Electronic Supplementary Material (ESI) for ChemComm.

Supporting information-

Full-colour carbon dots from energy-efficient synthesis to concentration-dependent photoluminescence properties

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1. Experimental Section

Sample characterizations. Fluorescence spectroscopy and absorption were collected on a Hitachi F4500 fluorescence spectrophotometer and a Shimadzu UV-2550 UV-vis spectrometer, respectively. The sample solution was dropped onto copper grids covered with an amorphous carbon film to prepare specimen for transmission electron microscopy (TEM) observation which were performed in a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. The infrared spectra were obtained on a Thermo Nicolet 260 FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) data of all samples was collected by a Kratos AXIS 165 mutitechnique electron spectrometer having an Al K_a X-ray source for determining the composition and chemical bonding configurations. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer. Raman spectra were collected with a confocal microprobe Raman system (Thermo Nicolet Almega XR Raman Microscope).

Preparation of CDs from coal pitch. Medium temperature coal pitch was used without further treatment and obtained from Hengshui Zehao rubber chemical co., LTD., China. The medium temperature coal pitch was grinded for 20 minutes with a mortar. 200 mg ultrafine powder was dispersed in 30 mL 88% of formic acid (HCOOH) and then mixed with 3 mL of 30% hydrogen peroxide (H_2O_2) solution. The obtained mixture was stirred with 800 rpm on magnetic stirring apparatus in the atmosphere without any external heating. The reaction time was 20 h. After removing unreacted power by centrifugation at 8000 rpm, the suspension containing CDs was obtained. The excess reaction solution was removed by solution boiling.

QY measurements: The QYs of CDs were obtained according to the procedure that we described in our previous reports: Hu et al., *J. Mater. Chem.* **2009**, *19*, 484; and *Chem. Asian J.* **2012**, *7*, 2711. The standard references were prepared based on the reference: A. M. Brouwer, *Pure Appl. Chem.* **2011**, *83*, 2213. Quinine sulfate in 0.1 M H_2SO_4, and Rhodamine B in EtOH were chosen as the standards that have the fixed and known fluorescence quantum yield values.

2. Supporting results

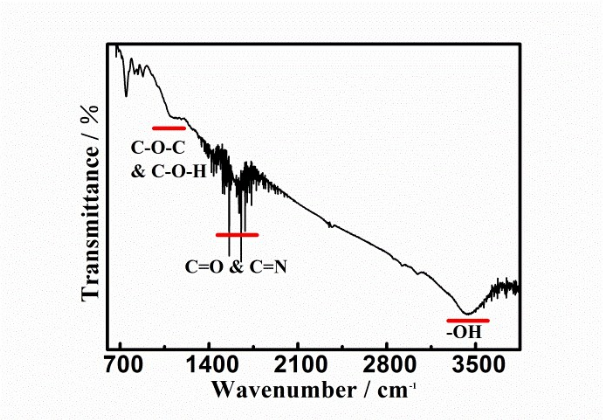


Figure S1 FTIR spectrum of coal pitch

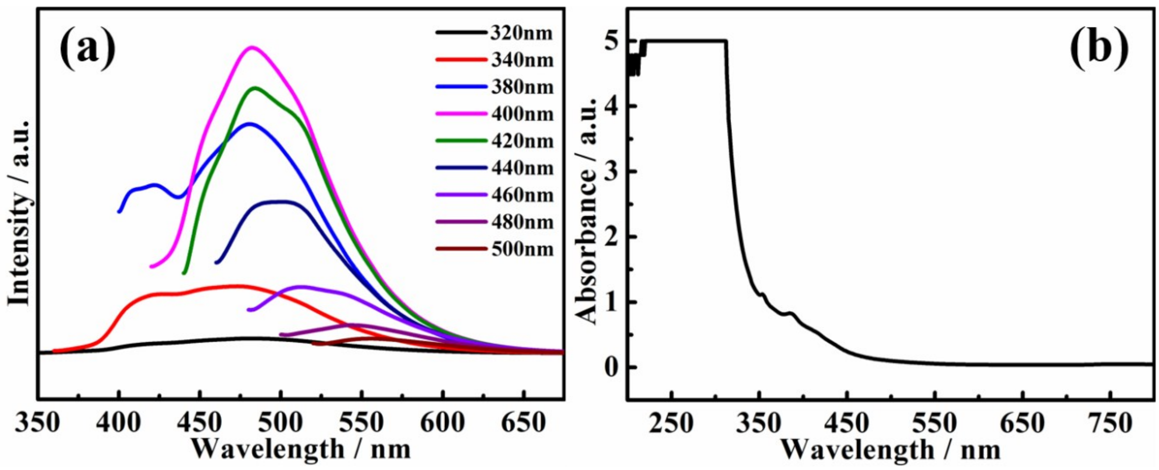


Figure S2 PL spectra (a) and UV-visible absorption spectrum (b) of the CDs obtained using H_2O_2 alone.

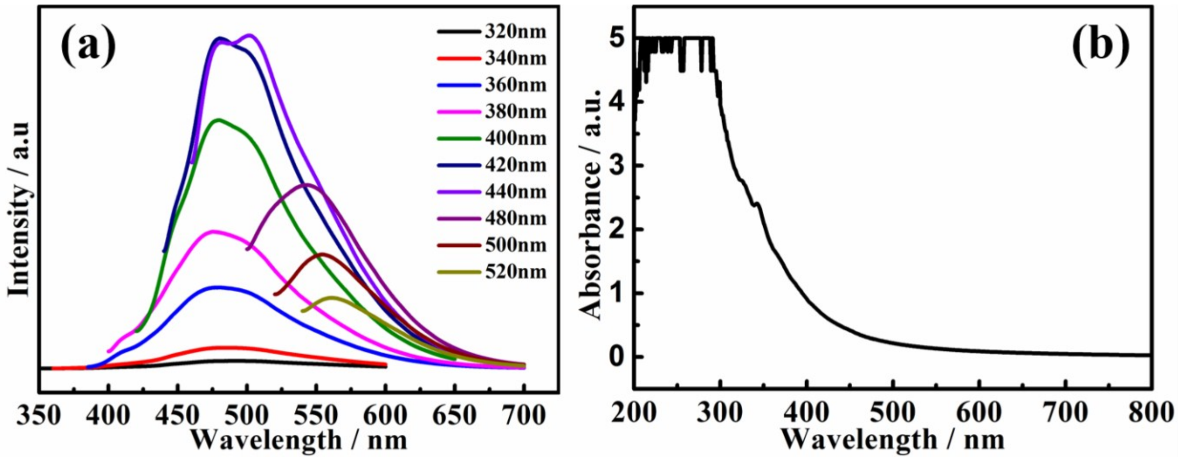


Figure S3 PL spectra (a) and UV-Vis absorption spectrum (b) of the CDs obtained using formic acid (HCOOH) alone.

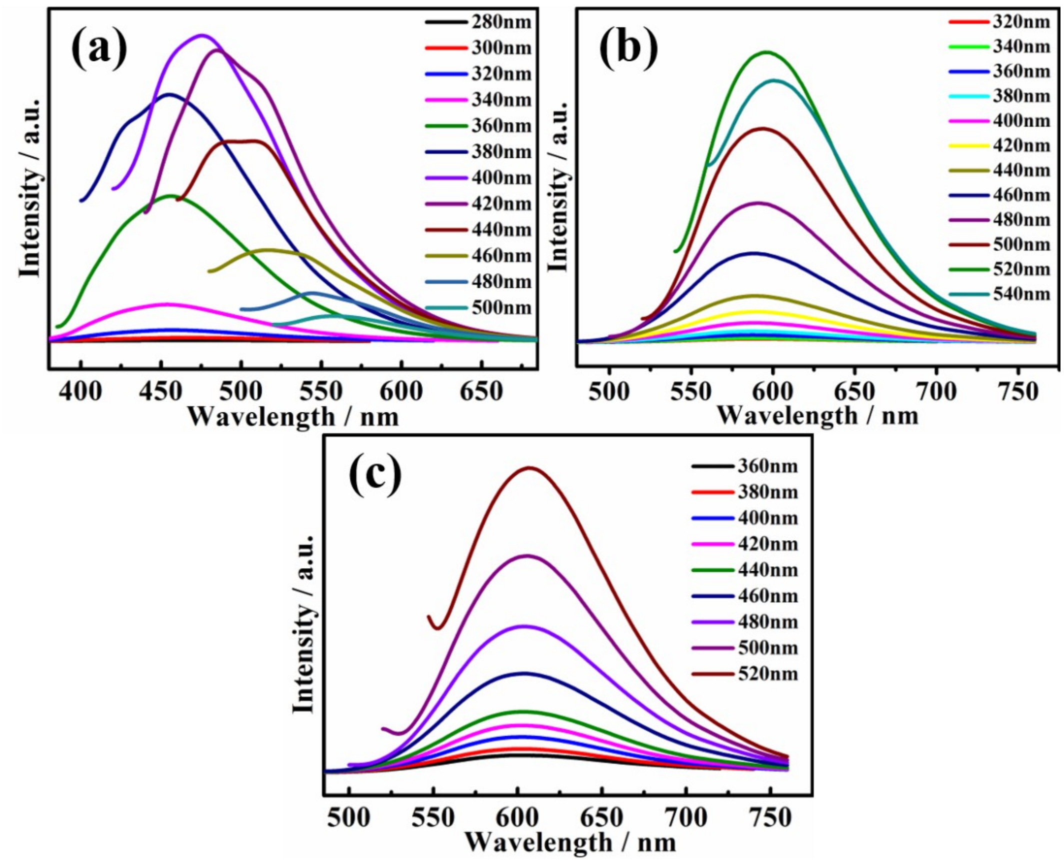


Figure S4 PL spectra of the CDs excited at different wavelengths, where the CDs were obtained at reaction time of 15 h using the mixture of formic acid and H_2O_2 at the ratios of ($HCOOH:H_2O_2$) 1:1 (a), 5:1 (b), 10:1 (c) as oxidation agent, respectively.

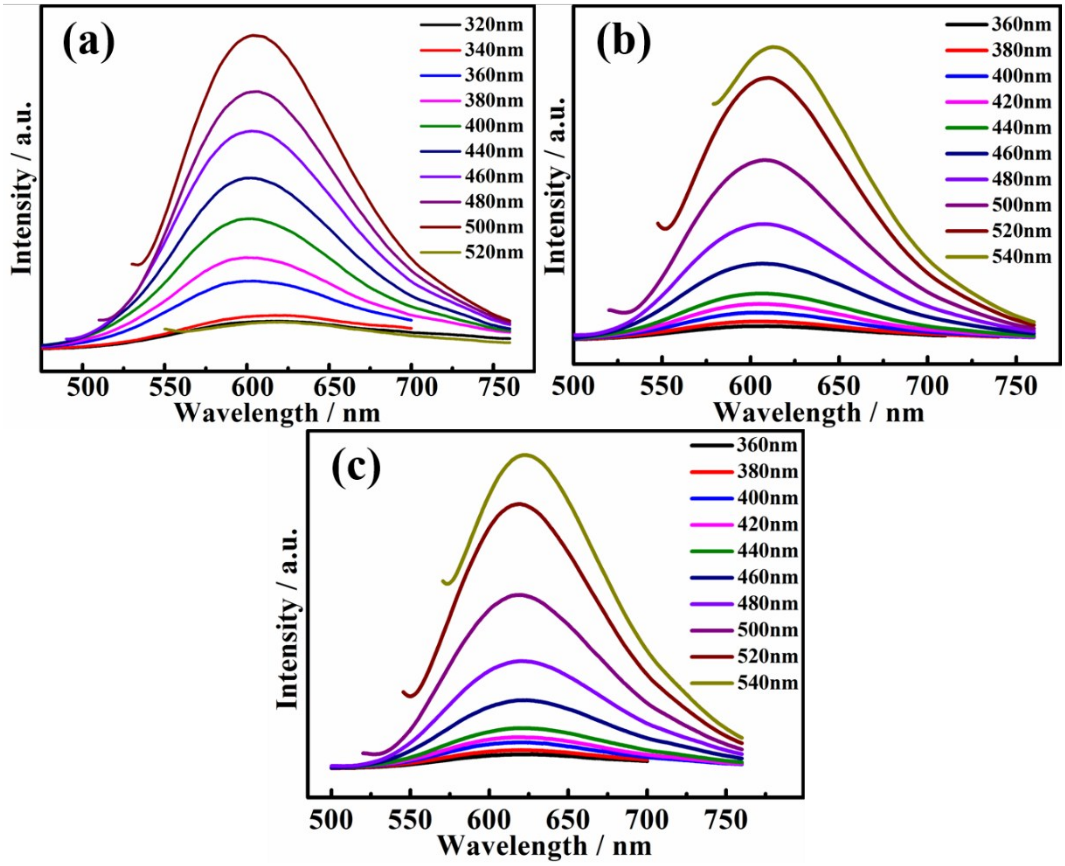


Figure S5 PL spectra of the CDs obtained at reaction time of 10 h (a), 15 h (b), 20 h (c), respectively, using the mixture of formic acid and H_2O_2 at a ratio of 10:1 as oxidation agent, excited at different wavelengths.

Figure S6 Photos of carbon dot solution diluted gradually with ethanol under the ambient light and a laser beam of 405 nm, respectively.

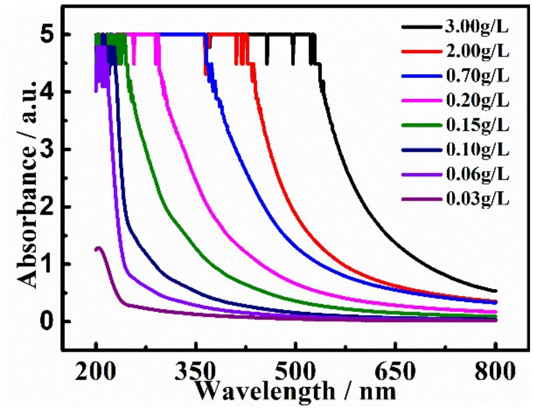


Figure S7 UV-Vis absorption spectra of the carbon dot solution with different concentrations.

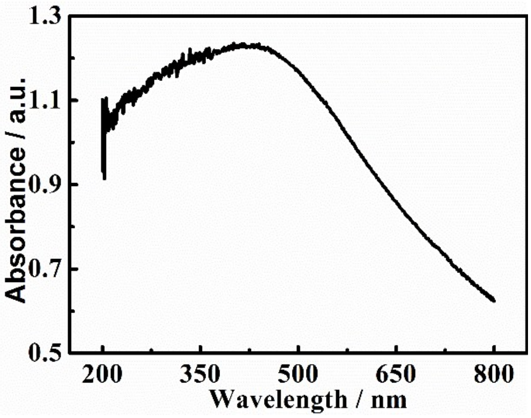


Figure S8 UV-Vis absorption spectrum of the solid CDs.

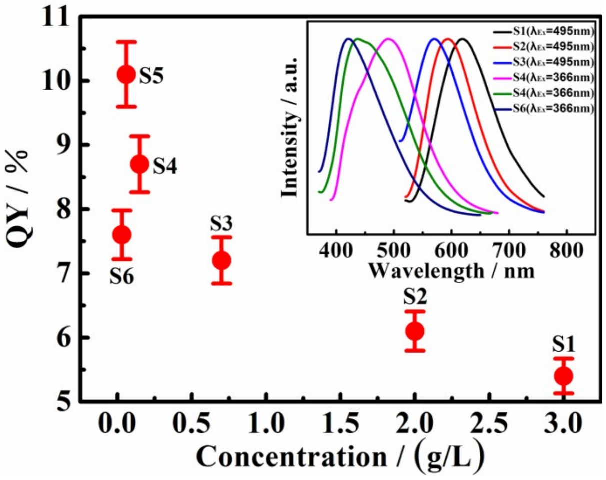


Figure S9 The fluorescence quantum yields of S1-S6; the inset is their PL spectra collected by the given excitation wavelengths during quantum yield measurement.

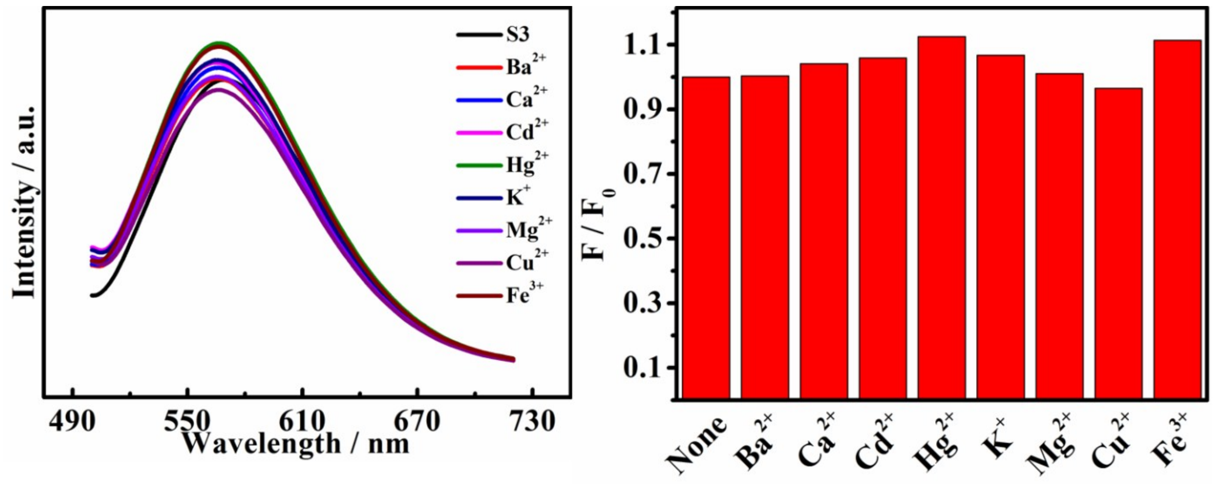
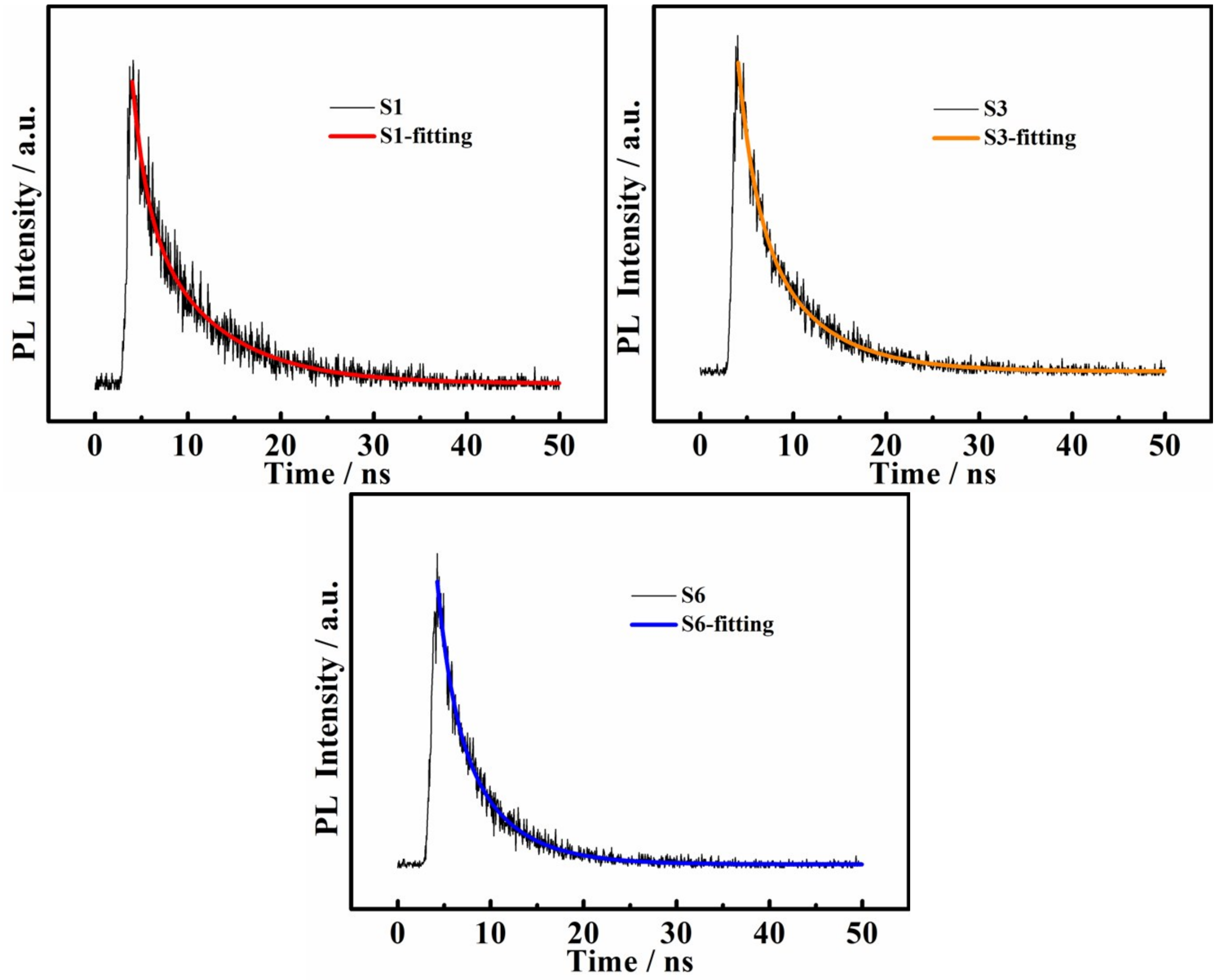


Figure S10 PL spectra of the S3 before and after adding 1 mM of different metal ions.



	t_1/ns	B_1%	t_2/ns	B_2%	t_{avg}/ns
S1	**1.43**	**9.23**	**7.23**	**90.77**	**6.72**
S3	**1.85**	**19.70**	**7.22**	**80.30**	**6.10**
S6	**2.03**	**22.55**	**5.62**	**77.45**	**4.81**

Figure S11 PL transient decay curves of the CDs from S1, S3 and S6, respectively, at 400 nm excitation.

Concentration-tuned PL mechanism (Detail explanation for Figure 5)

The concentration-tuned PL properties of CDs could be also ascribed to morphologic changes caused by their interactions. Although the natures of structure, size and chemical composition of an isolated carbon dot are unchanged, its surface states are varied with morphologies of CDs.[25] Surface states result from the dangling bonds of surface atoms, in which the unpaired electrons give rise to an electron state by their interactions.[12, 25] Due to the differences in free charge concentration between the inner and the surface, the charge redistribution near the surface induces a space charge region.[23] In this region, the energy band edges could be also shifted continuously toward the surface, thus producing an electric potential (V, Figure 5) described by the following Poisson's equation,[12, 25]

$$\frac{\partial^2 V(x,y,z)}{\partial x^2}+\frac{\partial^2 V(x,y,z)}{\partial y^2}+\frac{\partial^2 V(x,y,z)}{\partial z^2}=-\frac{\rho}{\varepsilon_r \varepsilon_0} \tag{1}$$

For a spherical nanoparticle with radius r, the V at the surface can be obtained by Poisson-Boltzmann equation, [25]i.e.

$$V=\frac{\rho D^2}{6\varepsilon_r \varepsilon_0}\left(3-\frac{2D}{r}\right) \tag{2}$$

where ρ, D, ε_r and ε_0 are the space charge density, the thickness of space charge region, the relative dielectric constant and the vacuum permittivity, respectively.

As one carbon dot approaches the other under the intermolecular interaction, (i.e. the distance between CDs reduces), their surface electric potentials could be influenced by one another, causing the V to be reduced. Due to a vital role of the V played in tuning recombination of excited electrons for CDs,[23,25] the recombination processes could be also varied with V reduction. From Figure 5 for an isolated carbon dot with large surface V, the electrons in the excited state are easily transferred to the surface and are subsequently trapped with the release of energy,[2] thereby emitting photons. This recombination route (R1) generally leads to excitation-dependent PL behaviors owning to the presences of many kinds of surface energy traps, which has been demonstrated by many works.[13, 21, 22, 24] The other recombination route (R2) could mainly originate from the structural defects though the electrons might also transfer from the defect energy levels to surface-trapped energy levels.[2] When the surface V becomes small, the driving forces of excited electron transfer to the surface are limited. In this case, the recombination route of R2 will be dominated in PL, which contributes to long wavelength emissions of samples with high concentration CDs.