A novel strategy towards designing a CdSe quantum dot – metallohydrogel composite material

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SEM, POM and fluorescence microscopy imaging of hydrogel-QD composite material
SEM and POM imaging were carried out on FEI sirion XL30 FEG SEM and Olympus C3040-ADU. The hydrogel-QD composite material was prepared by mixing equal volumes of aqueous NaCh [60 mM] solution and cadmium chloride (10 mM) solution containing CdSe QDs dispersed in CTAB (10 mM) micelle at room temperature. Then hydrogel-QD composite materia was drop cast on silicon wafer and dried under reduced pressure for overnight. For morphological analysis, the dried gel (xerogel) sample was coated with gold of thickness ~10 nm before FESEM operation. FESEM was operated at 20 KV. For POM and fluorescence microscopy, wet hybrid gel was drop cast on glass slide before experiment.

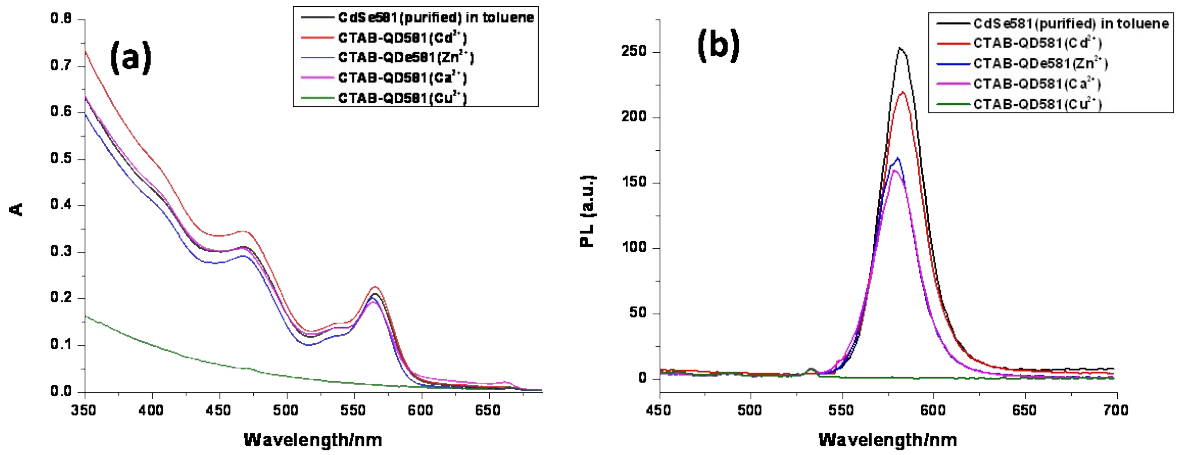
AFM imaging of CTAB-QD dispersion
In order to visualize the size, shape and morphology, freshly prepared CTAB-QD dispersion cast on mica sheet and dried under reduced pressure overnight. AFM imaging was carried out on a JPK NANO WIZARD II in in tapping mode at a scanning rate of 1.0 Hz.

TEM imaging of CTAB-QD dispersion and hydrogel-QD composite material
TEM images were recorded on JEOL 2100F. For TEM imaging CTAB-QD dispersion was cast on a carbon-coated copper grid (400 square mesh) and followed by high vacuum drying. Then sample was staining with 0.1% uranyl acetate. For hydrogel-QD composite was drop cast on carbon-coated copper grid and excess solvent was removed under vacuum. Then sample was staining with 0.1% uranyl acetate before experiment. The operating voltage for FETEM was 200 KV.

DLS and zeta potential measurement of CTAB-QD dispersion
DLS and zeta potential studies were carried out on Zetasizer Nano ZS. CTAB-QD dispersion was filtered through 0.45 μm nylon membrane. Then solution was immediately used for DLS and zeta potential measurement.

UV-visible, fluorescence, photoluminescent quantum yield and time resolved spectroscopy
Absorption and Fluorescence measurements were carried out on a Shimadzu UV-3600 spectrophotometer and Varian Cary Eclipse fluorescence spectrometer. UV-visible absorption and emission spectra of the CTAB-QD conjugate and hydrogel-QD composite were recorded on a UV-Vis spectrophotometer and emission at room temperature using quartz cuvette. The photoluminescent quantum yields were recorded on Edinburgh Instruments FLS980 fluorescence spectrometer equipped with an integrating sphere. A light emitting diode (IBH, nano LED, N-390) at 390 nm was used as excitation source. The instrument response function was measured by scattering the exciting light of aqueous milk powder. Fitting and analysis was performed using Origin8 software.

Photophysical properties of CTAB-QD System in presence of different metal ion:



(c)

System	PL QY (Ø)
CdSe QD581 in toluene (purified)	0.18
CTAB-QD581(Cd^{2+})	0.11
CTAB-QD581(Zn^{2+})	0.08
CTAB-QD581(Ca^{2+})	0.07

Fig S1. (a) UV, (b) photoluminescent spectrum and (c) photoluminescent quantum yields of CTAB-QD system in presence of different metal ion.

We have also used other metal ions, such as Ca^{2+}, Zn^{2+} and Cu^{2+}, in CTAB-QD system, where decreased of the PL quantum yields were observed. Interestingly, it has been observed that the luminescent property of the CTAB-QD is highly sensitive towards Cu^{2+}ion, where the PL intensity is completely quenched. Zhang and co-workers reported that the photoluminescence quenching was due to the decomposition of CdSe surface, as Cu^{2+} can replace the Cd^{2+} ions at the surface of QDs.[1]

DLS measurement of CTAB-QD dispersion:

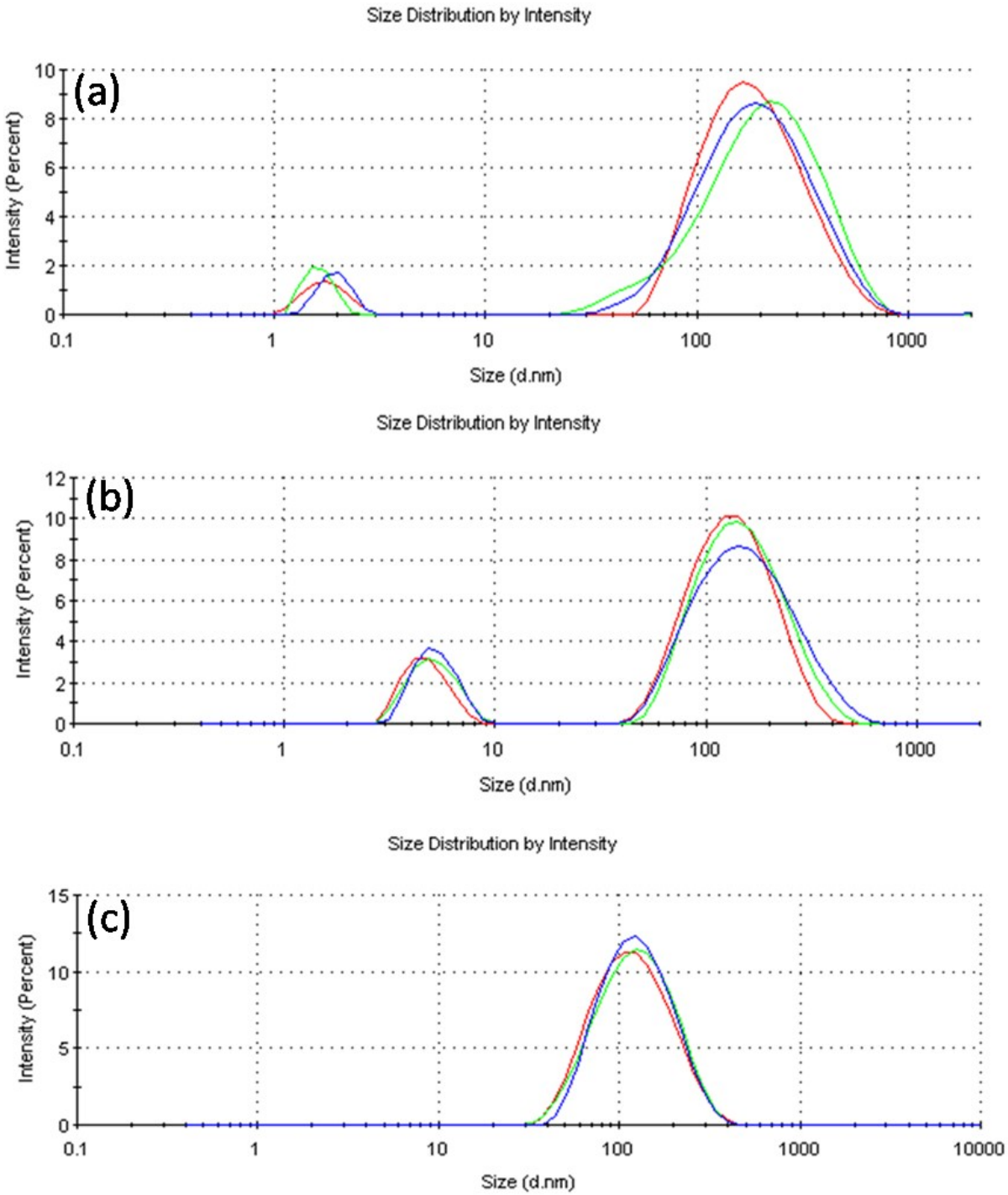
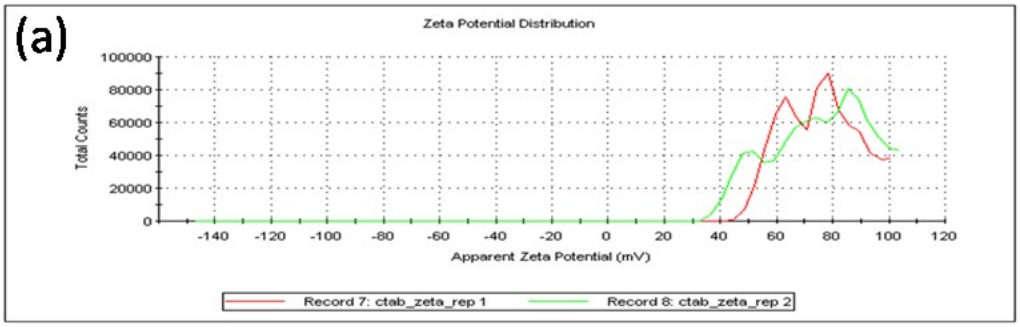


Fig S2. DLS measurement of (a) CTAB (10 mM) micelle, (b) cadmium chloride (10 mM) containing CTAB (10 mM) micelle and (c) CTAB-QD dispersion.

. **Zeta potential measurement of CTAB-QD dispersion**:

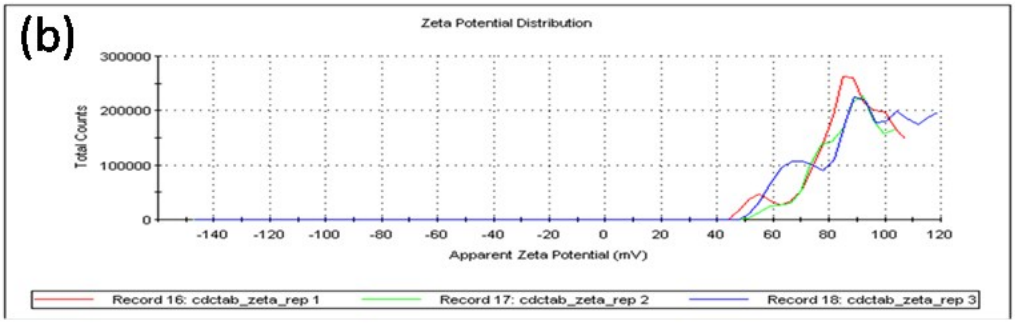
		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 75.7	Peak 1:	82.2	54.6	7.89
Zeta Deviation (mV): 13.3	Peak 2:	62.5	36.9	5.88
Conductivity (mS/cm): 0.271	Peak 3:	98.9	8.5	1.87

Result quality : Good



		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 87.6	Peak 1:	89.8	92.6	10.8
Zeta Deviation (mV): 13.6	Peak 2:	55.6	7.4	4.51
Conductivity (mS/cm): 1.04	Peak 3:	0.00	0.0	0.00

Result quality : Good



		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 89.8	Peak 1:	89.8	100.0	7.65
Zeta Deviation (mV): 7.65	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.874	Peak 3:	0.00	0.0	0.00

Result quality : Good

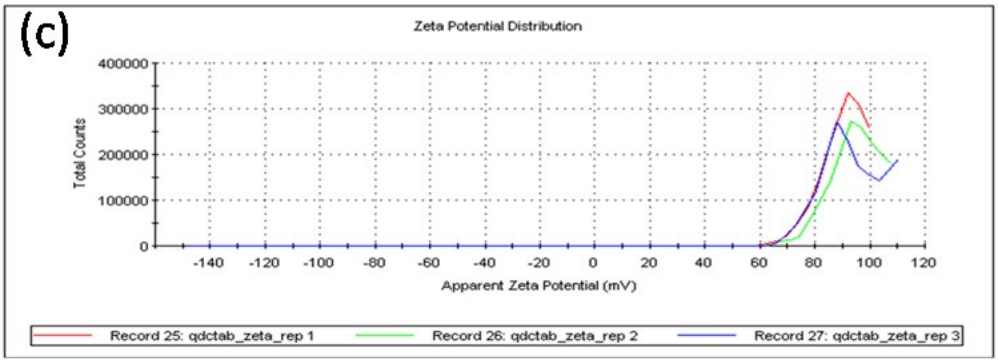


Fig S3. Zeta potential measurement of (a) CTAB (10 mM) micelle, (b) cadmium chloride (10 mM) containing CTAB (10 mM) micelle and (c) CTAB-QD dispersion.

AFM images of CTAB-QD dispersion:

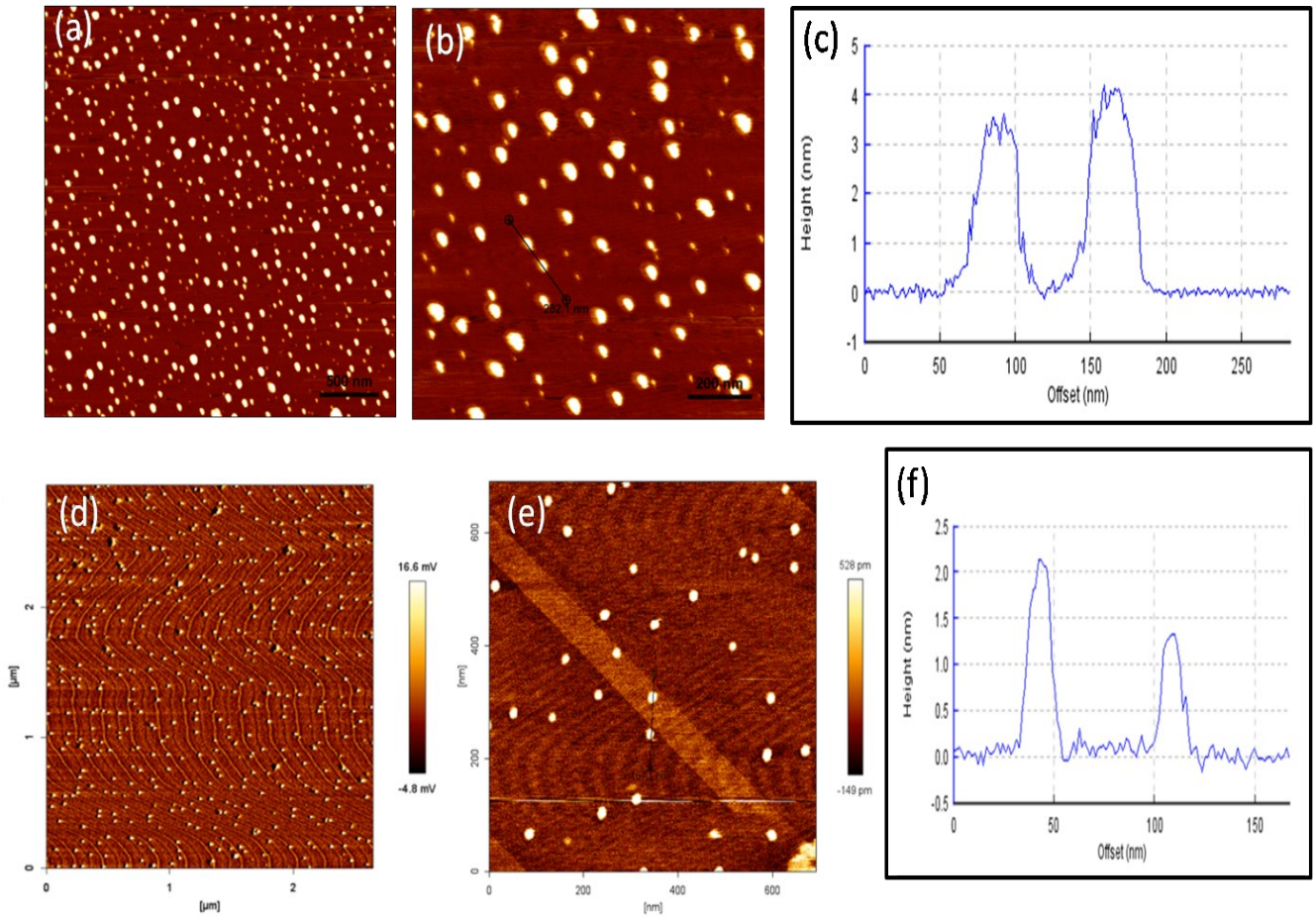


Fig S4. AFM images of (a, b) CTAB (10 mM) micelle[2] , (d, e) CTAB-QD dispersion and height profile of (c) CTAB (10 mM) micelle, (f) CTAB-QD dispersion.

Photophysical properties of yellow and red emitting *hydrogel-QD* composite:

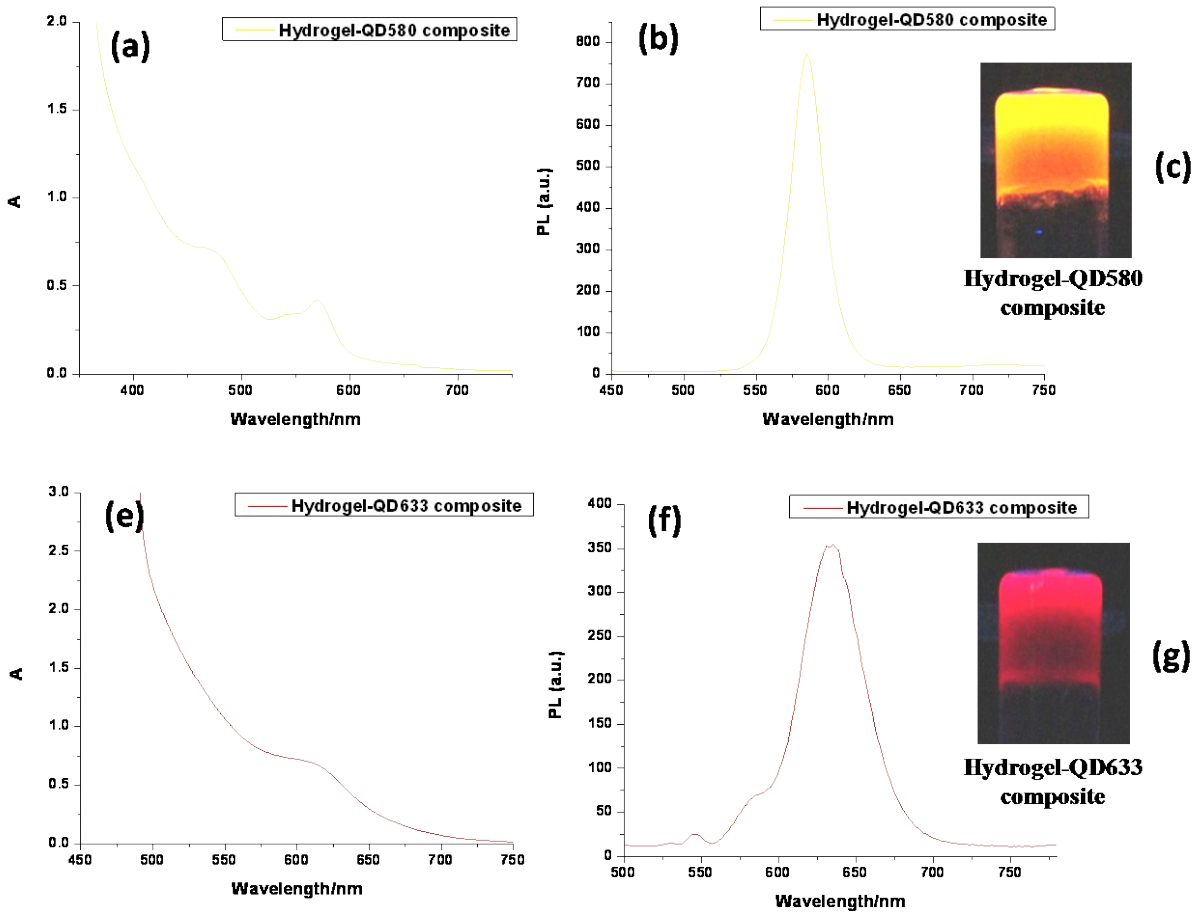


Fig S5. (a, e) UV, (b, f) photoluminescent spectrum and (c, g) photograph of yellow and red emitting *hydrogel-QD* composite.

The gelation tests were carried out by mixing equal volumes of aqueous NaCh [60 mM] solution and cadmium chloride (10 mM) solution containing CdSe QDs dispersed in CTAB (10 mM) micelle at room temperature. Yellow emitting photoluminescent *gels* was observed using yellow emitting QDs. upon irradiation with UV light (Fig c) and red emitting *hydrogel-QD* composite was obtained using the red emitting CdSe QDs (Fig g).

POM and fluorescence microscopic images *hydrogel*-QD composite (C-2):

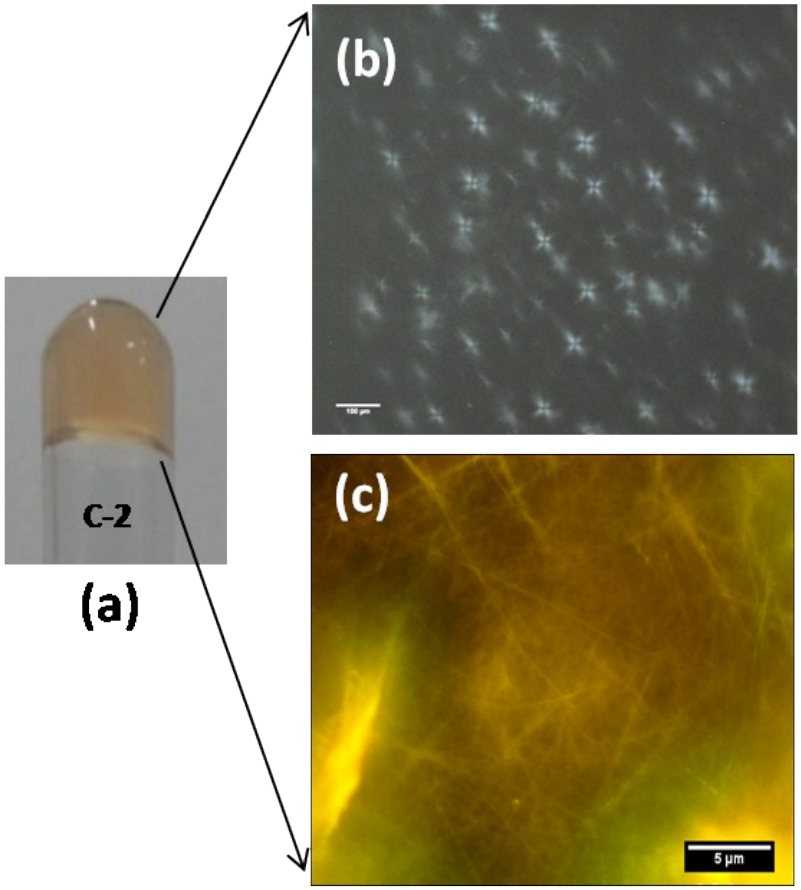


Fig S6. (a) Photograph, (b) POM and (c) fluorescence microscopic images of C-2.

SEM and TEM images *hydrogel*-QD composite (C-2):

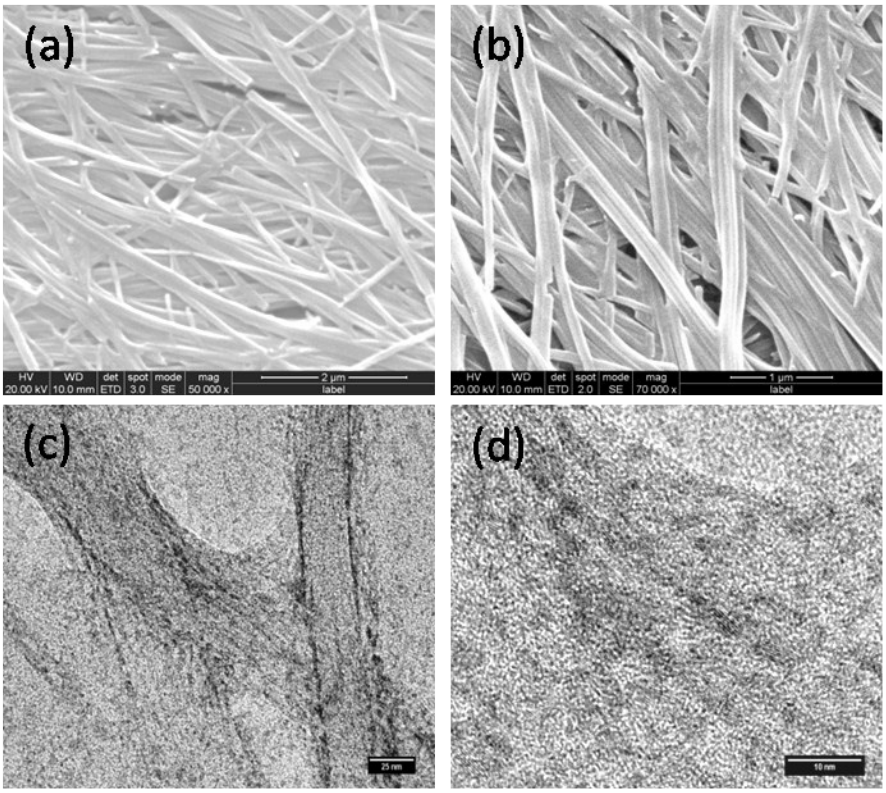


Fig S7. (a, b) SEM and (c, d) TEM images of C-2.

Absorption and photoluminescence spectra of yellow-orange emitting *hydrogel*-QD composite (C-2):

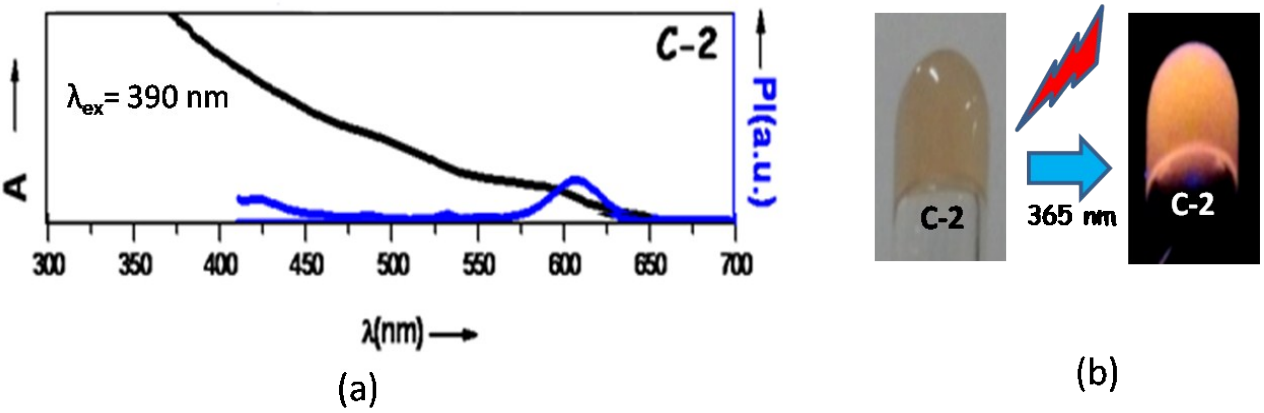


Fig S8. (a) Absorption and photoluminescence spectra and (b) yellow-orange emitting C-2 (UV excitation at 365 nm).

Table 1 Absorption, emission profiles and fluorescence lifetime values of *hydrogel*-QD composite (C-2):

Sample	λ_{abs}	λ_{em}	$\Delta\lambda$	FWHM	τ_1(ns)	A_1(%)	τ_2(ns)	A_2(%)	τ_3(ns)	A_3(%)	Adj. R^2 value	τ_{avr}(ns)
C-2	591.0 nm	609.0 nm	18.0 nm	36 nm	9.3	51	36.2	27	2.4	22	0.9996	15.0

λ_{abs} = maximum absorption wavelength, λ_{em}= maximum emission wavelength, $\Delta\lambda$ = Stokes shift, FWHM = full width half maxima value, A_1, A_2 and A_3 are the normalized amplitudes of the decay components, τ_1, τ_2 and τ_3 are the decay time constants and τ_{avr} = average life time

Absorption and photoluminescence spectra of *hydrogel*-QD composite materials at different concentration of NaCh:

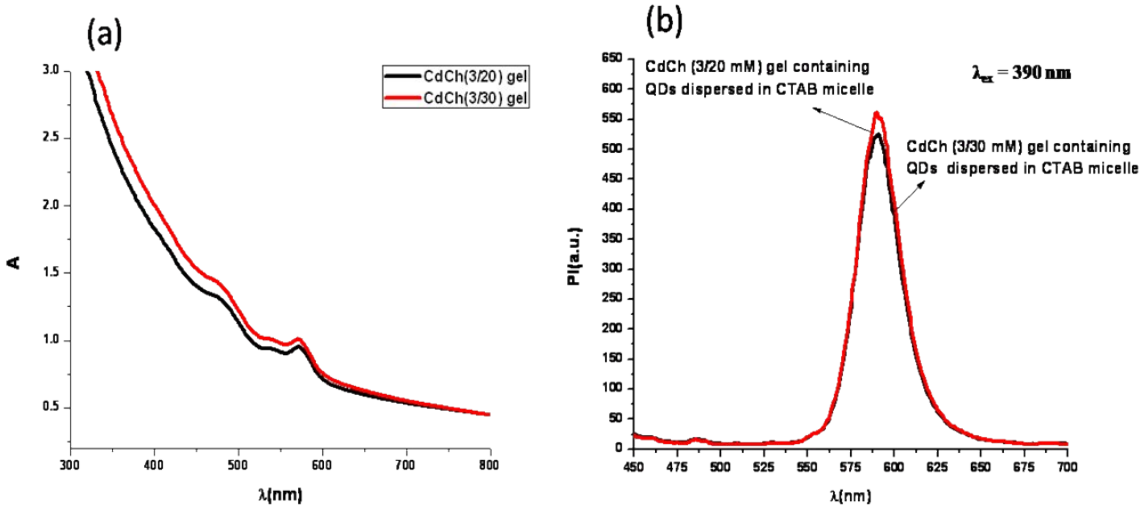


Fig S9. (a) UV and (b) photoluminescent spectrum of *hydrogel-QD* composite materials at different concentration of NaCh.

Reference:

1. X. Bu, Y. Zhou, M. He, Z. Chen and T. Zhang, *Dalton Trans.*, 2013, **42**, 15411–15420.