Preparation, characterization and cell cytotoxicity of Pd-doped CdTe quantum dots and its application as a sensitive fluorescent nanoprobe

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Abstract

Dopants strongly affect properties and optical behaviors of quantum dots, therefore doped-QDs considered as a novel class of luminescent materials. Following development doping approach and using Pd²⁺ ions as a dopant, for the first time, in this study, a facile preparation of Pd-doped CdTe QDs was reported with thioglycolic acid as a stabilizer. The essential parameters of the synthesis conditions such as dopant concentration, reaction time and optical properties of the Pd: CdTe QDs was studied. The Pd: CdTe QDs with excellent photostability and biocompatibility, exhibited a greenish emission at 529 nm. Interestingly, these nanoparticles display high fluorescence sensitivity to diazinon (DZN). Under optimal conditions, a proposed sensor was designed based on Pd: CdTe QDs which represented a wide range of linear response (2.3–100 µM), low detection limit [3.3 nM, (S/N=3)], high stability, and selectivity. Additionally, the newly sensing nanoprobe was used for the determination of DZN in environmental water samples with satisfactory results.

1 Introduction

Quantum dots (QDs) have been investigated during in the past few decades because of unique optical properties such as broad and strong absorption, high fluorescence quantum yield, narrow and symmetric emission with tunable colors [1–4]. These features make them an excellent candidate in diverse applications including solar cells, biosensors, and bioimaging probes [5–14].

Among the group II–VI semiconductors quantum dots, the Cadmium-based nanoparticles have attracted great attention because of specific features like as absorption coefficient, the narrow bulk band gap, and high photostability

[15–17]. However, the CdTe QDs typically contain the highly toxic heavy-metal atom, Cd, which increases concerns on the safety for various applications [18–27]. To date, numerous efforts have been dedicated to the design and fabricated of CdTe QDs with lower toxicity, highly efficient fluorescence and tunable emission wavelength [28–30].

Doping is a widely applied technological progress in nanomaterials science to yield materials with favorable properties and operation [31]. Doped quantum dots with variety of transition-metal ions namely Ag¹⁺, Mn²⁺, Cu²⁺, Ni²⁺, Cr³⁺, Eu³⁺ and Yb³⁺, show that, preserved almost all of the properties of the un-doped QDs and may have added some advantages, for example, reduction of the toxicity, enhanced thermal and environmental stabilities and also mitigated serious problems, for instance, electron–hole pair recombination and leaching [14, 29, 32–37]. Recent researches indicated that by the addition of noble metals like palladium in the host semiconductor nanoparticle, the optical features of some QDs by changing the band gap were improved [38–40]. So, considering aspects of favorable environmental effects of palladium, the properties of quantum dots can be improved by doped palladium ions and then, they can be used in various fields such as sensors and catalysts.

Diazinon (DZN) is a popular organophosphate insecticide which widely used on turf, alfalfa, lettuce, almonds, cotton, citrus, and other crops especially rice [41, 42]. Commonly, DZN released into the environment is moderately persistent,

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so that in the neutral water can stay 6 months. Unfortunately, the residual of the DZN in different parts of the living environment, as soil and water, may have great effects on the aquatic eco-systems and even at low concentrations can be very dangerous for human health [43, 44]. On the other hand, because of high agricultural production demand, pesticide usage is almost inevitable. Thus, the determination of the concentration and trace amounts of DZN in environmental waters with the affordable and highly sensitive analytical method is necessary [45, 46].

Here, in this study, a novel synthesis of thioglycolic acid (TGA) capped Pd: CdTe QDs was reported by hydrothermal method using palladium ions as a dopant. As it is shown in Fig. 1, the fluorescence intensity of the obtained QDs is quenched linearly in the presence of DZN. Thus, this novel nanoprobes was applied for highly sensitive and selective detection of DZN in environmental waters and displayed satisfactory results. Further, cytotoxicity assay using the Pd: CdTe QDs was also carried out successfully, that promises its brilliant prospect in the biological and medical application.

2 Materials and methods

2.1 Chemicals

Cadmium chloride, palladium(II) acetate, sodium hydroxide, tellurium powder, thioglycolic acid, and DZN were purchased from Sigma Aldrich (St. Louis, MO, USA). Other routine chemicals were purchased from Merck (Darmstadt, Germany) or Sigma Aldrich. Stock standard solutions of DZN with a concentration of $1 \times 10^{-3} \text{ mol L}^{-1}$ was prepared in the ultra-pure water and stored at 4 °C. All reactions were carried out in double deionized water.

2.2 Instrumentation

Perkin-Elmer LS-55 B fluorescence spectrometer was utilized to record the fluorescence spectra. FT-IR spectra were recorded by using a Perkin-Elmer Spectrum RXI FT-IR spectrometer. The ultraviolet (UV) absorption spectra to study the spectral properties of synthesized quantum dots were collected using an Agilent 8453 (USA) spectrophotometer. Transmission electron microscopy (TEM) images of the samples were obtained on Tecnai T20 microscope operating at 200 kV (FEI). X-ray diffractions (XRD) were performed on Panalytical X'pert PRO diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) under room temperature. The

Fig. 1 The schematic illustration for Pd: CdTe QDs sensor for detection of DZN

chemical composition of the nanocrystals was determined by using an SEM with energy dispersive X-ray (EDX) detector INCA Penta FETx3.

2.3 Preparation of Pd: CdTe quantum dots

Luminescent Pd: CdTe QDs dots were synthesized via one-pot hydrothermal method using thioglycolic acid (TGA) as a stabilizer. Briefly, 300 μL of palladium(II) acetate ($1 \times 10^{-3} \text{ mol L}^{-1}$) in acetonitrile was added to 0.15 g of CdCl_2 and TGA (80 μL) in the deionized water (50 mL). The pH of the mixture was adjusted to 10 by addition of NaOH solution and stirred for 3 h. Next, for the preparation of sodium hydrogen telluride (NaHTe), the 0.06 g of Te powder with 0.08 g of sodium borohydride added in of deionized water under stirred and N_2 purging for 3 h. Then, the prepared sodium hydrogen telluride was immediately injected into the above Cd solution. The resulting solution was transferred into a Teflon-lined stainless steel autoclave and heated in an oven at 100 $^\circ\text{C}$ for 3 h. The resultant product was washed with ethanol and kept at 4 $^\circ\text{C}$ in the dark for further use.

2.4 Fluorescence study

To observe the quenching effect of DZN upon the FL intensity of quantum dots, first, 5 mL of the Pd: CdTe QDs were dissolved in distilled water to achieve a solution of 1 μM . Afterward, the FL intensity of nanoparticles was recorded. Subsequently, 100 μL of the above solution with a various concentration of DZN added to 3 mL of Tris–HCl buffer ($1.0 \times 10^{-3} \text{ M}$, pH 7.1), after 1 min, fluorescence emission spectrum measured at 25 $^\circ\text{C}$. All the fluorescence measurements were recorded over the wavelength 400–650 nm upon the excitation wavelength at a 340 nm. The slit widths for excitation and emission were set on 10 nm. The quantum yield of quantum dots was determined using quinine sulfate ($\text{QY} = 0.54$ in 0.1 M H_2SO_4) as a reference chemical by using following the Eq. (1):

$$\text{QY}_x = \text{QY}_R \times A_R/A_x \times I_x/I_R \times \eta_x^2/\eta_R^2 \quad (1)$$

where I , A and η are the integrated area under the emission peak, the absorbance at the excitation wavelength and the refractive index of the solvent, respectively. R and X related to the standard and the sample of interest.

2.5 Determination of DZN

To confirm the feasibility of DZN detection in environmental water, samples were collected from a suburb of Kermanshah city and Gamasiab river. Before measurement, the 10 mL of the collected water samples were filtrated through

0.22 μm membrane filters to eliminate the suspended solids and then diluted ten times by Tris–HCl buffer ($1.0 \times 10^{-3} \text{ M}$, pH 7.1). Subsequently, the FL and absorbance spectra of the solution were recorded containing Pd: CdTe QDs (100 μL) and different amount of DZN after incubation for 1 min.

2.6 Cell viability assays

The cytotoxicity of Pd: CdTe QDs on fibroblast cells were evaluated by using the activity of the lactate dehydrogenase (LDH) method and reported by Linford with some minor changes. In this work, the primary culture of human fibroblast was used as a normal cell that is derived from human skin. The cells were seeded in 25-cm² tissue culture flasks and maintained in Dulbecco's MEM supplemented with inactivated fetal bovine serum 10%, penicillin 100 U mL^{-1} and streptomycin 100 $\mu\text{g mL}^{-1}$ for 48 h at 37 $^\circ\text{C}$ and 5% pCO_2 . In summary, the cells (in culture medium) were dispensed in 5×10^3 per well in 96-well microplates and allowed to incubate overnight. After 24 h of early cell culture, the fresh medium with nanoparticles at concentrations (1.0, 1.5, 2.0, 2.5, 3.0 μM) was renewed. Again, 100 μL of the media from each well was then transferred to new 96-well plates, and 100 μL of LDH stock was added to each well and cells were incubated at 37 $^\circ\text{C}$ for 30 min. Triton 1% was used as a positive control for the extraction test. The LDH release was estimated using a microplate reader at 495 nm according to the manufacturer's instructions. All measurements were done in triplicate and the mean cell viability was expressed as a percentage of the control.

3 Results and discussion

3.1 The optical properties of Pd: CdTe QDs

To optimize the synthetic method, the effect of dopant concentration and time reactions upon the quantum yield (QY) was investigated. First, to investigate the reaction time, the QDs were synthesized at different reaction time (0, 60, 120, 180, 240, and 300 min) and different-colored and QY (~2%, 13%, 23%, 28%, 22% and 20%) was obtained for Pd: CdTe QDs (Fig. 2a). During the reaction, the quantum dots size gradually increases with the reaction time. Along with passing the time, the red-shifts were observed in the emission and absorbance nanoparticle spectrum (Fig. 2b). This phenomenon is due to the quantum confinement effects that show the optical property of QDs is correlated with particle size [47, 48]. The result revealed the FL of Pd: CdTe QDs increased to 180 min and then by increasing the reaction time the FL were decreased. Thus, 180 min was selected as the optimal time required for the synthesis of Pd: CdTe QDs. The FL spectra in corresponds to the FL colors of doped

Fig. 2 **a** Photos of QDs under 365 nm UV light in different reaction times, **b** absorption and emission spectra of Pd: CdTe QDs with reaction time, 0–300 min (λ_{ex} = 340 nm), **c** normalized absorption and emission spectra of Pd-doped CdTe QDs

QDs. According to the previous studies, the FL intensity of doped-QDs is strongly influenced by the concentration of dopant [49]. With the aim to study the effect of dopant concentration, while the reaction time was 180 min, Pd: CdTe QDs was synthesized with three Cd/Pd precursor ratios (1/0.01, 1/0.05 and 1/0.1). It was found that the FL intensity of nanoparticles had a maximum value when the Pd^{2+} to Cd

precursor ratios was (1/0.05). In this case, the percentage of Pd^{2+} in the chemical structure was 4.1% and the quantum yield of nanoparticles was (~34%). While this value for the other ratios was (1/0.01 ~28%) and (1/0.1 ~31%) respectively. So, this concentration was used to synthesize the Pd doped CdTe QDs. As can be seen from the (Fig. 2c) the prepared Pd: CdTe QDs had a maximum emission at 529 nm (λ_{ex} = 340 nm). Also, the UV–Vis spectrum indicates a characteristic peak at 505 nm.

3.2 Characterization of Pd: CdTe QD

The XRD patterns of undoped CdTe and Pd-doped CdTe nanoparticles are shown in Fig. 3a. The XRD patterns of Pd: CdTe QDs, exhibits four peaks at around 26.57° , 42.70° , 51.82° and 66.54° that are corresponding to (111), (220), (311) and (331) planes, which their positions are consistent with the values of the standard diffraction patterns of the cubic structure of CdTe (JCPDS no. 03-065-1046). So, the XRD pattern demonstrates that samples had a similar cubic structure and proved Pd has been incorporated into the crystal lattice of CdTe without changing the cubic structure. The difference in ionic radii of Pd^{2+} and Cd^{2+} cause to a small variation in lattice parameter.

The average crystallite particle size of the Pd: CdTe QDs was calculated by using the Debye–Scherrer equation [50]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where λ , β and θ correspond X-ray wavelength, full width at half maximum (FWHM) of the diffraction peak and diffraction angle in radians, respectively. The K value is set to 0.9 due to the spherical geometry of the nanoparticles. By applying the Scherrer equation, 3.9 nm was obtained as the mean value of crystallite particle size.

The surface morphology and particle distribution of Pd: CdTe QDs were confirmed using TEM (Fig. 3b). As can be observed from these pictures, the nanoparticles have average sizes of about 3 nm, and the Pd-doped CdTe samples are well-developed with uniform spherical-shaped morphology with a little agglomeration.

Further evidence on the chemical composition of Pd: CdTe QDs can be obtained from the EDX analysis (Fig. 3c). The EDAX spectra revealed that the nanoparticles comprise an atomic percentage of Te (24.33%), Cd (31.93%) and Pd (4.1%), which show that the amount of palladium ions is not low. More signals like carbon, oxygen, and sulfur are verifying the presence of a capping agent.

To further investigate the existence of thioglycolic acid on the surface of the prepared Pd: CdTe QDs, the FT-IR spectra of free TGA and TGA-capped Pd: CdTe QDs were compared. As shown in Fig. 3d, the S–H stretching vibration bond at about 2569 cm^{-1} in TGA vanished completely in the

Fig. 3 **a** XRD patterns of CdTe QDs and Pd-doped CdTe QDs. Both nanocrystals display a cubic structure, **b** TEM image of the Pd: CdTe QDs, **c** EDX pattern of the prepared Pd: CdTe QDs, **d** FTIR spectra of TGA and TGA-capped Pd: CdTe QDs

spectrum of Pd: CdTe QDs that indicated TGA ligand was attached to Pd: CdTe QDs through covalent bonds between thiol groups and surface Cd and Pd atoms. The characteristic peaks of the asymmetric vibration -COOH at 1712 cm^{-1} shifted to 1578 cm^{-1} in Pd: CdTe QDs spectrum, it can be due to binding of the carboxyl group in TGA on to Cd^{2+} in Pd: CdTe QDs.

3.3 Optimization of analytical conditions

In order to optimal experimental design, the influence of reaction time, acidity and ionic strength were investigated.

3.3.1 Effect of reaction time

Initially, it was found that the fluorescence intensity of synthesized Pd-doped CdTe QDs was stable after 3 min in the solution (Fig. 4a). Then, the influence of reaction time on the fluorescence intensity of Pd: CdTe QDs–DZN system was studied. The experimental results support that the reaction finished within 1 min and the FL intensity could remain constant for more than 60 min. Further experiments were carried out by applying the time scale of 1 min.

3.3.2 Effect of acidity

FL intensity of QDs can be influenced by the pH value of the solution [51]. Therefore, to obtain a highly sensitive DZN detection, this parameter was studied for values between 3 and 9 in Tris–HCl buffer solution (Fig. 4b). In the absence of DZN, protonation of the surface binding thiolates in acidic pH cause decreasing the fluorescence intensity of Pd: CdTe QDs. In higher pH value, the deprotonation of the thiol group in the TGA molecule happens that could strengthen the covalent bond between Cd, Pd atoms, and the TGA molecules, which leads to increased FL intensity of nanoparticles. In the presence of 20 μL of DZN (10 μM) in pH 7.1, the results implied the change of fluorescence intensity reaches to its maximum. Hence, pH 7.1 was chosen to be a suitable pH for DZN detection.

3.3.3 Effect of ionic strength

The influences of ionic strength on the FL intensity of the sensing probe were investigated by NaCl solution (Fig. 4c). The results showed the reaction should be under a lower ionic intensity condition because, with increasing concentration of NaCl, the FL intensity of QDs strongly diminished. Furthermore, the high ionic strength due to the creation of an ion multi-layer barrier around quantum dots and diazinon can affect the formation of the DZN–Pd: CdTe quantum dots complex.

Fig. 4 **a** The influence of reaction time on the FL intensity of Pd-doped CdTe QDs, **b** effect of pH on the fluorescence quenching of Pd: CdTe by DZN under different pH value, **c** influence of ionic strength on the FL intensity of Pd: CdTe QDs after addition of 20 μL of DZN (10 μM), in the mixture of reaction

3.4 Determination of DZN with Pd: CdTe QDs

To evaluate the feasibility of the proposed method for DZN detection, under the optimum conditions mentioned above, the emission spectra of Pd: CdTe QDs with various concentrations (0 to 100 μM) of DZN in Tris–HCl buffer ($1.0 \times 10^{-3}\text{ mol L}^{-1}$, pH 7.1) were recorded. During the reaction, the fluorescence intensity of Pd: CdTe QDs decreases gradually with the addition of DZN amount. The quenching values of the fluorescence of nanoparticles were calculated by well-known Stern–Volmer Eq. (3):

$$F_0/F = 1 + K_{SV}[\text{DZN}] \quad (3)$$

here, F_0 and F are the FL intensity of Pd: CdTe QDs in the absence and presence of a quencher. K_{SV} represents the Stern–Volmer quenching constant and $[DZN]$ represents the concentration of DZN. Under the optimal experimental condition, the resulted plots exhibited a good linear Stern–Volmer relationships for DZN in the range of 2.3 to 100 μM with a correlation coefficient (R^2) of 0.9921. The (LOD) of this method was evaluated to be 3.3 nM. The good repeatability of the system was also confirmed by obtaining an RSD for DZN ($n=3$) is 3.4% at a DZN level of 5 μM (Fig. 5).

3.5 Mechanism of the “turn-off” fluorescent probe

Generally, quenching usually occurs through several mechanisms. Most common ones are as the dynamic quenching or collisional process and the static quenching (ground state complex formation) [52, 53], which can be recognized by exact investigation of the absorption spectra of the fluorophore. In the dynamic process, only the excited states have been influenced. Consequently, the fluorophore absorption spectrum does not change. In contrast, in the static process, the formation of the small molecules of ground state complex with the fluorophore, cause to change of the absorption spectrum [54]. For distinguishing the quenching mechanism of fluorescence of Pd: CdTe QDs by DZN, the UV–Vis absorption spectra of the Pd: CdTe QDs investigated in the presence and absence of DZN. After the addition of insecticide, the DZN through covalent interactions (via P=S bond) with Cd^{2+} and Pd^{2+} can be replacing the TGA ligands on the surface of QDs and as a result DZN-Pd: CdTe QDs complex is formed. The little blue shift (7 nm) in the emission peak proved that the TGA-capped DZN-Pd: CdTe QDs complex formed. At this time the fluorescence emission of Pd: CdTe QDs due to the transfer of electrons from DZN molecules to quantum dots through the photo-induced electron transfer

Fig. 5 Evolution of the FL spectra of Pd: CdTe QDs upon stepwise addition of different DZN concentrations (0 to 100 μM) in Tris–HCl buffer ($1.0 \times 10^{-3} \text{ mol L}^{-1}$, pH 7.1) after 1 min incubation and the linear relationship between the relative fluorescence intensity of the Pd-doped CdTe QDs and DZN concentration

(PET) Process decreases [55, 56]. Furthermore, comparison of cadmium telluride and Pd: CdTe QDs emission spectra in the presence of DZN (Fig. 6a) indicates the probable effect of palladium ions on the process of dehydrogenation of the DZN solution. The palladium can absorb hydrogen from the diazinon solution, and maybe develop an autocatalytic phenomenon to induce a chemical potential in solution. The induced chemical potential initiate electro-kinetic effect initiate in the formation of a chemical complex in DZN solution which can emit wavelength in the range of 520 to 530 nm [57–60].

According to Fig. 6b, the pure DZN show three strong absorption peaks at 219, 251 and 278 nm. During the

Fig. 6 a FL spectra of Pd: CdTe QDs and CdTe in the presence of DZN (100 μM), b UV–Vis absorption spectra of Pd: CdTe QDs, pure DZN, and DZN-Pd: CdTe QDs complex, c Stern–Volmer plot for the DZN-Pd: CdTe QDs solution at various temperatures

addition of DZN to the prepared Pd: CdTe QDs solution obvious spectral change occurs in the molar absorption coefficient of quantum dots and DZN, which indicates the quantum dot-DZN system is formed, and quenching type is static quenching. This mechanism was further confirmed by the Stern–Volmer equation. Using fluorescence spectroscopy, we achieved K_{SV} of QDs–DZN complex for various temperatures. The values of K_{SV} shown in (Fig. 6c). We observed that the temperature relationship with quenching constant (K_{SV}) is inverse, which confirms that the quenching occurs because of the static process.

3.6 Interference and selectivity studies

Selectivity is one of the most critical analytical parameters to assess the efficiency of a new fluorescent sensor [61, 62]. In order to the capability of the method for DZN detection, the interference of some common existing substances in the environmental water samples such as metal ions and other commonly used pesticides and herbicides were investigated on the sensing system. As displayed in Fig. 7a, among the common pesticides and herbicides only DZN, could quench the fluorescence of Pd: CdTe QDs significantly. Also, it can be seen a certain amount of coexisting substances does not interfere with the determination of DZN (Fig. 7b). These experiments revealed the nanoprobe based on Pd: CdTe QDs have a great selectivity for DZN detecting.

3.7 Assay of DZN concentrations in environmental water samples

To further explore the feasibility of the proposed method based on novel Pd: CdTe QDs sensor for practical purposes, it was employed for the determination of DZN in rainwater, tap and river water via the standard addition method. As shown in Table 1, the recovery ranged from 95.8 to 102.4%, and the relative standard deviation (RSD) was lower than 2.0%, these results show that our proposed sensor in spite the existence of various mineral and biological substances in the water samples could efficiently recognize DZN among other substance. Therefore, it can be efficiently applied to the analysis of DZN residues in environmental samples.

3.8 Cytotoxicity analysis

It is very important to gain QDs with low cytotoxicity for the purpose of realizing medicine and biological applications [63, 64]. LDH testing is one of the most commonly used techniques for cytotoxicity and cell viability. To measure the activity of Pd: CdTe QDs on the fibroblast cells, LDH assay, was accomplished and the results shown in (Fig. 7c). From the results, it is clear that the Pd: CdTe QDs exhibit dose-dependent cytotoxicity. However, this

Fig. 7 **a** FL spectra of Pd: CdTe QDs treated with different the common pesticides and herbicides, **b** FL intensity of DZN-Pd: CdTe QDs solution in absence and presence of interfering species, respectively. The concentration of DZN and other interfering species were 5 μ M and 100 μ M, respectively. The error bars represent standard deviations based on three independent measurements, **c** Cell viability of fibroblast cells mixed with the different concentration of Pd: CdTe QDs for 24 h and 48 h at 37 °C

Table 1 The determination of diazinon in tap, rain, and river waters

Sample	Spiked (μ M)	Value found (n = 3)	R.S.D (%)	Recovery (%)
Rainwater	5	5.1 ± 0.78	1.4	102.4
River water	5	4.88 ± 1.19	2.0	97.6
Tap water	5	4.79 ± 1.43	1.8	95.8

result reveals the nanoparticles have notable toxicity at 3.0 μ M, but, after treatment with the lower concentration of Pd: CdTe QDs (i.e., 1.0, 1.5, 2.0, 2.5 μ M) for 48 h, no cytotoxicity effects were observed. Nevertheless, the

dosage we use for experiments is much smaller than this concentration which does not have toxic effects.

4 Conclusions

In this study, a novel Pd: CdTe QDs was designed and synthesized by a facile hydrothermal method and characterized by various physicochemical techniques. Then, it applied as fluorescent nano-sensors for rapid detection of DZN residues in rainwater, tap and river water. Under optimum conditions, the suggested method achieved a good linear and low detection limit. Due to their low cost, simple procedure, low toxicity, rapid detection, and high sensitivity, we suggest that Pd: CdTe QDs as fluorescence sensor have the excellent potential for of low levels the insecticides residue detection in water samples. Furthermore, considering CdTe QDs are known to be toxic due to containing the highly toxic heavy-metal element cadmium, we have explored the toxicity of Pd: CdTe QDs, the results proved Pd: CdTe QDs did not show notable toxicity at the concentrations used in the experiments and, therefore it is proper for biological applications.

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