Supplementary Information (SI) for Nanoscale.

Supplementary Information

Multi Emissive Graphene Oxide Quantum Dots Showing Remarkable pH Responsive Long Wavelength Emission

Indrani Chakraborti[a], Udayan Basak[b], Subhadip Roy[c], Mahuya Pakhira[b], Arindam Das[a] and Dhruba P. Chatterjee[a]*

[a]Department of Chemistry, Presidency University, 86/1 College Street, Kolkata-700073, India

[b]School of Material Sciences, Indian Association for the Cultivation of Science, Raja S.C. Mullick Road, Jadavpur, Kolkata-700032

[c]Polymer Research Centre, Centre for Advanced Functional Materials, DCS, IISER Kolkata, Campus Rd, Mohanpur, Haringhata Farm, West Bengal 741246

*****Correspondence to: Dhruba P. Chatterjee (E-mail: ***dhruba.chem@presiuniv.ac.in*****)**

Preparation of PVA-GOQD Film

In this method 0.5 g of PVA was added in 5 mLof 10^{-2}(M) of HCl solution heated at 100°C for 30 minutes with constant stirring. After this 20 mg of solid GOQD was added to the reaction mixture. Then the mixture was put into petri-dish and allowed to dry at room temperature.

Preparation of PVA-GOQD gel

In this method 0.2 g of PVA was dissolved in 2 mL 0.0631(M) of NaOH solution heated at 100°C for 30 minutes with constant stirring. After this 8 mg of solid GOQD was added to the reaction mixture.The viscous solution was subjected to repetitive heating-cooling (in ice water) cycles before gel formation.

Characterization:

UV-Visible absorption Experiments

UV-Visible absorption measurements were carried out in Hewlett-Packard, model 8453 spectrometer. Aqueous GOQD solutions (2 mL) having concentration 0.1 mg/mL at different pH values were used in a typical quartz cuvette with a path length of 1 cm. During analysis of the effect of electrolyte, adequate amount of solid $NaNO_3$ was added in the above solutions to reach a concentration of 0.072 (M) at various pH values. The experiments were carried out at 298 K.

Photoluminescence Spectroscopy

Photoluminescence spectra of aqueous GOQD solution (1mg/mL) at different pH were recorded on a Horiba-JobinYvon Fluoromax-3 instrument using a four face transparent quartz cuvette of 1 cm path length. The excitation and emission slit width 2/2 with an increment of 1 nm wavelength having an integration time of 0.1 s. For excitation dependent emission spectral analysis, excitation wavelength were varied in the range of 300 nm to 640 nm. Similarly for excitation dependent solid state fluorescence the PVA-GOQD film was placed in a quartz surface by keeping the same excitation, emission wavelength and slit width. PL spectra of solid state were recorded in front-face geometry. For concentration dependent fluorescence measurement at pH 12.8, 2 mg GOQD was dissolved in 2 mL 0.0631 (M) NaOH solution for getting 1 mg/mL concentration which was subsequently diluted with the 0.0631 (M) NaOH solutions to get the lower concentrations. For salt added fluorescence measurement, adequate amount of different salts (NaCl, KCl, $NaNO_3$, Na_2SO_4, $MgCl_2$, $CaCl_2$) in solid form was added to reach concentration of 0.075 (M) in 2 mL (1 mg/mL) GOQD solution at different pH. The experiments were carried out at 298 K.

Photoluminescence quantum yield measurements

The relative PL quantum yield (QY) of GOQD solution at pH 12.8 was measured by using Rhodamine B (QY = 0.31 at λ_{em} 567 nm in water) [*J. Res. Natl. Inst. Stand. Technol.* 2008, **113**, 17-28] as a standard for the fluorescence quantum yield measurement. The concentration of GOQD solution was chosen 0.5 mg/mL with optical density value matching with that of the reference dye. Fluorescence quantum yield was estimated by this known reference quantum yield value using the following equation

$$QY_{Sample} = QY_{Std} \times [\frac{I_{Sample}}{A_{Sample}} \times \frac{A_{Std}}{I_{Std}}] \times \frac{\eta^2_{Sample}}{\eta^2_{Std}}$$

Where 'A' is the absorbance at excitation wavelength. All the measurements were carried out in dilute aqueous solutions therefore, the η_{Sample} and η_{Std} were assumed to be the refractive index of water. 'I' is the integrated area under the fluorescence emission curve at the same excitation wavelength. The details of the calculation is presented as below:

Sample	Integrated emission intensity (I)	Abs. at 555 nm (A)	Refractive index of the solvent (η)	Quantum Yield (QY)
Rhodamine B	179644	0.1103	1.33	0.31
GOQD	163744	0.1046	1.33	0.2979

The determination of the absolute PLQY of the GOQD-PVA composite film (containing 4% w/w GOQD)(casted at pH 2) and corresponding casting solution were conducted in FLS1000 photoluminescence spectrometer from Edinburgh Instruments under an optimal excitation wavelength. Absolute quantum yields were measured in an integrating sphere.

Transmission Electron Microscopy (TEM) study

The morphology of GOQDs at different pH was measured by HRTEM instrument (JEOL, 2010EX) operated at an acceleration voltage of 200kV and fitted with a CCD camera. The specimen for TEM study was made by spreading a small drop of aqueous solution of GOQD at different pH on Carbon-coated copper grid and allowing the drops to dry in air at 30°C and finally preserved at vacuum for 2 days.

Fourier Transform Infrared Microscopy (FTIR)

The FTIR spectra of dried GOQD's at different pH were made from KBr pellets of the samples in a Perkin-Elmer FTIR (FT-IR-8400S) instrument.

Dynamic light Scattering (DLS) Experiment

The DLS experiment and Zeta-potential of GOQD solution were performed by using Malvern instrument with a He-Ne laser of 632.8 nm at an angle of 173°. For pH-dependent DLS measurement, a series of GOQD solutions having concentration (1mg/mL) at different pH values were made. Similarly, measurement was also carried out with different $NaNO_3$ concentrations at pH 12.8 of aqueous GOQD solution/dispersion. All DLS experiments were carried out at 298 K.

Time-correlated Single–Photon-Counting (TCSPC) measurements

Time-resolved luminescence decay experiment were recorded on Edinburgh Instruments (Model: FLS1000-DD-STM). The samples of different pH were excited with 475 nm laser probe. The excited-state decay of the samples were collected by fixing the emission wavelength at a particular wavelength in the range of 470-630 nm. The decay curves were fitted in a triexponential decay function according to the following decay equation,

$$I(t) = \sum_{i=1}^{i=3} A_i e^{-t/\tau_i}$$

Where τ_i is the decay time and $A_i$represents amplitude of the corresponding decay.

X-ray Photoelectron Spectroscopy (XPS)

XPS analysis of the GOQD sample was performed by usingOmicron Nano Technology (model 0571) XPS spectrometer, using an aluminium anode and anAl Kα X-ray source (1486.8 eV).

Cyclic voltammetry experiments (CV)

Cyclic voltammetry (CV) were done by a CHI6087E electrochemical workstation (CHI, USA) by conventional three electrode systems.

Electrode fabrication and electrochemical measurements

Glassy carbon electrodes (GCE) (3 mm in diameter, surface area of 0.07 cm^2) are carefullypolished with 1, 0.3, and 0.05 μm alumina powder and sequentially washed through water andethanol with sonication at room temperature until a mirror finish was obtained before use. Here two working electrodes were prepared. First one by dissolving GOQDs in deionised water with the addition of Carbon black and Nafion in 2:1:1 weight ratio and the other one was devoid of GOQD in water medium. Then 5μL of both thesolutions (5 wt% in water) were drop-casted onto Glass Carbon Electrode. The coating is thendried in a vacuum oven at 60ºC for about 24 hours and subsequently electrochemical measurements are carried out in 0.1(M) H_2SO_4 medium. The casted electrode is used as the working electrode, Ag/AgCl as reference electrode and a Pt wire is used as counter electrode during measurement in three electrode cell configuration. CV curves were determined with the scan rate of 10 mV/s from 0 V to 1 V. Same procedure was followed for CV measurement in absence of GOQD.

Fabrication of GOQD doped PVA film for pc-LED:

Fabrication of phosphor converted pc-LEDs and related measurements: Commercially available InGaN chips (power = 3W, λ_{EL}= 390nm, VF = 3.1 V) were purchased from Amazon, India. 100 mg of PVA were dissolved in 1 mL of 0.0631(M) NaOH solutionand the mixture was heatedat 100^{o}C for 30 minutesunder stirring conditions. Thereafter, 4 mg of solid GOQDwas added to the PVA solution and 0.25 mL of the resulting solution was used for drop-casting on quartz substrate. The quartz substrate was then kept under high vacuum beforephotophysical studies.The emitted radiations were recorded in the FLS1000 photoluminescence spectrometer from Edinburgh Instruments.

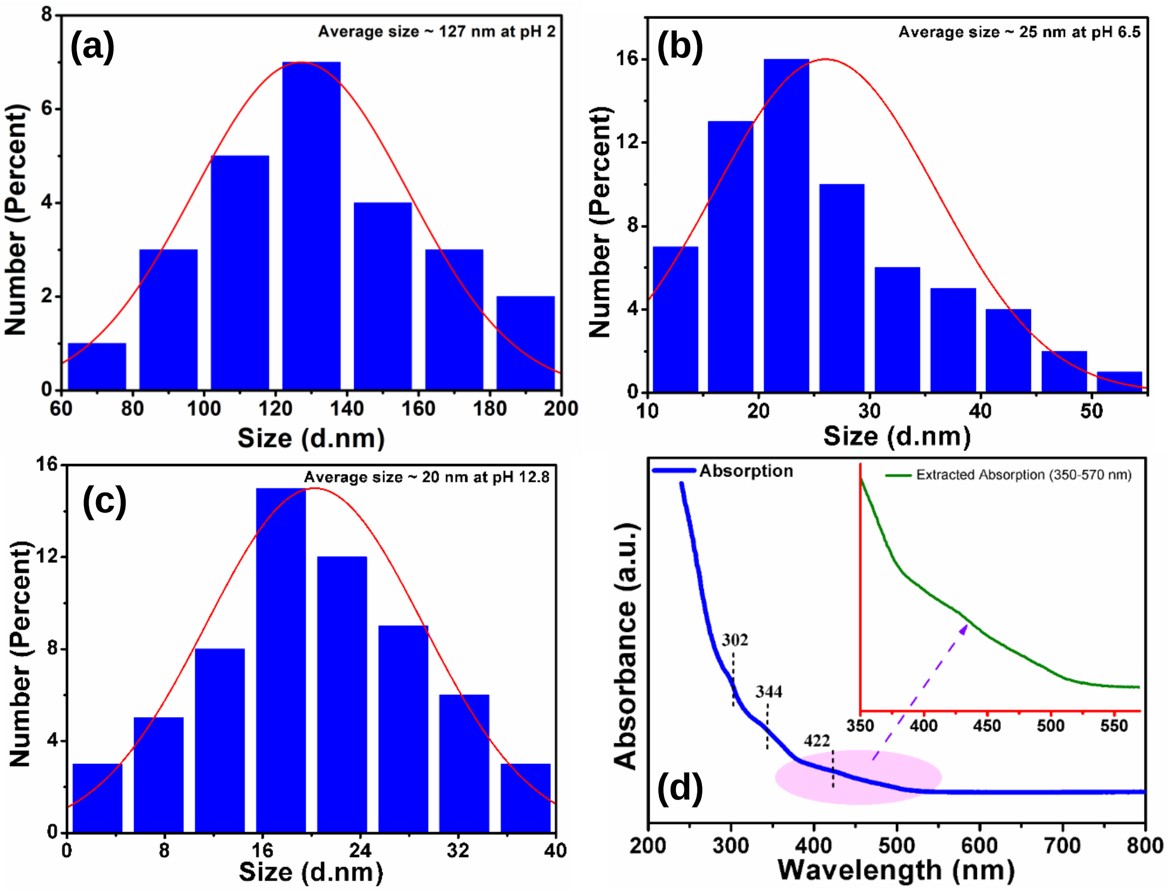

Fig. S1. Dynamic Light Scattering analysis of aqueous GOQD solutions (1 mg/mL) at a) pH 2, b) pH 6.5 and c) pH 12.8; (d) *absorption spectrum of aqueous GOQD at pH 2 (the inset shows expansion of the region in between 350-570 nm).*

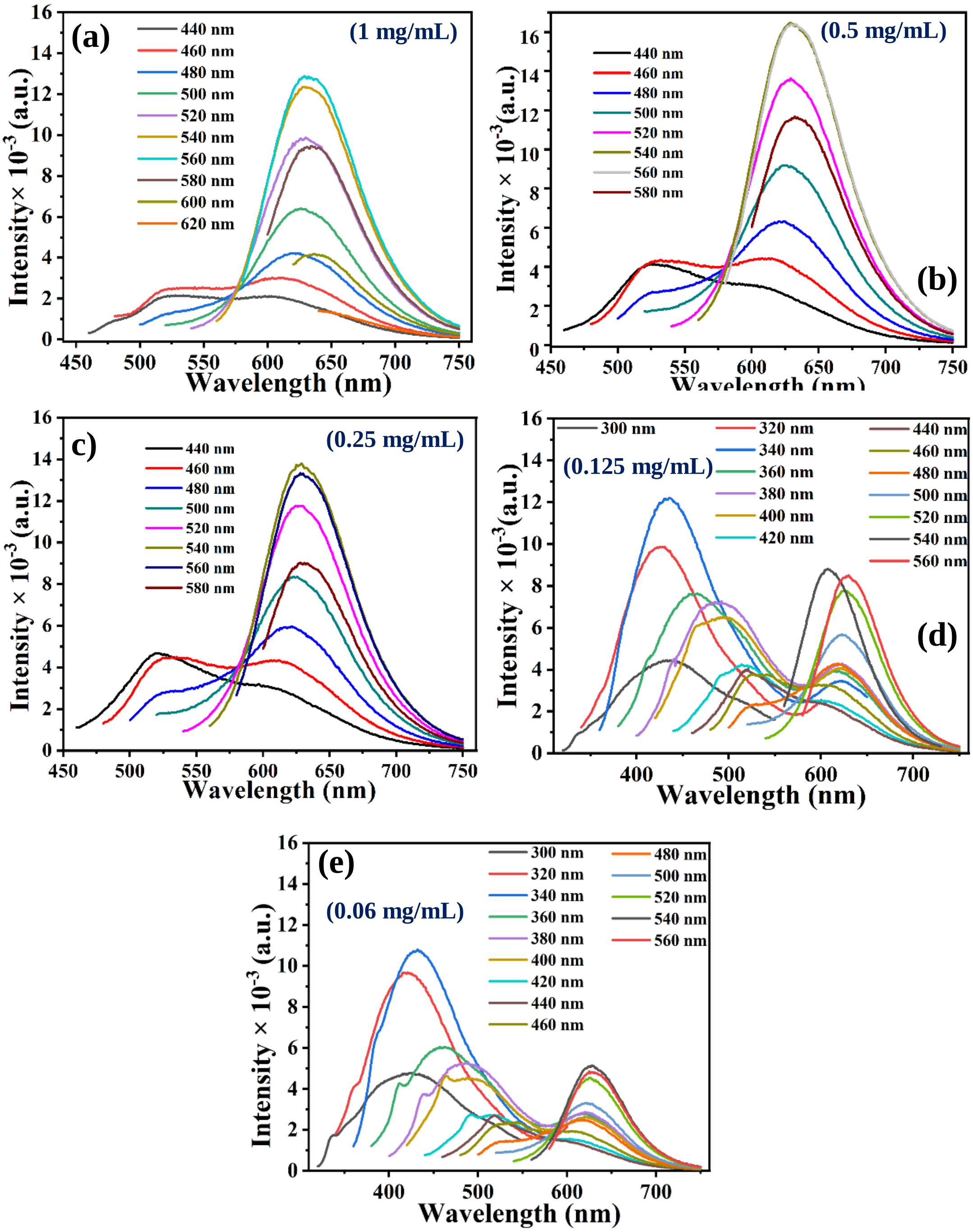

Fig. S2. PL spectra at pH 12.8 at concentrations (a)1 mg/mL, (b) 0.5 mg/mL, (c) 0.25 mg/mL, (d) 0.125 mg/mL and (e) 0.06 mg/mL.

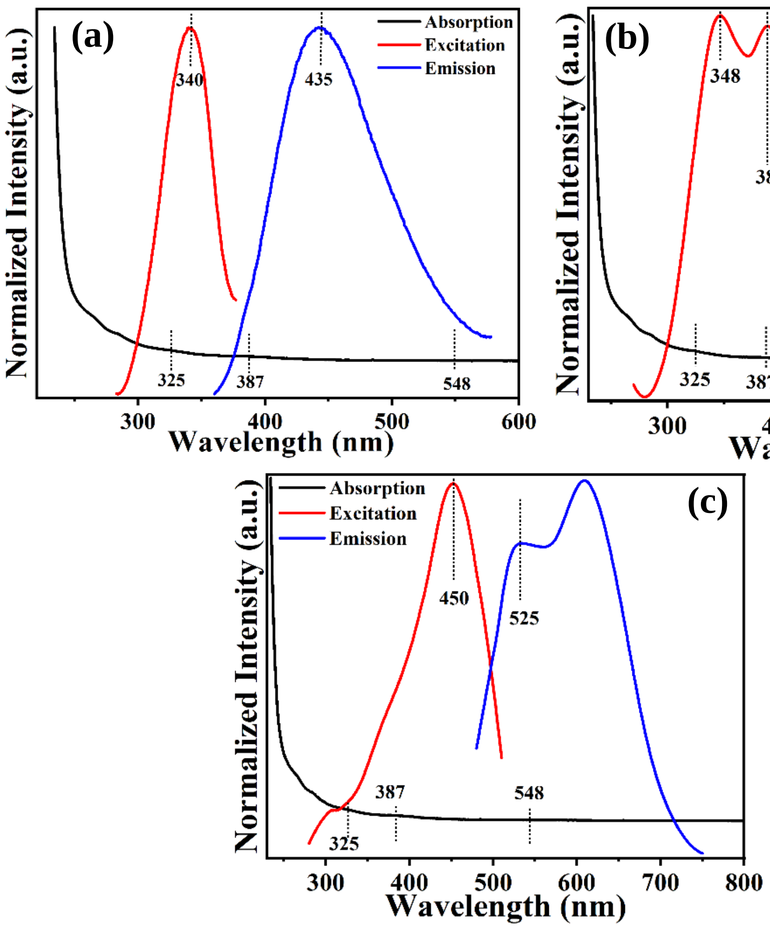

Fig. S3. Overlay of absorption, emission and excitation spectra for the emissions at 435 nm, 490 nm and 525 nm.

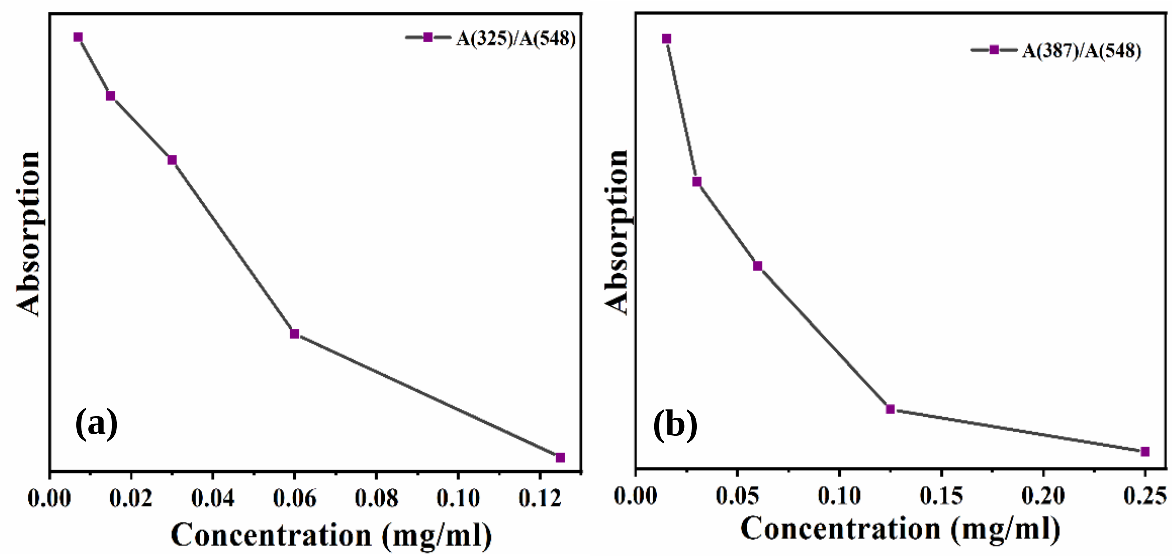

Fig. S4. Variation of absorbance ratios with concentration: Ratio of (a)absorbance at 325 nm with 548 nm and (b) absorbance at 387 nm with 548 nm.

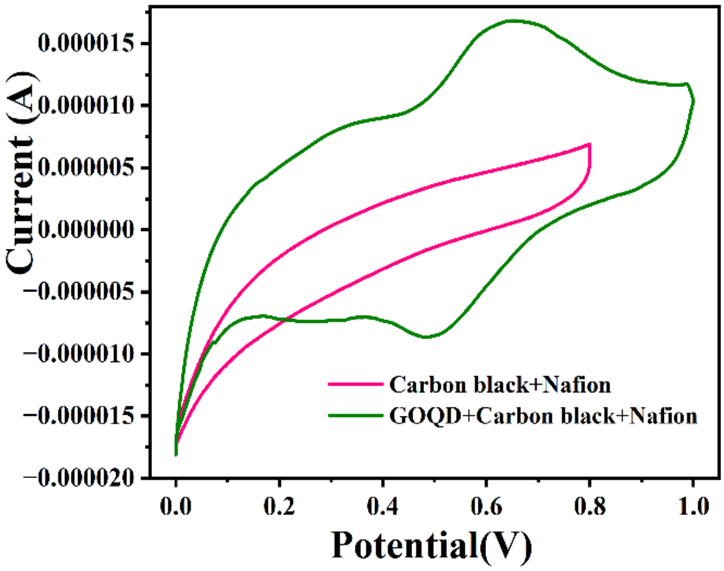

Fig. S5. Cyclic voltametric analysis of GOQD/carbon black composite and carbon black only. Both scans are run in 0.1 M H_2SO_4 with 10mV/s scan rate, with Ag/AgCl as reference electrode.

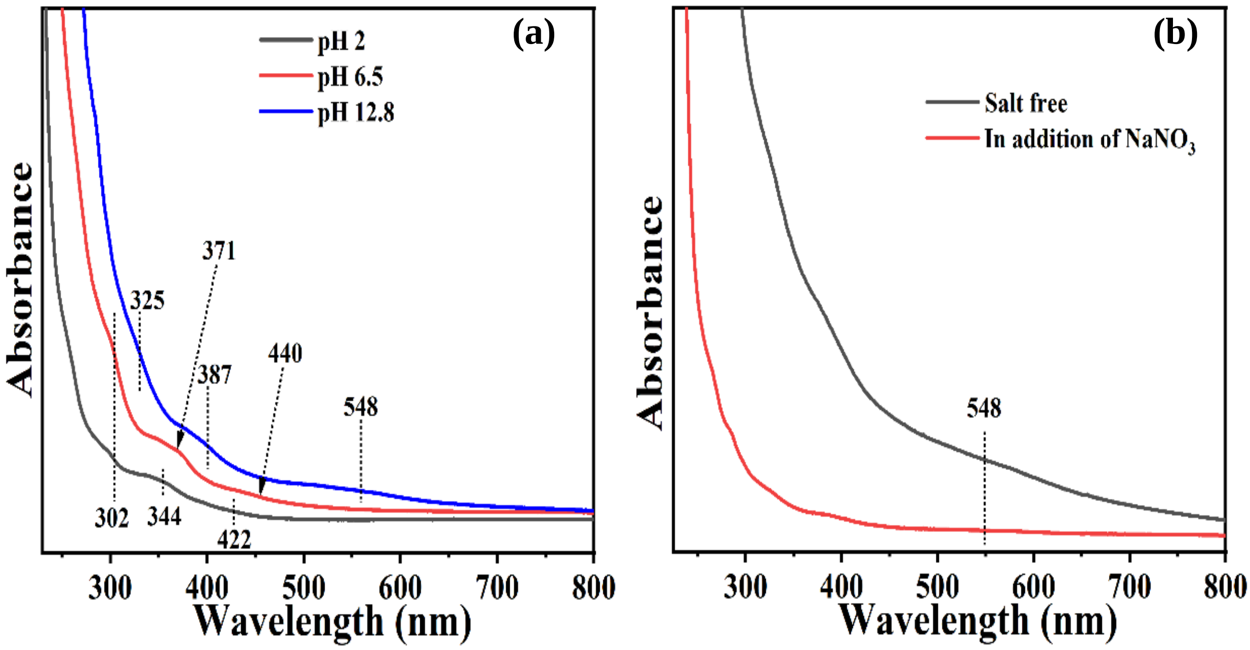

Fig. S6.(a) UV-visible absorption spectra of aqueous GOQD in presence of 0.075 (M) $NaNO_3$ at different pH values (b) UV-visible spectral overlay of aqueous GOQD in presence and in absence of 0.075 (M) $NaNO_3$ at pH 12.8.

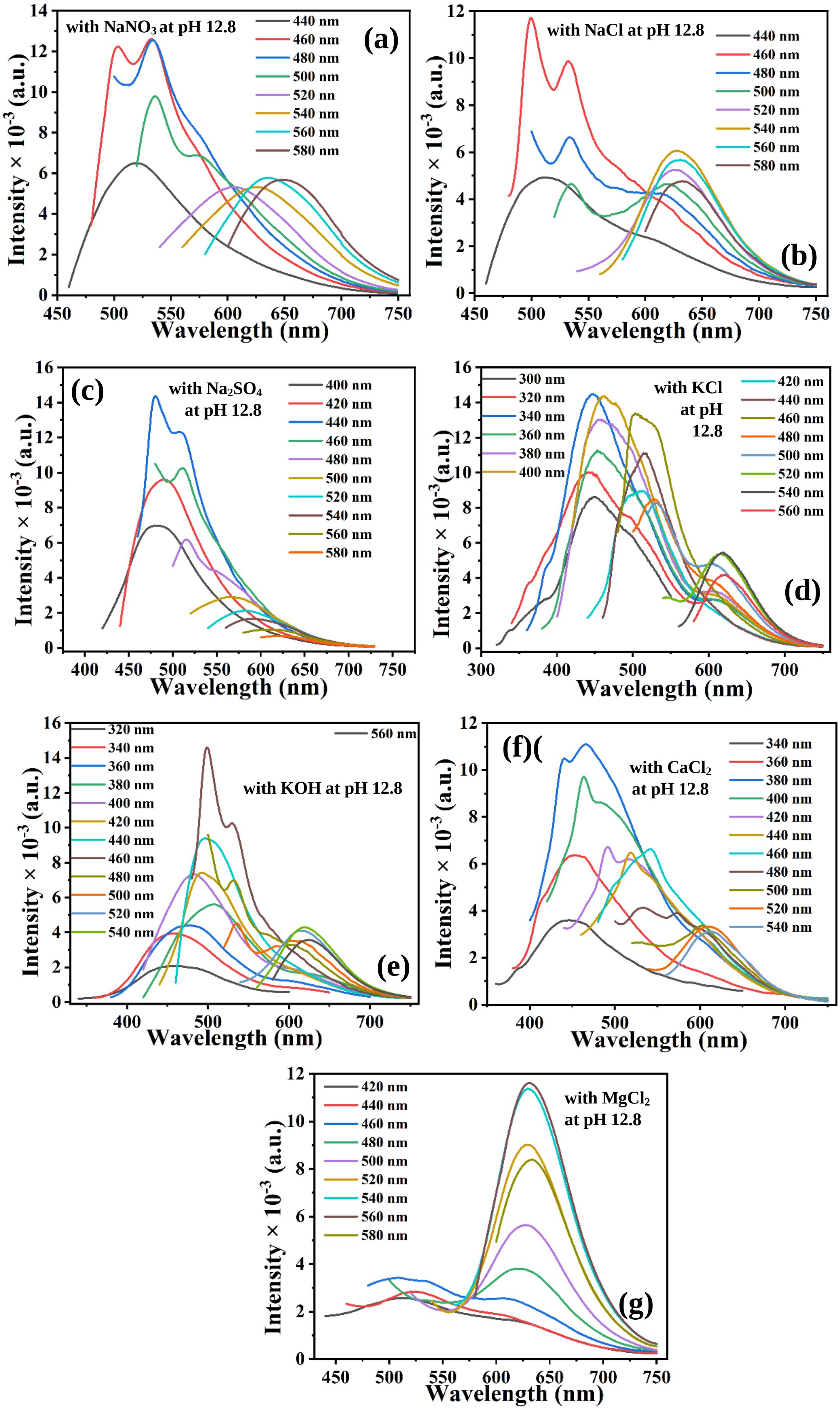

Fig. S7. Effect of salt at pH 12.8 (a) NaNO$_3$, (b) NaCl, (c) Na$_2$SO$_4$, (d) KCl, (e) KOH (f) CaCl$_2$ and (g) MgCl$_2$.

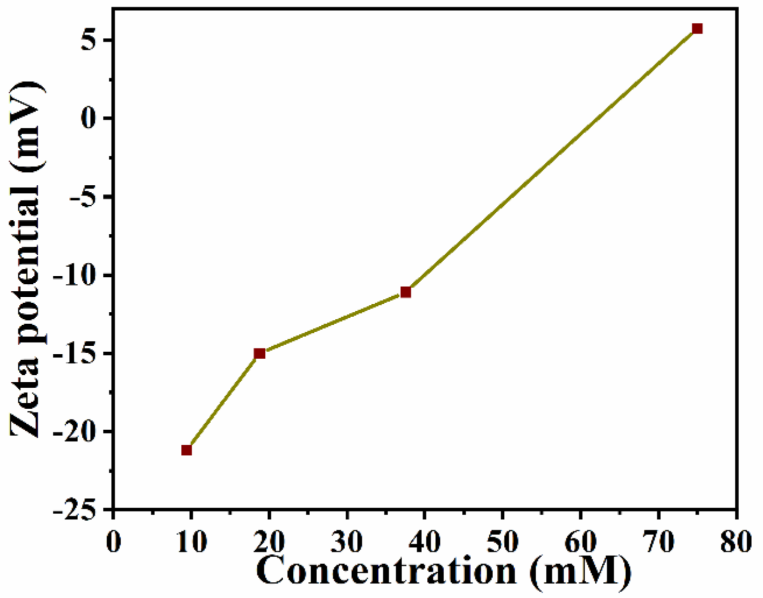

Fig. S8. Variation ofzeta potential of aqueous GOQD solution at pH 12.8 with increasing concentration of $NaNO_3$.

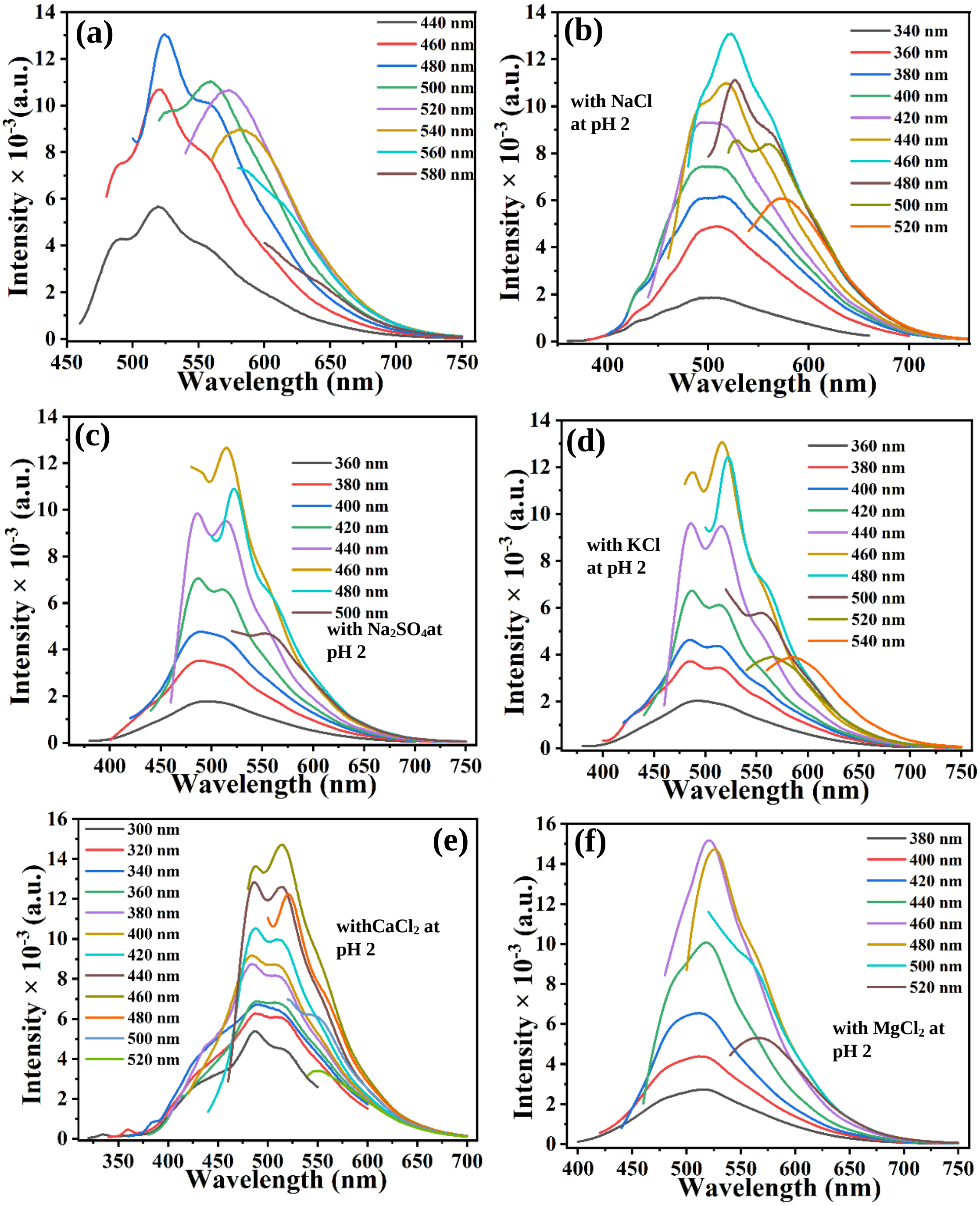

Fig. S9. Effect of salt 0.075 (M) at pH 2 (a) $NaNO_3$, (b) NaCl, (c) Na_2SO_4, (d) KCl, (e) $CaCl_2$ and (f) $MgCl_2$.

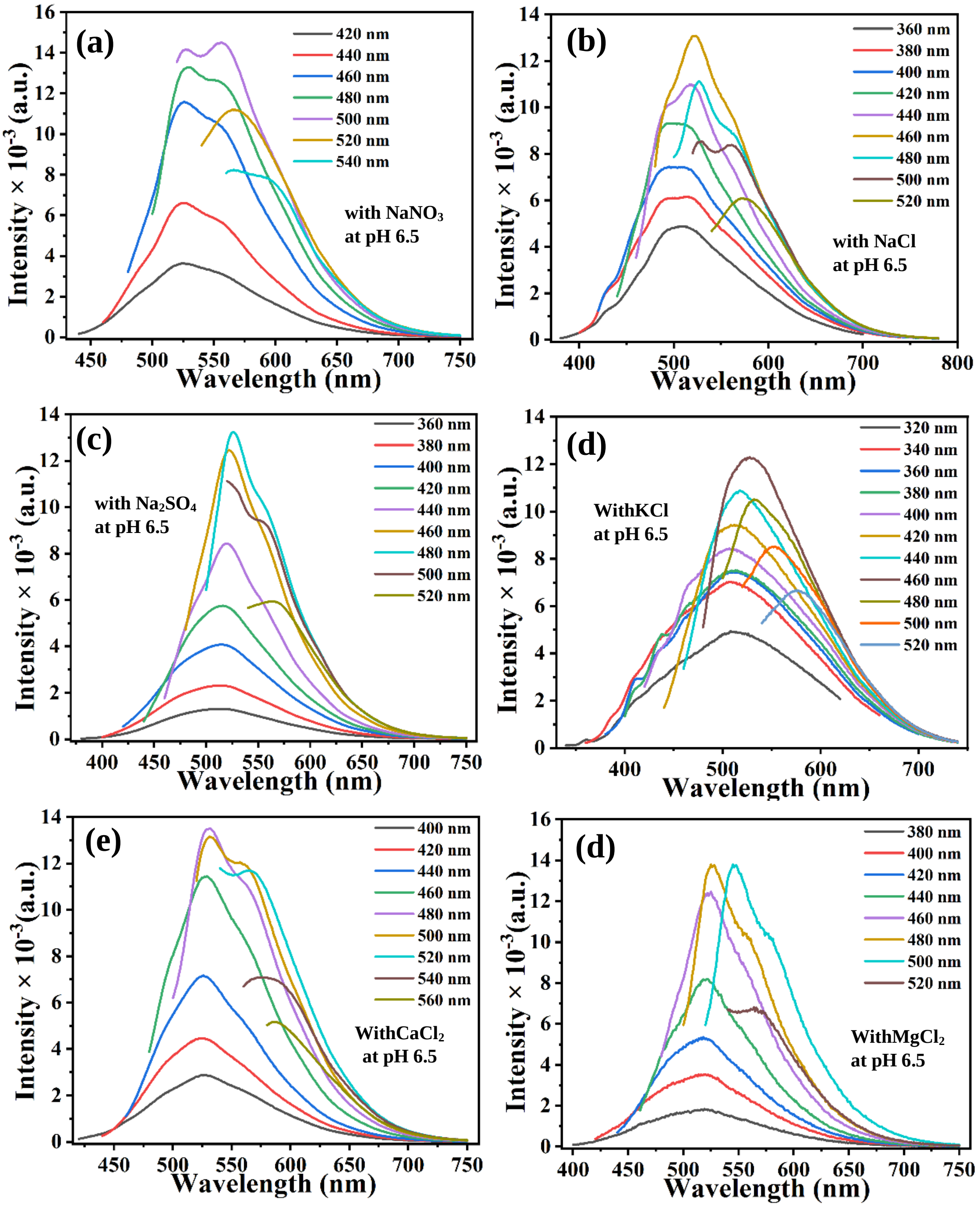

Fig. S10. Effect of salt 0.075 (M) at pH 6.5 (a) $NaNO_3$, (b) NaCl, (c) Na_2SO_4, (d) KCl, (e) $CaCl_2$and(f) $MgCl_2$.

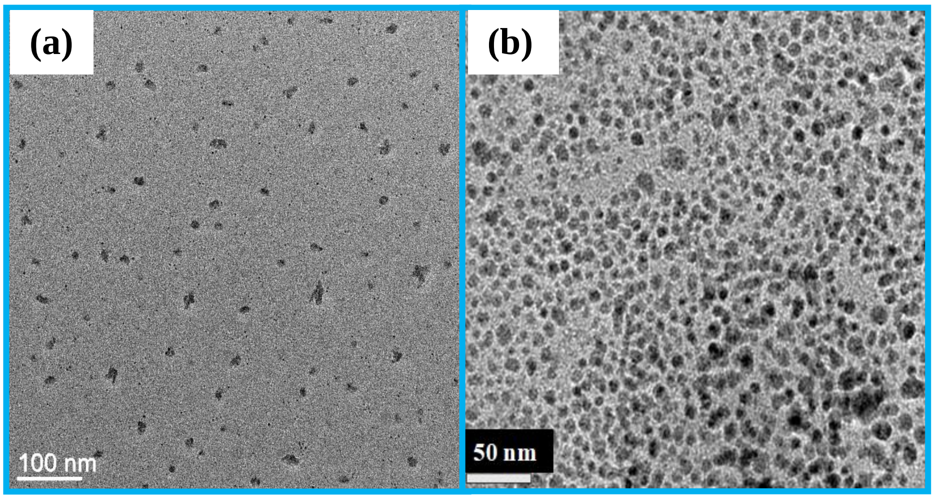

Fig. S11. TEM images of GOQD in presence of 0.075 (M) $NaNO_3$: (a) pH 2, (b) pH 6.5.

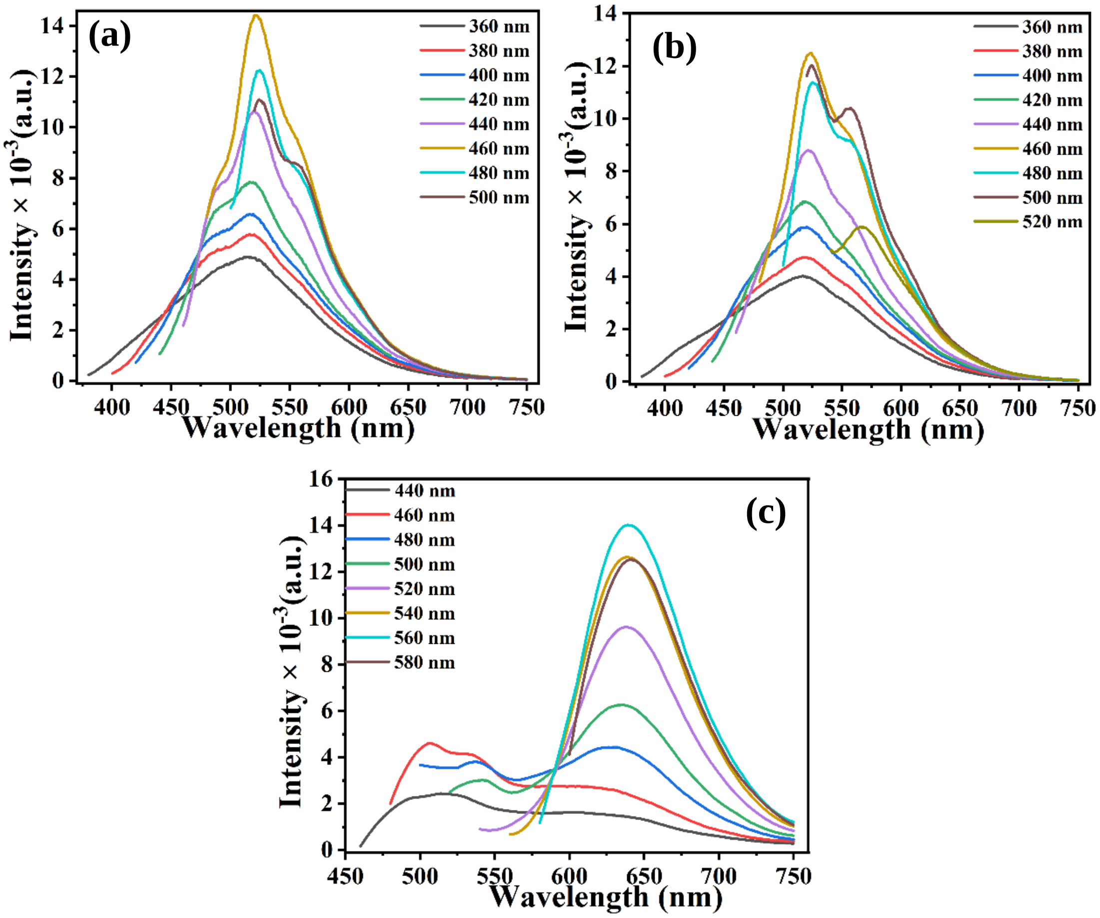

Fig. S12. Emission spectra of aqueous GQD after dialysis: a) pH 2, b) pH 6.5 and c) pH 12.8.

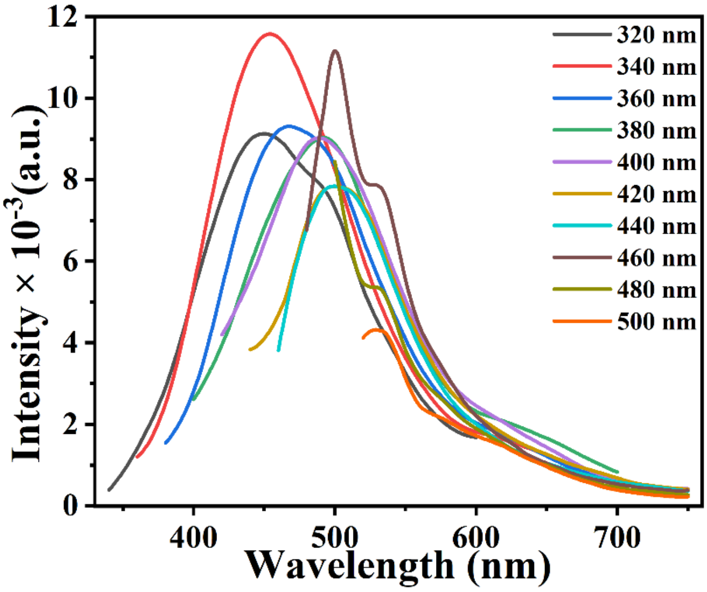

Fig. S13. Excitation wavelength dependent emission profile of PVA-GOQD film casted at pH 12.8.

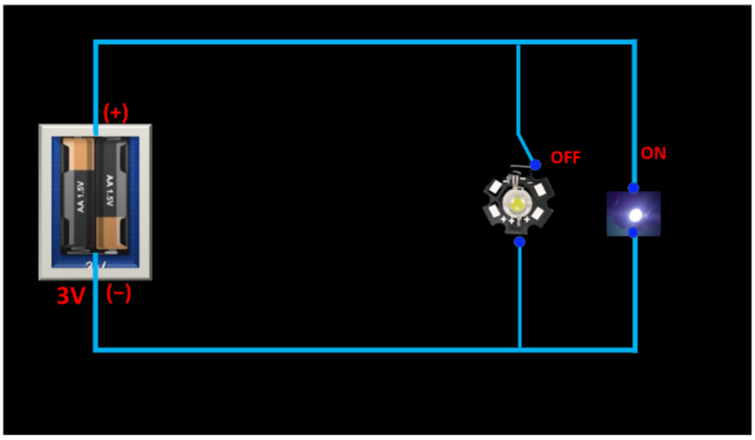

Fig. S14. Circuit diagram of the pc-LED setup.

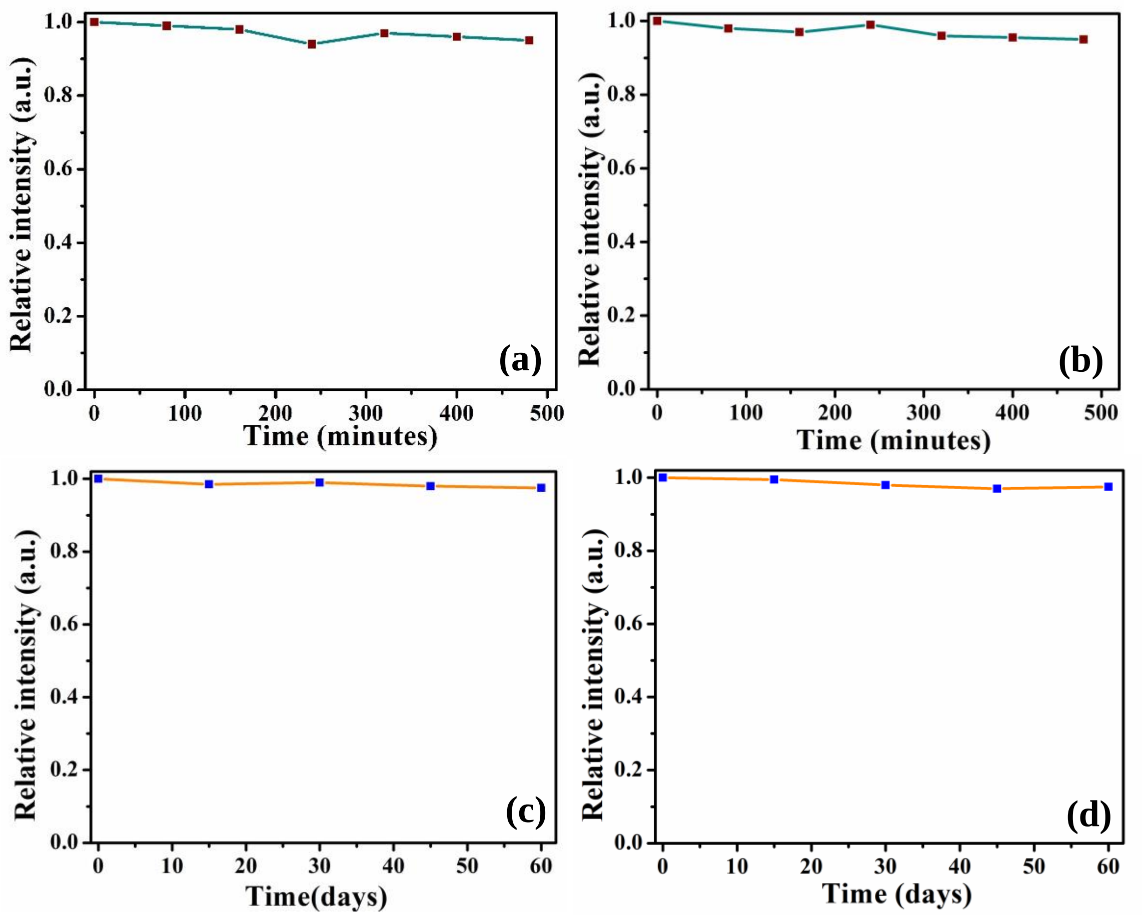

Fig. S15. Photo stabilityof PVA-GOQD emissive layers under UV radiation and sunlight: a) and c) solid film casted at pH 2, respectively; b) and d) orange-red gel film at pH 12.8 respectively.