Electronic Supplementary Information (ESI)

Amino acids as the source for producing carbon nanodots: microwave assisted one-step synthesis, intrinsic photoluminescence property and intense chemiluminescence enhancement

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Experimental Section

Chemicals and solutions: Histidine (HIS), arginine (ARG), lysine (LYS), threonine(THR), glutamic acid (GLU), glutamine (GLN), alanine (ALA) and proline (PRO) were purchased from Solarbio (Beijing, China) and used without further purification. All other reagents were of analytical grade and used as received. Ultra-pure water was prepared by a Millipore Milli-Q system and used throughout.

Synthesis of the fluorescent carbon nanodots (CDs): Fluorescent CDs were prepared from hydrophilic amino acids by a one-step acid or alkali assisted microwave treatment. In a typical procedure, 2 g histidine was dissolved in 20 ml ortho-phosphoric acid (0.5 mol L^{-1}) or NaOH (0.5 mol L^{-1}) solutions and then the mixture was heated in a domestic microwave oven (700W) for 2 min 40 s. After cooling, the obtained brownish-black solid powder was dissolved with 20 ml ultra-pure water. The supernatant was collected by centrifugation at 12,000 rpm for 20 min and then dialyzed against ultra-pure water through a dialysis membrane (molecular weight cut off = 1000, Shanghai Green Bird Science & Technology Development Development Co., China) for 48 h to remove the excess precursors and resulting small molecules. The resultant CDs (designated as CDs-HisH and CDs-HisOH) was maintained at 4 °C for further characterization and use. Fluorescent CDs were similarly prepared using other hydrophilic amino acids such as arginine, lysine, glutamine, glutamine, threonine, Alanine and Proline (designated as CDs-ArgH, CDs-LysH, CDs-GluH, CDs-GlnH, CDs-ThrH, CDs-AlaH and CDs-ProH, respectively).

Characterization: High resolution transmission electron microscopy (HRTEM) images of the prepared CDs-HisH were recorded on an electronic microscopy (Jeol, JEM-2100F, Japan). Ultraviolet-visible (UV-vis) absorption of the obtained CNDs was characterized by a UV-Vis spectrophotometer (Agilent 8453, USA). All fluorescent spectra of prepared CNDs were obtained by a fluorescence spectrophotometer (Hitachi, F-7000, Japan). X-ray diffraction (XRD) was carried out in a model D/max-rA diffractometer (Rigaku, Japan). X-ray photoelectron spectroscopy (XPS) was carried on an ESCALABMK II electron spectrograph (VG Scientific, UK) with Al KR radiation as the X-ray source. The fourier transform infrared (FT-IR) spectrum was obtained on a Bruker Vector-22 FTIR spectrometer (Bruker Instruments, Billerica, MA) in a KBr pellet, scanning from 4000 to 400 cm^{-1} at room temperature.

CL Measurements: Light-producing reactions were carried out in a well of microtiter plate with the batch method and detection was carried out using a microplate luminometer (Centro LB 960, Berthold, Germany). In a typical experiment, 50 μL of CDs dispersion was pipetted into a well of microtiter plate, and then 50 μL of 0.1 mol L^{-1} H_2O_2 solution and 50μL of 0.05 mol L^{-1} $NaIO_4$ solution was injected into the well successively. The light emission was measured by the microplate luminometer immediately.

The CL spectra were measured on a BPCL luminescence analyzer with high-energy cutoff filters from 400 to 640 nm between the flow CL cell and the PMT as described elsewhere.[1]

Quantum Yield Measurements: Quantum yield was measured according to established procedure (Lakowicz, J. R. *rinciples of Fluorescence Spectroscopy*, 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York).[2] The optical densities were measured on UV-vis spectra were obtained on a UV5800 Spectrophotometer. Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chose as a standard. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

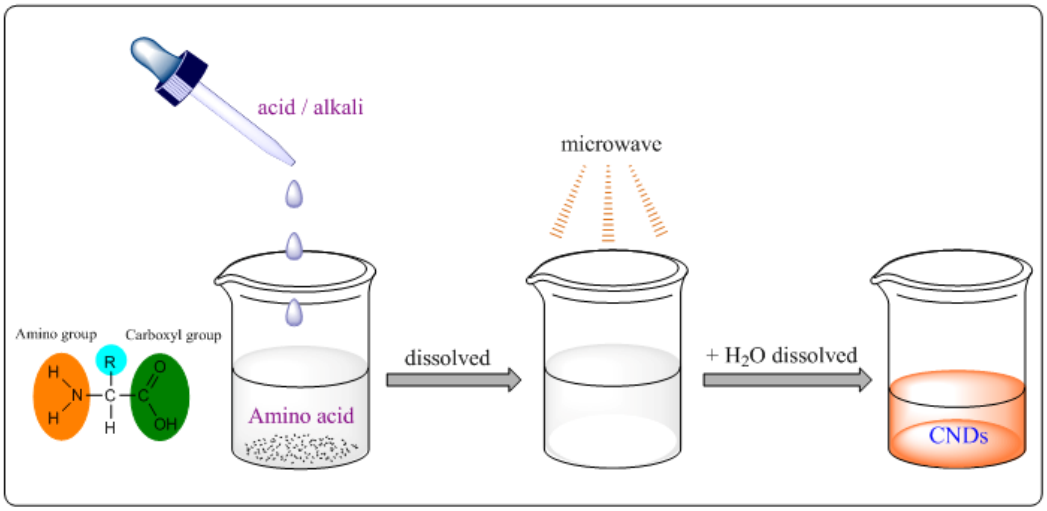
$$\varphi_x = \varphi_{std} \frac{I_x}{A_x} \frac{A_{std}}{I_{std}} \frac{\eta^2{}_x}{\eta^2{}_{std}}$$

Where φ is the quantum yield, I is the measured integrated emission intensity, and A is the optical density, and η is the refractive index. The subscript "std" refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (360 nm). Excitation and emission slit widths were set at 5.0 nm when recording their PL spectra.

The effect of acid or alkali in the synthesis: We consider that the acid or alkali served as catalysts for the formation of CDs from amino acids.

In the absence of acid or alkali, amino acids can produce CDs via the dehydration, polymerization, carbonization, and passivation process.[3] However, the experiment

should be conducted under strict conditions (high temperature above 300 °C for several hours), as the amidation and simultaneous dehydration reaction of amino acids is difficult. In our experiment, such a high temperature could not be obtained using open-vessel microwave irradiation of aqueous solution of amino acids, therefore, CDs could rarely be obtained. In the presence of acid or alkali, we suppose that amino acids will react to form amines at first. It is well known that amino acids can decarboxylate into amines and CO2 under high temperature by using acid or alkali as catalysts. Then the resultant amines may react with amino acids to produce CDs with less difficulty, as the amidation reaction between amines and amino acids is more easily compared with the amidation reaction of amino acids. Or the resultant amines probably produce CDs directly under microwave irradiation by using acid as catalysts according to the literature.[4-5] Accordingly, we consider that the acid or alkali served as catalysts for the formation of CDs from amino acids.



Scheme S1 Microwave assisted one-step synthesis of highly photoluminescent carbon nanodots from hydrophilic amino acid.

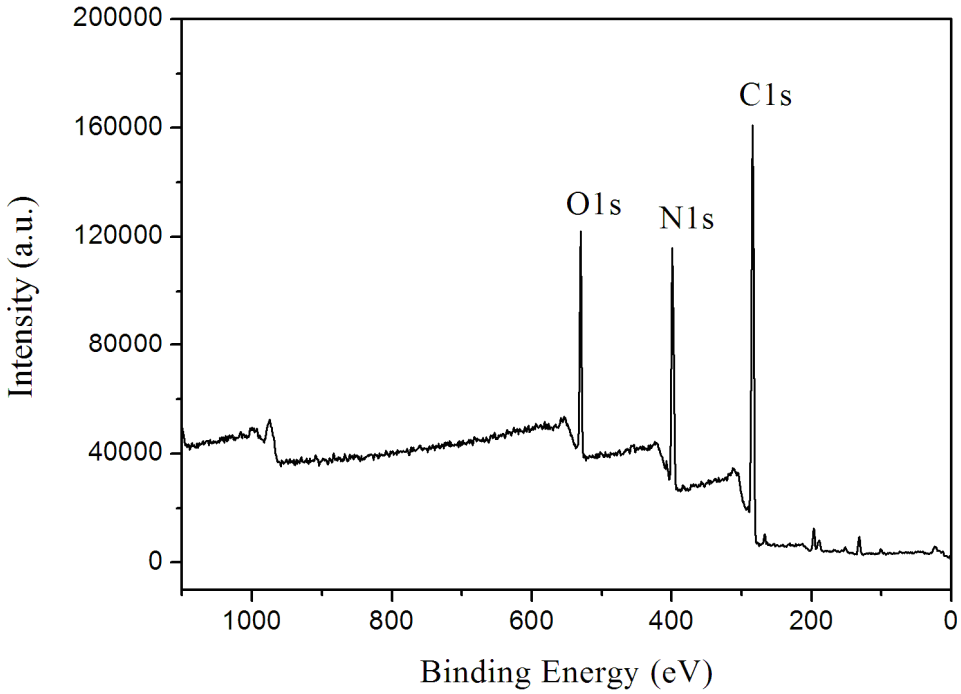


Fig. S1 Survey XPS spectra of CDs-HisH.

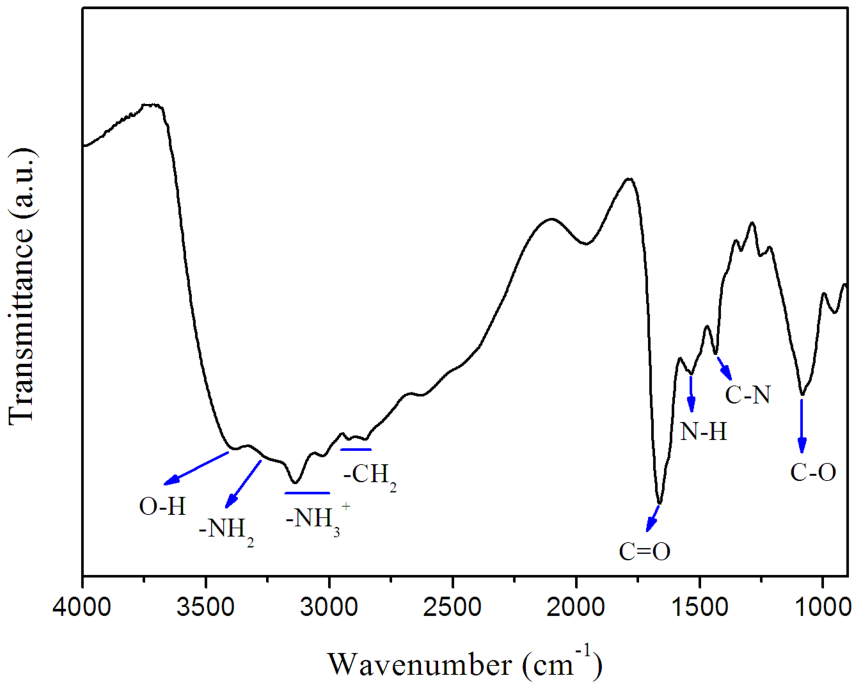


Fig. S2 FTIR spectra of CDs-HisH.

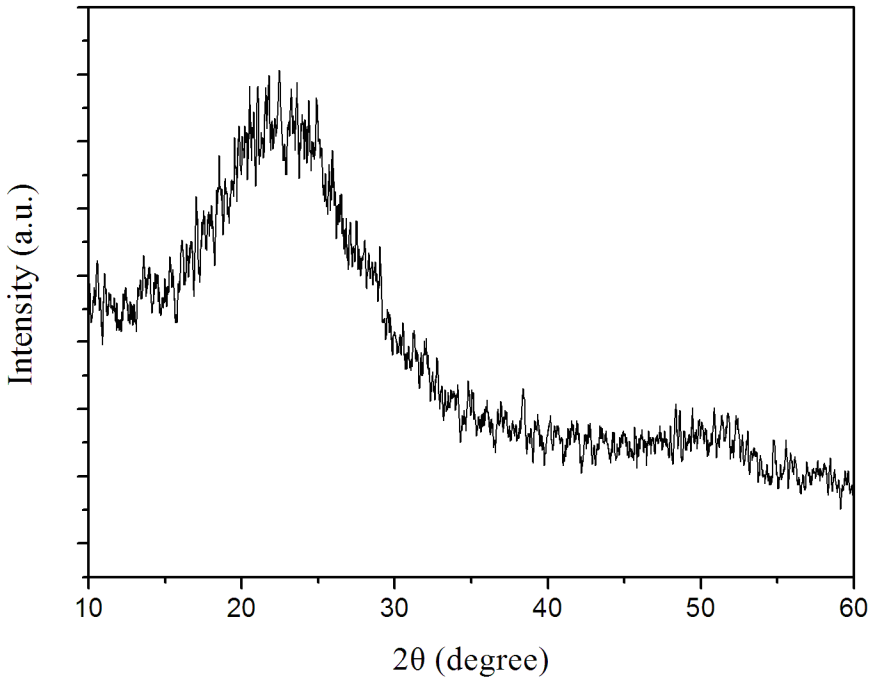


Fig. S3 XRD pattern of CDs-HisH.

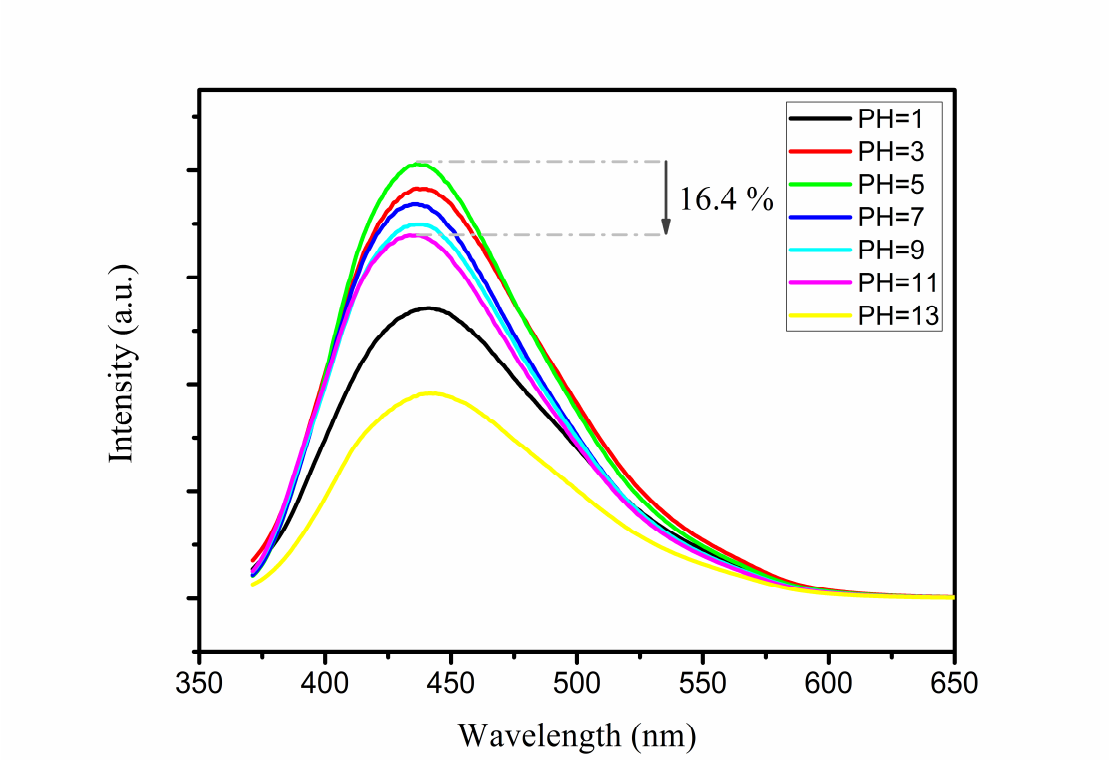


Fig. S4 The effect of the solution pH value on CDs-HisH fluorescence.

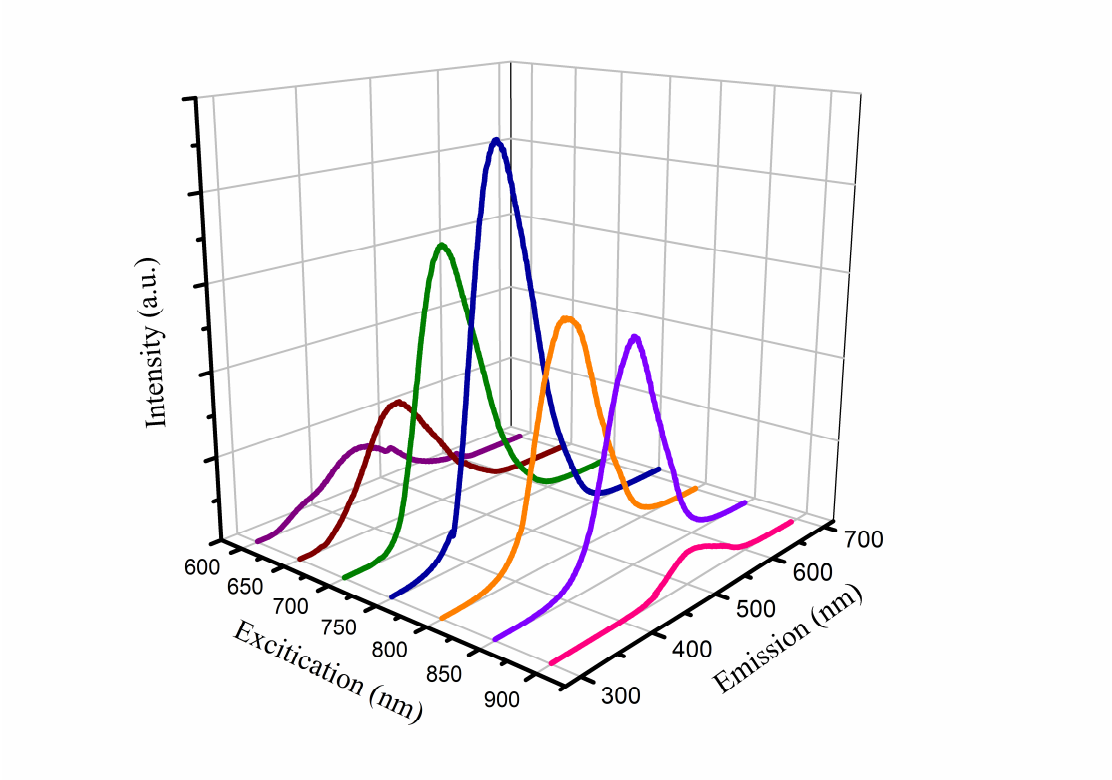


Fig. S5 The up-conversion photoluminescence spectra of CDs-HisH.

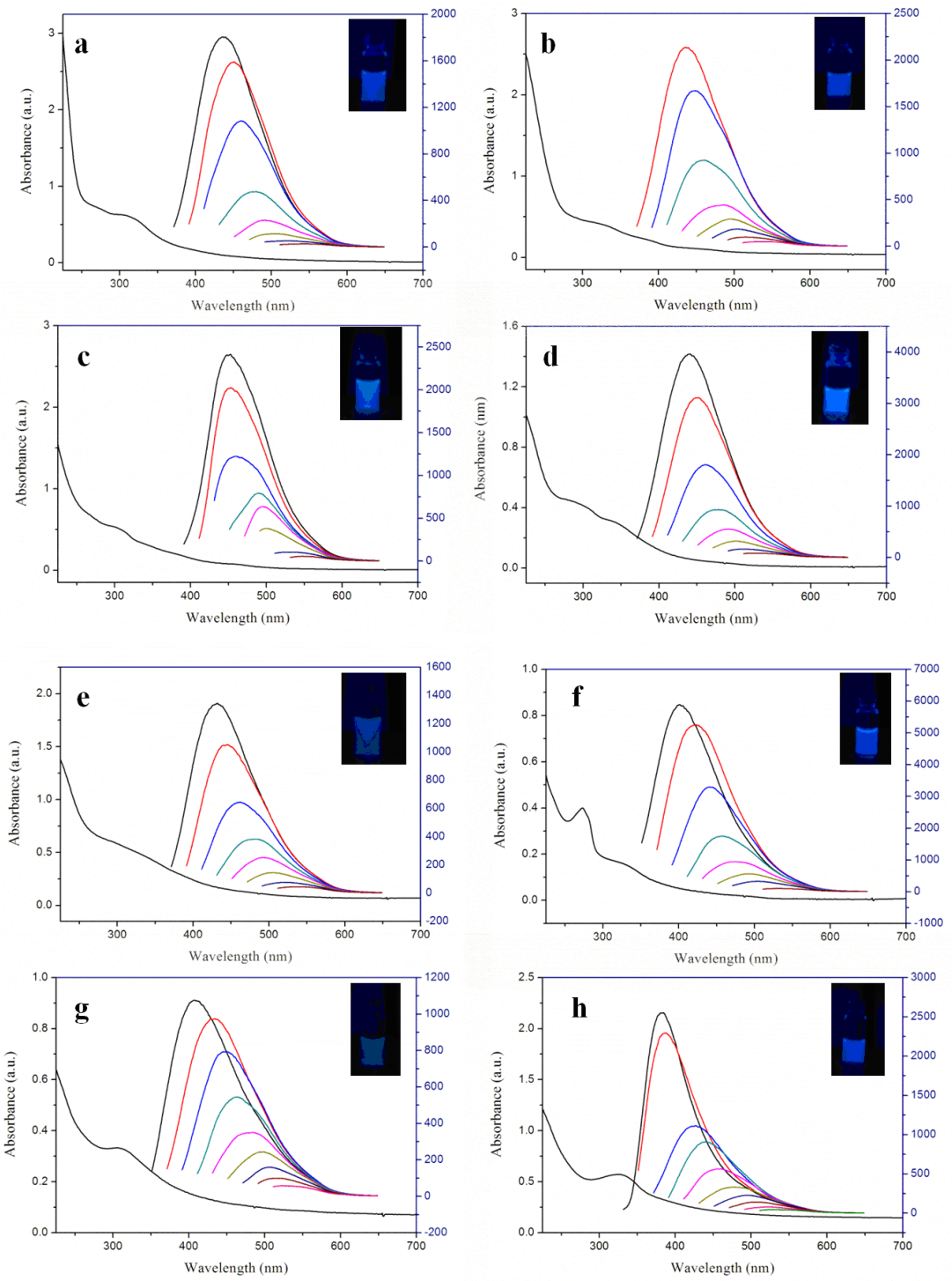


Fig. S6 UV-vis absorption and PL emission spectra of (a) CDs-HisOH, (b) CDs-ArgH, (c) CDs-LysH, (d) CDs-ThrH, (e) CDs-AlaH, (f) CDs-ProH, (g) CDs-GluH and (h) CDs-GlnH, respectively. Inset: the corresponding photographs in water under UV light (365 nm).

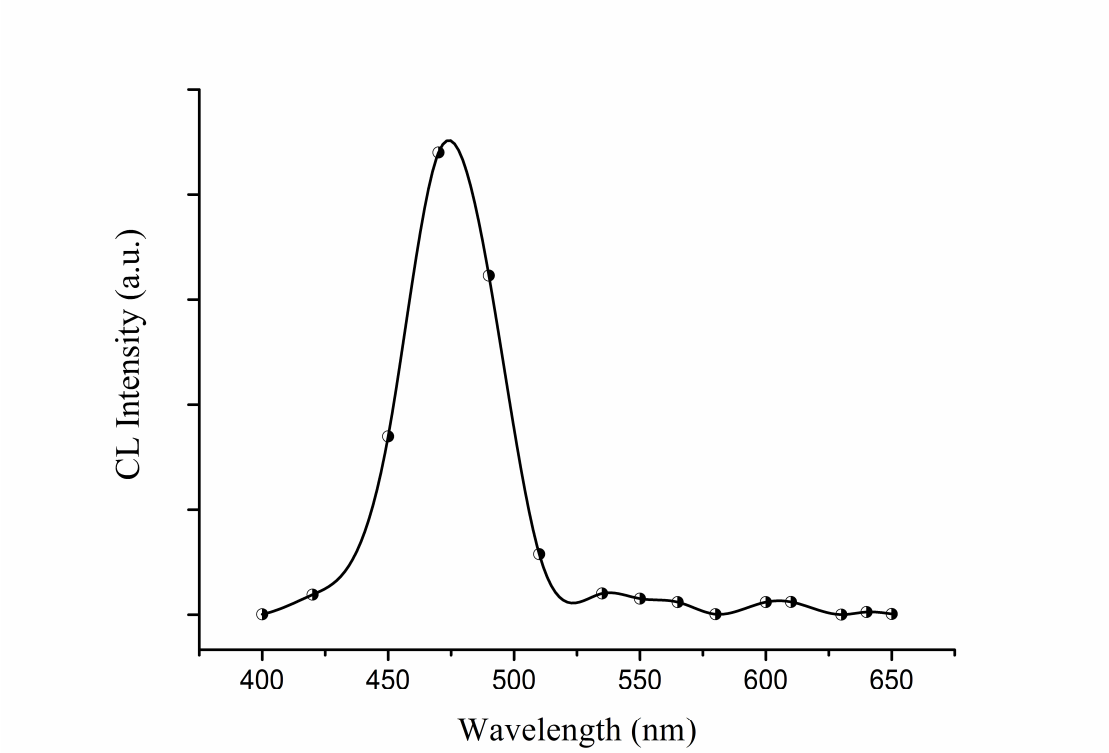


Fig. S7 CL spectrum of $NaIO_4$ – H_2O_2 system.

Supplementary References:

1 H. Cui, G. Z. Zou and X. Q. Lin, *Anal. Chem.*, 2003, **75**, 324.

2 J. R. Lakowicz, *rinciples of Fluorescence Spectroscopy*, 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York.

3 P. C. Hsu and H. T. Chang, *Chem. Commun.*, 2012, **48**, 3984.

4 S. Liu, J. Q. Tian, L. Wang, Y. L. Luo and X. P. Sun, *RSC Adv.*, 2012, **2**, 411.

5 S. Liu, L. Wang, J. Tian, J. Zhai, Y. Luo, W. Lu and X. Sun, *RSC Adv.*, 2011, **1**, 951.