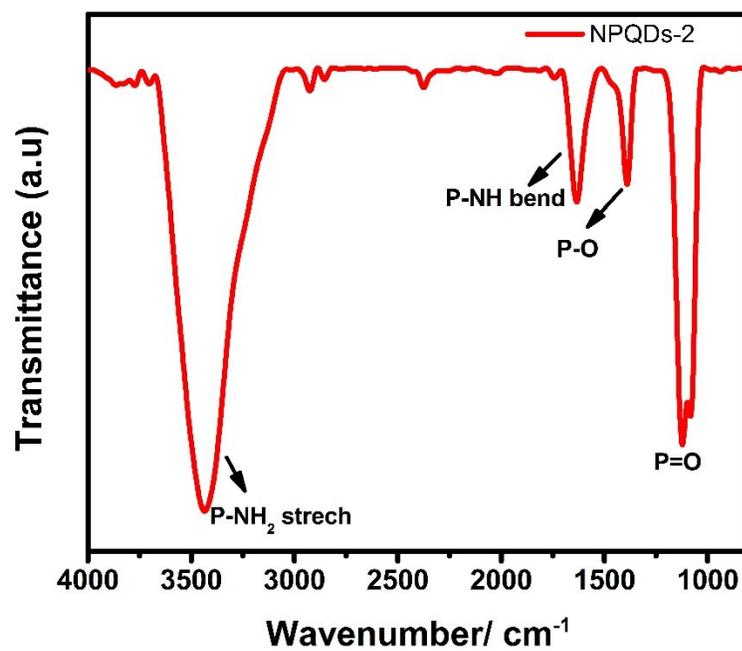


Figure S6. FT-IR Spectrum of NPQDs-2

7. Cyclic voltammograms of Black phosphorus before and after cathodic exfoliation

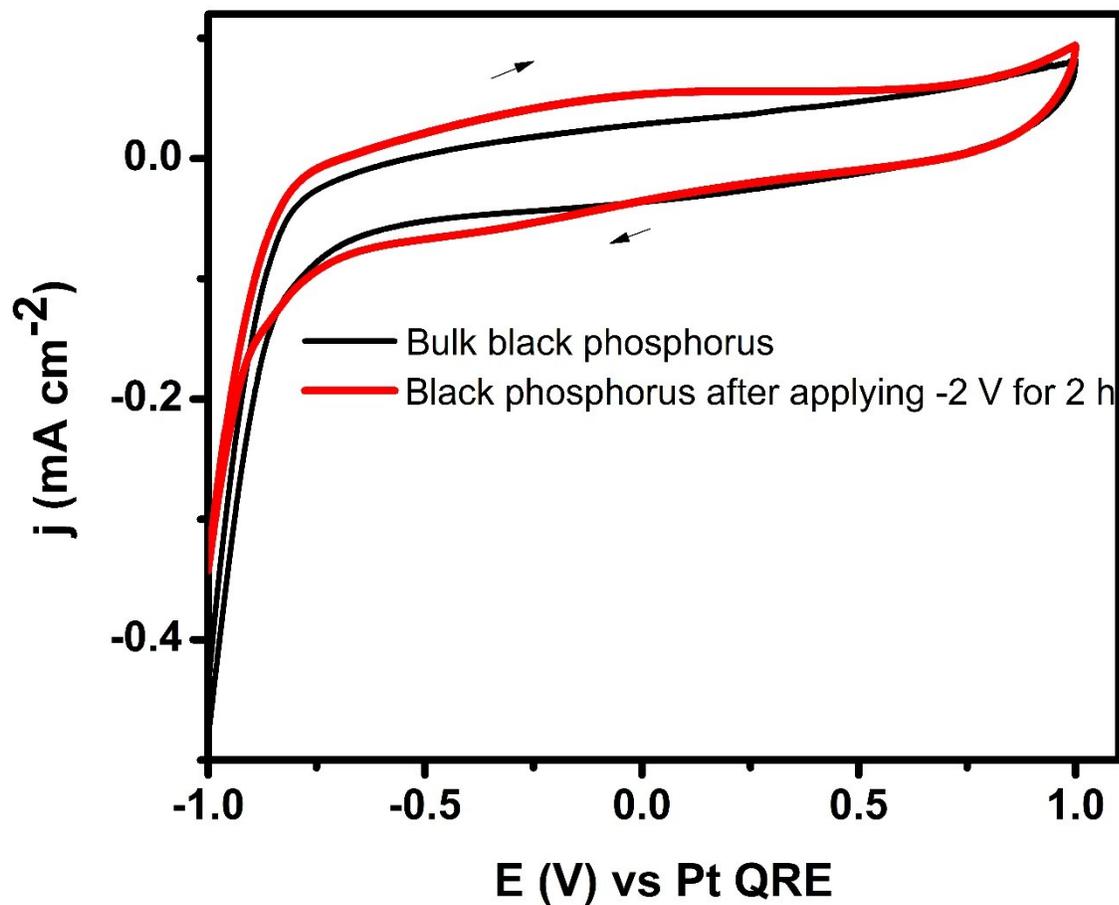


Figure S7. Comparative cyclic voltammograms of black phosphorus before and after applying -2.0 V for 2 h in 0.1 wt % Tetraethylammonium tetrafluoroborate in acetonitrile. Scan rate: 100 mV s⁻¹

References

- [1] S. Ge, L. Zhang, P. Wang, Y. Fang, *Sci. Rep.* 6 (2016) 27307.
- [2] J.V. Pustinger, W. Cave, M. Nielsen, *Spectrochim. Acta* 15 (1959) 909–925.
- [3] L. Daasch, D. Smith, *Anal. Chem.* 23 (1951) 853–868.