Electronic Supplementary Information

Bio-nanoplatforms based on carbon dots conjugating with F-substituted nano-hydroxyapatite for cellular imaging

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Experimental details

1. Synthesis of monodispersed NFAp

The oleic acid-capped monodisperse NFAp nanorods were synthesized *via* a hydrothermal method[S1]. In a Teflon-lined autoclave (50 mL), octadecylamine (0.5 g) were dissolved in oleic acid (6 mL) by heating at 100 °C. The solution was mixed with ethanol (24 mL) under agitation. Then, an aqueous solution of $Ca(NO_3)_2$ (0.28 M, 7.5 mL) and NaF (0.28 M, 1.4 mL) were added into the above solution orderly. After stirring for 10 min, $Na_3PO_4.12H_2O$ (0.16 M, 7.5 mL) aqueous solution was added and the mixture was agitated for about 10 min. After hydrothermal synthesized at 150 °C for about 12 h, the autoclave was cool down to room temperature. The products were collected and washed with cyclohexane and ethanol for several times. After that, the resultants were thoroughly redispersed in cyclohexane.

2. Quantum yield (QY) measurements

Fluorescence QYs of CDs and CDs-COOH were measured according to the standard method by comparing their integrated PL intensities. Quinine sulfate in 0.1 M H_2SO_4 (quantum yield 54%) was chosen as a standard as described. The QYs are calculated using following equation:

$$Q = Q_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n^2_R}$$

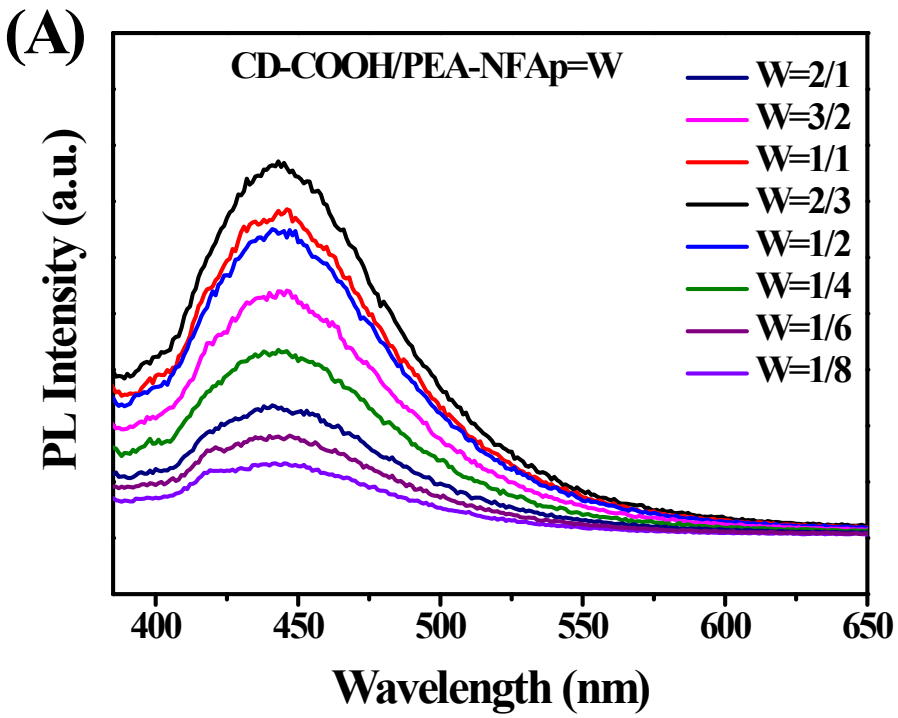
where Q is the QY, I is the integrated intensity, A means the UV-vis absorption intensity. The R refers to the reference, and n presents the refractive index with 1.33 as the default for both quinine sulfate and CDs solvent. Noteworthy, the optical density is kept under 0.05 to avoid inner filter effects.

3. Cell incubation

The human breast cancer cell (MCF-7) were maintained in a RPMI-1640 medium supplemented with FBS (10%), antibiotic-antimycotic solution (1%), L-glutamine (2 mM), and non-essential amino acids (1%) in 5% CO_2 at 37 °C.

The human liver hepatocellular carcinoma cell lines ($hepG_2$) were cultured in the DMEM medium supplemented with FBS (10%) and penicillin/streptomycin（1%）in 5% CO_2 and 95% O_2 at 37 °C.

The human colon carcinoma cell line(Caco-2) were maintained in Eagle's minimum essential (ATCC) medium supplemented with FBS (20 %) and antibiotic antimycotic solution (1%) in 5% CO_2 and 95% O_2 at 37 °C.



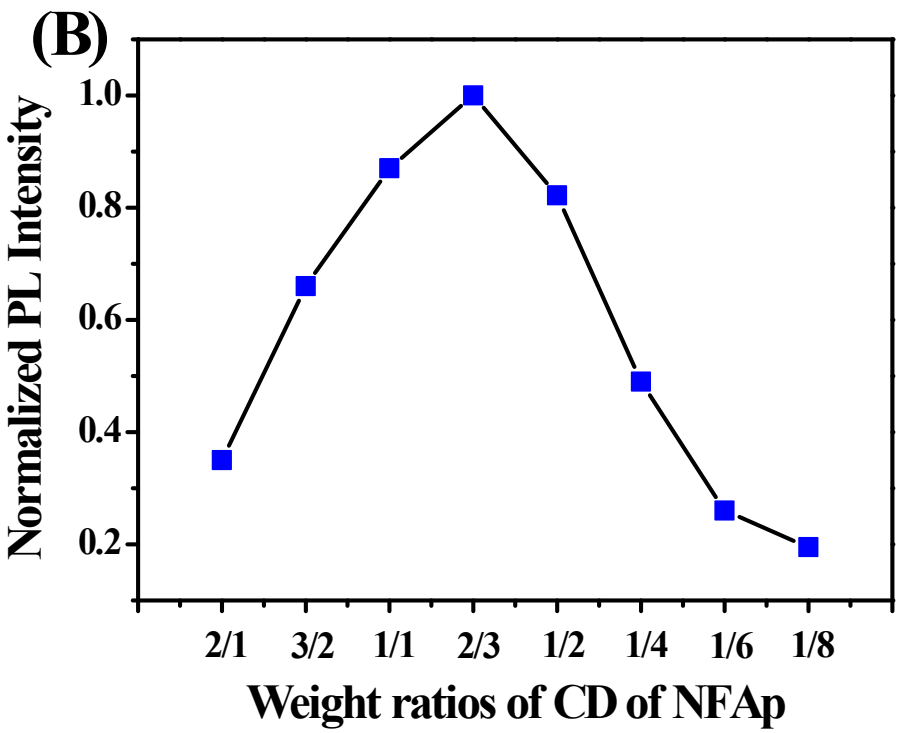


Figure S1. PL emission spectra of the CDS-COOH@PEA-NFAp conjugates with different CDs-COOH/PEA-NFAp weight ratios (A) and normalized fluorescence intensity (B). Excitation wavelength: 365 nm.

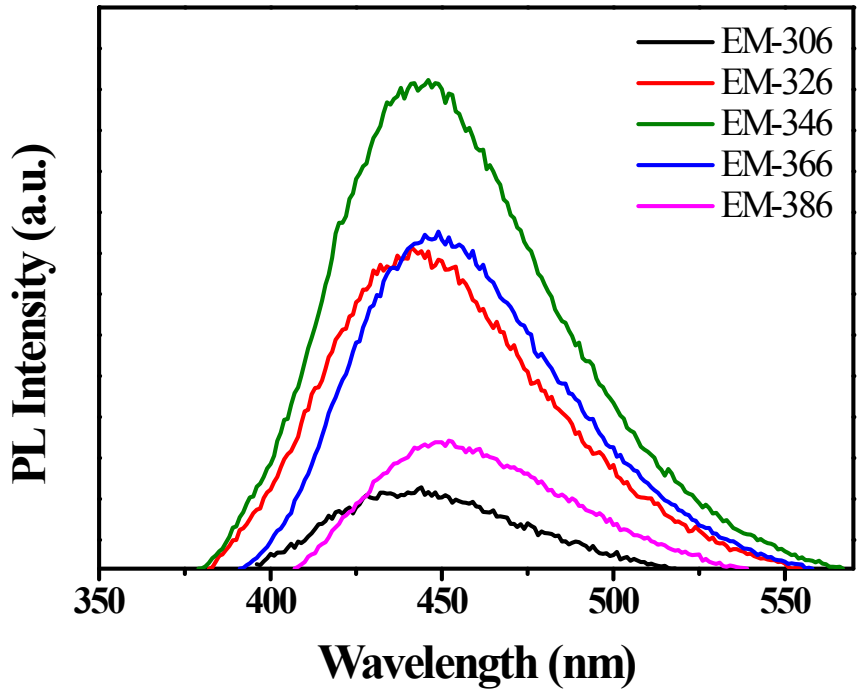


Figure S2. Excitation-dependent PL of CDs-COOH.

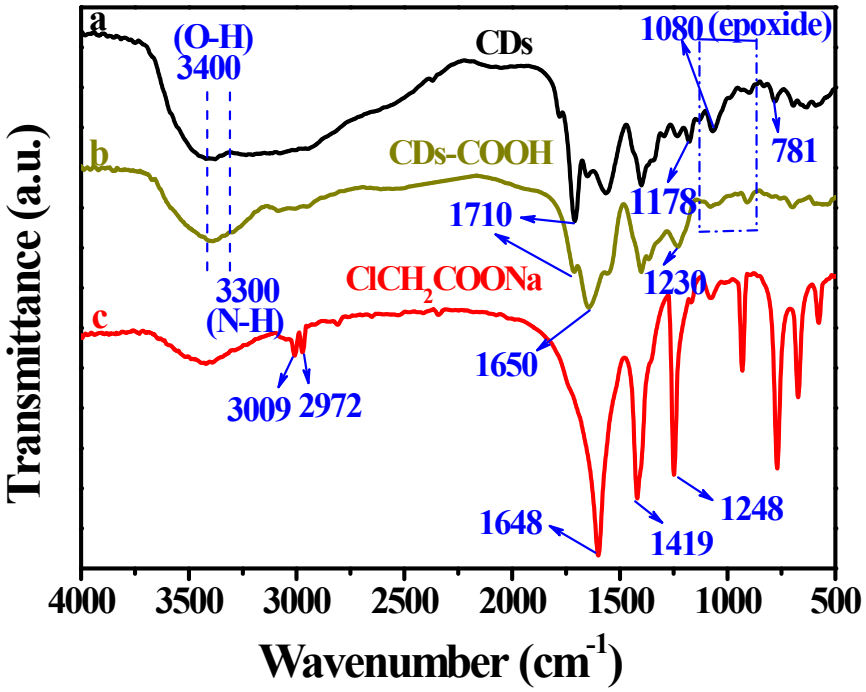
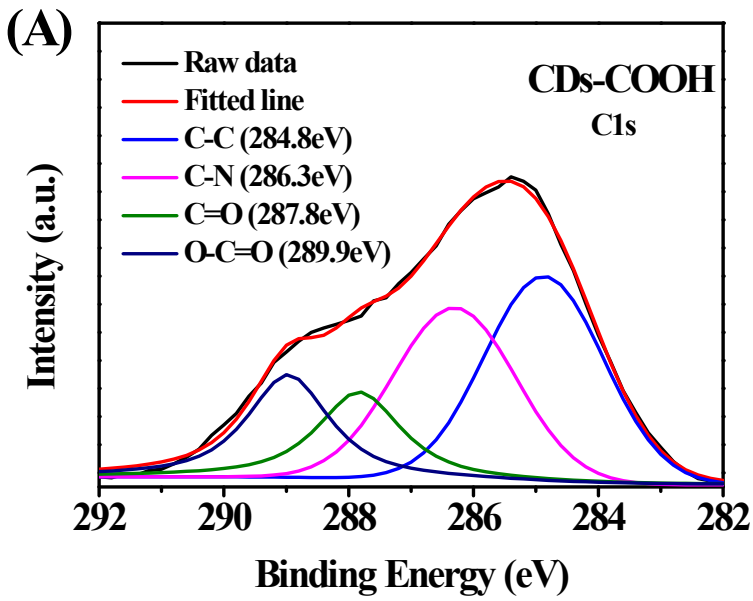
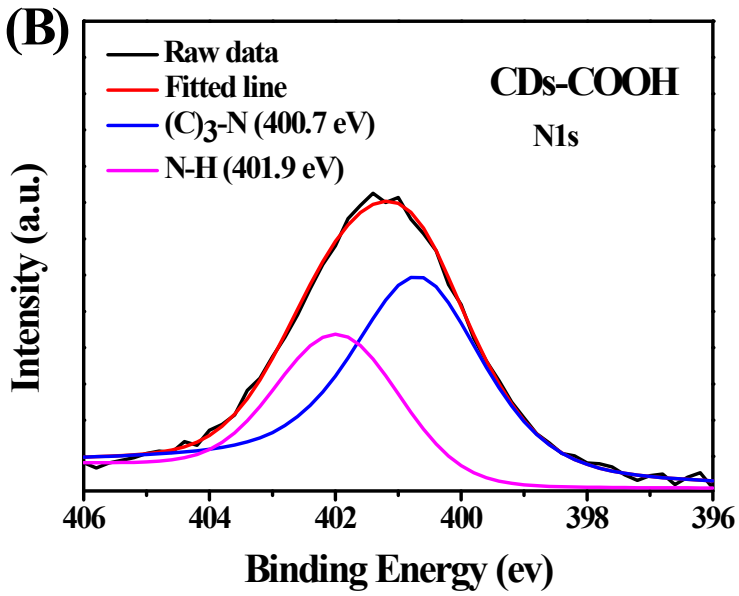
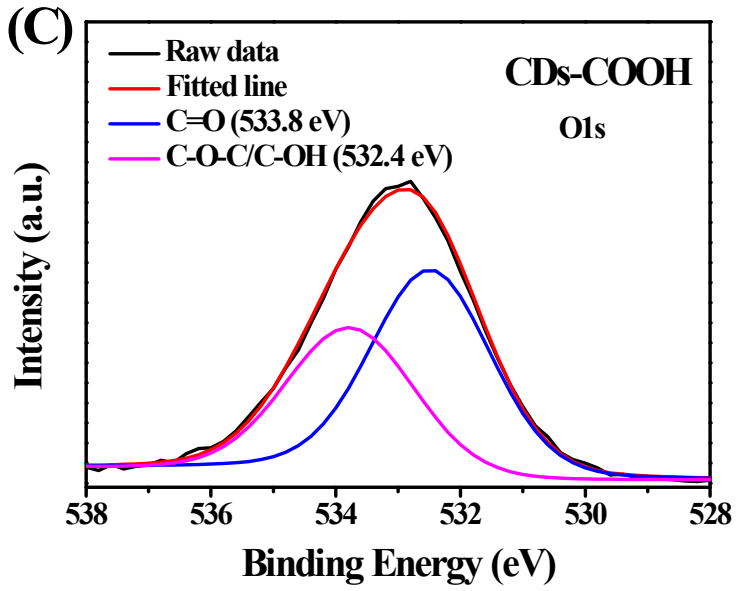
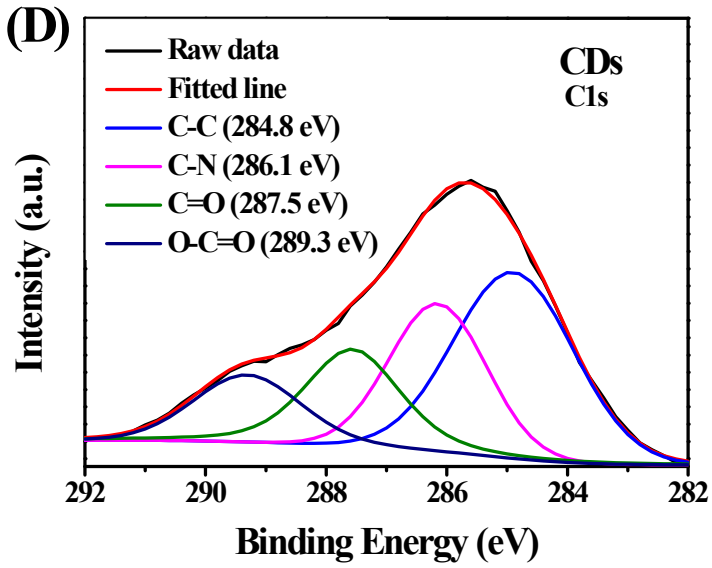


Figure S3. FTIR spectra of the CDs, CDs-COOH and $ClCH_2COONa$




(B)
Raw data
Fitted line
(C)3-N (400.7 eV)
N-H (401.9 eV)
CDs-COOH
N1s
Intensity (a.u.)
406
404
402
400
398
396
Binding Energy (ev)


(C)
Raw data
Fitted line
C=O (533.8 eV)
C-O-C/C-OH (532.4 eV)
CDs-COOH
O1s
Intensity (a.u.)
538
536
534
532
530
528
Binding Energy (eV)


(D)
Raw data
Fitted line
C-C (284.8 eV)
C-N (286.1 eV)
C=O (287.5 eV)
O-C=O (289.3 eV)
CDs
C1s
Intensity (a.u.)
292
290
288
286
284
282
Binding Energy (eV)

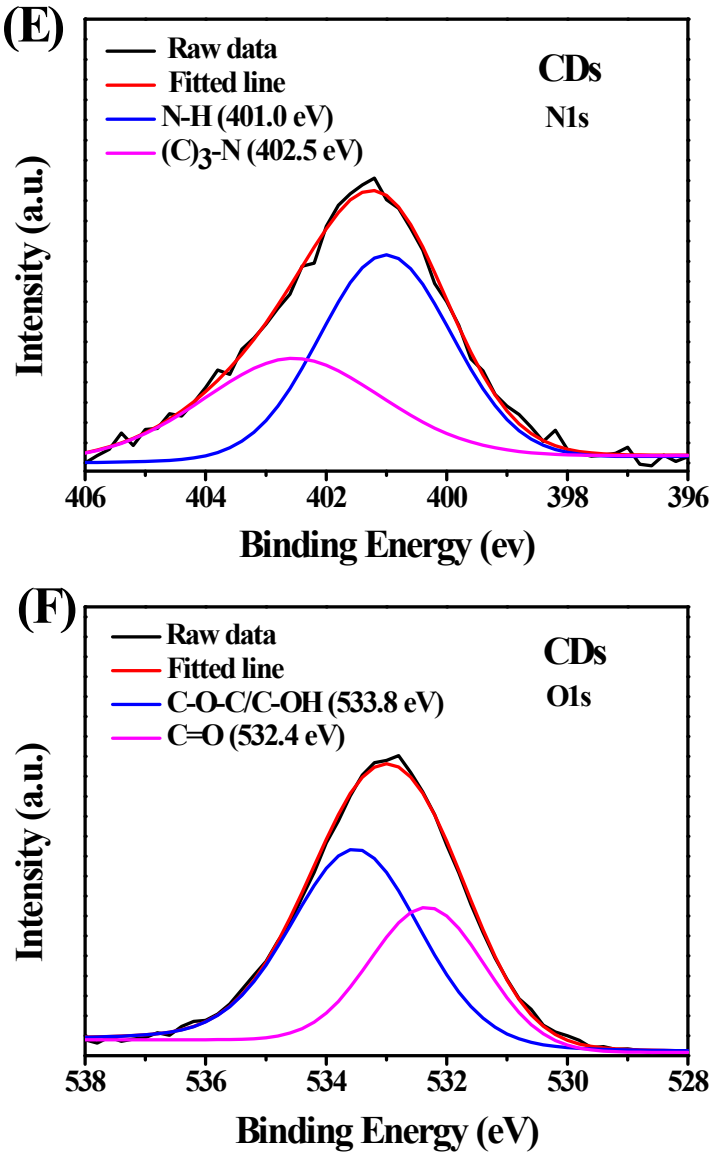


Figure S4. High-resolution XPS spectra of the as-prepared CDs-COOH (A-C) and CDs (D-F).

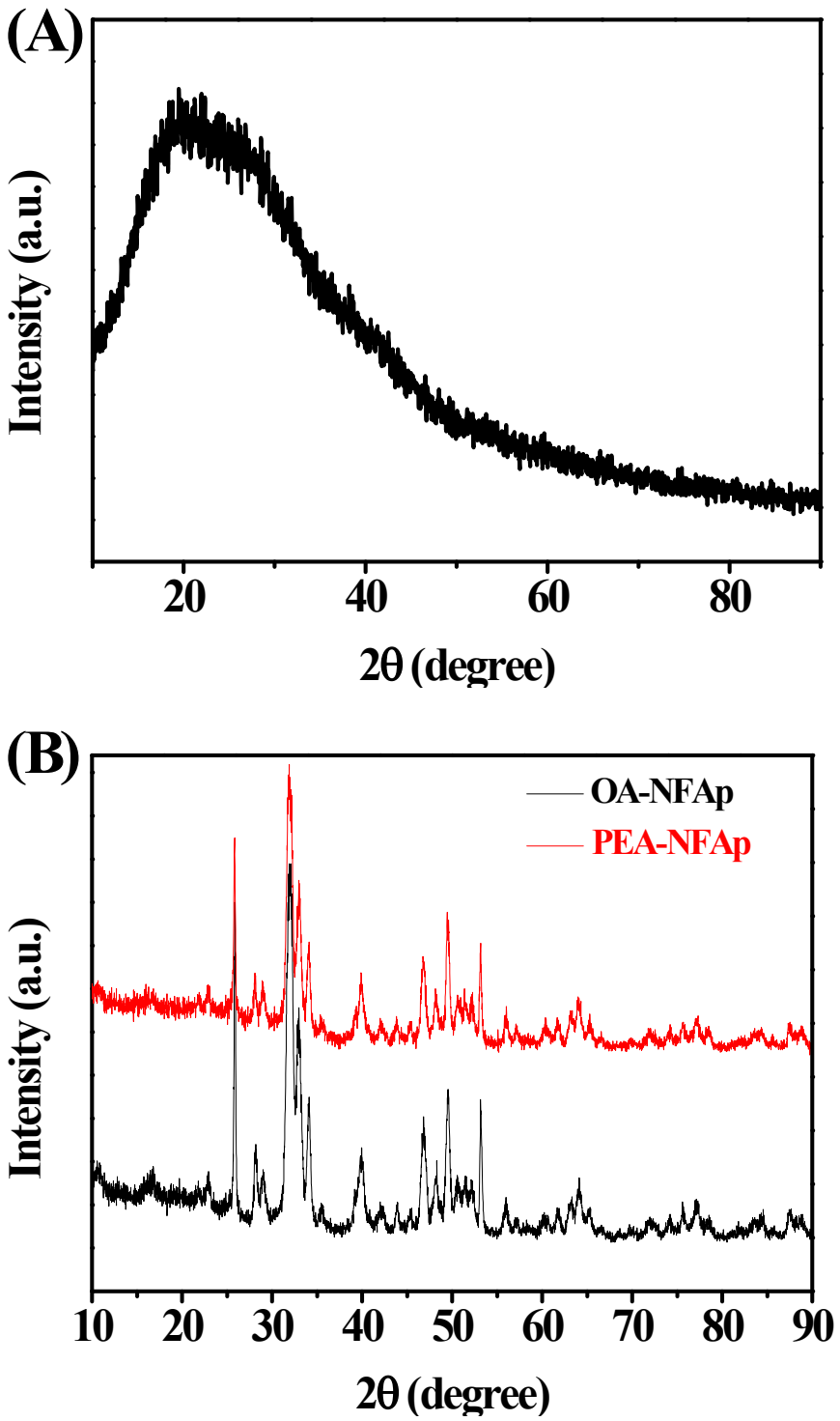


Figure S5. XRD pattern of the CDs-COOH (A); OA-NFAp and PEA-NFAp (B).

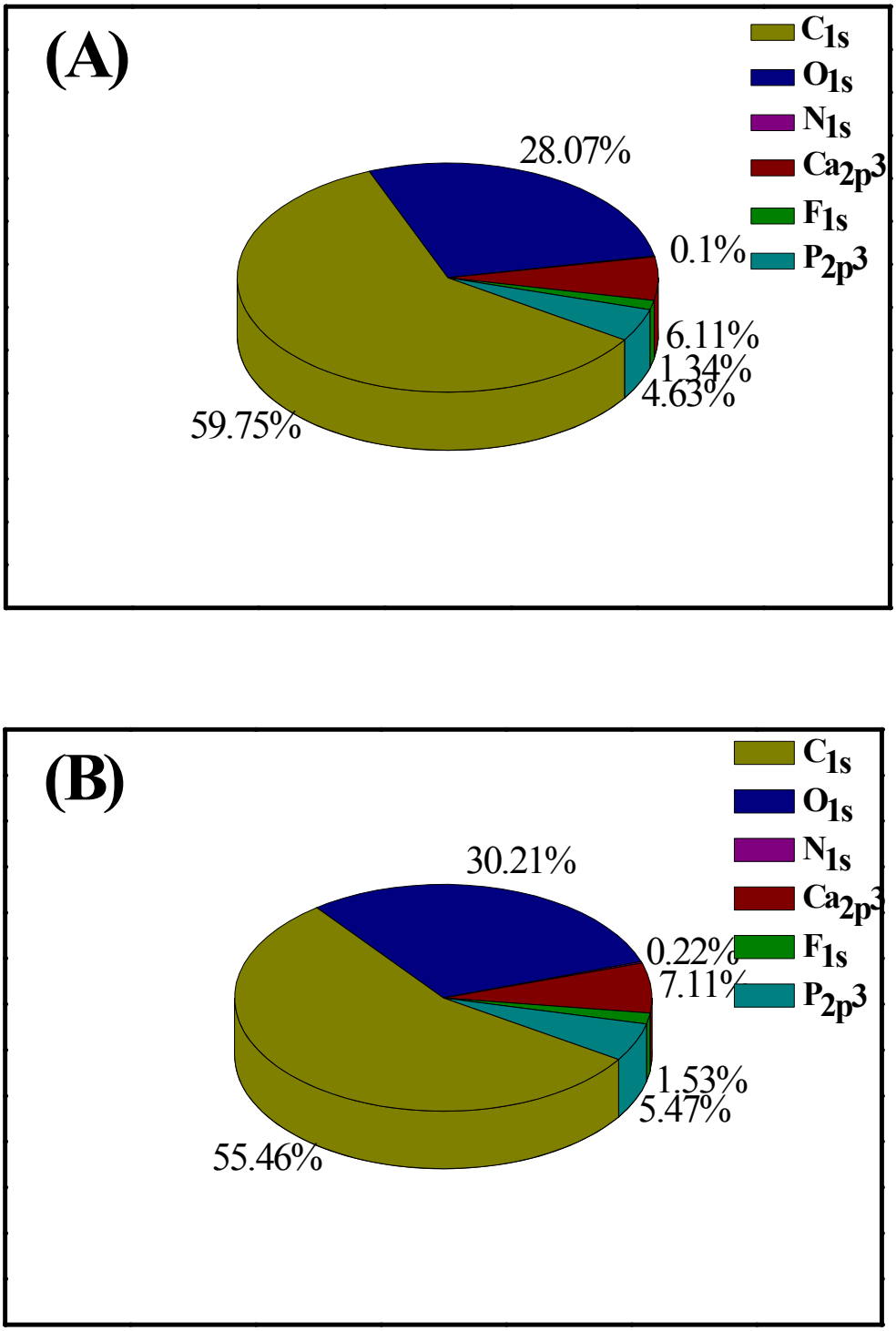


Figure S6. 3D color pie chart of element analysis (XPS) of OA-NFAp (A) and PEA-NFAp (B).

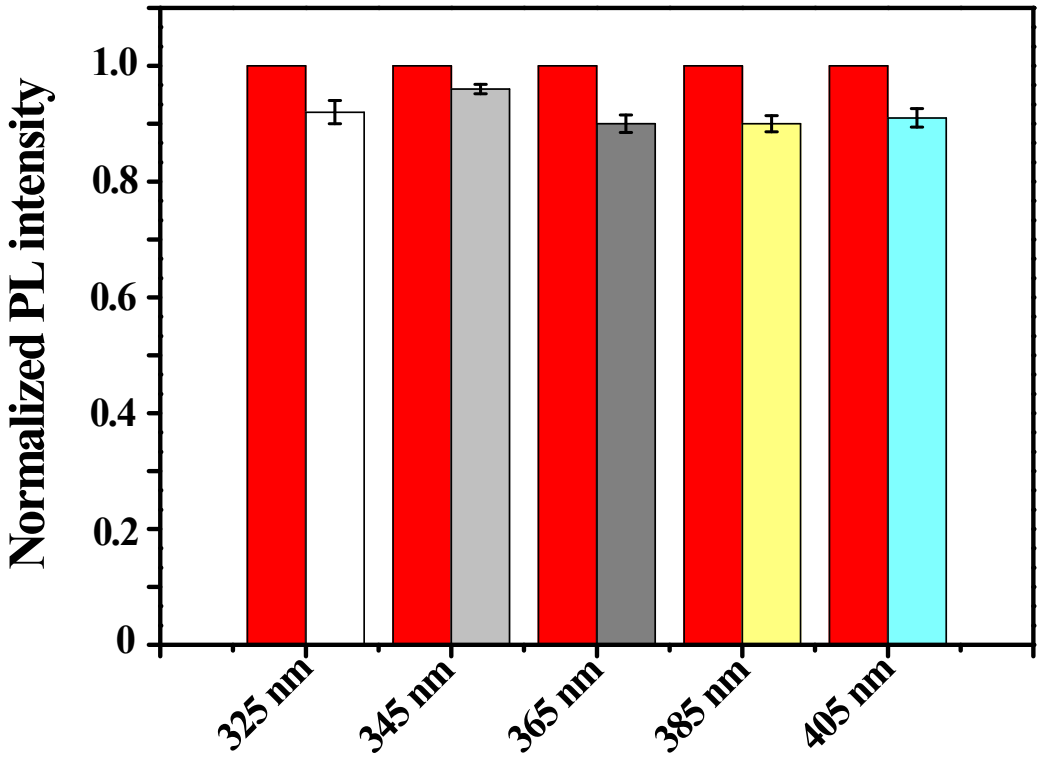


Figure S7. Photostability of CDs-COOH@PEA-NFAp conjugates irradiated with different excitation wavelengths (325, 345, 365, 385, 405 nm) over a period of 3 h. (red and other color bars represent normalized PL intensity before and after excitation, respectively.)

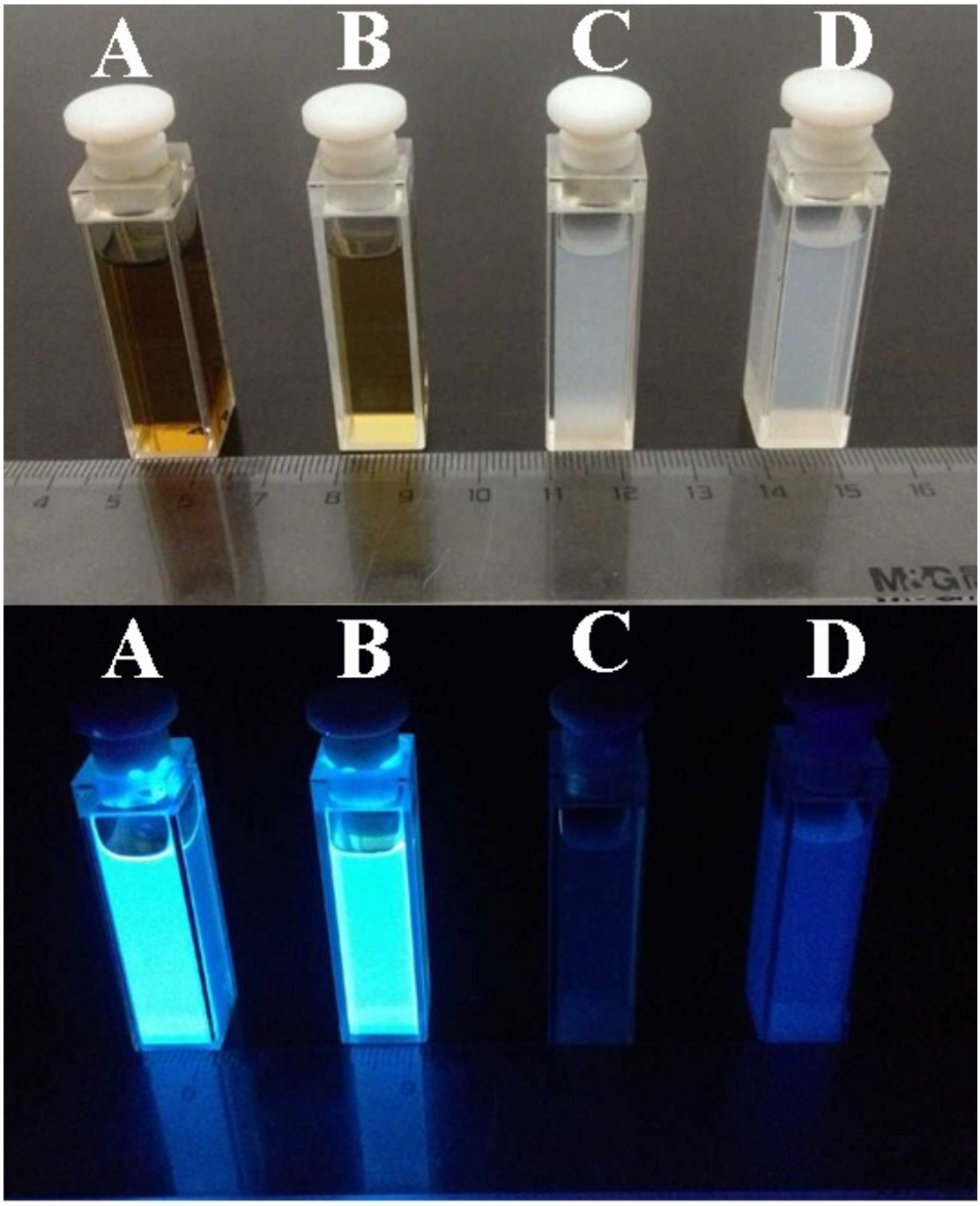


Figure S8. Bright-field photos and dark-field photos of CDs (A), CDs-COOH (B), PEA-NFAp (C), CDs-COOH@PEA-NFAp (D) under handhold UV Lamps at excitation wavelength 365 nm in Tris-HCl buffer solution.

Reference

S1. X. Wang, J. Zhuang, Q. Peng and Y. D. Li, *Adv. Mater.*, 2006, **18**, 2031-2034.