

Electronic Supplementary Information

Dielectric barrier discharge-mediated one-pot rapid synthesis of platinum nanoclusters for fluorescent sensing of malachite green

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Reagents and materials

Ultrapure water (18.2 M Ω cm) was prepared from a water purification system (PCWJ-10, Sichuan Ultrapure Technology Co., Ltd., Chengdu, China) and used throughout this work. Unless otherwise specified, chemicals used in this work were at least of analytical grade. Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), Tris(hydroxymethyl)aminomethane were purchased from Damas-beta (Shanghai, China). Dihydrolipoic Acid, Dithiothreitol, Citric Acid (Trisodium), Malachite green (MG), Tetracycline hydrochloride, Glyphosate, Melamine, Dopamine hydrochloride, Leucine (Leu), Lysine (Lys), Glutathione (GSH), Cysteine (Cys) and various chlorides of silver, magnesium, calcium, copper, zirconium, sodium, iron, and zinc were purchased from Aladdin Reagent Corporation (Shanghai, China). Ascorbic acid, NaOH, HCl and Urea were acquired from Chron Chemicals (Chengdu, China). Tris buffer (pH 5.0, 100 mM) was prepared using Tris(hydroxymethyl)aminomethane, NaOH and HCl.

Real water samples were obtained from Listening Lotus Pond, Wangjiang Campus, Sichuan University and Yanhu Lake, Chengdu University of Technology. Real water samples were first filtered using a 0.22 μ m membrane for FL analysis. Crucian and snakehead were purchased from a local supermarket, and the skin and bones were removed, and the back muscles were minced. First, 4 g of minced meat was placed in a 50 mL plastic centrifuge tube. Then, 20 mL of methanol-water mixture (1:1, v/v) was added to the tube. The supernatant was discarded after shaking for 10 minutes and centrifugation at 10,000 rpm for 10 minutes. Subsequently, 20 mL of hydrochloric acid (0.2 M) was added to the residue. After homogenization for 1 min, the mixture was placed in an ultrasonic bath for approximately 10 min and centrifuged at 10,000 rpm for 10 min. The pH of the supernatant was adjusted to 5.0 and the solution was filtered through a 0.22 μ m microfiltration membrane and used directly in the FL analysis.

Instrumentation and characterization

The DBD reactor consisted of a concentric quartz cylinder tube with an exterior electrode made of copper wire wrapped around the outside of the tube and an internal electrode made of a tungsten rod placed into the inner cylinder. Both electrodes were connected to an electrical power supply. Transmission electron microscope (TEM and STEM-Mapping) images were

accomplished with a Talos F200S and a FEI Titan Cubed Themis G2 300 transmission electron microscope (American FEI, Inc.). Photoluminescence and UV-Vis absorption spectra were measured using an F-7000 fluorescence spectrophotometer (Hitachi, Japan) and a UH5300 UV-Vis spectrophotometer (Hitachi, Japan), respectively. Photoluminescence quantum yield (PLQY) and lifetime measurements were conducted on an Quantaaurus-QY Plus UV-NIR (Hamamatsu, Japan) and a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon, USA). An X-ray diffraction spectrometer (EMPYREAN, Netherlands) with a Cu sealed tube was used to figure out the structure of synthesized GSH@PtNCs. Fourier-transform infrared (FTIR) analysis was carried out using a Nicolet IS10 FT-IR spectrometer (Thermo Inc., USA). X-ray photoelectron spectroscopy (XPS) spectra was recorded with an AXIS Ultra DLD spectrometer (Kratos, UK). The pH was measured by a Seven Compact pH meter (Mettler Toledo, Switzerland).

Synthesis of GSH-protected platinum nanoclusters (GSH@PtNCs)

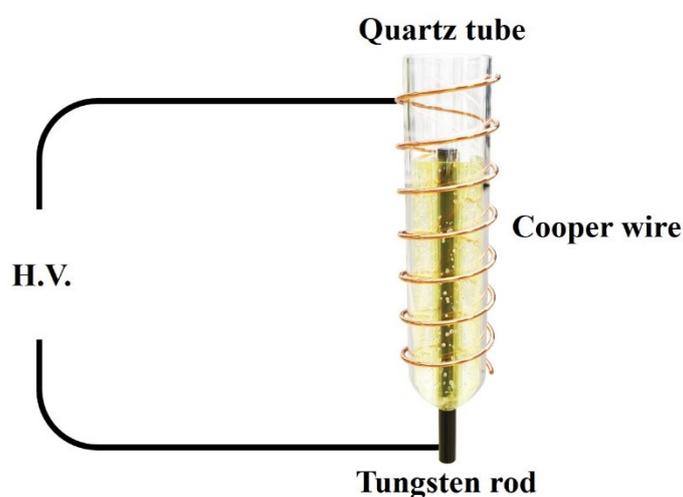


Fig. S1. The structure of the dielectric barrier discharge (DBD) device.

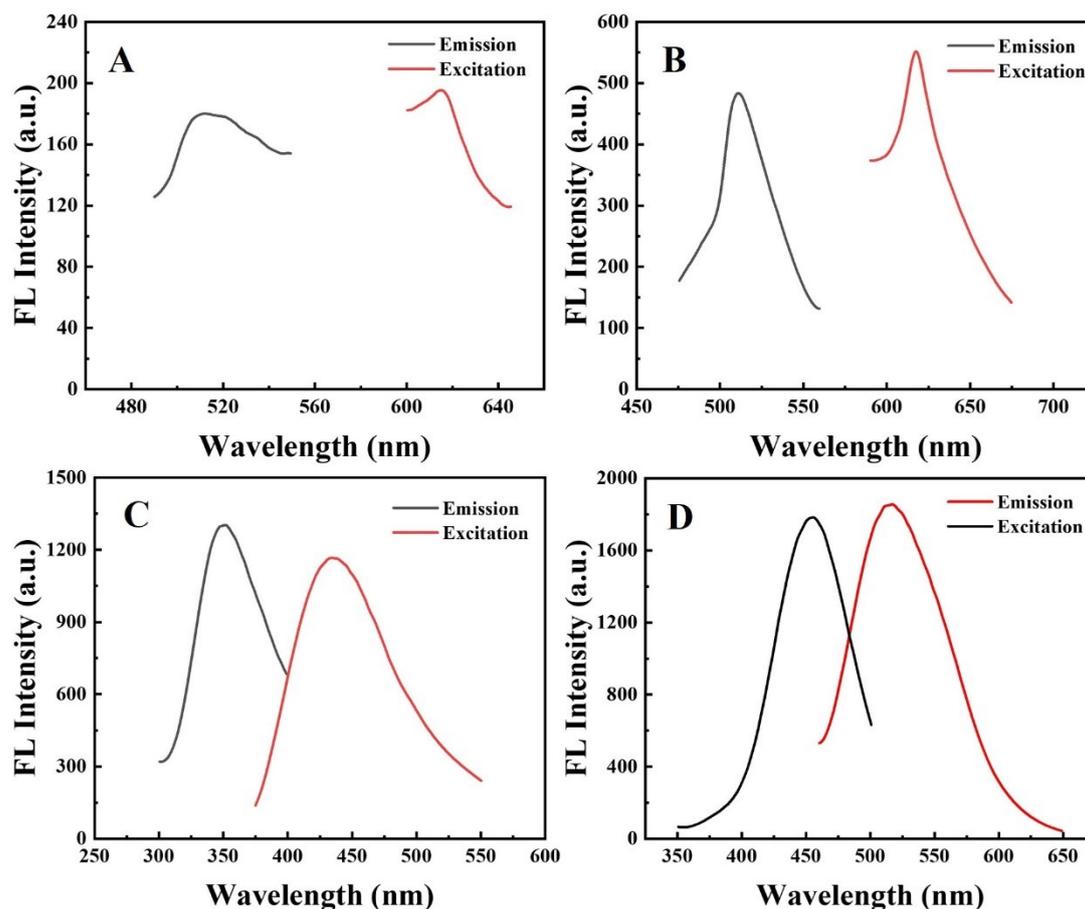


Fig. S2. The excitation and emission spectra of PtNCs protected by different ligands. (A) dihydrolipoic acid, (B) cysteine, (C) dithiothreitol, (D) glutathione.

For synthesizing PtNCs using DBD, we conducted ligand screening experiments and finally selected glutathione, which has high fluorescence intensity and stable signal, as the ligand for protecting the nanoclusters (Fig. S2). And the synthesis conditions of GSH@PtNCs were optimized by monitoring several factors as molar ratios of AA (reducing agent) and GSH (ligand) to the metal precursor Pt^{4+} in mixture solution, reaction time, DBD voltage, and the concentration of Pt^{4+} precursor (Fig. S3).

GSH@PtNCs might be unstable under strong reducing conditions and decomposed into complexes again. When the ratio of thiol to Pt^{4+} was low, the amount of ligand was not sufficient to completely chelate with Pt^{4+} , and the addition of reducing agent resulted in the formation of lumpy Pt, instead of dispersed particles; conversely, the chelating effect of the ligand with Pt^{4+} was so strong that the Pt:SR complex could not react with the reductant AA. Shorter synthesis time and lower voltage might lead to incomplete reaction, while longer synthesis time and higher voltage might cause some of the products PtNCs to be etched again

and aggregate into large particles of PtNPs, resulting in a decrease in the fluorescence of the material. We chose the concentration of Pt^{4+} with good performance of fluorescence intensity and saved the amount of raw materials as metal precursor to be added.^{1,2}

Finally, the optimal synthesis conditions were selected as follows: a molar ratio of 20:1 for AA to Pt^{4+} , a molar ratio of 5:1 for GSH to Pt^{4+} , a reaction time of 2.5 h, a DBD voltage of 32 V, and a Pt^{4+} concentration of 10 mM. The synthesized products GSH@PtNCs showed good salt tolerance and maintained stable spectral properties after being stored at room temperature for one month (Fig. S4).

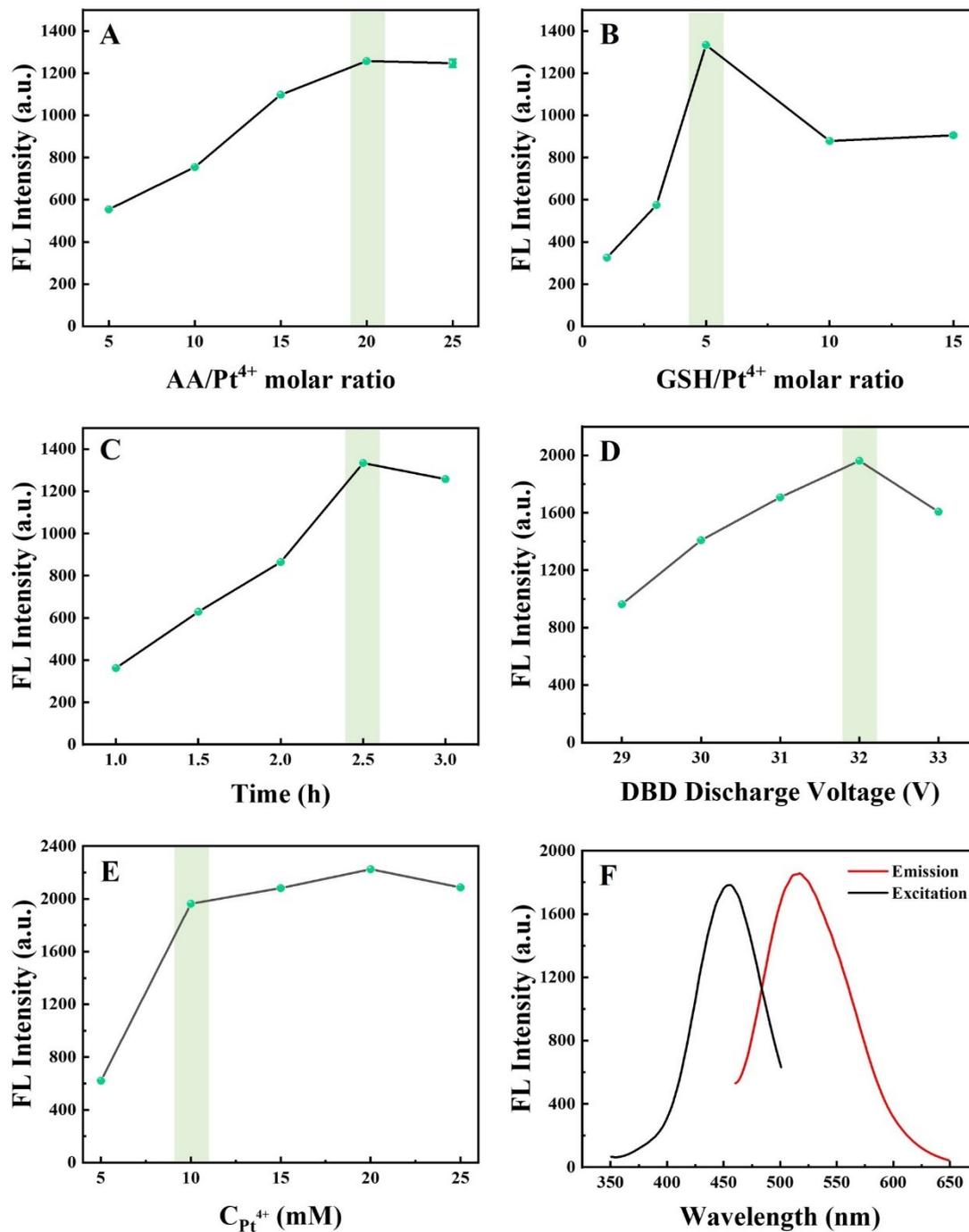


Fig. S3. Effects of (A) molar ratios of ascorbic acid (reducing agent) to Pt⁴⁺ precursor, (B) molar ratios of glutathione (ligand) to Pt⁴⁺ precursor, (C) reaction times, (D) DBD discharge voltages, (E) concentrations of Pt⁴⁺ precursor on the fluorescence intensity of GSH@PtNCs recorded under 440 nm wavelength excitation; and (F) the excitation and emission spectra of GSH@PtNCs.

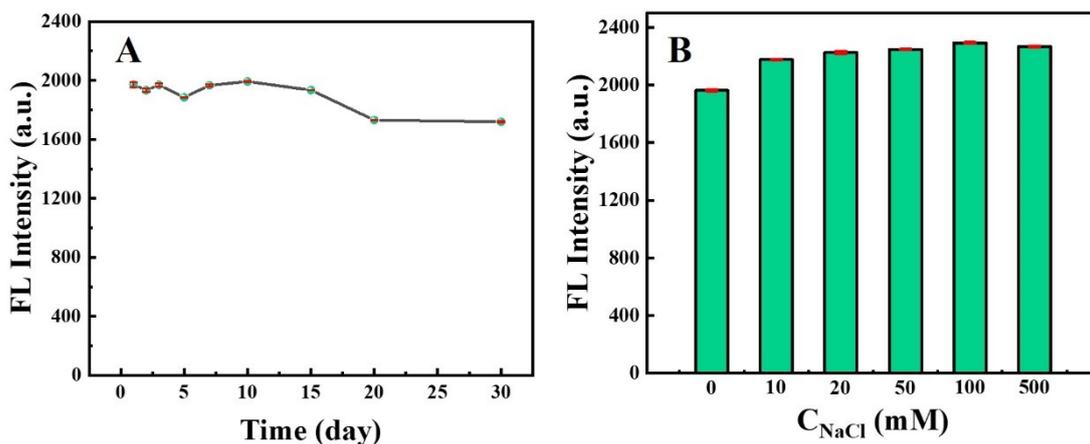


Fig. S4. (A) stability of the prepared GSH@PtNCs stored over time; (B) fluorescence intensity of GSH@PtNCs in different concentrations (0, 10, 20, 50, 100, 500 mM) of NaCl.

Table S1. Comparison of synthesis conditions of PtNCs in this work with those in other studies.

Preparation method	Reducing agent	Reaction condition	Reaction time	Ref.
Chemical synthesis	DMAB	25 °C	7 h	3
Chemical synthesis	DMF	140 °C	8 h	4
Chemical synthesis	GLP	60 °C	12 h	5
Chemical synthesis	BGP	80 °C	12 h	6
Chemical synthesis	Yeast extract	100 °C	12 h	7
Chemical synthesis	NaBH ₄	room temperature	15 h	8
Chemical synthesis	AA	35 °C	24 h	9
Ultrasonication	AA	300 W	5 h	10
DBD assisted synthesis	AA	32 V	2.5 h	This work

Fluorescent sensing of MG

GSH@PtNCs solution (350 μ L) was first mixed with Tris buffer (0.1 M, pH=5, 250 μ L), and then 200 μ L of different concentrations of MG was added. The fluorescence spectra were recorded after 1 min of incubation at room temperature.

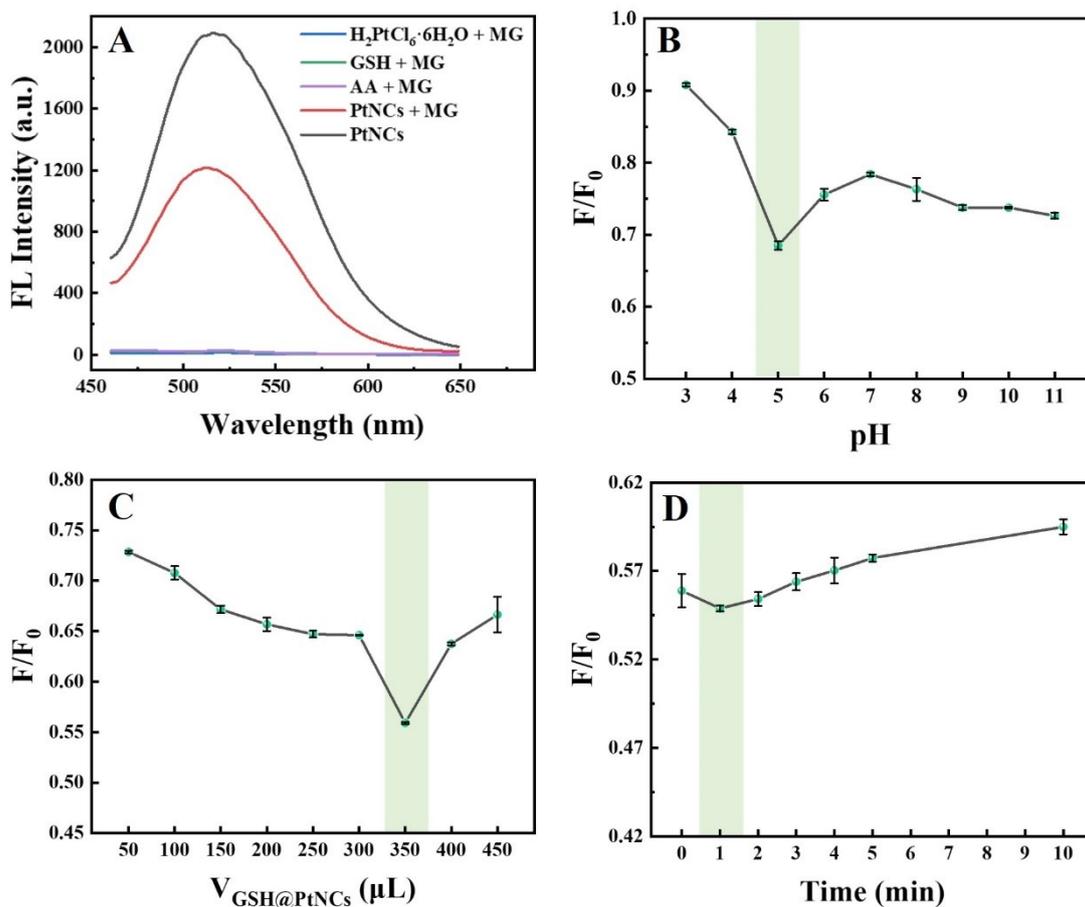


Fig. S5. (A) fluorescence spectra of PtNCs and MG mixed with $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, GSH, AA and PtNCs, respectively; and the effects of (B) buffer pH, (C) volume of added materials, and (D) incubation time on MG fluorescence sensing.

Table S2. The intra- and inter-day precision of the proposed method.

Concentration of MG ($\mu\text{mol/L}$)	Intra-day % RSD	Inter-day % RSD
40	3.3	4.1
100	2.0	2.7
300	1.5	1.6

Table S3. Comparison of the analytical performance of different sensing materials for the detection of MG.

Sensing material	Analysis methods	Linear range ($\mu\text{mol/L}$)	LOD (nmol/L)	Ref.
BSA-AuNCs	Fluorimetry	0.3-20	190	11
RhB@ZrT-1-OH	Fluorimetry	1.0-12	287.9	12
Tb _{0.6} Eu _{0.4} -MOF	Fluorimetry	2-180	1120	13
Al-MOF/RhB	Fluorimetry	14.5-548	4380	14
GSH@PtNCs	Fluorimetry	10-600	252	This work

Table S4. Determination of MG in real samples (n = 3).

Sample	Spiked ($\mu\text{mol/L}$)	Detected ($\mu\text{mol/L}$)	Recovery (%)
Pond water 1	0	ND	-
	40	40.7 \pm 0.6	101.8
	80	77.4 \pm 3.6	96.7
	300	298 \pm 3.9	99.5
Pond water 2	0	ND	-
	40	40.2 \pm 1.8	100.5
	80	76.8 \pm 3.4	96.0
	300	296 \pm 4.0	98.5
Crucian	0	ND	-
	30	28.4 \pm 1.2	94.8
	60	60.1 \pm 1.2	100.1
	80	79.7 \pm 3.7	99.6
Snakehead	0	ND	-
	30	29.1 \pm 1.3	97.1
	60	59.9 \pm 1.1	99.8
	80	78.9 \pm 2.9	98.7

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