Supplementary materials

A novel electrochemiluminescence aptasensor for sensitive detection of kanamycin based on the synergistic enhancement effects between black phosphorous quantum dots and silver-decorated high-luminescence polydopamine nanospheres

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Experimental section

1. Chemicals and materials

All drugs were of analytical grades and used directly without any treatment. All the solutions used throughout experiments were prepared with ultra-pure water (>18 MΩ). Kanamycin sulfate ($C_{18}H_{36}N_4O_{11}•H_2SO_4$) (≥98%) was purchased from Shanghai Biotechnology Co., Ltd. Bulk BP (99.998%) was obtained from XFNANO Materials Tech Co. Ltd. Disodium hydrogen phosphate ($Na_2HPO_4·12H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4·2H_2O$) were purchased from Shanghai Ling feng Chemical Reagent Co., Ltd. Dopamine hydrochloride ($C_8H_{11}NO_2•HCl$), anhydrous sodium citrate ($Na_3C_6H_5O_7•2H_2O$) were purchased from Shanghai Sa en Chemical Technology Co., Ltd. Hydrogen peroxide (H_2O_2) , 1-methyl-2-pyrrolidone (NMP) , potassium persulfate ($K_2S_2O_8$) , L-cysteine, 1-(3-(dimethylamine)-propyl)-3-ethylcarbodiimide hydrochloride (EDC, 98.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Silver Nitrate ($AgNO_3$) was purchased from Shanghai Shen bo Chemical Co., Ltd. Kanamycin aptamer was synthesized by Shanghai Sangon Biotech Co., Ltd. The sequence of the kanamycin aptamer was designed as: 5'-HOOC-AGA TGG GGG TTG AGG CTA AGC CGA-3'. All other reagents are analytically pure and can be used without further purification. Ultrapure water is used throughout the experiment.

2. Apparatus and methods

Transmission electron microscopy (TEM) images were studied by a JEOL transmission electron microscope (JEOL 2100, Japan). Fourier transform infrared spectroscopy (FT-IR) characterization was analyzed by a Nicolet In10 (Thermo Fisher Scientific, USA). Raman spectra were obtained by Raman Spectrometer (LabRAM HR Evlution, Japan). The Zeta potential values were obtained on a Laser particle size analyzer (Malveren Instruments, US). The UV-vis absorption spectra and the fluorescence spectra were obtained from an UV-2450 spectrophotometer (Shimadzu, Japan). ECL measurements were performed on MPI-B multifunctional ECL system (Xi'an Ruimai Analytical Instrument Co., Ltd.), with three-electrode system: a modified glassy carbon electrode (GCE) (Φ = 3 mm) as the working electrode, a platinum wire as the auxiliary electrode, and Ag/AgCl as the reference electrode. Electrochemical impedance spectroscopy (EIS) was studied by CHI660D electrochemical workstation (Shanghai CH Instrument Co., Ltd., China).

UV-vis absorption spectra provided more significant information on the successful immobilization of BPQDs onto the HLPNs@Ag. As shown in Fig. S1(A), the UV-vis spectrum of HLPNs@Ag (curve a) presents the characteristic peak of Ag at around 410 nm. The UV-vis spectrum of BPQDs (curve b) shows an obvious absorption peak at about 285 nm. The UV-vis spectrum of HLPNs@Ag/BPQDs (curve c) presents the characteristic peaks of Ag and BPQDs, indicating that HLPNs@Ag/BPQDs is successfully synthesized. Fig. S1(B) reveals that BPQDs can emit fluorescence at 350 nm with an excitation wavelength of 285 nm (Fig. S1(A), curve b). The light absorption can be observed at a lower wavelength, suggesting the potential spectroscopic application of these novel semiconductor quantum dots.

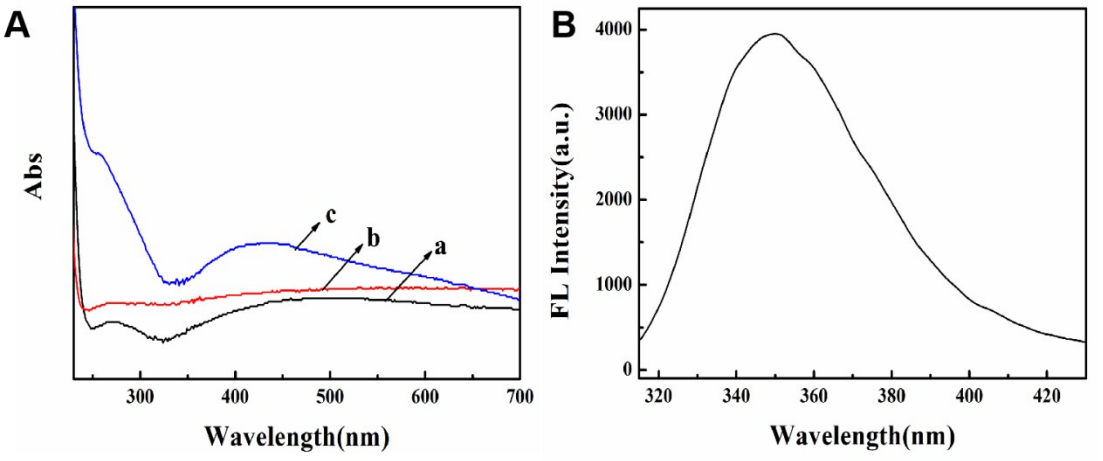

Fig. S1. (A)UV-vis absorption spectra of HLPNs@Ag (a), BPQDs(b), HLPNs@Ag/BP (c). (B) Fluorescence spectra of BPQDs

Tabel S1. The zeta potential of BPQDs, BPQDs−SH, HLPNs, HLPNs@Ag, HLPNs@Ag/BP

Materials	Zeta potential (mV)
BPQDs	-20.2
BPQDs−SH	15.1
HLPNs	-25.0
HLPNs@Ag	-24.9
HLPNs@Ag/BP	-12.6

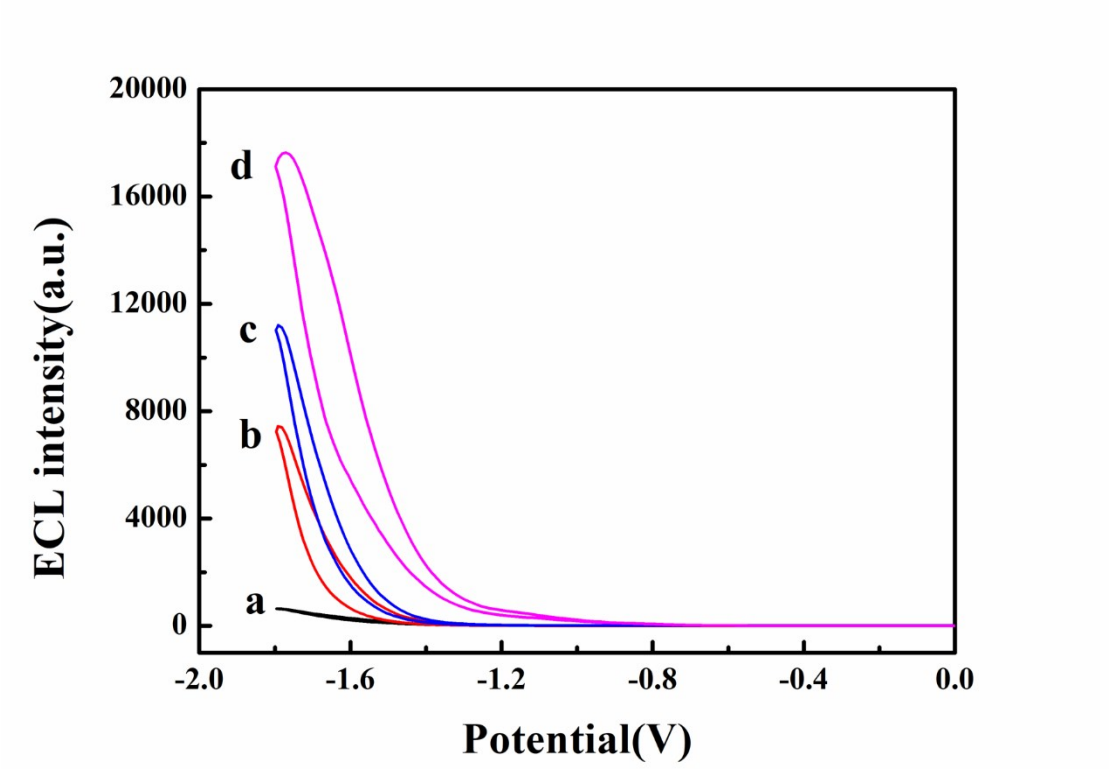

Fig. S2 ECL responses were collected synchronously by using the homemade three-electrode system (scan range: -1.8–0 V, vs Ag/AgCl; scan rate, 0.1 V/s): (a) $S_2O_8^{2-}$ solution, (b)BPQDs + $S_2O_8^{2-}$ solution, (c) HLPNs/BP + $S_2O_8^{2-}$ solution, (d) HLPNs@Ag/BP + $S_2O_8^{2-}$ solution.

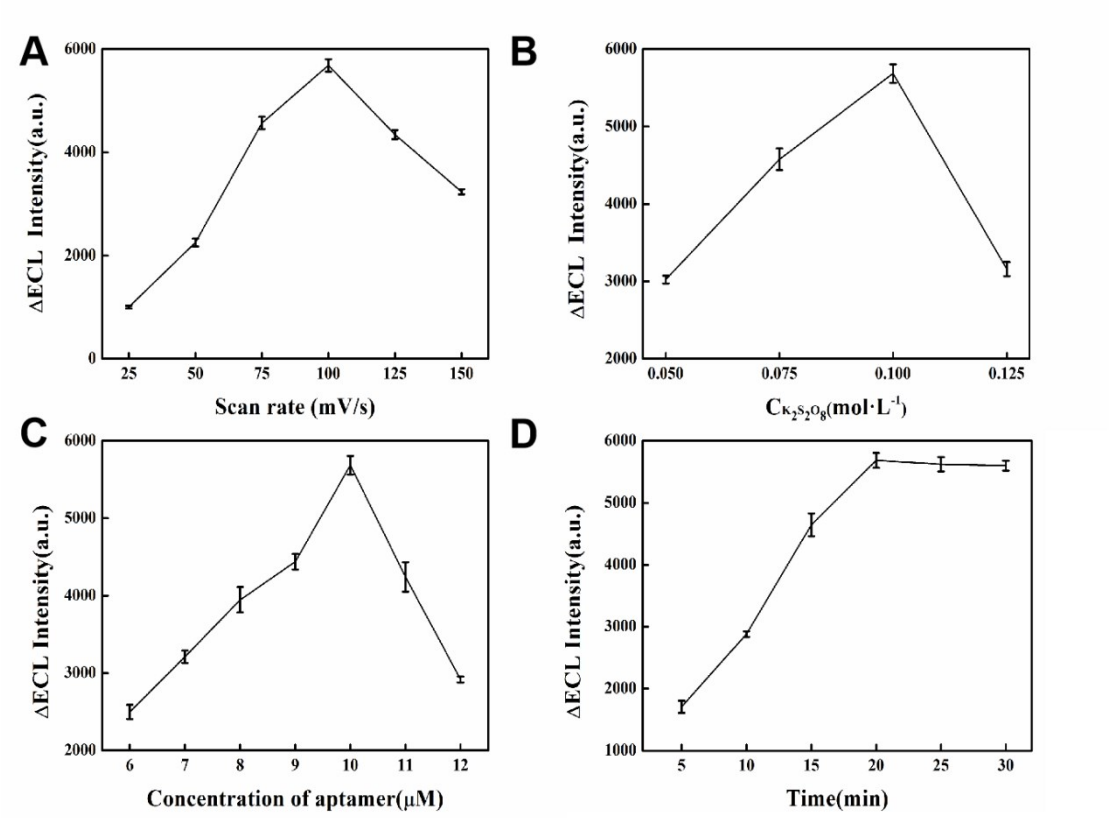

Fig. S3 Optimization of (A) Scan rate; (B) concentration of $K_2S_2O_8$; (C) incubated concentration of KAN aptamer and (D) incubation time of ECL aptamer-sensor in 1.0×10^{-9} M KAN solution.

Table S2. The comparison of different method to determine KAN

Method	Linear range (M)	LOD (M)	Reference
Fluorescence	5.0×10^{-9} ~ 7.1×10^{-8}	2.3×10^{-12}	1
PEC	2×10^{-10} ~ 2.5×10^{-7}	0.2×10^{-12}	2
Fluorescence	8×10^{-10} ~ 3.5×10^{-8}	0.3×10^{-12}	3
SPR	1×10^{-7} ~ 1×10^{-5}	4.33×10^{-11}	4
Colorimetry	3.35×10^{-9} ~ 5.375×10^{-8}	3.35×10^{-12}	5
Electrochemistry	1×10^{-8} ~ 1.5×10^{-7}	5.8×10^{-12}	6
ECL aptamer-sensor	1×10^{-12} ~ 1×10^{-7}	1.7×10^{-13}	This work

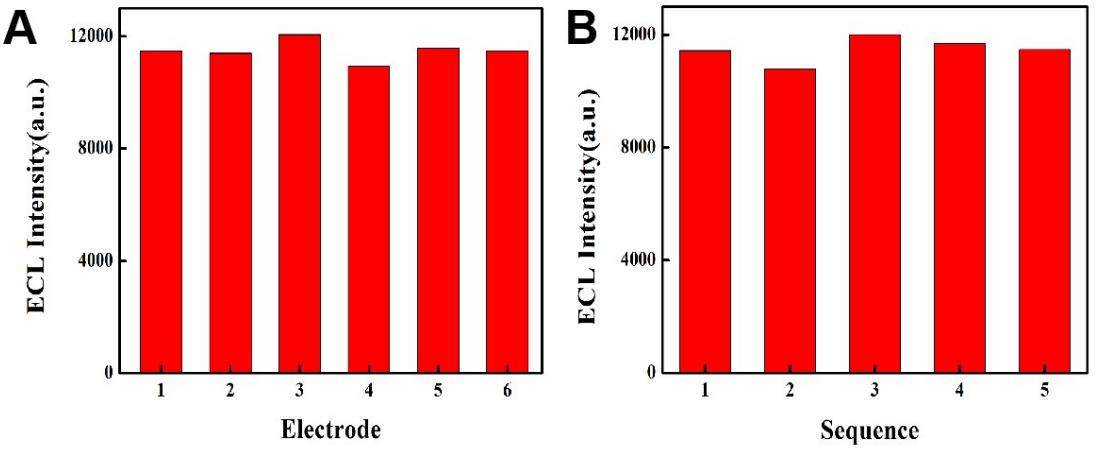

Fig. S4. (A)Repeatability of KAN detection by 6 parallel measurements; (B) Stability of KAN detection in five times. The concentration of KAN was 10^{-8}M.

Table S3. Application of the ECL aptasensor for KAN determination in real samples

Sample	Added (nM)	Found (nM)	Recovery %	RSD (%) (n=3)
Lake water	0	None	-	-
		0.97	97.0	
	1	1.03	103.0	3.04
		1.01	101.0	
		10.25	102.5	
	10	9.77	97.7	2.56
		9.86	98.6	
Pond water	0	None	-	-
		0.98	98.0	
	1	1.04	104.0	3.21
		0.99	99.0	
		10.32	103.2	
	10	10.17	101.7	2.48
		9.83	98.3	

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