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Highly Selective and Sensitive Recognition of Cobalt(II) Ions Directly in Aqueous Solution Using Carboxyl-Functionalized CdS Quantum Dots as a Naked Eye Colorimetric Probe: Applications to Environmental Analysis

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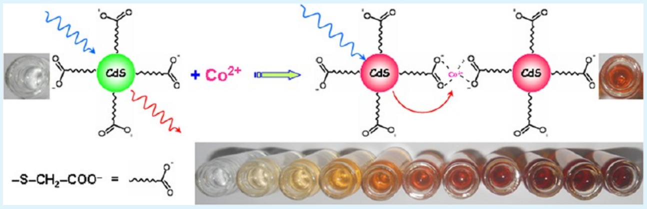
ABSTRACT: Quantum dots (QDs) are usually used as fluorescent probe, and they are difficult to use in colorimetric detection. However, in this report carboxyl-functionalized CdS (COF-CdS) QDs were synthesized in aqueous solution for colorimetric detection following a classic method. On the basis of inducing the aggregation of COF-CdS QDs, a simple naked eye colorimetric method with high sensitivity and selectivity was developed for the sensing of Co^{2+} ions in aqueous solutions. The Co^{2+} ions induced COF-CdS QDs results in a marked enhancement of the UV−vis absorption spectra at 360 nm, and the process was accompanied by a visible color change from colorless to yellowish brown within 5 min, which proves a sensitive detection of Co^{2+} ions. The sensing of Co^{2+} ions can therefore be easily achieved by a UV−vis spectrophotometer or even by the naked eye. Under the optimized circumstances, this method yields excellent sensitivity (LOD = 0.23 μg mL^{-1}) and selectivity toward Co^{2+} ions. The calibration plot of $(A - A_0)$ at 360 nm against concentration of Co^{2+} ions was linear over the range from 0.5 to 14 μg mL^{-1} with a correlation coefficient of 0.9996. The accuracy and reliability of the method were further ascertained by recovery studies via standard addition method with percent recoveries in the range of 99.63−102.46%. The plausible mechanism for the color change reaction has also been discussed. Our attempt may provide a cost-effective, rapid, and simple solution for the inspection of Co^{2+} ions in the presence of a complex matrix from environmental aqueous samples.



KEYWORDS: *CdS quantum dots, functionalized, colorimetric, Co^{2+} ions, recognition, environmental*

INTRODUCTION

Cobalt is a naturally occurring element in rocks, soils, water, animals, and plants. The development of highly sensitive and selective analytical methodology of Co^{2+} ions is of great importance to avoid its toxic effects. Humans may be exposed to cobalt compounds from diet and occupational exposure in several industries such as the hard metal, diamond polishing, porcelain, chemical, and pharmaceutical industries.[1] Exposure to cobalt may cause toxicological effects, including vasodilatation, flushing, and cardiomyopathy in humans and animals.[2,3] Thus, it is critical to detect trace amounts of cobalt samples in the environment. So far numerous methods have been employed to detect Co^{2+} ions based on different analytical strategies.[4−9] However, these methods have their own limitations and are unsuitable for real-time detection. Therefore, it is challenging to develop an onsite method for real time detection of Co^{2+} ions. Colorimetric methods can avoid these problems, and the detection signal can be observed by the naked eye.[10,11]

At the moment, functionalized semiconductor quantum dots (QDs) have been generated incredible interest in the fields of physics, chemistry, biology, and engineering owing to their ideal optical properties in the past decade. The unique photophysical properties of colloidal semiconductor QDs attributed to quantum confinement effects have elicited intensive research for sensing, labeling, and imaging applications. In comparison to traditional organic dyes and fluorescent proteins, QDs offer advantages in many aspects such as a high quantum yield, broad absorption spectra, narrow size-tunable symmetric emission from visible to infrared wavelengths, high level of brightness, and photochemical stability.[12]

As a group of narrative fluorescence (FL) probes, QDs with variable surface capping ligands have comprehensively been used as fluorescent probes for cell labeling, tumor imaging, and clinical diagnoses in biology and medicine particularly in analytical chemistry.[13] They have also been applied in quantitative determination of biological macromolecules.[14] On the basis of the FL quenching of the CdSe QDs by spironolactone, Liang et al. presented a simple, rapid, and specific method for spironolactone

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determination, which considered that the changed surface-bound organic molecules of QDs were induced by spironolactone.[15] Li et al. and Liu et al. have detected ciprofloxacin and sulfadiazine respectively by surface modified CdS QDs based on gradual quenching of the luminescent intensity of the QDs.[16,17] Recently, functionalized CdS QDs as a FL probes were described for the direct determination of ranitidine hydrochloride by Gore et al.[18] These researches revealed that QDs can be used as FL probes for drug molecules based on the changes of their luminescent properties. So far, many papers have focused on the detection of metal ions such as Pb(II), Cu(II), Hg(II), Ag(I), and CN^- with functionalized QDs via analyte−induced changes in photoluminescence.[19−23]

Recently, a variety of highly selective and sensitive colorimetric sensors based on functional metal nanoparticles have been designed, especially of gold and silver nanoparticles (Ag NPs), due to their extremely high extinction coefficients and the strongly distance−dependent optical properties.[24] For example, dispersed silver nanoparticles are slight yellow in color, whereas aggregated ones are red. More importantly, the introduction of ligands onto Ag NPs surfaces provides not only stability to these nanoentities in different solvents, but also desirable surface functionalities.[25−30] When the introduced ligand give a special response to analysis of substrate, the change in color and UV−vis spectroscopy can be detected because of the aggregation of these Ag NPs. However, if only the simple modification of metal NPs with single recognition site is used, they can not be very sensitivite or selectivite. It has been reported that bifunctionalized sensors can further improve the sensing efficiency, because of the cooperative effect of ligands.[7] Lin and co-workers have found that thioctic acid and crown bifunctionalized Au-NPs can recognize K^+ more quickly.[31] Huang and co-workers have further improved the selectivity of the probe by modifying the Rhodamine B−Au NP surfaces with thiol ligands.[32] However, the use of such noble metal nanoparticle based probes in day-to-day laboratory practices is expensive and these methods have their own limitations.

However, little attention has been paid to the use of QDs as colorimetric probes for metal ion detection and sensing. More recently Yang et al published a paper on naked eye colorimetric analysis of Hg^{2+} with bicolor CdTe quantum dot multilayer films.[33] But, the preparation of multilayer thin films and sensing of accurate concentration of analyte in the solid state is a very difficult task. So the development of a new colorimetric nanosensor for the direct detection of analyte in the presence of a matrix is of great significance in trace determination.

In this work, we present a new strategy for the efficient recognition and determination of Co^{2+} ions in aqueous solution using carboxyl-functionalized CdS (COF-CdS) QDs. In our proposed approach, the interaction between metal ions and thioglycolic acid (TGA) can provide coordination site for metal ions.[34] The metal ions are thus expected to bind with carboxyl group through metal−ligand interaction. In this context, we have showed that COF-CdS QDs can have an effect on recognition of Co^{2+} ions, resulting in appreciable changes in color and absorption properties over other metal ions tested. COF-CdS QDs can demonstrate the role of ligands, making to show good sensitivity and selectivity. Up to date, there are very few reports on COF-CdS QDs. The research of COF-CdS QDs is of great significance since they can be designed as smart probes, which have potential applications in environmental and biosensing. Furthermore the colorimetric probe has been successfully applied for the direct determination of Co^{2+} ions from different environmental samples without any interference in presence of matrix by standard addition method. Moreover, probable mechanism for color change of COF-CdS QDs selectively induced by Co^{2+} ions was also discussed.

■ EXPERIMENTAL SECTION

Equipment. The absorption spectrum was acquired at room temperature on UV 3600 Shimadzu UV−vis−NIR spectrophotometer with the use of 1.0 cm quartz cell. Fluorescence measurement of solutions were made with PC based spectrofluorophotometer (JASCO Model FP-750, Japan.) equipped with xenon lamp source and 1.0 cm quartz cell. Both excitation and emission slits were fixed at 10 nm. The particle size distribution and zeta potential of QDs in aqueous suspension was measured by dynamic light scattering (DLS) with a Zetasizer Nano ZS (Malvern Instruments Ltd., U. K.). High-resolution transmission electron microscopy (HR-TEM) images were recorded on a Tecnai transmission electron microscope (HR-TEM, FEI Tecnai 300). The pH of solutions was measured with digital pH meter model LI-120 (ELICO Hyderabad, India) with a combined glass electrode.

Reagents. All chemical reagents were of analytical reagent grade and used as received without further purification. All aqueous solutions were prepared with doubly distilled water. Cadmium chloride ($CdCl_2.H_2O$), sodium sulphide (Na_2S), and thioglycolic acid (TGA) was purchased from S d fine-chem Ltd. (Mumbai, India). All reagent required for Carmody buffer preparation, potassium dihydrogen orthophosphate dihydrate (KH_2PO_4 $2H_2O$), and dipotassium hydrogen orthophosphate (K_2HPO_4) for phosphate buffer preparation were procured from Spectrochem Chemicals (Mumbai, India). The stock solution of Co^{2+} ions was prepared by dissolving cobalt chloride ($CoCl_2·6H_2O$) in water. All the metal salts used were purchased from S d fine-chem Ltd. (Mumbai, India). Doubly distilled water was used for preparing all solutions throughout the experiments.

Synthesis of COF-CdS QDs. COF-CdS QDs were synthesized via the procedures described by Winter et al. with some modifications.[35] Appropriate amounts of $CdCl_2·H_2O$, Na_2S, and TGA were first dissolved in doubly distilled water separately. A 10 mL portion of 0.1 mol L^{-1} $CdCl_2·H_2O$ solution was added dropwise into 2.5 mL of 1.0 mol L^{-1} TGA solution slowly with continuous stirring at room temperature. Then pH between 6.0−7.0 was adjusted by the dropwise addition of 0.1 mol L^{-1} NaOH solution with constant stirring. The solution was deaerated with N_2 for 30 min under vigorous stirring, 5.0 mL of 0.1 mol L^{-1} Na_2S was dropped slowly in the flask, and a clear yellowish suspension of CdS QDs was obtained. The solution turned yellow shortly after the addition of sodium sulfide due to the formation of COF-CdS QDs. After stirring overnight (12 h), the mixture was diluted to 100 mL with doubly distilled water and stored at 4 °C in the dark for further use. The concentration of resultant COF-CdS QDs was 5×10^{-3} mol L^{-1} (calculated through the concentration of the S^{2-} added) which was used for further measurements.

Colorimetric Determination of Co^{2+} Ions with COF-CdS QDs. The colorimetric detection of Co^{2+} ions in aqueous solution was performed at room temperature. The desired concentration of aqueous solution of Co^{2+} ions was prepared by dissolving $CoCl_2·6H_2O$ in doubly distilled water. The solutions for all metal ions were prepared by dissolving their respective salts in doubly distilled water and stored at room temperature. For a typical colorimetric titration of metal ions with COF-CdS QDs, to a 10 mL standard flask solutions were added according to the following order: 2.0 mL of COF-CdS QDs stock solution (5×10^{-3} mol L^{-1} the concentration of colloids is represented by the final concentration of Na_2S was added), 2.0 mL of 0.1 mol L^{-1} phosphate buffer solution (pH = 7.5), and a known volume of standard metal ions solution. Then the solutions were diluted with water, mixed thoroughly, and maintained at room temperature for 5.0 min, and then, they were transferred separately into quartz cuvettes. Their absorption bands were recorded by UV−vis spectrophotometer. The photographs were taken using Cannon digital camera.

■ RESULTS AND DISCUSSION

Characterization of COF-CdS QDs. First and foremost, synthesized COF-CdS QDs were characterized by the UV−vis and FL spectra (Figure 1a and 1b). It can be seen that the line width of the FL spectrum (λ_{em} = 513 nm) is narrow, which showed that as prepared COF-CdS QDs were nearly monodisperse and homogeneous. The particle size of the prepared COF-CdS QDs was calculated from absorption maximum (A = 0.82 at λ_{max} = 360 nm) of the UV–vis spectra according to the calculation method specified in the literature.[36] The results showed that the particle diameters of the prepared COF-CdS QDs were 2.3 nm and had a concentration of 0.058 μM. In addition to that, we measured size of the particles using HR-TEM. Figure 2a shows that COF-CdS QDs are highly dispersed and uniform in aqueous solution, with particle sizes nearly ranging from 3–10 nm.

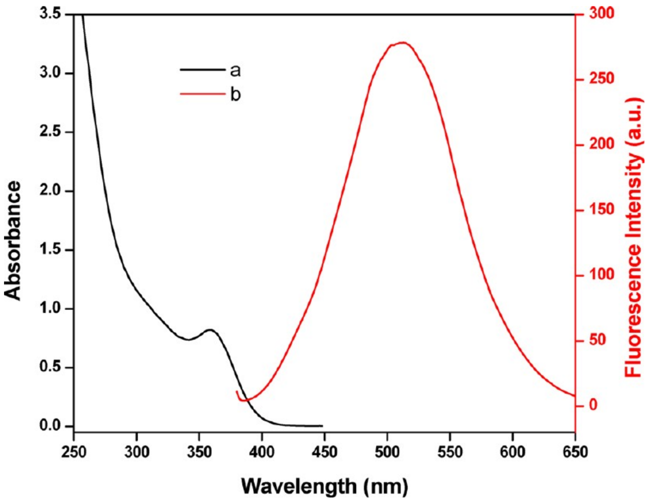


Figure 1. UV–visible absorption spectrum (a) at λ_{max} = 360 nm and emission spectrum (b) at λ_{em} = 513 nm (excited at 370 nm) of the COF-CdS QDs (2×10^{-4} mol L^{-1}) in aqueous colloidal solution.

Particle size measurement of COF-CdS QDs was also carried out in the suspension by DLS experiments. Figure 3 shows the typical size and size distribution of synthesized COF-CdS QDs measured by DLS. The average size of COF-CdS QDs as determined by DLS is 13 nm, and the size distribution is found within the range of 8–18 nm, which is considerably larger than predictable from HR-TEM and absorption maximum of the UV–vis spectra. This is because, the DLS technique gives us a mean hydrodynamic diameter of the COF-CdS QD core surrounded by organic and solvation layers, and this hydrodynamic diameter is influenced by the viscosity and the concentration of the solution.[37]

Zeta (ζ) potential measurement was performed for COF-CdS QDs in order to characterize the surface charge of QDs as well as stability to confirm the effectiveness of the carboxyl capping. The obtained zeta potential of the COF-CdS QDs at alkaline pH was found to be −27.7 mV. For small sufficient QDs, a high zeta potential will confer stability i.e. the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate.[38] Therefore colloids with high zeta potential

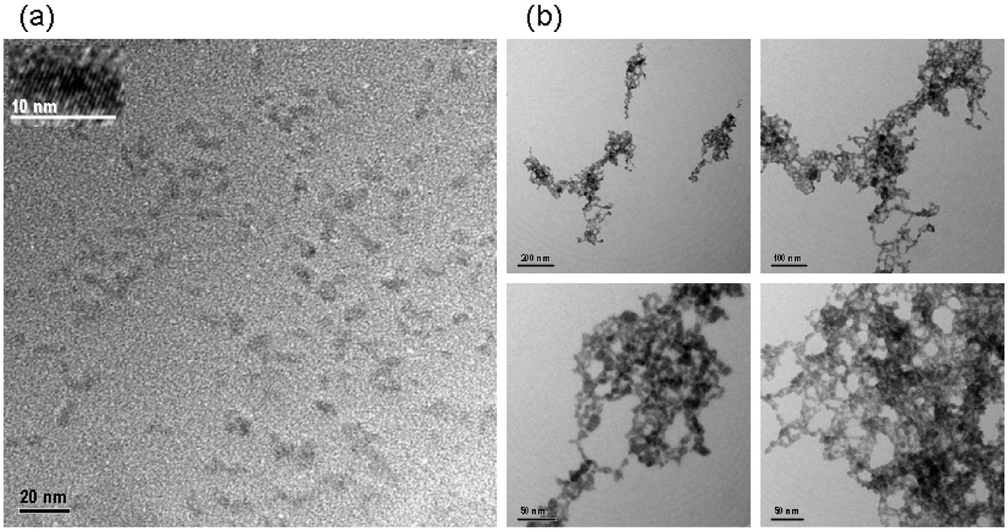


Figure 2. HR-TEM images of the (a) COF-CdS QDs and (b) after 10 μg mL^{-1} Co^{2+} ions added in COF-CdS QDs colloidal solution.

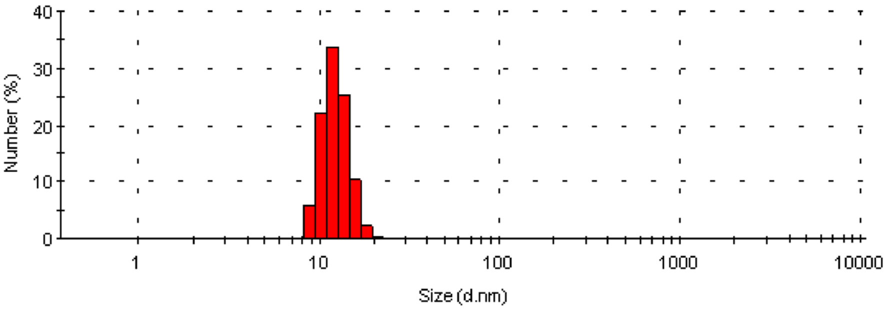


Figure 3. Particles size distribution measured by DLS of the COF-CdS QD colloidal solution (2×10^{-4} mol L^{-1}). Average size is 13 nm, 96% of the particles are in between 8 and 18 nm.

(negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

Effect of pH Value and Reaction Time. In the present study, the effect of pH value of the solution on the absorbance intensity of COF-CdS QDs was studied in the presence of Co^{2+} ions (5.0 μg mL^{-1}) which is shown in Figure 4. From the figure, it is observed that pH values between 2.0 and 12 with Carmody buffer were tested and it was found that the most sensitive pH lies in the range of 6.0−9.0 in order to get full complexation. Therefore, for every measurement in the present work phosphate buffer solution having pH = 7.5 was chosen throughout the experiment. Additionally, time required to form the distinct color change was also monitored by using kinetic mode on UV−vis spectrophotometer in presence Co^{2+} ions (5.0 μg mL^{-1}) over 5 min. It was observed that after mixing of Co^{2+} ions with COF-CdS QDs dramatic color change is observed and absorbance is stable for above 5 min (Figure 5). So it is not necessary to wait for prolonged times for color development after addition of Co^{2+} ions prior to analysis during experimental study.

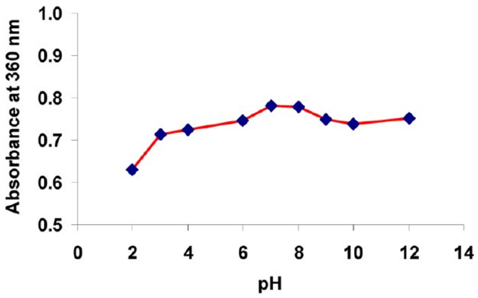


Figure 4. pH-dependent changes of absorption at 360 nm of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution in the presence Co^{2+} ions (5.0 μg mL^{-1}).

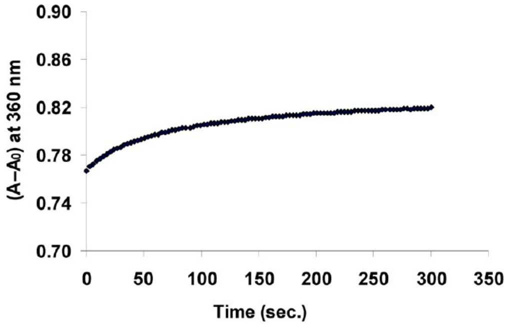


Figure 5. Plot of the time-dependent absorption at 360 nm of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution in the presence Co^{2+} ions (5.0 μg mL^{-1}) over 5 min.

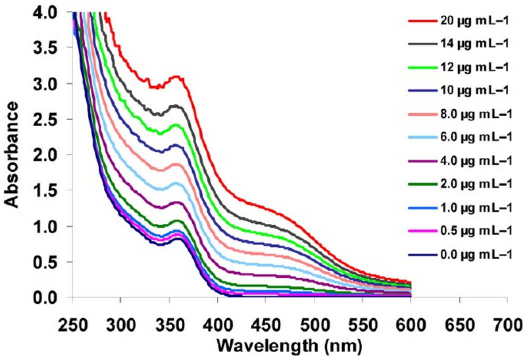


Figure 6. UV−vis absorption spectra of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution with various concentrations of Co^{2+} ions. The concentrations of Co^{2+} ions from bottom to top 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 12, 14, and 20 μg mL^{-1}.

Selective Recognition of Co^{2+} Ions by COF-CdS QDs. It has been established that carboxylic acid groups can bind with metal ions through metal−ligand interaction.[34] On the basis of this approach, we have synthesized COF-CdS QDs for metal

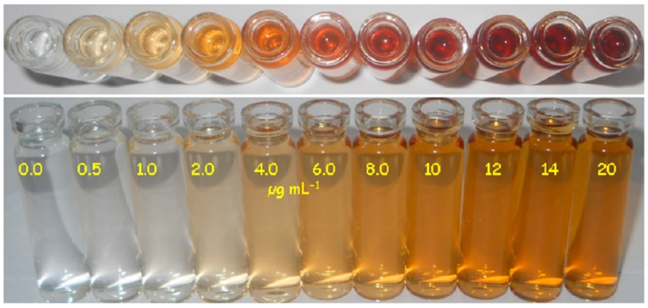


Figure 7. Photo images of the COF-CdS QDs (2×10^{-4} mol L^{-1}) with various concentrations of Co^{2+} ions. The concentrations of Co^{2+} ions from left to right are 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 12, 14, and 20 μg mL^{-1}.

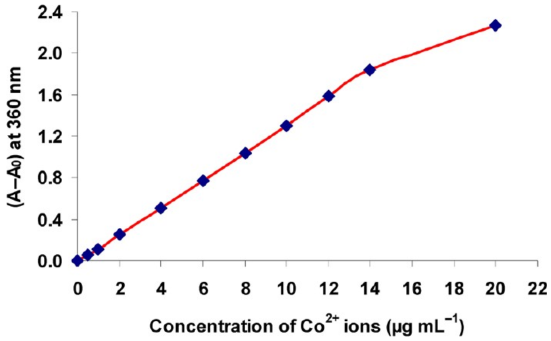
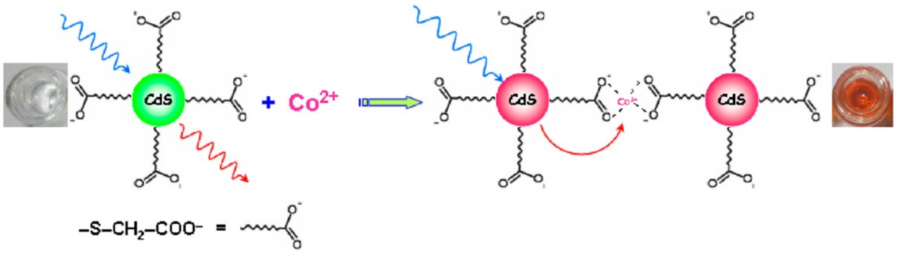


Figure 8. Equilibrium curves between ($A - A_0$) of the COF-CdS QDs solution (2×10^{-4} mol L^{-1}) at 360 nm and the Co^{2+} ions concentration. The concentrations of Co^{2+} ions are 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 12, 14, and 20 μg mL^{-1}.

Scheme 1. Schematic Representation for the Colorimetric Recognition of Co^{2+} Ions Using COF-CdS QDs



ions sensing and observed that they have a good recognition for Co^{2+} ions. The sensing ability of COF-CdS QDs for Co^{2+} ions was investigated by UV−vis absorption spectroscopy. In the absorption spectrum (Figure 6), COF-CdS QDs led to a dramatic increase in the absorbance intensity at 360 nm, which can be attributed to metal−ligand interaction of COF-CdS QDs. When the standard solution of Co^{2+} ions was added, the absorption peak at 360 nm was gradually increased without noticeable shift in absorption wavelength, but at the same time an additional broad absorption band was observed at about 470 nm possibly due to the formation of colored complex between them (Scheme 1). This absorption maxima corresponds to a distinct color change of the solution from colorless to yellowish brown with increasing concentration of Co^{2+} ions (Figure 7), representing a strong interaction between the COF-CdS QDs and Co^{2+} ions. As shown in Figure 8, no further variation was measured after 14 μg mL^{-1} Co^{2+} ions had been added to COF-CdS QDs (2×10^{-4} mol L^{-1}) solution, indicating that the saturable concentration of Co^{2+} ions on the surface of CdS QDs was reached, because of that no more ligand sites were available for complexation with Co^{2+} ions. These facts indicates that the carboxyl ligand of each COF-CdS QDs surface coordinates to Co^{2+} ions. Importantly as shown in Figure 9, the addition of Co^{2+} ions causes FL quenching of COF-CdS QDs simultaneously with appreciable red shift from 513 to 531 nm. This is possibly due to the trapping of charge from the photoexcited (excited at 370 nm) COF-CdS QDs that results in a strong FL quenching. All these observations strongly suggest that the color change is due to metal−ligand interaction of COF-CdS QDs with Co^{2+} ions indicating the formation of a ground state nonfluorescent complex.[39]

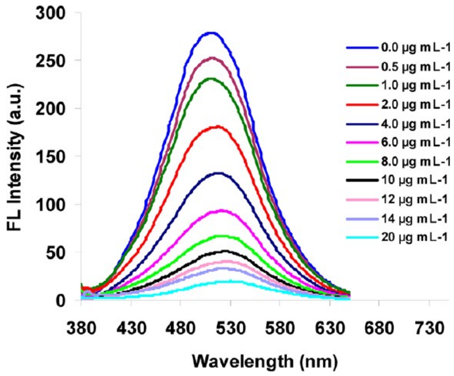


Figure 9. Fluorescence (excited at 370 nm) quenching spectra of COF-CdS QDs (2×10^{-4} mol L^{-1}) upon addition of different concentrations of Co^{2+} ions. The concentrations of Co^{2+} ions from top to bottom are 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 12, 14, and 20 μg mL^{-1}.

High selectivity is necessary for an excellent sensor. In the present work, the optical responses of COF-CdS QDs were extended to other metal cations in aqueous solution. Figure 10a and 10b (bar graph and photographic images, respectively) show the selectivity of the COF-CdS QDs as an optical sensor. As shown in Figure 6 (absorbance) and Figure 7 (photographs), only the addition of Co^{2+} ions led to drastic absorbance change of the COF-CdS QDs, and no significant color changes were observed upon addition of other metal cations such as Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+}, Hg^{2+} Zn^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Na^{+}, K^{+}, and Sb^{3+} indicating that only Co^{2+} ions involved strong interaction with COF-CdS QDs, resulting in the color change (Figure 10a and 10b). Moreover, competitive experiments were also carried out by adding Co^{2+} ions to solutions of COF-CdS QDs in the presence of other cations. As shown in Figure 10c,

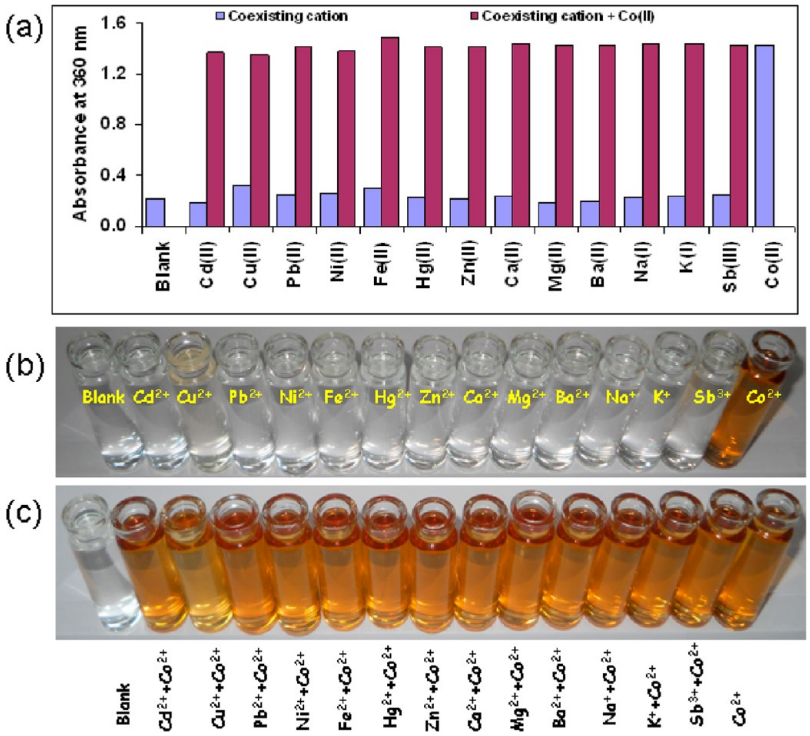


Figure 10. (a) Absorption intensity of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution at 360 nm shows the specificity test for Co^{2+} ion (5.0 μg mL^{-1}) over other coexisting metal ions (10 μg mL^{-1}). Blue bars denote the responses of individual metal ions while red bars show the responses of Co^{2+} ions (5.0 μg mL^{-1}) in the presence of other coexisting metal ions (10 μg mL^{-1}). Photographic images (b and c) of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solutions corresponding to the blue bars and red bars in part a, respectively.

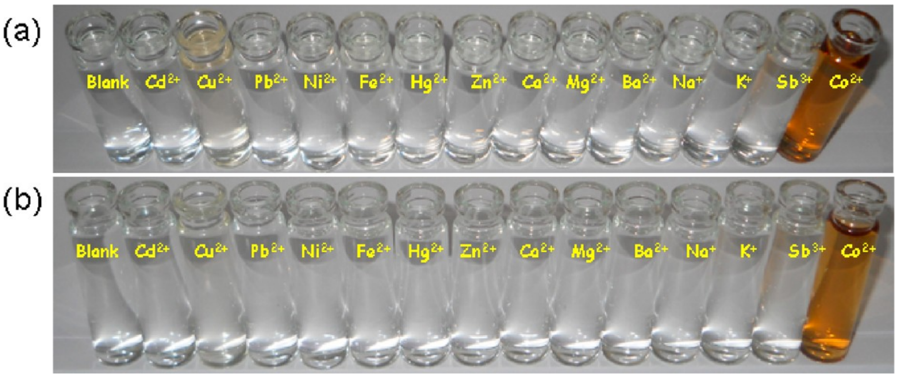


Figure 11. (a) Photographic images of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution for Co^{2+} ions (5.0 μg mL^{-1}) over other coexisting metal ions (10 μg mL^{-1}). (b) Photographic images of the COF-CdS QDs (2×10^{-4} mol L^{-1}) solution after 5 days shows the stability test for Co^{2+} ions (5.0 μg mL^{-1}) over other coexisting metal ions (10 μg mL^{-1}).

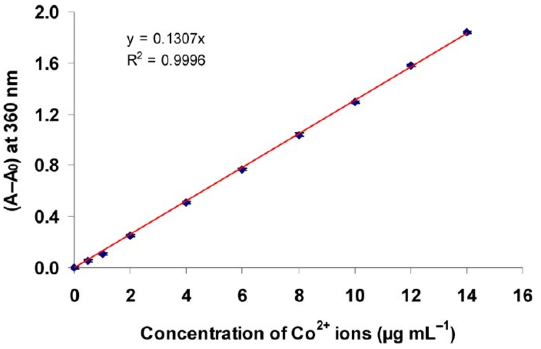


Figure 12. Graph shows the dependence (linearity) of the ($A - A_0$) values COF-CdS QDs solution (2×10^{-4} mol L^{-1}) at 360 nm on the increasing concentration of Co^{2+} ions: 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 12, and 14 μg mL^{-1}.

whether in the absence or presence of other cations, significant spectral changes were observed for COF-CdS QDs upon addition of Co^{2+} ions. The results indicate that the sensing of Co^{2+} ion by COF-CdS QDs is hardly affected by these commonly coexisting ions.

In our proposed approach, the carboxyl group on the surface of COF-CdS QDs can provide coordination site for Co^{2+} ions selectively among the other metal ions. It is well know that TGA forms different colored thiolate complexes with a various metal ions.[40] It is reported that TGA forms colored complex with Co^{2+} ions based on the masking of interfering ions, this concludes that free thiol group (−SH) contributes for color change and liable to form complexes with most of the interfering ions.[40] But in our proposed model (Scheme 1) thiol group of TGA is covalently bonded to QDs core leaving carboxylate group free and can provide selective coordination site only for Co^{2+} ions indicating the key role of QDs. Therefore, COF-CdS QDs can act as a highly selective and sensitive naked eye colorimetric probe for Co^{2+} ions. Furthermore, the stability of the color produced after interacting COF-CdS QDs with Co^{2+} ions was also investigated. It was observed that, the Co^{2+} ions induced color is quite stable in comparison with other metal cations tested at room temperature over 5 days without any noticeable change in the color (Figure 11a and 11b). This means that COF-CdS QDs can be used as a stable colorimetric probe for detection of Co^{2+} ions in aqueous solution at room temperature.

Quantitative analysis was performed by titrating the Co^{2+} ions and monitoring the UV−vis absorption spectra and the color of the system changes. Figures 6 and 7 show the typical

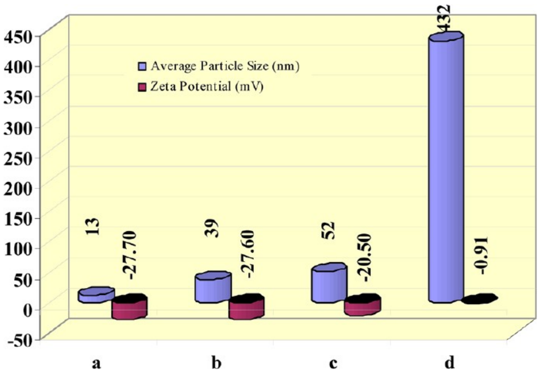


Figure 13. Representing average particle size of COF-CdS QDs and zeta potential measured by DLS varies in response to the addition of Co^{2+} ion concentrations in COF-CdS QDs (2×10^{-4} mol L^{-1}): (a) in the absence of Co^{2+} ions, (b−d) in the presence of 0.5, 2.0, and 10 μg mL^{-1} Co^{2+} ions, respectively.

UV−vis spectroscopic response and images of COF-CdS QDs solution after adding different concentrations of Co^{2+} ions over 5 min, a clear color progression from colorless to yellowish brown with increasing Co^{2+} ions concentration was observed (Figure 7). The absorption intensity of the COF-CdS QDs at 360 nm increased with increasing concentration of Co^{2+} ions (Figure 6). There is an equilibration curve between ($A - A_0$) and Co^{2+} ions concentration from 0.5 to 20 μg mL^{-1}. The curve can reach a platform when the concentration of Co^{2+} ions is above 14 μg mL^{-1} (Figure 8). A linear correlation exists between ($A - A_0$) and the concentration of Co^{2+} ions over the range of 0.5 to 14 μg mL^{-1} (Figure 12). The linear equation is $A - A_0 = 0.1307x$ with a linearity coefficient of 0.9996. The limit of detection (LOD) is defined by the equation LOD = ($3\sigma/k$), where σ is the standard deviation of the y-intercepts of regression lines and (k) is the slope of calibration graph.[41] The colorimetric LOD for Co^{2+} ions is 0.23 μg mL^{-1}. However, a colorimetric sensor can realize onsite and rapid detection with a signal that can be observed by the naked eye.

Mechanism for Color Change of COF-CdS QDs with Co^{2+} Ions. Consecutively to explore the color change of the COF-CdS QDs solution induced by Co^{2+} ions, we have performed a variety of experiments. We proposed that the color change of COF-CdS QDs is possibly due to the ability of carboxyl group to bind with Co^{2+} metal ions through metal−ligand interaction. Our proposed mechanism is different from that suggested by other researchers.[42,43] It has been reported

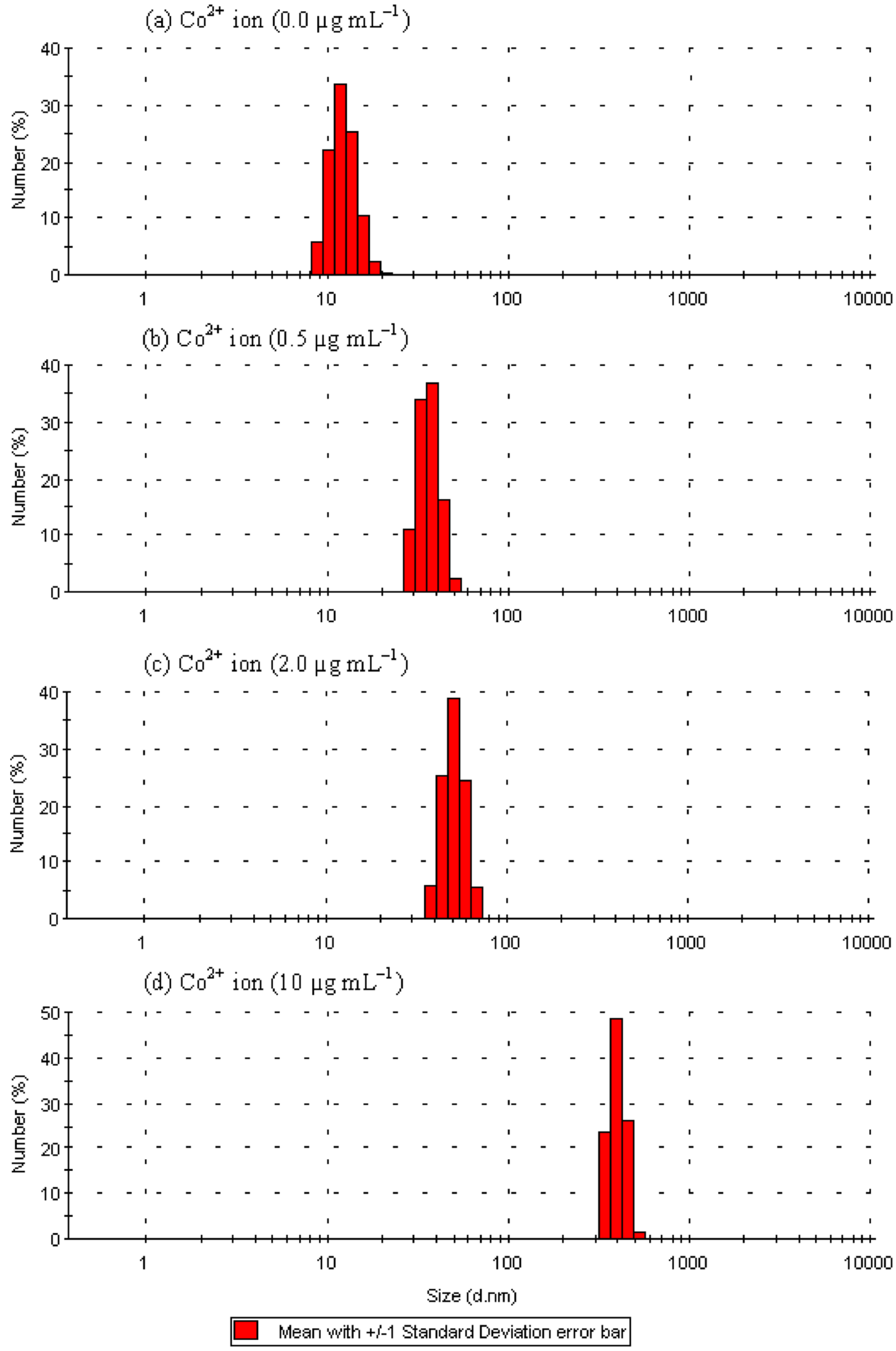


Figure 14. Demonstrating that size distribution measured by DLS varies in response to the addition of Co^{2+} ion concentrations in COF-CdS QDs (2×10^{-4} mol L^{-1}): (a) in the absence of Co^{2+}, (b–d) in the presence of 0.5, 2.0, and 10 $\mu g\ mL^{-1}$ Co^{2+} ions, respectively.

that heavy metal ions displace the Cd in the CdSe and CdTe QDs due to its higher binding affinity to Te and Se, as indicated by its lower K_{sp} values. Isarov and Chrysochoos investigated the quenching emission of CdS with copper ions[44] and found that copper ions formed ultrafine complexes of Cu_xS (x = 1, 2). To further understand the underlying mechanism in our system, we have employed a variety of analytical methods, including UV–vis absorption spectroscopy, spectrofluorometery, DLS, and HR-TEM.

In the absorption and emission measurement of COF-CdS QDs solution in presence of Co^{2+} ions (0.5–20 $\mu g\ mL^{-1}$) noteworthy changes are observed. No significant shifts were noted in the absorption spectra (Figure 6) at 360 nm, but simultaneously a new hump was observed during measurement at about 470 nm which consequently increases with addition of Co^{2+} ions. Similarly FL emission spectra of COF-CdS QDs also quenches strongly accompanied by a considerable red shift from 513–531 nm with addition of Co^{2+} ions (Figure 9). Moreover, COF-CdS QDs solution containing Co^{2+} ions was also excited at 470 nm to decide whether the formed complex is fluorescent or not. An additional emission peak was not observed in the FL spectra. Hence, it is assumed that color change of COF-CdS QDs was due to metal–ligand interaction of COF-CdS QDs with Co^{2+} ions demonstrating the formation of ground state nonfluorescent colored complex through carboxyl group in the TGA with Co^{2+} ions.[39]

Table 1. Determination of Co^{2+} Ions in Water Samples from Different Water Sources by the Standard Addition Method ($n = 3$)

water samples studied	amount of standard Co^{2+} ions added (μg mL^{-1})	total Co^{2+} ions found ($n = 3$) (μg mL^{-1})	recovery of Co^{2+} ions added (%)	RSD (%)	relative error (%)
drinking water (Dept. of Chemistry, SUK[a])	2.00	2.01	100.66	1.80	0.66
	4.00	3.99	99.63	0.21	−0.37
	6.00	6.00	100.02	0.29	0.02
tap water (Dept. of Chemistry, SUK)	2.00	2.01	100.25	1.65	0.25
	4.00	4.10	102.46	1.46	2.46
	6.00	6.11	101.86	1.09	1.86
lake water (Rajaram Lake, Near SUK)	2.00	2.01	100.53	1.45	0.53
	4.00	4.01	100.32	1.04	0.32
	6.00	6.10	101.68	1.23	1.68
Panchganga River (Kolhapur, MS, India)	2.00	2.01	100.39	1.67	0.39
	4.00	4.02	100.46	0.62	0.46
	6.00	6.08	101.35	1.06	1.35

[a] SUK = Shivaji University, Kolhapur

However, it would be difficult to rationalize the selective response of COF-CdS QDs toward Co^{2+} ions based on this hypothesis. To further evaluate this hypothesis, the DLS, Zeta potential, and HR-TEM experiments were also performed. The particle sizes and zeta potentials of the COF-CdS QDs before and after the sequential addition of Co^{2+} ions (0.5, 2.0, and 10 μg mL^{-1} Co^{2+} ions) are graphically represented in Figures 13 and 14. The average particle size of COF-CdS QDs was found to be 13 nm, and on addition of 0.5 μg mL^{-1} Co^{2+} ions, it was increased from 13 to 39 nm. The size was enlarged to 52 and 432 nm on the addition of 2.0 and 10 μg mL^{-1} Co^{2+} ions, respectively (Figure 14), showing the tendency toward the formation of aggregates. The formation of aggregated assembly is reflected again in the color change of COF-CdS QDs solution from colorless to yellowish brown (Figure 7).

As shown in Figure 13, the zeta potential of the COF-CdS QDs was reduced from −27.70 to −27.60 mV, on addition of 0.5 μg mL^{-1} Co^{2+} ions. When 2.0 μg mL^{-1} Co^{2+} ions was added to COF-CdS QDs, the charge was reduced to −20.50 mV and subsequently to −0.91 mV on the addition of 10 μg mL^{-1} Co^{2+} ions. The considerable reduction in zeta potential also indicates the tendency for the formation of aggregates. The carboxyl group of TGA on the surface of COF-CdS QDs can bind with Co^{2+} ions through metal−ligand interaction, which could reduce anionic character of the COF-CdS QDs, bringing down the negative zeta potential.[38] The magnitude of the measured zeta potential is an indicator of the net charge over the QDs and can be used to predict the long-term stability of the particles. If all the particles in suspension have either a large negative or a positive zeta potential, there will not be any tendency for them to come closer due to strong repulsion. However, if the particles have low zeta potential values, the probability of them coming together to form an aggregate is higher.[38,45] The COF-CdS QDs synthesized in our laboratory did not show any sign of aggregation even after 6 months under refrigerated conditions.

In addition to all above study, we also measured the size of the particles by using HR-TEM. Figure 2a shows the size of the COF-CdS QDs as 3−10 nm. Figure 2b displays the sizes of the COF-CdS QDs on interaction with 10 μg mL^{-1} Co^{2+} ions. The size of the COF-CdS QDs increased on adding increasing quantities of Co^{2+} ions. When 10 μg mL^{-1} Co^{2+} ions was added, the size was increased, it became close to about 150−200 nm, and a total complex like aggregate was formed on adding 10 μg mL^{-1} Co^{2+} ions. However, HR-TEM showed lower values for the size of the COF-CdS QDs compared to DLS measurements (Figure 14). DLS measurement records higher values since the light is scattered by the core particle and the layers formed on the surface of the particles, on the other hand, HR-TEM shows the size of the metallic core only. He et al. have also made similar observations earlier.[46] The idea that Co^{2+} ion induced aggregation of COF-CdS QDs leading to color change may be due to the carboxyl binding with Co^{2+} ions through metal−ligand interaction is well-supported by the absorption, FL quenching, DLS measurements and HR-TEM investigations. The plausible mechanism for color change is schematically depicted in Scheme 1.

Table 2. Results of Analysis of Water Samples from Different Sources Containing Spiked Co^{2+} Ions by the Proposed Methods and Comparison with the Established Methods

	Co^{2+} ions found[b] (% recovery ± SD)	
water samples studied[a]	proposed method	reference method (AAS)
drinking water (Dept. of Chemistry, SUK[c])	100.10 ± 0.52	100.13 ± 0.15
tap water (Dept. of Chemistry, SUK)	101.52 ± 1.14	100.28 ± 0.24
lake water (Rajaram Lake, Near SUK)	100.84 ± 0.73	100.80 ± 0.56
Panchganga River (Kolhapur, MS, India)	100.73 ± 0.54	100.3 ± 0.74

[a] Water samples were collected from different water sources in the university campus. [b] Average of three determinations. [c] SUK = Shivaji University, Kolhapur

Application of COF-CdS QDs for the Determination of Co^{2+} Ions from Different Environmental Water Samples. To demonstrate the potential use of a developed colorimetric probe, COF-CdS QDs were used in the analysis of different environmental water samples. The applications of the proposed method were evaluated for determination of Co^{2+} ions in water samples from different sources collected throughout the university campus. The sample collected was first filtered through filter paper (Whatmann No. 40) to remove suspended matter, impurities etc., and then boiled for 5 min to remove chlorine and dissolved gases. After that, water samples were spiked with standard Co^{2+} ions at different concentration levels, then the sample was diluted within the working linear range and analyzed with the method proposed via the standard addition method. The results are summarized in Table 1, which shows good agreement between the expected and found values. The results obtained with proposed method were also in good agreement with those obtained using the established method (AAS), and results are tabulated in Table 2. These results demonstrate that the designed probe is applicable for naked eye detection of Co^{2+} ions from different environmental water samples in the presence of a matrix.

■ CONCLUSIONS

In conclusion, we have synthesized COF-CdS QDs as a single shot naked eye colorimetric probe that specifically detect Co^{2+} ions over 13 other cations in aqueous solution. The Co^{2+} ion induced COF-CdS QDs results in a marked enhancement of the UV−vis absorption spectra at 360 nm and a visible color change from colorless to yellowish brown, which proves a sensitive detection of Co^{2+} ions. This study presents a highly sensitive and selective method for the determination of Co^{2+} ions in aqueous solutions. Compared to traditional methods, the proposed method is superior due to its simplicity and speed of detection. First, no complicated sample pretreatment like separation or preconcentration was needed. Second, the color change induced by Co^{2+} ions can be easily observed by the naked eye, suggesting excellent applicability to field tests. Beneath the optimal conditions, the developed probe gave good linearity for the calibration graph ($A - A_0$) at 360 nm against concentrations of Co^{2+} ions in the range from 0.5 to 14 μg mL^{-1} with a correlation coefficient of 0.9996. The COF-CdS QDs can be capable of evaluating the exceeding standard of Co^{2+} ions in environmental water samples with a lowest colorimetric detection limit (LOD = 0.23 μg mL^{-1}) by the standard addition method. This method may offer a new cost-effective, rapid, and simple solution to the inspection of Co^{2+} ions in water samples in the presence of a complex matrix.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) El-Safty, S. A. *Adsorption* **2009**, *15*, 227−239.
(2) Gharehbaghi, M.; Shemirani, F.; Farahani, M. D. *J. Hazard. Mater.* **2009**, *165*, 1049−1055.
(3) Khorrami, A. R.; Hashempur, T.; Mahmoudi, A.; Karimi, A. R. *Microchem. J.* **2006**, *84*, 75−79.
(4) Monteil-Rivera, F.; Dumonceau, J. *Anal. Bioanal. Chem.* **2002**, *374*, 1105−1112.
(5) Lin, W. Y.; Yuan, L.; Long, L. L.; Guo, C. C.; Feng, J. B. *Adv. Funct. Mater.* **2008**, *18*, 2366−2372.
(6) Maity, D.; Govindaraju, T. *Inorg. Chem.* **2011**, *50*, 11282−11284.
(7) Yao, Y.; Tian, D.; Li, H. *ACS Appl. Mater. Interfaces* **2010**, *2*, 684−690.
(8) Zhen, S. J.; Guo, F. L.; Chen, L. Q.; Li, Y. F.; Zhang, Q.; Huang, C. Z. *Chem. Commun.* **2011**, *47*, 2562−2564.
(9) Au-Yeung, H. Y.; New, E. J.; Chang, C. J. *Chem. Commun.* **2012**, *48*, 5268−5270.
(10) Ai, K.; Liu, Y. L.; Lu, L. H. *J. Am. Chem. Soc.* **2009**, *131*, 9496−9497.
(11) Xiong, D. J.; Li, H. B. *Nanotechnology* **2008**, *19*, 465502−465507.
(12) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538−544.
(13) Gao, X.; Yang, L.; Petros, J. A.; Marshall, F. F.; Simons, J. W.; Nie, S. M. *Curr. Opin. Biotechnol.* **2005**, *16*, 63−72.
(14) Chen, X. D.; Wang, X. B.; Liu, L.; Yang, D. C.; Fan, L. *Anal. Chim. Acta* **2005**, *542*, 144−150.
(15) Liang, J.; Huang, S.; Zeng, D.; He, Z.; Ji, X.; Ai, X.; Yang, H. *Talanta* **2006**, *69*, 126−1307.
(16) Li, D.; Yan, Z. Y.; Cheng, W. Q. *Spectrochim. Acta Part A* **2008**, *71*, 1204−1211.
(17) Liu, M.; Xu, L.; Cheng, W.; Zeng, Y.; Yan, Z. *Spectrochim. Acta Part A* **2008**, *70*, 1198−1202.
(18) Gore, A. H.; Mote, U. S.; Tele, S. S.; Anbhule, P. V.; Rath, M. C.; Patil, S. R.; Kolekar, G. B. *Analyst* **2011**, *136*, 2606−2612.
(19) Wu, H.; Liang, J.; Han, H. *Microchim. Acta* **2008**, *161*, 81−86.
(20) Wang, L.; Chen, H.; Wang, L.; Wang, G.; Li, L.; Xu, F. *Spectrochim. Acta, Part A* **2004**, *60*, 2469−2473.
(21) Bo, C.; Ping, Z. *Anal. Bioanal. Chem.* **2005**, *381*, 986−992.
(22) Liang, J. G.; Ai, X. P.; He, Z. K.; Pang, D. W. *Analyst* **2004**, *129*, 619−622.
(23) Chen, B.; Yu, Y.; Zhou, Z.; Zhong, P. *Chem. Lett.* **2004**, *33*, 1608−1609.
(24) Liu, J. W.; Lu, Y. *Chem. Commun.* **2007**, *46*, 4872−4874.
(25) Li, H. B.; Bian, Y. H. *Nanotechnology* **2009**, *20*, 145502−145507.
(26) Bae, D. R.; Han, W. S.; Lim, J. M.; Kang, S. W.; Lee, J. Y.; Kang, D. M.; Jung, J. H. *Langmuir* **2010**, *26*, 2181−2185.
(27) Ling, J.; Sang, Y.; Huang, C. Z. *J. Pharm. Biomed. Anal.* **2008**, *47*, 860−864.
(28) Xiong, D. J.; Chen, M. L.; Li, H. B. *Chem. Commun.* **2008**, *7*, 880−882.
(29) Li, H. B.; Yao, Y.; Han, C. P.; Zhan, J. Y. *Chem. Commun.* **2009**, *32*, 4812−4814.
(30) Xiong, D. J.; Chen, M. L.; Li, H. B. *Chem. Commun.* **2008**, *7*, 880−882.
(31) Lin, S. Y.; Chen, C. H.; Lin, M. C.; Hsu, H. F. *Anal. Chem.* **2005**, *77*, 4821−4828.
(32) Huang, C. C.; Chang, H. T. *Anal. Chem.* **2006**, *78*, 8332−8338.
(33) Yang, F. P.; Ma, Q.; Yu, W.; Su, X. G. *Talanta* **2011**, *84*, 411−415.
(34) Kim, Y. K.; Johnson, R. C.; Hup, J. T. *Nano Lett.* **2001**, *1*, 166−167.
(35) Winter, J. O.; Gomez, N.; Gatzert, S.; Schmidt, C. E.; Korget, B. A. *Colloid Surf. A* **2005**, *254*, 147−157.
(36) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854−2860.
(37) Wu, Y. L.; Lim, C. S.; Fu, S.; Tok, A. I. Y.; Lau, H. M.; Boey, F. Y. C.; Zeng, X. T. *Nanotechnology* **2007**, *18*, 215604−215612.
(38) Lyklema, J. In *Fundamentals of Interface and Colloid Science: Solid−Liquid Interfaces*, 1st ed.; Academic Press: London, 1995; Vol. 2, p 3.208.
(39) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2006; Vol.*1*, p 278−327.
(40) Anand, V. D.; Deshmukh, G. S.; Pandey, C. M. *Anal. Chem.* **1961**, 33, 1933−1937.
(41) International Conference on Harmonization (ICH) of Technical Requirements for Registration of Pharmaceuticals for Human Use, Topic Q2 (R1): Validation of Analytical Procedures: Text and Methodology, 2005, www.ich.org.
(42) Liang, J. G.; Ai, X. P.; He, Z. K.; Pang, D. W. *Analyst* **2004**, *129*, 619−622.
(43) Dong, C.; Qian, H.; Fang, N.; Ren, J. *J. Phys. Chem. B* **2006**, *110*, 11069−11075.

(44) Isarov, A. V.; Chrysochoos, J. *Langmuir* **1997**, *13*, 3142−3149.

(45) *Measuring Zeta Potential*; Application Note by Malvern Instruments Ltd: Worcestershire, U. K., March 30, 2012; http://www.malvern.co.uk.

(46) He, Y. Q.; Liu, S. P.; Kong, L.; Liu, Z. F. *Spectrochim. Acta Part A* **2005**, *61*, 2861−2866.