Supplementary Information

Observation of pH-, Solvent-, Spin-, and Excitation-dependent Blue Photoluminescence from Carbon Nanoparticles

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Preparation of luminescent CNPs. The CNPs were prepared by a pyrolytic method from EDTA-2Na·2H_2O. In a typical procedure, a quartz boat filled with EDTA-2Na·2H_2O (AR, 0.5 g) was thrust into a quartz tube and calcined in a tube furnace for 2 h at a heating rate of 10 ℃/min and a N_2 flow rate of 0.1 L/min. After cooled down, a black product was collected with a yield of ~40%. The product was dissolved in acetone (20 mL) and then centrifuged at a high speed (15000 rpm) for ten minutes. The upper brown solution was collected and evaporated in a rotary evaporator at 50 ℃. Pure luminescent CNP powder was obtained by drying the concentrated solution at 70 ℃ for 15 h. The powder can be soluble in water and organic polar solvents.

Characterization. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2010F electron microscope operating at 200 kV. X-ray powder diffraction (XRD) patterns were obtained from Japan Regaku D/max-2500 using Cu Kα radiation. Absorption and fluorescence spectra were recorded at room temperature on a Hitachi 3100 spectrophotometer and a Hitachi 7000 fluorescence spectrophotometer, respectively. Fourier transform infrared (FTIR) spectra were recorded with a Bio-Rad FTIR spectrometer FTS165. Raman spectra were recorded

on Renishaw in plus laser Raman spectrometer with λ_{exc} = 785 nm. EPR spectra were recorded in solid states at room temperature on an EMX-10/12 spectrometer.

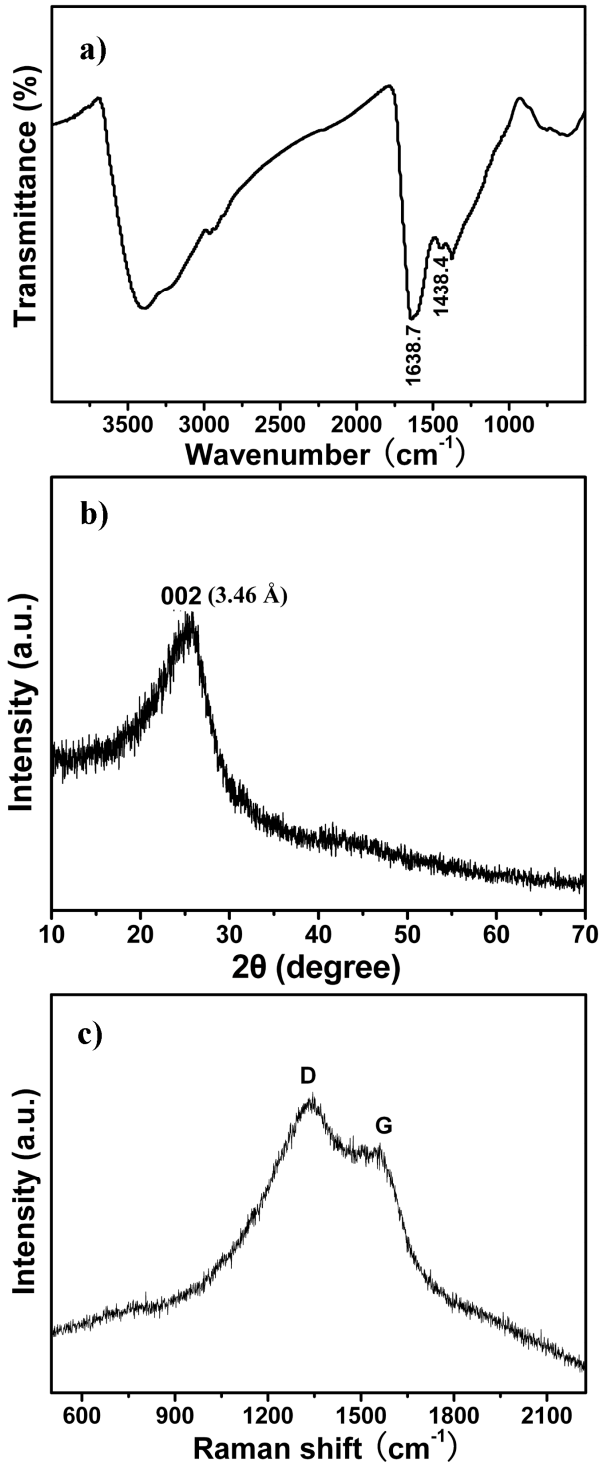

Fig. S1. FTIR spectrum (a), XRD pattern (b) and Raman spectrum (c) of the

fluorescent CNPs prepared at 400 ℃.

Fluorescence Measurements.

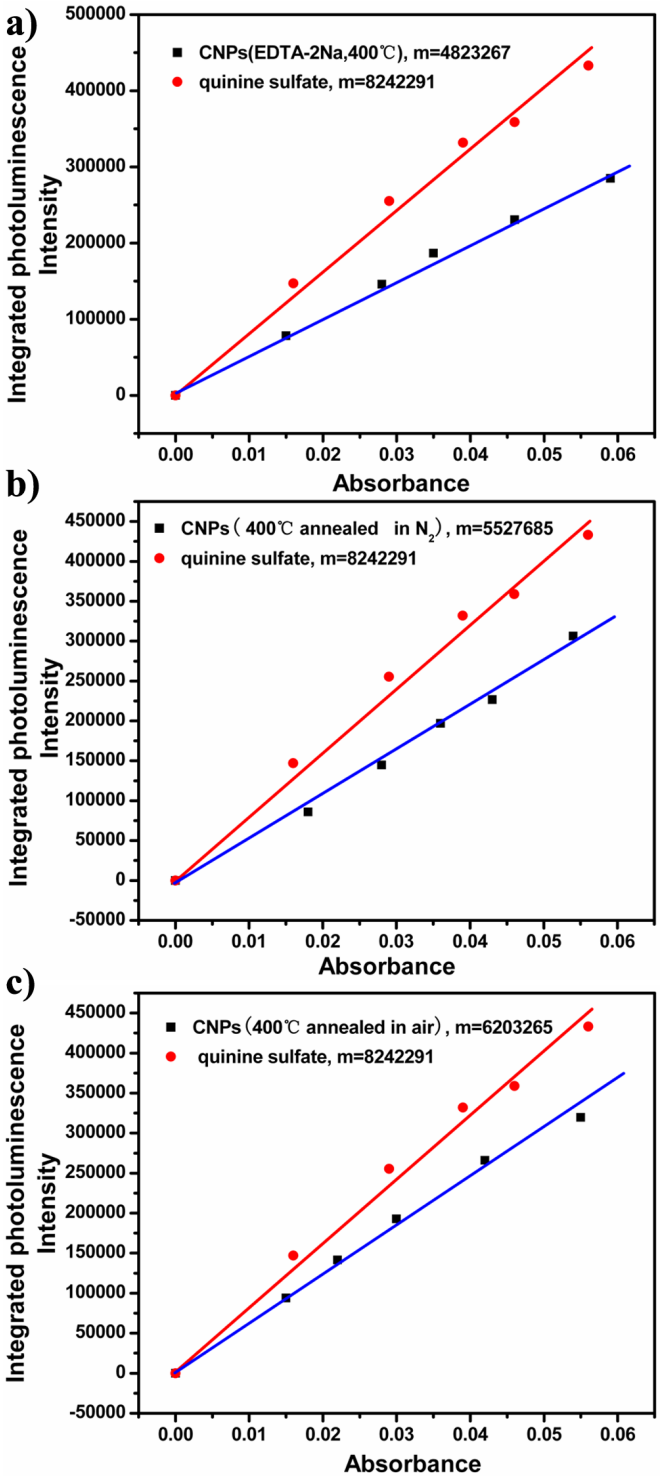

Fig. S2. Photoluminescence and absorbance of the CNPs prepared at 400 ℃ (a), and the CNPs annealed in N_2 (b) and in air (c). Quinine sulfate is used as a reference.

The QYs of the CNPs were determined by comparing the integrated photoluminescence intensities (excited at 320 nm) and the absorbency values (at 320 nm) of the CNPs using quinine sulfate in 50 mM of H_2SO_4 aqueous solutions as a reference. This method was reported to be used to measure the QY of blue fluorescent carbon nanocrystals (J. Zhou, C. Booker, Zhou, R. X. Li, T. Sham, X. Sun, Z. Ding, *J. Am. Chem. Soc.* **2007**, *129*, 744-745). Different concentrations of the reference and the carbon samples were made, all of which had absorbance less than 0.1 at 320 nm.

QYs were calculated using the following equation:

$$QY_s = QY_r (m_s/m_r) (\eta_s/\eta_r)^2$$

Where *m* is the slopes determined by the curves in Figure S1, η is the refractive index of the solvent (water). The subscripts of s and r refer to the sample and the reference, respectively. For these aqueous solutions, $\eta_s/\eta_r=1$.

From Fig. S2, the *m* values can be determined to be 8242291 ,4823267 , 5527685 , 6203265 for quinine sulfate, as-prepared CNPs, CNPs annealed in N_2 and CNPs annealed in air, respectively. For quinine sulfate, QY_r = 54% (literature), the QYs of the three carbon samples can thus be determined to be 31.6%, 36.2% and 40.6%.

The same method was used to measure the QYs of other CNP samples prepared at lower temperatures (250, 300, 350 ℃). Their QYs are determined to be 4.8%, 14.7%, and 19.2%, respectively.

Interestingly, we found that the more distinct or stronger the ~ 320 nm absorption band is, the higher the QYs are (Fig. S5). For example, for the CNPs prepared at 250

℃, which has the lowest QY in all these samples, the corresponding 320 nm absorption band can not be observed owing to the strong disturbance from non-luminescent background absorption. This fact indicates that the ~400 nm PL is directly correlated with the ~ 320 nm absorption band. We note that for previously reported CNPs (references 1-11), their QYs are very low (<10%) and there are no marked absorption bands observed near the excitation wavelengths, like one of our samples, the CNPs prepared at 250 ℃. These facts show that in our CNPs with high QYs (36% ~ 40%), there is a high concentration of luminescent cores that produce the marked absorption band at ~ 320 nm. This can explain why our CNPs are highly luminescent although their exact luminescence mechanism needs to be studied further.

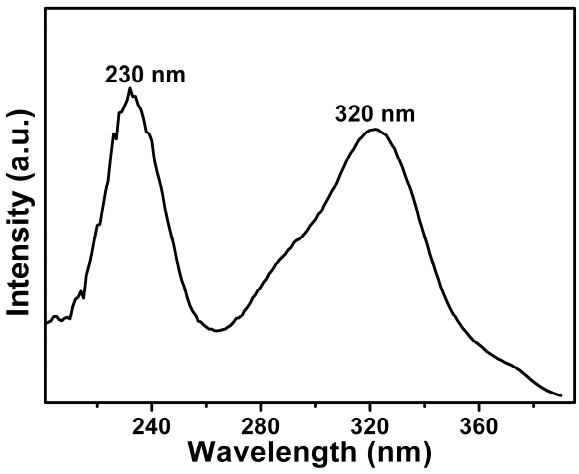

Fig. S3. PLE spectrum of the fluorescent CNPs with the detection of the emission at 400 nm.

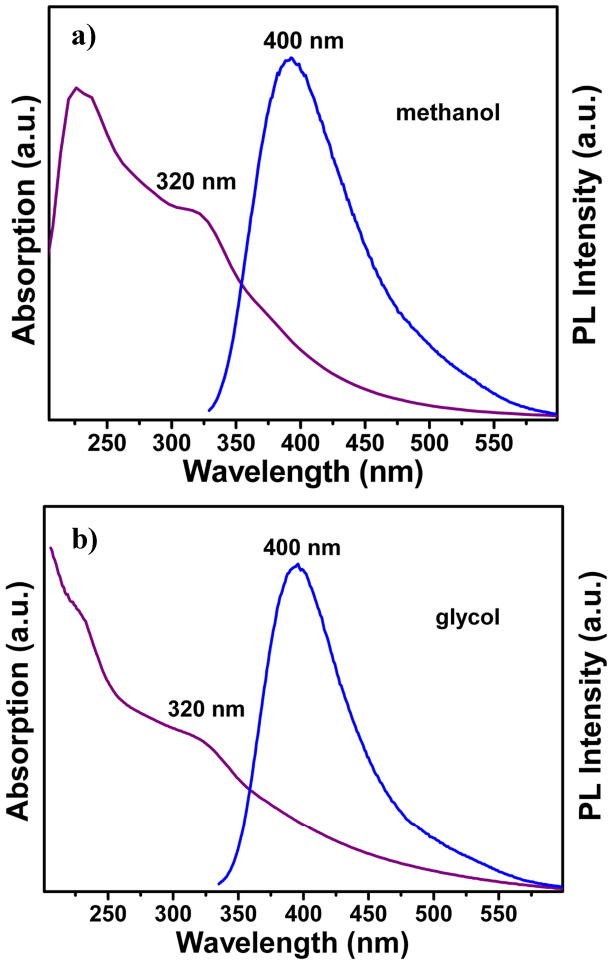

Fig. S4. UV-vis absorption and PL spectra of the CNPs dispersed in methanol (a) and glycol (b).

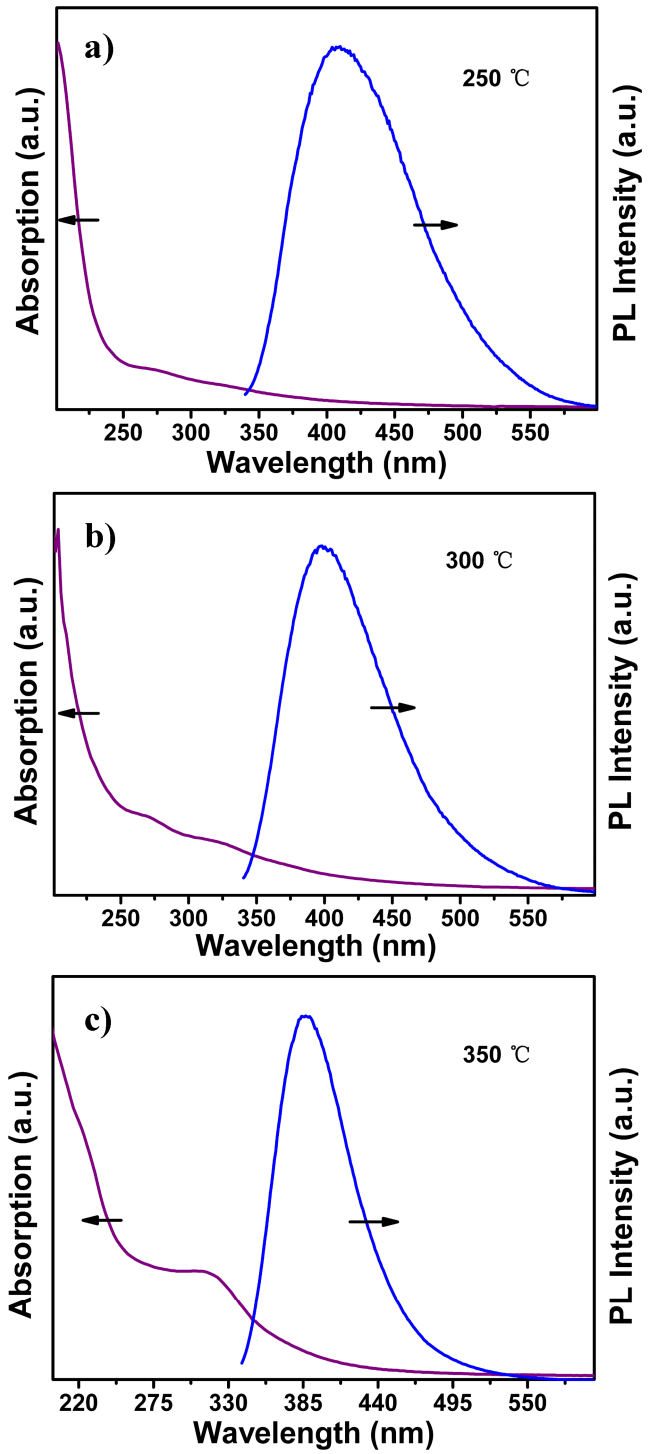

Fig. S5. UV-vis absorption and PL (320 nm excitation) spectra for the CNPs prepared at 250 ℃ (a), 300 ℃ (b) and 350 ℃ (c) dispersed in DI water.