Highly crystalline N and S co-doped carbon dots as selective turn off-on sensor for Cr(VI) and ascorbic acid and turn off sensor for Metanil yellow

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S1 EXPERIMENTAL

S1.1 Reagents

Mesaconic acid, ethylenediamine and sulfuric acid were purchased from Sigma Aldrich and were used without further purification. Metanil Yellow was procured from TCI chemicals. All other chemicals not mentioned here were of analytical reagent grade and were obtained from Sigma Aldrich and were used as received. Double distilled water was used in the synthesis of nanosensor

S1.2 Instrumentations

The Hitachi F-2700 spectrometer was used to record fluorescence spectra. Electronic spectral studies were done on a Perkin Elmer Lamda 365 UV-VIS spectrometer. FT-IR spectrum was obtained from Perkin Elmer Spectrum Two FT-IR Spectrometer. EDX spectrum was obtained on JSM-6510LV, JEOL, Japan . TEM was carried out in a JEM-2100F JEOL, Japan operating at the maximum accelerating voltage of 200 kV. For this, 5 µL of the sample was drop coated on a carbon-coated copper TEM grid followed by air drying. Acquired micrographs were analyzed using ImageJ (http://imagej.nih.gov/ij/download.html) by randomly selecting individual nanoparticles in the TEM images to compute size distribution histograms. X-ray diffraction experiments were carried out using SMARTLAB Rigaku with Cu-Kα1radiation..

Flash EA 1112 analyzer was employed to carry out elemental analysis. Fluorescence lifetime measurements were done on HORIBA Jobin Yvon Fluorocube-01-NL fluorescence lifetime by using Time correlated Single Photon Counting (TCSPC) method.

S1.3 Preparation of test solutions and general procedure for UV-Vis and fluorescence spectrometry determination

For determination of Cr(VI) and Metanil yellow, 3ml of double distil water was mingled with 200 µL of 2mg/ml NS CDs, then series of appropriate volumes of 1mmol Cr(VI) and Metanil yellow were added and the fluorescent intensities were measured. For determination of ascorbic acid 3ml of double distil water was mingled with 200 µL of 2mg/ml NS CDs. Then 150 µM Cr(VI) was added in order to form nanoprobe (NS CDs/Cr(VI)). Then fluorescent intensities were recorded by adding appropriate volumes of 1mmol ascorbic acid.

S1.4 Synthesis of NS CDs

NS CDs were synthesized by hydrothermal method. 2 gm mesaconic acid was dissolved in 50 ml of 15% EDA solution. The mixture was transferred to 100 ml Teflon lined stainless steel autoclave and heated constantly at 180^0C for 10 hours. The mixture was cooled down naturally after reaction. Than 70% sulfuric acid was added to the mixture till the mixture becomes neutral. The resulting solution was kept in hot air oven at 60^0C for 24 hours to obtain the NS CDs powder.

S 1.5 Detection of metanil yellow in turmeric powder sample

Turmeric powder was purchased from a local supermarket and was confirmed that no metanil yellow dyes was claimed from their lists of ingredients. metanil yellow was spiked into the turmeric powder.

The samples for analysis were prepared by adding increasing amounts of metanil yellow (0.1 mg/1000 mg of sample) into turmeric powder. Samples were thoroughly mixed. The prepared mixtures were extracted ultrasonically by 30 ml distil watet for 30 minutes and centrifugal

sedimentation was carried out for 10 minutes at 10,000 rpm. Finally the supernatant (also called as extracted solution) was collected for detection. Fixed aliquots of extracted solution of different samples were added to NS CDs aqueous solution.

S2 DETECTION LIMIT OF NS CDs NANOSENSOR

The detection limit was calculated based on fluorescence titration for tested analytes. To determine the δ/S ratio, emission intensity of nanosensor without tested anolytes was measured 10 times and standard deviation from blank measurements was determined. The detection limit was then calculated with the equation : detection limit = 3 δ/S where δ is the standard deviation of blank measurements and S is the slope of intensity vs sample concentration. δ from intensity measurements was calculated to be 2.5.

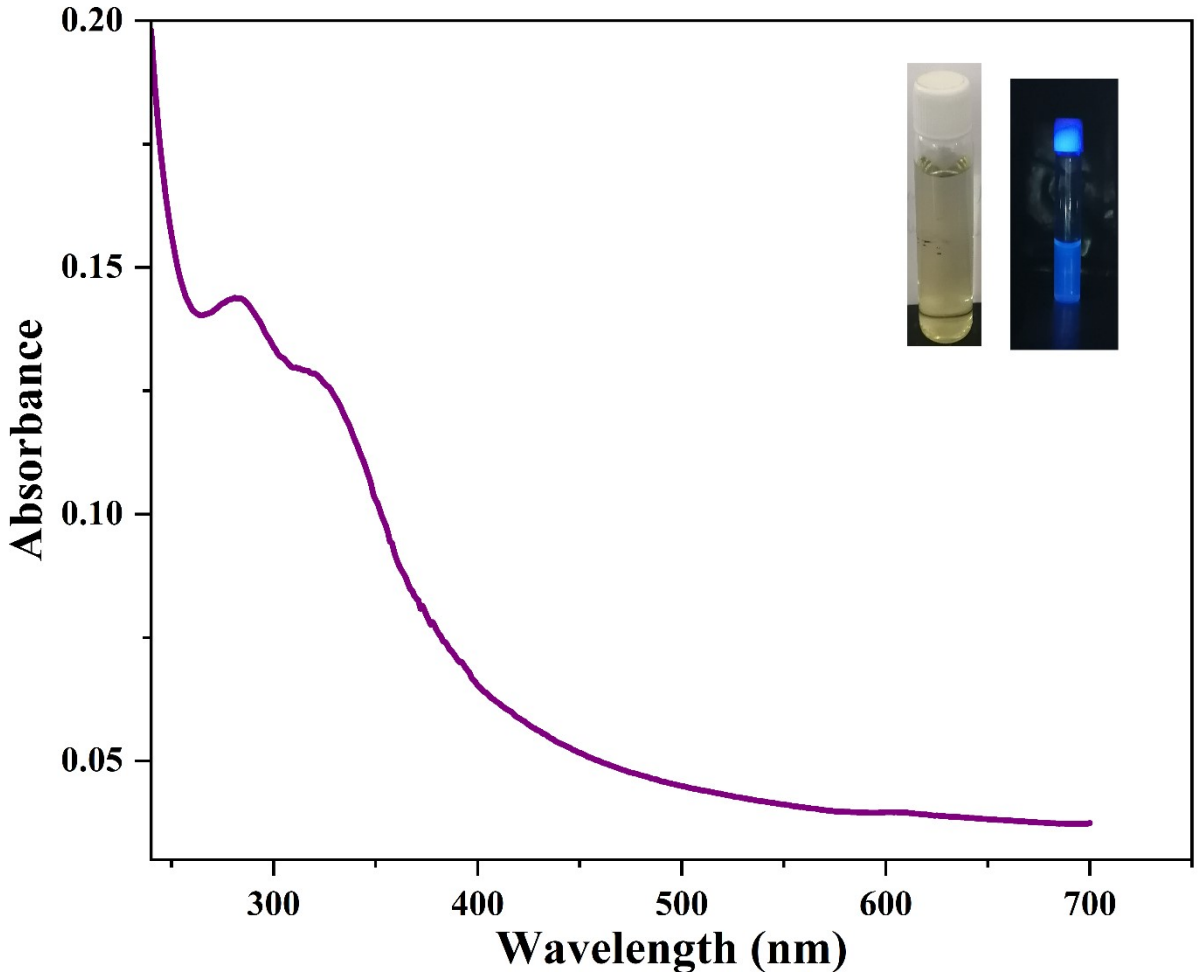


Fig. 1S Absorption spectrum of NS CDs

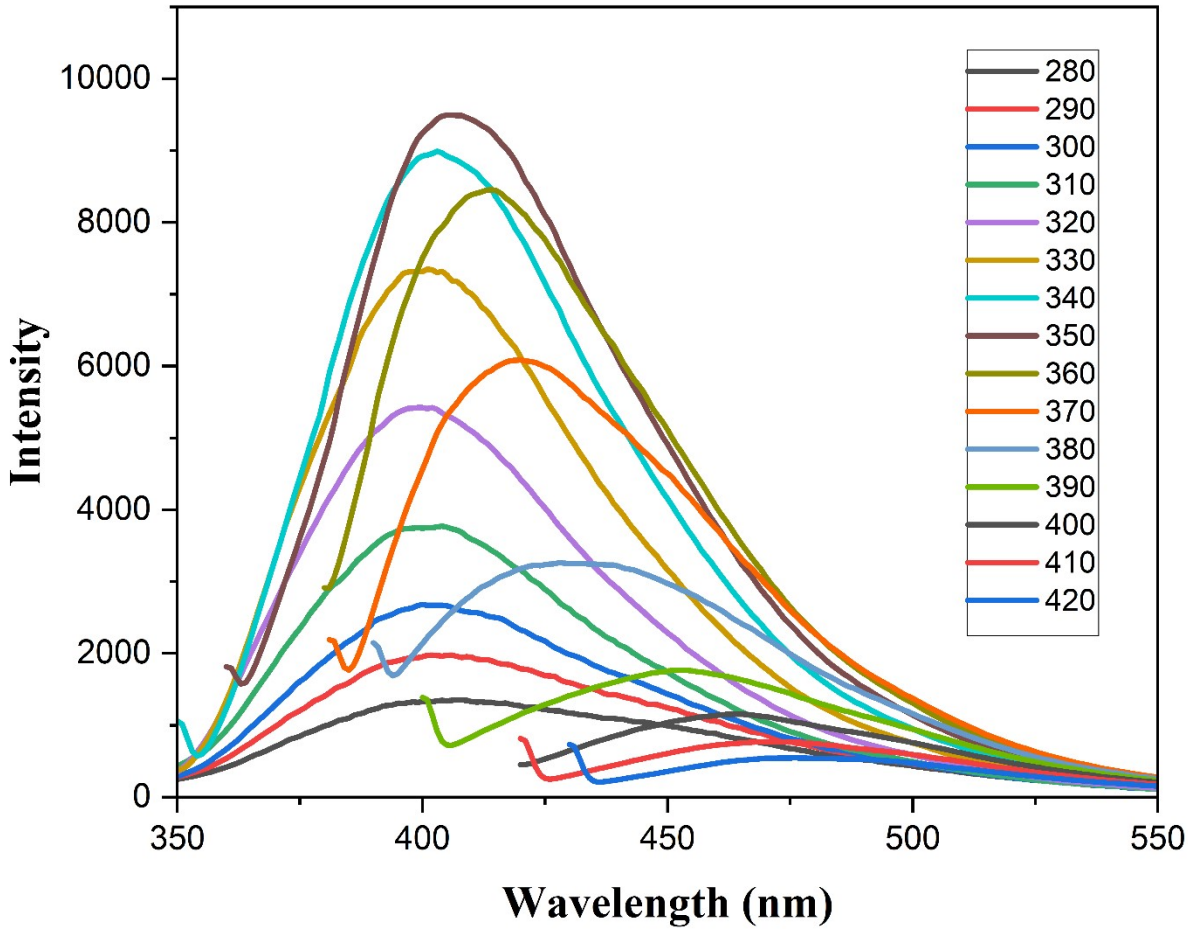


Fig. 2S Emission spectrum of NS CDs at different excitation wavelengths.

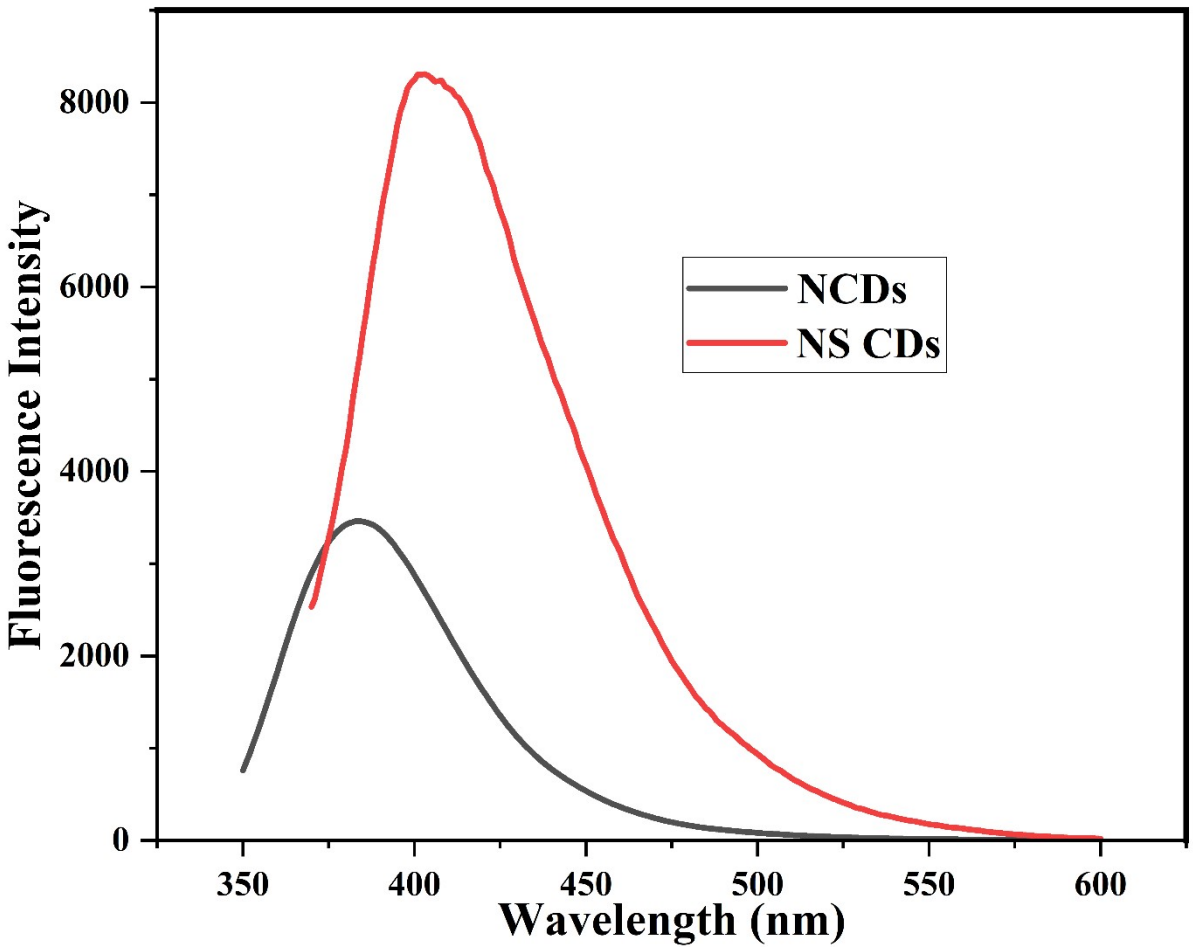


Fig. 3S Comparison of fluorescent intensity of NCDs and NS CDs.

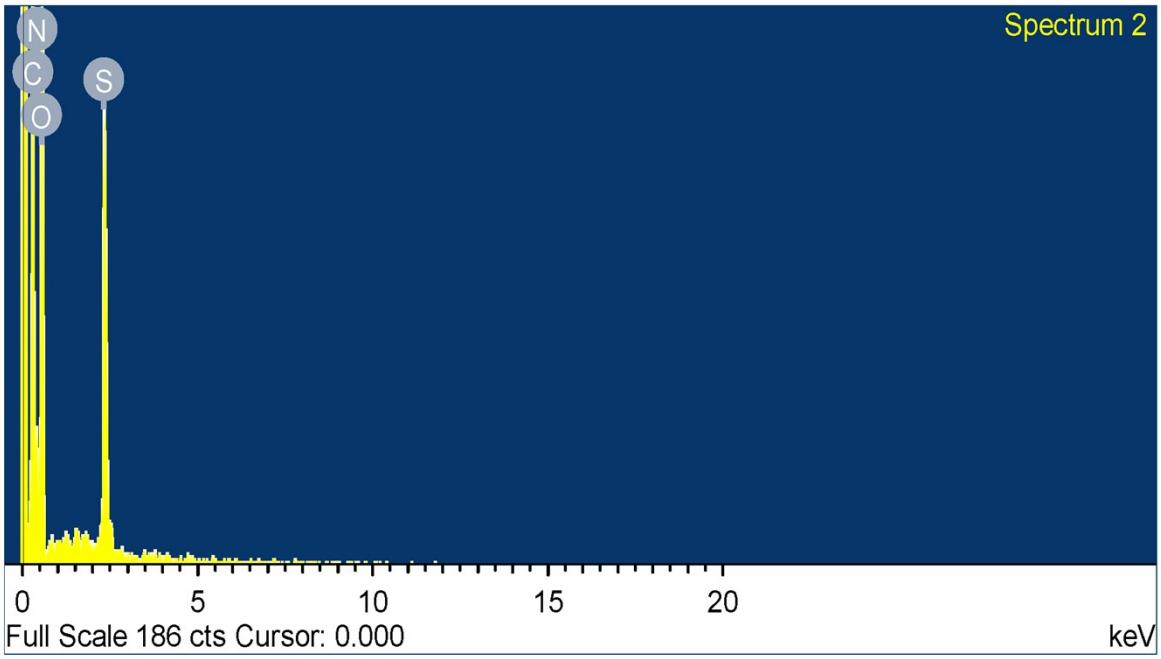


Fig. 4S EDX spectrum of NS CDs

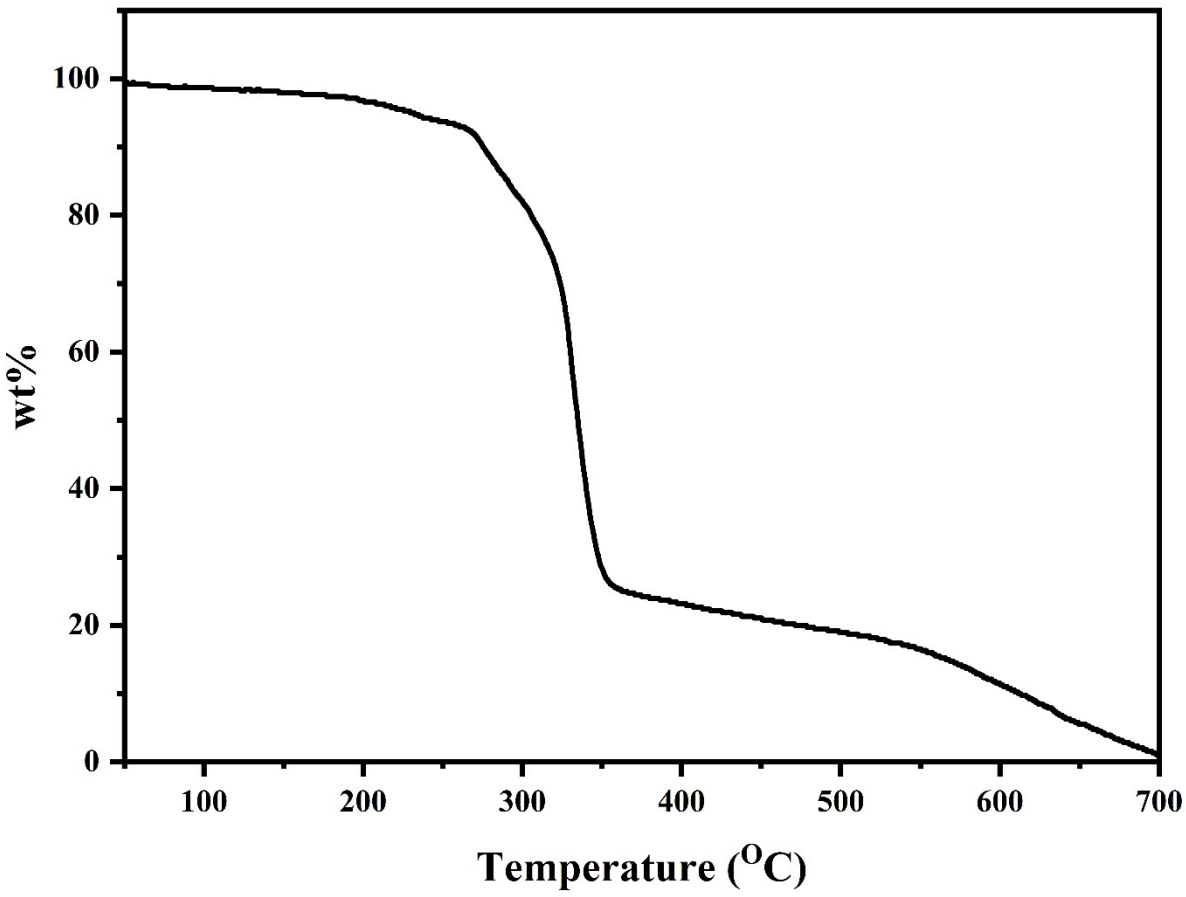


Fig. 5STGA spectrum of NS CDs

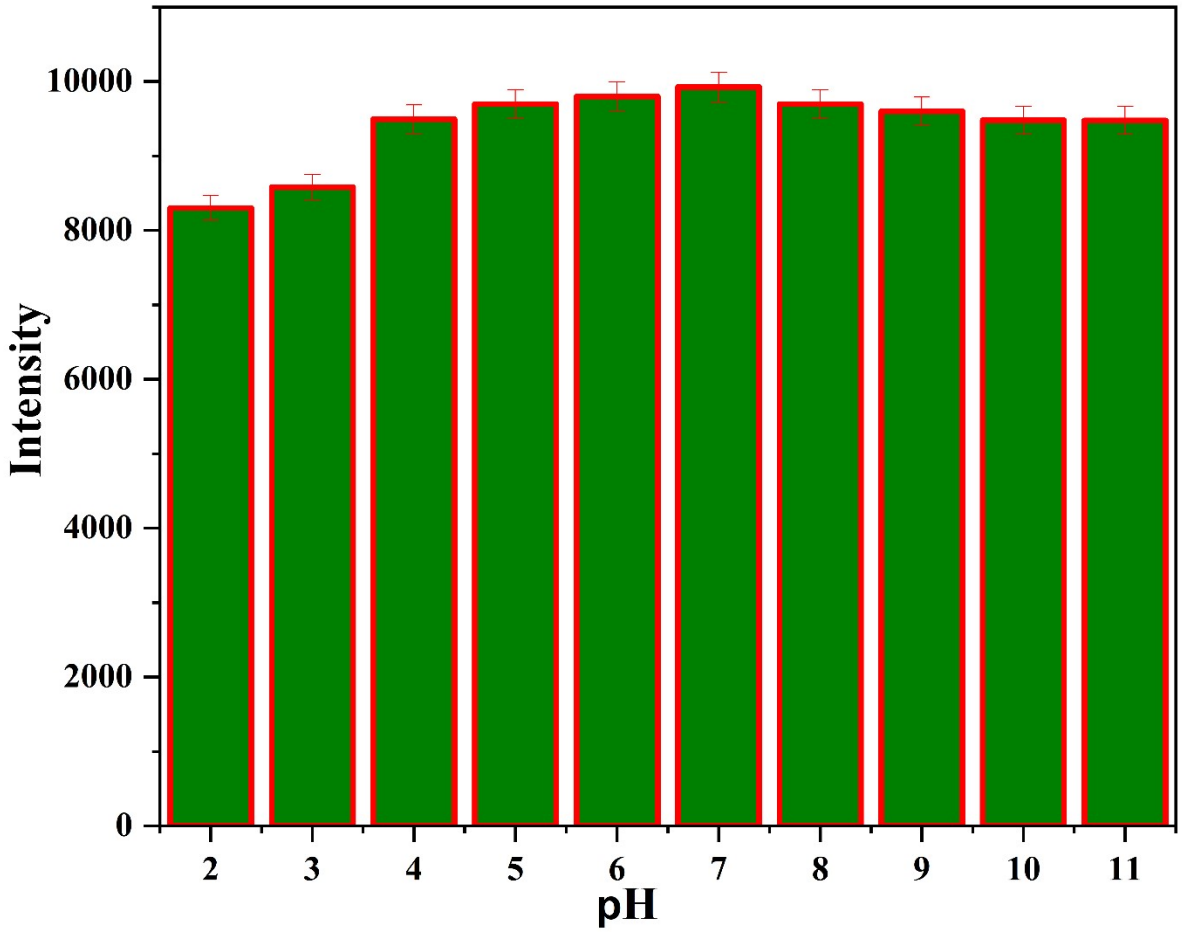


Fig 6S Effect of pH on fluorescent intensity of NS CDs

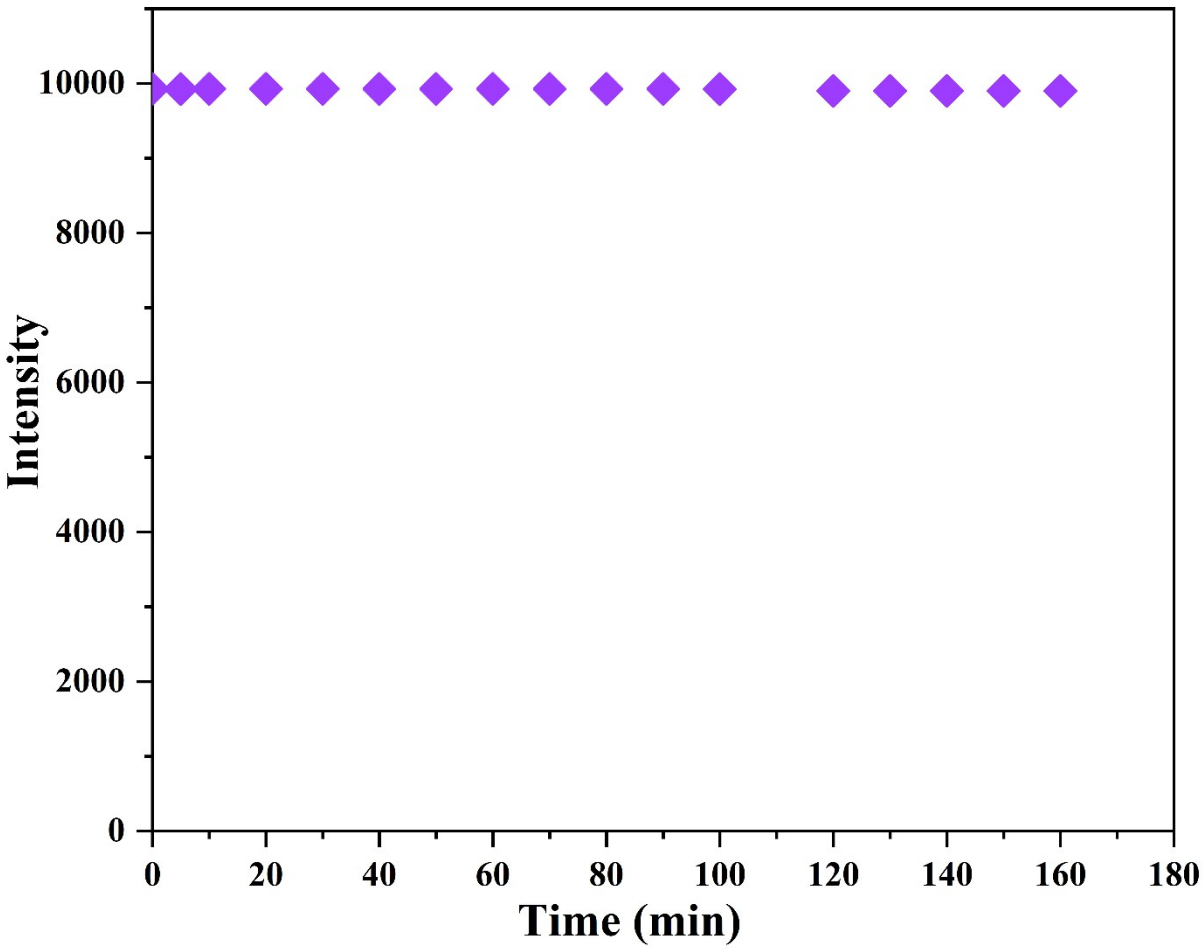


Fig 7S Effect of irradiation time on fluorescent intensity of NS CDs

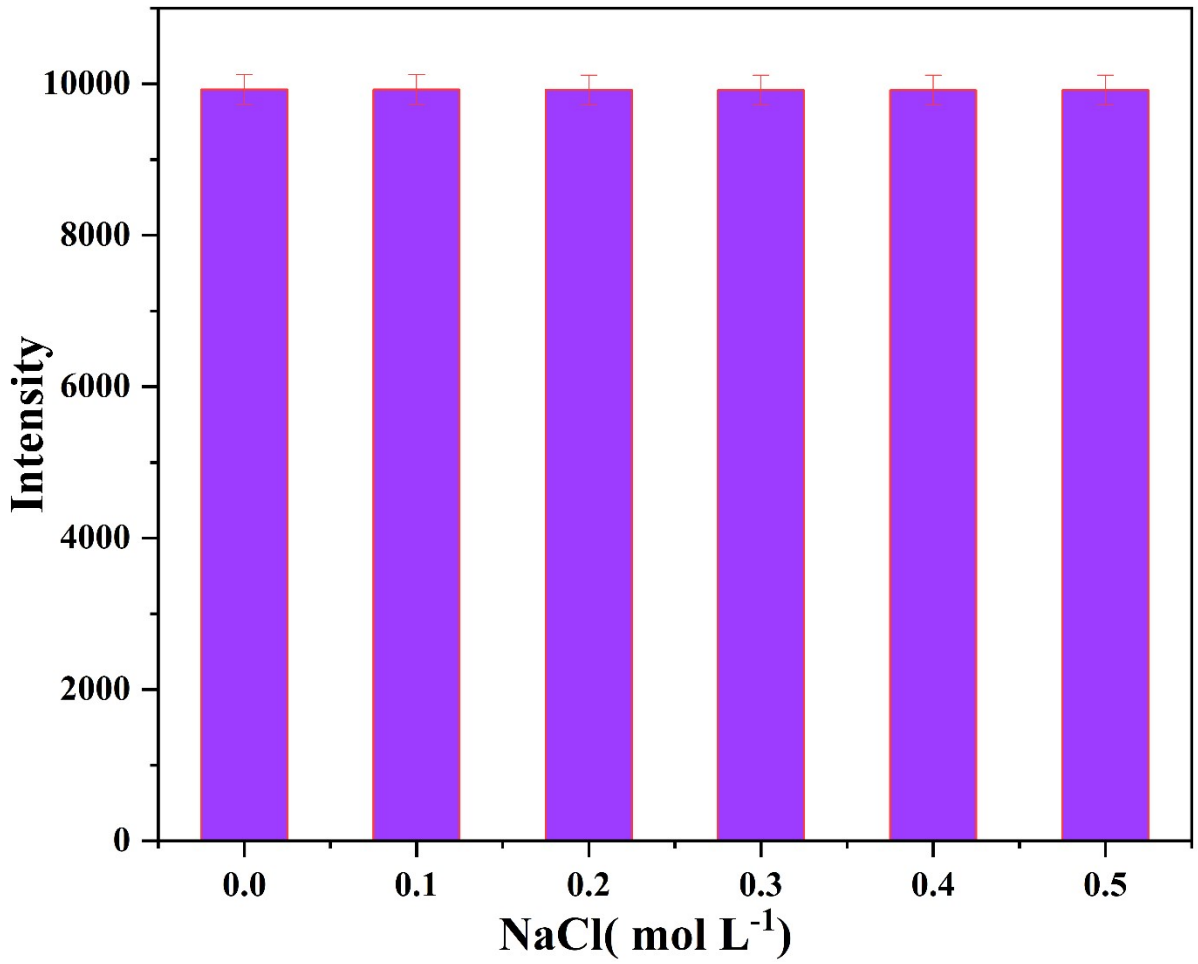


Fig 8S Effect of ionic strength on fluorescent intensity of NS CDs

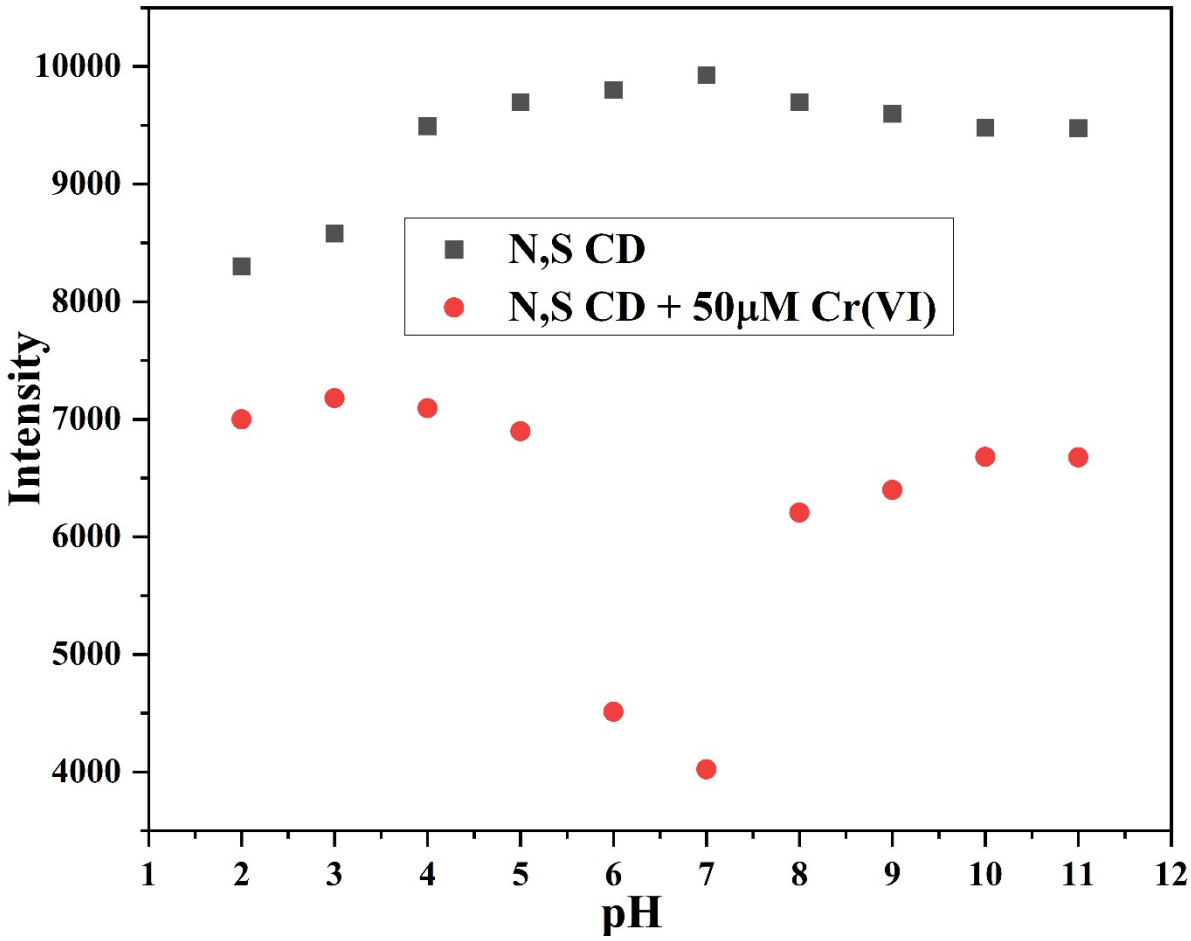


Fig. 9S Effect of pH on fluorescence intensity of nanosensor-Cr(VI) solution

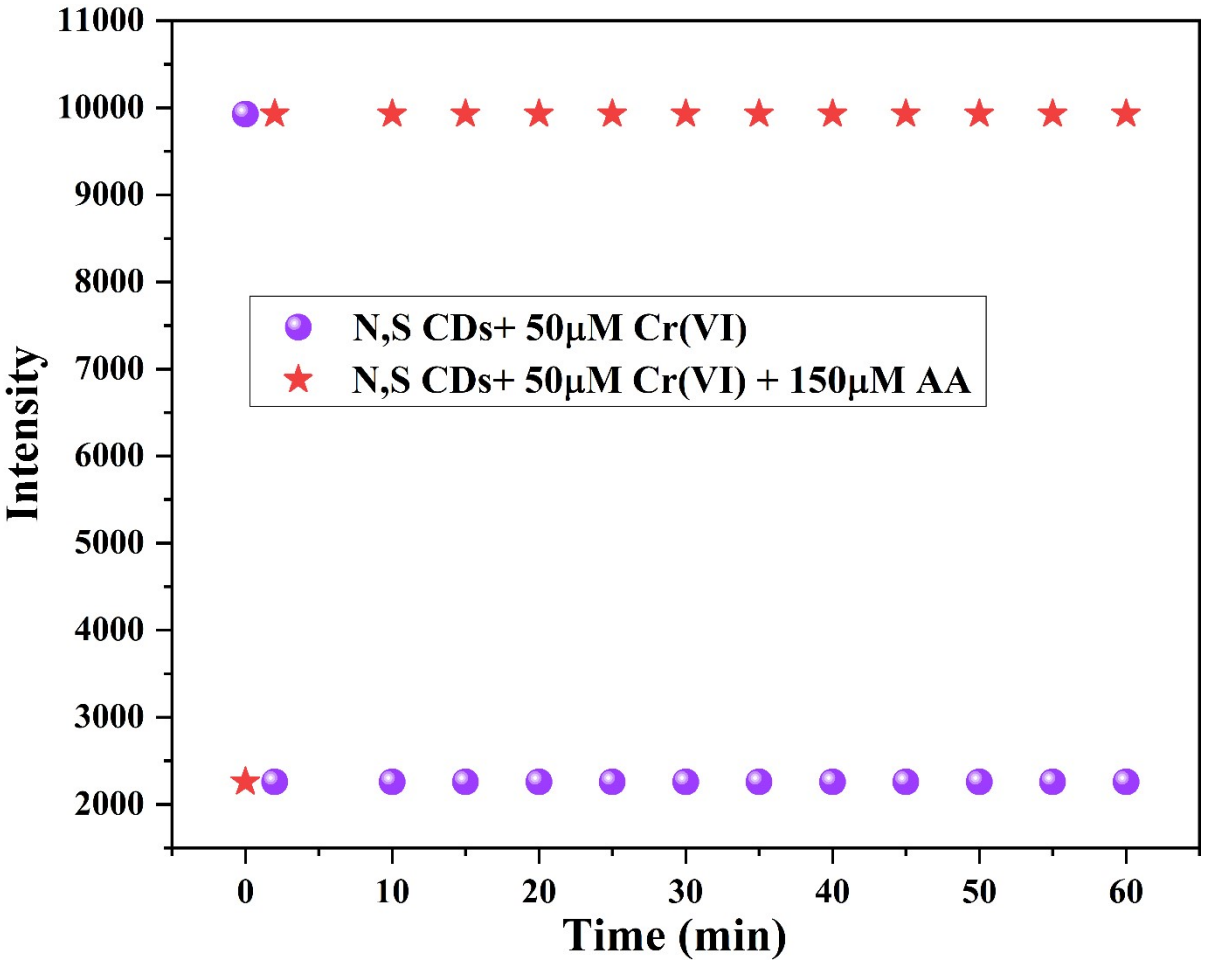


Fig. 10S Kinetic characteristics of the florescence intensity of nanosensor with 50 μM Cr(VI) solution and 150 μM ascorbic acid

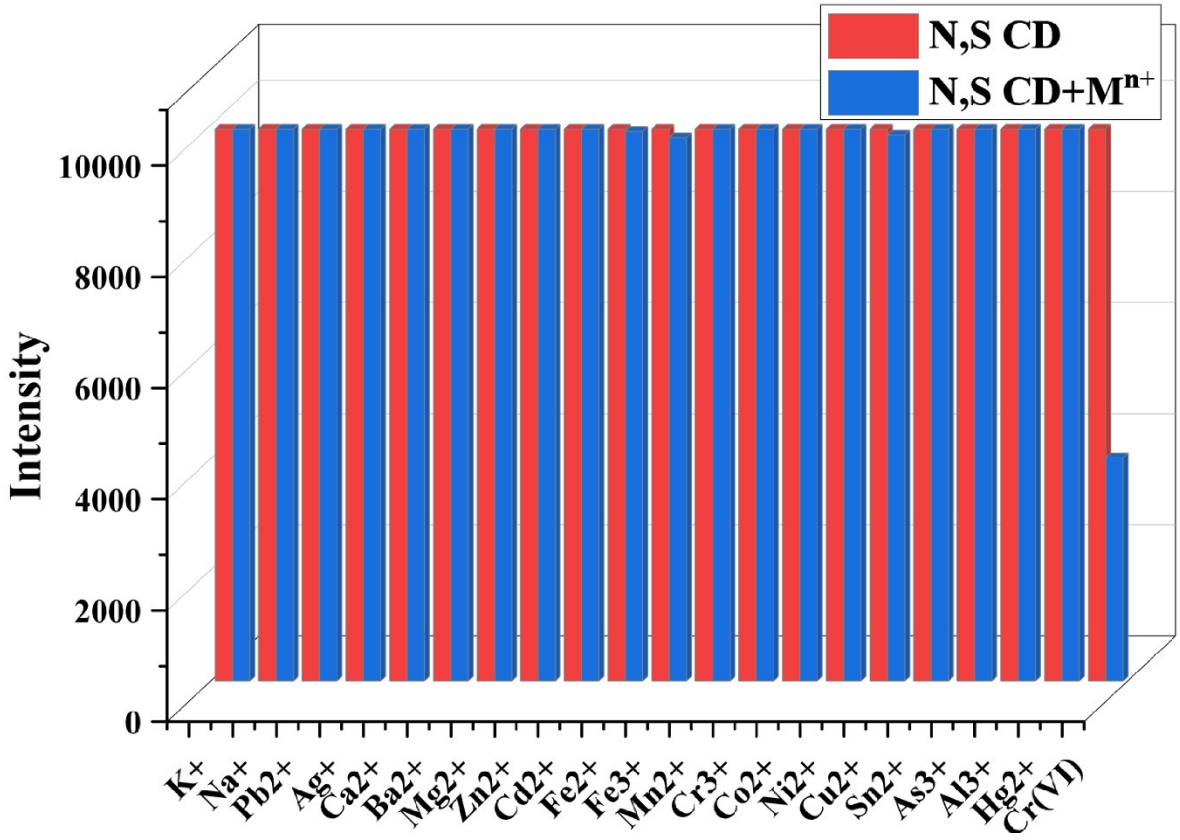


Fig. 11S Effect of other metal ions on fluorescent intensity of NS CDs (200µL, 2mg/ml).The concentrations of various metal ions 1500 µM

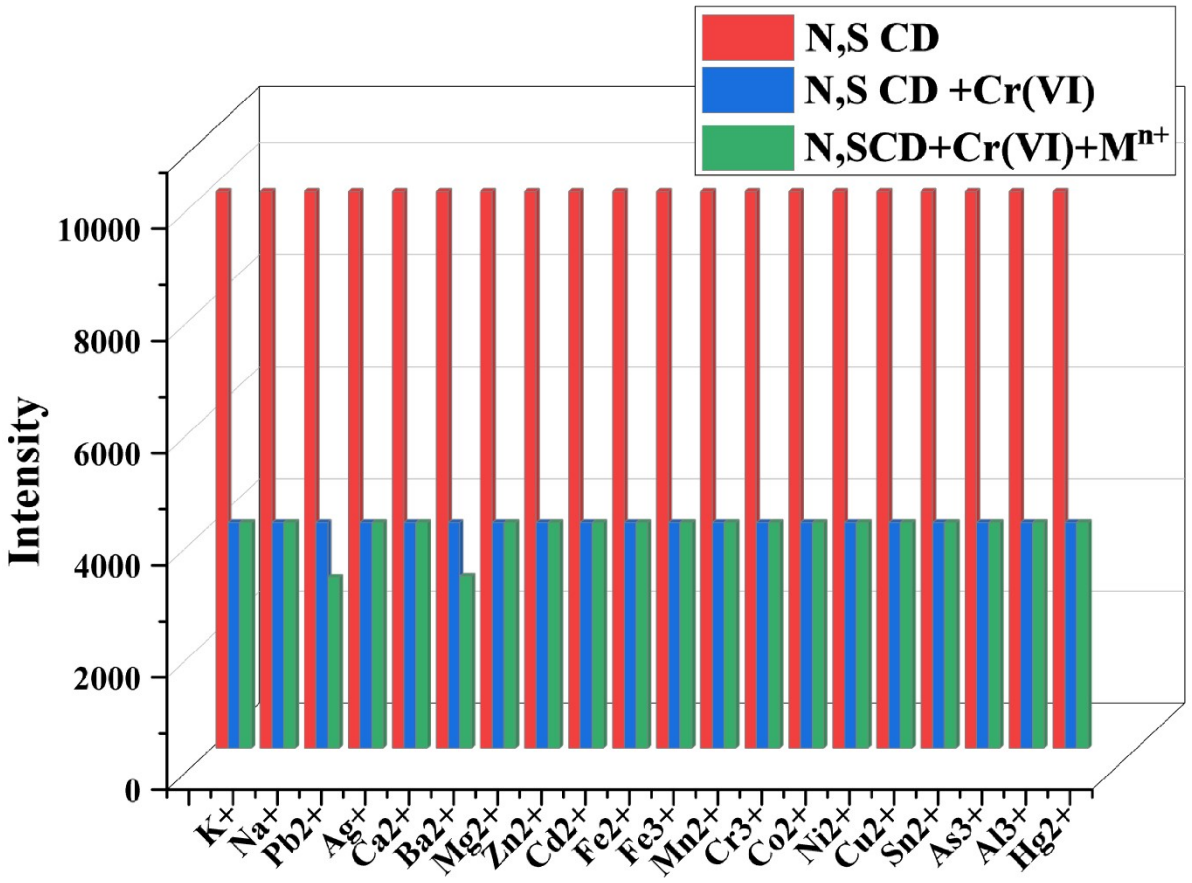


Fig. 12S Interference spectrogram of NS CDs-Cr(VI

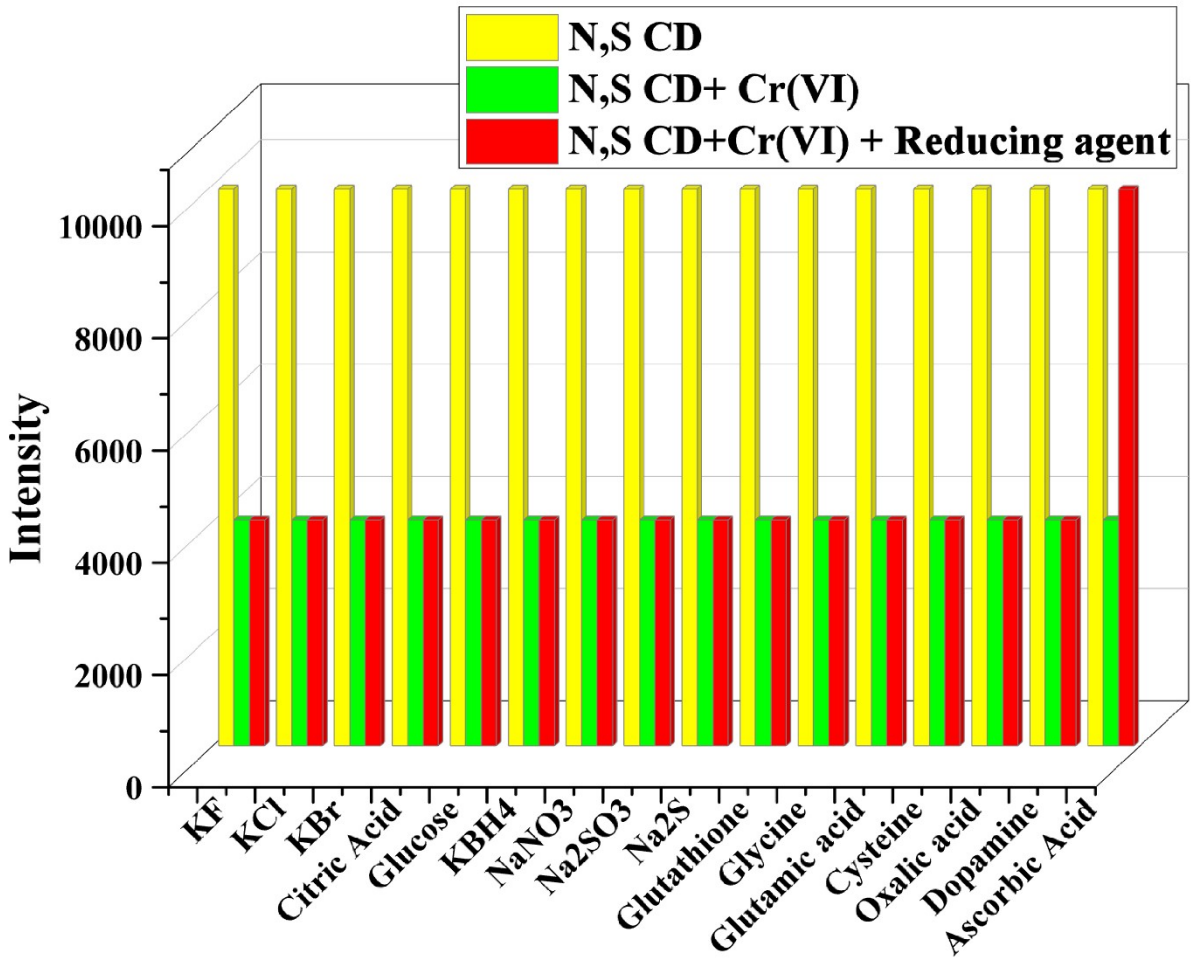


Fig 13S Effect of other reducing species on fluorescent intensity of NS CDs+Cr(VI) ensemble . The concentrations of various reducing species are 160 μM

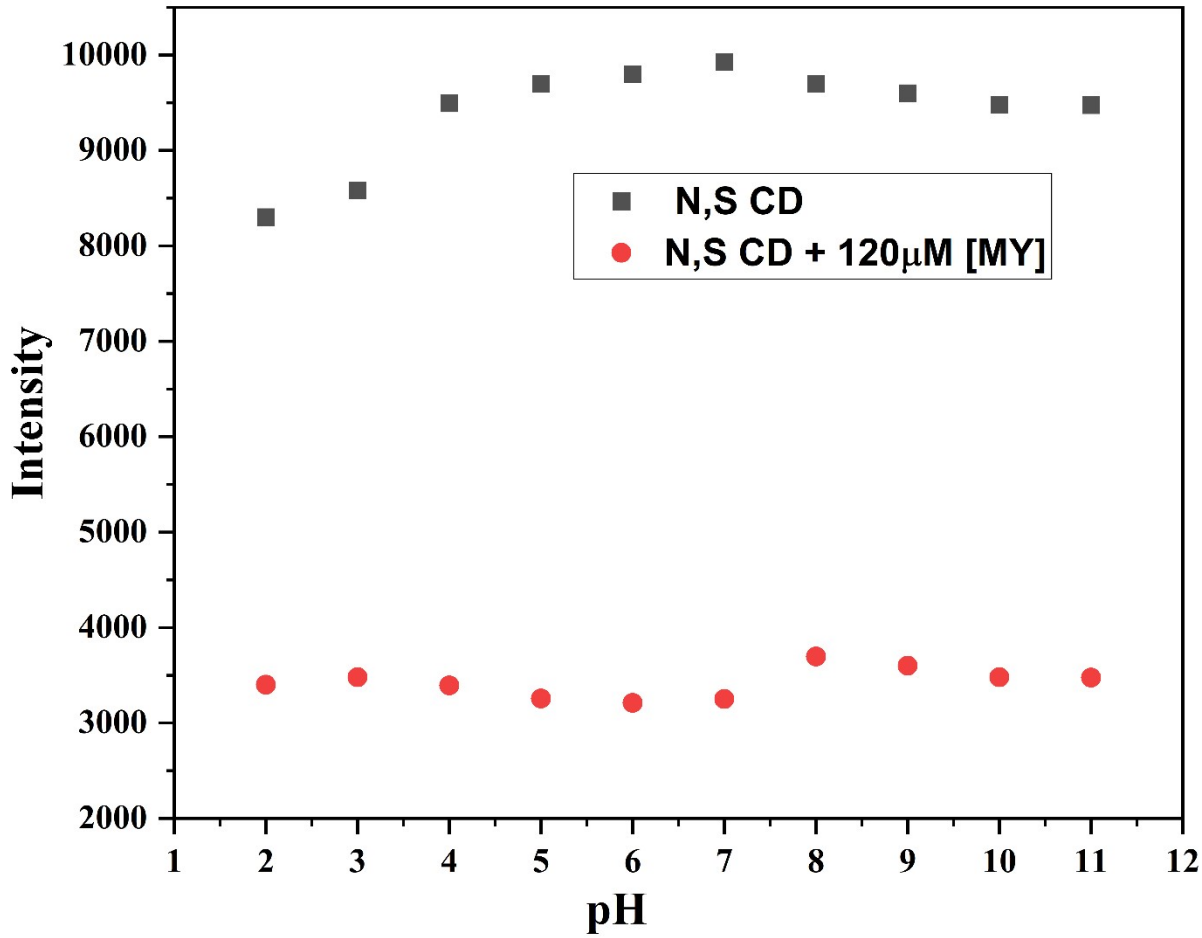


Fig. 14S Effect of pH on fluorescence intensity of nanosensor- metanil yellow solution.

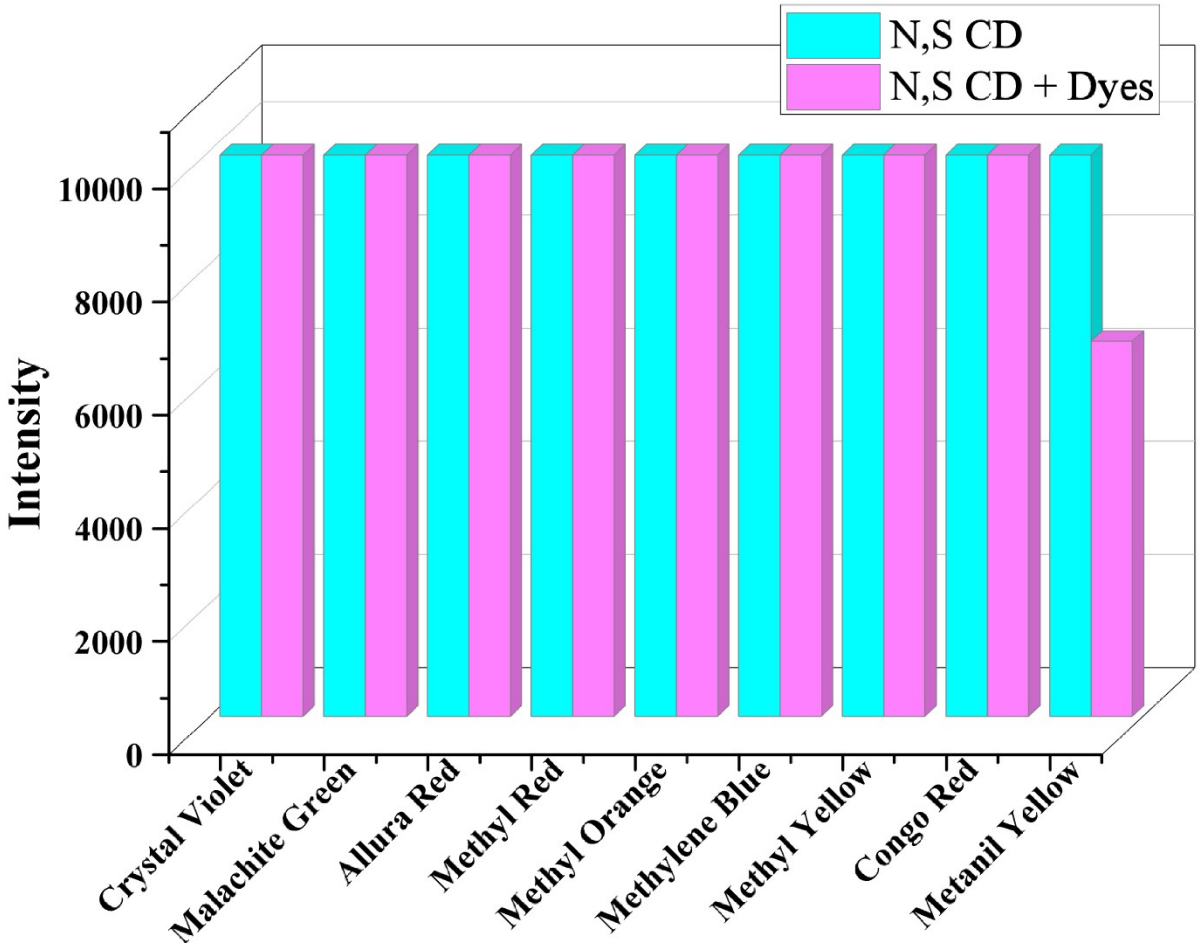


Fig 15S Effect of other dyes on fluorescent intensity of NS CDs

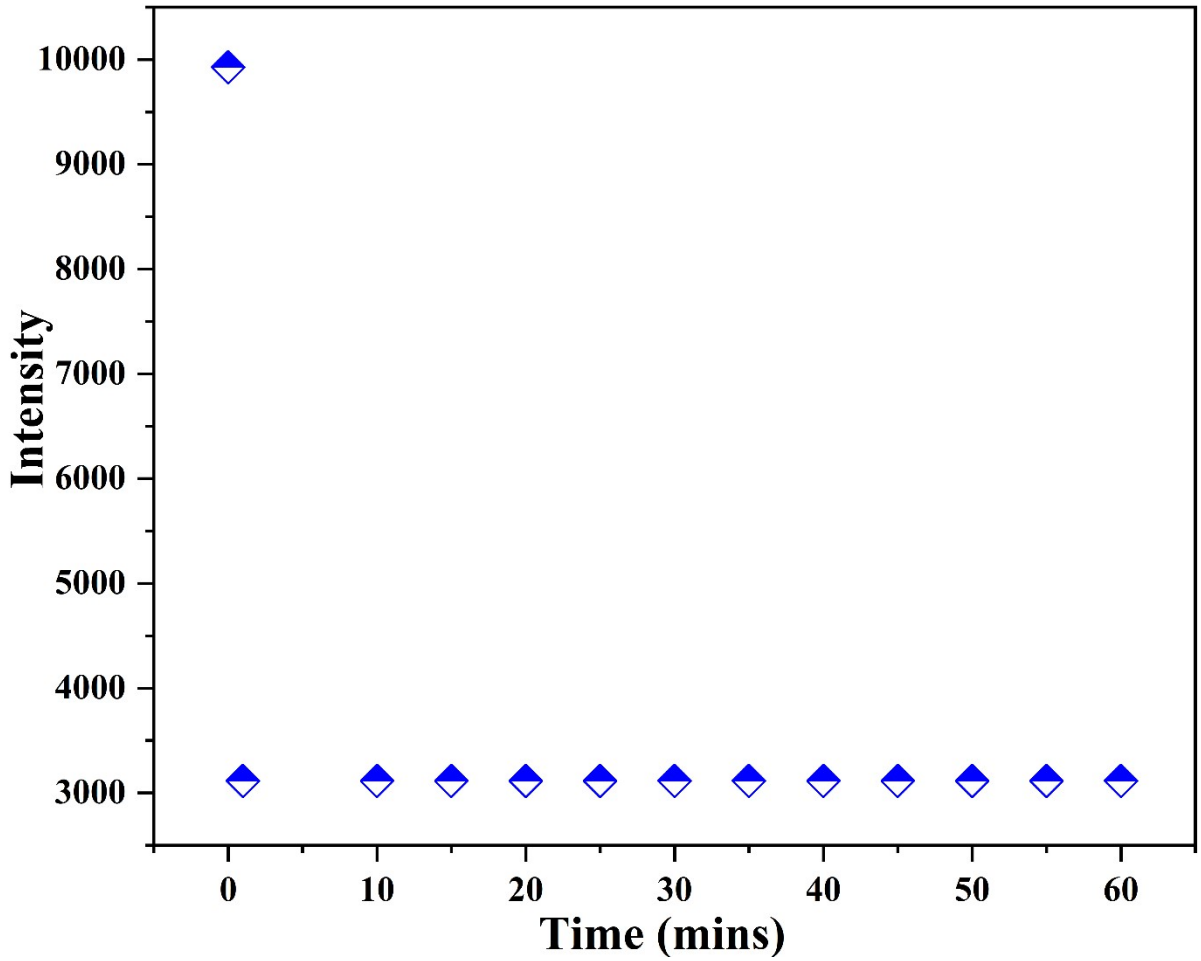


Fig 16S The stability of NS CDs-MY solution

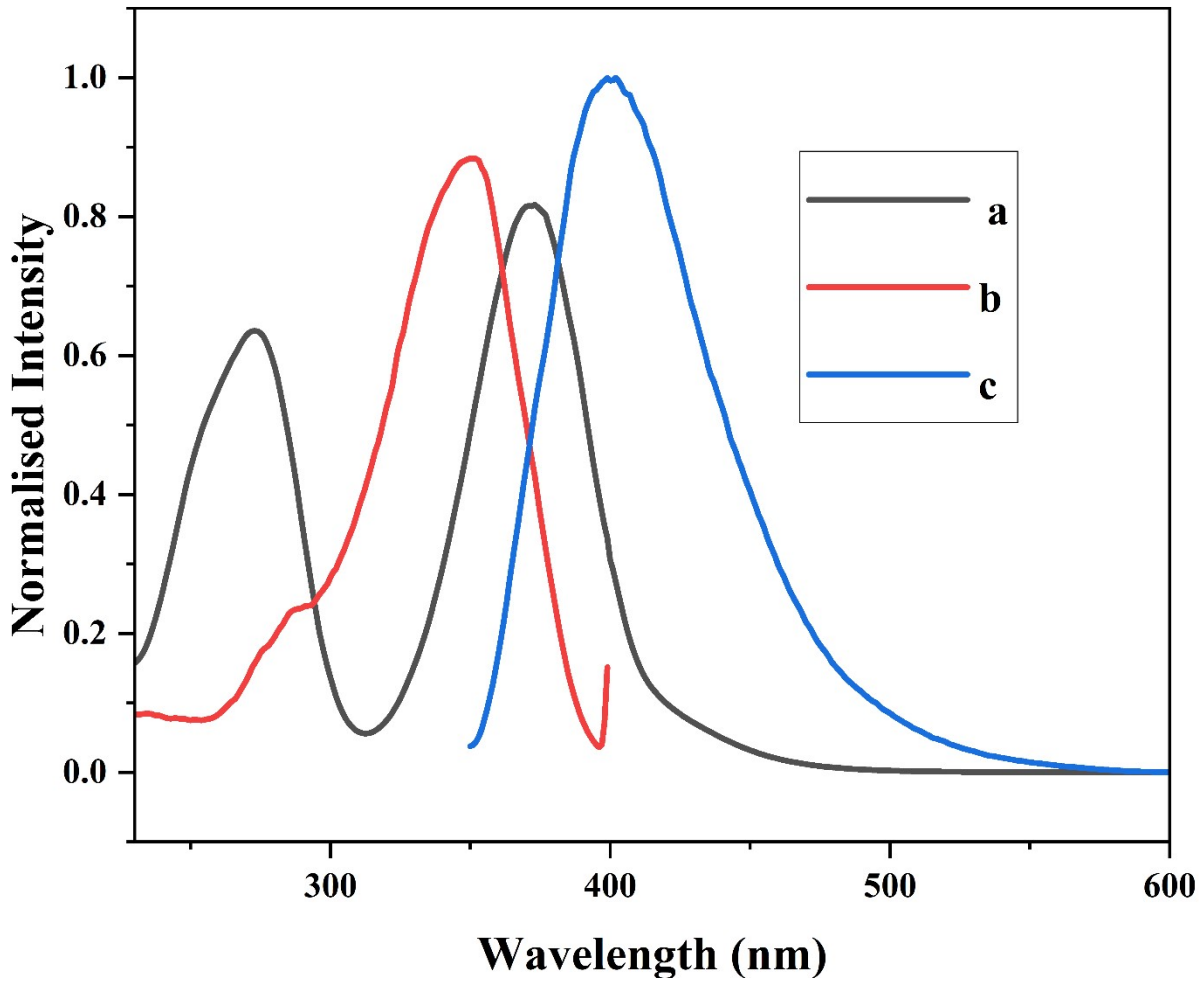


Fig. 17S Spectral overlap of absorption spectrum of Cr(VI) (a) with emission (c) and excitation spectrum(b) of NS CDs

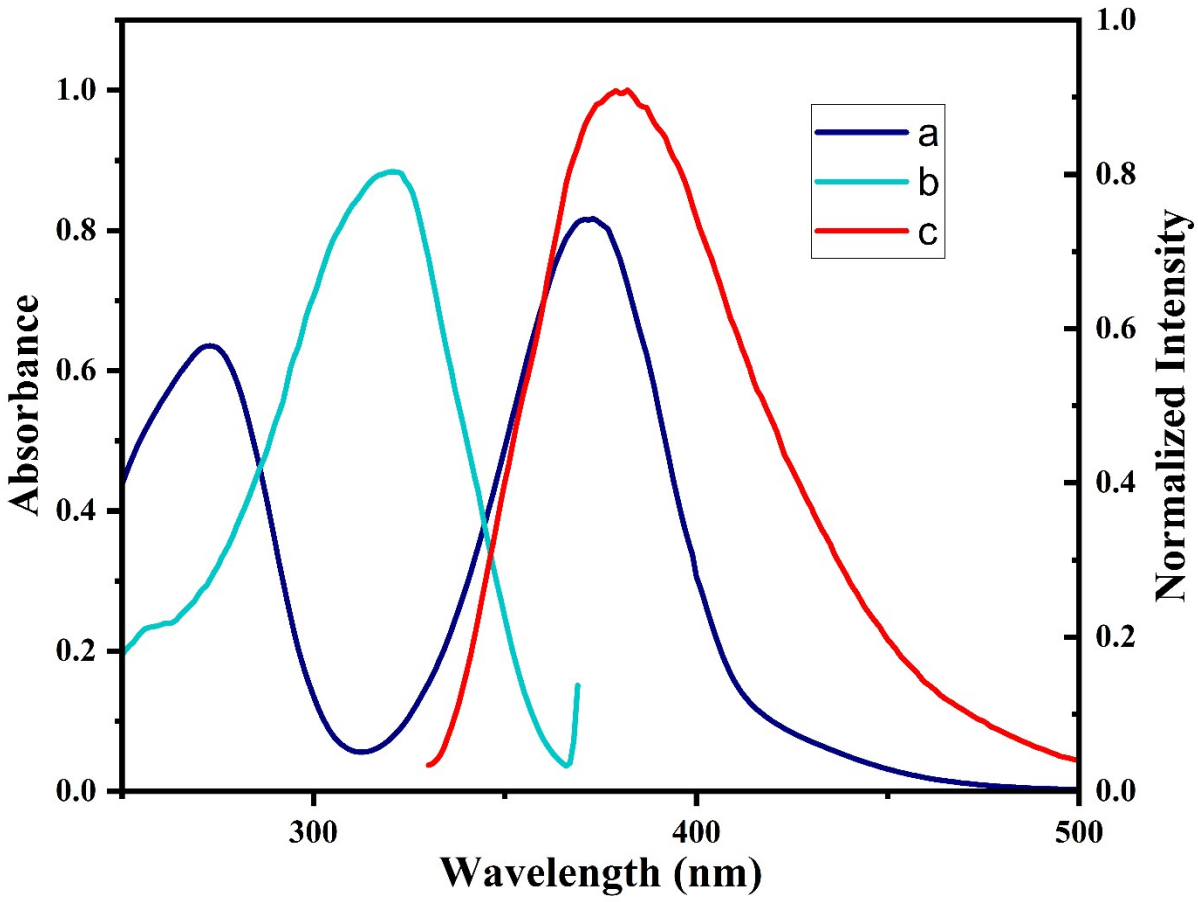


Fig. 18S Spectral overlap of absorption spectrum of Cr(VI) (a) with emission (c) and excitation spectrum(b) of NCDs

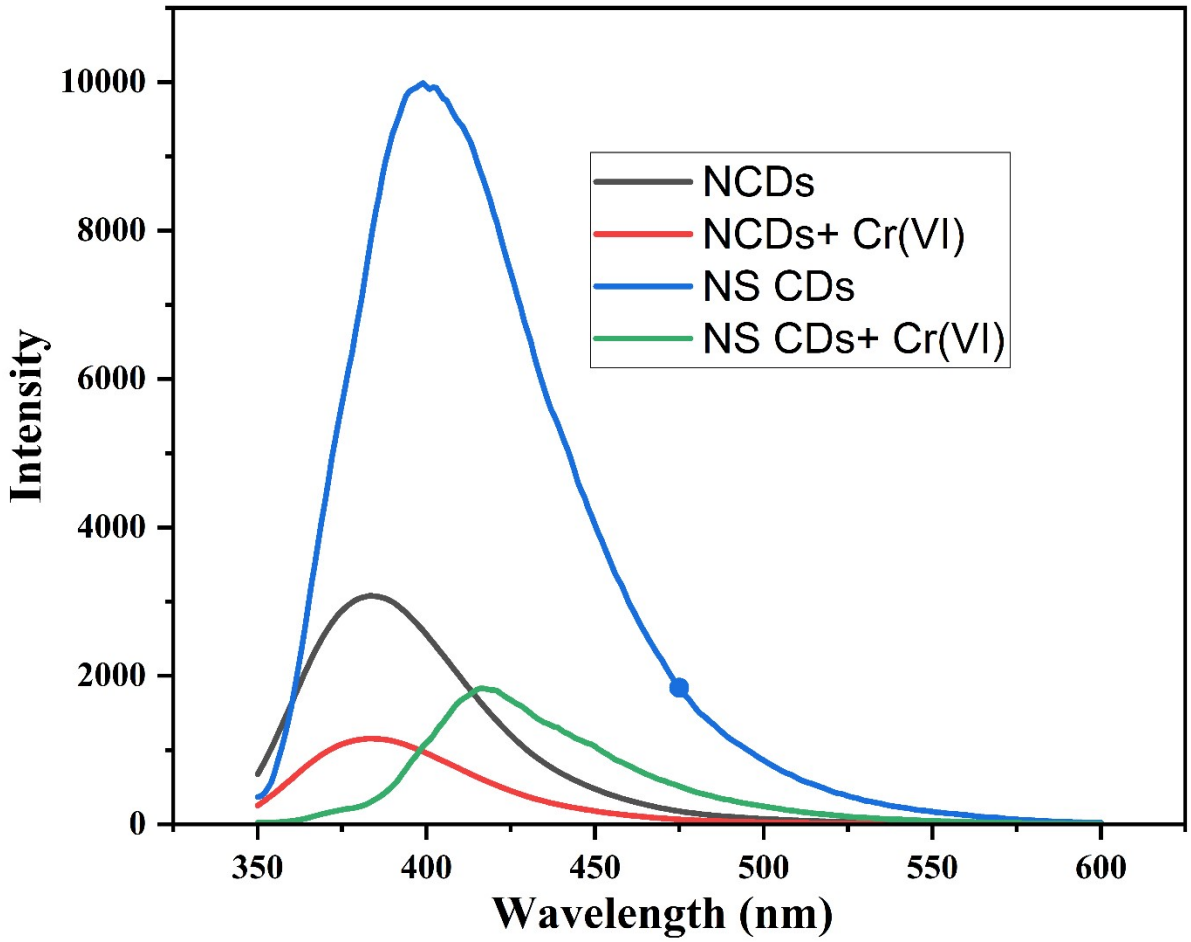


Fig 19S. Fluorescence quenching spectra of NCDs and NS CDs with Cr(VI).

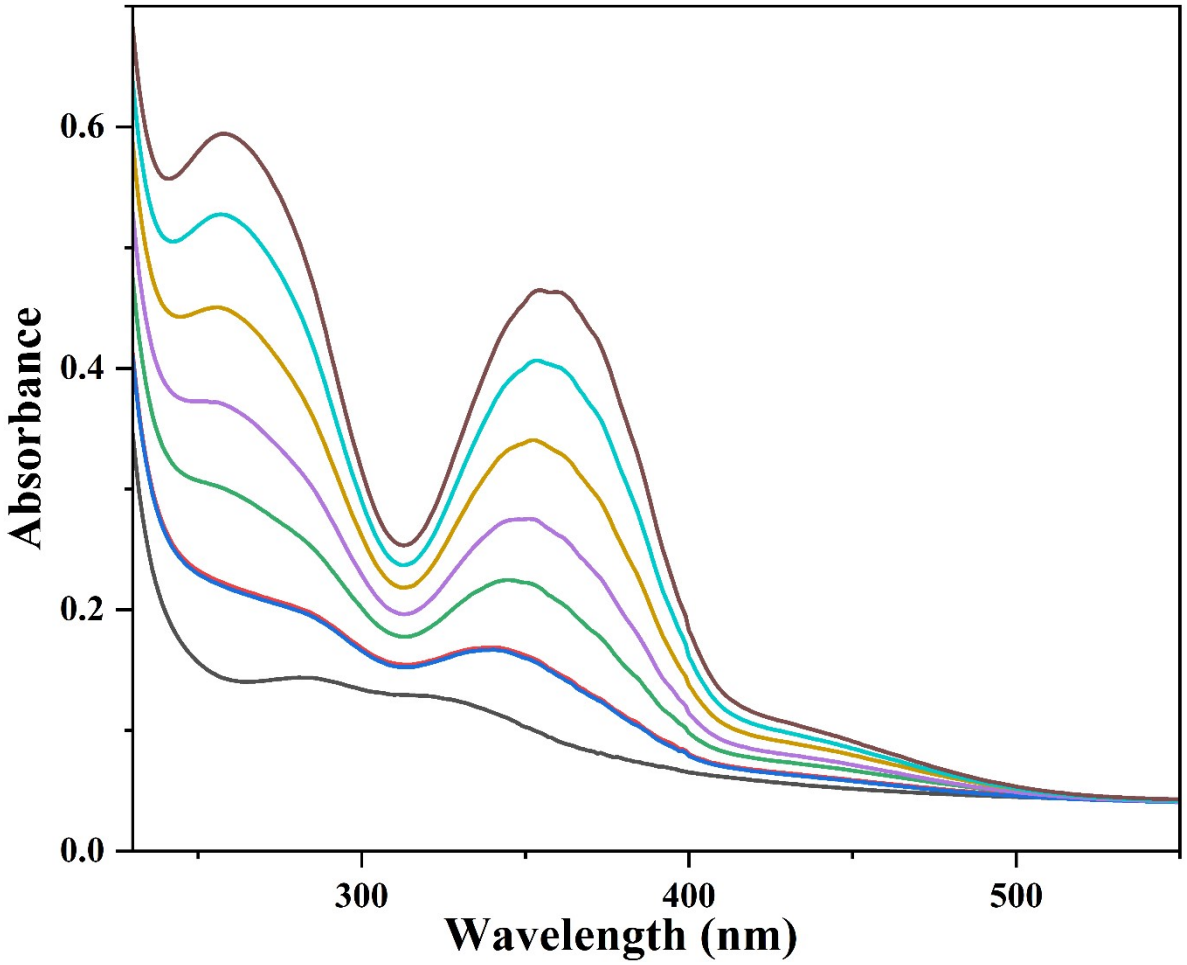


Fig 20S Absorption spectrum of NS CDs in presence of increasing concentration of Cr(VI)

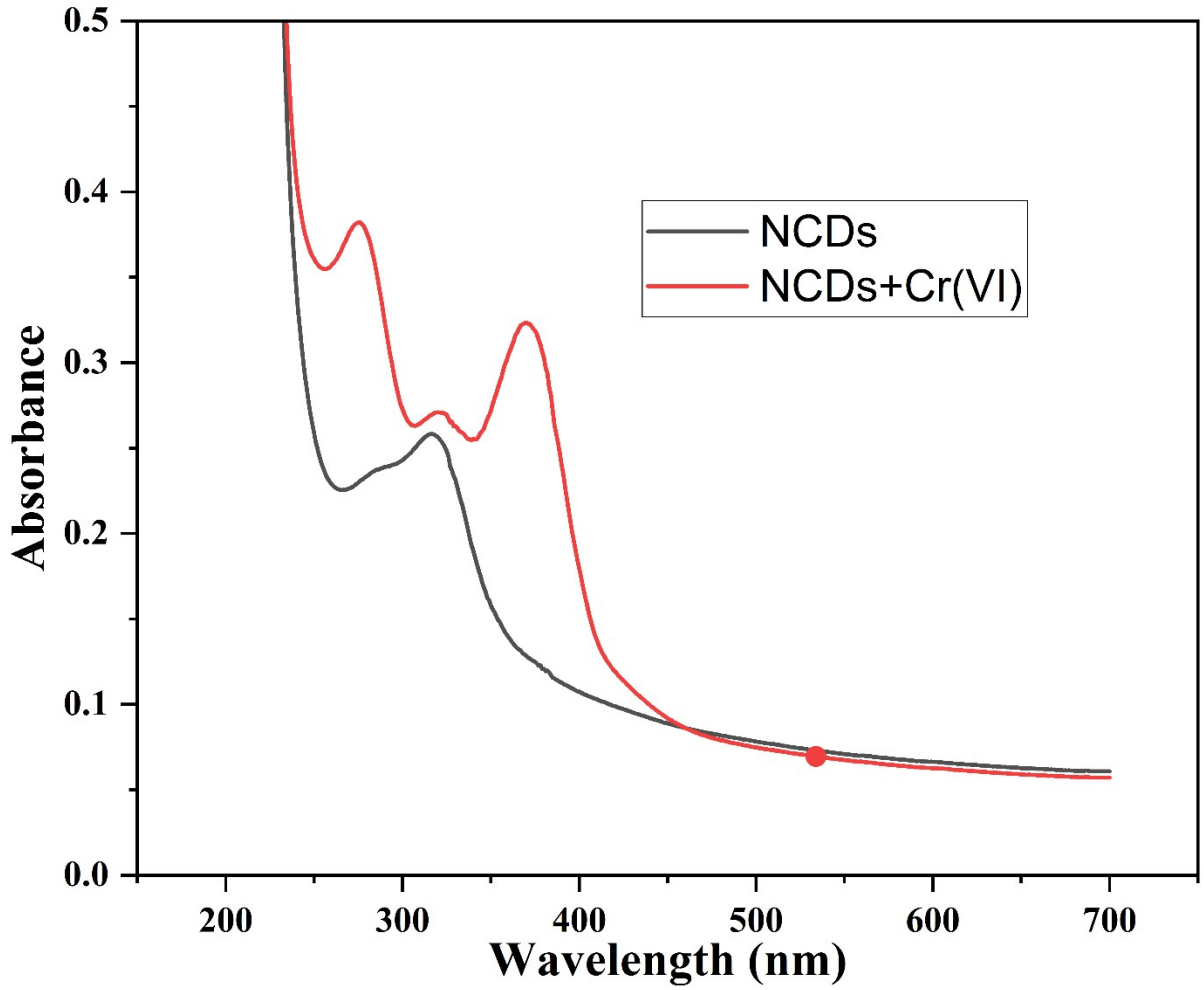


Fig 21S Absorption spectrum of NCDs in presence of Cr(VI)

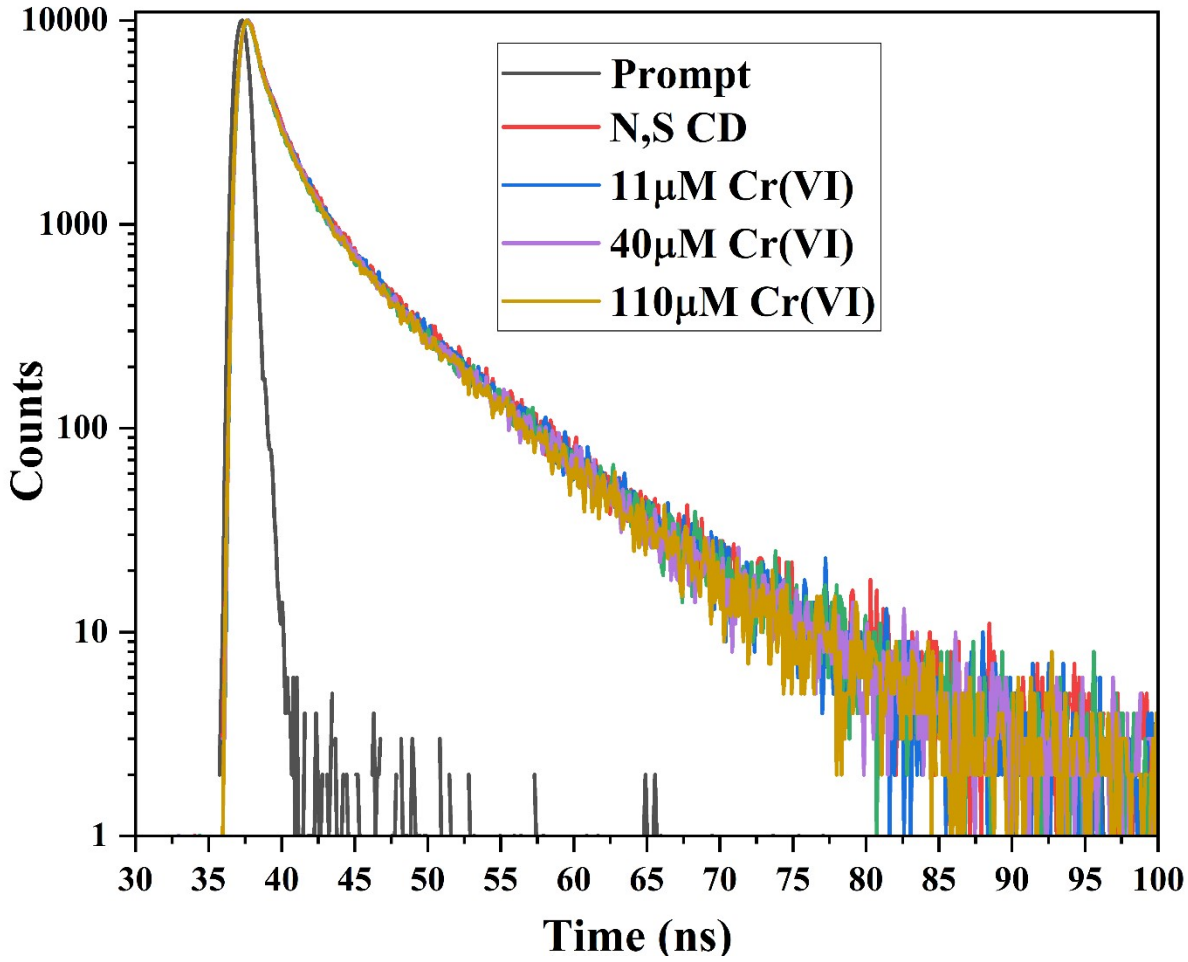


Fig 22S Decay time profile of NS CDs in absence and presence of Cr(VI)

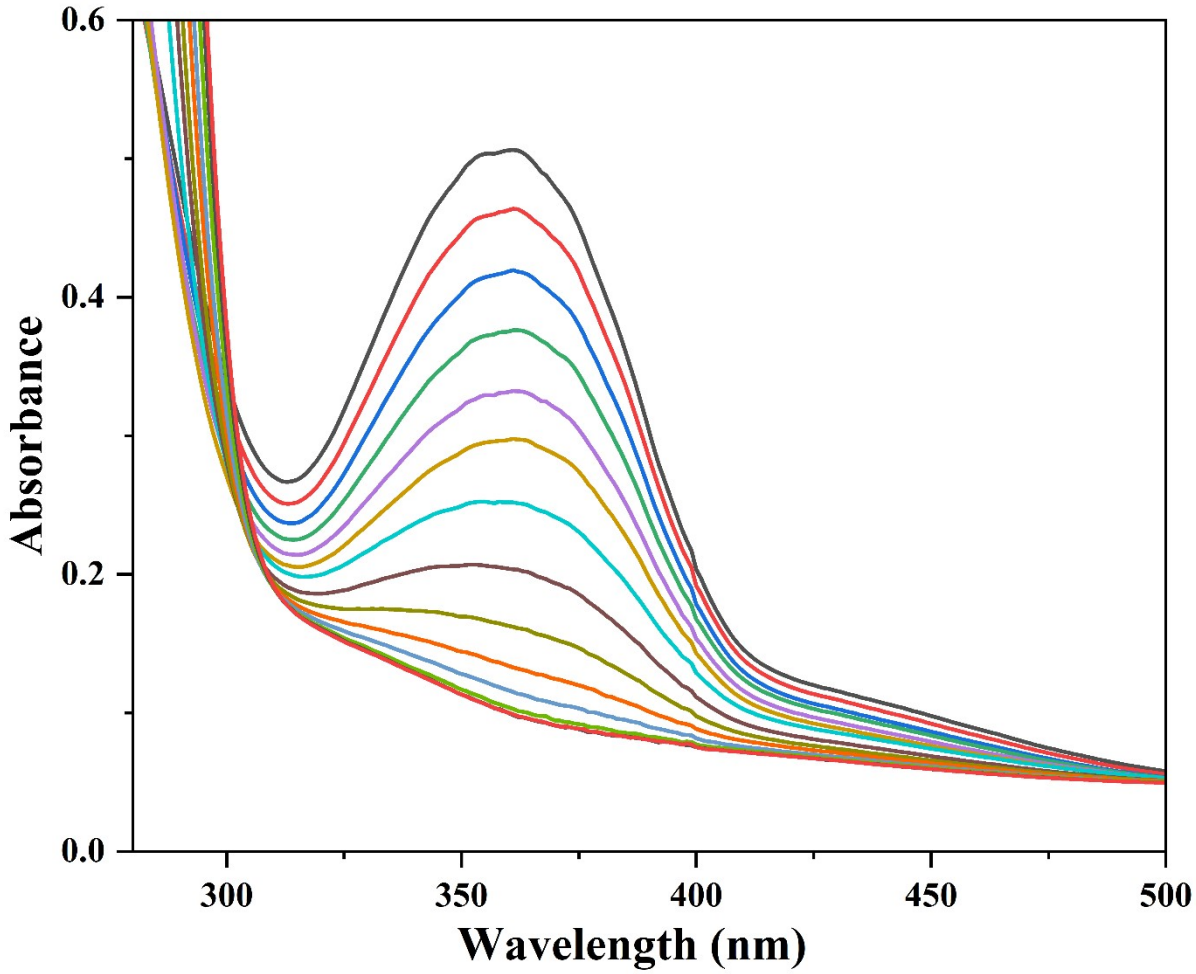


Fig 23S Absorption spectrum of NS CDs – Cr(VI)in presence of increasing concentration of ascorbic acid

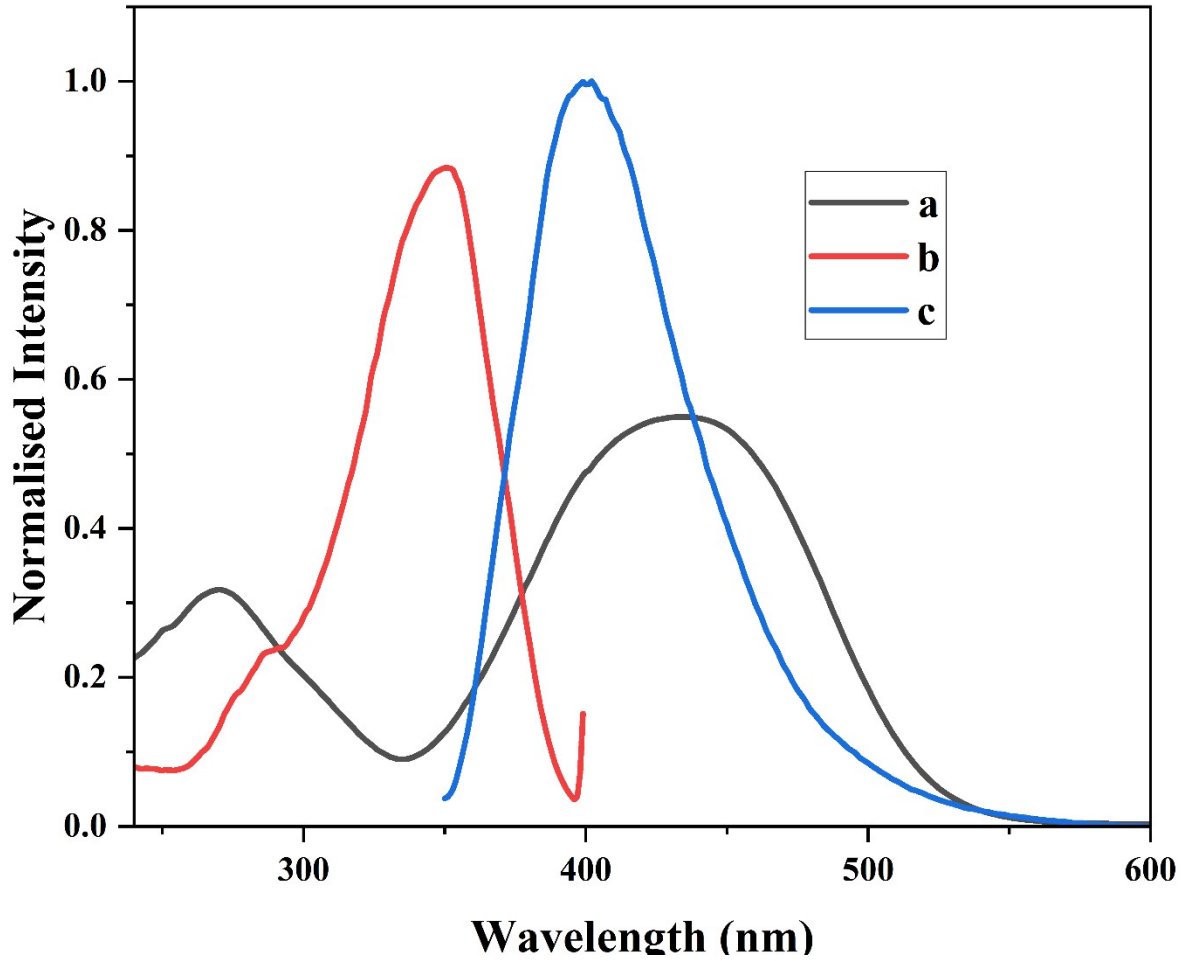


Fig. 24S Spectral overlap of absorption spectrum of Metanil Yellow (a) with emission (c) and excitation spectrum (b) of nanosensor

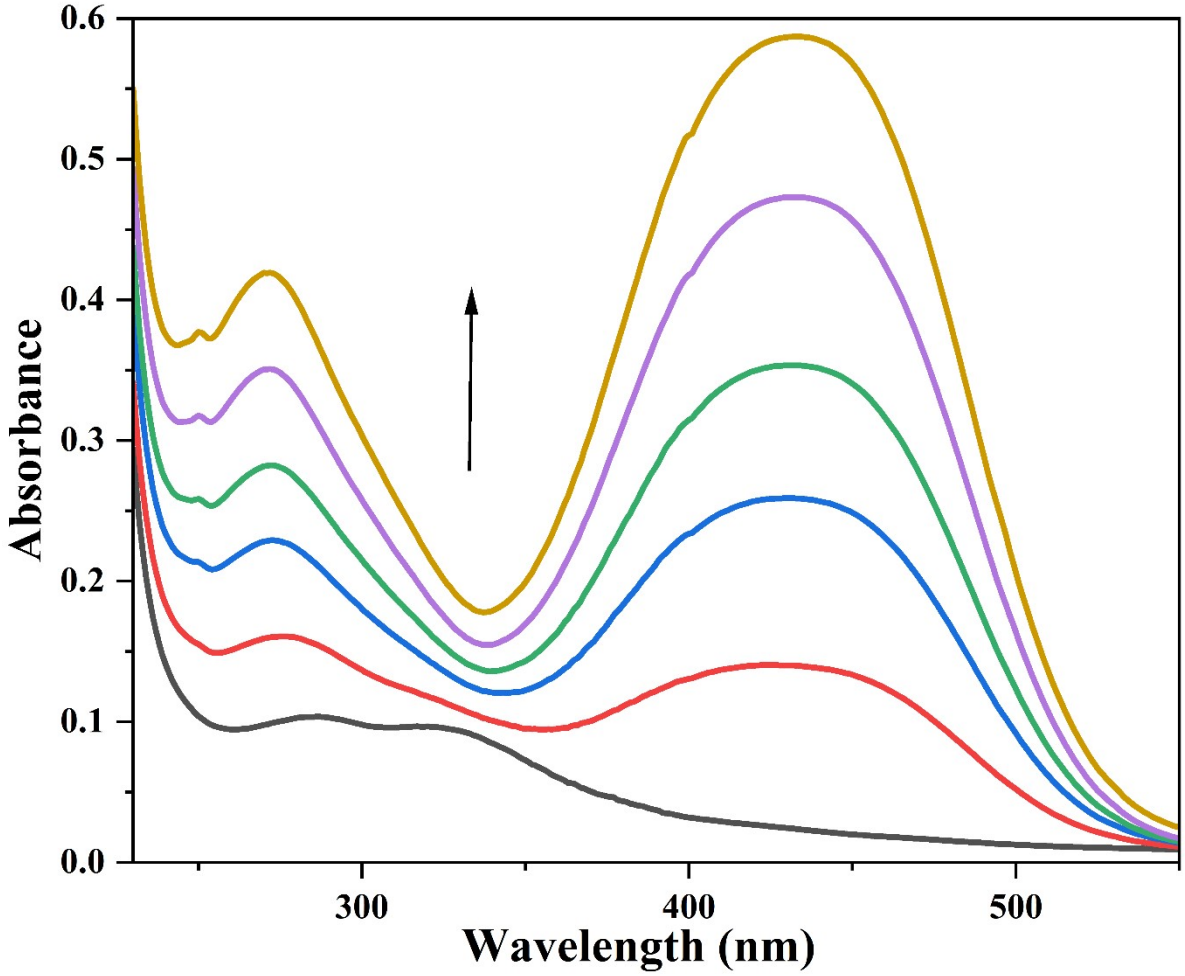


Fig. 25S Absorption spectrum of NS CDs – Cr(VI)in presence of increasing concentration of Metanil yellow.

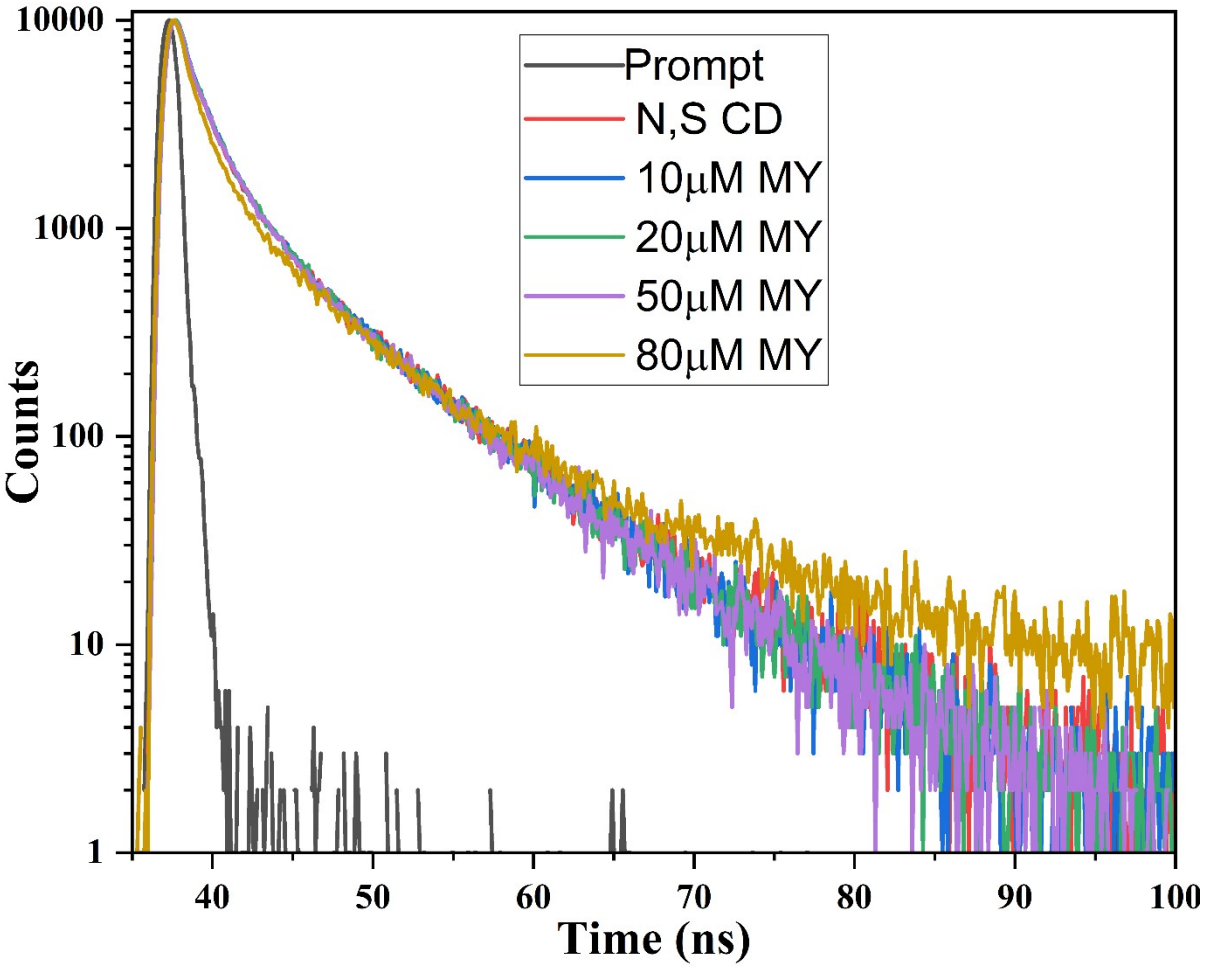
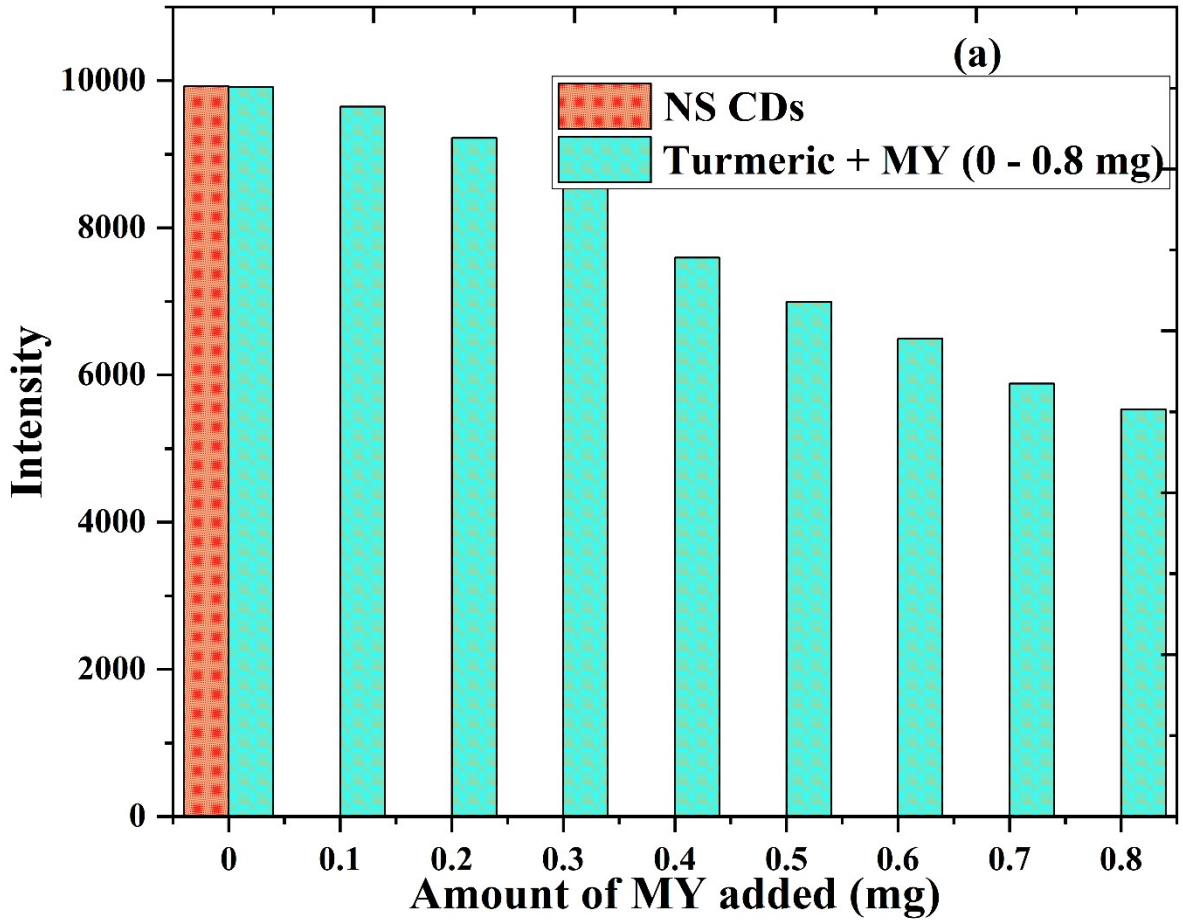


Fig. 26S Decay time profile of NS CDs in absence and presence of Metanil yellow.


(a)
NS CDs
Turmeric + MY (0 - 0.8 mg)
Intensity
10000
8000
6000
4000
2000
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Amount of MY added (mg)

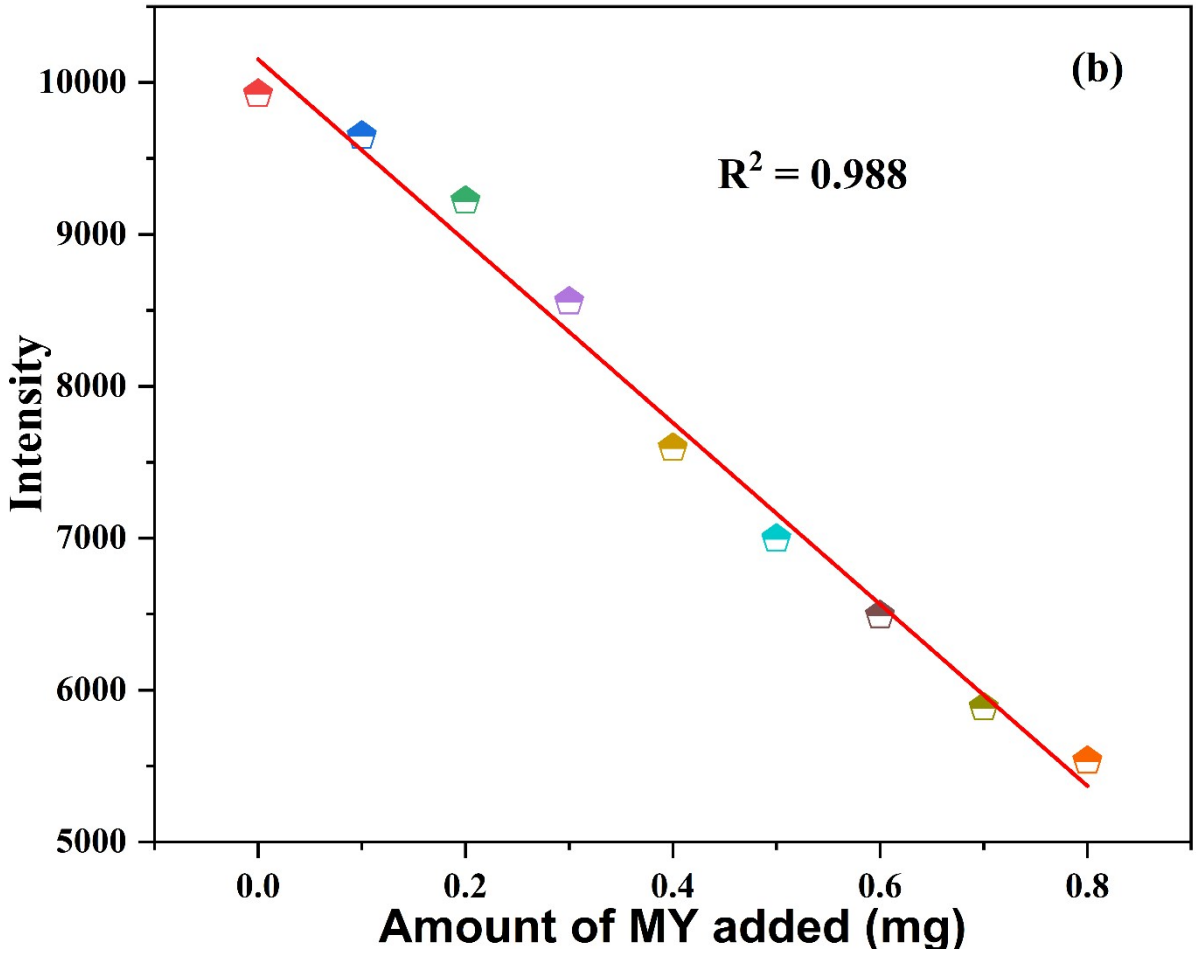


Fig. 27S The relationship between fluorescence intensity v/s the amount of Metanil Yellow (0−0.8 mg per 1000 mg turmeric powder) added in Turmeric Powder.

Table 1S Quantum Yield Calculation Integrated fluorescence intensity against absorbance

Formula used for calculation:

$$Q = Q_{ref}\, \eta^2/\eta^2_{ref}\, I/A\, A_{ref}/I_{ref}$$

η = Refractive Index of the solvent used.

η_{SAMPLE} = 1.333 for Water

η_{ref} = 1.33 for 0.1M H_2SO_4

Q_{ref} = 0.546 (Quantum yield of QUININE SULFATE)

I = Integrated Fluorescence intensity of NS CDs

I_{ref} = Integrated Fluorescence intensity of reference

A = Absorbance at the excitation wavelength of NS CDs

A_{ref} = Absorbance at the excitation wavelength of reference

QY of reference	Area of NS CDs	OD of Reference	Refractive index of sample solvent	Area of Ref	OD of NS CDs	Refractive index of ref solvent	QY
0.546	70793281	0.026221	1.333	110724735	0.027619	1.33	0.32778
0.546	97870331	0.032273	1.333	156091030	0.032325	1.33	0.33804
0.546	182198157	0.052567	1.333	273899865	0.057418	1.33	0.32886
0.546	202953529	0.065006	1.333	330025815	0.064582	1.33	0.33426
					Average QY		**0.33223**

Table 2S Quantum Yield Calculation Integrated fluorescence intensity against absorbance

Formula used for calculation:

$$\mathbf{Q = Q_{ref}\ \eta^2/\eta^2_{ref}\ I/A\ A_{ref}/I_{ref}}$$

η = Refractive Index of the solvent used.

η_{SAMPLE} = 1.333 for Water

η_{ref} = 1.33 for 0.1M H_2SO_4

Q_{ref} = 0.546 (Quantum yield of QUININE SULFATE)

I = Integrated Fluorescence intensity of NCDs

I_{ref} = Integrated Fluorescence intensity of reference

A = Absorbance at the excitation wavelength of NCDs

A_{ref} = Absorbance at the excitation wavelength of reference

QY of reference	Area of NCDs	OD of Reference	Refractive index of sample solvent	Area of Ref	OD of NCDs	Refractive index of ref solvent	QY
0.546	28387980	0.026221	1.333	110724735	0.027619	1.33	0.133499857
0.546	41230820	0.032273	1.333	156091030	0.032325	1.33	0.144642024
0.546	73109135	0.052567	1.333	273899865	0.057418	1.33	0.134027717
0.546	83596770	0.065006	1.333	330025815	0.064582	1.33	0.139840574
					Average QY		**0.138002543**

Table 3S Comparison of methods for Cr(VI) determination

Detection method	Linear Range	Detection Limit	Reference
Electrochemical Technique	2-200 µM	0.9 µM	[1]
Graphite Furnace Atomic absorption Spectroscopy	0.038-3.1 µM	0.001 µM	[2]
Spectro fluorimetry	0.05-2 µM	0.0055 µM	[3]
Colorimetric assay	0.16-24 µM	0.15 µM	[4]
Colorimetric assay	0- 100 µg/L	1.43 µG/L	[5]
Electrochemical Technique	0.10-105 µM	0.03 µM	[6]
Fluorescence Spectroscopy	0.05-500 µM	0.0037 µM	[7]
Fluorescence Spectroscopy	0.05-10 µM	0.015 µM	[8]

Fluorescence spectroscopy	3-60 μM	0.056 μM	This work

Table 4S Comparison of methods for Metanil yellow determination

Detection method	Linear Range	Detection Limit	Reference
FT-IR	not given	5% concentration	[9]
Fluorescence	not given	3.83 nM/ml	[10]
Electrochemical	not given	9.8 nM	[11]
Electrochemical	not given	not given	[12]
Fluorescence	3 -100 μM	0.0073 μM	[13]

Table 5S Triple exponential fitting parameters of NS CDs and ND CDs-Cr(VI) decay curves

Concentration of Cr(VI) (μM)	τ_1 (nm)	B_1	τ_2 (nm)	B_2	τ_3 (nm)	B_3	τ (nm)	CHISQ
0	1.88	43.25	0.135	23.79	7.53	32.96	3.3	1.04
11	1.76	36.83	0.0832	32.97	7.26	30.20	2.87	1.05
40	1.82	37.70	0.0864	31.92	7.11	30.38	2.87	1.05
110	1.71	37.65	0.0884	30.92	6.85	31.43	2.82	1.05
$\tau = \tau_1 \times B_1 + \tau_2 \times B_2 + \tau_3 \times B_3$ ($\Sigma B_i = 1$, for good fit , CHISQ should be less than 1.2								

Table 6S Triple exponential fitting parameters of NS CDs and ND CDs-metanil yellow decay curves

Concentration of Cr(VI) (μM)	τ_1 (nm)	B_1	τ_2 (nm)	B_2	τ_3 (nm)	B_3	τ (nm)	CHISQ
0	1.88	43.25	0.135	23.79	7.53	32.96	3.3	1.04
10	1.81	39.58	0.0782	29.66	7.26	30.76	2.97	1.03
20	1.88	44.45	0.142	22.52	7.36	33.03	3.3	1.02
50	1.84	43.14	0.126	23.51	7.15	33.34	3.2	1.04
$\tau = \tau_1 \times B_1 + \tau_2 \times B_2 + \tau_3 \times B_3$ (Σ B_i =1, for good fit , CHISQ should be less than 1.2								

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