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Supporting Information

Black phosphorus quantum dots as novel electrogenerated chemiluminescence emitters for the detection of Cu^{2+}

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Part I. Experimental details

Reagents and materials. N-Methyl-2-pyrrolidinone (NMP, AR) and NaOH were obtained from Aladdin Reagents. Bulk BP (99.998%) was obtained from XFNANO Materials Tech Co. Ltd. (Nanjing, China). Deionized distilled water was used throughout the experiments. $K_2S_2O_8$, Na_2HPO_4 and NaH_2PO_4 were obtained from Beijing Chemicals Inc. (Beijing, China). 0.1 M phosphate-buffered solution (PBS, pH 7.2) composed of Na_2HPO_4, NaH_2PO_4, and 0.1 M NaCl was used as the electrolyte in ECL analysis.

Apparatus. Transmission electronic microscopy (TEM) images were recorded with a Hitachi H-800 instrument (Japan). High-resolution TEM (HRTEM) images were acquired with a JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer (Thermo ESCALAB 250) with Al Kα as the radiation source. Raman spectra are obtained by FT-Raman Spectrometer (VERTEX 70v). The surface roughness data were obtained by using the NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. UV-Vis spectra were recorded using a UV-2501PC spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were obtained on a RF-5301PC spectrophotometer (Shimadzu, Japan). The ECL spectra were recorded by collecting the ECL data during the cyclic potential sweep with a series of optical filters at 535, 555, 575, 590, 605, 620, 640, 665, 690 nm. Cyclic voltammetric and ECL measurements were carried out with a Model MPI-E Electrochemiluminescence Analyzer (Xi'an Remex Analytic Instrument Co., Ltd, Xi'an, China). The voltage of the photomultiplier tube was set at 800 V in the process of ECL detection. A conventional three-electrode system was used in the experiment with a bare or modified GCE as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode (saturated KCl) as the reference electrode.

Synthesis of BPQDs. BPQDs were prepared according to our previously reported method[1]. Briefly, 20 mg of black phosphorus crystals were first grinded into black phosphorus powder with protection of NMP. Then black phosphorus powder solution, 200 mL of NMP, and 200 mg NaOH were added in a flask and kept vigorous stirring for 6 h at 150 °C under the protection of N_2. At last, the resulting suspensions were centrifuged for 20 min at 7000 rpm to separate the precipitation and supernatant, and the supernatant was centrifuged for 10 min at 10000 rpm to obtain BPQDs with a size of 4.18 nm. BPQDs is obtained from the exfoliation of black phosphorus crystals, by changing the reaction temperature to 100 °C, the BPQD with a size of 9.65 nm can be obtained by centrifugation through the above steps.

Preparation of BPQDs modified glassy carbon electrodes (BPQDs/GCE). Prior to use, the glassy carbon electrode (GCE, diameter 3 mm) was polished carefully with 1.0, 0.3 and 0.05 μm alumina slurry, respectively, followed by washing thoroughly with water. Then the electrode was sonicated in water and allowed to dry in a stream of N_2. 6 μL of BPQDs suspension was dropped on the surface of the clean GCE and dried at room temperature as the BPQDs/GCE.

Part II. Supplementary figures

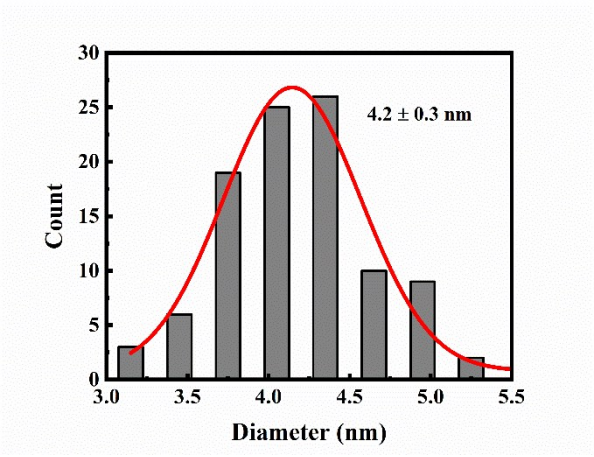

Fig. S1 Statistical analysis of the lateral sizes of 100 BPQDs determined by TEM.

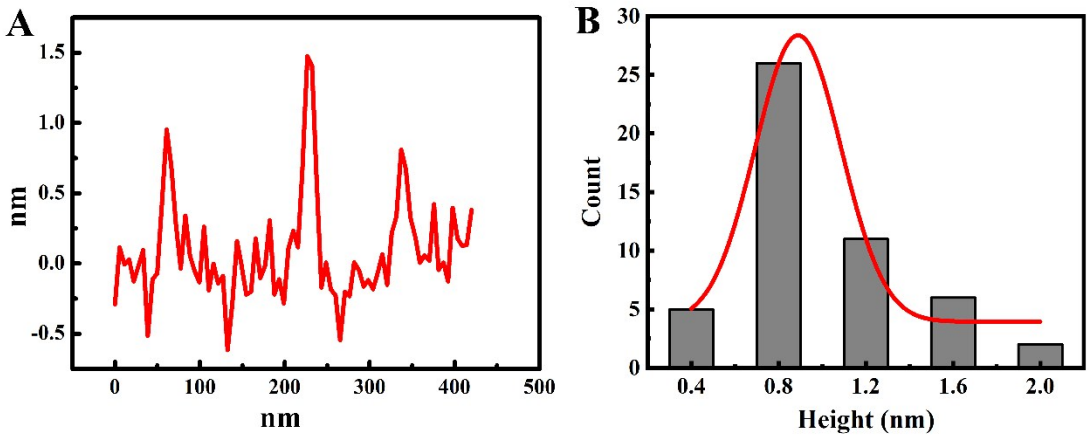

Fig. S2 (A)Along the red line in the AFM image. (B) Statistical analysis of the heights of 50 BPQDs determined by AFM.

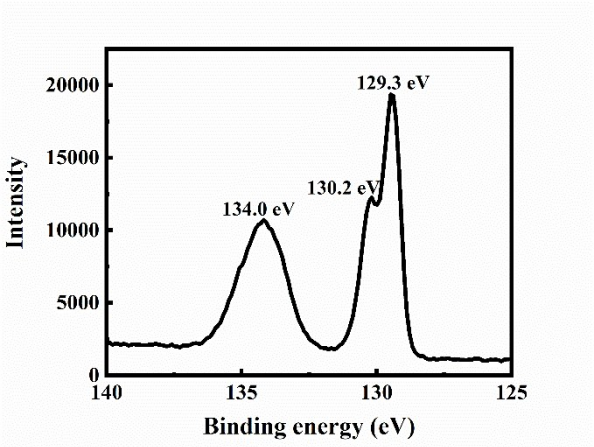

Fig. S3 XPS spectrum of P 2p in BPQDs.

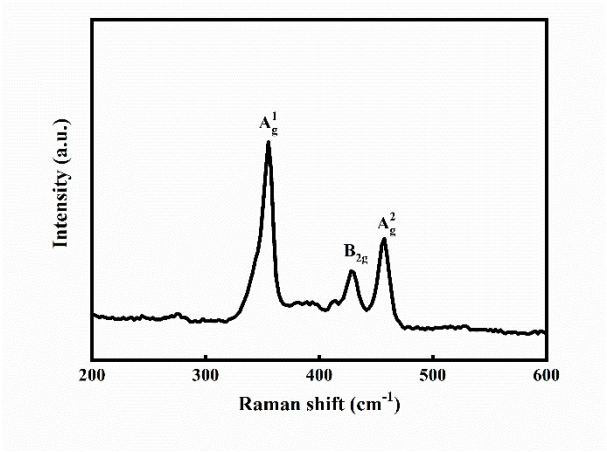

Fig. S4 Raman spectrum of BPQDs.

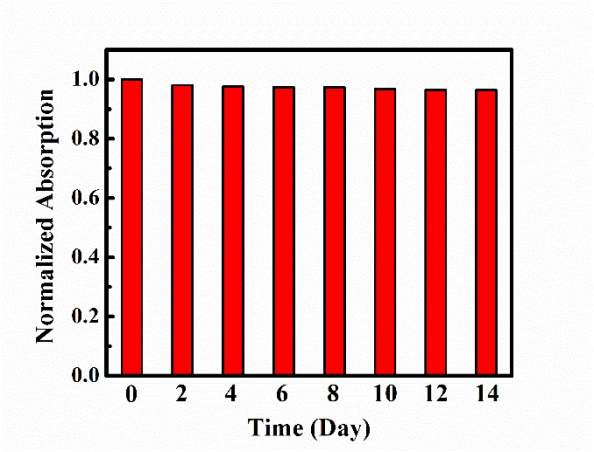

Fig. S5 Absorption intensity at 310 nm of the BPQDs after storing in NMP for different periods of time.

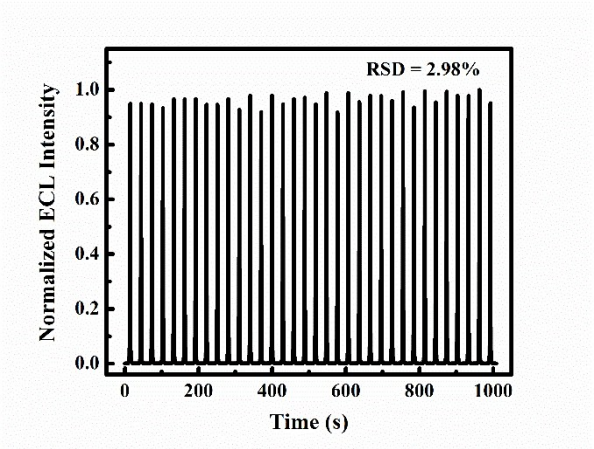

Fig. S6 Time-dependent ECL signals collected of BPQDs/GCE in 0.1 M PBS (pH 7.2) containing 0.1 M $K_2S_2O_8$ at a scan rate of 100 mV s^{-1}.

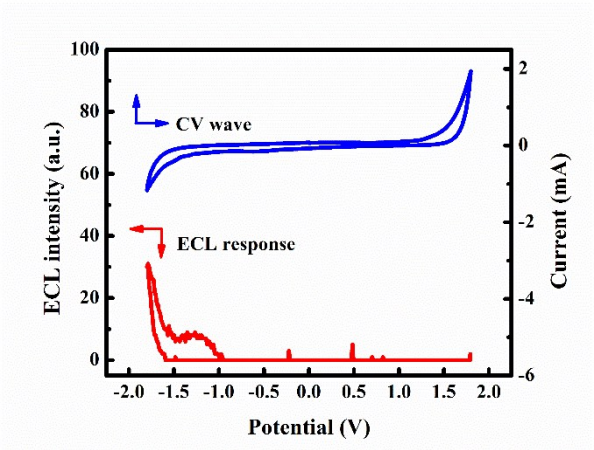

Fig. S7 CV (blue line) and ECL (red line) of BPQDs/GCE in nitrogen-saturated 0.10 M PBS, pH 7.2 at a scan rate of 100 mV s^{-1}.

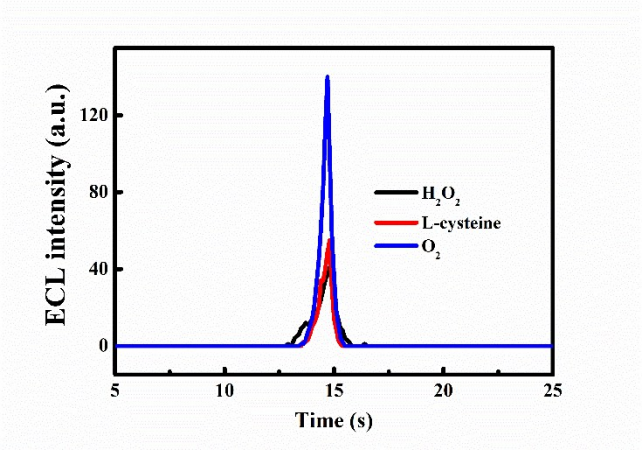

Fig. S8 ECL-time curves of the BPQDs/GCE with different co-reactants including H_2O_2 (black line), L-cysteine (red line) and O_2 (blue line), respectively.

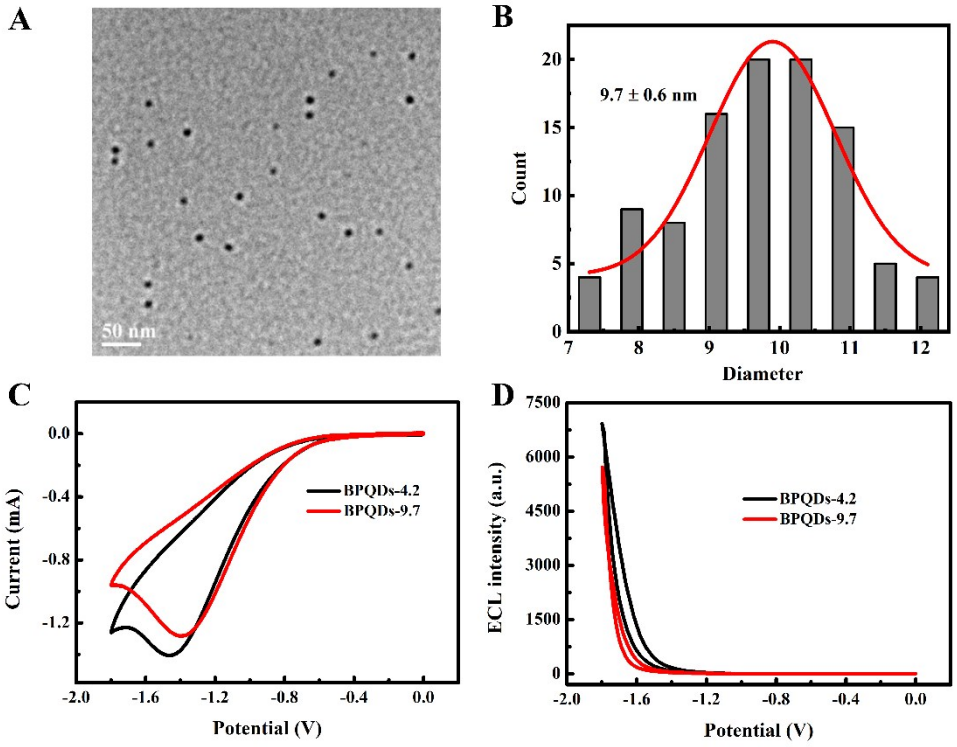

Fig. S9 (A) TEM image of BPQDs with a size of 9.7 nm. (B) Statistical analysis of the size of 100 BPQDs with a size of 9.7 nm based on the TEM images. (A) CV and (B) cathodic ECL of BPQDs-4.2/GCE (black line) and BPQDs-9.7/GCE (red line) in N_2-saturated 0.10 M PBS, pH 7.2, containing 0.1 M $K_2S_2O_8$ with a scan rate of 100 mV/s.

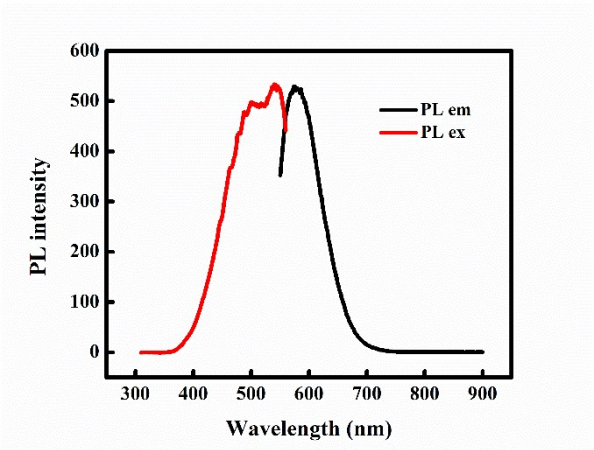

Fig. S10 PL excitation spectrum (red line) and PL emission spectrum (black line) (blue line) of BPQDs with the sizes of 9.7 nm.

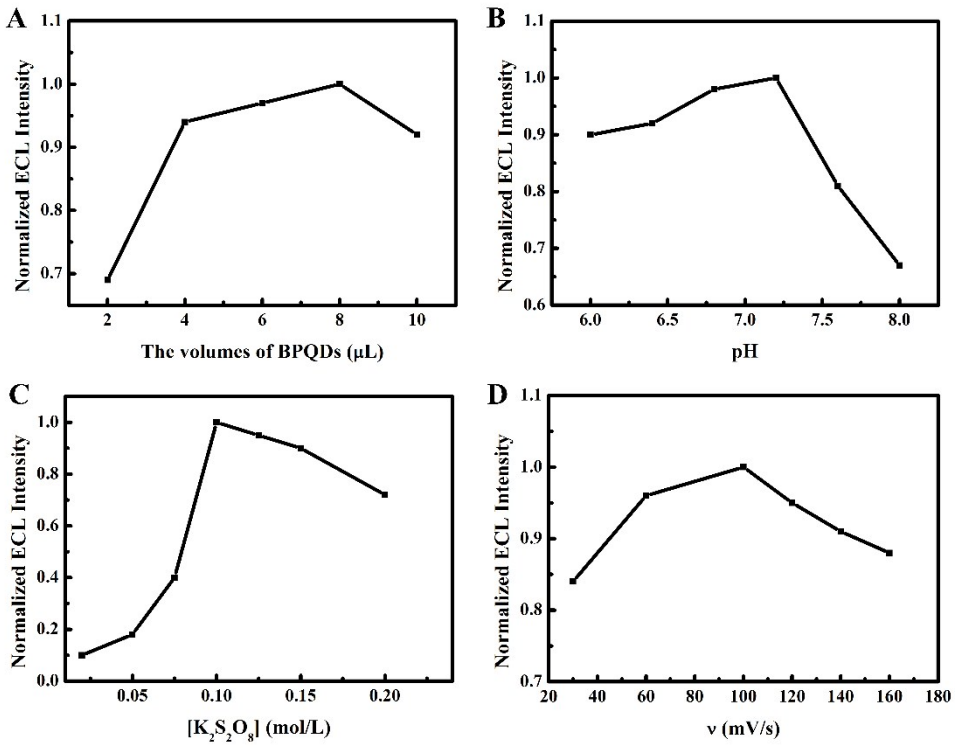

Fig. S11 Effects of the volumes of BPQDs dropped on surface of GCE (A), solution pH (B), $K_2S_2O_8$ concentration (C), and scan rate (D) on the ECL intensity of BPQDs/GCE.

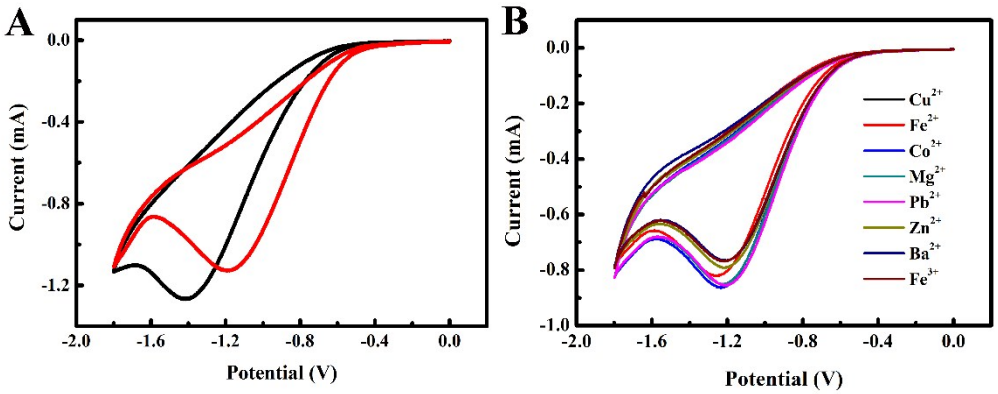

Fig. S12 (A) Cyclic voltammograms of BPQDs modified on the GCE without (black line) and with (red line) 10 nM Cu^{2+} in 0.1 M PBS (pH 7.2). (B) Cyclic voltammograms of BPQDs modified on the GCE with Cu^{2+} and other interfering ions on Cu^{2+} in 0.1M PBS (pH 7.2).

Table S1 Comparison of new BPQDs/ $K_2S_2O_8$-based ECL system with other ECL systems for Cu^{2+} detection

ECL system	Linear range	LOD	Ref
CdS/ZnS QDs/ $K_2S_2O_8$	0.0025–0.20 μM	0.95 nM	2
g-C_3N_4	2.5–100 nM	0.9 nM	3
CNNS/ TEA	0.4–6 μM	250 nM	4
CdTe/CdS/O_2	100–10000 nM	20 nM	5
C,N-QDs@NSs	$5x10^{-4}$ – 10 μM	0.2 nM	6
P-CQDs/H_2O_2	1 – 1000 nM	0.27 nM	7
BPQDs/ $K_2S_2O_8$	0.5–1000 nM	0.07 nM	This work

Table S2 The thermodynamic parameters of the reactions between BPQDs and metal ions at room temperature (T = 298 K, Pb-P has no thermodynamically stable form.)

Reaction	△H(kJ)	△S(J/K)	△G(kJ)	logK
$7P + 5CoCl_2 + 8H_2O = 5CoP + 10HCl + 2H_3PO_4$	–364	948	–647	113
$16P + 15ZnCl_2 + 24H_2O = 5Zn_3P_2 + 30HCl + 6H_3PO_4$	1921	3014	1022	–179
$16P + 15MgCl_2 + 24H_2O = 5Mg_3P_2 + 30HCl + 6H_3PO_4$	3759	2944	2872	N/A
$16P + 15BaCl_2 + 24H_2O = 5Ba_3P_2 + 30HCl + 6H_3PO_4$	6437	3166	5493	N/A
$12P + 5FeCl_2 + 8H_2O = 5FeP_2 + 10HCl + 2H_3PO_4$	–255	811	–497	87
$13P + 5FeCl_3 + 12H_2O = 5FeP_2 + 15HCl + 3H_3PO_4$	–579	1386	–992	174
$11P + 15CuCl_2 + 24H_2O = 5Cu_3P + 30HCl + 6H_3PO_4$	–1072	3114	–2001	308

All calculations were performed using HSC software (HSC Chemistry, Outotech Research).

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