

## Microwave Assisted Synthesis and Optical Properties of Highly Fluorescent N-Doped Carbon Dots

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Herein, a rapid microwave assisted solid state method is reported for the synthesis of highly fluorescent N-doped carbon dots (NCDs) using citric acid as carbon source and guanidine hydrochloride as N-dopant. Synthetic parameters such as microwave power, irradiation time and reactants ratio were optimized to produce high quality N-doped carbon dots. The N-doped carbon dots were well characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), SEM-EDS, FTIR, UV-visible and fluorescence spectroscopies. N-Doped carbon dots exhibited bright emission with a quantum yield of 11 %. Detailed study of their optical properties revealed their excellent property of resistance to photo bleaching, high ionic strength and solution pH. Further they exhibited excitation dependent emission behaviour, high aqueous solubility and a long shelf life of 60 days. This strong fluorescence emission combined with high stability make N-doped carbon dots a promising fluorescent probe for wide range of applications.

**Keywords:** N-Doping, Carbon dots, Citric acid, Guanidine hydrochloride, Fluorescence.

### INTRODUCTION

Luminescent carbon dots (CDs) serendipitously discovered in the year 2004, have grabbed the attention of many research groups with their spectacular properties [1]. They are fool proof and robust materials with unique, versatile and novel properties such as chemical inertness, superior stability against photo bleaching, biocompatibility and low cytotoxicity which made them find wide applicability in various fields [2,3]. They are best known for their strong and stable fluorescence ability. These are the nanoparticles of carbon and considered as rising star of the carbon nanomaterials family with sub 10 nm of diameter. Since their first discovery, several researchers came up with a wide variety of approaches ranging from laser ablation, arc discharge, thermal and electrochemical treatments to ultrasonication, hydrothermal and microwave treatments for the production of carbon dots (CDs) [4-6]. Furthermore, application of CDs to numerous areas including biomedicine, biomedicine delivery, sensing, catalysis and optoelectronic conversion were also widely explored [7-9]. Carbon dots (CDs) can be viewed

as promising alternatives to traditional fluorescent substances with their superior features of good water dispersibility, non-toxic nature, and high tolerance to photo bleaching [10].

Although considerable progress has been made towards the production and usage of CDs to diversified fields, much more research needs to be focused on synthesizing CDs in ways of overcoming the major drawbacks like poor fluorescence quantum yields [7,11]. Doping of heteroatoms particularly N and S into the carbon core is considered to be promising in this regard. Currently, researchers are making several attempts in developing novel strategies for the production of improved CDs with doping [11]. In most of the studies, hydrothermal treatment is successfully applied for CDs production by employing many natural resources, waste materials and various organic small molecules [12]. However, hydrothermal treatments generally require long reaction times. Recently, usage of microwave radiation for the synthesis of carbon dots (CDs) have gained much attention and diverse starting materials including small organic molecules like hydrocarbons, acids, esters and natural resources [6,13]. Microwave radiation assisted fabri-

cation offers advantages such as operational simplicity, cost effectiveness and a rapid reaction times and avoids the traditional harsh treatments like strong acids, elevated temperatures, and lengthy reaction times [14].

Here in this work, we report a simple microwave assisted production of N-doped carbon dots (NCDs) with fluorescent quantum yield as high as 11 %. Citric acid is used as carbon source and guanidine hydrochloride as dopant and various synthetic conditions like microwave power, irradiation time and mole ratio of reactants are optimized. The as-fabricated NCDs were systematically characterized by various analytical techniques and their optical properties are studied.

## EXPERIMENTAL

Citric acid and guanidine hydrochloride were procured from S.D. Fine Chemicals Ltd. Mumbai, India. All the chemicals and reagents used in the present study are of analytical grade and used without further purification. Double distilled water was used throughout the study.

**Synthesis of N-doped carbon dots (NCDs):** Appropriate amounts of citric acid and guanidine hydrochloride (mole ratio of 1:2) were placed in an agate mortar and grounded into a uniform powder. Then the mixture was taken in a glass vial, placed in a domestic microwave oven and heated at 500 W for 5 min followed by the addition of 10 mL of double distilled water to obtained a char like material. The obtained brown coloured solution containing N-doped carbon dots (NCDs) is then centrifuged and filtered to remove large particles. Unreacted reactant molecules and other small molecules were removed by dialysis (MWCO 3500Da).

Fluorescence spectral measurements were carried out using a JASCO spectrofluorometer (FP-8500) set with excitation and emission slit widths at 2.5 nm. UV-visible spectral studies were conducted on Shimadzu UV-VIS-NIR 3600 spectrophotometer. Transmission electron microscopy (TEM) images were acquired on a JEOL 3010 microscope operating at 200 kV by drop casting an appropriate dilution of NCDs aqueous solution onto the carbon-coated copper grids. Fourier Transform Infrared (FT-IR) spectrum was recorded on Shimadzu IR Prestige-21 spectrophotometer. X-ray diffraction (XRD) patterns of NCDs were obtained using an X'pert Pro powder X-ray diffractometer (Netherlands) with Cu K $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ .

**Quantum yield calculation:** Quantum yield (QY) of N-doped carbon dots (NCDs) was determined by comparing the integrated fluorescence intensities and absorbance values

with those of reference compound (quinine sulfate). Quinine sulfate ( $\Phi = 0.54$ ) was dissolved in 0.1M H<sub>2</sub>SO<sub>4</sub> ( $\eta = 1.33$ ) and the NCDs were present in double distilled water ( $\eta = 1.33$ ). To avoid inner filter effect, absorbance values were kept less than 0.1. Finally, quantum yields were calculated by employing the following equation:

$$\Phi = \Phi_R \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

where  $\Phi$  is the quantum yield, I is the recorded integrated emission intensity, A is the absorbance at excitation wavelength, and  $\eta$  is the refractive index. The subscript R denotes reference compound (quinine sulfate).

## RESULTS AND DISCUSSION

**Synthesis of N-doped carbon dots (NCDs):** In this work, a simple, green, microwave assisted solid state synthesis of N-doped carbon dots is reported. Citric acid is used as carbon source and guanidine hydrochloride as dopant. Synthetic conditions such as microwave power, heating time and reactants ratio were optimized by taking quantum yield of the produced N-doped carbon dots (NCDs) as a parameter. Firstly, mole ratio of reactants was optimized by keeping the microwave power at 500 W and heating time at 5 min. As shown in Fig. 1a, the mole ratio of 1:2 (citric acid to guanidine hydrochloride) resulted NCDs with high quantum yield.

Similarly, microwave power was also optimized by keeping other conditions constant. As shown in Fig. 1b with increase in the microwave power from 180 to 500 W, the quantum yield also increased. However, further increase in microwave power resulted in a drastic decrease in the quantum yield and water insoluble char like product was obtained at a microwave power above 900 W. Furthermore, microwave irradiation time was optimized by keeping other parameters constant. Increase in the irradiation time from 1 min to 5 min resulted in a clear increase in the quantum yield and reached the maximum value (Fig. 1c). However, at higher irradiation time, NCDs with relatively low quantum yield were obtained. This can be ascribed to the fact that increased reaction times will lead to the over carbonization of the formed carbon dots which in turn would lead to the decrease in the quantum yield [15]. Thus, the optimized synthetic conditions are 1:2 mole ratio of citric acid and guanidine hydrochloride, microwave power of 500 W and irradiation time of 5 min.

**TEM analysis:** The structure, morphological features and size distribution of NCDs obtained under optimal synthetic

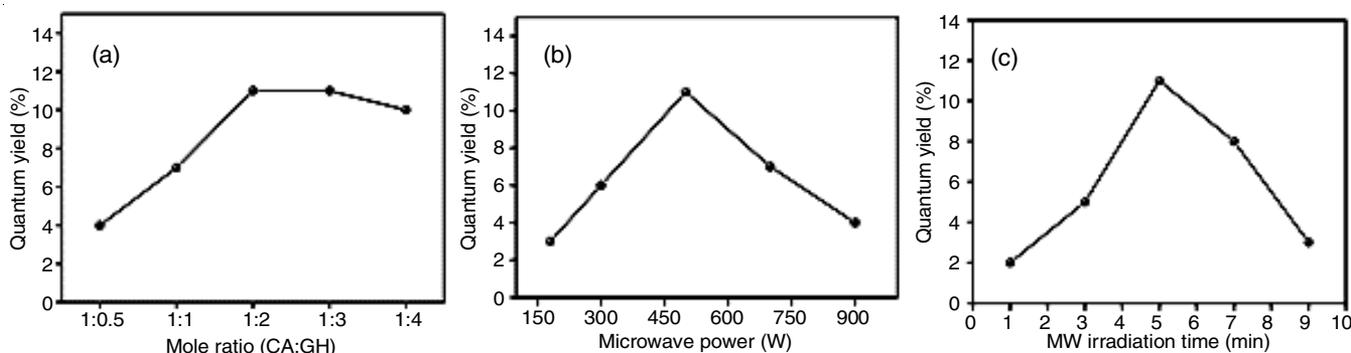


Fig. 1. Optimization of synthetic conditions: QY as a function of (a) mole ratio (b) microwave power and (c) microwave irradiation time

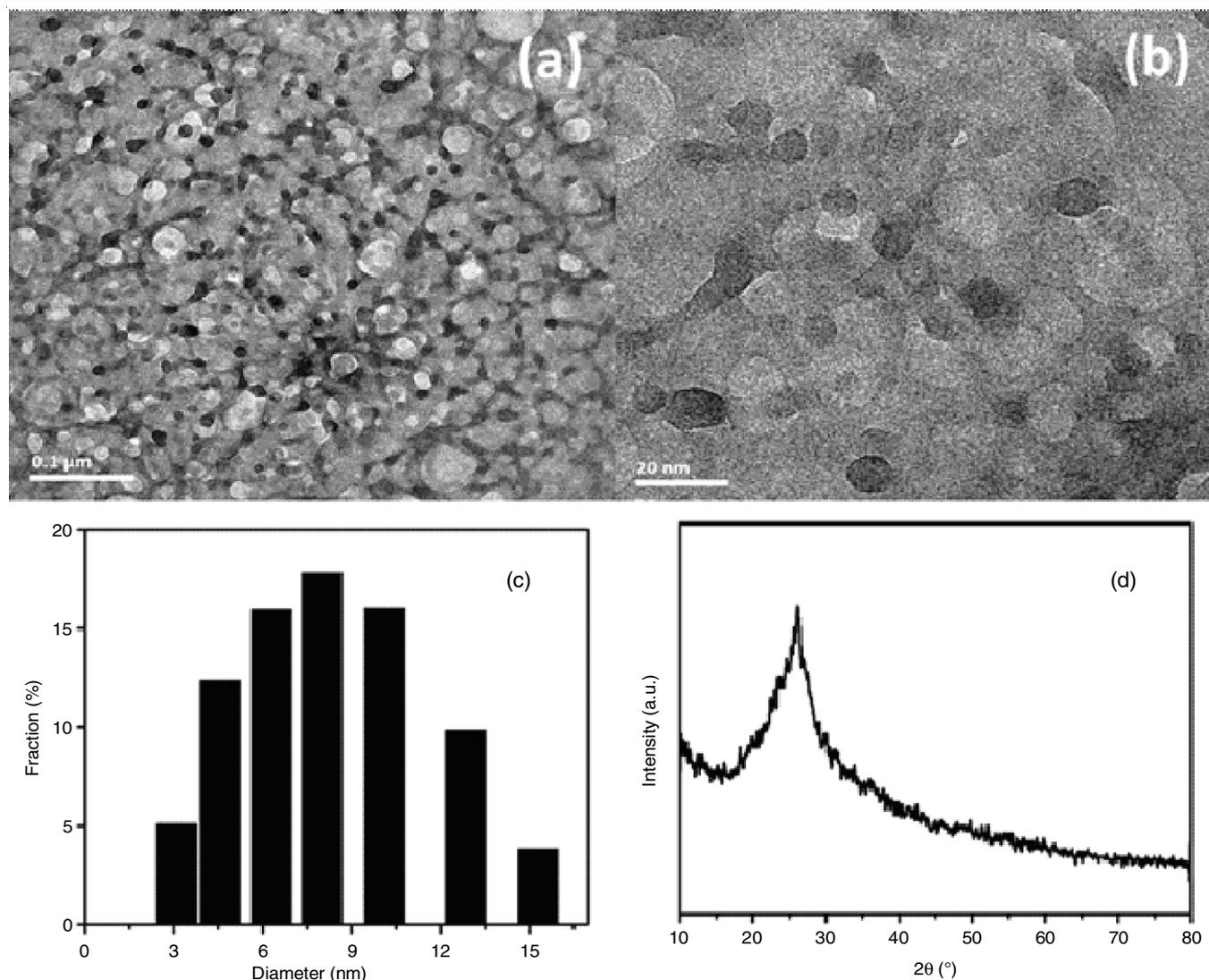


Fig. 2. TEM images of NCDs (a) low magnification (b) high magnification and (c) corresponding particle size distribution (d) powder XRD pattern of NCDs

conditions were studied by using TEM analysis. TEM image shown in the Fig. 2a clearly revealed the spherical morphology of NCDs and the particles were well separated from each other without undergoing any agglomeration.

Corresponding size distribution histogram is shown in Fig. 2b suggested the size of NCDs ranging from 3 to 15 nm with an average diameter of 8 nm. Powder XRD patterns of NCDs (Fig. 2c) exhibited a single broad peak centred at  $2\theta = 26.2^\circ$  indexed to the (002) lattice spacing of graphitic carbon indicating the graphite like structure of NCDs [15]. The interlayer spacing  $d$  (0.37 nm) is larger than that of graphite (0.34 nm) suggesting the incomplete graphitization or amorphous nature and can be attributed to the existence of polar functional groups on the surface [16].

**SEM-EDS analysis:** The chemical composition of NCDs is evaluated by using SEM-EDS analysis. As shown in Fig. 3, the NCDs are composed of carbon (56.57 %), nitrogen (14.55 %) and oxygen (28.88 %).

**FTIR analysis:** In the FTIR spectrum (Fig. 4), the broad vibration band in the range of  $3500\text{--}3200\text{ cm}^{-1}$  can be ascribed to the characteristic -OH and -NH stretching vibrations. The

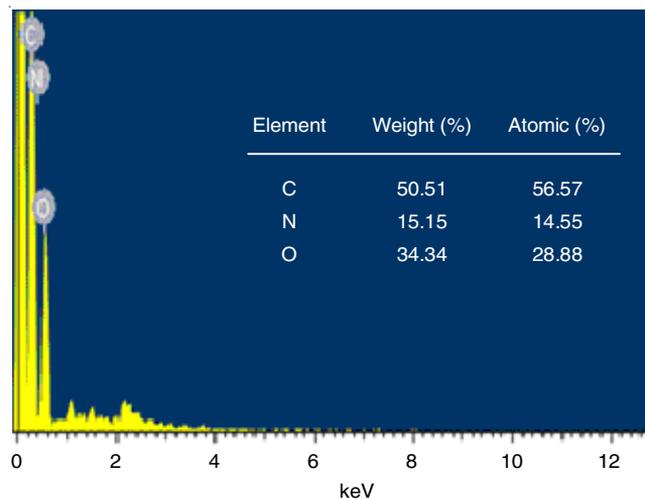


Fig. 3. SEM-EDS analysis of N-doped carbon dots

peak at  $1643\text{ cm}^{-1}$  represents the carbonyl stretching, while the peaks in the range of  $1600\text{ to }1400\text{ cm}^{-1}$  can be assigned to C=C stretching vibrations of polycyclic aromatic hydrocarbons

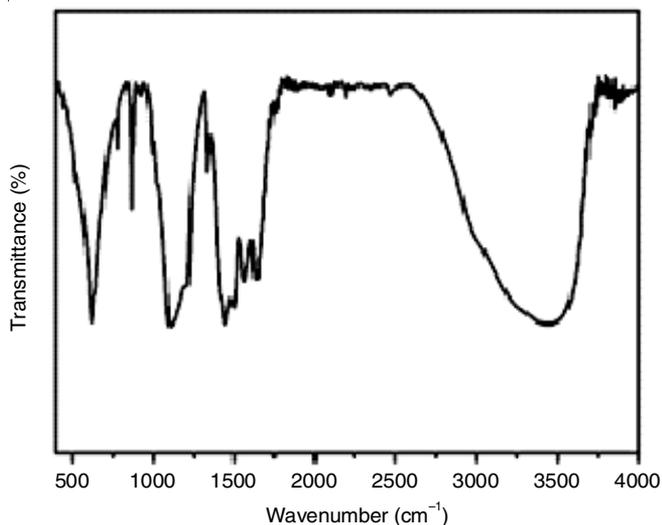


Fig. 4. FT-IR spectra of N-doped carbon dots

indicating the presence of  $sp^2$  hybridization. Further, the peaks at 1211 and 1100  $cm^{-1}$  can be ascribed to the stretching and bending vibrations of C-O bonds in carboxyl groups. These results manifest that the NCDs comprise multiple functional groups like -OH, -COOH and NH on their surface which makes them highly soluble in water. Further, these functional groups can act as linkers for the attachment of biomolecules to serve NCDs as nano-carriers [17].

**Optical properties:** UV-visible and fluorescence spectroscopic techniques were employed to study the optical properties of NCDs. Under day light, aqueous solution of NCDs appeared transparent and pale yellow coloured whereas the same solution exhibited bright blue emission under 360 nm UV lamp (Fig. 5). The absorption spectra and emission spectra of NCDs aqueous solution at ambient conditions is presented in Fig. 5. In the absorption spectra, two poorly resolved bands can be observed at around 290 and 370 nm. These bands might be aroused from the  $\pi-\pi^*$  transition of carbogenic core and  $n-\pi^*$  transition of heteroatomic surface functionalities, respectively [10]. The emission spectra of NCDs presented a strong peak

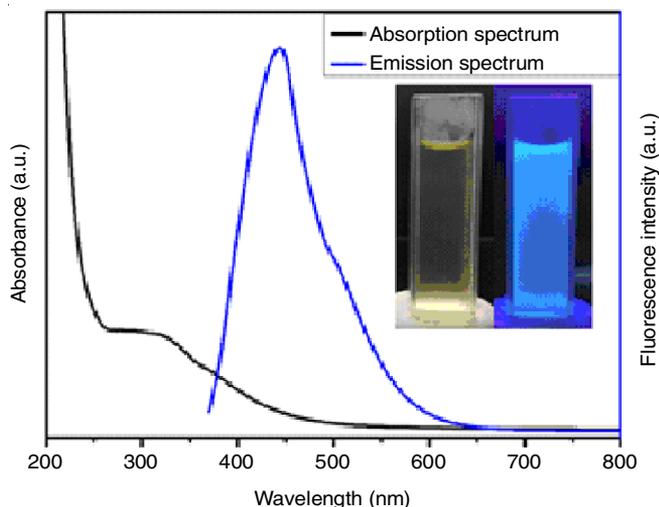


Fig. 5. Absorption and fluorescence emission spectra of NCDs, inset: photographs of NCDs aqueous solution exposed to day light (left) and 360 nm UV light (right)

centred at 445 nm ( $\lambda_{ex} = 360$  nm) with a stoke shift of 85 nm and full width at half maximum (FWHM) of 90 nm. These observations are well in accordance with the previous reports.

**Fluorescence spectra:** The emission spectra of NCDs was recorded at various excitation wavelengths. As shown in Fig. 6, the emission intensity increased with increase in the excitation wavelength from 300 to 360 nm. However, further increase in the excitation wavelength resulted in a clear decrease in the emission intensity. Furthermore, with increase in the excitation wavelength from 300 to 480 nm a clear red shift in the emission peak position from 437 nm to 535 nm was observed. These results suggest that the CDs do not obey Kasha's rule which suggest that the emission peak position of a fluorophore will not depend on the excitation wavelength. This kind of excitation dependent emission nature is considered as the characteristic feature of CDs and makes them as fluorescent probe for multi-colour imaging [18]. The origin of this excitation dependent nature is either due to the optical selection of differently sized nanoparticles (quantum effect) and/or different emissive traps on their surface or some other mechanism altogether, is presently unresolved and a matter of debate among the scientific community [1]. Quantum yield of NCDs determined by using quinine sulphate as reference compound is found to be 11 %, which is higher than several previous reports [19-21]. The reason for this higher quantum yield can be attributed to the doping with nitrogen element [22].

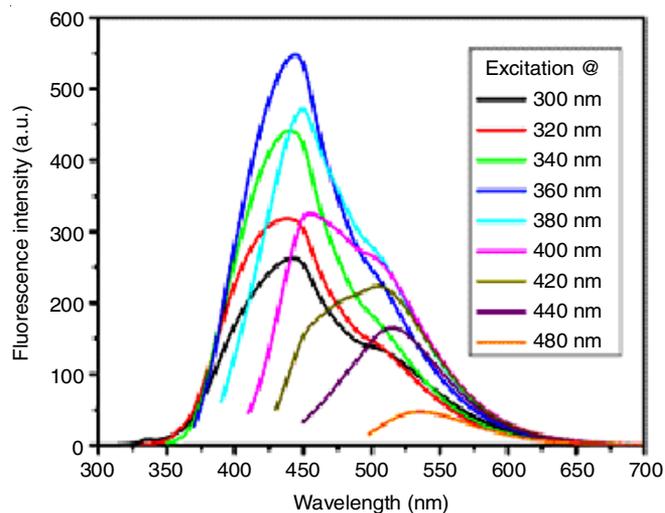


Fig. 6. Emission spectra of NCDs at different excitation wavelengths

**Fluorescence stability:** It is well known that the emission intensity of many fluorescent probes will be disrupted by complex environmental conditions. Hence to test the ability of NCDs to be used as a fluorescent probe for various practical applications, their fluorescence stability was tested under diverse conditions. Firstly, we have examined the effect of ionic strength by recording the emission spectra of NCDs at various KCl concentrations. As shown in Fig. 7a, only a slight decrease in the emission intensity appeared even at a high KCl concentration of 2M. This verifies the tolerance of NCDs to high ionic conditions and further extends their applicability to similar ion rich biological environments [23]. As shown in Fig. 7, solution pH has some significant effect on the emission intensity

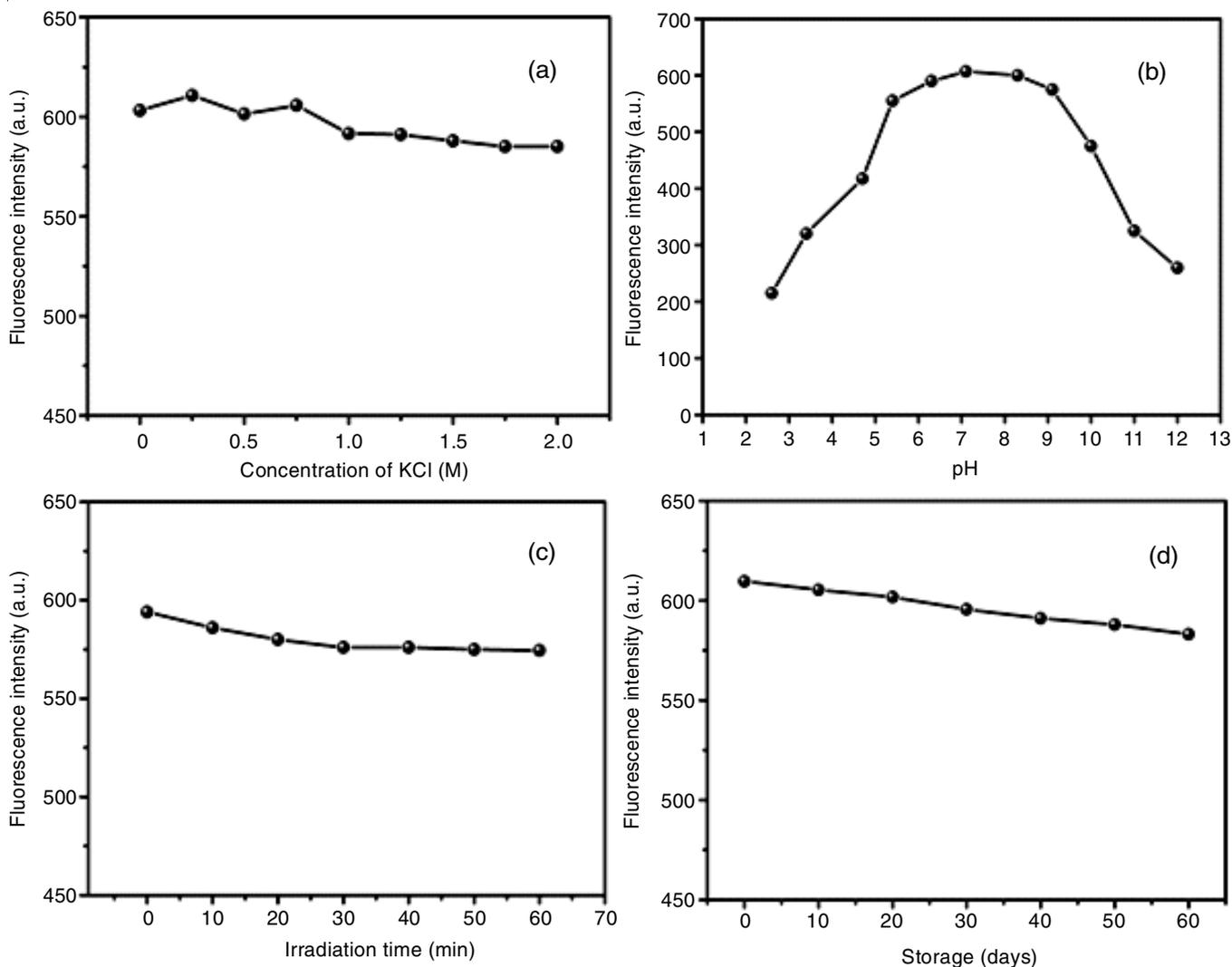


Fig. 7. Effect of (a) concentration of KCl (b) solution pH (c) UV light exposure time and (d) storage on the fluorescence intensity of NCDs ( $\lambda_{em} = 445$  nm and  $\lambda_{ex} = 360$  nm)

but fortunately the emission intensity was high and remained almost constant in the pH range of 5 to 9 which is the common pH range of many environmental and biological samples.

Strong acidic and basic conditions cause some severe protonation and deprotonations on the surface of NCDs which might lead to the aggregation of nanoparticles and result in decreased fluorescence emission [24]. Photostability or resistance to photo-bleaching is an important characteristic for a fluorophore to be used in various applications ranging from imaging to optoelectronics. Photostability studies were performed by continuously irradiating the aqueous solution of NCDs under 360 nm UV lamp for 1 h. No significant decrease in the emission intensity was observed even after 1 h of exposure (Fig. 7c), indicating the superior photo stability of NCDs. Furthermore, the shelf life of NCDs aqueous solution was evaluated by storing it under ambient conditions. Again, no substantial decrease in the emission intensity was observed even after storing for 60 days and the solution remained clear, implying the great stability and long shelf life of NCDs (Fig. 7d). All these results suggested that the produced NCDs are highly stable and can serve as excellent candidates for diverse applications.

## Conclusion

To summarize, we have successfully demonstrated a simple microwave assisted method for the production of N-doped carbon dots with quantum yield as high as 11 %. The synthesized NCDs contain various polar surface functionalities which impart favourable aqueous solubility. N-doped carbon dots (NCDs) displayed excitation dependent emission behaviour which is crucial in multicolour imaging. Further, NCDs exhibited strong fluorescence emission which is stable to various environmental conditions such as high ionic strength, solution pH and continuous irradiation. Furthermore, they showed long shelf life of 60 days. All these properties make NCDs an excellent fluorescent probe for wide variety of applications ranging from bioimaging and chemical sensing to optoelectronic devices.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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