

Bilimbi (*Averrhoa bilimbi*) fruit derived carbon dots for dual sensing of Cu(II) and quinalphos

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Abstract

Synthesis of highly fluorescent carbon dots from an agro crop through facile one-pot microwave method has been reported. Bilimbi fruit derived carbon dots named as BCDs, exhibited excellent photoluminescent properties and stability. Fluorescence of the system selectively quenched on interaction with Cu(II), due to the complex formation between amine, hydroxyl and carboxyl groups in the surface of the BCDs with Cu(II). The non-fluorescent complex displayed a selective and sensitive turn-on fluorescence behavior on adding organophosphorus pesticide quinalphos. And hence, the prepared system is used for dual sensing purposes with nanomolar level of detection limits. The limit of detection of Cu(II) and quinalphos was estimated as 115 nM and 510 nM, respectively. The entire detection process was visible under UV light of 365 nm. Moreover, the BCDs@Cu(II) nanoprobe was effectively applied as fluorescence sensor of quinalphos in real samples of rice and tea where its presence is frequently reported, with good level of recovery percentages.

Introduction

In the modern agricultural practices, organophosphorus pesticide are considered to be an essential element to assure high productivity of agricultural crops by providing protection against various diseases and wide variety of insecticidal attacks [1]. The wide acceptability of this type of pesticides are mainly because of their fast action against broad spectrum of pests by disturbing the carboxylic ester hydrolases functioning inside the body of pests [2]. The exceeded usage of pesticides adversely affects the health of all beings directly and indirectly. Besides, the excessive pesticide content in several food crops leads to rejection and recession in the importing of these crops and pose a black mark to the field. And in a broad sense the over usages of pesticide make impact not only on the health sector but also in the economy. O,O-diethyl-O-quinoxalinyI phosphorothioate generally known as quinalphos, a popular pesticide from the family of organophosphorus pesticides, is frequently applied in different types of crops including rice, tea and variety of fruits etc. [3]. Reports on the health issues caused by the quinalphos exposure reveals that, the trace amount of this pesticide has been affects central nervous system and other body functioning in a drastic manner. Intoxication of this pesticide occurs through many ways like inhalation, ingestion and skin absorption and all these leads to several health issues such as hypernatremia, pancreatitis, renal failure, weakness, low scoring memory and learning abilities [3, 4]. Therefore, precise profiling of this pesticide has been very crucial to ensure safeguarding of crops and appropriate pesticide managements. Various analytical techniques including chromatographic methods like gas chromatography [5], high performance liquid chromatography-mass spectrometry/ mass spectrometry [6], spectrofluometric assays [7] and enzyme-linked UV-Vis spectroscopy [8] are in practice to monitor quinalphos in agricultural commodities. However, the above methods have several drawbacks like requirement of sophisticated instruments, trained technicians, costly bio-reagents like antibodies and time consuming complicated procedures. On account of these facts and perceiving the merits of fluorescence sensing methods, fluorescent based sensor was developed for the selective and sensitive detection quinalphos.

Out of the most commonly used fluorescent sensor, carbon based nanomaterials mainly carbon dots, tremendously received wide acceptability due to many salient factors associated with it. They are the quasi- spherical photoluminescent carbon nanomaterials with particle size range under 10 nm. The major features of carbon dots, including biocompatibility, excellent water solubility, photobleaching resistance, lesser cytotoxicity, photostability, interesting and adjustable optical properties effectively contribute to its popularity [9, 10]. Owing to the aforementioned properties of carbon dots especially the fluorescent nature, they found many applications in several fields of science and technology in the past few years such as bio-imaging and bio-sensing, as fluorescent ink [11, 12], and several metal, non-metal and pollutant sensing in water and environmental samples [13, 14].

Carbon dots can be prepared from variety of sources, out of which biogenic carbon dots; carbon dots from biomass and bio-waste materials recently received more appraisal. The major facts behind this acceptance are accredited to its renewability, availability, cost effective, non-toxicity and environmental benign nature [15, 16]. In the present work, carbon dots are prepared from the bilimbi (*Averrhoa bilimbi*) fruit extract. This is considered as an acidic fruit enriched with acids like oxalic and ascorbic acids, various nutrients and several carbohydrates. It is considered as an excellent source of antioxidants and minerals and it used as medicine for variety of diseases in the indigenous system of medicine [17]. The acids present in the fruit extract believe to play an important role in the facile formation of carbon dots. Here, materialization of this biomass is carried out by the aid of greener microwave method, without using any other chemicals. The bio-resources utilized for the fabrication of a dual sensor through an eco-friendly method. Microwave heating is opted for the synthesis due to its inherent features like short reaction time and direct and homogeneous heating through which simultaneous time and energy savings can be achieved [18].

Through this piece of work an efficient dual sensing probe was fabricated from a single bio-source by the aid of microwave energy. This one-pot synthetic method completely devoid of any hazardous chemicals and expensive instruments and strictly followed all the greener principles. The as prepared system with strong fluorescence was firstly used as selective fluorescent turn off probe for the sensing Cu(II) and the resulting non-fluorescent system executed as the turn on fluorescent probe for the organophosphorus pesticide, quinalphos. The limit of detection of both falls in the nanomolar range (115 nM for Cu(II) and 510 nM for quinalphos). The quinalphos sensing is also carried out in real rice and tea samples with good recovery percentage. The real samples are purposefully selected because the content of this particular pesticide is frequently noticed in rice and tea; the samples were collected from the local market of Kerala, a popular consumer state in India.

Experimental Section

Chemicals and apparatus

Bilimbi fruit were collected from the nearby garden in the month of June. All chemicals used in the present work were of analytical grade and were used as such without further purification. Copper sulfate

pentahydrate, cobalt nitrate, nickel nitrate, mercuric chloride, lead nitrate, aluminium sulphate, cadmium chloride and ferric chloride hexahydrate were procured from Merck Pvt. Ltd., India.

The prepared system was characterized with several analytical techniques. Morphology examination and particle size distribution of the as synthesized carbon dots (BCDs) were evaluated from the transmission electron microscope (TEM) images. Selected electron diffraction (SAED) pattern was used to study the crystalline nature of the BCDs. Both were captured with JEOL JEM 2100. Surface functionalities of BCDs were identified and studied with PerkinElmer Fourier transform infrared (FTIR) spectrum instrument. The all FTIR spectra were recorded with average scan rate of 64 scans in the range of 4000-500 cm^{-1} . The optical properties of the system was explored using PerkinElmer UV-Visible spectrometer and PerkinElmer FL6500 fluorescence spectrometer instruments. All the fluorescence spectra were recorded at 25 °C in the range of 200-800 nm. The luminescence nature of BCDs was observed by using ROTEX UV cabinet, photographs of fluorescent BCDs also taken from the same cabinet.

Synthesis of carbon dots

Bilimbi fruits were washed thoroughly with water and were cut in to small pieces and crushed using mortar and pestle. The resultant fruit paste was transferred to a beaker with 30 mL of hot distilled water, and it was magnetically stirred for 30 minutes. Afterwards the solution was filtered and placed in domestic microwave oven at 500 W for 20 minutes of time with frequent cooling in every 5 minutes. The as obtained residue was stirred with 30 mL of distilled water, filtered, centrifuged to remove large and unreacted particles. Finally the solution was dialyzed (dialysis membrane with 3 KDa molecular weight cut off) against distilled water for 48 hrs. The resultant brownish solution of carbon dots designated as BCDs was stored at 4°C.

Quantum yield calculation

The quantum yield of the prepared system was determined as per the standard method using quinine sulfate in 0.1M H_2SO_4 as standard. It was calculated by the equation 1.

$$Q_S = Q_{\text{BCDs}} [M_{\text{BCDs}} / M_S] (n_{\text{BCDs}}^2 / n_S^2)$$

Where Q is the quantum yield, M is the slope of the linear graph obtained from the plot of integrated fluorescence intensity with corresponding absorbance. S and BCDs are representing the standard and carbon dots, respectively. n is the refractive index of the solvents used to dissolve the standard and BCDs.

Quinalphos detection

Quinalphos sensing was carried out using fluorescence spectra studies. Firstly the fluorescence spectrum of BCDs solution was recorded at an excitation of 430 nm giving emission maxima at 531 nm. The native fluorescence of BCDs was quenched by the addition of different concentration of Cu(II) solution. This BCDs@Cu(II) was utilized as the probe solution for the quinalphos pesticide sensing. The sensing probe was developed by the following procedure; 2 mL of BCDs solution was taken in the quartz cuvette and the

fluorescence spectra of the bare BCDs was recorded at 430 nm, then different concentration of Cu(II) solution was introduced to the system by using a micropipette. The spectra were recorded after an incubation time of 5 minutes using the same instrument and intensity of emission spectra were noted down in each addition and all spectra were recorded at the same excitation wavelength. As concentration of Cu(II) increases the intensity was gradually decreased. The selectivity of BCDs towards Cu(II) has been studied by recording the spectra of BCDs with different metal ions (Co(III), Ni(II), Hg(II), Pb(II), Al(III), Cd(II) and Fe(III)). The probe for quinalphos sensing have been developed by the addition of definite concentration of Cu(II) solution to the BCDs and termed as BCDs@Cu(II). Then quinalphos detection by the probe was conducted as follows; about 2 mL of BCDs@Cu(II) was taken in the cuvette, fluorescence spectrum of the probe was recorded. Subsequently different concentrations of quinalphos were added to the probe solution by the aid of micropipette and were kept for 10 minutes as incubation time and spectra were recorded by the same experimental conditions as above. The intensity of emission spectra was monitored.

The fluorescence response of the probe with different pesticides such as glyphosate, marathion, dichlorovos, chloropyrifos and diethylthiocarbamate were screened to study the selectivity of the probe towards quinalphos. The selectivity investigation follows the same procedure with same concentration and experimental conditions as above.

Real sample analysis

To assert the practicability of the developed probe, the sensing was carried out using real samples. Two different agricultural crops, rice and tea were selected as real samples and were collected from the local market. For this study rice and tea extract were prepared as follows; about 5g of each samples were gently grinded and soaked in hot distilled water for 2 hrs of time in two beakers. Later the mixture was filtered and centrifuged. The resulting extracts were spiked with different concentration of quinalphos solution, and were kept stand for 24 hrs. The spectra of the spiked samples with BCDs@Cu(II) probe were recorded at the excitation wavelength of 430 nm after an incubation of 10 minutes. The detection was carried out by monitoring the fluorescence response of the probe. The corresponding recovery percentage was calculated in each case.

Results And Discussion

Synthesis and characterization

BCDs were prepared by the microwave heating of bilimbi extract. Bilimbi extract consists of plenty of acids and carbohydrates [17]. The suggested carbon dot formation mechanism falls under the category of bottom-up synthesis; formation of nano-dimensional particles from smaller molecules by various steps like, condensation, polymerization, carbonization and nuclear burst under the microwave irradiation. The acids presents in the extract, like oxalic acid plays an important role in the initiation of hydrolysis and dehydration of carbohydrates present in the extract by utilizing the microwave energy. Then the formation of water soluble fluorescent nano-materials, through various reactions including,

decomposition, condensation, carbonization and aromatization reactions on the dehydrated carbohydrate products [18–20]. The Transmission electron microscope images were used to examine the morphology and particle size of the BCDs and were found to be nearly spherical in shape (Fig. 1a). The selected electron diffraction pattern of the particle was used to examine the crystalline or amorphous phase structure of BCDs. As shown in Fig. 1b, it does not possess bright spots or clear well defined pattern indicating that the crystallinity of the BCDs is very poor [21].

Fourier transform infrared spectroscopy has been used to identify the functional groups associated with the prepared nanomaterial and the spectrum is displayed in Fig. 2. Two bands at 3363 and 3268 cm^{-1} was arises due to combined effects of O-H and N-H stretching vibrations. A peak at 2930 cm^{-1} is attributed to stretching vibration of C-H, a medium band at 1719 cm^{-1} was accredited to C=O stretching. A comparatively strong band arising due to stretching vibration of C=C bond at around 1625 cm^{-1} implies the existence of aromatic sp^2 clusters [20]. Asymmetric and symmetric stretching vibration of COO^- indicated by the two bands located at 1521 and 1436 cm^{-1} . Bands at 1360 and 1026 cm^{-1} was contributed by the C – N stretching vibrations [20, 22], whereas peak centered at 1208 cm^{-1} attributed to the stretching vibrations of C-O group. As a whole the spectral data reveals that the surface of BCDs enriched with plenty of carboxyl, hydroxyl and amine functionalities and these hydrophilic groups plays a vital role in the excellent stability and solubility of the system in aqueous medium.

The luminescent behavior of the system was explored the UV-Vis absorption and fluorescence spectroscopes. The absorbance spectrum of BCDs exhibits a strong peak at 309 nm originated due to the $n\text{-}\pi^*$ transitions of C=O bonds present in the BCDs [23], and the corresponding spectrum is shown in Fig. 3a. The fluorescence nature of the BCDs was studied by the fluorescence spectrum and its excitation dependence nature was investigated by recording the spectra at different wavelength ranging from 290 nm to 450 nm (Fig. 3b). The results reveals that the system having excitation wavelength dependent nature, and this behavior may derived from the polydispersity and electronic transitions of surface attached functional groups like C=C and C-NH₂ bonds. This implies that the fluorescence peak is adjustable with excitation wavelength and it shows tunable nature of the system. Moreover, the full width half maximum of the fluorescence curve was about 90 nm indicating that the range of size distribution of BCDs comparatively narrow [22]. The excitation dependence study also reveals that the BCDs shows maximum emission peak when excited at 430 nm and the emission band is centered at 531 nm (Fig. 3c). These values were selected as excitation and emission wavelength for further studies. In addition, the prepared system exhibits strong bluish fluorescence under UV light and the photographs of the BCDs in normal light and UV light of 365 nm is shown in Fig. 3d along with the fluorescence excitation and emission graphs of BCDs. The fluorescent quantum yield of the synthesized system was about 3.4%, determined by using quinine sulphate as standard with quantum yield of 54%.

The stability of the prepared system was investigated against different ionic atmosphere, UV irradiation and time. It was found to be stable up to nine weeks of time at 4°C and its stability is comparatively lesser in atmospheric temperature and open atmosphere storage leads lesser stability and kind of fungal

infections are noticed over time. Under UV light (365 nm) the system shows apparent stability up to 3 hours of continues irradiation, after that fluorescence slightly reduced. The fluorescence intensity of BCDs not shows any significant effect in presence of different concentration of KCl solution. All these facts reveals that the system have good stability features.

Fluorescence sensing and detection of Cu(II) and quinalphos

The fluorescence property of the as prepared BCDs was utilized for dual sensing purpose. Firstly, the fluorescence response of the system with addition of different concentration of Cu(II) solution was studied. A gradual decrease in the native fluorescence of BCDs was observed on increasing Cu(II) concentration. This quenching of fluorescence is shown in Fig. 4a, indicating the fluorescence intensity of the emission peak centered at 531 nm decreased with Cu(II). The plot of F_0/F with concentration of Cu(II) was shown in Fig 4b, where F_0 and F was the fluorescence intensity of BCDs before and after the introduction of Cu(II). A good linear relationships between relative fluorescence intensity and concentration of Cu(II) was maintained in the concentration range of 0- 20 μM with linear equation $F/F_0 = 0.06[\text{Cu(II)}] + 0.97$ with $R^2 = 0.9986$. Limit of detection for copper was calculated from this linear range and it was found to be 115 nM. To investigate the selectivity of the system towards Cu(II), fluorescence response of BCDs with different metal ions like Co(III), Ni(II), Hg(II), Pb(II), Al(III), Cd(II) and Fe(III) were tested under the same experimental conditions. It reveals that the quenching efficiency of Cu(II) was comparatively higher than the other metal ions under study (Fig. 4c).

On account to the fluorescence quenching by the addition of Cu(II) a new probe was developed from BCDs and was successfully employed for the sensing of quinalphos. As mentioned earlier the probe was prepared by adding definite concentration of Cu(II) to BCDs solution and termed as BCDs@Cu(II). Fluorescence response of BCDs@Cu(II) with different concentration of quinalphos (0- 10.32 μM) was evaluated and the corresponding spectra is shown in Fig 5a. A significant enhancement of fluorescence intensity was noticed with increasing concentration of quinalphos. This fluorescence turn on behavior is clear from the figure. The relationships between relative fluorescence intensity with concentration of quinalphos was linear from 0 to 10.32 μM range of quinalphos concentration and it is depicted in Fig. 5b, with linear regression equation $F/F_0 = 0.46[\text{QP}] + 1.09$ ($R^2 = 0.9977$). Where F and F_0 are the fluorescence intensity of BCDs@Cu(II) after and before the addition of quinalphos, respectively. The corresponding limit of detection was 510 nM based on $3\sigma/\text{slope}$ equation, where σ is representing standard deviation and slope is obtained from the linear plot. The selectivity of the nanoprobe against quinalphos was investigated by selectivity studies. The fluorescence response of BCDs@Cu(II) with different organophosphorous pesticides were screened. The fluorescence enhancement was much higher for quinalphos on comparing with others (Fig. 5c). Photographs of BCDs, BCDs@Cu(II) and BCDs@Cu(II)+QP under UV light of 35 nm is given in Fig. 5d.

Probable sensing mechanism

In the present study two different fluorescence responses was encountered. Firstly the fluorescence of BCDs getting reduced by the addition of Cu(II) and this quenching may attributed to non-radiative ground state complex formation between Cu(II) and surface functionalities of BCDs. FTIR data reveals that the surface contains plenty of hydroxyl, carboxyl and amino functional groups. Especially the amino group present in the BCDs readily forms cupric amine complexes with Cu(II) and this may result in the fluorescence quenching and this type of quenching coming under the category of static quenching. The absorbance spectra of BCDs, Cu(II) and BCDs@Cu(II) was recorded and the changes in the absorbance and wavelength was noticed in the spectra of BCDs and BCDs@Cu(II) representing the static quenching mechanism. Moreover there is an extra peak formation in BCDs@Cu(II) spectra around 345 nm and it may attributed to new complex formation (Fig. 6a). This non-fluorescent complex was further utilized as a probe for quinalphos sensing applications. When quinalphos was introduced to the system a remarkable fluorescence increment was noticed and it could be ascribed to the following. The non-fluorescent nature of the BCDs@Cu(II) was losses gradually due to the release of BCDs from the complex. The quinoxaliny and phosphorothioate groups present in quinalphos have been profound chelating ability to Cu(II), therefore the quinalphos addition rupture the non fluorescent BCDs@Cu(II) complex and thus resulting to the recovery of native fluorescence of BCDs [3]. The UV-Vis spectra of BCDs, quinalphos, BCDs@Cu(II) and BCDs@Cu(II)+QP (QP is quinalphos) were investigated to further confirm the facts (Fig. 6b). The changes in the absorbance of spectrum BCDs@Cu(II)+ QP with that of BCDs@Cu(II) and decrease in absorbance of the newly formed peak by the addition of quinalphos were clear from the spectral data, implies that the formed complex somewhat disturbed by the addition of quinalphos and hence the BCDs recovers its fluorescence. In consideration of above results the sensing mechanism of the prepared system attributed to static quenching followed by the recovery of fluorescence through release of BCDs from the non-fluorescent complex via competitive chelation of Cu(II) with quinalphos.

Analysis of quinalphos in rice and tea samples

The feasibility of the probe was assessed for the detection of quinalphos in spiked rice and tea samples, where the quinalphos content was observed often. The illustrated procedure consists of comparatively simple steps and follows standard addition method. The samples were separately prepared and spiked with different concentration of quinalphos (0, 4, 6, 8 μ M) and were estimated through aforementioned procedure. The results were given in Table 1, the recovery ranges of the quinalphos in rice and tea samples were found to be 95.25 – 97.83 % and 95.33 – 102.12 %, respectively. The corresponding error percentages also show satisfactory levels of accuracy and precision. These results manifested that the fabricated probe could be employed to practical on- field samples.

Table 1 Determination of quinalphos in real samples

Sample	Added quinalphos (μM)	Found (μM)	Recovery (%)	Error (%)
Rice	0	Not found	–	–
	4	3.81	95.25	4.75
	6	5.87	97.83	2.16
	8	7.75	96.88	3.12
Tea	0	Not found	–	–
	4	3.87	96.75	3.25
	6	5.72	95.33	4.66
	8	8.17	102.12	2.12

Conclusion

In summary, a selective and sensitive dual sensor was developed through a simple one step microwave heating process. The produced carbon dots (BCDs) characterized well and owing to the strong fluorescent behaviour, it has been used as a fluorescent probe for the sensing of Cu(II) and quinalphos. In the presence of Cu(II), the native fluorescence of the system gets quenched due to the formation of ground state, non-fluorescent BCDs@Cu(II) complex. This turn off behavior of the system was accredited to static quenching mechanism. The fluorescence of the BCDs@Cu(II) gets turn on by the addition of quinalphos and this fluorescence enhancement is due to the strong chelating interaction between Cu(II) and quinalphos, making the BCDs free from the complex and regain its luminescence. The limit of detection of Cu(II) and quinalphos was found to be about 115 nM and 510 nM, respectively. Based on the simplicity and efficacy of the illustrated method of detection, the BCDs@Cu(II) probe was successfully employed for quinalphos detection in real rice and tea samples. The good level of precision and accuracy with recovery percentage ranging from 95.25–102.12% are promising to use the system for detecting quinalphos in commercial samples.

Declarations

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Author Declarations

1. Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Vidya N. The first draft of the manuscript was written by Vidya N. Review, editing and supervision of work was performed by Venugopalan P. All authors read and approved the final manuscript.

2. Conflicts of interest/Competing interests

The authors declare they have no competing interests.

3. Funding

No funding was received for this study.

4. Ethics Declaration statement

Not applicable

5. Consent to Participate

Not applicable

6. Consent for publication

Not applicable

7. Availability of data and material/ Data availability

All data generated or analysed during this study are included in this published article

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Figures

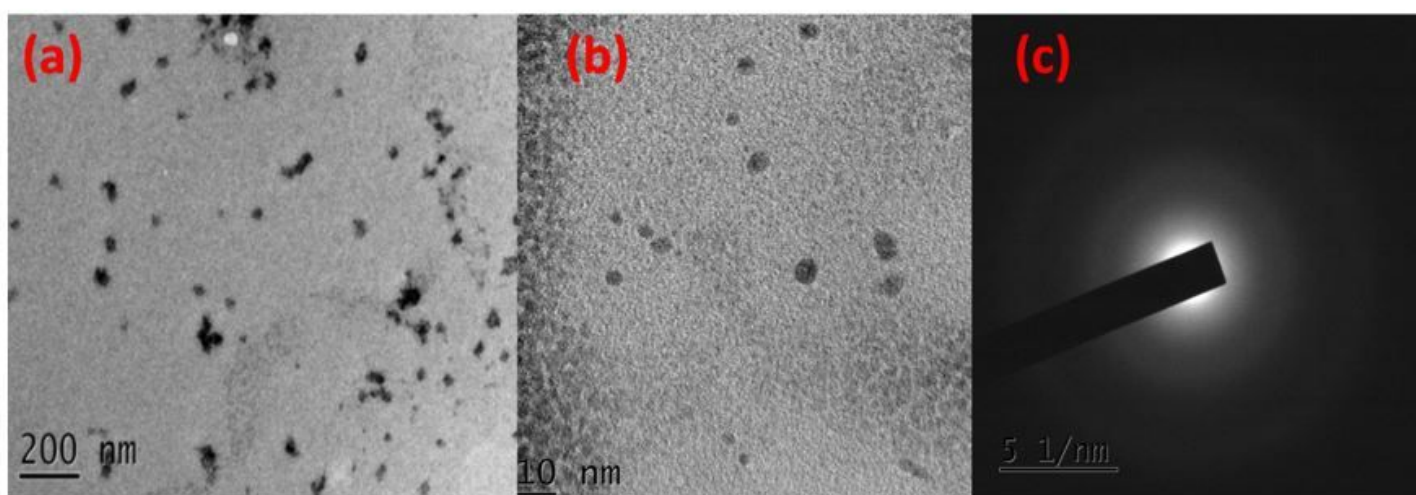


Figure 1

a, b TEM images of BCDs at different magnification **c** SAED pattern of BCDs

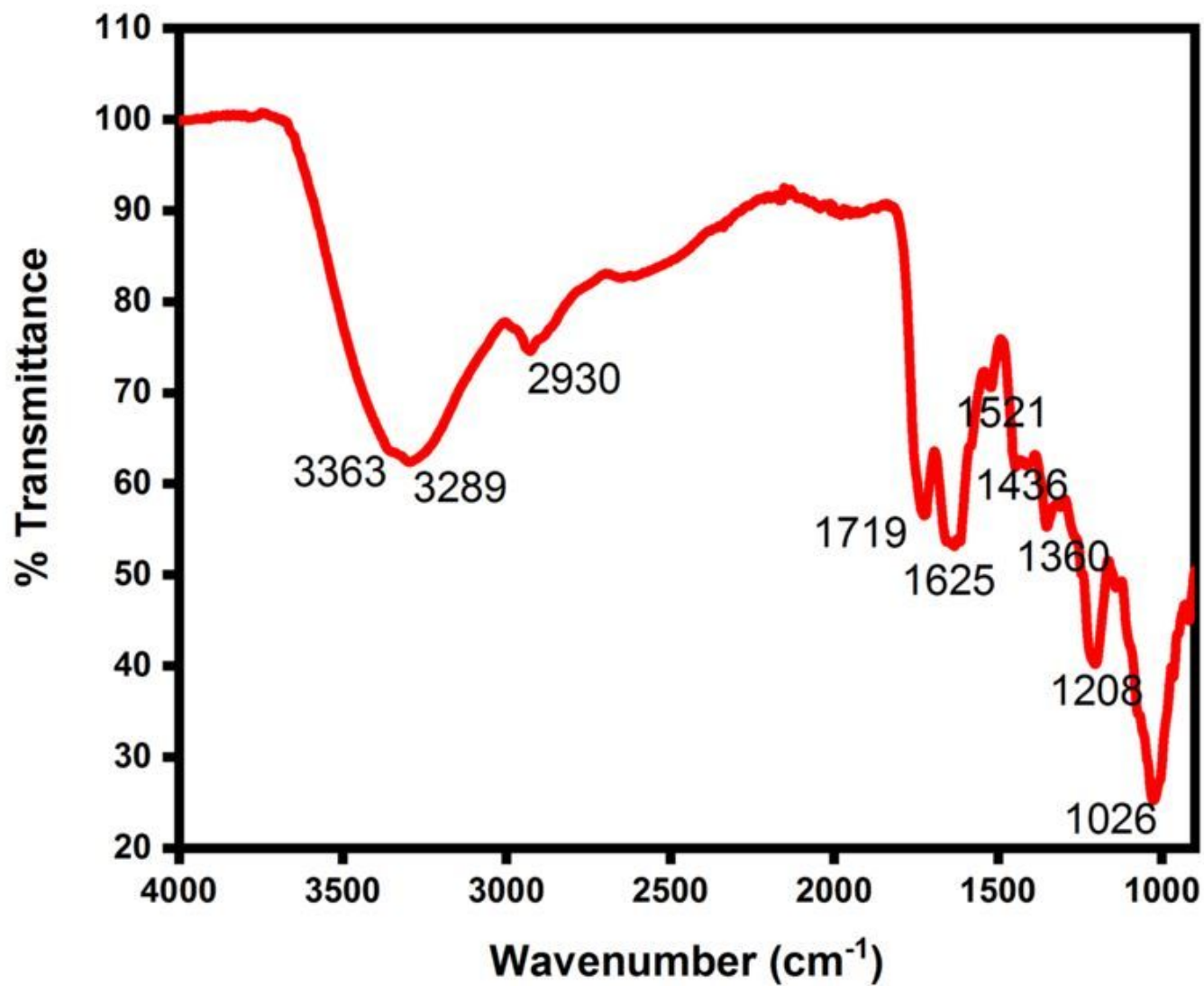


Figure 2

FTIR spectrum of BCDs

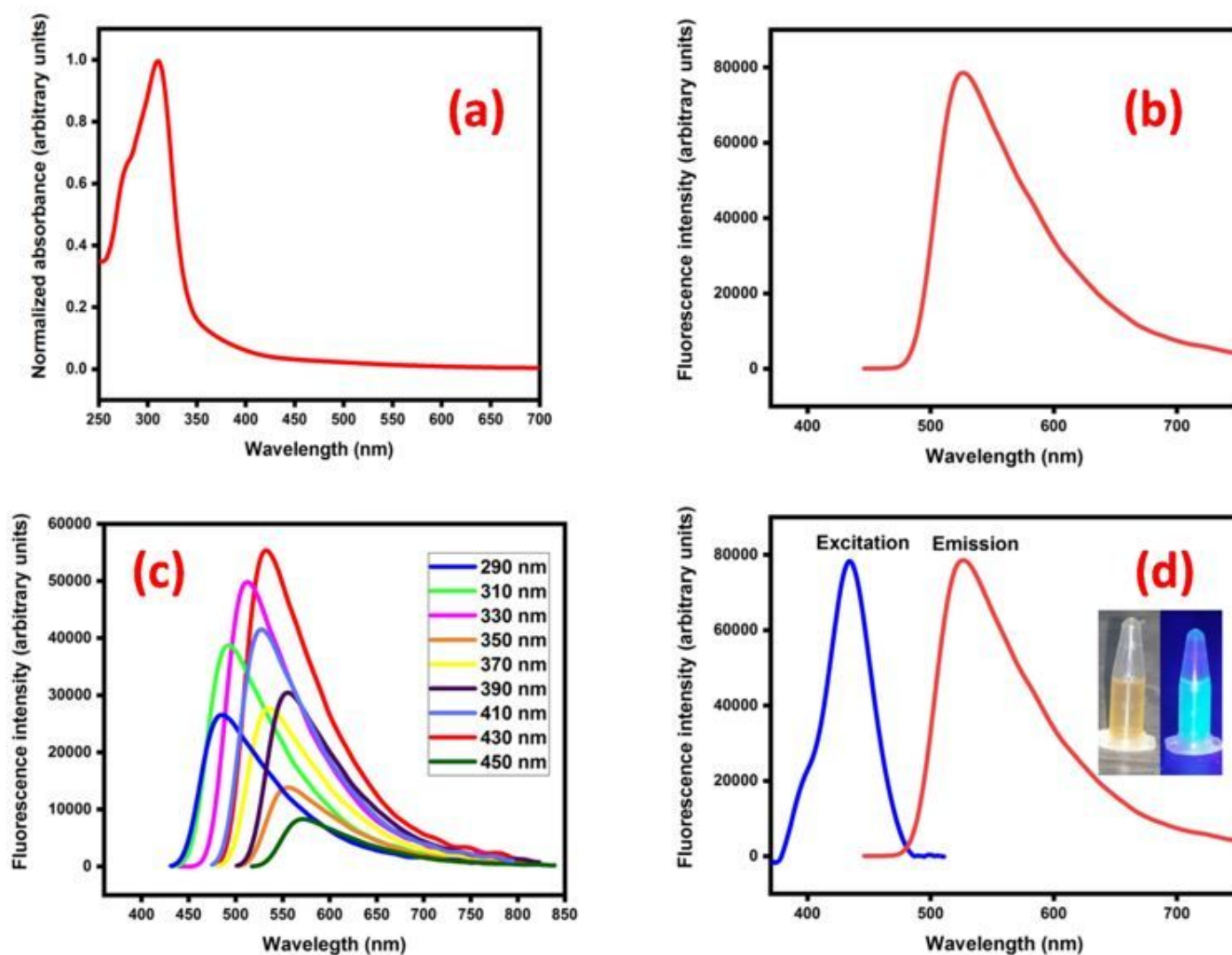


Figure 3

a Normalized UV-Vis absorption spectrum of BCDs **b** Fluorescence spectrum of BCDs **c** Excitation dependent emission spectra of BCDs from 290 nm to 450 nm **d** Excitation and emission spectra of BCDs (inset: BCDs at normal light(left) and BCDs at UV light(right))

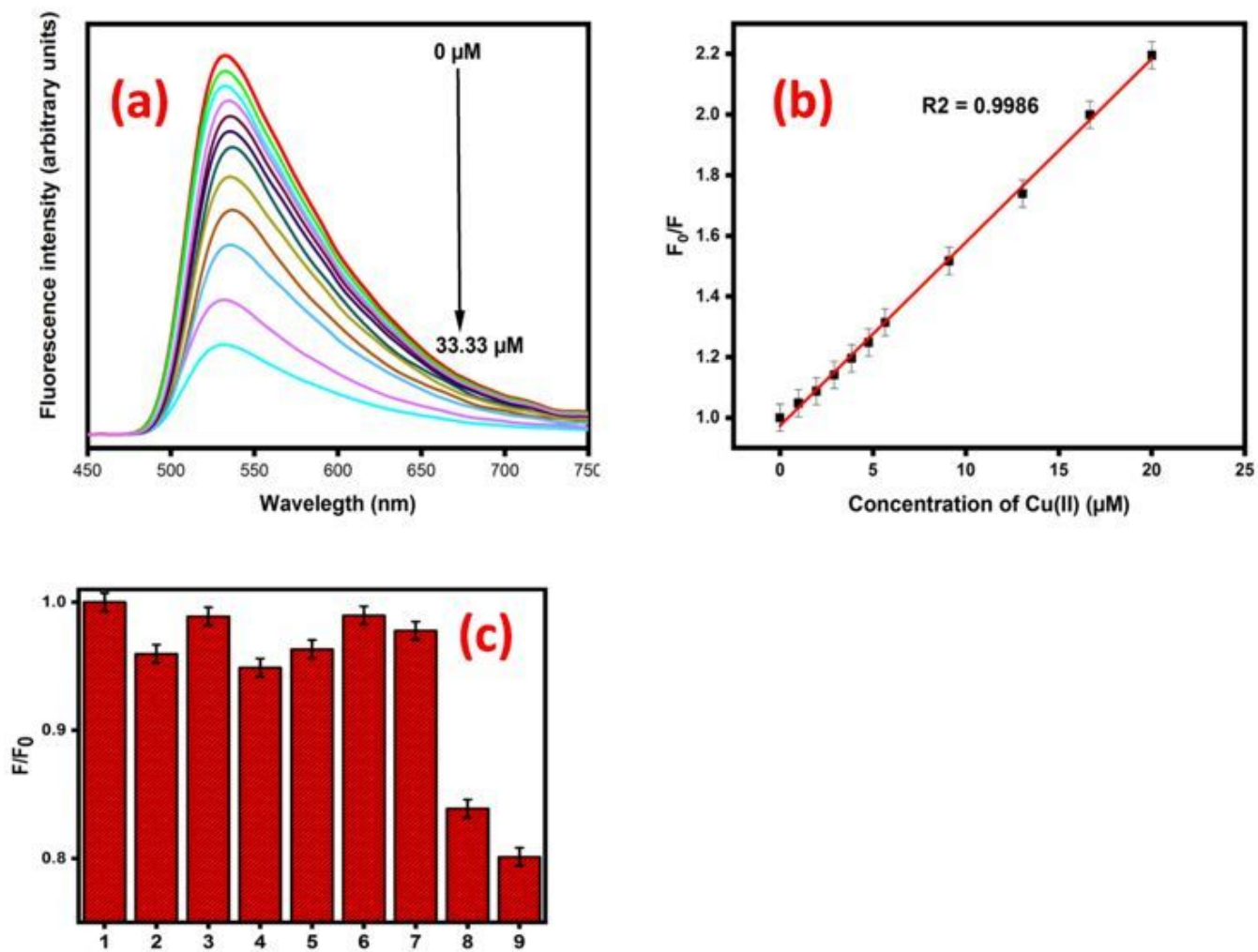


Figure 4

a Fluorescence emission spectra of BCDs with different concentration of Cu(II) **b** Relative fluorescence intensity with concentration of Cu(II) **c** Relative fluorescence intensity of BCDs with different metal ions (1 to 9 representing BCDs, Co(III), Ni(II), Hg(II), Pb(II), Al(III), Cd(II), Fe(III) and Cu(II))

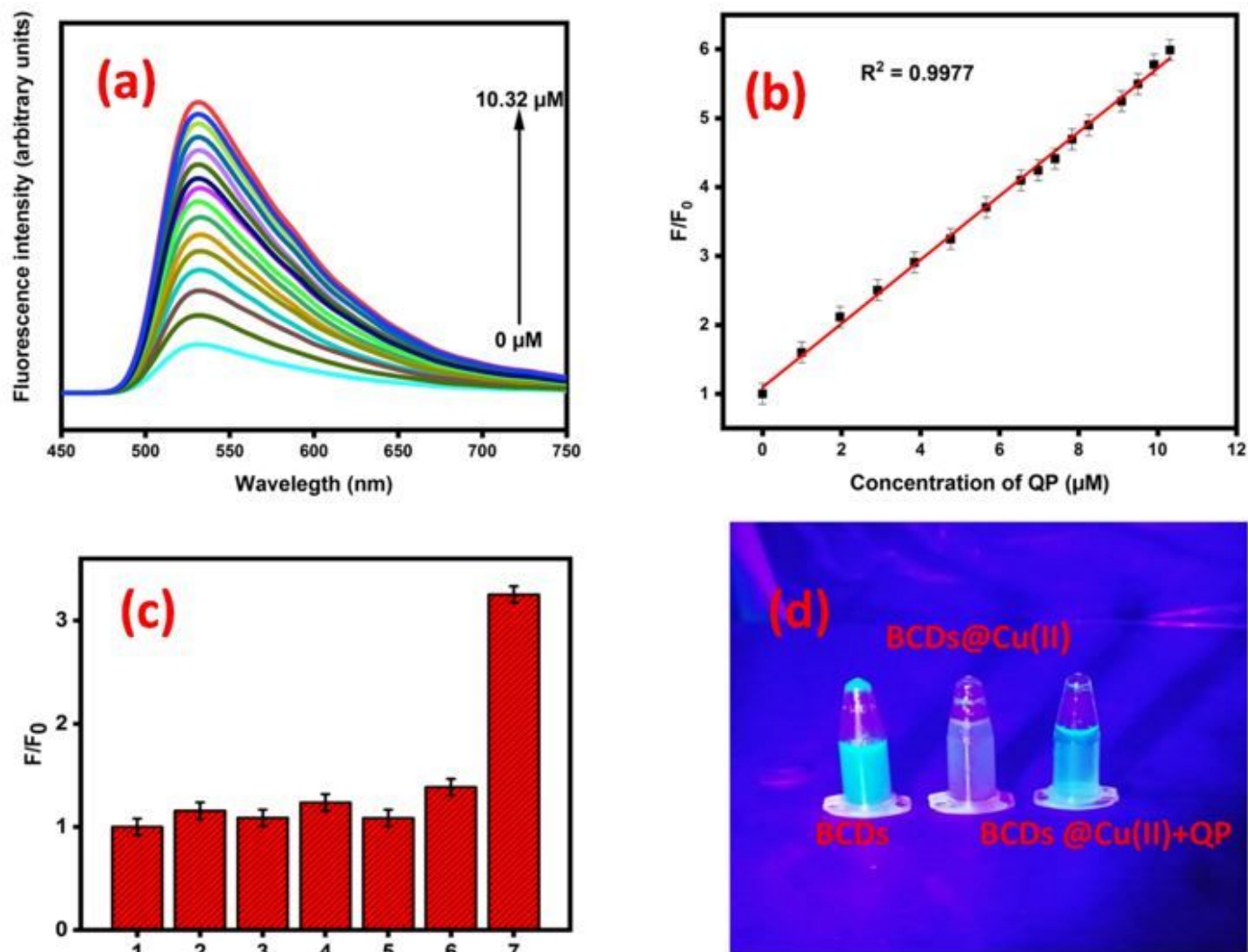


Figure 5

a Fluorescence emission spectra of BCDs@Cu(II) with different concentration of quinalphos **b** Relative fluorescence intensity with concentration of quinalphos **c** Relative fluorescence intensity of BCDs@Cu(II) with different pesticides (1 to 7 representing BCDs@Cu(II), glyphosate, marathion, dichlorovos, chlorpyrifos, diethylthiocarbamate and quinalphos) **d** UV cabinet photographs of BCDs, BCDs@Cu(II) and BCDs@Cu(II)+QP at 365 nm

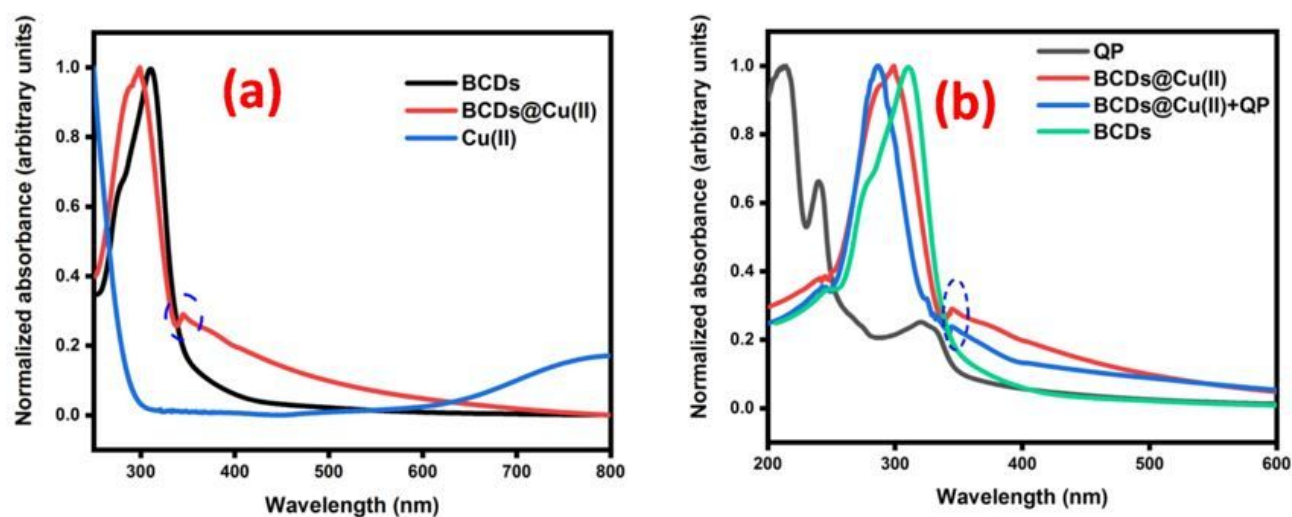


Figure 6

a Normalized UV-Vis absorption spectra of BCDs, BCDs@Cu(II) and Cu(II) **b** Normalized UV-Vis absorption spectra of quinalphos (QP), BCDs@Cu(II), BCDs@Cu(II)+QP and BCDs