

Role of Structural Distortion in Stabilizing Electrosynthesized Blue Emitting Phosphorene Quantum Dots

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1. Experimental section

1.1 Synthesis of PQDs

2.0 mg/mL dispersion of black phosphorus (ACS materials) is prepared in deaerated ethanol. 50 μ L of the dispersion is mounted onto a 3 mm glassy carbon working electrode (GCE) and allowed to dry. The room-temperature electrochemical exfoliation is carried out in a three-electrode cell where the black phosphorus coated GCE is employed as the working electrode, Pt wire as the quasi reference electrode and Pt mesh as the counter electrode. Lithium perchlorate (LiClO_4 , 0.1 wt%) in Argon-saturated propylene carbonate was used as the electrolyte. An electric field of strength $5.2 \times 10^8 \text{ V m}^{-1}$ is applied for 24 h. The product obtained from the electrolyte by centrifugation and was used for further characterization.

1.2 Calculation of Electric field strength:

We have calculated the electric field strength approximately using the applied potential with Debye length ' λ_D ' (which is the characteristic thickness of the double layer) . The debye length is calculated according to the following expression:

$$\lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 K_B T}{\sum_{\text{all ions}} (Z_i e)^2 C_i^*}}$$

Where,

ϵ_r =dielectric constant of the solvent (here propylene carbonate)

ϵ_0 =permittivity of free space

K_B = Boltzmann constant

T = Temperature

Z_i = Charge of ions

e = Charge of electron

C_i = concentration of ions per cubic meter

The calculated debye length for our system is 3.87×10^{-9} m and the strength of electric field inside the double layer is 5.2×10^8 V m⁻¹

Reference: *Electroanalytical Methods: Guide to Experiments and Applications, Second edition* by Fritz Scholz, (Chapter 1.1 ,Page 8.)

1.3. Experimental optimization details of PQDs synthesized by various applied potentials, electrolyte and supporting electrolytes .

Potential	Electrolyte	Supporting electrolyte	Average size (nm)
+2 V	Propylene carbonate	Lithium perchlorate	7
-2 V	Propylene carbonate	Lithium perchlorate	8
-2 V	Acetonitrile	Tetraethylammoniumtetrafluoroborate	6
-2 V	Acetonitrile	Lithium perchlorate	10

Table S1.Summary of PQDs synthesized by various applied potentials ,electrolyte and supporting electrolytes

2. DFT Studies

All the calculations in the study were performed under the framework of Density Functional Theory (DFT), using a linear combination of Gaussian orbitals as implemented in deMon 4.3.2 code.¹ The geometries were optimized using the Perdew-Burke-Ernzerhof (PBE) exchange and correlation

functional.² No additional polarization functions are added. The GEN-A2 auxiliary functions are used to fit the charge density.³ The convergence of the geometries is based on gradient and displacement criteria with a threshold value of 10^{-5} a.u and the criteria for convergence of an SCF cycle was set to 10^{-6} a.u. It has been noted that, in earlier theoretical studies, particularly on Phosphorene Quantum Dots (PQDs), modelled with phosphorus atoms ranging from P_{16} to P_{374} had been used.⁴⁻⁶ A latest study on gas sensing applications of PQDs showed a P_{54} model with a partial edge passivation by S atoms.⁶ In addition to this, considering a model with higher number of P atoms will increase the computational demand in terms of power and time. Therefore, in the current study, a minimal model with 54 phosphorous atoms (P_{54}) have been chosen to represent the structure of synthesized PQDs.

3. Materials characterization

X-ray photoelectron spectroscopy is carried out using a ThermoScientific Multilab 2000 Base system with a Twin Anode Mg/Al(300/400 W) X-Ray Source. The diffraction patterns were 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 was carried out using an FEI, Tecnai 20 G2 electron microscope. Absorption spectra were collected using a VARIAN Cary 500 scan UV-Vs-NIR double beam spectrophotometer. Fluorescence measurements were carried out using a VARIAN Cary Eclipse Fluorescence Spectrophotometer with a Xenon Pulse lamp as the source. Electro-chemical synthesis was done using a Bio Logic SP-150 model potentiostat.

1 **4. Results and Discussion**

2 **4.1 Transmission electron micrographs of electrosynthesized PQDs at various applied**
3 **potentials and electrolyte –supporting electrolyte systems.**

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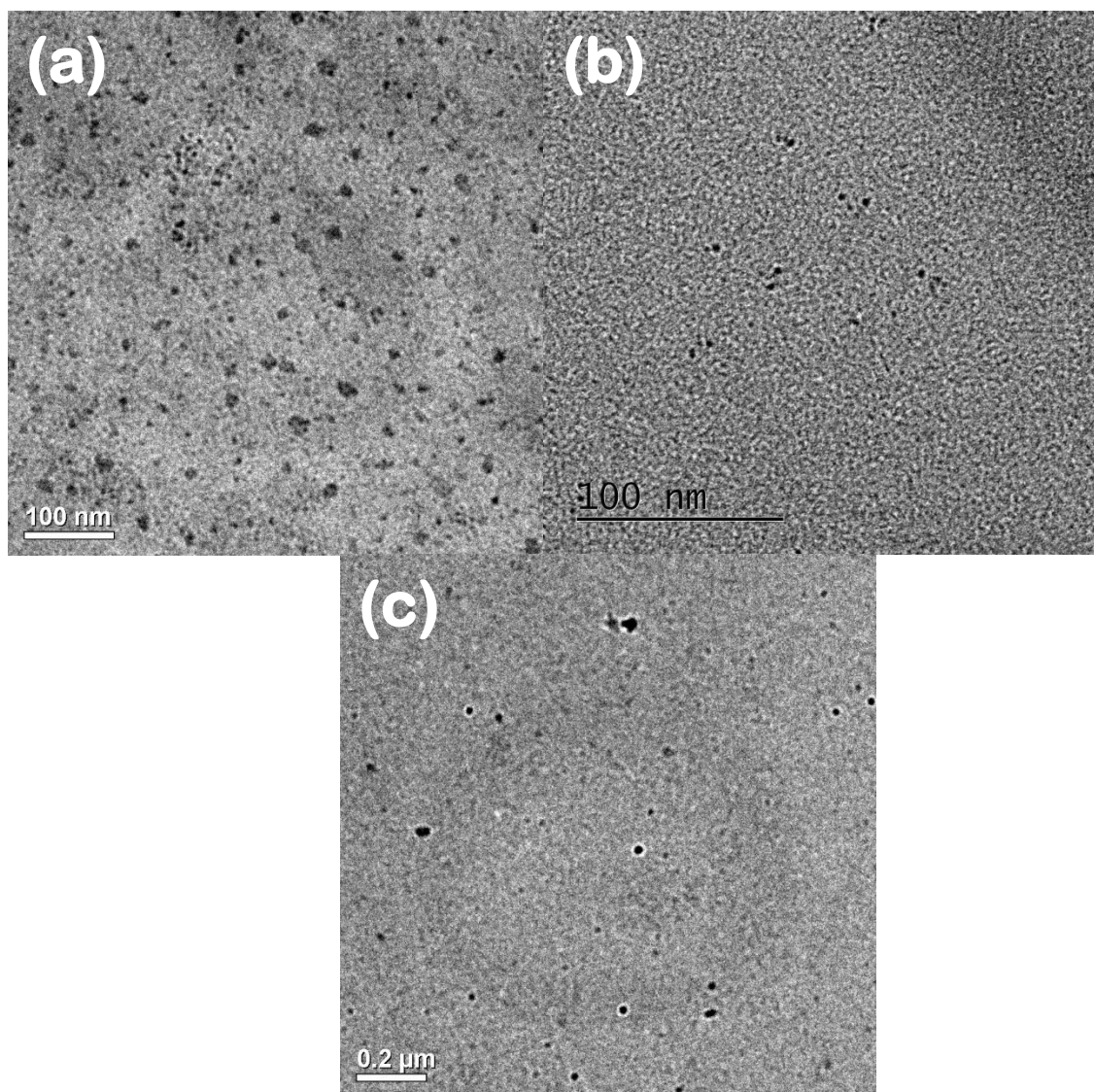


Figure S1.(a) PQDs synthesized by applying -2V for 2 h in Acetonitrile/lithium perchlorate electrolyte-supporting electrolyte (b) PQDs synthesized by applying +2V for 24 h in Propylene carbonate/lithium perchlorate electrolyte-supporting electrolyte (c) PQDs synthesized by applying -2V for 2 h in Acetonitrile/tetraethylammonium tetrafluoroborate electrolyte-supporting electrolyte

4.2 Atomic micrograph of electrosynthesized PQDs

Figure S2 shows the atomic force micrograph (contact mode) of the electrosynthesized PQDs along with the height profile. The van der Waals distance of black phosphorus is 0.53 nm and therefore approximately 2-3 layers are observed for PQDs.

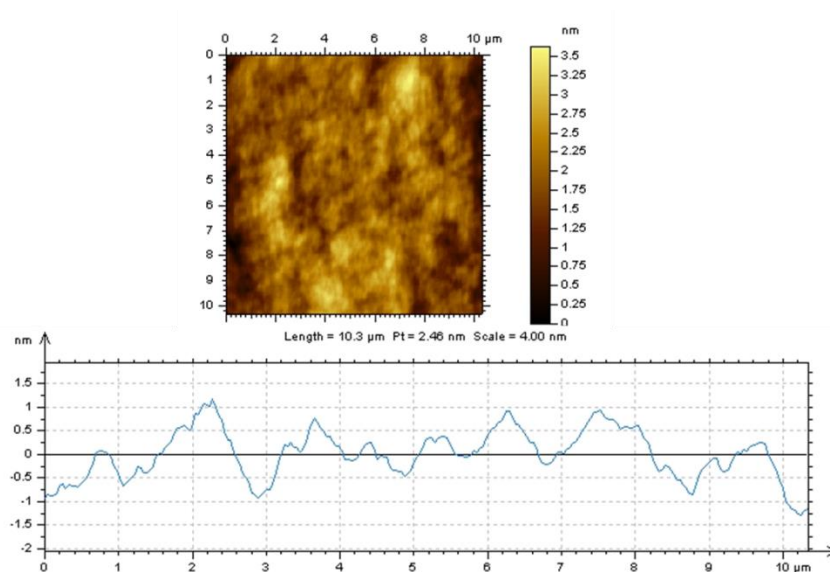


Figure S2. Atomic Force Micrograph and corresponding height profile of PQDs

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3 *4.3 FT-IR spectrum of PQDs*

4 FT-IR spectrum of electrosynthesized PQDs showing P=O stretching vibration at 1100 cm^{-1}

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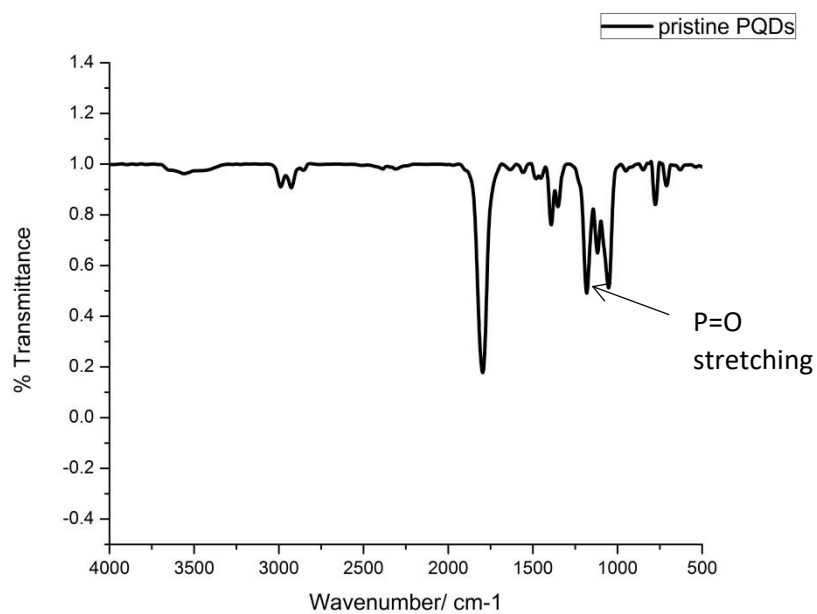


Figure S3. FT-IR Spectrum of PQDs

4.4 Cyclic Voltammograms of black phosphorus before and after exfoliation

The cyclic voltammogram of black phosphorus physisorbed on a glassy carbon electrode at 100 mVs⁻¹ scan rate in propylene carbonate containing 0.1 wt % LiClO₄ shows a slight oxidation around +1.5 V and a reduction with onset around -1 V due to traces of dissolved oxygen. Upon applying an electric field for 24 h, the voltammogram shows an increase in capacitive current as indicated by the change in the non-faradaic region.

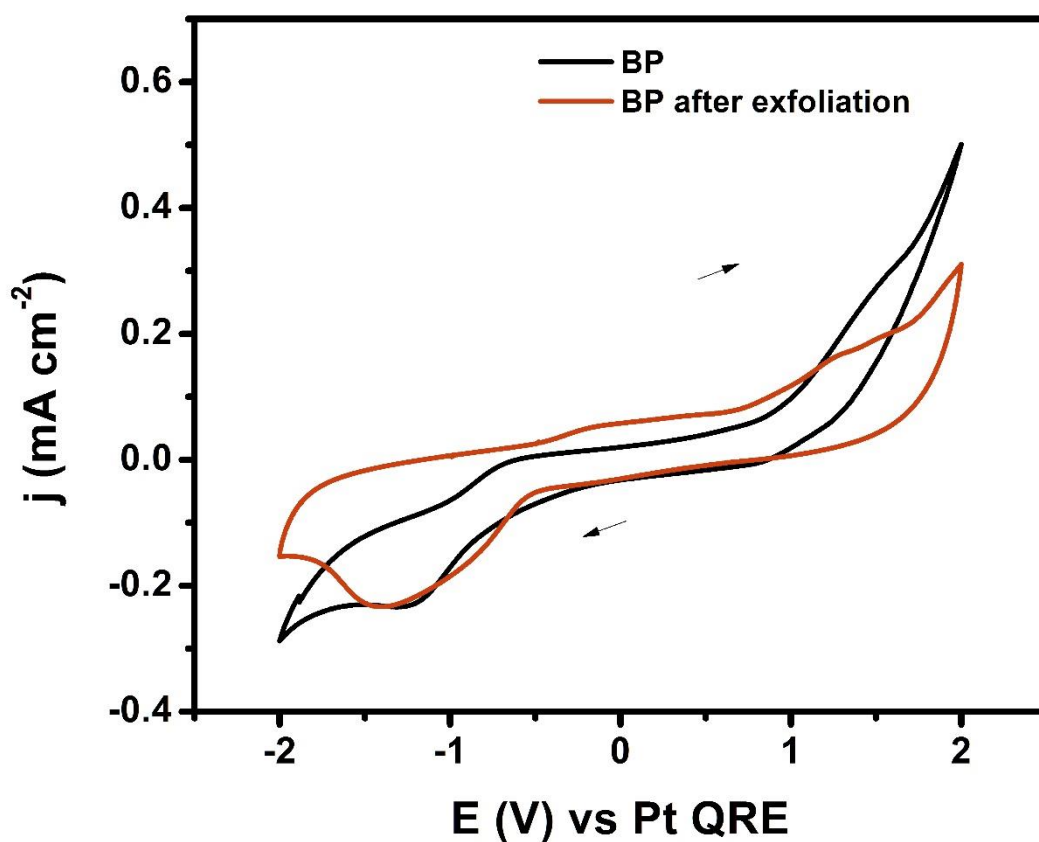


Figure S4. Comparative cyclic voltammograms of BP before and after exfoliation at scan rate of 100 mV s⁻¹ in propylene carbonate containing 0.1 wt % LiClO₄ as supporting electrolyte

4.5 Fitted results of life-time measurements of electrosynthesized PQDs

System	Excitation wavelength λ_{ex} (nm)	Emission wavelength λ_{em} (nm)	τ_1 (a ₁) [ns]	τ_2 (a ₂) [ns]	τ [ns]
PQDs -2V	370	420	0.856(0.99)	10.9 (0.01)	0.956

Table S1.Fitted results of life-time measurements of PQDs

4.6 UV-Visible and Photoluminescence spectrum of quinine sulfate in 1N H₂SO₄ used as standard for determination of photoluminescence quantum yield

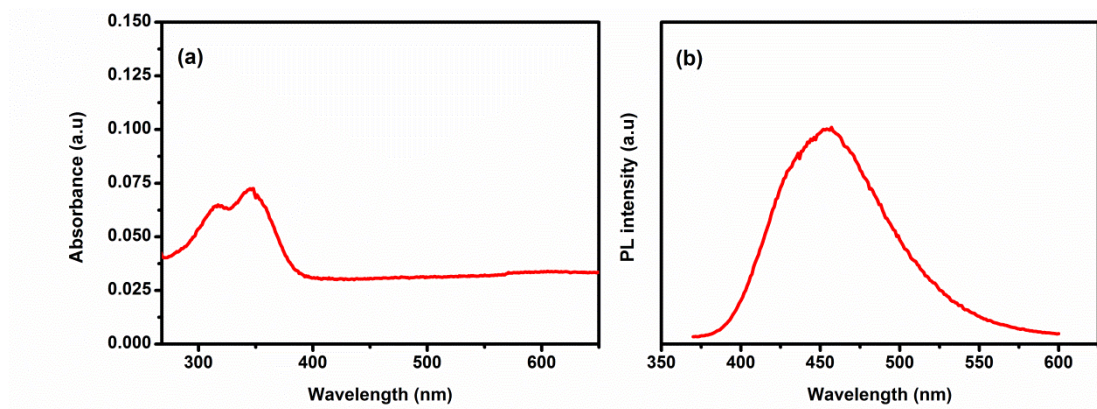


Figure S5. UV-Visible and photoluminescence spectrum of quinine sulfate in 0.1 N H₂SO₄ (excitation wavelength 360 nm)

Justifications for using quinine sulfate as standard for quantum efficiency calculation

For a compound to be chosen as quantum yield standard, it must meet the following criteria:

1. The photoluminescence emission and the absorption range of the standard should match with that of the sample to eliminate the detector-calibrator errors.

2. The absorption and the emission of the standard should not overlap

3. The standard should be soluble and stable in the same solvent (if the standard is not taken in the same solvent, a refractive index correction has to be done while calculation the fluorescence quantum yield)

4. The quantum yield of the standard must be accurately known and should be independent of excitation wavelength.

5. The quantum yield of the standard should not be affected by the concentration and oxygen quenching.

Since the photoluminescence emission of quinine sulfate standard and PQDs fall in the same range of wavelength and quinine sulfate meets all of the above-mentioned criteria,^{7,8} we used quinine sulfate monohydrate as a standard for our quantum yield measurements. The quantum yield of quinine sulfate in 1 N H₂SO₄ is 0.54. The concentration of quinine sulfate was maintained such that the optical density is below 0.05 to avoid inner filter effects.

References

1. A. M. Koster, P. Calaminici, M. E. Casida, R. F. Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J. M. del Campo, S. Patchkovskii, J. U. Reveles, A. Vela, D. R. Salahub. *deMon2k*, 2006.

2 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple *Phys Rev Lett* 1996, **77**, 3865.

3 P. Calaminici, F. Janetzko, A. M. Koster, R. Mejia-Olvera and B. Zuniga-Gutierrez, Assessment of density functional theory optimized basis sets for gradient corrected functionals to transition metal systems: The case of small Nin ($n \leq 5$) clusters *J. Chem. Phys.*, 2007, **126**, 044108.

4. Rajbanshi, B.; Kar, M.; Sarkar P.; Sarkar P. Phosphorene quantum dot-fullerene nanocomposites for solar energy conversion: An unexplored inorganic-organic nanohybrid with novel photovoltaic properties. *Chem. Phys. Lett.* **2017**, 685, 16.

5. Niu, X.; Li, Yunhai.; Shu, Huabing.; Wang, J. Anomalous Size Dependence of Optical Properties in Black Phosphorus Quantum Dots *J. Phys. Chem. Lett.* **2016**, 7, 370.

6. Abdelsalam, H.; Saroka, A. V.; Younis, W. O. *Physica E: Low-dimensional Systems and Nanostructures* **2019**, 107, 105.

- 1 7. J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd ed., Springer, New York, 2006.
- 2 2.J.N Demas and G.A Crosby, Measurement of photoluminescence quantum yields. A Review, Journal of
- 3 Physical Chemistry, 1971, 75, 991.