

Supplementary information of

Cool white, persistent room-temperature phosphorescence in carbon dots embedded in silica gel matrix

Julin Joseph, Aji A. Anappara*

Department of Physics, National Institute of Technology Calicut (NITC),
Kerala-673601, India

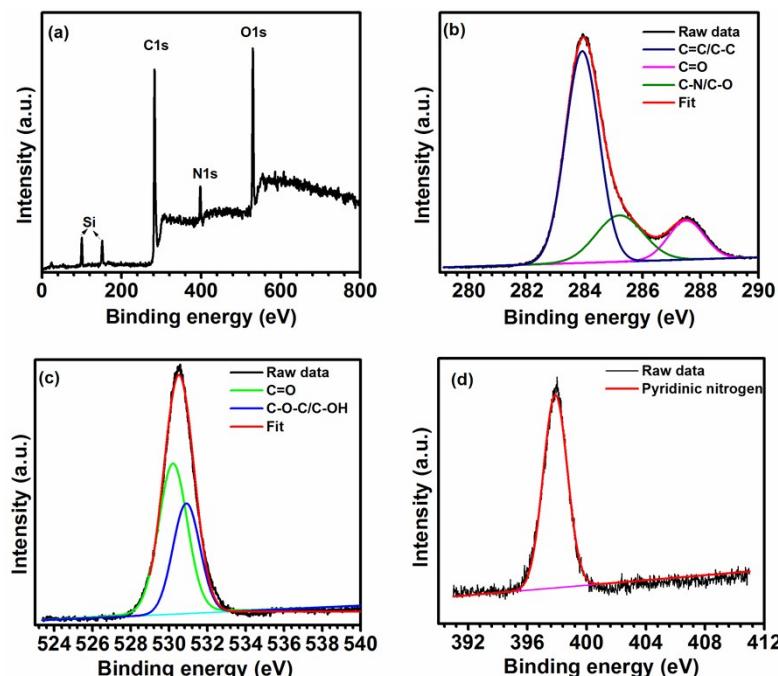


Fig.S1 (a) Wide scan XPS spectrum of the CDs. The peaks of silicon arise from the glass substrate. (b) High resolution XPS spectra of C1s (c) O1s (d) N1s.

* Corresponding author. Tel: +91 495 2285107. E-mail: aji@nitc.ac.in (Aji A. Anappara)

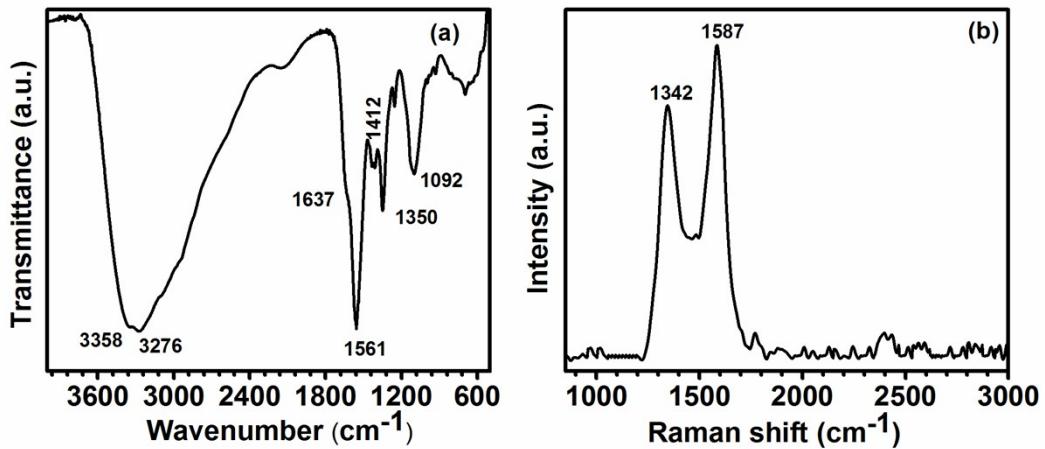


Fig. S2 (a) FTIR spectra of carbon dots. (b) Raman spectra of CDs. The excitation wavelength of the laser was chosen to be 532 nm. The peak at 1342 cm⁻¹ represents D band and 1587 cm⁻¹ corresponds to G band.

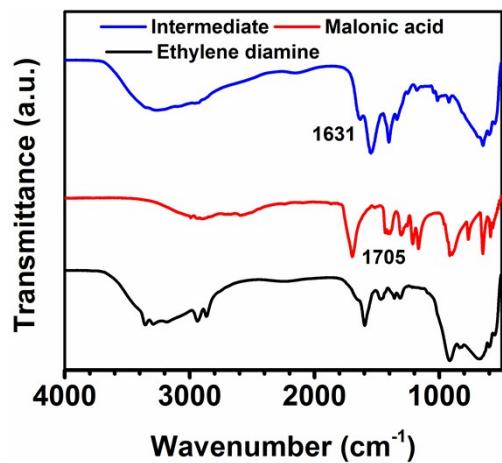


Fig.S3. FTIR spectra of precursors and the intermediate state of carbon dots formation.

	λ_{ex} (nm)	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	τ_{avg} (ns)
CDs in water	340	44.65	4.9	11.13	1.18	44.22	11.3	9.2
CDs in silica gel	340	45.15	4.54	13.66	0.94	41.20	11.65	9.36

Table S1. Excited state decay parameters of CDs dispersed in water and silica gel obtained from TCSPC measurements, with an excitation wavelength of 340 nm.

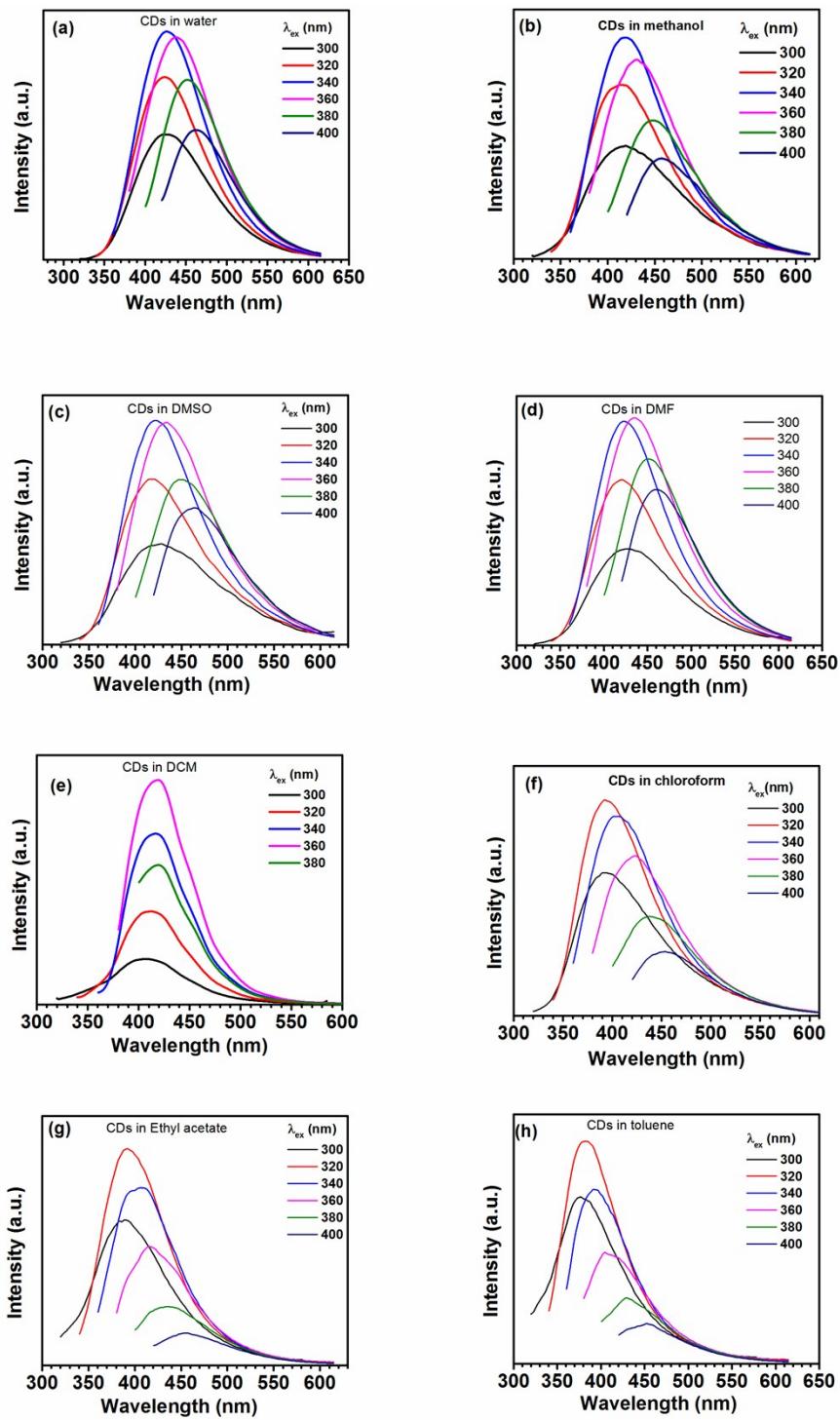


Fig.S4. Fluorescence spectra of carbon dots dispersed in various organic solvents at different excitation wavelengths.

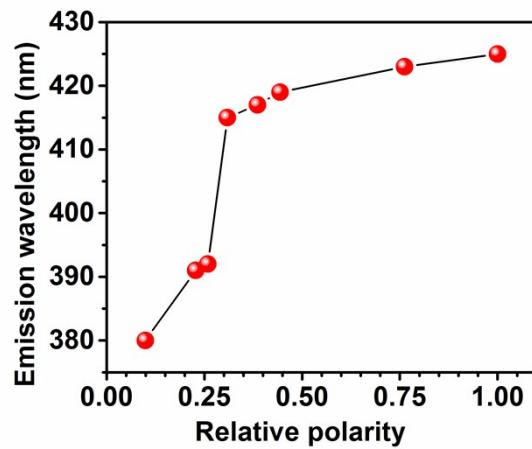


Fig.S5. Variation of emission peak of fluorescence spectra as a function of solvent polarity parameter.

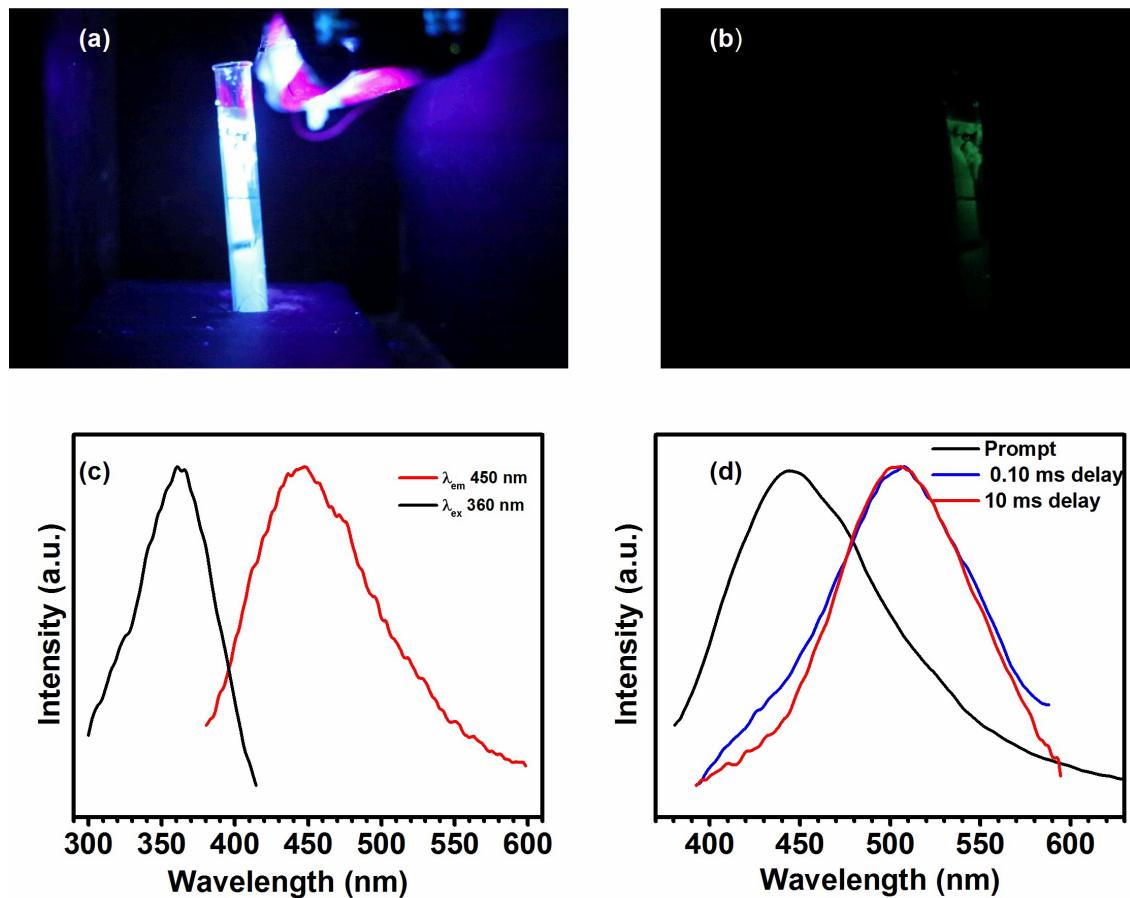


Fig.S6 (a) Digital photograph of CDs in silica gel under 365 nm UV lamp (b) CDs in silica gel a few seconds after turn-off the UV lamp (c) Fluorescence excitation (black) and emission spectra (red) of CDs dispersed in silica gel (d) Spectra of prompt (0 delay time) is represented as black curve and spectra which taken after 0.1ms (blue) and 10 ms (red).

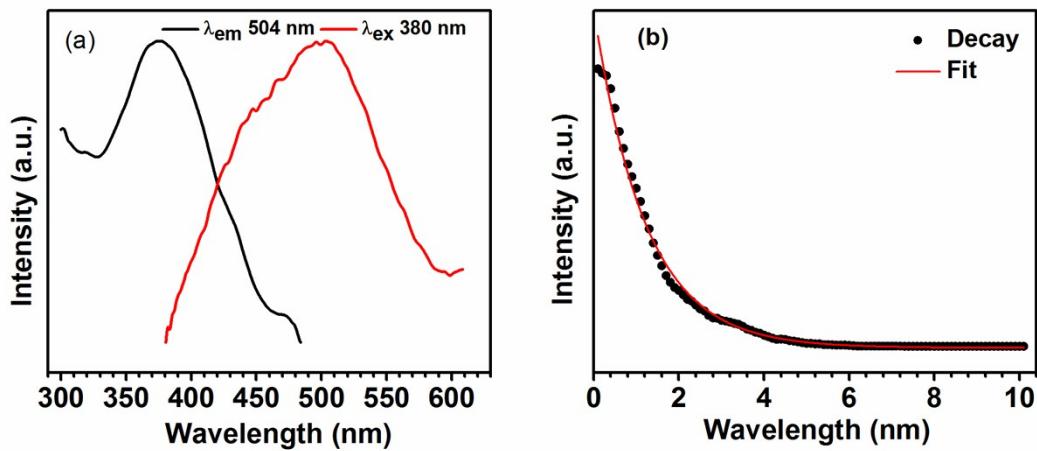


Fig.S7 (a) Phosphorescence excitation (black) and emission spectra (red) of CD. (b) Phosphorescence decay curve of CDs in silica gel.

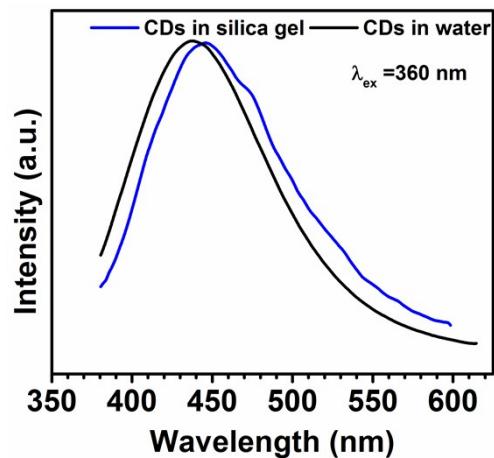


Fig.S8 Comparison of fluorescence spectra of carbon dots dispersed in solution and solid state.

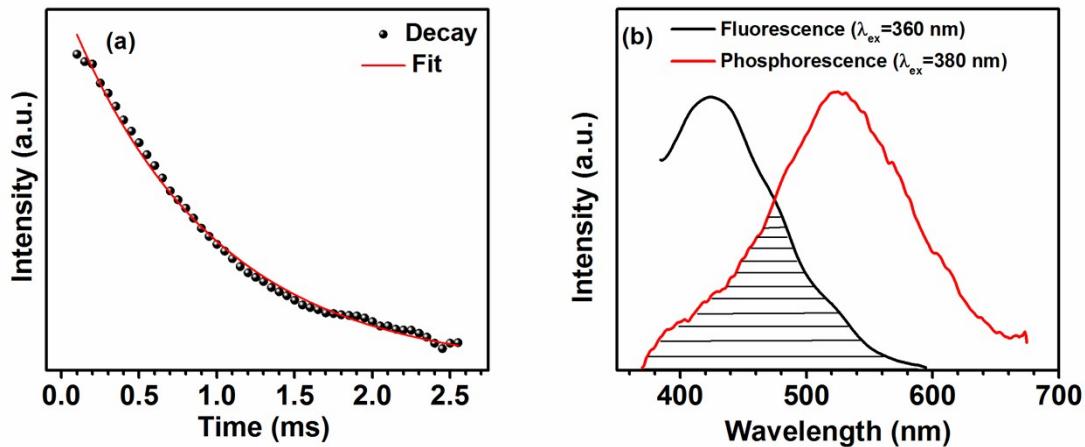


Fig.S9 (a) Decay measurements of carbon dots dispersed in silica gel collected at 360 nm excitation and 420 nm emission (b) Comparison of fluorescence and phosphorescence emission of carbon dots.

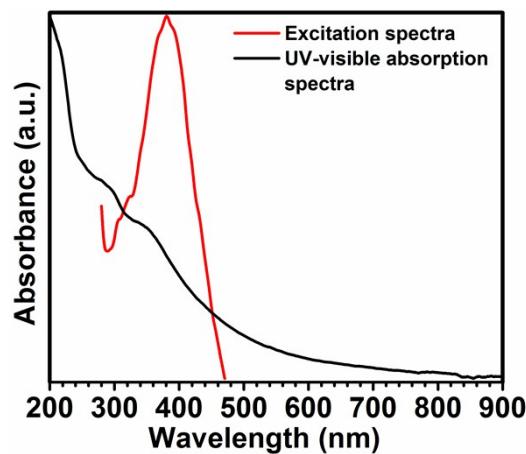
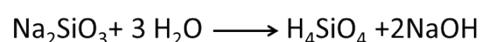


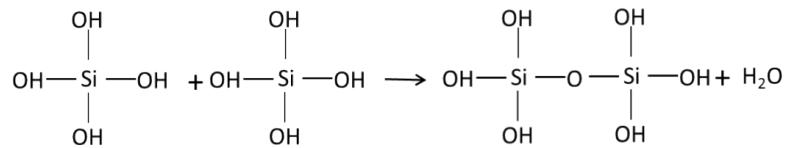
Fig.S10 (a) UV-visible spectrum of CDs dispersed in silica gel and phosphorescence excitation spectrum of CDs.

Silica gel formation

For the preparation of silica gel 5gm of sodium meta silicate is dissolved in 250mL of water and the density was further adjusted to 1.04 g/cm³. When sodium meta silicate is dissolved in water monosilicic acid is produced and the reaction is



The monosilicic acid can polymerize in the presence of acid with the liberation of water as shown below.



This process continues until a 3D network of Si-O links established. The Si-O chains connect among themselves by hydrogen bonding. On introducing CDs in to these system which have C=O, OH and COOH functional groups, C=O may form hydrogen bond with OH functional groups on the polymerised silicic acid and the hydroxyl functional groups may form siloxy bond which is demonstrated as below.

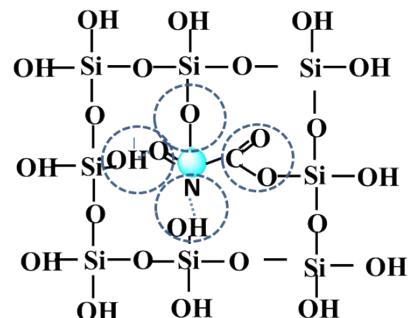


Fig. S11. Schematic representation of carbon dots in silica gel.

The gelation period and hydrogen bond formation is very sensitive to pH value. At pH 11 the gel formation is very slow. Since the rate gelation is low the CDs could easily form bonds with silicic acid. Because of this hydrogen bond and strong siloxy bond formation the intermolecular motion of the CDs are blocked and it may favour the radiative transition from the triplet state and phosphorescence occurs. This bond formation of CDs with silicagel may be helpful to suppress the non-radiative transitions.

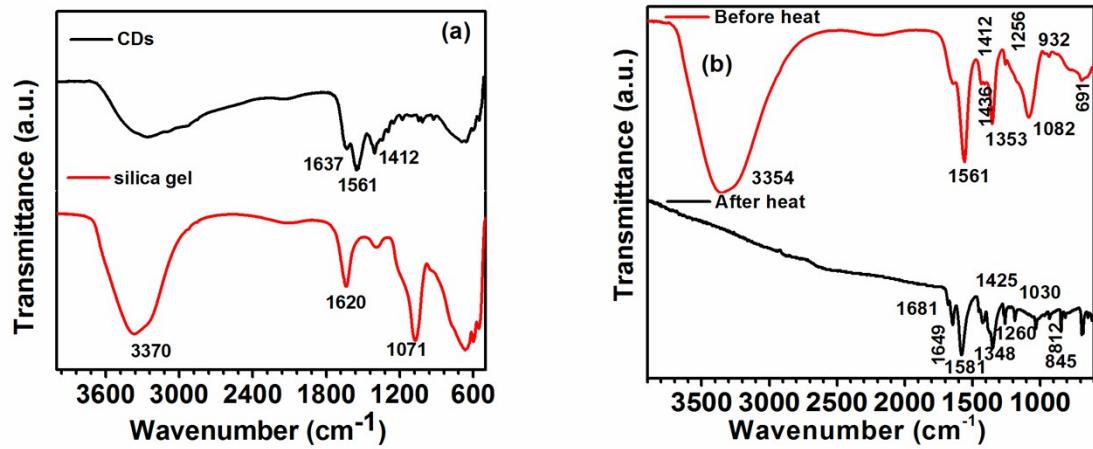


Fig.S12 (a) FTIR spectrum of CDs (black curve) and silica gel (red curve) (b) FTIR spectrum of CDs dispersed in silica gel before (red curve) and after (black curve) heat treatment.

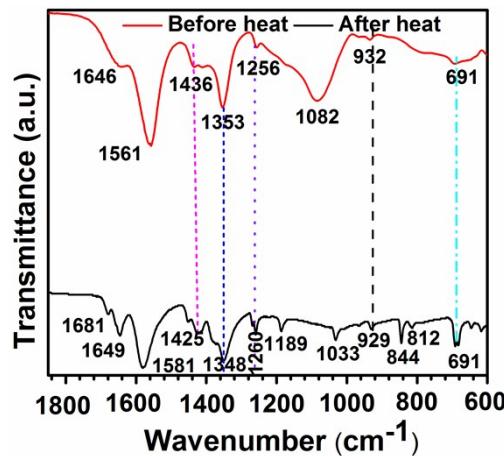


Fig.S13. FTIR spectrum in the region 600 cm⁻¹ to 1800 cm⁻¹ of carbon dots dispersed in silica gel before and after heat treatment.

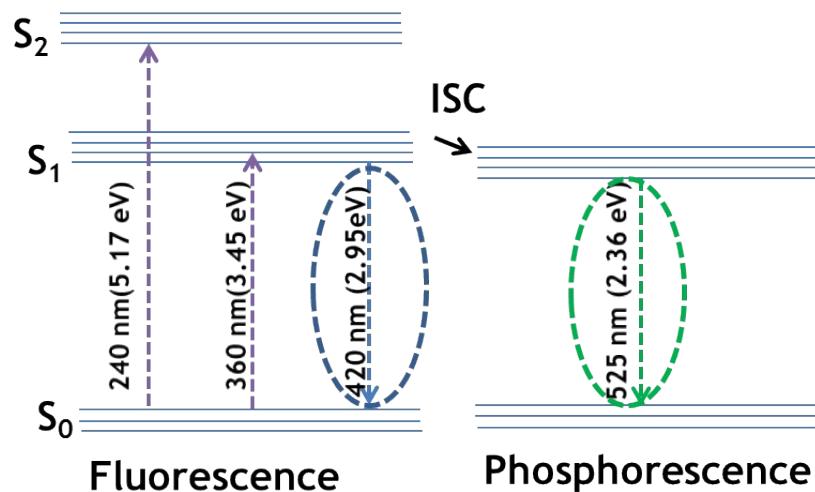


Fig. S14. The proposed photoluminescence mechanisms of CDs in silica gel.

Quantum Yield (Q.Y.) calculation

The PL quantum yield was estimated using quinine sulphate as the standard, in water. The quantum yield of quinine sulphate was taken as $Q_R = 0.54$ at 340 nm. The QY of the CDs

were calculated according to the following equation, $Q = Q_R \frac{I A_R n^2}{I_R A n_R^2}$, where Q and Q_R are the quantum yield of the sample and reference, and I and I_R are the integrated PL intensities of the sample and the reference, and A and A_R are the absorbance of the sample and the standard at the excitation wavelength; n and n_R are the refractive indices of the sample and reference respectively [1,2].

References

1. The manual of "A Guide to Recording Fluorescence Quantum Yields" by HORIBA Jobin Yvon IBH Ltd.
2. J. Wang, C. Cheng, Y. Huang, B. Zheng, H. Yuan, L. Bo, M. Zheng, S. Yang, Y. Guo and D. Xiao, J. Mater. Chem. C, 2014, 2, 5028-5035.