Electronic Supplementary Material (ESI) for RSC Sustainability.

Green Transformation of Biomass-Derived Indian Gooseberry into Fluorescent Intrinsic Nitrogen-Functionalized Carbon Quantum Dots for Real-Time Detection of Vitamin B_2 in Nanomolar Range

Mandeep Kaur, Mily Bhattacharya*, Banibrata Maity*

Department of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology

Patiala 147004, India

*Corresponding Authors

Mily Bhattacharya and Banibrata Maity

Email: mily.bhattacharya@thapar.edu and banibrata.maity@thapar.edu

Figure S1

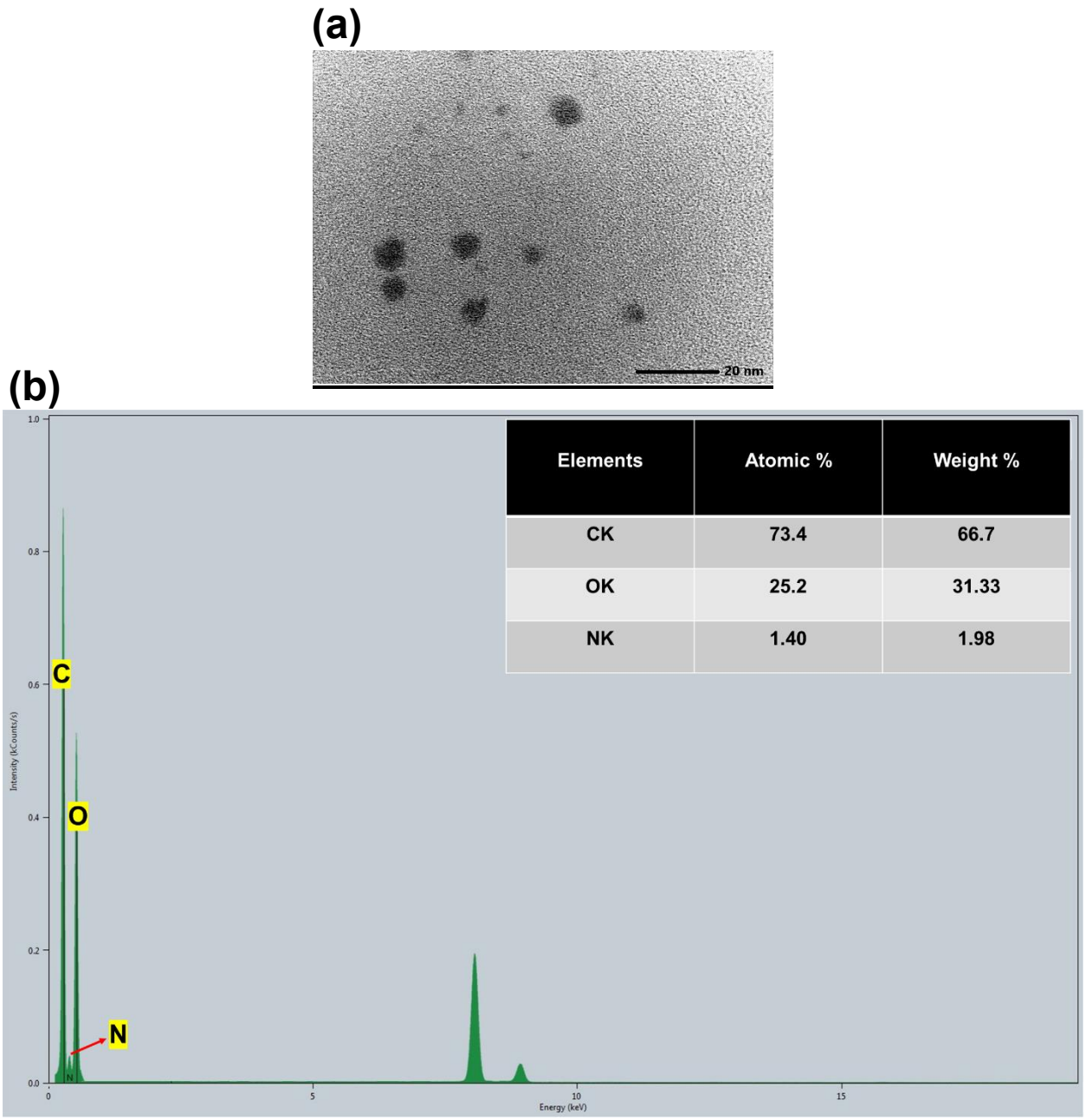

Figure S1. (a) HR-TEM image of N-CQDs, (b) Energy dispersive spectroscopy (EDS) spectrum of N-CQDs showing the presence of different elements on the surface of N-CQDs. The table (inset) denotes the percentage composition of each element present in the N-CQDs.

Figure S2

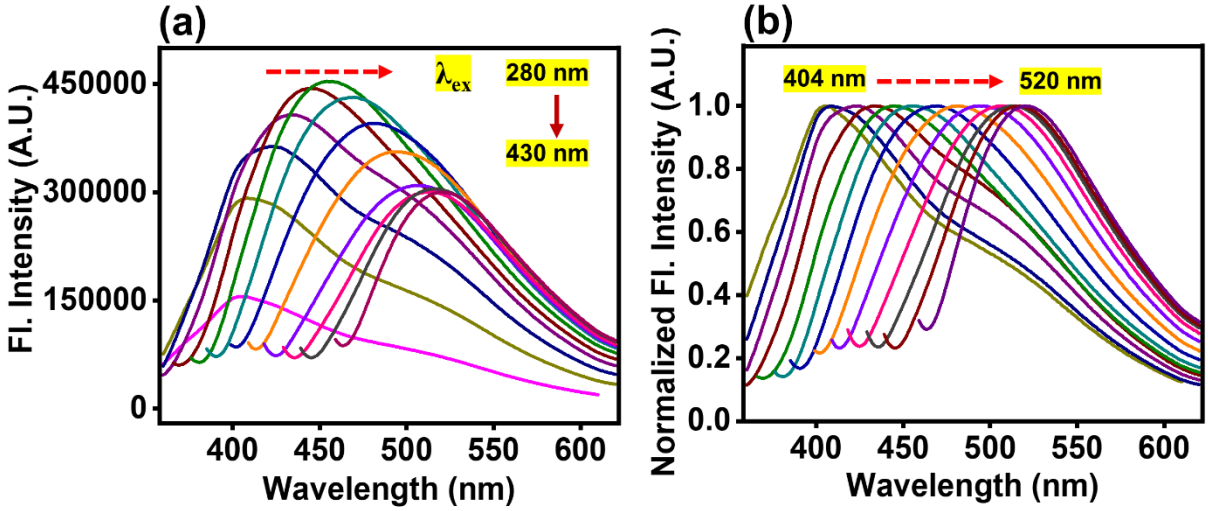

Figure S2. Excitation wavelength-dependent (a) changes in fluorescence emission spectra and (b) Peak position-normalized fluorescence emission of N-CQDs clearly depicting the spectral shift from 404 nm to 520 nm in pH 7.4 HEPES buffer. The red dashed-arrow indicates a red-shift in the fluorescence emission upon changing the excitation wavelength (λ_{ex}: 280 nm to 430 nm).

Figure S3

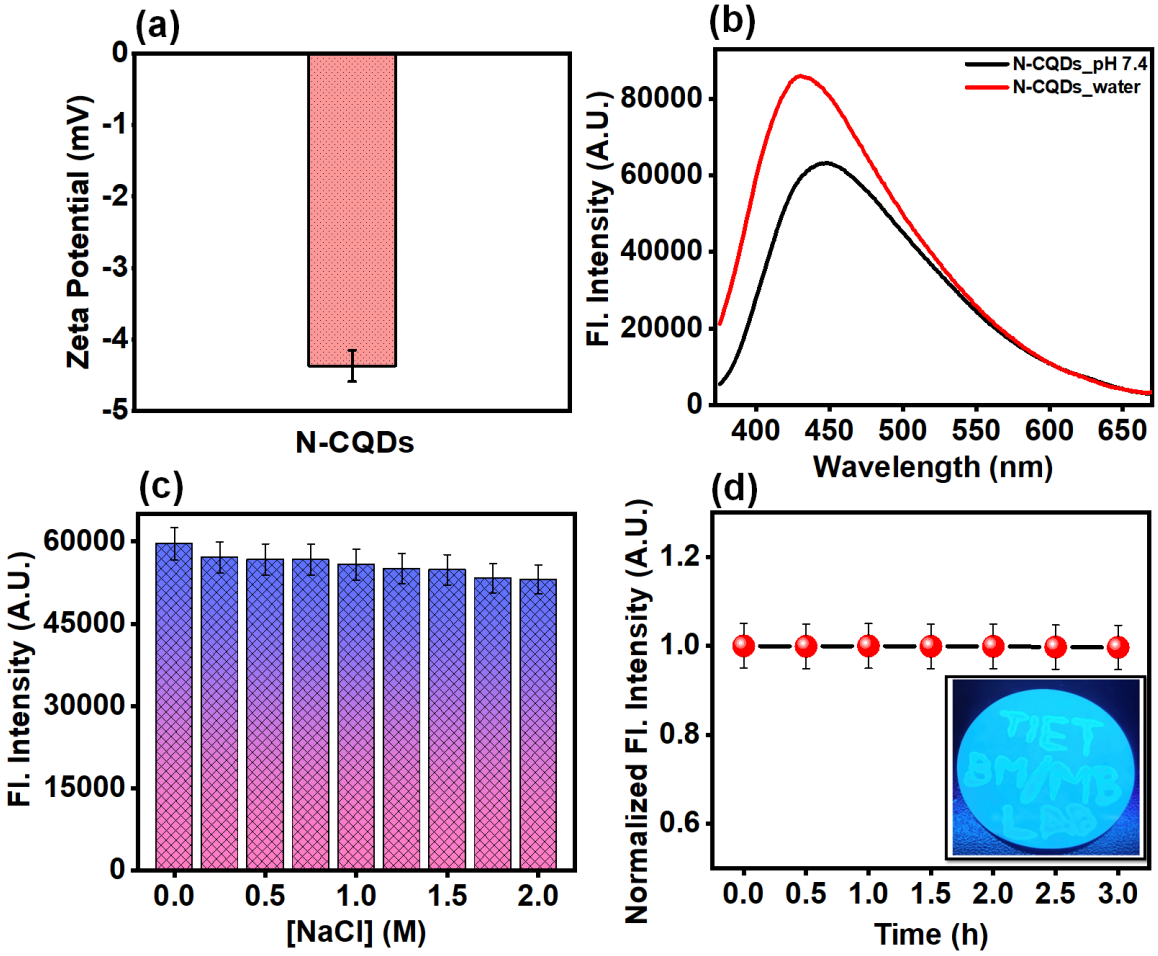

Figure S3. (a) Zeta potential of N-CQDs, (b) FL intensity of N-CQDs in aqueous and HEPES buffer at pH 7.4 (c) impact of ionic strength of the medium on N-CQDs emission at 430 nm in the presence of variable concentrations of NaCl (0-2 M) and (d) impact of photo-irradiation by a xenon arc lamp on the emission of N-CQDs at 430 nm as a function of time, (inset) photograph demonstrates practical utility of N-CQDs as a fluorescent ink. Error bars represents standard error of measurements obtained from three independent experiments.

Figure S4

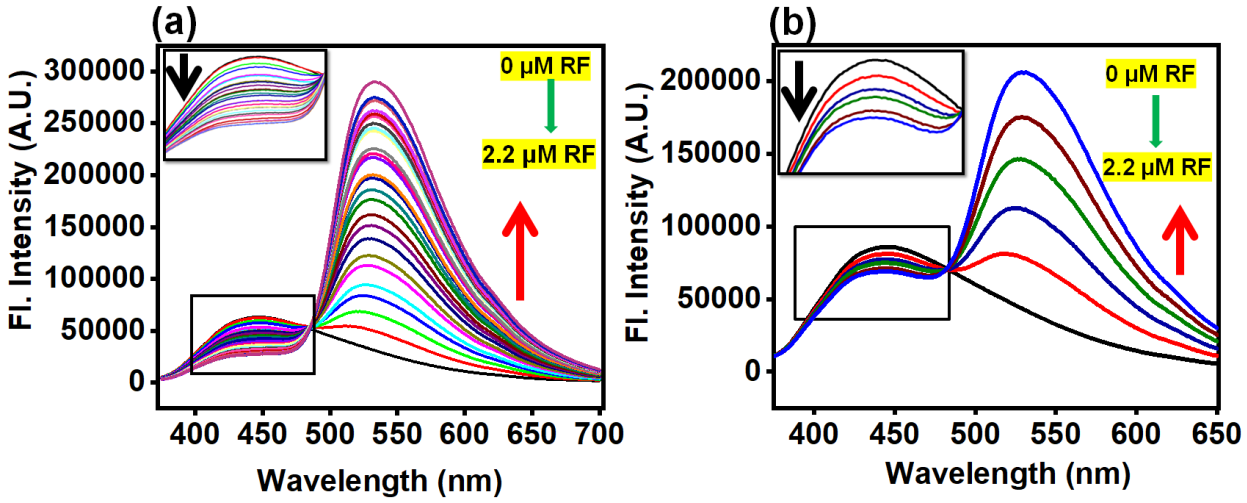

Figure S4. Variation in fluorescence emission of N-CQDs in the presence of different concentrations of RF (0-2.2 µM) with inset image showing fluorescence quenching (a) in HEPES buffer at pH 7.4 and (b) upon addition of a real sample of Vitamin B_2. Black arrow depicts the progressive decrease of fl. intensity of N-CQDs at shorter emission wavelength, while steady increase at longer emission wavelength is represented by red arrow.

Figure S5

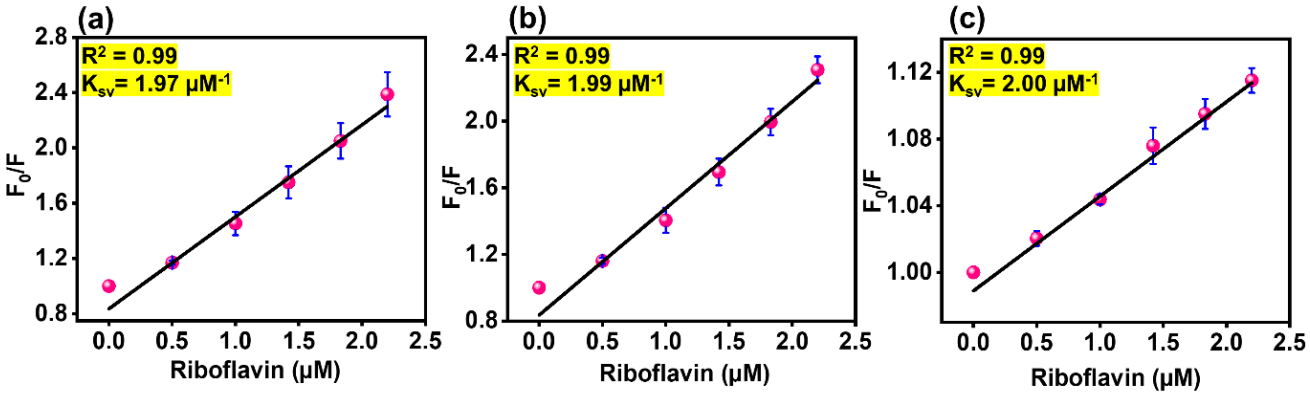

Figure S5. Stern-Volmer plots of N-CQDs in (a) aqueous medium, (b) HEPES buffer at pH 7.4 and (c) real sample of vitamin B_2. The parameters 'F_0' and 'F' indicate the fluorescence intensity in the absence and presence of vitamin B_2, respectively. 'K_{sv}' signifies Stern-Volmer quenching constant, which was estimated from the slope of the plots. The black line indicates the linear fit of the data using OriginPro 2021 and R^2 denotes the goodness of the fits. Error bars represents standard error of measurements obtained from three independent experiments.

Figure S6

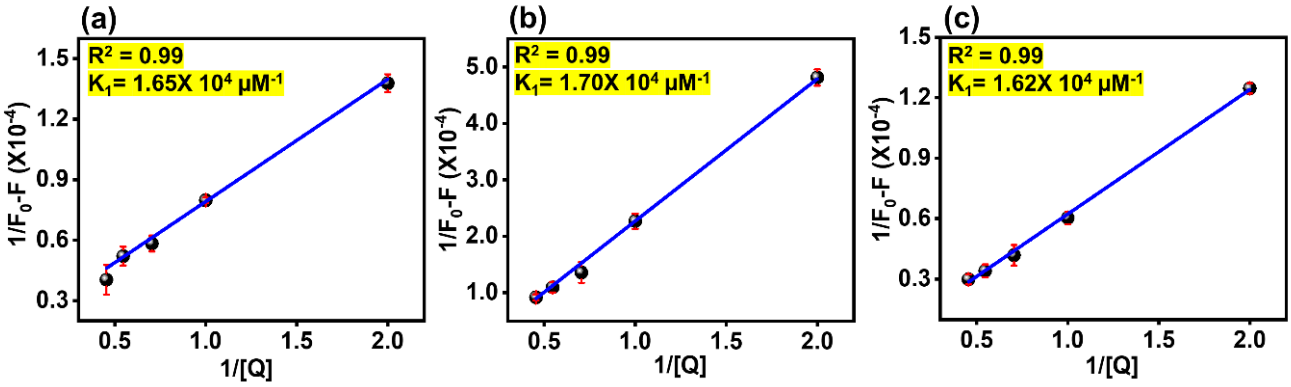

Figure S6. Benesi-Hildebrand plot of N-CQDs in (a) aqueous medium, (b) HEPES buffer medium at pH 7.4 and (c) real sample of vitamin B_2. The parameters 'F_0' and 'F' indicate the fluorescence intensity in the absence and presence of vitamin B_2, respectively. Q indicates the concentration of the quencher (i.e. vitamin B_2) and K_1 depicts the binding constant, which was estimated from the reciprocal of the slope of the plots. The blue line indicates the linear fit of the data using OriginPro 2021 and R^2 denotes the goodness of the fits. Error bars represents standard error of measurements obtained from three independent experiments.

Figure S7

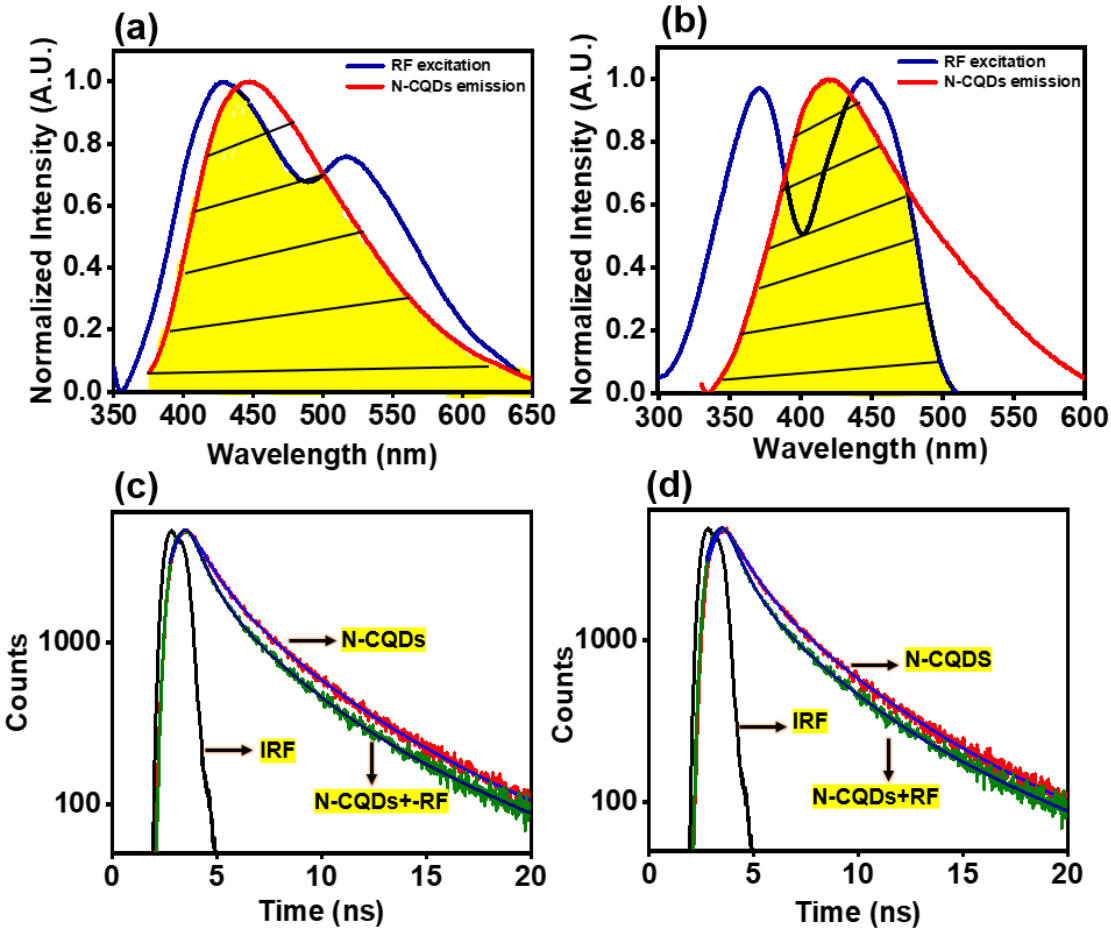

Figure S7. Spectral overlap between emission spectrum of N-CQDs (red) and excitation spectrum of RF (blue) where the yellow color demonstrates the overlapped region in (a) HEPES buffer at pH 7.4, (b) real sample of Vitamin B_2, (c) Fluorescence lifetime decays of N-CQDs in pH 7.4 HEPES buffer where, the sharp, thin black line represents the instrument response function, the red and olive lines represent the actual intensity decays in the absence and presence of RF respectively. The blue and royal blue lines correspond to fits obtained in the absence and presence of RF, respectively using tri-exponential function (See eq. 3; Experimental Section), (d) Fluorescence lifetime decays of N-CQDs in the presence of a real sample of Vitamin B_2 where, the sharp, thin black line represents the instrument response function, the red and olive lines represent the actual intensity decays in the absence and presence of RF respectively. The blue and royal blue lines correspond to fits obtained in the absence and presence of RF, respectively using tri-exponential function (See eq. 3; Experimental Section).

Figure S8

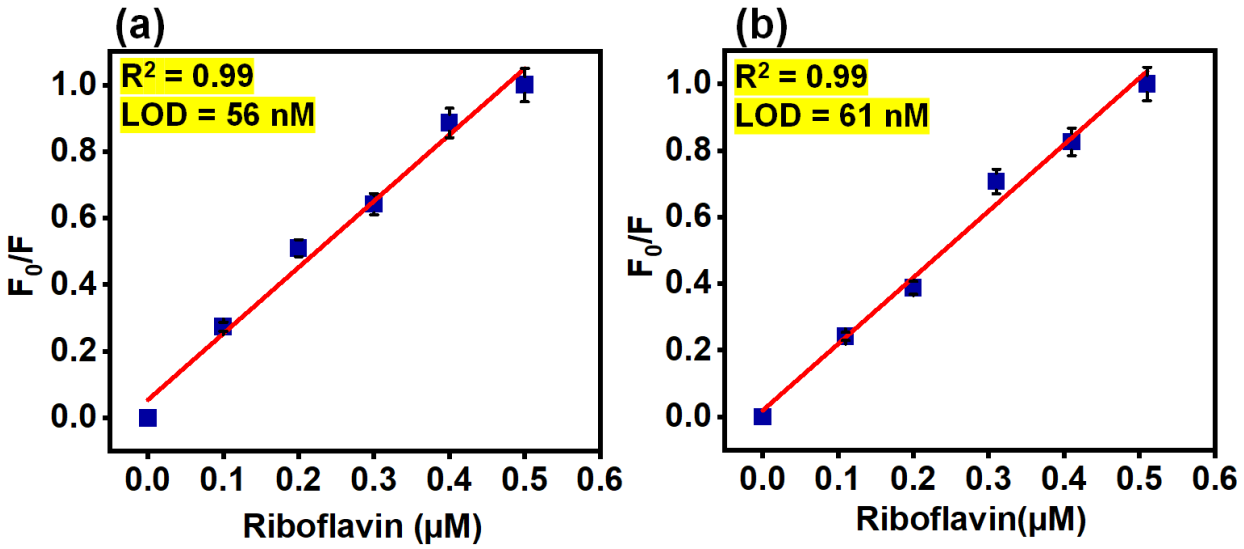

Figure S8. Linear relationship of fluorescence response (F_0/F) of N-CQDs with different concentrations of RF (0-2.2 μM) in (a) HEPES buffer at pH 7.4, (b) real sample of Vitamin B_2. The parameters 'F_0' and 'F' indicate the fluorescence intensity in the absence and presence of vitamin B_2, respectively. LOD signifies limit of detection. The red line indicates the linear fit of the data using OriginPro 2021 and R^2 denotes the goodness of the fits. Error bars represents standard error of measurements obtained from three independent experiments. See Experimental Section for all the required details.

Table S1

Table S1: Details of various parameters obtained during the deconvolution of the XPS data

Elements	**Peak position (functional groups present)**	**No. of deconvoluted spectra**	**Relative population (Peak Area %)**
Carbon (C1s)	283.3 eV (-C=C, -C-C), 285.3 eV (C=N, -C=O), 287.2 eV (-O-C=O)	3	45 42 13
Oxygen (O1s)	531.8 eV (-C=O, -C-O-C)	1	100
Nitrogen (N1s)	399.3 eV (-C-N-C), 401.1 eV (-C_3N)	2	93 7

Table S2

Table S2: Fluorescence lifetime components of N-CQDs and their respective coefficients along with the mean fluorescence lifetimes in aqueous and pH 7.4 medium. The lifetimes were extracted by fitting the time-resolved emission decays using a tri-exponential function. χ^2 represents the goodness of the fits.

System	τ_1 (ns) (α_1)	τ_2 (ns) (α_2)	τ_3 (ns) (α_3)	τ_m[#](ns)	χ^2
N-CQDs (aqueous medium)	0.95 (0.57)	3.06 (0.36)	8.76 (0.07)	2.26	1.13
N-CQDs (aqueous medium) +RF	0.99 (0.72)	1.79 (0.23)	7.90 (0.05)	1.55	1.13
N-CQDs + real sample of vitamin B_2 tablet	0.68 (0.69)	2.68 (0.26)	8.49 (0.05)	1.60	1.12
N-CQDs (HEPES buffer pH 7.4)	1.00 (0.60)	3.27 (0.33)	9.30 (0.06)	2.24	1.08
N-CQDs (HEPES buffer pH 7.4) + RF	0.68 (0.72)	2.78 (0.23)	8.80 (0.05)	1.57	1.13

[#] $\tau_m = \alpha_1\tau_1+\alpha_2\tau_2+\alpha_3\tau_3$

Table S3

Table S3: Application of the developed nanosensor for detection of real sample of RF in Tablet

Conc. added (µM)	Conc. detected (µM)	Recovery rate	Recovery error	Relative standard deviation (RSD)
0.5	0.48	93%	4%	2.3
1.42	1.39	97%	2%	2.3
2.2	2.19	99%	0.4%	0.3