Electronic Supplementary Information (ESI)

Carbon nanodots–ORMOSIL fluorescent paint and films†

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1. Experimental section

1.1 Materials. pluronic P123 (EO70PO20EO70; M_{av} = 5800) tetraethylorthosilicate (TEOS) and 3-glycidyloxypropyl-trimethoxy silane (GLYMO) (98 %), quininesulfate dihydrate were purchased from Sigma Aldrich. Absolute EtOH (99.99 %), ethyl acetate (99.5 %), n-hexane (99.99 %), H_2SO_4 (98%) and NH_3 was purchased from Merck India. Aluminium acetylacetonate ($Al(acac)_3$) was supplied by Lancaster, water (18 MΩ) used for solvent extraction was obtained from Milli-Q System (Millipore) and soda-lime glass slides for coating deposition were purchased from Reviera. For column chromatography silica gel (60-120 mesh) was purchased from Sisco research laboratory Pvt. Ltd. India.

1.2 Synthesis of organically modified silica hybrid (ORMOSIL) sol

In order to prepare the hybrid (ORMOSIL) sol,[24] 2.33:1 molar ratio of TEOS and GLYMO has been taken in a round bottom flask containing 21 g of n-butanol and stirred for proper mixing. To this, a mixture of catalytic amount of 1(N) HCl acid (0.586 g), water (10.9 g) and methanol (1.43 g) was added and stirred for next 30 min. The above resultant mixture was refluxed at 80 °C for 90 min and allowed to cool at room temperature. The sol obtained was aged for 24 h in closed condition at ± 5 °C temperature. $Al(acac)_3$ (0.02 mol per mol of GLYMO) was then added and stirred until it get dissolved for initiating the epoxy polymerization. The final equivalent SiO_2 content of the sol was 21 wt%. The sol was aged for 24 h in refrigerator (± 5 °C) prior to use.

1.3 Synthesis of CNDs in ethanol and fabrication of CNDs-ORMOSIL films

0.5 g P123 was stirred with 2 g H_2SO_4 (36 N) for 30 min which leads to a dark brown solution. 20 g EtOH was slowly added to the above solution at same stirring condition (200 rpm) for next 30 min and then neutralised with NH_3 (conc). Neutralisation leads to the salt formation in solution and colour of the solution changes from dark brown to golden yellow. Eventually the solution was filtered using 0.22 µm polyvinylidene fluoride (PVDF) membrane and residue was washed several times with EtOH. The collected filtrate solution was used for further use and characterisation. For film fabrications collected filtrate was concentrated to 5 ml (using rotary evaporator at 60 °C) and extracted in n-hexane/ water (3:1 v/v) mixture. In the process CNDs get well dispersed in hexane and excess P123 along with unwanted salt remained in water part. The hexane part was seperated and extracted again by the additon of fresh water in the same ratio as mentioned above. This process was repeated for 4 times and finally n-hexane part was evaporated to dryness at 60 °C and 5 g of prehydrolysed ORMOSIL sol was mixed with it. To obtain a transparent sol for coating purpose the solution was stirred for 30 min and dip-coating was performed using glass and silicon wafer substrates at an withdrawal velocity of 21 cm min^{-1}. All coatings were cured at 70 °C for 6 h.

To fabricate films with extra pure CNDs, extracted n-hexane part was dried upto 2-3 ml and used for column chromatography using SiO_2 stationary phase and n-hexane/ethylacetate (99:1 v/v) mobile phase. Eluted part was again evaporated to dryness and 3 g of ORMOSIL sol was mixed with it (since some hydrophilic CNDs stuck in the SiO_2 stationary bed, less amount of ORMOSIl was added to avoid dilution of CNDs). Mixture was stirred for 30 min and dip-coating was performed as mentioned above.

1.4 Characterization

UV-Visible absorption and emission spectra of the films were recorded with Cary 50, Varian Inc and PTI QM-30 spectrometers, respectively. Fourier transformed infrared (FTIR) absorption spectra of the film samples deposited on Si wafer were recorded using a Nicolet 380 FTIR spectrometer. High angle XRD measurements of the CNDs-ORMOSIL films and transmission SAXS measurement of CNDs in solution were performed with a Rigaku SmartLab X-ray diffractometer operating at 9 kW (200 mA; 45 kV) using Cu-Kα (λ= 1.5405 Å) radiation. For SAXS analysis, Rigaku nanosolver software was used. Transmission electron microscopic (TEM) measurements were carried out with JEOL JEM 2100F operating at 200 kV. For this purpose hexane dispersed CNDs and scratched off film samples (dispersed in methanol with ultrasonication) were used and placed on lacey carbon coated Cu-grids and analyzed. Thickness of films were measured by surfcorder SE-2300 profilometer (Kosaka Laboratory Ltd., Japan). A ZEISS SUPRA 35VP field-emission scanning electron microscope was used for scanning electron microscopy (SEM) analysis. For this purpose films deposited on silicon wafer were used. The pencil hardness of coatings was measured by ASTM D3363 specifications using a BYK Gardner pencil hardness tester and adhesion of the films on glass substrates was evaluated using the method as per ASTM D3359 cross-cut tape test. Fluorescence imaging of CNDs-ORMOSIL films was done under Olympus BX51 system microscope. The ultimate power falling on the 6x6 inches film was measured by a UV power puck (S/N-8000; EIT Inc). For the same purpose film was kept 2 cm apart from lamps of 8 Watt. Refractive index of CNDs-ORMOSIL film was measured by spectroscopic Ellipsometer (J. A. Woollam). The luminescence decay measurements were performed by time correlated single-photon counting (TCSPC) method. For decay measurements, samples were excited at 375 nm using a picosecond diode laser (IBH Nanoled-07) at a repetition rate of 1 MHz. The typical FWHM of the system response is about 200 ps. The fluorescence decays were analyzed using IBH DAS6 software. The quality of fitting was evaluated from the χ^2 value and DW parameters, and the PL decay curves were fitted using a triexponential function.

1.5 Quantum yield (QY) measurement

Relative quantum yield measurement of CNDs was done with respect to 10^{-4} M quininsulfate in 0.01N H_2SO_4 solution as a standard. In order to minimize re-absorption effect diluted CND solution was used for QY measurement. Relative QY was calculated using equation S1:

$$QY_{sample} = \left(\frac{F_{sample}}{F_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \text{X } QY_{ref} \qquad \text{-------------} \text{ (S1)}$$

F ⟶ Integrated area under the PL emission curve

A ⟶ Absorbance at excitation wavelength

n ⟶ Refractive index of the samples

QY_{sample} ⟶ Quantum yield of the sample

QY_{ref} ⟶ Quantum yield of the reference (here quininsulfate)

Table S1: Calculated quantum yield of CNDs (in hexane) with respect to 10^{-4} M standard quinine sulfate solution

Sample name	Absorbance at excitation wavelength (365 nm)	Integrated emission area	Refractive index of the medium	Quantum yield %
10^{-4} M quininsulfate (in water)	0.061	1615	(H_2O)= 1.33	54
CNDs (in hexane)	0.04	212.2	(hexane) = 1.38	10

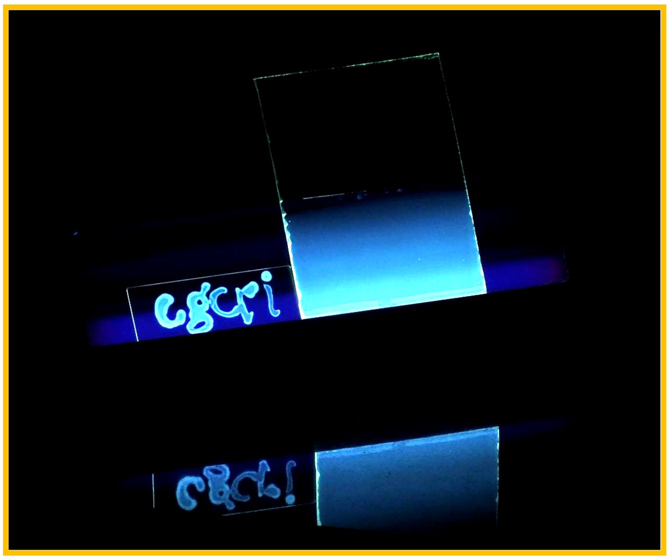

Fig. S1 Digital picture of CNDs–ORMOSIL used for writing on a glass slide and scratch resistant film on a 6 x 6 inch^2 glass under UV-lamp of wavelength 365 nm. Bottom is the reflection image.

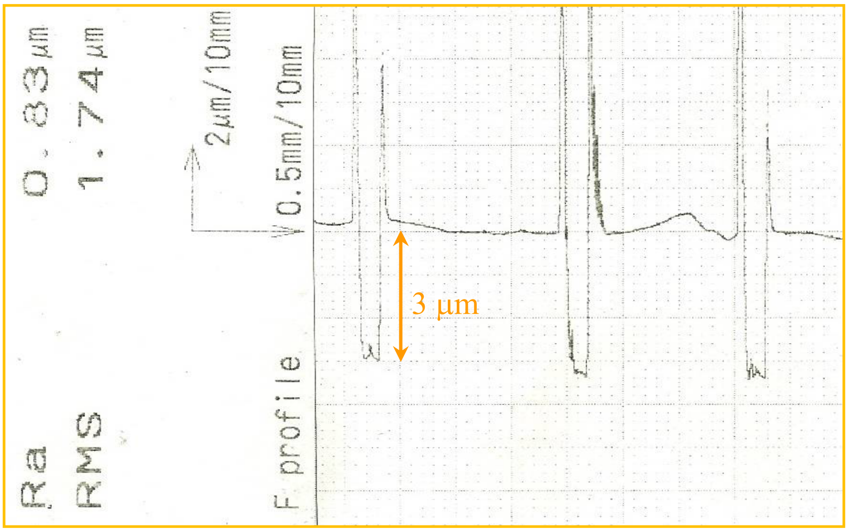

Fig. S2 Profilometric traces at 3 different places of one representative CND-ORMOSIL film deposited on glass substrate. Surface of the as-prepared film (dried at room temperature) was first scratched with a sharp steel blade followed by heat treatment at 70 °C for 6 h.

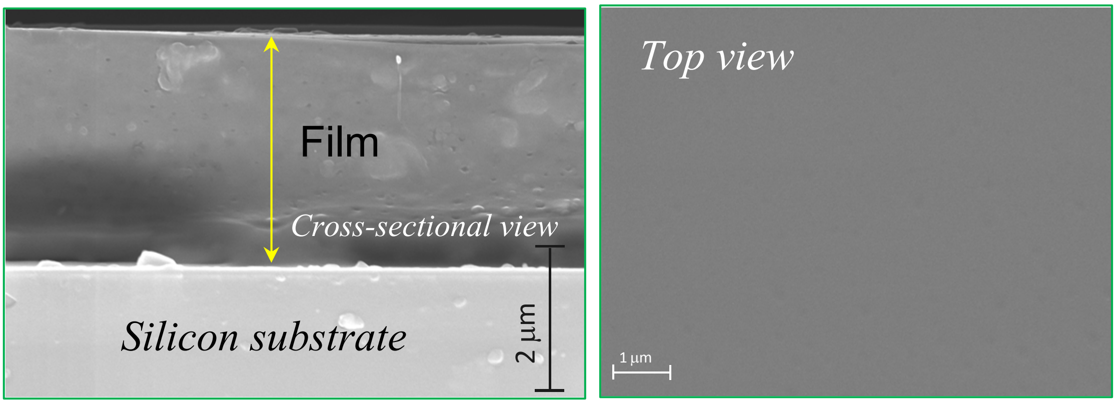

Fig. S3 FESEM images showing the cross-sectional and top view of the CNDs-ORMOSIL film. The cross-sectional view shows a thickness value close to 3 µm. The crack-free homogeneous surface can be observed from the top view. The film has been deposited on silicon wafer maintaining the silmilar experimental conditions as that of glass substrate.

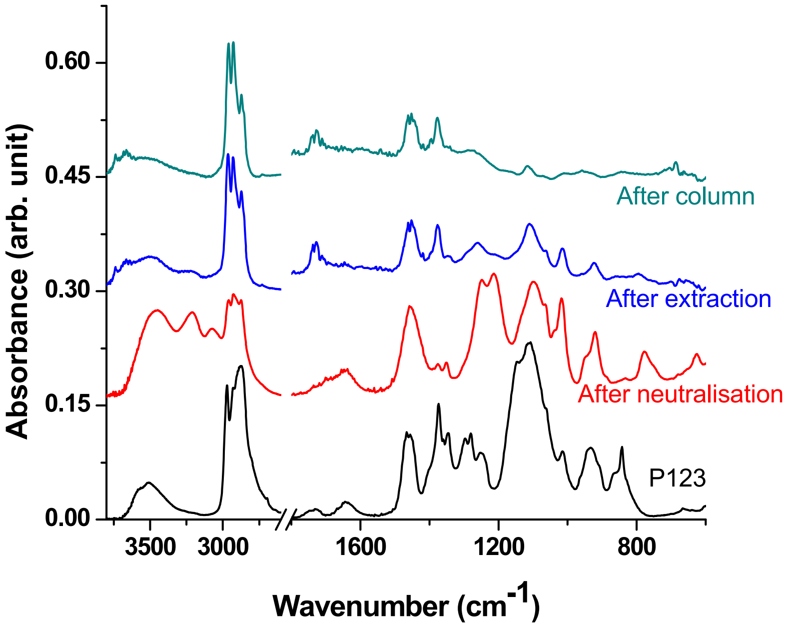

Fig. S4 FTIR spectra of P123 and CNDs at different stages of synthesis.

Fig. S5 Digital picture of CNDs in aqueous and organic solvents under day light (left panel) and UV-light (right panel).

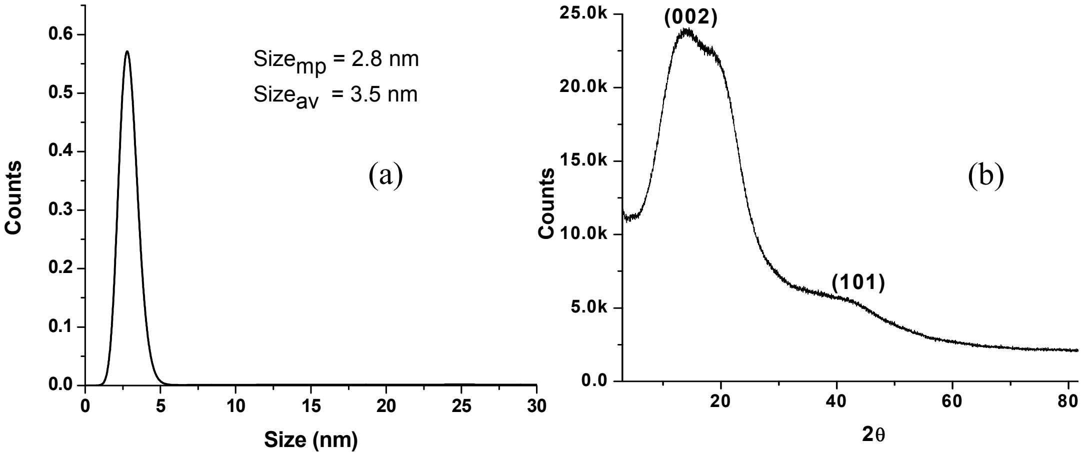

Fig. S6 (a) Transmission SAXS showing the size distribution of CNDs in hexane; (b) High angle XRD pattern of CNDs.

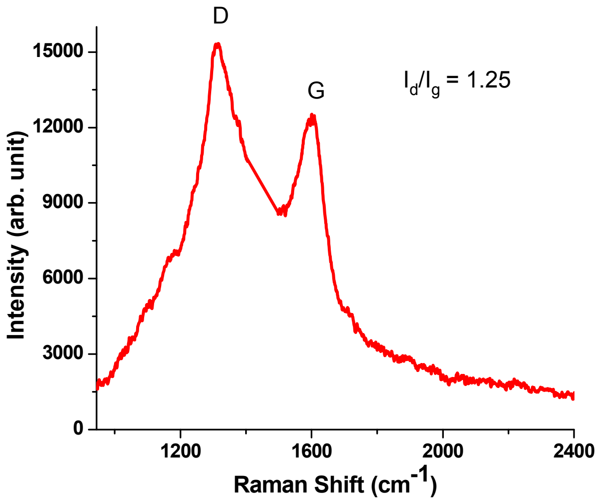

Fig. S7 Raman spectrum of bare CNDs (measured on aluminium substrate using 514 nm laser).

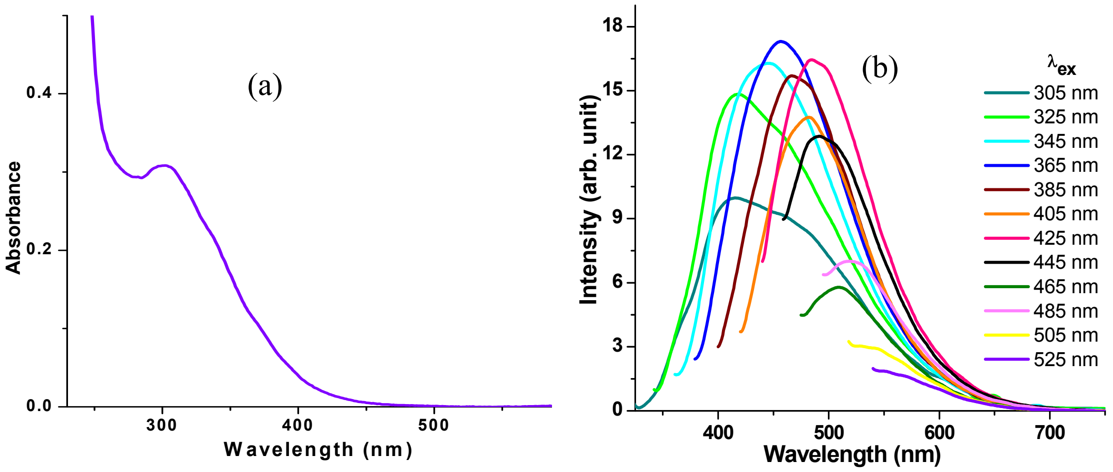

Fig. S8 UV-visible (a) and PL (b) spectra of CNDs in EtOH.

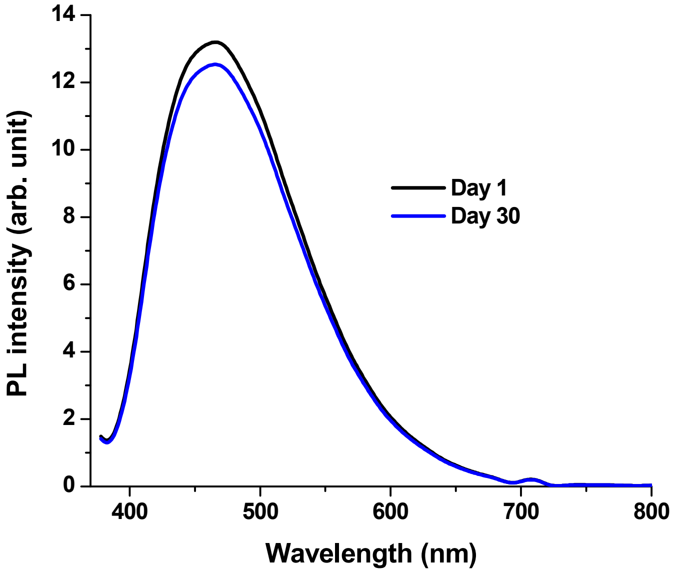

Fig. S9: PL curves showing the photostability of CNDs-ORMOSIL films under ambiant condition.

Table S2 Calculated average lifetime (from fitting data) of CNDs in hexane and CNDs-ORMOSIL films.

Sample name	**a_1**	**a_2**	**a_3**	**τ_1(ns)**	**τ_2(ns)**	**τ_3(ns)**	**τ_{av}(ns)**	**χ^2**
CND (in hexane)	0.39	0.34	0.25	2.13	0.59	4.78	2.22	1.02
CNDs-ORMOSIL film	0.931	0.019	0.887	1	4.4	0.918	1.82	1.17