Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

A highly fluorescent nitrogen-doped carbon dots with excellent thermal and photo stability and applied as an invisible ink for loading important information and anti-counterfeiting

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Experimental Section

Materials

Citric acid monohydrate was purchased from Bejiing Chemical Works. Tri(hydroxymethyl)aminomethane (Tris) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Polyvinyl alcohol (PVA, MW: 1750±50) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized (DI)-water was provided by Changchun Institute of Applied Chemistry Chinese Academy of Chinese. All chemical reagents were used as received without any further purification.

Preparation of nitrogen doped-carbon dots (N-CDs)

Critic acid (1.054 g) and Tris (0.6084 g) were dissolved in 10 ml DI-water. Then, the solution was transferred into a 20 mL Teflon-lined stainless autoclave at 200℃ for 6 h. After the reaction, the reactor was cooled by running water. The crude product was dialyzed against de-ionized water in a membrane tube (molecular weight cut-off (MWCO) of 3500) for 48 h to remove weakly fluorescent large particles, and then the dialysate outside membrane tube was concentrated by the evaporation of water using rotary evaporation system. The concentrated sample was further dialyzed in a membrane tube (MWCO of 500) against de-ionized water to remove unreacted reagent and small molecular species, the nitrogen doped-carbon dots (N-CDs) were collected from sample inside membrane tube.

Preparation of N-CDs invisible ink

After dialysis treatment against MW 3500 and 500, respectively, the N-CDs invisible ink was fixed at a concentration of 4.1 mg/mL.

Preparation of N-CDs/PVA anti-counterfeiting film

1.2 g PVA was added into 18 mL DI-water, then the mixture was heated to 95℃. After the PVA was dissolved in water, 4.1 mg/mL N-CDs was added to the PVA solution under vigorous stirring. The obtained solution was used for preparing flexible-transparent N-CDs/PVA composite film by using our home-made instrument.

Characterization

Transmission electron microscope (TEM) analyses were performed on FEI Tecnai G^2 F20 microscope. Atomic force microscopy was recorded on Veeco Model D3100. X-ray diffraction (XRD) measurement was performed on a Bruker D8 Focus powder diffractometer with Cu-Kα radiation. Raman spectra were performed on Renishaw InVia Raman spectrometer using laser excitation at 514 nm. Fourier transform infrared (FT-IR) spectrum was recorded on a VERTEX 70 FT-IR spectrometer. Fluorescence emission spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. UV-Vis spectra were conducted on a Shimadzu UV-VIS-NIR 3600 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using PHI 5000 Versa Probe (ULVAC-PHI, Japan). The irradiant intensity on the tested samples from 250 W mecury lamp was measured by optical power/energy meter (Model 842-PE, Newport).

Fluorescence QY measurement

Fluorescence QYs of the as-prepared N-CDs were measured in accordance with a relative method. Quinine sulfate in 0.1 M H_2SO_4 (QY=54% at 350 nm excitation) was chosen as a reference. The QY of a sample was calculated according to the following equation[1]:

$$\phi_{\mathrm{x}} = \phi_{\mathrm{Re}\,f}\left(\frac{I_x}{I_{\mathrm{Re}\,f}}\right)\left(\frac{A_{\mathrm{Re}\,f}}{A_x}\right)\left(\frac{\eta_x^2}{\eta_{\mathrm{Re}\,f}^2}\right) \tag{1}$$

Where ϕ is the fluorescence quantum yield of the tested sample, I is the integrated emission intensity, A is the optical density, and η is the refractive index of solvent. The subscripts “x” and “Ref” refer to the tested sample and reference fluorescence dye, respectively. QY was determined by slope ratio calculated from the linear regression of integrated PL intensity *vs* absorbance. In order to minimize the re-absorption effects, the absorbance of the as-prepared N-CDs aqueous and reference fluorescence at excitation wavelength were kept under 0.1.

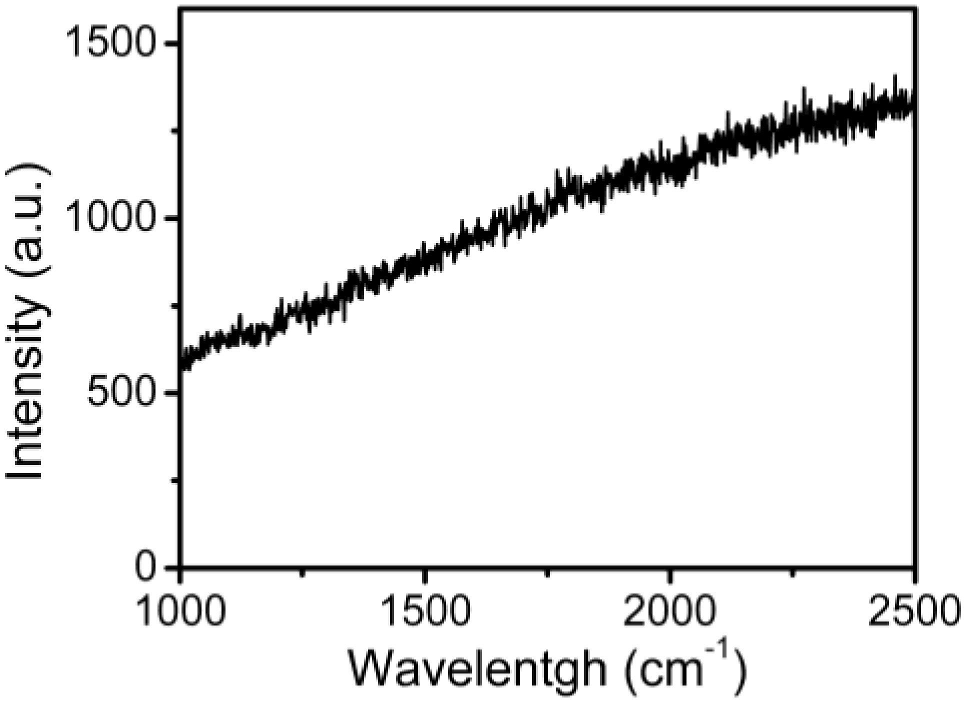

Fig. S1 Raman spectra of N-CDs.

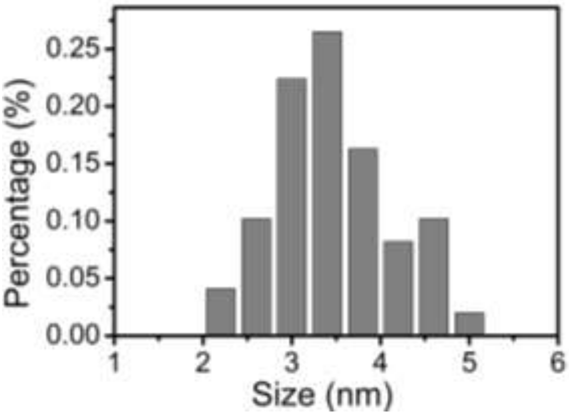

Fig. S2 Histogram of particle size distribution of N-CDs.

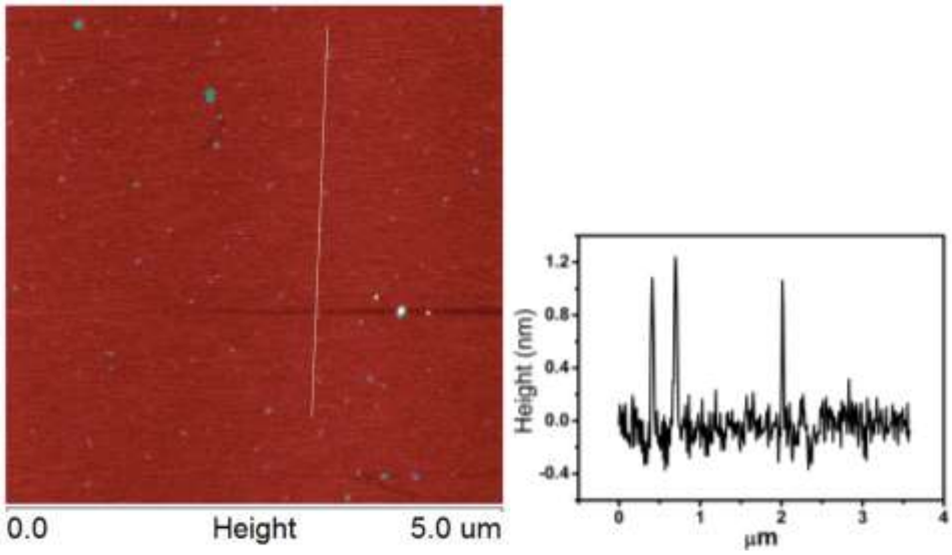

Fig. S3 AFM image of N-CDs

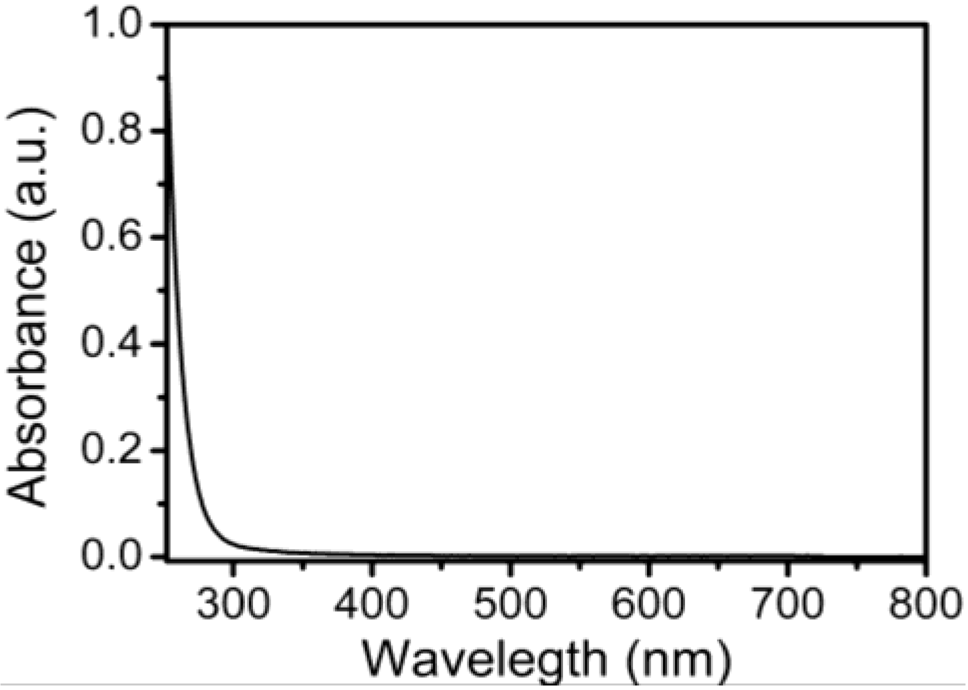

Fig. S4 Absorption spectra of CA under hydrothermal treatment of 200℃ for 6 h.

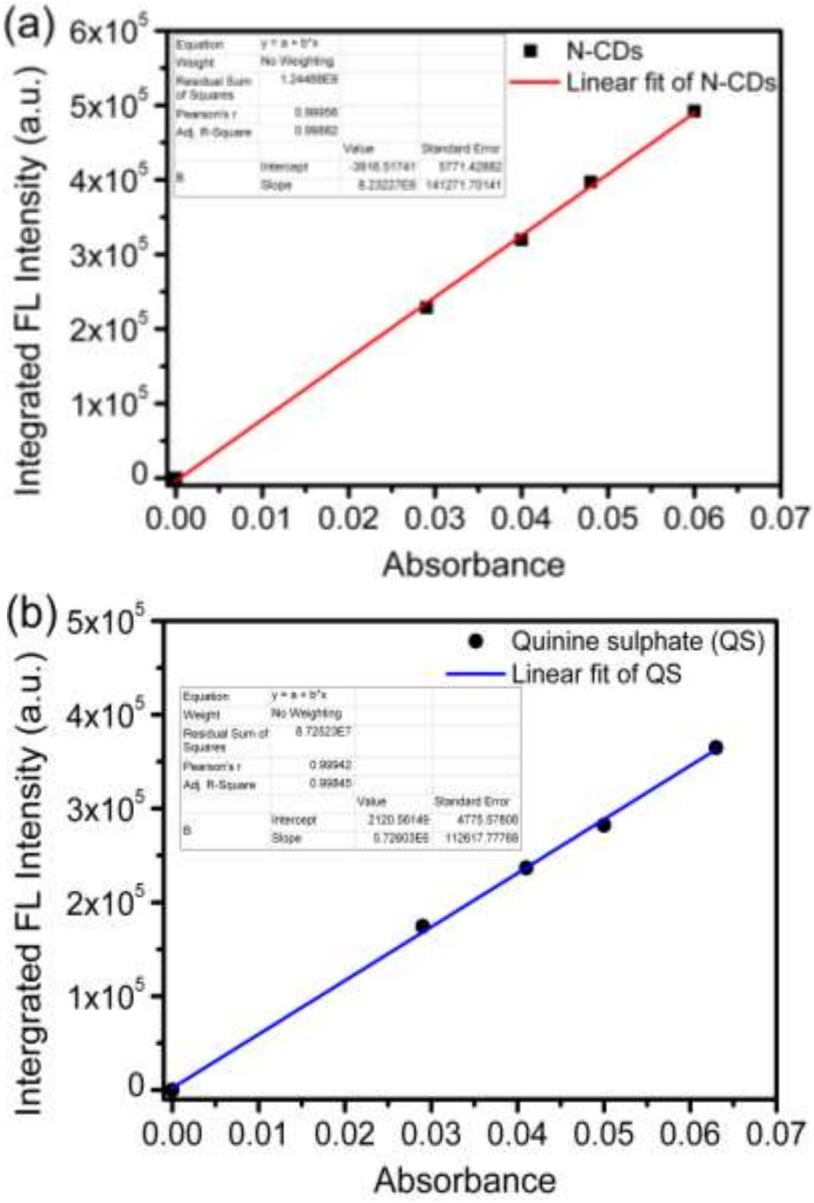

Fig. S5 Plots of integrated FL intensity of (a) N-CDs and (b) referenced quinine sulfate as a function of absorbance at 350 nm.

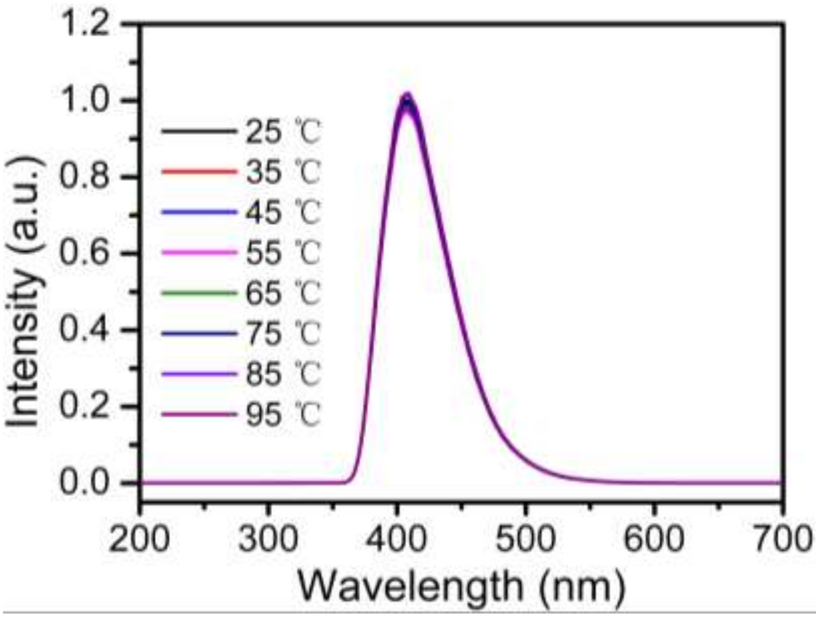

Fig. S6 Fluorescence intensity of N-CDs at testing temperature range from 25 to 95℃.

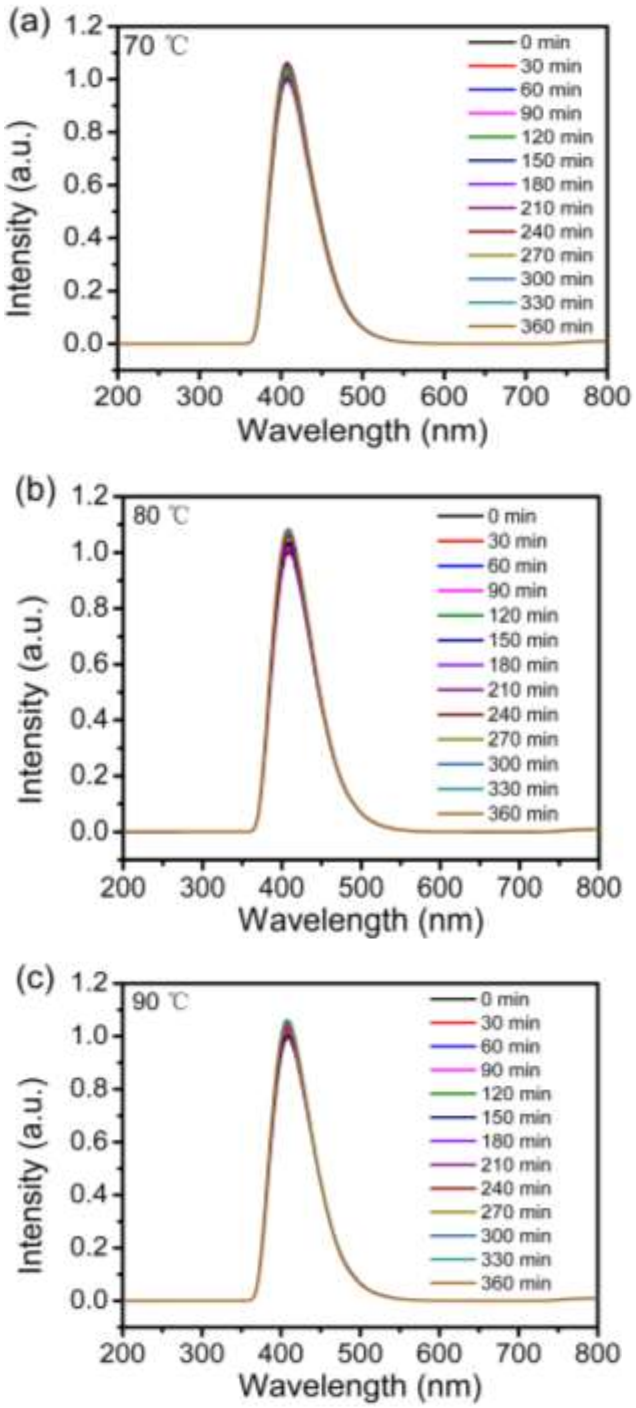

Fig. S7 Fluoresce intensity of N-CDs at fixed temperature (a) 70℃, (b) 80℃ and (c) 90℃ for testing time of 360 min.

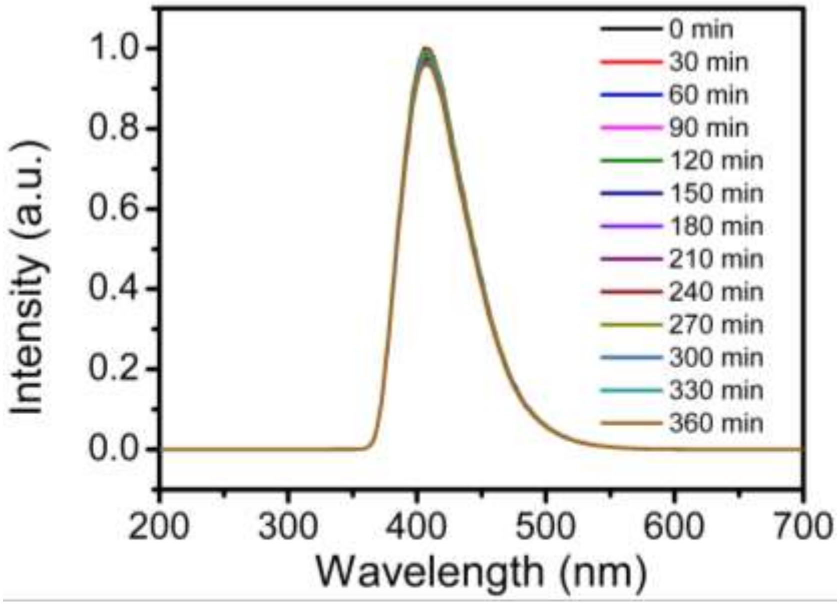

Fig. S8 Fluorescence intensity of N-CDs exposed to 20 mW/ cm^2 UV illumination from 250 W mecury lamp for testing time of 360 min.

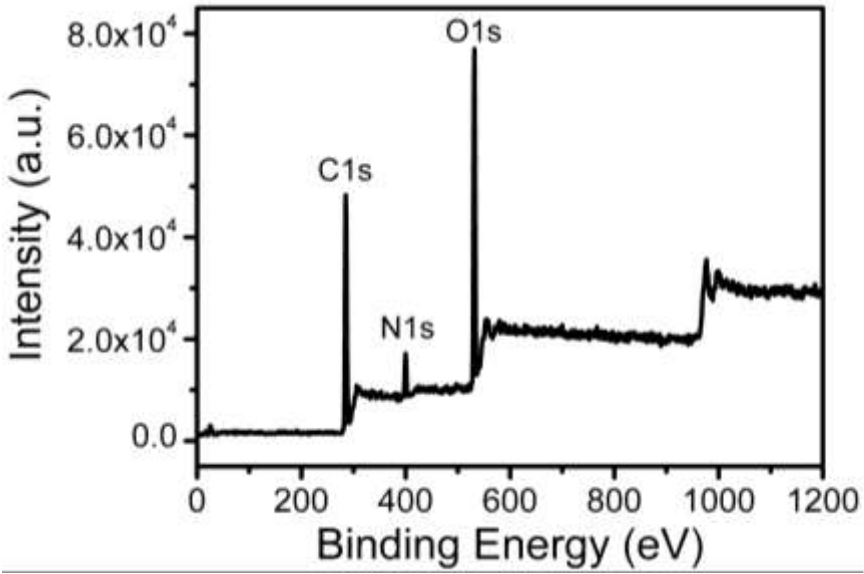

Fig. S9 The XPS spectra of N-CDs.

Table S1 Elemental composition of N-CDs by XPS spectra

C (At %)	N (At %)	O (At %)
63.47	6.06	30.47

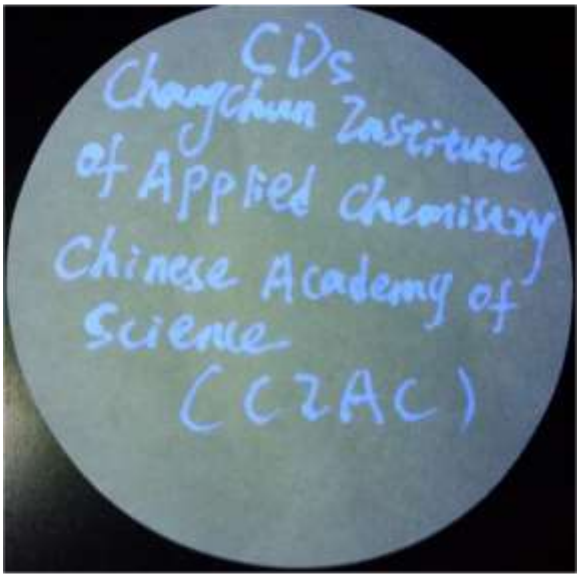

Fig. S10 The reproducibility of the information loaded on commercial filter paper under 365 nm hand-held UV lamp for 90 days storage under ambient air.

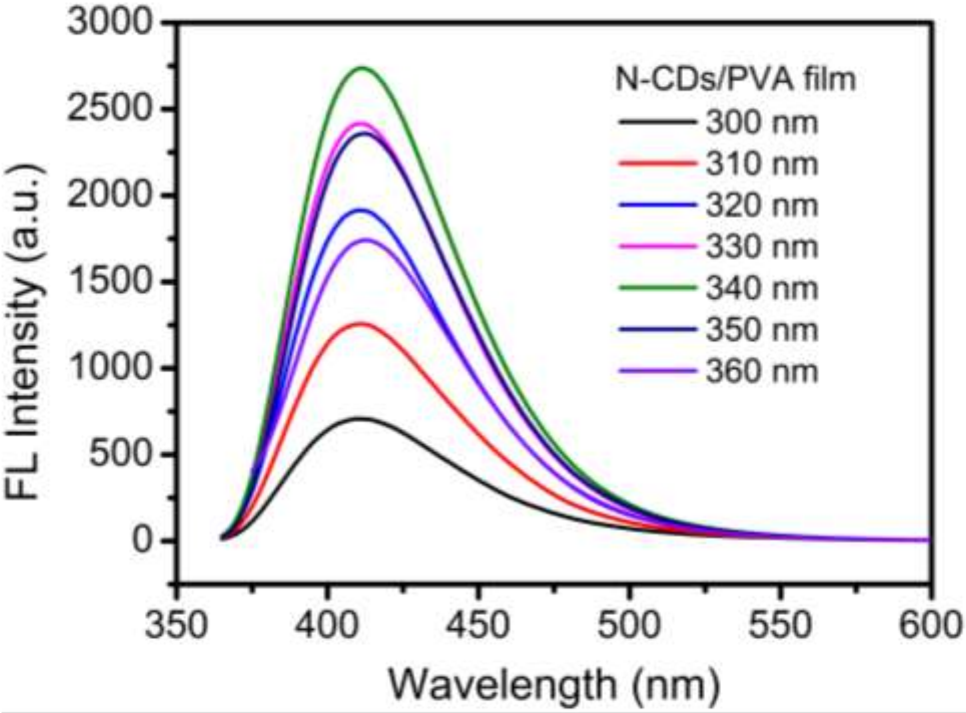

Fig. S11 Fluorescence emission spectra of N-CDs/PVA film under different excitation wavelength.

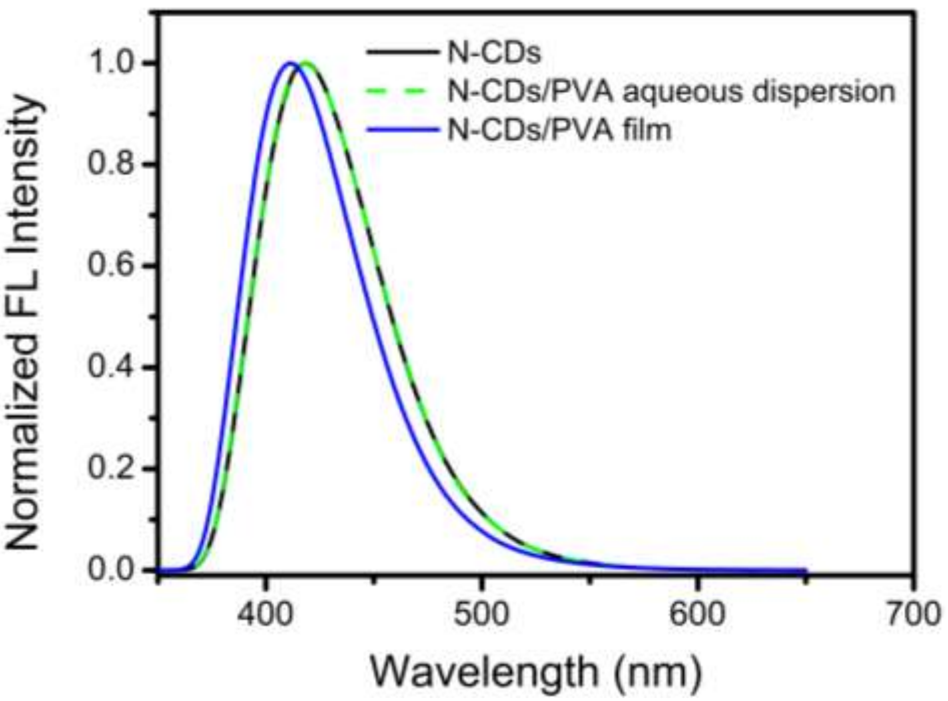

Fig. S12 Fluorescence spectra of N-CDs aqueous solution, N-CDs/PVA aqueous dispersion and N-CDs/PVA film.

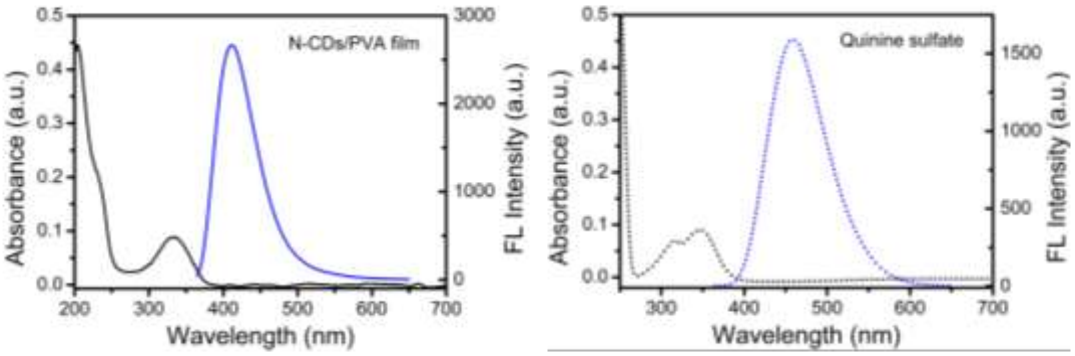

Fig. S13 Absorption and fluorescence spectra of N-CDs/PVA film and quinine sulfate for determining QY of N-CDs in PVA film.

Table S2 The result of quantum yield of N-CDs/PVA film

Sample	Absorbance	Integrated FL intensity	η	QY
N-CDs/PVA film	0.89	189904	1.52	0.92
Quinine sulfate	0.91	142003	1.33	0.54

References:

1. M. Grabolle, M. Spieles, V. Lesnyak, N.Gaponik, A. Eychmüller and U. Resch-Genger, *Anal. Chem.* 2009, **81**, 6285.