

Electronic Supplementary Information

Highly sensitive photoluminescent energy transfer detection for 2,4,6-trinitrophenol using photoluminescent carbon nanodots

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Experimental Section

Chemicals and materials. Yam, also called rhizoma dioscoreae, is a plant used as traditional Chinese medicine and can be seen everywhere in our daily life. It was collected from the local countryside (Dazhou, China) and washed with water for further use. Na₃PO₄, Na₂CO₃, Na₂SO₄, NaNO₃, KCl, CaCl₂, CrCl₃, CuCl₂, AgNO₃, CdCl₂, BaCl₂ and FeCl₃ were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Phenol, 2,4,6-trinitrotoluene (TNT); 2,4-dinitrotoluene (DNT), p-nitrotoluene (NT), nitro-benzene (NB) and 2,4,6-trinitrophenol (TNP) were purchased from Aladdin Reagent (Shanghai, China). Other chemicals were analytical-reagent grade and used as received. Doubly distilled water was used throughout all experiments. 0.1 M phosphate buffer solutions were used throughout photoluminescent detection for TNP.

Apparatus. Photoluminescence spectra were recorded on a Hitachi Model F-2700 FL Spectrophotometer (Tokyo, Japan). Transmission electron microscopy (TEM) measurements were made on a HITACHI H600 electron microscope (Tokyo, Japan) with an accelerating voltage of 100 kV. Samples for TEM measurements were prepared by placing a drop of colloidal solution on carboncoated copper grid and then

dried at room temperature. Fluorescent photographs of photoluminescent C-Dots under 365 nm UV light were operated with ZF-20D ultraviolet analyzing equipment from Gongyi City Yuhua Instrument Co., Ltd. temperature. The fluorescence lifetime measurements were recorded on a Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometer equipped with a time-correlated single photon counting (TCSPC) system. The photoluminescence lifetime for TNP detection system using C-dots was measured with excitation wavelength of 280 nm and emission wavelength of 405 nm. S-25 digital pH meter (Shanghai Jingke Industry Company, Shanghai, China) was used to detect the acidity of the solution.

Preparation procedures of C-dots. C-dots were prepared via a hydrothermal reaction by heating yam (also called rhizoma dioscoreae) according to literatures. In a typical synthesis, 0.5 g yam was immersed into 30 mL water, transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 3.5 h. The yellow C-dots solution was collected by removing large dots through filtration and centrifugation at 8000 rpm for 10 min and finally dried under vacuum for 48 h. The dried C-dots were dispersed in distilled water at a concentration of 0.25 g/L for further characterization and use.

Procedures for TNP detection. 500 μ L 0.2 M buffer solution (pH 7.0), 100 μ L 0.25 g/L C-dots solution, different concentrations of TNP and water were successively pipetted into a 1.5 mL vial to keep the final volume of 1 mL. Then, the mixture was thoroughly vortex mixed and kept at room temperature for 1 min. Then photoluminescence spectra were measured at the excited wavelength of 330 nm.

Procedures of TNP detection in water. Industry wastewater samples were first treated by ultrafiltration with 10 kD ultrafiltration membrane. Tap water samples were used directly. 100 μ L wastewater and tap water was respectively added into 500 μ L 0.2 M buffer solution (pH 7.0). For the determination of recoveries, a given amount of TNP, two different amounts of TNP was added to the above solutions to keep the final concentrations of TNP at 10 μ M and 40 μ M, respectively. Then, 100 μ L 10-fold diluted C-dots solutions and water were added to keep the final volume of 1 mL for the analysis of TNP in tap water and industry wastewater.

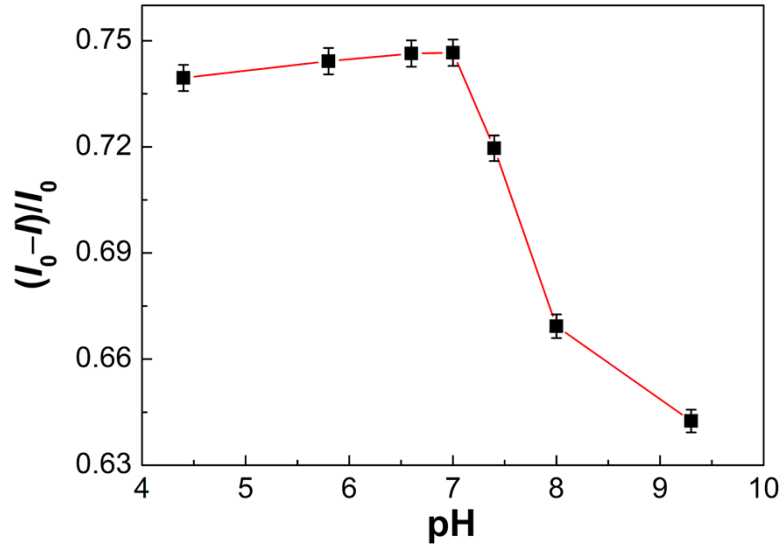


Fig. S1 Effect of pH on TNP detection system using C-dots. I represents photoluminescent intensity after the addition of TNP; I_0 represents photoluminescent intensity of the control sample; $(I_0 - I)/I_0$ (blue triangles) represents photoluminescent intensity quenching efficiency after the addition of TNP. $c(\text{TNP})$, 80 μM ; $c(\text{C-dots})$: 0.025 g/L; λ_{ex} : 330 nm; 0.1 M phosphate buffer pH, 4.4, 5.8, 6.6, 7.0, 7.4, 8.0, 9.3; Each point is an average of three successive measurements.

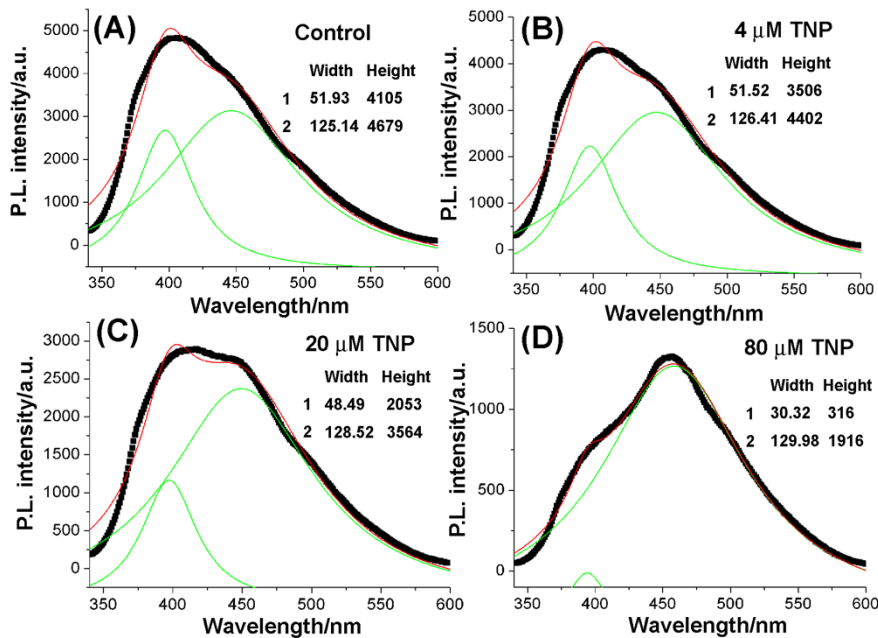


Fig. S2 Lorentzian fitting results of photoluminescent spectra for C-dots before (A) and after the addition of TNP (B-D); $c(\text{TNP})$, from B to D): 4, 20, 80 μM ; $c(\text{C-dots})$: 0.025 g/L.

Table S1. Comparison of different methods for the detection of TNP.

Methods	Fluorescent probes	Linear ranges	Detection limits	References
Fluorescence	8-hydroxyquinoline aluminum-based bluish green fluorescent composite nanospheres	0.2 – 30.6 μ M	140nM	[1]
Fluorescence	fluorescent organic nanoparticles: pentacenequinone derivative	2.2– 35.0 μ M	2.2 μ M	[2]
Fluorescence	near infrared ratiometric fluorescent compound based on intramolecular charge transfer	5–100 μ M	70nM	[3]
Fluorescence	fluorescent p-phenylenevinylene-based molecules	–	11.8nM	[4]
Photoluminescence	triazine derivatives NPhDCzT and DNPhCzT	0.06– 0.4 μ M	65.5nM	[5]
Surface plasmon resonance	Trinitrophenol–BSA conjugate and anti-TNP antibody	0.044nM– 0.4 μ M	0.044 nM	[6]
Colorimetry	Synthesized N-acylhydrazone L	2–10 mM	2mM	[7]
Colorimetry	Synthesized compound with N-acylhydrazone group	–	100 μ M	[8]
Simultaneous Chronoamperometry	molecularly imprinted thiophene polymers	–	0.69mM	[9]
Photoluminescence	Photoluminescent C-dots prepared by yam	0.08 – 100 μ M	22nM	Present work

Table S2. Determination of TNP in real water samples according to the proposed photoluminescent method.

Samples	Added (μM)	Found (μM)	Recovery (%)	RSD (n=3) %
Tap water	1	0.96	96%	3.7
Tap water	10	10.21	102.1	3.5
Tap water	40	40.38	103.8	4.2
Industry wasterwater	1	1.03	103%	2.2
Industry wasterwater	10	10.43	104.3	3.1
Industry wasterwater	40	38.54	96.3	2.9

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