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Chelation-enhanced fluorescence of phosphorus doped carbon nanodots for multi-ion detection

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Abstract The present paper reports on a chelation enhanced fluorescence (CHEF) effect that is observed on addition of certain metal ions to phosphorus doped carbon nanodots (P-CNDs). The effect is accompanied by a large shortwave shift of the emission peak. Highly passivated P-CNDs with sizes of around 3 nm were prepared from lactose and phosphoric acid, using a one-pot low temperature solvothermal method. The nanoparticles were purified according to polarity and size. The extent of blue shift and strength of enhancement depend on metal ions and actual pH value. For instance, the P-CND complex with Al(III) has a fluorescence that is shifted to shorter wavelengths, and the fluorescence quantum yield is enhanced from 12% (for the free P-CNDs) to almost 62% at 490 nm. The fluorescence is also enhanced and shifted by the ions Zn(II) and Cd(II). It is quenched by the ions Fe(II), Fe(III), Hg(II), Cu(II) and Sn(II), among others. The enhancement is attributed to the chelation of metal ions with the passivated surface functional groups of P-CNDs, mainly those of phosphorus. Phosphorous free CNDs (prepared via HCl instead of H₃PO₄) and low-passivated **P-CNDs** (prepared for longer period of time; typically 8 h) show no enhancement. The metal ion induced enhancement led to the design of a

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² Komar Research Center, Komar University of Science and Technology, Sarchinar-Qularaise district, Sulaymania City, Kurdistan Region, Iraq fluorometric assay for the detection of these ions. The detection limits are 4 nM for Al(III) and 100 nM for Zn(II). The two ions were quantified in spiked pharmaceutical formulations. Recoveries typically are 102% (for n = 7).

Keywords Carbon nanodots · Enhancement · CHEF · Fluorescence enhancement · Phosphorus doped carbon dots · Quantum yield

Introduction

After the first report on the preparation and characterization of fluorescent cabon nanodots by Xu et al. [1] there is a great motivation to understand the mechanism, behavior, and potential applications of this interesting family of carbon materials.

Fluorescent carbon nanodots (**CNDs**) have become one of the most interesting nanomaterials, due to their high luminescence, biocompatibility, photostability, water solubility, and flexible functionalization, which are applicable to chemical and biological sensors, bioimaging, light emitting devices, electrocatalysts, photocatlysts, and cancer therapy [2, 3].

The term "carbon dots" refers to fluorescent carbon materials with an inner graphitic core and an outer shell composed of chemical functional groups [4]. Due to their fluorescent emission, researchers have been trying to use them as sensors either with label or without label. Most sensors based on fluorescent carbon nanodots are only suitable for one type of metal ion detection, and they are mostly based on quenching. [2] Quenching is based on photoelectron transfer from the excited species to the metal ion orbitals or vise-versa [5].

Chelation-Enhanced Fluoroscence (**CHEF**) for molecular fluorophores in solutions was first observed by Czarnik et al. [6, 7]. They attributed the enhancement of molecular

fluorophore to some type of complexation with nonquenching metal ions, like Zn^{2+} and Cd^{2+} [8, 9]. **CHEF** also has been observed for different types of luminophores and luminogens after combining with Al^{3+} , Pb^{2+} , and Cu^{2+} as well [10–12]. It is believed that CHEF leads to decreasing the rate of photo-induced electron transfer (**PET**), hence enhancing the radiative decay pathway. Yet, to the best of our knowledge, **CHEF** for carbon nanodots has not been reported.

Pramanik et al. [13] reported photoluminescence enhancement of graphene quantum dots (not **carbon nanodots**) by divalent ions, like; Zn^{2+} , Cd^{2+} and Sn^{2+} . They ascribed the enhancement to internal charge transfer; however, they did not observe tuning of emission wavelength. Zhang et al. [14] reported that quinolone derivative-functionalized carbon dots showed good response towards the detection of Zn^{2+} ion, but this approach was not label free, and the enhancement mechanism was based just on the complexation of quinolone derivative with zinc ions.

Herein, we report low-temperature, one-pot solvothermal synthesis of pH-dependent, high-passivated phosphorous doped fluorescent carbon nanodots (**P-CNDs**). The fluorescence emission of as-prepared **P-CNDs** was enhanced and spectrally shifted upon combining with certain metal ions and quench with some other metal ions. To our knowledge, it is the first report on this interesting phenomenon for **CNDs**. Metal ions such as Al³⁺ can enhance dramatically the fluorescence intensity with quantum yield up to 62%. Fig. 1 shows a scheme of enhancing and quenching of the fluorescence emission of **P-CNDs**. The enhancement is accompanied by shifting of the fluorescence emission, which makes **P-CNDs** for metal ion detection more selective. The prepared water

soluble fluorescent **P-CNDs** were used for quantitative analysis of Al^{3+} and Zn^{2+} elements in pharmaceutical formulations.

Experimental section

Chemicals

All chemicals used were of high analytical grade. Lactose (99%), H_3PO_4 (85%) were purchased from Merck (Darmstadt, Germany) and used as received. Chloroform with ACS grade were purchased from Sigma-Aldrich (Sigma Aldrich, 99%, USA). Metal nitrates, sulfates and sodium salts of anions were purchased from Aldrich and Merck. Deionized water (DI) was used for all the experiments with 18 M Ω .cm.

Instruments

The size and morphology of the nanoparticles were studied using a JEM-2100 transmission electron microscopic (TEM; JEOL, Japan) at 200 KV. The TEM samples were prepared by casting a drop of dilute solution of **P-CNDs** onto a carboncoated copper grid. UV-Vis absorption spectra were recorded on a Cary 60 Spectrophotometer (Agilent technologies, USA). Fluorescence measurements (PL) were recorded on Cary Eclipsed Fluorescence Spectrophotometer (Agilent Technologies, USA). FTIR spectra were obtained on Cary 660 ATR-FTIR connected to ATR (Agilent technologies, USA). X-ray diffraction (XRD) spectra were obtained on Empyrean X-ray diffractometer, (PANalytical, Netherland).



Fig. 1 A scheme illustrating the enhancement and quenching of the fluorescence emission of P-CNDs upon combining with metal ions

X-ray Photoelectron spectrophotometry (XPS) spectra were carried out using Kratos Axis Ultra DLD instrument with the monochromated aluminum source, with two analyses points per sample. Survey scans were collected between 1200 to 0 eV binding energy, at 160 eV pass energy and 1.0 eV intervals. In addition, high-resolution O 1 s, C 1 s and P 2p spectra were collected over an appropriate energy range at 20 eV pass energy and 0.1 eV intervals.

Preparation of phosphorous doped carbon Nanodots (P-CNDs)

In a typical synthesis, 3.0 g of lactose was dissolved in 15 mL of concentrated H₃PO₄, then the solution was heated in a water bath for 20–30 min until the color changed from colorless to pale yellow, dark yellow then dark brown (Fig. 2). The black solution was diluted with 1.0 M sodium hydroxide solution and the pH adjusted between 3 and 4, and the solution left for 24 h. The solution was centrifuged at 14000 rpm for 20 min to remove the larger particles. The **P-CND**s in the aqueous solution were extracted and purified using chloroform (first purification step). Then the solution was heated slowly to evaporate the chloroform, leaving the **P-CND**s, which were later dissolved in water, then dialyzed for another 24 h using dialysis membrane 1000 MWCO (second purification step). The clear pale yellow solution of **P-CND**s was obtained and used for characterizations and applications.

For the **P-CNDs-1**, **P-CNDs-2**, **P-CNDs-3**, **P-CNDs-5**, **P-CNDs-8** all were prepared same way as **P-CNDs**, except they were different in the heating time, and the numbers refer to the heating times in hours.

Quantum yields

The quantum yields of the **P-CNDs** were calculated using a known standard [15]. The integrated photoluminescence intensity was plotted against absorbance for several concentrations, and the gradients of the sample and reference fluorescent materials, such as fluorescein, QY 0.95 [16] and Rhodamine 6G, QY 0.95, [17] were used to obtain the quantum yield, using common formula:

$$\phi x = \phi st (Gradx/Gradst)(\eta x^2/\eta st^2)$$

Where St and X represents standard and Sample respectively, ϕ is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance of different concentrations, and η the refractive index of the solvent. The absorbance should be below 0.1 in order to avoid inner filter effect.

Preparation of zinc tablet and antacid tablet

10 tablets of each formulation were purchased in a local pharmacy, and grinded to make a tablet powder. 1.0 g from the tablet powder was dissolved in 10–25 mL of 0.1 M HNO₃, then heated to 80-90 °C for 20 min with stirring. The solution was filtered to remove big and undissolved particles, then the clear solution was diluted to 100 mL with DI water. This tablet solution was used for the analysis purposes.

Results and discussion

A low temperature solvothermal method was used for preparation of high-passivated P-CNDs in aqueous solution. Concentrated phosphoric acid was added directly to lactose powder followed by heating for 20-30 min at 80-90 °C. Here, dehydration, polymerization, carbonization and passivation of the surface, all take place in one pot producing a dark brown solution of carbon dots within 20-30 min (Fig. 2). Following synthesis of P-CNDs, purification was carried out to gain pure nanodots. In the first purification step, simple extraction procedure was used for extracting the P-CNDs to the organic part and leaving the ions formed during the solvothermal process in the aqueous layer. Chloroform was used as the best organic solvent for the extraction. Here, not all P-CNDs dissolve in CHCl₃, very hydrophilic nanodots (here green emitters) will stay in the aqueous solution, and yellow luminescent P-CNDs transfer to chloroform layer. The second purification step, yellow emitters then further purified using dialysis. Chloroform was used for purification based on polarity (polarity-based purification) to obtain similar functional groups, and dialysis was used for more purification based on size (size-based purification) to obtain monodisperse nanoparticles. Two step purification based on polarity and size make the nanodots similar size and polarity.



Fig. 2 Scheme illustrating the solvothermal preparation of water soluble fluorescent P-CNDs

Short heating times and low temperatures make high-passivated **P-CNDs**, while long period of time and high temperatures lead to low passivated **P-CNDs** [18].

Size and surface composition

The size, shape and morphology of **P-CNDs** were examined from transmission electron microscopy (TEM).

The TEM image presented in Fig. 3a and b show that the **P**-**CND**s have spherical shapes and the sizes of the particles are around 3.0 nm. The XRD pattern exhibits broad diffraction spectrum peak around 27° (Fig. 3c), which is attributed to highly disordered carbon atoms [19].

In order to identify the functional groups on the surface of the particles, FTIR spectra were used at different pHs (Fig. 3d). In the FTIR spectra, a broad peak between 2900 and 3400 cm⁻¹ is assigned to stretching of the carboxylic and hydroxyl groups, and a peak at 1610 cm⁻¹ is assigned to a stretching vibration of C = O [20]. The FTIR spectra show that the **P-CND**s have hydrophilic surfaces, which make the nanoparticles water soluble and useful for real applications, such as sensors, bioimaging and other fluorescent-based applications.

X-ray photoelectron spectroscopy (XPS) results were used to further characterize the composition of the functional groups and elements on the surface of the carbon dots.

The XPS survey spectra presented in Fig. 4a show three main peaks: O 1 s (531 eV), C 1 s (286 eV), P 2p (133 eV). In the high resolution XPS spectra, the C 1 s spectrum can be deconvoluted to four peaks as shown in Fig. 4b: sp^2 carbon (C = C, 284.5 eV), sp^3 carbon (C-O, 286.5), carbonyl carbon (C = O, 288.2 eV), and carboxyl carbon (COOH, 289.4 eV)

[21–23]. The O 1 s band contains two peaks (Fig. 4c): carbonyl oxygen (C = O, 531.5 eV), and hydroxyl oxygen (C-OH or C-O, 532.8 eV) [24]. Another band at 133.5 eV just contains one peak and attributed to P 2p of phosphorous group (Fig. 4d) [25]. Phosphorous peak in XPS assigns for that the prepared nanodots are phosphorus doped. The present results were in a good agreement with literature, as **CNDs** that were solvothermally prepared with phosphoric acid, such as in the present case, have phosphorus atoms on the surface or doped with phosphorous [26].

Optical properties

The optical properties of the P-CNDs were examined in the aqueous solutions. The UV-Vis absorption spectra of the P-CNDs exhibit weak absorption peak at 220-225 nm, as shown in Fig. 5, that can be attributed to a π - π * transition of aromatic C = C of graphitic sp² domains of graphene in the dots. Strong characterization absorption peak was observed at 283 nm, which can be ascribed to the n- π^* transition of C = O groups [2, 27]. A small, broad absorption peak can be seen at 400-425 nm, which matches the maximum excitation wavelength that may be assigned to $n-\pi^*$ of the phosphorous group. In order to prove the broad peak of 400-420 nm is from phosphorous group, CNDs were prepared via HCl instead of H₃PO₄ (Fig. 5a inset). It shows that **P-CNDs** prepared via HCl do not show this 400-425 nm broad absorption peak. A small absorption peak at the maximum excitation wavelength (420-425 nm) might be an indicator for the full passivation of the surface, as 30 min heating time with low temperature hydrothermal approach (90 °C) leads to cover or highly passivate the surface of nanoparticle with functional groups [18].









The excitation spectrum and absorbance spectra are not resemble each other, which can be attributed to the fact that the fluorescence is partly from individual surface emitter [28].

The photoluminescence emissions of **P-CNDs** from pHs 1-12 give bright yellow color centered around 560 nm with a quantum yield of almost 12% (excited at 425 nm). Above pH 12 and below pH 1, the PL is drastically weakened and shifts to 580 nm (Fig. S3). This pH effect has been observed in carbon nanodots, and is attributed to the change in protonation of the functional groups on the surface of **CNDs** [2].

In contrary to excitation-dependent PL which is a common effect in carbon nanodots, and is due to the various surface state (molecular state, surface traps, and defects), the present carbon dots show excitation independent PL which is rarely observed (Fig. 5b). However, Zeng et al. [18] showed that low passivation of carbon dots (formation of carbon dots at higher temperatures) lead to multi-mode absorptions, i.e. the formation of different levels below the HOMO, which results in asymmetric and structureless absorption peaks, while high passivation carbon dots (usually obtain in low temperature preparation conditions) shows a single transition mode, giving symmetric and structured absorption spectra (such as in the present **P-CNDs**, Fig. 5a). The same phenomena was observed for the PL spectra. In high passivation mode, there is a single transition, i.e. the PL will be excitation wavelengthindependent. In low passivation, as there are multi transition modes, there should be excitation-wavelength dependent PL.

Chelation—Enhanced emission (CHEF)

Adding aluminum, zinc, or cadmium tuned the PL wavelengths as presented in Fig. 1 and Fig. S4, from the 560 nm emission of free **P-CNDs** to 490 nm for **P-CND:Al³⁺**, 525 nm for **P-CND:Zn²⁺**, and 530 nm for **P-CND:Cd²⁺**.

Fig. 5 a Absorption (*blue line*), Excitation (*black line*), and fluorescence (*orange*) spectra of the free **P-CNDs** in an aqueous solution (pH 3–5); inset: absorption spectra of **P-CNDs** prepared by H₃PO₄ (*black line*) and

HCl (red line). **b** Fluorescence emission of the **P-CNDs** (pH 3.5) at different excitation wavelengths, the wavelengths are indicated in the graph

Interestingly, adding these metal ions to the solution of **P**-**CNDs** resulted in unprecedented observation in carbon nanodots' field. Aluminum ions enhanced the fluorescence quantum yield from 12% (for free **P-CNDs**), to almost 62%, for **P-CND:Al³⁺** and shifted the emission maximum from 560 nm to 490 nm (Fig. 6). Such a high fluorescence quantum yield (62%) is uncommon in carbon nanodots, and it makes the **P-CNDs** a good candidate for aluminum sensor. Other metals like; zinc and cadmium ions both enhanced and tuned the emission, zinc ions enhanced and tuned the PL emission maximum, to 525 nm and raised the QY to ~40%, and cadmium ions tuned the emission maximum to 530 nm, and raised the QY to ~32% (Fig. 6).

The interaction of the **P-CNDs** and metal ions was pH dependent, depending on the protonation state of the functional groups on the surface of **P-CNDs** as shown in Fig. 6. As the **P-CND:AI³⁺** works best in the pH range from 0.5 to 5, after pH 5, the aluminum starts to precipitate as $Al(OH)_3$ (Ksp = 4 × 10⁻³⁴). Still **P-CND:AI³⁺** gives emission even below pH 1 (Fig. 6c). Interestingly, below pH < 1, **P-CND:Zn²⁺** and **P-CND:Cd²⁺** are non-fluorescent, which makes **P-CNDs** more selective for Al^{3+} below pH 1 (Fig. 6c). The pH range of fluorescence of **P-CNDs** with metal ions is limited by the formation of hydroxide precipitate with the metal ions (Fig. 6d-f). Thus, the best range for **P-CND:Zn²⁺** is between 1 and 6 (Ksp Zn(OH)₂ = 5 × 10⁻¹⁷), and from **P-CND:Cd²⁺** from 1 to 7 (K sp Cd(OH)₂ = 7.2×10^{-15}).

The prepared **P-CNDs** are affected and quenched by some metal ions, like; Mn^{2+} , Hg^{2+} , Fe^{3+} , Fe^{2+} , Cu^{2+} , Co^{2+} , Cr^{2+} , and Ni²⁺ as shown in Fig. S5. The quenching effect is attributed to electron transfer between the metal ions and excited **P-CNDs**, which increase the non-radiative decay pathway [29]. However, some metal ions do not show any effect on the PL emission, like; Mg^{2+} , Ca^{2+} , and K^+ .

Excitation-independent PL was observed of the **P-CND:Al³⁺**, **P-CND:Zn²⁺**, and **P-CND:Cd²⁺**, as it indicates that the metal ions are not introducing different surface traps to carbon nanodots. They are only binding (chelating) with the surface functional groups (Fig. S6).

The enhancement and tuning mechanism is rather difficult to be lonely assigned and attributed to perturbation of the photoelectron transfer (PET) as mentioned in literature. The reason can be due to that the origin and mechanism of fluorescence emission of carbon dots is still a matter of debates, explanations in literature are sometimes controversial and contradictory.

In general, two models of fluorescence enhancement mechanism have been observed, the first model is Metal Enhanced Fluorescence (**MEF**) or Surface Plasmon Enhanced Fluorescence (**SPEF**), which was first observed by Drexhage et al. [30–32]. MEF or SPEF is a physical phenomenon that occurs when a fluorophore is located at nanometric distance from a metallic surface, i.e. is the interaction between the excited states of a fluorophore and the induced surface plasmon of a metal nanoparticles or a metallic surface. The

Fig. 6 a Comparison of fluorescence emission spectra of **P-CNDs** with and without metal ions (enhancers) at pH 3, orange line: free **P-CNDs**, cyan-greenish: **P-CND:**AI³⁺, green line: **P-CND-Zn²⁺**, green yellowish line: **P-CND:**Cd²⁺. **b** Comparison of the fluorescence spectra of free **P-CNDs** with and without Zn²⁺ ions at two different pHs, green line **P-CND:**Zn²⁺ (pH 3.5); Black line: free **P-CND** (pH 3.5); orange line: **P-CND:**Zn²⁺ (pH 1), red line: free **P-CNDs** (pH 1). **c** Comparison of the

fluorescence spectra of P-CND:Al³⁺ (cyan-greenish color) with free P-CNDs (orange color), CND:Zn²⁺ (green color), and P-CND:Cd²⁺ (green-yellowish) all at pH 1. Inset: enlarging the graphs of P-CND:Zn²⁺, P-CND:Cd²⁺, free P-CNDs at pH 1. d and e pH effect on P-CND with enhancer enhancers. (F) pH range graph for P-CND:Al³⁺ and P-CND:Zn²⁺. Excitation wavelength for P-CNDs, P-CND:Zn²⁺, P-CND:Cd²⁺ is 425 nm, for P-CND:Al³⁺ is 405 nm

second model is Chelation-Enhanced Florescence (**CHEF**) which attributes complexation of the functional groups with metal ions [6, 7].

The MEF model applies for enhancement by metals, due to plasmonic effect. Chen et al. [33] reported photoluminescence enhancement of carbon nanodots due to silver nanoclasuter, which can be via MEF. To cross-check whether the present enhancement is from MEF or not, a large concentration of OH⁻ or sulfide ions (from NaOH and Na₂S) was added to the solution of **P-CND:Al³⁺**. Upon addition of the ions, the strong cvan-green emission of **P-CND:Al³⁺** disappeared (490 nm), and the original yellow emission of free P-CNDs restored (560 nm), with precipitation of Al₂S₃ or Al(OH)₃ at the bottom of the tube (Fig. 7a). The same experiment was repeated for P-CND:Zn²⁺ and P-CND:Cd²⁺ when N,N'biyridine or sulfide ions were added, the green emission disappeared and yellow emission restored (Fig. 7b). Restoring of the original yellow emission (560 nm) is a good indicator for non-reducing of the metal ions on the surface or the vicinity of cabon nanodots. Hence, it rules out the MEF to be the mechanism of the enhancement.

Regarding **CHEF** mechanism, the absorption and emission spectra for **P-CNDs** with and without metal ions at different pHs were compared (Fig. S7). It has been shown that adding metal enhancers at particular pHs changes the long wavelength broad peaks between 400 and 425 nm in the absorption spectra. For instance, at pH 0.5 and 1, **P-CND:Zn²⁺** shows no fluorescence, and in the absorption spectra, any observable peak around 400–425 nm cannot be observed, as presented in Fig. S7C. While for **P-CND:Al³⁺**, there is a small new peak at around 400–410 nm (Fig. S7C), which can be attributed to the chelation and bond formation between **P-CNDs'** functional groups with aluminum ions, here **P-CNDs** make chelation with Al^{3+} ions and hence give fluorescence, while **P-CND:Zn**²⁺ does not emit fluorescence (Fig. S7 A-D). The chelation between surface functional groups and metal ions may decrease this intramolecular electron transfer (PET), and enhances the emission [34, 35]. At pH 2, for **P-CND:Zn**²⁺ a small peak around 420 nm in the absorption spectra was formed, and at this pH, **P-CND:Zn**²⁺ emits fluorescence emission (Fig. S7B, E, F). This is assigned to chelation between zinc ions with functional groups on the carbon dot surface. Therefore, **CHEF** is a likely the mechanism for the enhancement of fluorescence.

The reason **P-CND:AI**³⁺ is emissive below pH 1, i.e. it chelates with **P-CNDs**, and **P-CND:Zn**²⁺ is not might be due to the greater attraction that aluminum's with 3+ charge has for the **P-CND**. Fig. S8 shows a schematic mechanism of the chelation of Al³⁺ and Zn²⁺ with **P-CNDs**.

Effect of heating time on CHEF

In order to further prove the chelation-enhanced mechanism, **P-CNDs** were prepared at different heating times, based on the assumption that the more heating time, the more lowpassivated **P-CNDs** are formed [18] with increasing heating time, for instance 8 h (**P-CNDs**-8) the broad absorption peak around 400–425 totally disappeared and the PL will be very weak at 560 nm (QY < 0.5) and no enhancing with metal ions (Fig. S9). In a more quantitative measurement, absorbance intensity at 280 nm over absorbance at 400 nm (A280/ A400) were correlated to the solvothermal heating time, as presented in Fig. S9B. Ratio of A280/A400 represents the ratio of n to π^* transition of C = O groups over electronic

Fig. 7 Restoring of yellow emission color (560 nm) of free P-CNDs, after adding chelating agents a OH⁻ for P-CND:Al³⁺, b N, N' bipyridine or sulfide for P-CND:Zn²⁺ ions. Excitation wavelength for P-CNDs, P-CND:Zn²⁺, P-CND:Cd²⁺ is 425 nm, for P-CND:Al³⁺ is 405 nm

transitions of phosphorus groups on the surface of carbon nanodots. With increasing heating time, from 30 min, 1 h to 2 h, the ratio of A280/A400 is slowly increased, and the fluorescence quantum yields are 20%, 18%, 15% respectively, and the excitation-independent PL was observed (Fig. S9C, and S10), it is assigned for high-passivated surface. Higher heating times, 3, 5, and 8 h, the ratio of A280/A400 is dramatically increased to nearly 32, and excitation-dependent PL were observed (Fig. S9D, and S10) assigning for low-passivated surface.

Chelation of Al^{3+} and Zn^{2+} with **P-CNDs** prepared in different heating times were investigated. At low passivated zone, the enhancement emission was very low, indicating for few amount of phosphorous groups on surface of **CNDs**, as their absorption spectra presented in Fig. S10 show decreasing of chelation within increasing of heating time. While, in low heating times (high passivation) chelation is more, and PL enhancement is high as well (Fig. S11 and S10).

Form the above mentioned results, one can conclude that the broad peak between 400 and 425 nm is related to phosphorous group and is associated with chelation to metal ions, and accordingly responsible for **CHEF** mechanism.

Analytical application of P-CNDs as sensor

The prepared **P-CND**s used for quantitative determination of total zinc in Zinc Tablets, and total aluminum in Antacid Tablet, as their matrices contain no quenchers and other enhancers as interferences. However, if analysis of zinc and

aluminum in different matrices are required, then masking agents should be used for increasing the selectivity.

Calibration graphs for series standard solutions for both Al^{3+} and Zn^{2+} ions were constructed (Fig. 8). The lower limit of detection, LOD (LOD = 3 SD/m, SD: standard deviation of the blank, m: is the slope of calibration) for Al^{3+} was 4 nM, and for Zn^{2+} it was 100 nM. Spiked recoveries for both were 103% and 102% for seven replicates. Such a label free nanoprobe with such a low LOD is very important in analytical chemistry especially for trace analysis. This is especially valuable, because one type carbon nanodot shows different emission when combined with different metal ions. Efforts to increase selectivity and sensitivity of the nanodots are underway in our lab.

Conclusions

Chelation-enhanced fluorescence of phosphorous doped carbon nanodots was observed after combining them with certain metal ions. Al³⁺, Zn²⁺ and Cd²⁺ show enhanced and tuned emission, some metal ions can quench the emission, like d¹⁻ ⁹ metal ions, while Alkali and Alkali earth metal ions neither show enhancement nor quenching. The enhancement mechanism can be attributed to complexation of the metal ions (enhancers) with high passivated surface functional groups of **P-CNDs**. The prepared label free fluorescent **P-CNDs** can used for detection of metal ions in interference free media, like pharmaceutical formulations, such as Zinc Tablets and Antacid Tablets. Detection limits as minimum as 4 nM was

Fig. 8 Fluorescence spectra and calibration graphs of a P-CND:Al³⁺, b P-CND:Zn²⁺. Photograph of free CNDs and different solutions of CND with c P-CND:Al³⁺, and d P-CND:Zn²⁺. The pH of P-CNDs with and without metals are 3–4. Excitation wavelength for P-CNDs, P-CND:Zn²⁺, P-CND:Cd²⁺ is 425 nm, for P-CND:Al³⁺ is 405 nm

obtained for Al^{3+} ions and 400 nM for Zn^{2+} ions. The main limitation of the nanodots for real sample analysis is lack of high selectivity and their universal response to many ions either quenchers or enhancers. The selectivity can be improved using proper masking agents.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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