



Synthesis of a Fluorescent Sensor by Exploiting Nitrogen-Doped MXene Quantum Dots for the Detection of Dopamine

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Abstract

MXene quantum dots (QDs) are emerging two-dimensional materials from the MXene family that possess unique physicochemical properties and are employed in divergent disciplines, such as energy storage, conversion, catalysis, medicine, and biosensing. In this study, we synthesized MXene QDs using the MAX phase of MXene into its sheets by acidic treatment, followed by doping with ethylenediamine (EDA), and produced nitrogen-doped QDs (NMQDs) via the hydrothermal method. The resulting NMQDs showed excellent fluorescence quenching with a neurotransmitter, i.e., dopamine (DA). These NMQDs showed a strong blue fluorescence with a photoluminescence (PL) emission wavelength maximum of 400 nm under the excitation wavelength maximum of 330 nm. The optical properties of NMQDs were investigated using UV–Vis and PL spectroscopy techniques. The morphological, elemental constitution, and phase composition features were characterized by employing HRTEM, SEM, XPS, XRD, FTIR techniques, etc. The NMQDs delivered high sensitivity towards DA with a limit of detection (LOD) of 18 nM within the linear concentration range between 20 and 100 nM. These results suggest that these NMQDs have the potential to be used as fluorescent sensors for neurotransmitter detection.

Keywords MXene · Nitrogen-doped quantum dots · Fluorescence · Dopamine · Detection

Introduction

MXenes, a class of two-dimensional layered materials consisting of transition metal carbides or nitrides, are often synthesized using a process known as selective etching. This process involves the removal of A layers, where M represents an early transition metal, A represents an element from groups 13 and 14 (referred to as A-group elements), and X represents carbon and/or nitrogen. MXene, a novel class of materials, exhibits inherent hydrophilicity and natural electrical conductivity due to the presence of hydrophilic groups within its structure. This unique characteristic renders MXene materials very suitable for many applications, such as biosensing [1], biological imaging [2], and photodynamic therapy [3].

Compared to other two-dimensional materials, MXene has many unique benefits, such as being hydrophilic,

biocompatible, easy to functionalize on the surface, and having high metallic conductivities. These features distinguish them from conventional two-dimensional materials, which are hydrophobic, less compatible with living cells, have negligible electrical conductivity, and have difficulty in the fabrication of functional groups on their surfaces.

MXene 2D material is layered, self-stacks itself, and agglomerates due to interaction between Vander Waals forces and hydrogen bonds between its layers [4]. These MXene sheets are undergoing a hydrothermal process to cut down their size to about less than 10 nm. They show some distinct advantages with a large surface area, good biocompatibility, and ease of doping over the parent MXene blocks. Recently, by tuning its size by changing reaction conditions, Ti_3C_2 quantum dots (QDs) showed better PL properties than 2D Ti_3AlC_2 sheets [5]. These MXene QDs (MQDs) easily get oxidized and lose their structure and chemical composition when exposed to air, resulting in changes in their properties. This easy oxidation of MXene is prevented by modifying it with any doping elements to enrich their properties for sensing applications. The PL performance was enhanced using surface modification through functionalization and elemental doping. Some studies demonstrate

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surface modification using polymers [6] and other small molecules [7] to enhance their PL performance. In general, QDs with elemental doping using different elements, such as nitrogen, sulphur, and potassium, can enhance their quantum yield. Using nitrogen as a doping element, it has been shown that an increase in the quantum yield and enhanced intensity in the blue-colored PL emission are possible due to its electron-withdrawing property [8].

Previously, several studies were carried out using nitrogen-doped QDs for dopamine detection. Nitrogen-doped carbon dots were synthesized using polyacrylamide as both carbon and nitrogen sources for the detection of DA. This fluorescent probe shows good water solubility and strong fluorescent properties with a detection limit of 0.05 μM [9]. For instance, recently, nitrogen-doped carbon dots were synthesized using ferrocene (FC) and dimethylaminomethyl ferrocene (DFC) as a carbon source by a one-pot hydrothermal process. The fluorescent probe from this carbon source showed the fluorescent quenching effect towards DA and exhibited a limit of detection (LOD) of about 5.12 mM [10]. Recently, nanomaterials and their doped structures were found to be promising fluorescent probes for the detection of DA.

DA is one of the neurotransmitters belonging to the catecholamine group, is present in the brain, and plays a vital role in the transmission of neuronal signals in the central nervous system and peripheral nervous system [11]. It has numerous roles in brain functions, including behavior response, feelings, working memory, sleep, mood, and attention [12]. Improper function of the dopamine system has been implicated in diseases related to the nervous system. An increase in secretion is related to Huntington's disease, which results in a loss of energy metabolism, and eventual death will occur [13]. Low concentrations of DA will relate to apraxia, Alzheimer's, and Parkinson's disease. A sensitive detection system is needed to detect irregular concentrations of DA and make early diagnoses of DA-related diseases [14]. Many conventional methods were employed for the detection of DA, but they required expensive equipment, were labor-intensive, and were not applicable for rapid detection at low concentrations. Nanomaterials, including QDs or CDs with biocompatibility, high fluorescence, photochemical stability, and an easy-to-pass blood–brain barrier characteristics, were used as drugs for the treatment of various brain disorders and also for the detection and bioimaging of DA in various parts of the brain [15, 16]. Fluorescence-based sensing systems nowadays give more attention to detecting even low-level concentrations with rapid, sensitive, and selective detection. Recently, the fluorescence-based technique using graphdiyne (GDY) QDs, which are synthesized using urea as a nitrogen source, showed highly sensitive and selective detection of DA with an LOD of 0.14 μM [17]. The increase in fluorescence property and quantum yield of the synthesized QDs

are achieved by elemental doping, which is of significant importance.

In this work, we synthesized NMQDs using EDA as a doping agent through a hydrothermal process. The amine ($-\text{NH}$) group in the EDA molecule assisted in the formation of NMQDs during the hydrothermal reaction [18]. The synthesized NMQDs were thoroughly characterized and utilized for the detection of DA at nanomolar levels. These NMQDs are highly suitable as a sensitive and selective probe for DA detection.

Experimental

Materials

Ti_3AlC_2 powders (98% purity, 200 mesh) were purchased from Sigma-Aldrich. Ethylenediamine (EDA) and hydrofluoric acid (HF) were purchased from JT Bakers. Dopamine hydrochloride (DA), epinephrine (EP), norepinephrine (NE), γ -aminobutyric acid (GABA), potassium chloride (KCl), magnesium chloride (MgCl_2), sodium chloride (NaCl), glucose, and L-cysteine (L-Cys) were purchased from Sigma-Aldrich (USA). We used deionized water (DI) for the experiments that were required. The dialysis membrane (MWCO of 100–500 D) was acquired from Spectrum Laboratories, Inc.

Instruments and Measurements

Synthesized NMQDs were diluted in water, and dark field images were taken using a PTI UV illuminator at 365 nm. UV spectra of the diluted solution of NMQDs were obtained by a Varian Cary 100 UV–Vis spectrophotometer. SEM images were acquired from a Hitachi SU8600. Imaging was performed in a high vacuum at a cold cathode field emission electron gun. The resolution is 0.6 nm at 15 kV and 0.7 nm at 1 kV. Magnification and voltage are 20–1000000 $\times$ and 0.1–30 kV. HRTEM images were recorded using the TecnaiTM G2 F30 Series, the ultimate nano-analysis system, which was equipped with 300 kV Schottky FEG with high maximum beam current, a patented S-TWIN objective lens, 0.17 nm of HR STEM resolution, 0.20 nm of point resolution, and 0.102 nm of line resolution and was purchased from Hillsboro, USA. Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex high-resolution 70 FTIR spectrometer. X-ray diffraction (XRD) patterns were processed by a Rigaku Ultima III X-ray diffractometer equipped with a Cu-sealed tube of $\lambda = 1.54$, 178 Å, 40 kV, 30 mA, and a scan speed of 2°/min in continuous scanning 2 θ mode. XPS spectra were measured using the Thermo Scientific K-AlphaTM X-ray Photoelectron Spectrometer with a range of motion (100–4000 eV), a 128-channel detector,

and a double-focusing hemispherical analyzer (180°) with a micro-focused X-ray source (Al K α). Fluorescence measurements were performed by Quanta Master, Photon Technology International (PTI), NJ, USA, equipped with a Xe lamp of Arc Lamp Housing, A-1010BTM, a monochromator, and the power supply (Brytebox). The pH was measured by the Thermo Scientific pH meter.

Synthesis and Purification of Ti_3AlC_2

The preparation of MXene QDs contains the following steps, and the method was adopted from a slight modification of previous studies [19]. 1 g of Ti_3AlC_2 was treated with HF for 24 h at room temperature, and after the solution was centrifuged, the pellet was washed with double-distilled water until its pH reached 6. The powder was delaminated with dimethyl sulfoxide (20 mL) for about 24 h at room temperature. The resultant powder pellet was sonicated with distilled water for about 10 h at room temperature. The powder was dried at 60°C about 20 h, to get the MXene sheet. About 300 mg of MXene sheet was sonicated with double-distilled water for about 15 min before being transferred to hydrothermal treatment. To obtain N-doped MQDs, 2 mL of EDA was added to the mixer and transferred to a Teflon-lined stainless-steel autoclave at 120°C for about 6 h. The NMQDs could be obtained by centrifugation, and the supernatant was filtered through a $0.22\text{ }\mu\text{m}$ membrane, freeze-dried, and kept in the refrigerator until used.

Fluorescence Assay for Dopamine

For a typical sensing assay for dopamine, 900 μL of phosphate buffer solution (PBS) of pH 7.4 with 100 μL NMQDs solution (1 mg/mL) were mixed thoroughly; subsequently, the fluorescence intensity at 400 nm (under excitation of 330 nm) was recorded and denoted as initial fluorescence intensities (F_0). The variable concentrations of DA (20–100 μM) were introduced into the above mixture. After incubation for 5 min, the fluorescence intensities were recorded as final fluorescence intensities (F).

Selectivity Assay for Dopamine

The selective detection of dopamine is essential for each sensing material, especially for real sample analysis. To investigate the selective detection of DA, different neurotransmitters and ions were selected. The concentration of neurotransmitters and ions was fixed at 10 μM . The detection conditions were adopted as above, and the fluorescence response of the interference substance was recorded at the excitation wavelength of 330 nm.

Results and Discussion

Synthesis of NMQDs

The NMQDs were synthesized from the MAX by two-step acid refluxing and hydrothermal processes (Fig. 1). In the acid refluxing process, HF was used for about 24 h of continuous stirring, and MXene sheets were obtained. Using MXene sheet, hydrothermal treatment along with elemental doping using ethylenediamine were carried out at 120°C in 50 mL of a Teflon-lined autoclave for 6 h. The as-prepared NMQDs show efficient blue color emission under ultraviolet (UV) illumination. The NMQDs' solutions were separated via centrifugation at 10,000 rpm for 20 min, filtered, freeze-dried, and kept in the refrigerator for further use.

Material Characterization

We investigated SEM, TEM, and XRD studies to observe the morphology and phase composition of MXene sheets and the NMQDs that were synthesized (Fig. 2). First, employing Ti_3AlC_2 as the raw material, MXene sheets were prepared by strong acid reflux and etching with HF. The obtained MXene sheet was subjected to a hydrothermal process to produce N-doped MXene quantum dots. The SEM image of MXene sheets is shown in Fig. 2a. In Fig. 2a, we observed the stacking layer of MXene sheets that are perfectly layered and clearly separated from the unreacted raw material, and Al is completely removed from the Ti_3C_2 [20]. We investigated the TEM analysis to obtain the morphological details of the synthesized NMQDs. Figure 2b shows a TEM image of prepared NMQDs using EDA as a doping element, showed small spherical-shaped dots with a uniform distribution with an average size of 2 nm based on the particle-size distribution curve (Fig. 2d). It is confirmed that the prepared QDs successfully transformed into a zero-dimensional structure compared to the parent compound. The HRTEM image

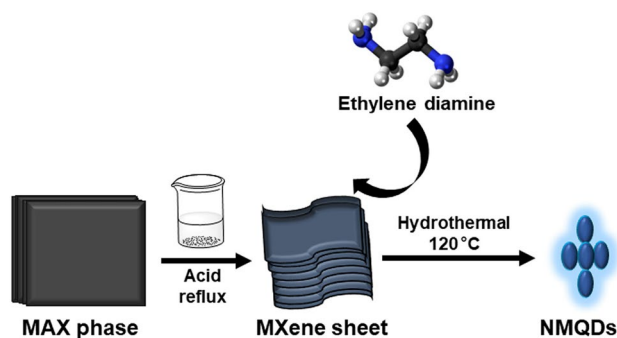


Fig. 1 Schematic representation for the synthesis of NMQDs by the hydrothermal method

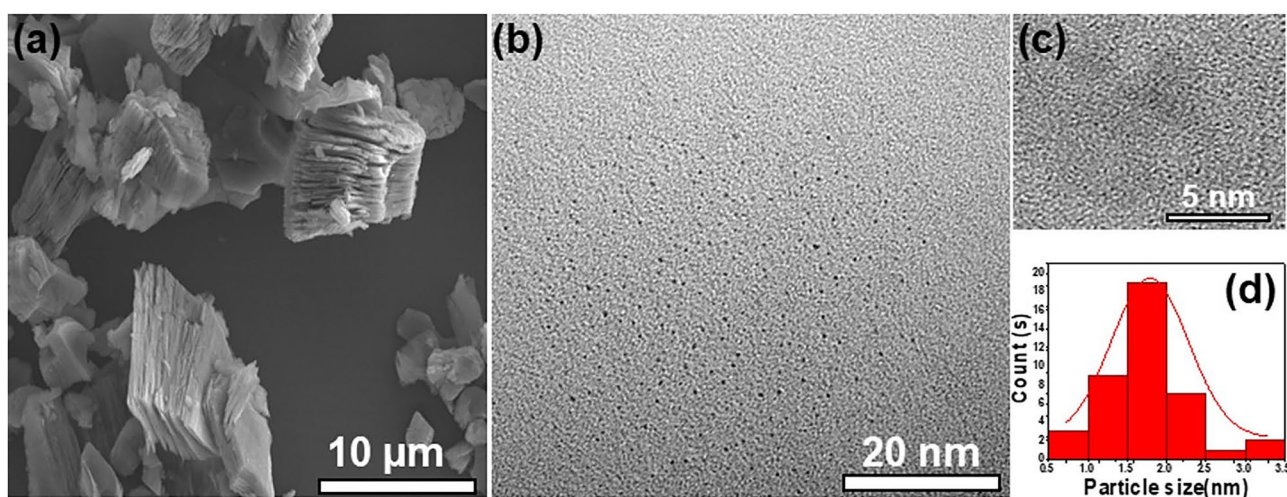


Fig. 2 **a** SEM image of MXene sheets; **b** TEM image of NMQDs; **c** HRTEM image of NMQDs; **d** particle-size distribution curve of NMQDs

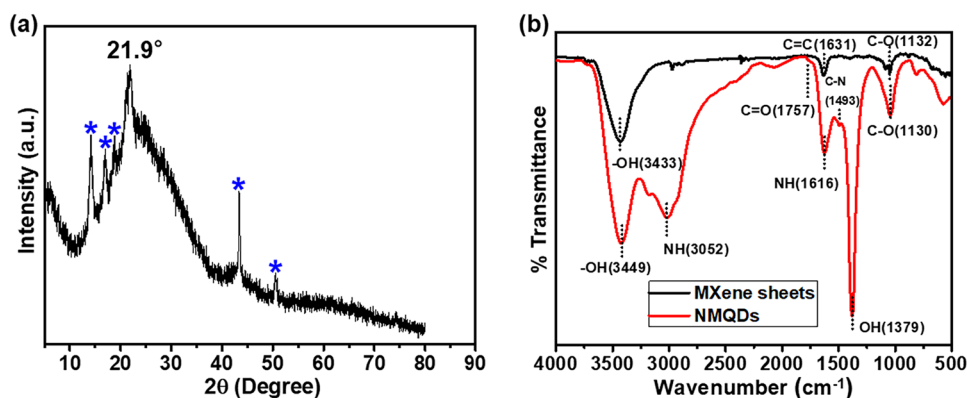
(Fig. 2c) of the synthesized NMQDs has demonstrated their moderately amorphous nature without distinct crystalline planes, which corroborates the formation of QDs. Furthermore, we investigated the TEM analysis for the MQDs without EDA doping. The MQDs were synthesized using the same hydrothermal treatment without doping with EDA. The resulting TEM image of the MQDs is shown in Fig. S1. The irregular shapes were not defined as spherical QDs; moreover, they appear to be like a sheet with an irregularly layered structure [21]. This may be due to severe oxidation that may occur in the Ti backbone, and EDA reduces the degree of oxidation and protects the Ti backbone during the synthesis of NMQDs.

From XRD studies, a broadening amorphous peak was observed at 21.9° , attributed to the presence of a carbon-rich structure in NMQDs, and the sharp peaks (denoted by stars) indicated crystalline phases of the MXene, and these results suggested that NMQDs were well synthesized (Fig. 3a) [22]. FTIR analysis was carried out to understand the surface functional characterization of MXene sheets and NMQDs, as

shown in Fig. 3b. The characteristic absorption peaks from the FTIR spectra of the NMQDs at 3052 and 1493 cm^{-1} are attributed to the N–H- and C–N-stretching vibrations, which provides evidence regarding the successful doping of EDA in the NMQDs [23]. The peaks at 1130 , 1379 , 1616 , and 1757 cm^{-1} correspond to the stretching vibrations of C–O, O–H, N–H, and C=O bonds, respectively. The presence of O–H, C=O, and N–H moieties on the surface of NMQDs is responsible for the improved hydrophilicity, which can enhance the dispersion and solubility of NMQDs in aqueous solutions [24]. Also, the FTIR spectra of MXene sheets were analyzed to verify the successful doping of EDA in MQDs. It showed stretching vibrations of O–H, C=C, and C–O bonds around 3433 , 1631 , and 1132 cm^{-1} , respectively. However, there was no evidence for the stretching vibrations of N–H or C–N groups, suggesting the N-doping of MXene sheets to form NMQDs.

To explore the elemental composition of synthesized NMQDs, XPS analysis was performed (Fig. 4). From Fig. 4a, the total survey spectrum shows four main peaks at 284.5 ,

Fig. 3 **a** XRD pattern of NMQDs; **b** FTIR spectra of MXene sheets and NMQDs



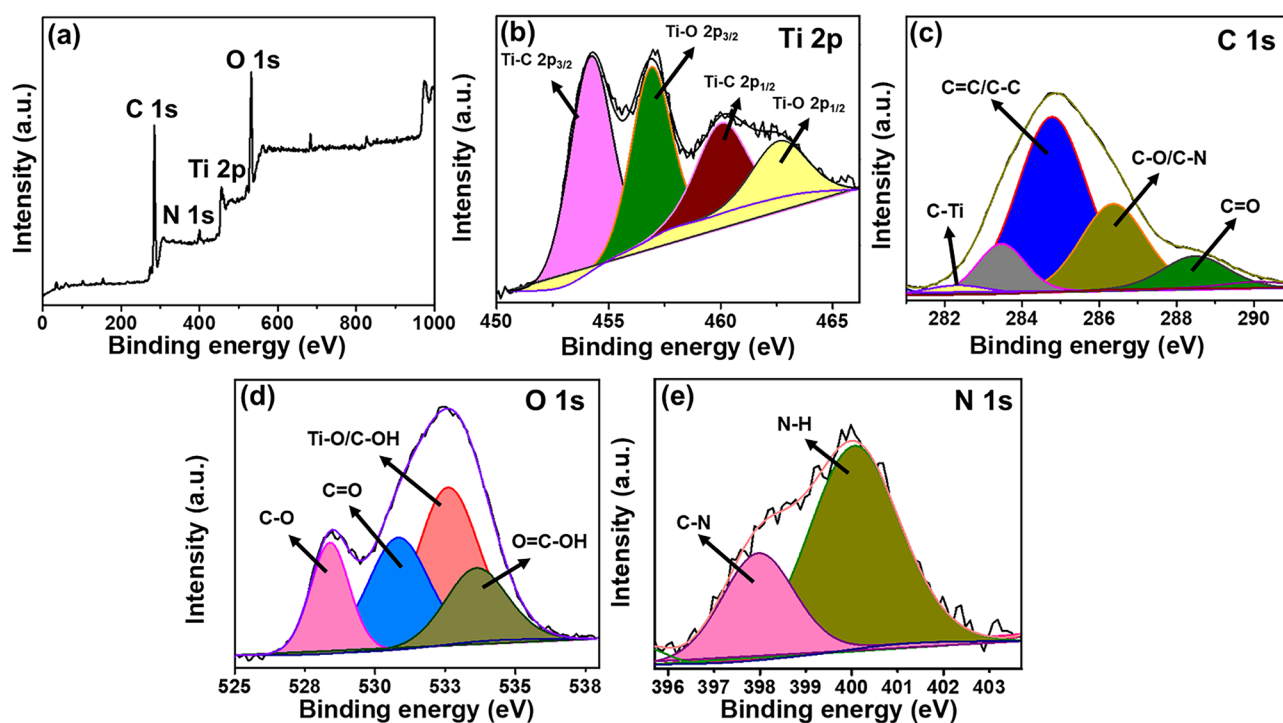


Fig. 4 **a** XPS total survey spectrum of NMQDs; **b–e** high-resolution spectra of Ti 2p, C 1s, O 1s, and N 1s, respectively

399.2, 455.2, and 531.8 eV, which are attributed to C 1s, N 1s, Ti 2p, and O 1s, respectively. The high-resolution spectra of Ti 2p show four deconvoluted peaks at 454.19, 456.88, 460.02, and 462.61 eV, which are assigned to Ti–C 2p_{3/2}, Ti–O 2p_{3/2}, Ti–C 2p_{1/2}, and Ti–O 2p_{1/2}, respectively. The above-mentioned results show that NMQDs preserve the MXene structures (Fig. 4b). The C1s high-resolution spectra show four deconvoluted peaks at 282.33, 284.77, 286.36, and 288.49 eV, which are responsible for C–Ti, C=C/C–C, C–O/C–N, and C=O, respectively (Fig. 4c). The O1s spectra mainly demonstrate four deconvoluted peaks at 528.4, 530.82, 532.59, and 533.61 eV, which are attributed to C–O, C=O, Ti–O/C–OH, and O=C–OH, respectively (Fig. 4d). From Fig. 4d, the presence of O₂ content in the synthesized NMQDs with balanced sp² and sp³-carbon atoms can tune the fluorescent properties of NMQDs [25]. Figure 4e shows the high-resolution XPS spectra of N 1s, which demonstrated peaks around 397.96 and 400.05 eV, which are ascribed to the C–N and –NH moieties. The composition of nitrogen content in the NMQDs can influence the fluorescence properties of the synthesized NMQDs, and it is well reported that the doping of nitrogen atoms increases the fluorescent emission properties of QDs [26].

Sensitivity, Selectivity, and Stability Studies of NMQDs

The sensing mechanism for the fluorescence detection of DA based on NMQDs was precisely investigated using UV–Vis absorption spectroscopy (Fig. 5a). For this, the absorption spectra of NMQDs and NMQDs-treated DA were studied. The absorption spectra of NMQDs and NMQDs-treated DA showed a π – π^* transition at 231 nm. However, the absorption spectra of NMQDs alone did not demonstrate the n – π^* transition, but NMQDs-treated DA exhibited a distinct absorption peak at 298 nm, which is attributed to the n – π^* transition. Generally, the absorption spectra for DA show the n – π^* transition in this wavelength region. Hence, it is suggested that the prepared NMQDs interacted with DA and participated in the fluorescence sensing mechanism. The fluorescence properties of the NMQDs were studied in an aqueous solution, which exhibited a maximum PL emission wavelength of 400 nm, as shown in Fig. 5b. The inset images show the visual photographs of NMQDs in DI water under daylight (left) and UV illumination (right), respectively. The excitation wavelength-independent emission behavior was observed from the NMQDs in DI water at

Fig. 5 **a** UV–Vis absorption spectra of NMQDs alone (black curve), NMQDs-treated DA; **b** PL emission spectrum (λ_{em} : 400 nm) of NMQDs. Inset shows the photographs of NMQDs in DI water under bright-field (left) and blue-colored emissive NMQDs in the presence of UV illumination (365 nm); **c** PL excitation-independent emission spectra of NMQDs under different excitation wavelengths ranging from 290 to 350 nm

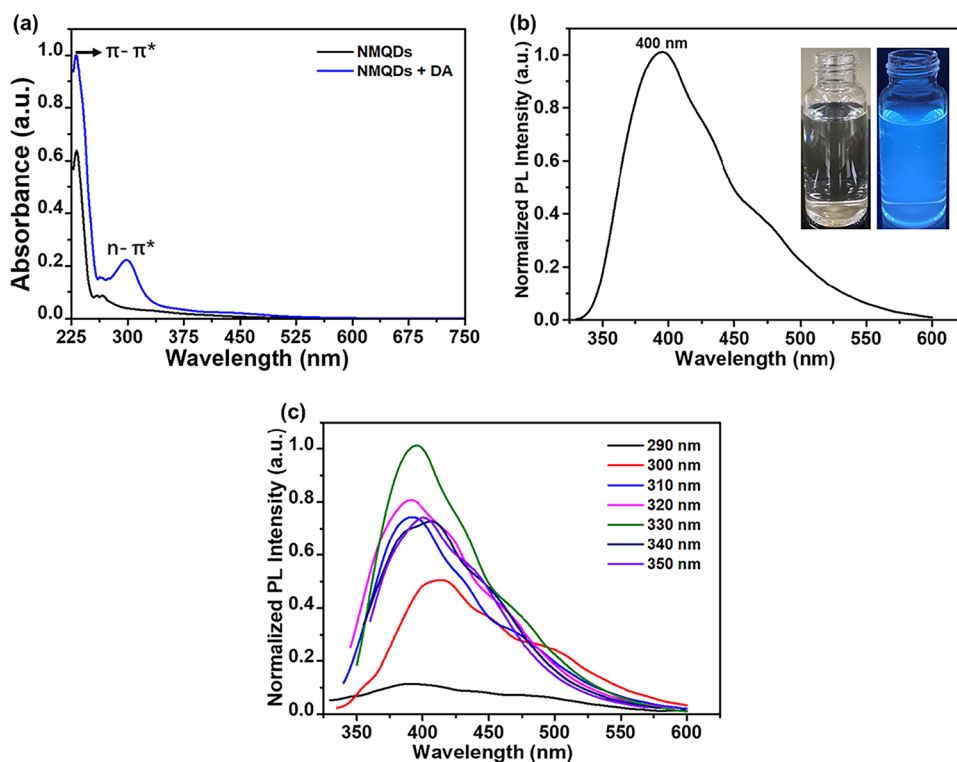
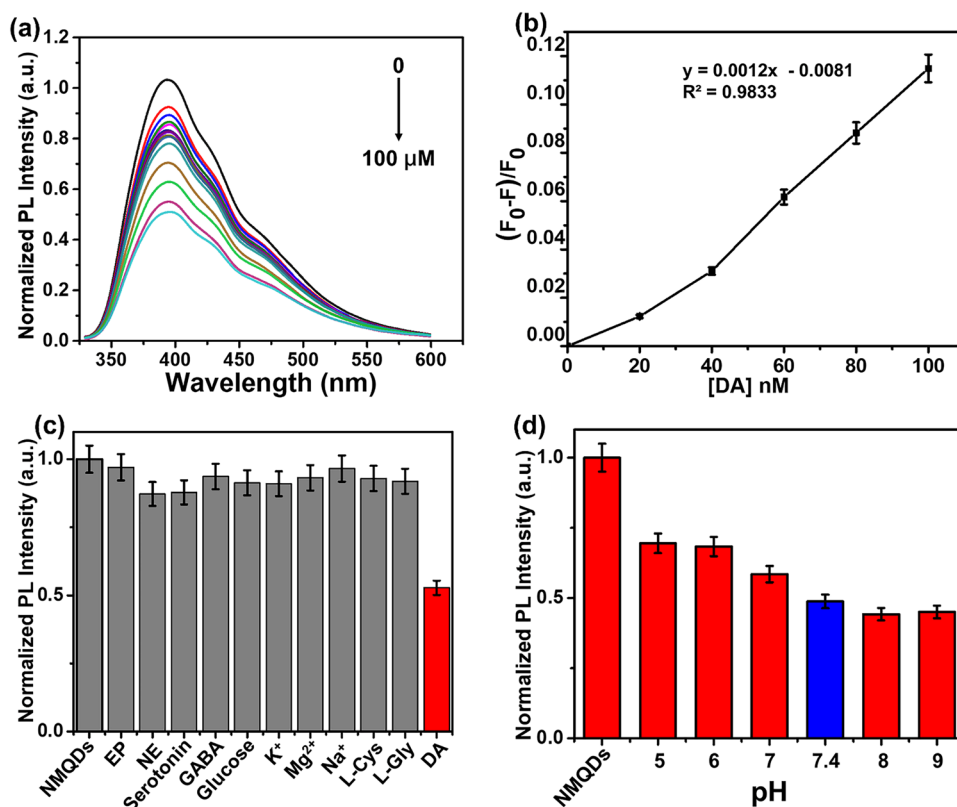


Fig. 6 **a** PL emission spectra of NMQDs with different concentrations of DA (20, 60, 80, 100, 400, and 800 nM; 2, 6, 10, 40, 60, 80, and 100 μ M); **b** linear regression curve between $(F_0-F)/F_0$ and DA concentrations (0–100 nM); **c** selectivity of NMQDs for DA sensing against divergent interferents. **d** The fluorescence response of NMQDs alone and NMQDs-treated DA in different pH solutions (pH 5, 6, 7, 7.4, 8, and 9)



various excitation wavelengths ranging from 290 to 350 nm, as shown in Fig. 5c.

The fluorescence quenching response of NMQDs was investigated by treating them with different concentrations of DA (20, 60, 80, 100, 400, and 800 nM; 2, 6, 10, 40, 60, 80, and 100 μ M), as shown in Fig. 6a. The fluorescence intensity of NMQDs decreased steadily after adding different concentrations (nanomolar to micromolar) of DA. From these results, we have drawn the linear regression curve between $(F_0 - F)/F_0$ and DA concentration (Fig. 6b). The good regression coefficient value (R^2) around 0.9833 was achieved within the linear concentration range of DA (0–100 nM), and the LOD was found to be 18 nM. The normal concentration of DA in the dopaminergic pathway in the brain ranges from 10^{-8} to 10^{-5} M [27]. Hence, the proposed probe has delivered a significant sensitivity within a suitable linear range of DA, starting from nanomolar to micromolar levels. These results signify that the proposed probe is adequately excellent for DA sensing as compared to the previously reported fluorescent analytical probes [9, 10, 17, 22] (Table 1).

We also investigated the selectivity test to understand the interference effect of other interfering molecules that showed a possible quenching effect on NMQDs. Figure 6c shows that there is a decrease in the fluorescence intensity of NMQDs while adding DA to the reaction system, whereas other molecules such as amino acids (L-cysteine), ions (including K^+ , Na^+ , Mg^{2+} , and Ca^{2+}), sugar like glucose, and other neurotransmitters such as EP, NE, serotonin, and GABA did not show significant changes in the fluorescent quenching. From Fig. 6c, it was shown that the fluorescence quenching of NMQDs was towards NE, and serotonin has a high fluorescence quenching next to DA. The fluorescence quenching effect of NMQDs towards NE shows 27% of the quenching effect due to structural similarities between DA and NE. In a living system, the concentration of NE is 300 pg/mL (1.8 nM), which is ten times less than the concentration of DA (26–40 nM) [28]. In real sample analysis, the influence of NE is negligible on the detection of DA. Next to NE, serotonin showed fluorescence quenching with NMQDs; the maximum intensity was observed at 380 nm instead of 400 nm. The difference in the excitation wavelength shows the low impact of interfering biomolecules in real sample analysis [29]. At 400 nm, both NE and serotonin

have a lower fluorescence quenching than dopamine. The above-mentioned results suggest that the prepared NMQDs are more significant as fluorescent probes with high selectivity and sensitivity.

The fluorescence response of NMQDs towards DA is carried out in PBS buffer at a pH of 7.4. Further, we measured the PL intensity of the NMQDs with DA by adjusting the pH from 5 to 9. The results showed that as the pH increased from 5 to 8, the fluorescence quenching increased but then slightly decreased (Fig. 6d). It is well reported that the mechanism by which changes in pH will affect the fluorescence intensity may be due to the energy level changes caused by H^+/OH^- groups present on the surface of NMQDs [30]. In alkali conditions at pH 8, the DA molecule gets oxidized easily into dopaquinone under ambient O_2 conditions, and maximum quenching was observed in this range. However, at pH 9, the deprotonation process may occur, which could eliminate the hydrogen-bonding effect, resulting in a decrease in energy levels, and vibrational coupling will lead to a decrease in fluorescence quenching [31]. This system showed about a 50% quenching effect at this pH for detecting DA in real samples. The synthesized NMQDs were stored in the refrigerator and tested their PL quenching effect at different time intervals in a time period of 50 days, where no significant fluctuations were observed in PL quenching up to 25 days (Fig. S2). However, after 25 days, a minimal fluorescence quenching was observed.

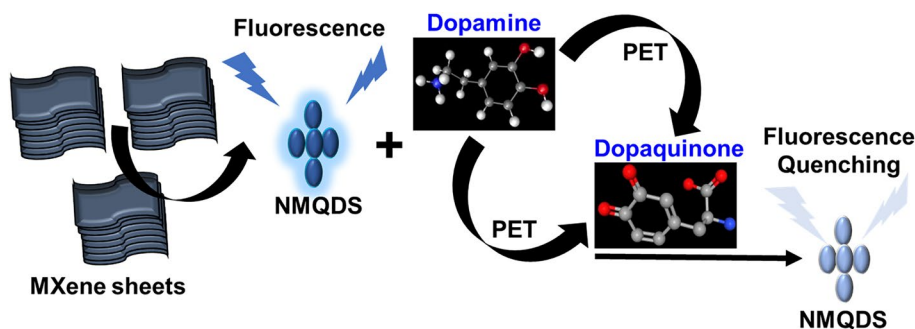
Plausible Mechanism for DA Detection

Using UV absorption spectra, the fluorescence quenching mechanism of NMQDs with DA was discussed. The quenching mechanism is either static or dynamic based on the changes in the absorption spectrum of NMQDs, whether they cause a new product to be produced or not. From Fig. 5a, the absorption spectra of NMQDs before and after the addition of DA showed a change in absorption spectra, which may be due to the formation of new products. It is well known that at ambient O_2 under alkali conditions, dopamine gets oxidized to dopamine quinone [32]. It is already reported that the product dopamine quinone acts like an electron acceptor, which allows fluorescence quenching with NMQDs [33]. Finally, the probable quenching mechanism for the developed NMQDs sensing

Table 1 Comparison for the previously reported fluorescent analytical probes with the proposed sensing probe for DA sensing

Analytical probe	Sensing approach	Linear range μ M	LOD	References
N-carbon dots	Fluorescence	0.1–200	0.05 μ M	[9]
N-carbon dots	Fluorescence	3.3–400	5.12 μ M	[10]
N-graphdiyne QDs	Fluorescence	0.32–500	0.14 μ M	[17]
N-graphene dots	Fluorescence	1–200	0.07 μ M	[22]
N-MXene quantum dots	Fluorescence	20 nM–100 nM	18 nM	Present work

Fig. 7 Schematic of DA detection mechanism by NMQDs



system is photo-induced electron transfer (PET), which ensures that the electrons are transferred from the NMQDs to dopamine quinone (Fig. 7).

Conclusion

In this study, MAX phase and EDA served as precursors for the hydrothermal synthesis of NMQDs. The purpose of doping is well achieved by preventing the oxidation of NMQDs and exhibiting strong fluorescence quenching. The synthesized QDs have a spherical-like structure, good water solubility, an average size of about 2 nm, and are efficiently quenched upon the addition of DA. These properties make NMQDs a fascinating nanomaterial for bio-imaging and in vivo detection of DA in real samples. The possible mechanism discussed in this sensing system was the transfer of electrons from the NMQDs to the dopamine quinone, which is produced via oxidation in DA under ambient O_2 in an alkali condition. A good linear relationship between 20 and 100 nM was found with an LOD of about 18 nM. This study demonstrates the great potential of NMQDs as fluorescence probes for the detection of DA in real sample analysis.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11814-024-00144-y>.

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Data availability Data available on request.

Declarations

Conflict of Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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