Supplementary Information (SI) for Analytical Methods.
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Supporting Information

Electrochemiluminescence immunosensor for sensitive determination of pancreatic neuroendocrine tumors biomarker chromogranin B based on graphdiyne quantum dots

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Experimental

Chemicals and Materials

GDY was donated by Prof. Yuliang Li (Institute of Chemistry, Chinese Academy of Sciences, Beijing, China). CgA, CgB and anti-CgB monoclonal antibodies were purchased from Abcam (USA). Human immunoglobulin G (IgG) was purchased from Beijing Bioss Biotechnology Co., Ltd. (Beijing Chian). Bovine serum albumin (BSA) was obtained from Beijing BioDee Biotechnology Co., Ltd. (Beijing, China). Ethyleneiminepolymer (PEI), N-Hydroxysuccinimide (NHS), 1-(3-dime-thylaminopropyl)-3-ethylcar-bodiimide hydrochloride (EDC), and Chloroauric acid ($HAuCl_4$) were purchased Beijing Inno-chem Technology Co., Ltd. (Beijing, China). Potassium persulfate ($K_2S_2O_8$) was obtained from Fortune Chemical Reagent Co., Ltd. (Tianjin, China). Deionized distilled water (DDW) was used in all experiments.

Apparatus

Transmission electronic microscopy (TEM) images were taken on a Hitachi HT7700 instrument (Japan). High-resolution TEM (HRTEM) images were taken on a JEOL JEM-2100 microscope (Japan). Atomic force microscope (AFM) images were obtained by using the NanoScope IIIa microscope from Veeco Instruments (USA). X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer (Thermo ESCALAB 250) (USA). Raman spectra are obtained by LabRAM Aramis Raman Spectrometer with a 532 nm excitation laser (France). Fourier Transform Infrared (FT-IR) spectra were measured on a Bruker Vertex 70 FT-IR spectrometer using KBr pressed disks (Germany). UV-Vis spectra were recorded using

a UV-2501PC spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were obtained on an 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 400, 440, 490, 535, 575, 620, 640, 665, and 715 nm. Cyclic voltammetric tests were recorded by a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments, Co., Ltd, Shanghai, China). ECL measurements were carried out with a Model MPI-E Electrochemiluminescence Analyzer (Xi'an Remex Analytic Instrument Co., Ltd, Xi'an, China).

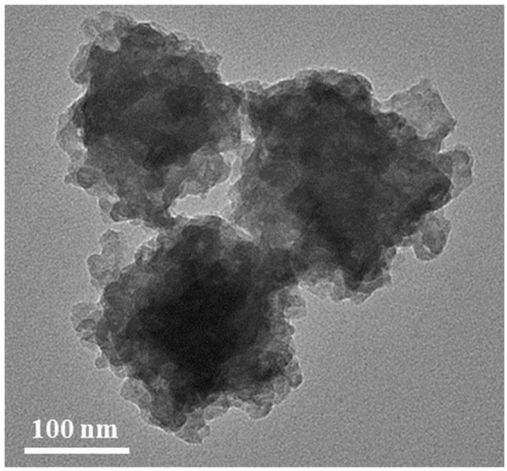

Fig. S1 TEM image of GDY.

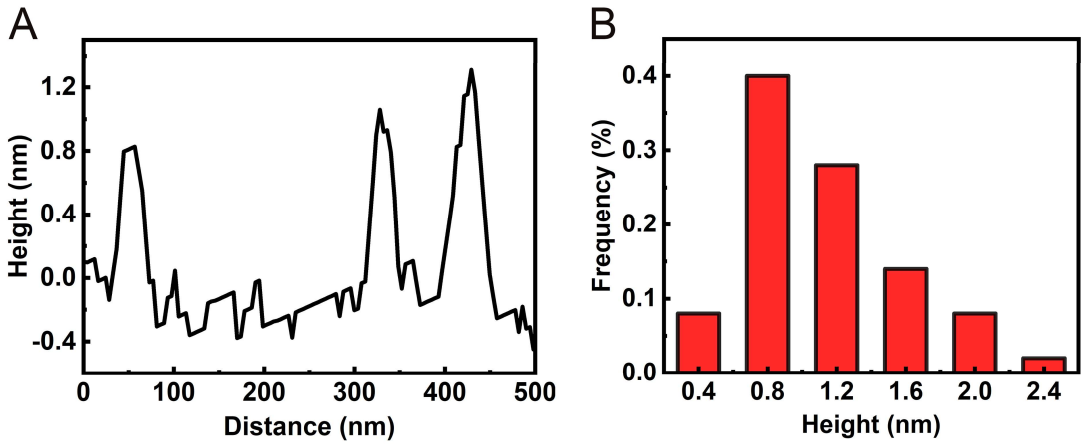

Fig. S2 (A) The height profiles along the red lines in the AFM image of Fig. 1C. (B) Statistical analysis of the heights of 50 GDY QDs determined by the AFM image of Fig. 1C.

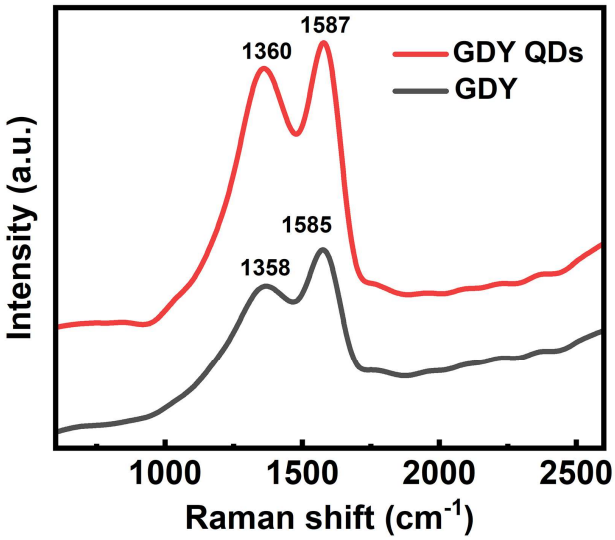

Fig. S3 Raman spectra of GDY and GDY QDs.

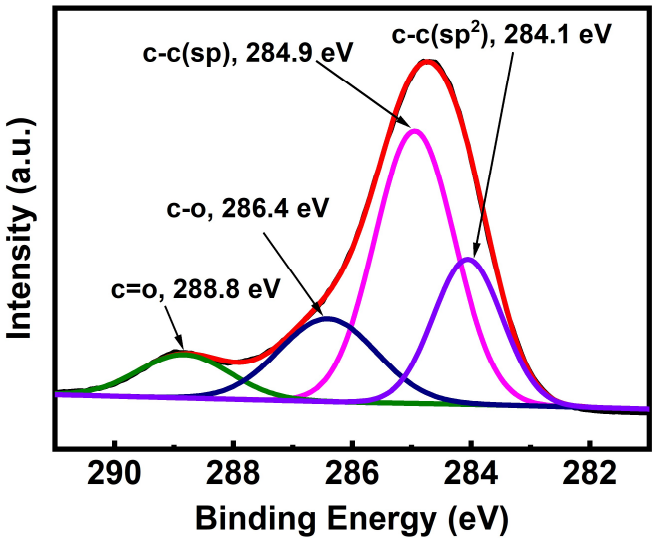

Fig. S4 High-resolution C 1s spectrum of GDY.

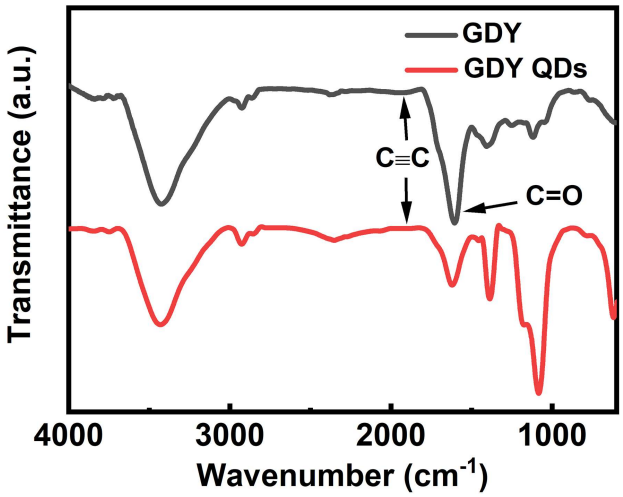

Fig. S5 FT-IR spectra of GDY and GDY QDs.

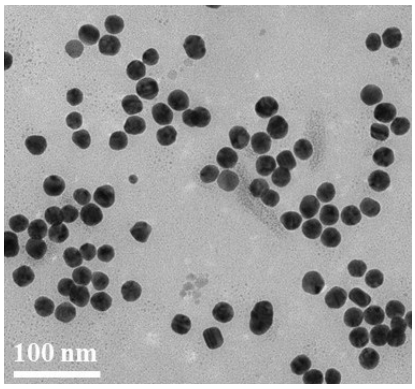

Fig. S6 TEM image of Au NPs.

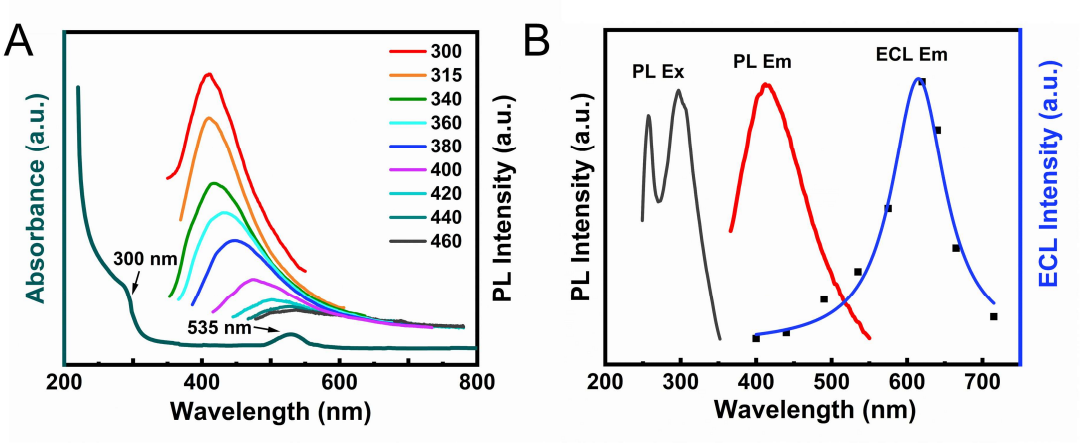

Fig. S7 (A) UV-Vis absorption spectrum and fluorescence spectra at different excitation wavelengths of GDY QDs@Au NPs. (B) PL excitation, emission and ECL emission spectrum of GDY QDs@Au NPs.

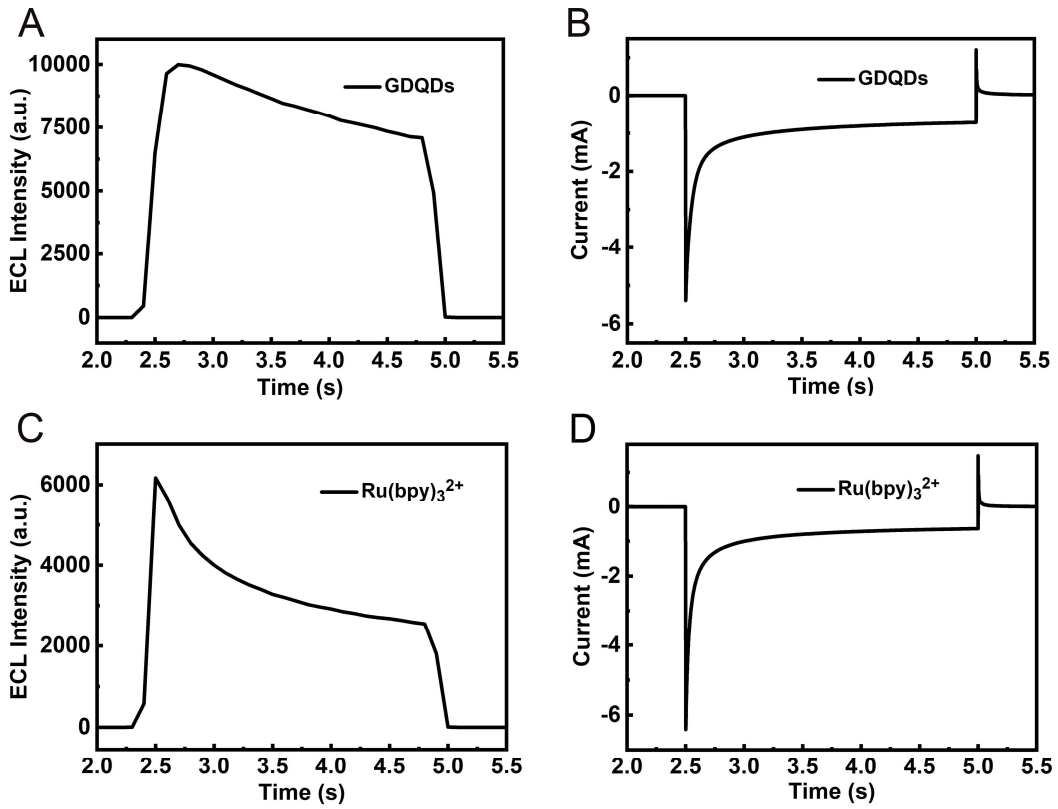

Fig. S8 ECL curves of GDY QDs (A) and $Ru(bpy)_3^{2+}$ (C), corresponding chronoamperometry curves (B, D) in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} $K_2S_2O_8$.

The Φ_{ECL} of the GDY QDs-$K_2S_2O_8$ system was calculated according to the following equation used in the previous works[1, 2]:

$$\Phi_{ECL}=\frac{\left(\frac{\int ECL\,dt}{\int Current\,dt}\right)_x}{\left(\frac{\int ECL\,dt}{\int Current\,dt}\right)_{st}}\times 100\% \qquad \text{(S1)}$$

Herein, ECL and current are the ECL intensity and electrochemical current values, respectively, *st* stands for the $Ru(bpy)_3^{2+}$-$K_2S_2O_8$ system as standard and *x* refers to the GDY QDs-$K_2S_2O_8$ system.

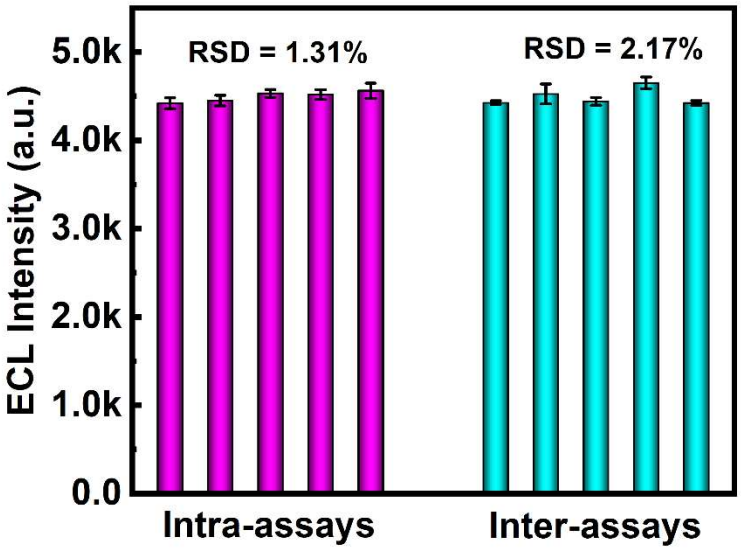

Fig. S9 Intra-assays and inter-assays study of anti-CgB/GDY QDs@Au NPs/GCE incubated with 100 pg mL^{-1} CgB in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} $K_2S_2O_8$.

Table S1 The proposed immunosensor detects CgB in human serum samples (n=3).

Samples number	Added (pg mL^{-1})	Measured (pg mL^{-1})	RSD (%)	Recovery (%)
1	0.1	0.099	4.0	98.81
2	10.0	10.050	3.1	100.46
3	1000.0	1020.230	2.0	102.02

References

1 R. Zhang, J. R. Adsetts, Y. Nie, X. Sun and Z. Ding, *Carbon*, 2018, **129**, 45-53.

2 C. Venkateswara Raju, G. Kalaiyarasan, S. Paramasivam, J. Joseph and S. Senthil Kumar, *Electrochim. Acta*, 2020, **331**, 135391.