Supporting information

Green fluorescent graphitic carbon nitride nanosheets for sensing of copper ions in living cells

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Preparation of PDCN nanosheets

In a typical procedure, 10 g urea and 0.0186 g trimesic acid were dissolved in hot water. After dried at 80-90℃, the mixture was ground into powder, and then put in an alumina crucible with a cover and heated to 500℃ for 2 h with a heating rate of 5 °C min^{-1} under nitrogen protection. After cooling to room temperature, the powder was collected for further characterization and treatment.

Next, 100 mg bulk PDCN powder was refluxed in 15 mL HNO_3 (16 mol L^{-1}) at 80℃ for 3 h. After cooling down to room temperature, the yellow product was centrifuged at 12000 rpm for 5 min, washed with ultrapure water to neutral pH. Finally, the precipitate was sonicated in 30 mL water for 10 h. The resultant solution was centrifuged at 8000 rpm for 5 min to remove the large PDCN nanosheets. The concentration of PDCN nanosheets was approximately 900 μg mL^{-1}.

Characterizations

Absorption spectrum was obtained on a Perkin-Elmer Lamda 750 UV-Vis-NIR spectrometer. Transmission electron microscopy (TEM) image was collected with a FEI Tecnai G2F20 transmission electron microscope at an accelerating voltage of 200 kV. The thickness of PDCN nanosheets was collected by a Bruker Multimode III scanning probe microscope. X-ray photoelectron spectroscopy (XPS) spectrum was collected by a VG ESCALAB 250 X-ray photoelectron spectrometer. X-ray diffraction (XRD) pattern was investigated by a Rigaku Ultima IV diffractometer equipped with Cu Kα radiation (40 kV, λ=1.5418Å). The particle size distribution and zeta potential of PDCN nanosheets were measured by dynamic light scattering (DLS) method using a Malvern zetasize nano-zs90 nanoparticle size potential analyzer. The fluorescent spectrum was performed on an Edingburgh Instruments FLS920 fluorescence spectrometer. The fluorescent images were taken on a Nikon C2 confocal fluorescence microscope.

Absolute Quantum Yield:

The absolute quantum yield of PDCN nanosheets was determined by using an EI

FLS920 spectrofluorometer equipped with an integrating sphere. 3 mL dispersion solution of PDCN nanosheets was sealed in a quartz cell (10 mm × 10 mm), and its absorption intensity at 310 nm was controlled in the range of 0.15-0.40. The same volume of water was used as the blank sample. The excitation wavelength was set at 310 nm. The scattering spectral range was set from 290 nm to 360 nm, and the emission spectral range was set from 400 to 720 nm.

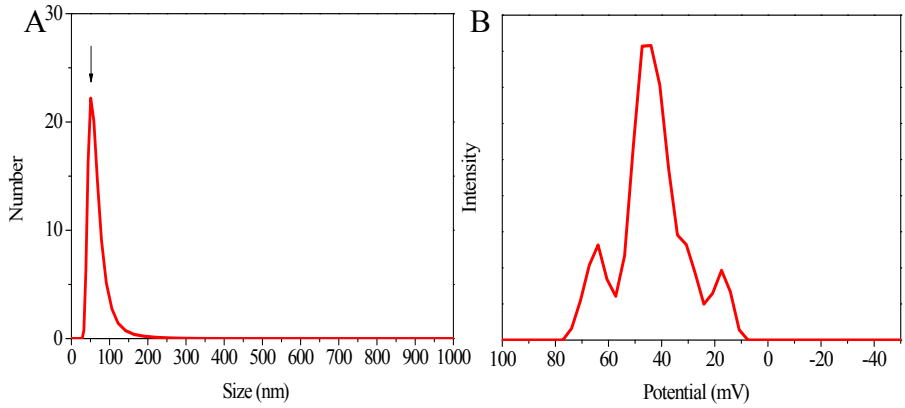

Fig. S1. (A) Particle size distribution and Zeta potential distribution (B) of PDCN nanosheets by dynamic light scattering

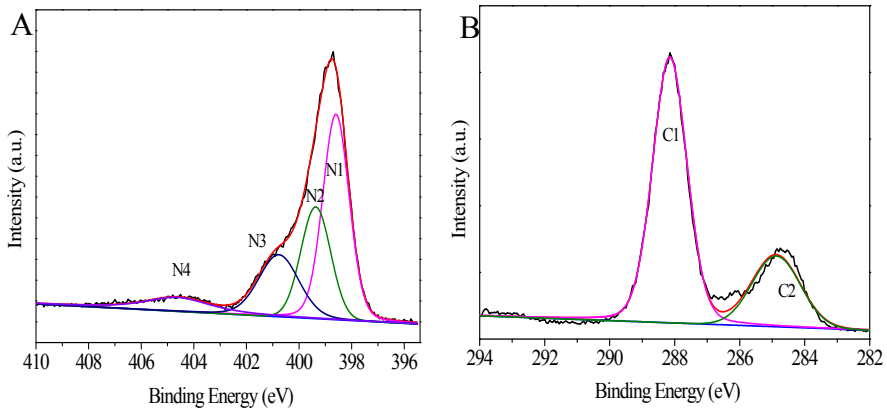

Fig. S2. (A) N 1s and C 1s (B) core-level XPS spectra of bulk PDCN

The C 1s core-level spectrum of bulk PDCN could be divided into two peaks at 284.7 (C2) and 288.1 e V (C1), corresponding to C-C and N-C=N, respectively. For N 1s core-level spectrum of bulk PDCN, four different peaks at 398.5 (N1), 399.3 (N2), 400.7 (N3), 404.5 eV (N4) were assigned as pyridinic nitrogen (C=N-C), pyrrolic nitrogen (C-N-C), primary amine nitrogen atoms ($-NH_2$), and charging effects or positive charges localization in the heterocycles, respectively.

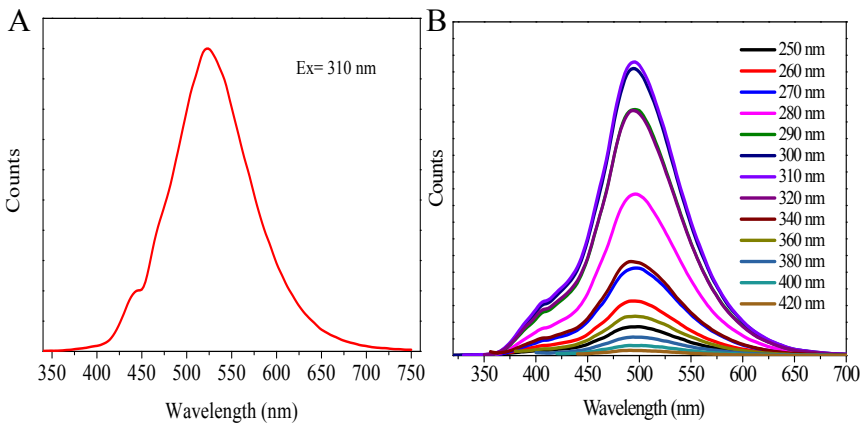

Fig. S3. (A) Fluorescent spectrum of bulk PDCN under excitation of 310 nm; (B) Fluorescent spectra of PDCN nanosheets dispersion under different excitation wavelength.

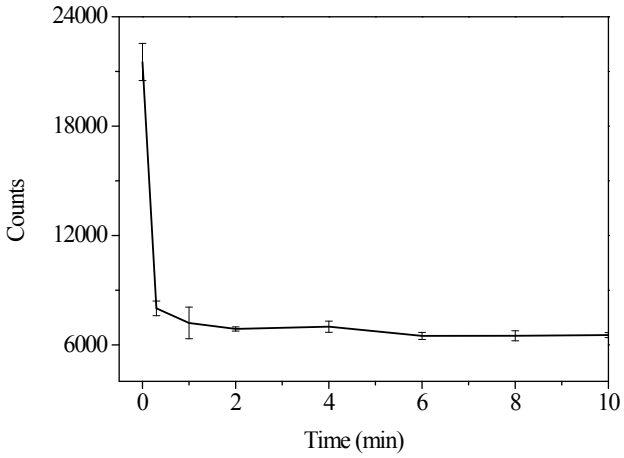

Fig. S4. Fluorescent intensity of PDCN nanosheets at 498 nm as a function of reaction time on addition of 2.0 μmol L^{-1} Cu^{2+}. Error bars were calculated from three repeated measurements

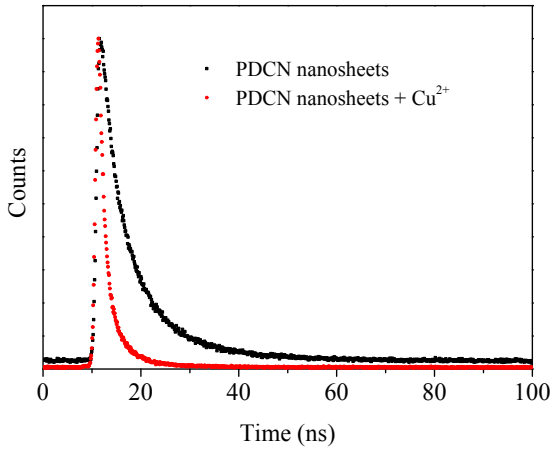

Fig. S5. The decay curves of PDCN nanosheets and PDCN nanosheets with 2.0 μmol L^{-1} Cu^{2+} when excited with a 340 nm laser and emission at 500 nm.

Table S1. Fluorescence lifetime parameters of PDCN nanosheets before and after adding 2 μmol L^{-1} Cu^{2+}

	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ_3 (ns)	Rel (%)	χ^2	$\tau_{average}$ (ns)
PDCN nanosheets	2.65	29.62	6.66	51.15	17.97	18.90	1.052	6.36
PDCN nanosheets + Cu^{2+}	1.23	27.84	3.79	51.71	12.36	20.45	1.011	2.73

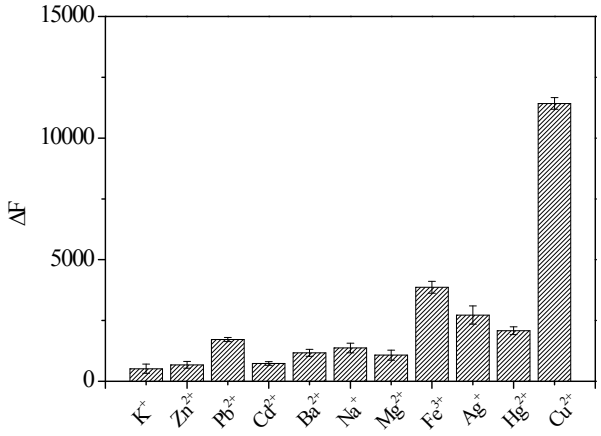

Fig. S6. Fluorescent quenching of PDCN nanosheets on addition of different metal ions (The concentrations of K^+, Zn^{2+}, Pb^{2+}, Ba^{2+}, Na^+, Mg^{2+}, Fe^{3+} are 5.0 μmol L^{-1} and the concentrations of Ag^+, Hg^{2+}, Cu^{2+} are 2.0 μmol L^{-1})

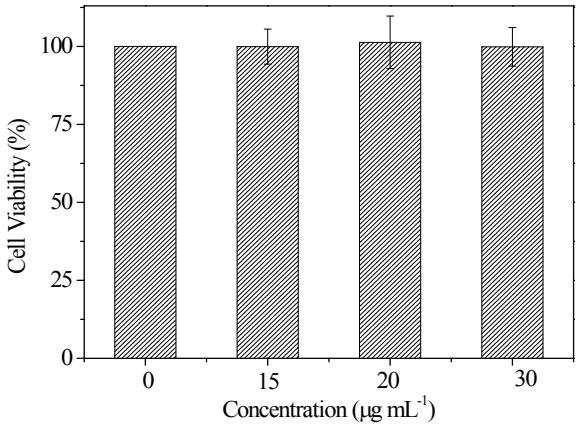

Fig. S7 Cell viability of HeLa cells in the presence of different concentrations of PDCN nanosheets

Table S2. Comparison of sensing performance of different carbon nitride fluorescent probes for Cu^{2+} detection.

Fluorescent probes	Fluorescent color	Detection limit (nmol L^{-1})	Linear range (μ mol L^{-1})	Ref.
c-mpg-C_3N_4	Blue	12.3	0.01-0.1	S1
Ultrathin g-C_3N_4 nanosheets	Blue	0.5	0-10	S2
g-C_3N_4 nanosheets	Blue	0.5	-	S3
F-g-C_3N_4 dots	Blue	0.5	-	S4
P,O-g-C_3N_4 nanodots	Blue	2.0	0-1.0	S5
CNNF	Blue	60	0-1.0	S6
BCN nanosheets	Blue-green	70	0.1-1.0	S7
PDCN nanosheets	Green	39	0.1-2.0	This work

Reference

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