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Supporting Information

Investigation of luminescent mechanism: N-rich corbon dots as the luminescence center of fluorescent Hydroxyapatite prepared by a typical hydrothermal process

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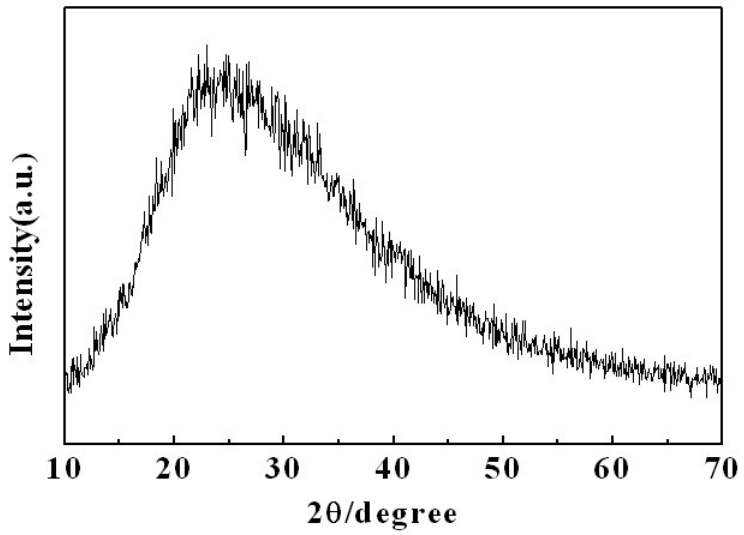


Fig. S1 XRD patterns of the luminescence center

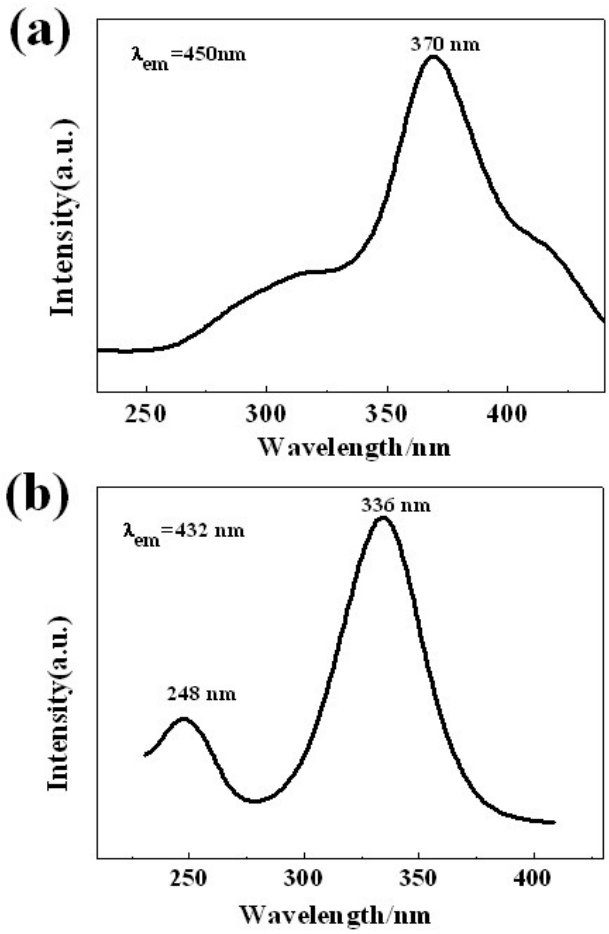


Fig. S2 Fluorescence excitation spectra of (a) the luminescence center and (b) sample S6

Sample	Raw materials involved in the hydrothermal system	Hydrothermal reaction parameters
S1	$Ca(NO_3)_2$, CTAB, sodium citrate, $(NH_4)_2HPO_4$	190 ℃, 24 h
S2	$Ca(NO_3)_2$, sodium citrate, $(NH_4)_2HPO_4$	190 ℃, 24 h
S3	$Ca(NO_3)_2$, $(NH_4)_2HPO_4$	190 ℃, 24 h
S4	$Ca(NO_3)_2$, CTAB, sodium citrate, Na_2HPO_4	190 ℃, 24 h
S5	$Ca(NO_3)_2$, sodium citrate, Na_2HPO_4	190 ℃, 24 h
S6	$Ca(NO_3)_2$, ammonium citrate, Na_2HPO_4	190 ℃, 24 h
C1	sodium citrate	190 ℃, 24 h
C2	ammonium citrate	190 ℃, 24 h
CDs	ammonium citrate	190 ℃, 24 h

Table S1 Summary of the raw materials and the hydrothermal reaction parameters of Samples S1-6, C1, C2, and CDs

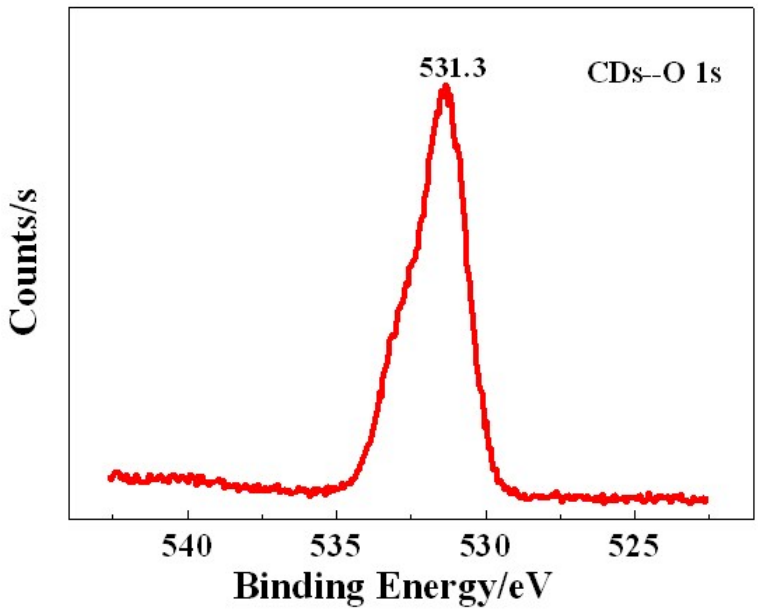


Fig. S3 XPS narrow scan spectrum of O1s of CDs

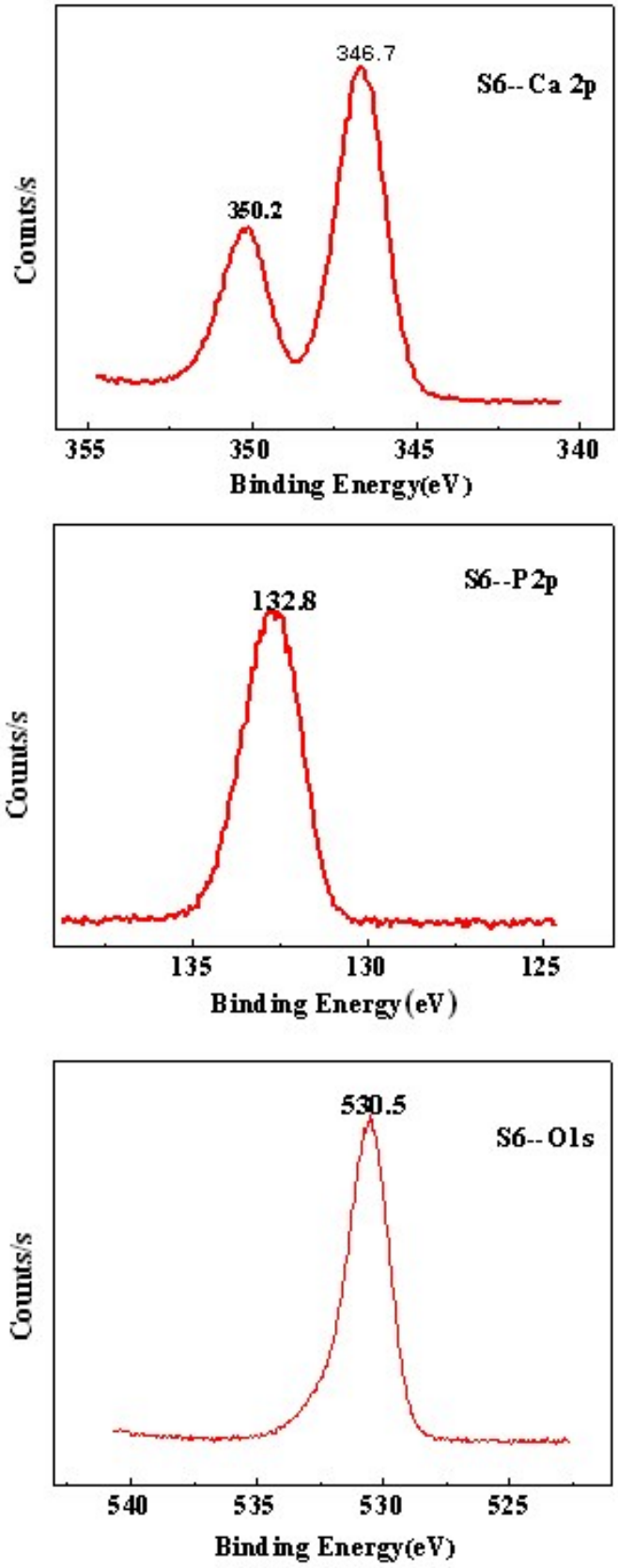


Fig. S4 XPS narrow scan spectrum of Ca 2p, P2p, and O1s of sample S6

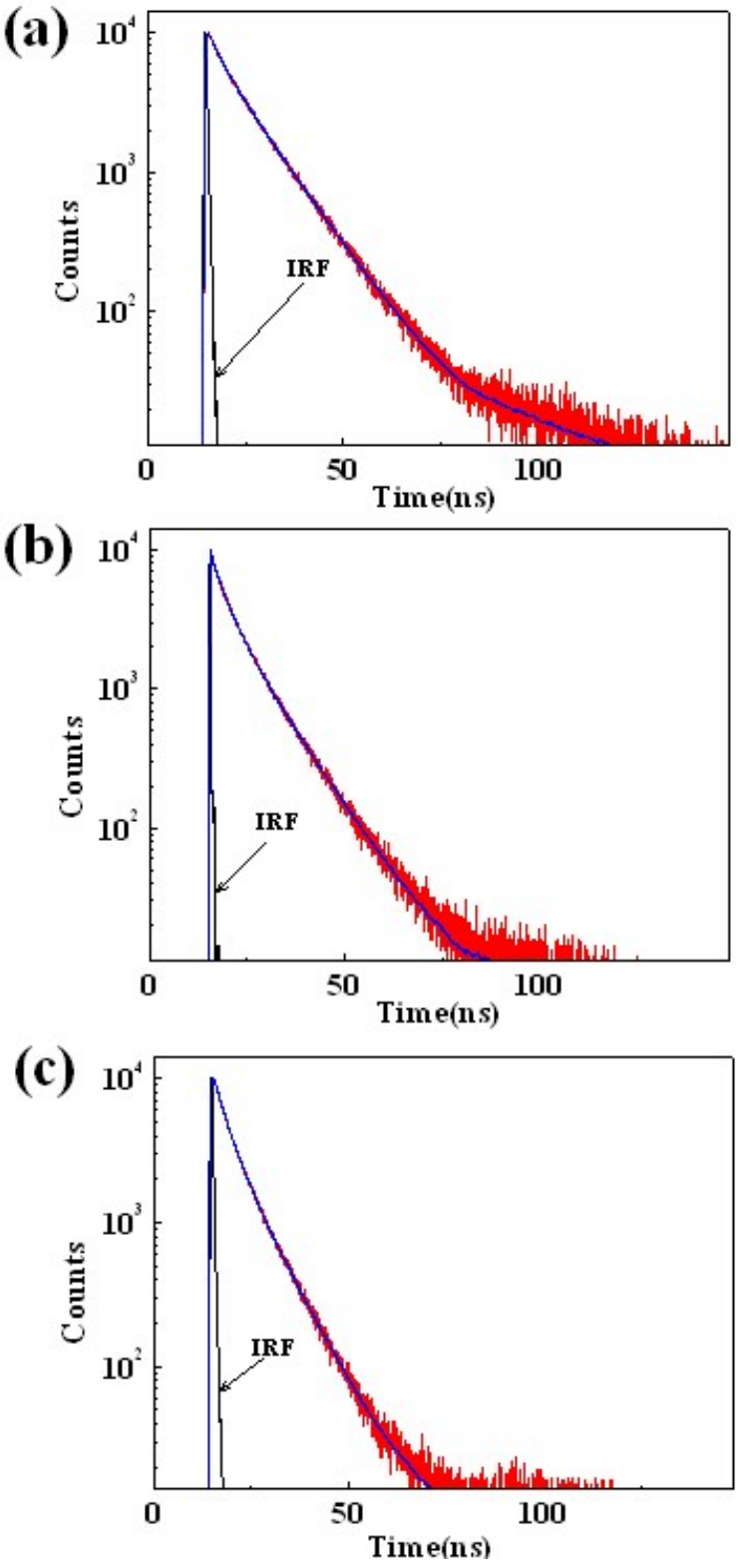


Fig. S5 Fluorescence lifetime decay profiles: (a) CDs, λ_{ex}=320 nm, emission monitored at 430 nm; (b) CDs, λ_{ex}=371 nm, emission monitored at 450 nm; (c) S 6, λ_{ex}=320 nm, emission monitored at 430 nm.

States	CDs		S6
λ_{ex} (nm)	320	370	320
$\lambda_{em.max}$(nm)	430	450	430
τ (ns)	4.65 (15.4%) 11.2 (82.0%) 0.68 (2.6%)	3.94 (31.2%) 11.4 (65.9%) 0.42 (2.9%)	3.64 (36.6%) 8.75 (58.9%) 0.73 (2.9%)
τ_{av}(ns)	6.94	4.71	4.36
χ^2	1.05	1.22	1.08

Table S2 Lifetime data of CDs and sample S6

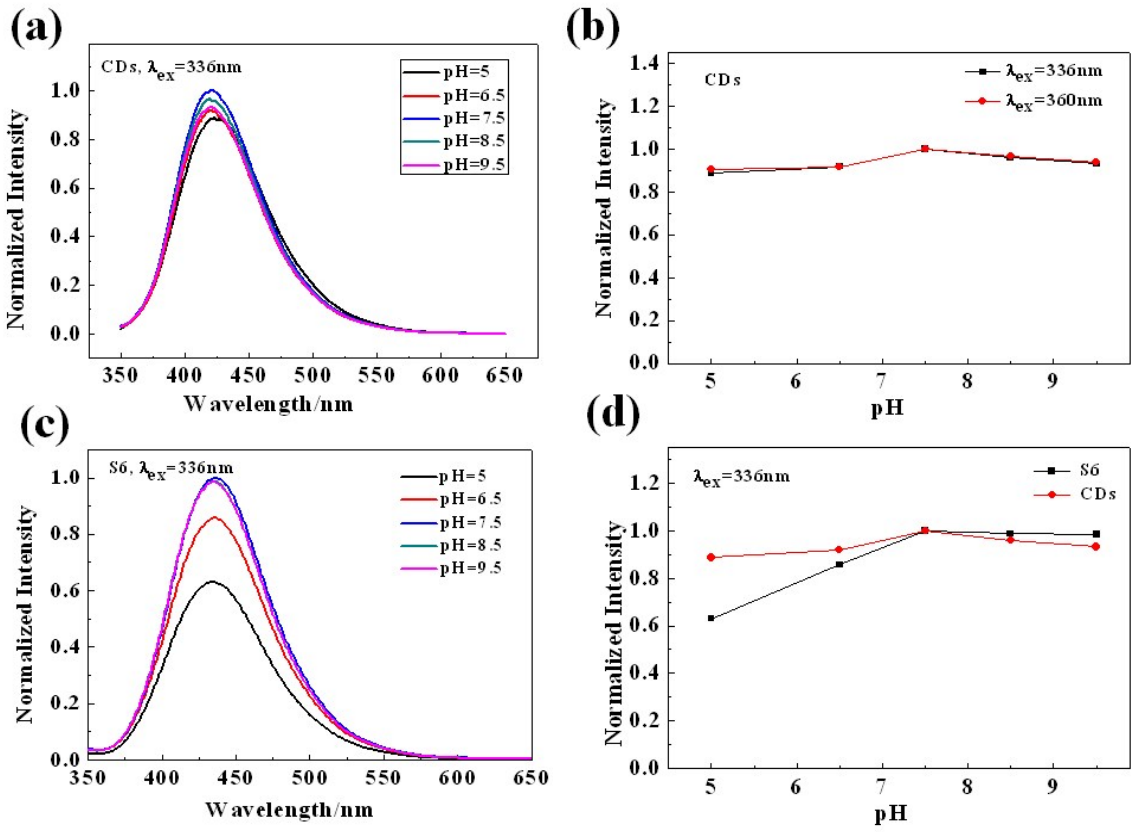
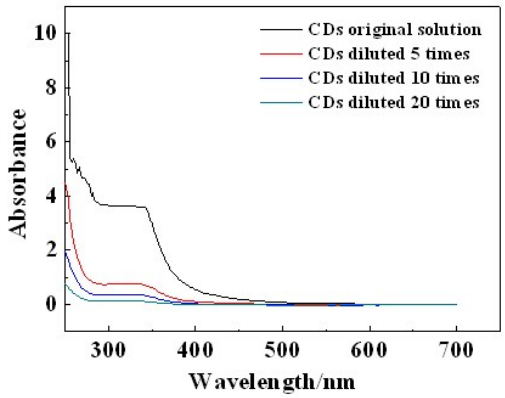


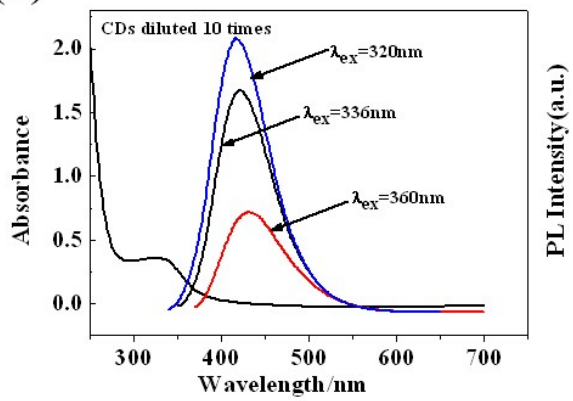
Fig. S6 (a) Emission spectra of CDs at different pH values (λ_{ex}=336 nm); (b) Normalized fluorescence intensity of CDs at different pH values excited at 336 nm or 360 nm; (c) Emission spectra of sample S6 at different pH values (λ_{ex}=336 nm); (d) A comparison of the fluorescence intensity variation of CDs and sample S6 at different pH values (λ_{ex}=336 nm)

(The experiments were performed in phosphate buffer saline (PBS) solution with 2 M HCl or 2 M NaOH to adjust the pH values. Sample S6 powder was dispersed in the above solution with a designated pH value by ultrasonic method to form nearly transparent suspensions/solutions with a mass concentration of 250 μg/mL. The CDs solution for testing is prepared by mixing the CDs original solution and the above PBS solution with a designated pH value by a volume ratio of 1:9, and then trace amounts of 2 M HCl or 2 M NaOH was used to fine-tune the pH value of the as-prepared mixture. All the specimens were kept in a 37 °C oven for 2 h before the fluorescence measurements.)

(a)



(b)



(c)

Solution	CDs diluted 10 times		
λex(nm)	320	336	360
QY	62.64%	40.16%	32.17%

Fig. S7 (a) UV-vis absorption spectra of CDs at different concentrations; (b) UV-vis absorption and PL spectra of a diluted CDs solution (10 times) at various excitation wavelengths; (c) The QY values of a diluted CDs solution at various excitation wavelengths

(notes: As shown in **Fig. S7(a)**, the absorbance of CDs original solution and its 5 times diluted solution are very high in the wavelength range of 250nm~380nm, which may cause self-quenching and will not satisfy the QY measurement because of the re-absorption effects. Herein, the QY of its 10 times diluted solution were listed (**Fig. S7(c)**) for discussion because it can meet the demands of the QY measurement since its re-absorption effect is weaker (**Fig. S7(b)**).)

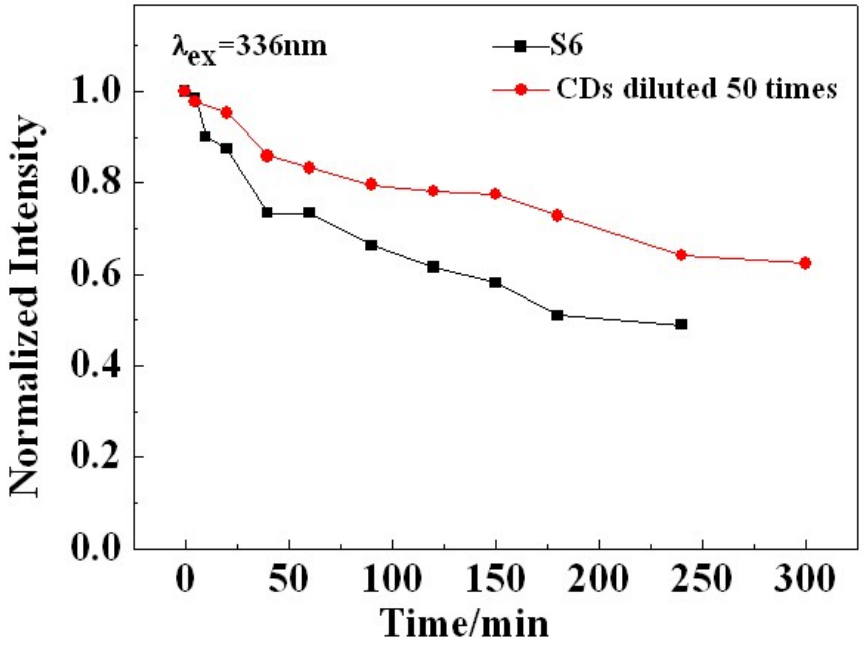


Fig. S8 Normalized fluorescence intensity of sample S6 and 50 times diluted CDs solution at different stages under UV exposure (These photostability tests were performed at room temperature. The 50 times diluted CDs solution was placed in a culture dish and the S6 powder was spread on a paper. The ultraviolet lamp (365 nm, 12 W) was placed 10 cm away from the diluted CDs solution and S6 powder. The fluorescence intensities of the specimens after different irradiation time were measured.).

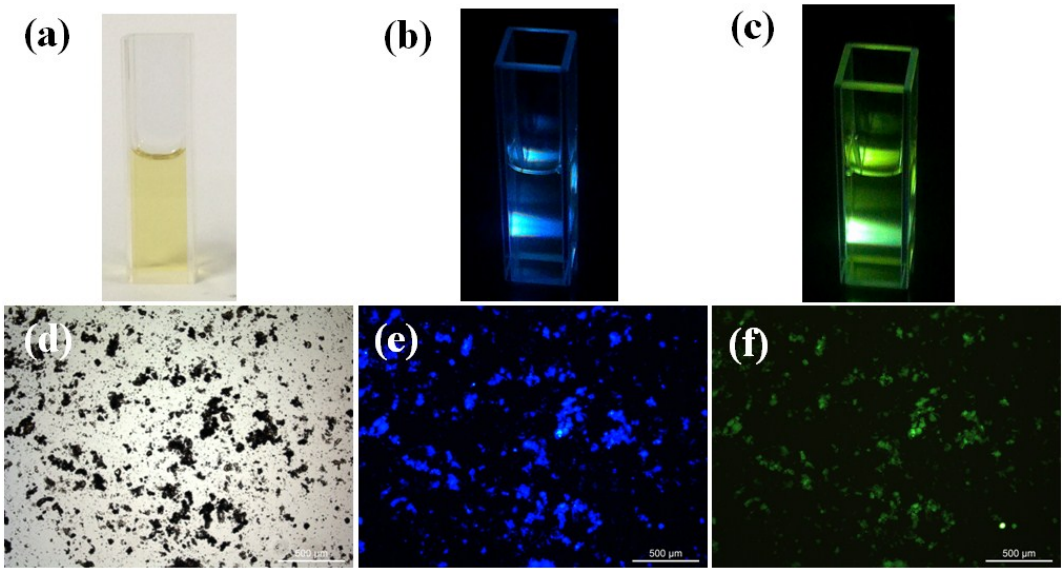


Fig. S9 Images of the CDs solution (a-c) and HAp (d-f) powders under different excitation light/mode: (a) day light; (b) λ_{ex}=370nm; (c) λ_{ex}=440nm; (d) bright field (BF), (e) fluorescence filter cube A and (f) fluorescence filter cube I3.

(The HAp with tunable fluorescence emission was prepared in another hydrothermal synthesis system also with the CDs as fluorescence center. The fluorescent images of CDs were taken on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The images of HAp powders were obtained on a Leica DMI4000B automated inverted microscope and the sample was prepared by a small amount of HAp powder placing on a glass slide.)