Supporting Information

Template Free Hydrothermal Synthesis of Amphibious Fluorescent Carbon Nanorice towards anti-counterfeiting application and unleashing its Nonlinear Optical properties

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Formation mechanism of CNR structures:

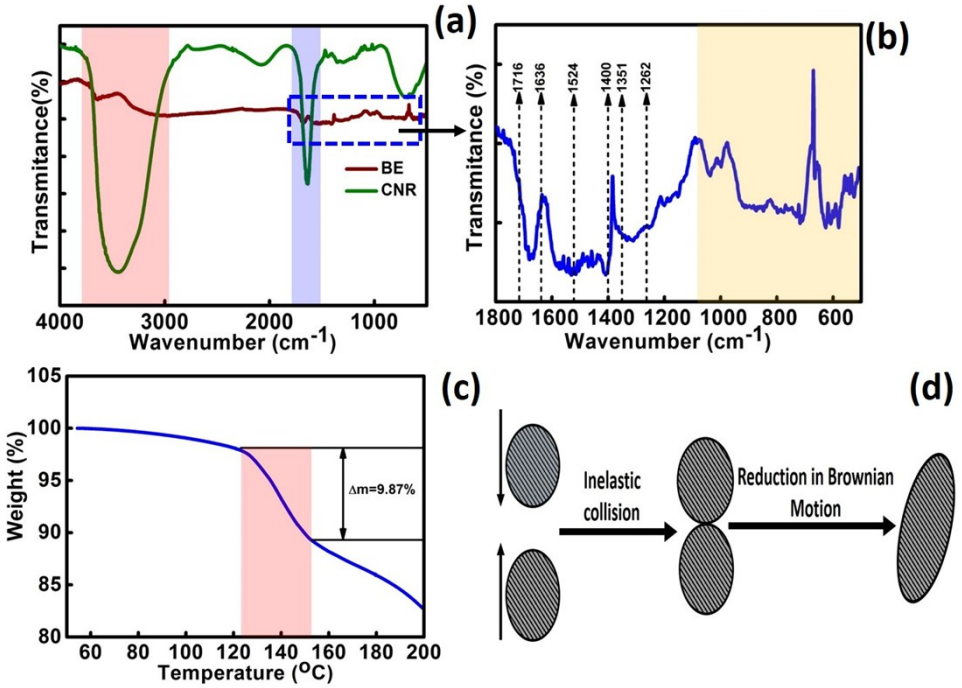

Fig. S1 (a) The FTIR spectra of the precursor BE and synthesized CNR sample. (b) FTIR spectrum of the precursor BE in the spectral range of 1800 - 500 cm^{-1}. (c) TGA curve of the precursor BE. (d) Schematic representation of formation of CNR structures from small spherical carbon nanocrystals with comparable lattice parameter via inelastic collations and coalescence mechanism.

The formation of CNR takes place via two intermediate growth mechanisms. At first carbon nanocrystals are formed by following four steps: dehydration, polymerization, carbonization and passivation during the hydrothermal process. It has been reported earlier by different chromatographic techniques[36] that the precursors used for the synthesis of CNR may contain different types of essential and non-essential natural amino acids such as alanine, isoleucine, threonine, phenylalanine, *L*-tryptophan, etc. The presence of these essential and nonessential amino acids with in the BE precursor also has been confirmed by the FTIR spectra and presented in Fig. S1a. The amino acids are expected form zwiterionic structure in aqueous medium and hence all modes vibrations corresponding to NH_3^+ and $–COO^-$ can be expected from FTIR spectra of BE extract in aqueous medium due to the presence of different types of essential and non-essential amino acids. The modes of vibration due presence of NH^{+3} group has been observed at ~ 1636 cm^{-1} (anti-symmetric deformation mode of vibration) and at ~ 1524 cm^{-1} (symmetric mode of vibration).[1-2] The IR absorptions at ~ 1716 cm^{-1} , 1400 cm^{-1} and 1262 cm^{-1} are originated due to protonated form of amino acids. The reason of IR absorption at these individual positions has been presented in Table S1 and has been compared with data available in literature. Moreover the broad IR absorption band in the region 1070-500 cm^{-1} is due to the vibrations originated due to C-N and several other C-C stretching modes in association with $CH_3(CH_2)$ rocking modes.

Table S1 Summary of amino acid head groups and different protonated states present in precursor BE

Head groups of amino acids	Position of IR absorption from experimental results (cm^{-1})	Position of IR absorption reported in literature [1,2] (cm^{-1})	Modes of vibration responsible for IR absorption
NH^{+3}	1636	1630	Anti-symmetric deformation-
	1524	1520	Symmetric deformation
COOH	1716	1720	Stretching (C=O)
	1400	1400	Deformation (C-OH)
	1262	1260	Stretching (C-O)
Others	1351	1350	Deformation (CH_2 and CH_3)
	1070-500	1100-500	Stretching (C-N and C-C) and rocking (CH_3CH_2)

In order to investigate hydrothermal process steps, we have compared the FTIR spectrum of the synthesized CNR sample with the precursor BE and presented in Fig. S1b. The board absorption band in the region 3670-2935 cm^{-1} has been observed in case of synthesized CNR sample and it assigned due to the stretching mode of vibrations of O-H, N-H, and polycyclic aromatic C-H bonds. Whereas the IR absorption band cantered at ~1630 cm^{-1} is due to starching mode of vibration of aromatic C=C bonds. This huge IR absorption due to O-H, N-H, C-H and C=C bonds is almost absent for the precursor BE. The presence of O-H bonds suggests dehydration of the precursor during the hydrothermal treatment. Whereas, the presence polycyclic aromatic C-H and C=C suggests the formation of polycyclic aromatic graphitic structure due to carbonization during hydrothermal process.[3] Furthermore, the thermogravimetric analysis (TGA) curve of precursor BE shows (Fig. S1c) weight loss of amount 9.87% within a temperature range of 120^{O} C- 150^{O} C, which confirms the dehydration [4] of the precursor during the hydrothermal process at a temperature range of 120^{O}C - 150^{O}C. whereas, Fig. S1d schematically represents formation of CNR structures from small spherical

carbon nanocrystals with comparable lattice parameter via inelastic collations and coalescence mechanism.

References:

1. M. Wolpert and P. Hellwig, *Spectrochim. Acta Mol. Biomol. Spectrosc.,* 2006, **64**, 987-1001.
2. S. Y. Venyaminov and N. N. Kalnin, *Biopolymers*, 1900, **30**, 1243-1257.
3. Z. Wang, B. Fu1, S. Zou, B. Duan, C. Chang, B. Yang, X. Zhou and L. Zhang, *Nano Res.*, 2016, **9**, 214-223.
4. E. Deydiera, R. Guileta, S. Sardaa and P. Sharrockb, *J. Hazard. Mater.*, 2005, **121**, 141-148.

Linear optical properties of synthesized CNR

Quantum yield (QY) of the synthesized CQDs

The QY (Φ) of the synthesized CNR sample has been estimated by comparing its integrated PL intensity (excited at 350 nm) and the absorbance value (at 350 nm) with that of the quinine sulphate in 0.05 M H_2SO_4 solution (literature quantum yield 0.54 at 350 nm [5]). The following equation been used to calculate the value of Φ of synthesized CNR structures.

$$\Phi_S = \Phi_R \left(\frac{A_R(\lambda_R) I_S}{A_S(\lambda_S) I_R} \right) \left(\frac{\eta_S}{\eta_R} \right)^2 \quad (1)$$

Where Φ_S and Φ_R are the quantum yields of the sample and reference respectively; $A_R\ (\lambda_R)$ and $A_s\ (\lambda_s)$ are absorbance of the reference and sample respectively. Here η_s and η_R are the refractive index or the sample and reference medium respectively. I_s and I_R are the integrated PL intensities of sample and reference, respectively.

References:

5. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.

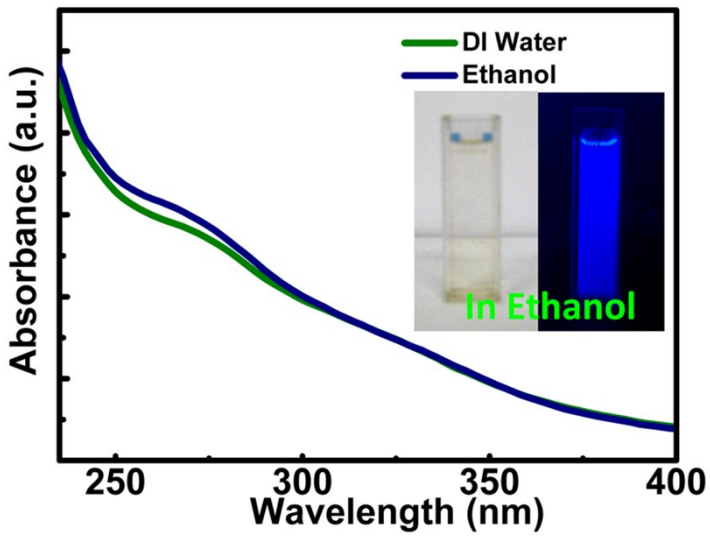

Fig. S2 UV-Vis absorption spectra of synthesized sample dispersed in DI water and ethanol. The inset shows the digital camera image of the sample dispersed in ethanol under daylight (left) and under UV lamp (right).

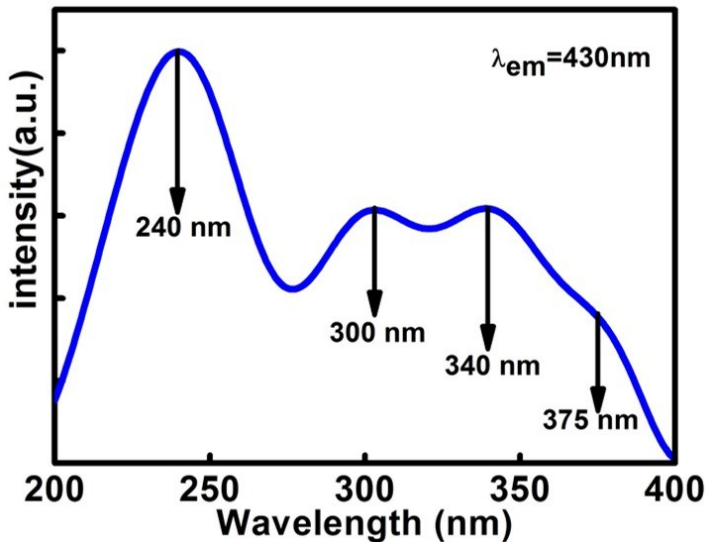

Fig. S3 The PL excitation (PLE) spectra of the synthesized CNR sample (0.014mg/ml) collected for emission at 430 nm in aqueous medium.

The observed blue luminescence in synthesized CNR structures can be correlated with PL excitation (PLE) spectrum collected for emission at 430 nm and it is been presented in Fig.

S3. The PL excitation (PLE) spectrum clearly shows the presence of three distinct peaks at ~ 240 nm, ~ 300 nm and ~ 340 nm due to σ-π^*, π-π^*, and n-π^* transitions respectively in CNR structure.[6-7] Whereas, The observed shoulder PLE peak ~ 375 nm is related to the energy bands induced by the functional groups attached on the surface of sp^2 carbon core and other defect related states.[8]

References:

6. D. Pan, J. Zhang, Z. Li and M. Wu, *Adv. Mater.*, 2010, **22**, 734-738.

7. J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. R-Aburto, L. Ge, L. Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaipparettu, A. A. Marti, T. Hayashi, J-J. Zhu and P. M. Ajayan, *Nano Lett.*, 2012, **12**, 844-849.

8. F. Liu, M. H. Jang, H. D. Ha, J. H. Kim, Y. H. Cho and T. H. Seo, *Adv. Mater.*, 2013, **25**, 3657-3662.

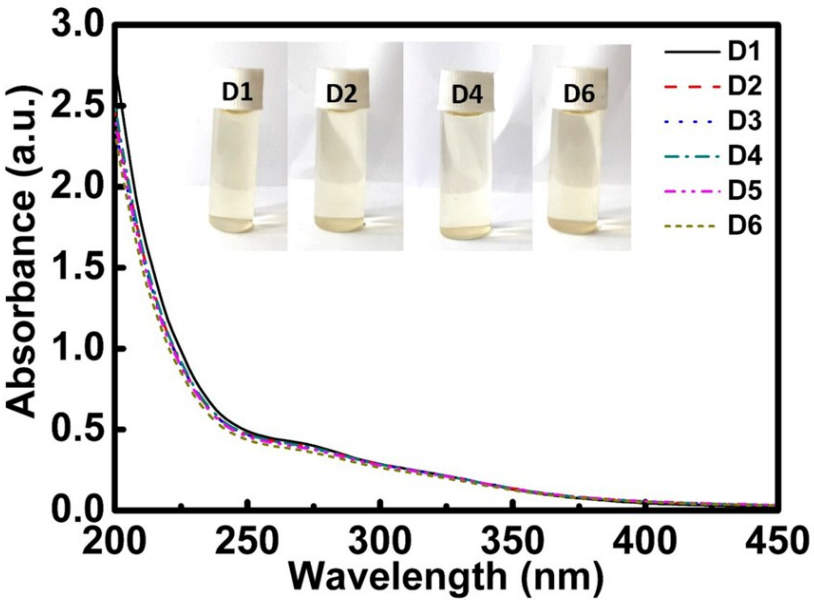

Fig. S4 Aging study of the synthesized sample after diluting in DI water for six days (a) UV-Vis absorption spectra of sample taken in each day (day 1-6) and inset is the Digital image of the sample on day 1 (D1), day 2(D2), day 4 (D4) and day6 (D6).

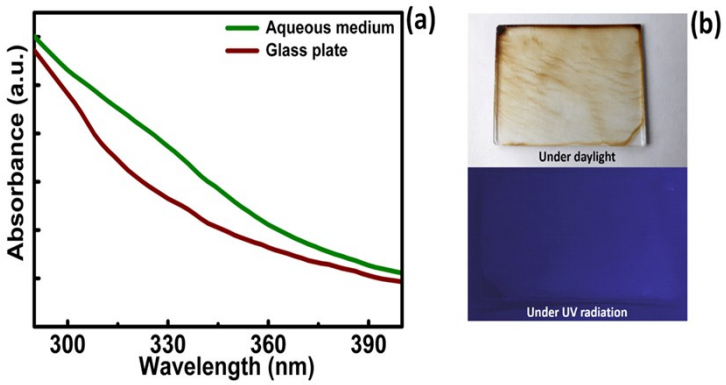

Fig. S5 UV-vis absorption spectra of the as synthesized CNR sample in original aqueous solution and dried over a glass slide. (b) Digital image of the CNR sample dried over glass slide under daylight and under 365 nm UV irradiation.

Nonlinear optical response of CQDs

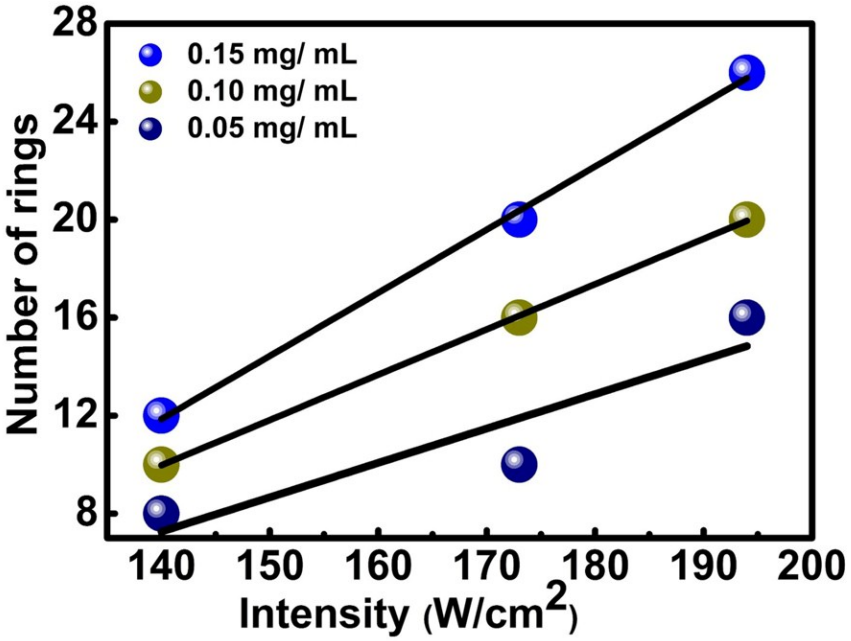

Fig. S6 Variation of numbers of rings on the intensity of the incident laser radiation.