Highly Sensitive and Selective Fluorescent Sensor for Ag^+ in Using β-Cyclodextrin / Chitosan Polymer Coated S QDs Based on Aggregation Caused Quenching Mechanism

Shan Wang (shanwang2002@163.com)
Xianyang Normal University
Huan Wang
Xianyang Normal University
Jianshe Yue
Xianyang Normal University
Yi Lu
Xianyang Normal University
Tian Jia
Xianyang Normal University
Jie Chen
Xianyang Normal University

Research Article

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Abstract

A fluorometric sensor based on poly (β- cyclodextrin/chitosan) with H bonded S QDs/CTSCD nanocomposites was synthesized by self-assembly. They were characterized by FTIR, UV–Vis spectroscopy, XPS, and TEM. The S QDs on the chain of the polymer could coordinate with transition-metal ions due to surface electronegativity. The distance between the S QDs on the different chains of polymer could construct the bridge bond of S–Ag^{+}–S with silver ions leading to fluorescence aggregation-caused quenching. The linear range of the method was from 1.0×10^{-5} -5.5×10^{-5}mol/L. The correlation coefficient was 0.9992 with a detection limit of 66.7 nM. This method could be used to detect silver ions in real samples with excellent sensitivity and selectivity, indicating its potential as a novel sensor.

Highlights

Facile fabrication of a novel bionanomaterials to detect silver ions in water by aggregation-caused quenching mechanism

(1) A green coordination mechanism-based S QDs fluorescence sensor was easily fabricated.

(2)The S QDs/CTSCD nanocomposites could coordinate with Ag^{+} due to surface electronegativity.

(3) The aggregation caused quenching mechanism of the sensor form the bridge bond of S-Ag^{+}-S with Ag^{+}.

1. Introduction

Silver ions were a precious metal with special bactericidal, catalytic, and optical properties [Velmurugan, 2014]. The metal was widely used in electronics, photo-sensing, and electroplating industries, causing silver ions to enter the environment in various forms. Silver ions were one of the most toxic metal ions for aquatic organisms even at 0.5% concentration [Singh, 2020; Nasrollahzadeh, 2021; Zhang,2020]. At the same time, a large amount of silver-containing industrial waste was constantly released into the environment. The 17 μg/L concentration of silver ions was also harmful to the fish and microorganisms. Thus, the detection silver ions had become an important topic of health, epidemic prevention, and environmental monitoring. There were many ways to detect heavy metal ions such as stripping voltammetry, [Mikelova,2007] atomic absorption spectrometry, [Chamsaz,2008] inductively coupled plasma mass spectrometry [Barriada,2007] et al. But all of these were non-portable, expensive, time consuming [Lin, 2010;]. Therefore, the design of novel detection methods for selectivity and sensitivity to silver ions was crucial for the maintenance of the environment and human health. Fluorescence analysis, a highly sensitive and selective determination method had developed rapidly in recent years. Because this method could not only overcome the above shortcomings, but also solve the serious drawbacks such as low sensitivity, hydrophobicity, low selectivity, and toxicity, et al [Jaiswal,2012;Zheng,2013;Ding ,2010].

As long as the appropriate fluorescent substances were selected, fluorescence quenching for detecting trace silver ions could be established [Singha,2015]. A few fluorescent sensors for sulfur atoms have been reported for silver ions determination in recent years[Goh,2017;Hwang,2017; Lotfı,2017]. However, many of them had poor biocompatibility and poor water solubility, which hindered their application in water and biological environment. Therefore, the development of biocompatible and water-soluble fluorescent sensors for silver ions was one of the areas which scientists focus on. So far, a wide variety of fluorescent probes had been developed, including metal nanoparticles, semiconductor quantum dots and dye molecules to solve the disadvantages of low sensitivity, low selectivity, insoluble, toxic and so on[Gao,2015]. S QDs have good stability, low cytotoxicity and high biocompatibility. It was found that there were almost no fluorescent probe to detect silver ions by using S QDs in the literature [Fu,2020]. Therefore, it was necessary to develop high-sensitivity, green, portable, and low-cost S QDs fluorescence sensors to detect silver ion.

Several coordination mechanism-based sensors for detecting ions had been exploited [Luidmila,2017; Xiao,2010]. However, most of these coordination polymers were macroscopic solid-state substances, which had very limited solution-based behavior. Given the hydrophobic ligands of the prepared complex polymers, the sensing reaction was primarily performed in an organic solvent. This characteristic remarkably limited their application in biosensors. The polymers had a tailorable and diversified structure and provide a new possibility for their use as biosensors [Spokoyny, 2009; Lotfia,2017; Vaishnav,2019;Jiang,2018].

We proposed a new method to detect silver ions with high sensitivity and excellent selectivity. Chitosan (CS) and β-cyclodextrin was formed a novel polymer crosslinked by formaldehyde (CTSCD). The S quantum dots (QDs) were combined with the amino group in the CTSCD by an electrostatic effect to form the S QD/CTSCD nanocomposites.The S QD /CTSCD nanocomposites rapidly aggregated in the presence of silver ions because of its attraction to the surrounding of S QD/CTSCD nanocomposites through electrostatic interaction. S–Ag^{+}–S was formed with the S QD/CTSCD nanocomposites leading to remarkable particle aggregation and aggregation-caused quenching (ACQ) occurred during its fluorescence detection. The possible mechanism was shown in Figure 1.

2. Experimental

2.1 Reagents and instruments

All chemical reagents were bought from Aladdin Reagent (Shanghai) Co., Ltd and used without further purification. Secondary distilled water was used throughout the experiments. Fluorescence was recorded on a Fluoromax-F 7000 spectrofluorometer with a 10 nm slit and UV–vis spectra were determined using a Shimadzu UV-24500 equipment. XPS data were obtained with an Axisultra DLD electron spectrometer from Shimadzu. FTIR spectra were recorded on Nicolet Magna 550 spectrometer.

2.2 Preparation of CTSCD.

Exactly 3.00 g of CS was completely dissolved in 300mL (0.1mol/L) of hydrochloric acid, and 15.00 g of β-cyclodextrin was dissolved in 600 mL of distilled water. The above mentioned prepared solution was mixed in a 1000 mL beaker. The temperature was increased to 60℃, and 25.00% of the formaldehyde (14.40 mL) was added slowly. The temperature was then increased to 90℃, and the reaction was carried out at stirring for 80.00 mins. After the reaction was completed, NaOH was added dropwise to the solution until pH reached 11.00, and a yellow precipitate was produced. The same temperature was maintained, and the reaction was continued for 45 mins. The reaction solution was filtered, washed to neutral, and washed with acetone and ethanol twice. The extract was dried to a constant weight at 45℃. The resulting product was a CTSCD with a red-brown color.

2.3 S QDs functionalized CTSCD

Exactly 0.031 g of CTSCD was dissolved in 6.0 mL of anhydrous ethanol. Then, 1.50 mL (3 mg/mL) of S QDs was added to the solution. The tube was placed in an ultrasonic instrument to complete self-assembly synthesis, and the sample S QD/CTSCD nanocomposites were obtained.

2.4. Fluorescence properties of S QD/CTSCD nanocomposites

The fluorescence sensing silver ions in the sample by S QD/CTSCD nanocomposites was determined as follows: different concentrations of silver ions were mixed with 500 μL of S QD/CTSCD nanocomposites and 2.5 mL ultrapure water. After 5 min, the solution was transferred to the luminous measurement with an excitation wavelength of 295 nm. The excitation wavelength (λ_{ex}) of S QDs/CTSCD nanocomposites was 295 nm in all tests, and the emission was monitored from 320 nm to 580 nm. The width of excitation and emission slit was 5 nm.

The selectivity of silver ions was investigated by preparing the same samples following the above mentioned. Fe^{3+}, Ca^{2+}, Pb^{2+}, Na^{+}, Cr^{3+}, Bi^{3+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Sr^{2+}, Hg^{2+}, Ni^{2+}, and other solutions were added to each sample until the same concentration (10 μM) was reached. All of the mixtures were incubated at room temperature for 20 mins. The fluorescence spectra were recorded at the excitation wavelength of 295 nm.

2.5 Application in actual water samples

The practicability of the method was evaluated by detecting the actual water samples from the iron bridge, Xianyang Lake, Canal water, and tap water. The impurities were removed by filtration and centrifugation, and silver ions in river samples was detected by standard addition method. The detection procedure was the same as the above mentioned.

3. Results And Discussion

3.1. FTIR and DSC analysis of the S QD/CTSCD nanocomposites

Fig.2A showed the infrared spectra of the S QDs, CTSCD, and S QD/CTSCD nanocomposites. The peak at 1640 cm^{-1} was a typical S QDs [Shan,2019], and the peak at 896 cm^{-1} was β-(1, 4)-glycosidic bonds of CS. The peak at 1042 cm^{-1} indicated the presence of the a-(1,4)-glycosidic bond of β-CD. The peak at 1640 cm^{-1} corresponded to the S QDs, indicated that S QDs was successfully introduced to CTSCD. The peaks at 1560–1640 cm^{-1} and 2100 cm^{-1} were belonging to amino ($–NH_2$), alicyclic amine I (C=O), and cyclic amine II (N–H) groups. The absorption peak of the S QD/CTSCD nanocomposite was reduced due to the reaction with the amino group.

The results of DSC analysis of CTSCD (a) and S QD/CTSCD nanocomposites (b) were shown in Fig. 2B. Curve a showed an obvious endothermic peak at 97.25℃attributed to the crystalline water that evaporated in the CTSCD. The melting peak of CS was approximately 225℃ due to the internal H bond, whereas the melting peak of CTSCD was approximately 228℃, which was more stable than that of the CS monomer [Djerahov,2016Teng, 2020. Rao, 2020, Lin,2020, Li, 2020]. From the curve b in Fig.2B, an obvious endothermic peak was found at 100℃. The hydrophobicity and thermal stability of CTSCD were evidently improved by the S QDs. The exothermic peak at 259.48℃ was the degradation peak of S QD/CTSCD nanocomposite chain skeleton, which was due to the weakening of hydrogen bond interaction and the destruction of crystal structure regulation by S QDs. The two lines in Fig.2B showed that with increased degradation temperature of the chain skeleton, the thermal stability of S QD/CTSCD nanocomposites were improved.

3.2. Optical property and TEM of the S QD/CTSCD nanocomposites

The optical properties of S QDs/CTSCD were studied on the basis of the UV absorption spectra and fluorescence spectra at room temperature. Fig.3A showed a 298 nm centered absorbance band in the UV absorption spectrum. The ultraviolet absorption of S QDs, which was modified by the CTSCD polymer, was stronger than that of S QDs. Therefore, as shown in Fig.3A, the solution of S QD/CTSCD nanocomposites was light yellow (A) in sunlight but bright blue when irradiated at 365nm UV light (B), indicating the blue fluorescence properties of S QD/CTSCD nanocomposites. When excited at 295 nm, the fluorescence spectrum showed excellent emission peak at approximately 411 nm, which was shown in Fig.3B.

The TEM micrographs (Fig. 4A) showed the good dispersion of S QDs. The particles mostly have a regular spherical shape with approximately 2-3 nm in size. A typical amorphous structure was observed with no visible lattice. These results showed that the synthetic S QDs had excellent nanoparticle properties for metal-ion sensors. The atomic force microscopy image shows the shape and height of the S QDs. The average height was 2.8 nm (Fig. 4B). The TEM image showed the good dispersion of SQD/CTSCD (Figs.4B and 4C) with a relatively uniform size distribution. The average diameter of the S QDs/CTSCD was 2.5 nm.

3.3. XPS of S QD/CTSCD nanocomposites

The composition, surface group, and structure of S QDs/CTSCD were studied by XPS. The four peaks of the nanocomposites at 284.30, 398.8, 532.04, and 165.9 eV were C1s, N1s, O1s, and S2p in the Fig.5A, respectively. The C1s spectrum (Fig.5B) had two peaks at 282.73 and 285.9 eV, which could be attributed to C–C and C–OH. Two peaks were found at 165.75 and 165.5eV in the S 2p spectra (Fig. 5C) attributed to S in $SO_2^-(2p^{2/3})$, $SO_2^-(2p^{1/2})$, $SO_3^-(2p^{2/3})$, and $SO_3^-(2p^{1/2})$ bands [Prasannan,2013]. The three peaks of 395.9, 396.05, and 397.1eV in the N1s spectrum (Fig.5D) were from the C–N–C and C–N groups, respectively. The O1s spectrum (Fig.5E) had two peaks at 532.7 and 531.9eV, which were due to the C-OH/C–O–C and C=O bands [Park,2015;Teng,2020;Wu,2020]. This finding indicated that S atom was added to the CTSCD prepared in the present study. These results were consistent with those of FTIR.

3.4 Effect of pH on the fluorescence of S QD/CTSCD nanocomposites

Fig.6 showed the effect of pH (4–10) on the fluorescence intensity of the S QD/CTSCD aqueous solution. In the experiments, 0.1 M HCl and NaOH were added to the solution to obtain the desired pH. In the strong acid environment(pH≤4), the amino groups on chitosan will protonate [Gao,2020;Yang,2020], which would destroys the weak self-assembly between the polymer and sulfur quantum dots. The sulfur quantum dots fall from the polymer chain, the fluorescence intensity increased significantly (pH=4). With increased pH from 4 to 10, fluorescence intensity decreased by approximately 7%. This negligible change might be the result of a small change in the quantum confinement due to the functionalization of the S QDs/CTSCD. S QD/CTSCD samples did not change their maximum fluorescence value and the same spectral shape was changed. Under these experimental conditions, the S QD/CTSCD samples were monodispersed and the fluorescence emission was stable [Dager,2019].

3.5. Selectivity of the sensor

Selectivity was an important parameter for assessing the fluorescence property of S QD/CTSCD nanocomposites. The effect of various metal ions, such as Fe^{3+}, Ca^{2+}, Pb^{2+}, Na^+, Cr^{3+}, Bi^{3+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Ag+, Sr^{2+}, Hg^{2+}, and Ni^{2+} which concentration was 1.0×10^{-5}mol/L of fluorescence was examined. As shown in Figure 7 (A), the fluorescence intensity of S QD/CTSCD nanocomposites was quenched to a remarkable extent in the presence of silver ions, whereas the fluorescence intensity in other metal ions (alkali, alkali soil, and transition-metal ions) had negligible change or remain unchanged in the presence of a single cation at 1.0×10^{-5}mol/L. Thus, the sensor based on S QDs/CTSCD had good selectivity to silver ions.

3.6. Quenching of the S QD/CTSCD nanocomposite to silver ions.

Under optimum conditions, the sensitivity of the S QD/CTSCD nanocomposite to silver ions was investigated. In a typical operation, S QD/CTSCD solution (0.01mg/mL) was dispersed in water and mixed with different amounts of silver ions. After the samples were incubated at room temperature for 20 mins, the fluorescence emission spectra (λ_{em}=411nm) were recorded and performed in triplicate. The fluorescence intensity was calibrated by changing the silver ions concentration. F_0 and F were the

fluorescence intensities of S QDs/CTSCD in the absence and presence of silver ions at different concentrations, respectively.

Fig.7B showed that the fluorescence intensity of the S QD/CTSCD nanocomposites gradually decreased with increased concentration of silver ions increased because S–Ag^+–S bond formed between silver ions and S QDs/CTSCD. Based on these phenomena, a favorable linear correlation (R^2=0.9992) existed between I and silver ions concentration in the range of 1.0×10^{-5}-5.5×10^{-5}mol/L (Fig.7C), and the detection limit for silver ions was approximately 66.7 nM. The effectiveness of silver ions fluorescence detection with S QDs/CTSCD as fluorescence probe was verified and provided a platform. The selectivity of S QDs/CTSCD to silver ions might be due to the synergistic effect of S and O functional groups on S QDs/CTSCD [Lu,2014]. Where F_0 (F_0 was [C]=0), F was the fluorescence intensity before and after adding silver ions, K_{SV} was the quenching effect coefficient of the sensing material, [C] was the molar concentration of the analyte (C).This quenching effect could be rationalized by the Stern–Volmer equation: $I_0/I=1+0.0029C$(R^2=0.9966). The concentration of silver ions was in the range of 1.0×10^{-5} – 5.5×10^{-5} mol/L (Fig.7D). The results also showed that the S QD/ CTSCD nanocomposite was a more sensitive silver ions fluorescence sensor than others [Gao, 2020; Dager, 2019; Jiang, 2015; Lu,2014; Yang, 2020]. The sensitivity of the sensor was higher than that of other methods reported in literature [Lv, 2014; Gao, 2015; Wang, 2007;Bian, 2017]. As shown in Table1, the detection limit and the analytical concentration range of different technologies. Furthermore, it could be used to directly detect silver ions in the actual sample.

3.7 Sensor mechanism

The structure of S QDs/CTSCD should have a molecular-recognition capability to detect a certain type of substrate and provided the necessary spatial-structure arrangement for binding sites and functional groups. The functionalization of S QDs by the CTSCD structure was determined by the ability of a receptor with a heteroatom (S from S QDs, N from NH_2) with lone pairs to bind silver ions. The hydration radius of silver ions could exactly match the distance on the S QDs/CTSCD nanocomposites. S QDs functionalized by the crosslinking CTSCD supramolecular structures as a component of self-assembly structure was promising because their structure contains potential coordination centers of metal cations (bridged sulfur atoms and negative charge NH_2 groups). The bridged S QDs in polymer structure formed S–Ag^+–S bonds, which combined with colloidal particles with noncovalent bonds, thereby forming the dendritic fractal structure of aggregates based on silver ions. The experimental results showed that ACQ has occurred.

3.8 Effect of coexisting metal ions

To further investigate the selectivity of S QDs/CTSCD nanocomposites to silver ions, the competitive experiments were carried out by measuring the fluorescence intensity of S QDs/CTSCD nanocomposites in the presence of silver ions and additional metal ions. The effect of some co-existing cations on the detection of silver ions was shown in Figure 8. Fig.8 (B) showed the fluorescence response of the sensing

system to silver ions in the presence of other metal ions. The emission peak at 411 nm was almost no changed of most coexisting metal ions except Ni^{2+}.It could be concluded that most coexisting metal ions did not interfere with the binding of the silver ions to the S QD/CTSCD nanocomposites except Ni^{2+} ions that had a weak effect on detection. Therefore, the selective binding of silver ions could be carried out in the presence of most competitive and coexisting metal ions.

3.9. Detecting silver ions in environmental sample

Environmental sample from the Xianyang Lake, Gudu Canal, and Nanhu Lake was collected. The standard Ag^{+} solution was added to the water samples and analyzed via standard addition method. The results showed that the recovery of silver ions in the samples were 98.44-110.76% (Table 2).The results showed that the designed sensor was reliable and practical for detecting silver ions in different environmental water samples.

4. Conclusion

A convenient and green strategy of S QD/CTSCD nanocomposites was developed via simple self-assembly, which included a prior crosslinking experiment of CS and β-cyclodextrin. The advantages of the method lied in the aspects as follows. (1) S QDs were successfully linked to the CTSCD polymer chain through a simple and convenient self-assembly reaction and exhibited excellent fluorescence behavior. (2) S QDs/CTSCD showed a selective and sensitive response to silver ions. (3) A simple and direct method of silver ions detection was realized with fast response, wide linear range, and low detection limit. (4) Distilled water, tap water, and water from the Xianyang Lake, Nanhu Canal, and Gudu Canal were analyzed. The experimental results showed that the detection of silver ions was achieved in actual water samples. In brief, the S QDs/CTSCD nanocomposites provides new opportunities within the personal healthcare and environmental monitoring domains.

Declarations

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Authorship contribution statement

Shan Wang: Investigation, Methodology, Writing - original draft. Yi Huang: Data curation. Yi Lu: Editing. Tian Jia and Chenyun Cai: Experiments.

Declaration of Competing Interest

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

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Authors' information (Optional)

Shan Wang : School of Chemistry and Chemical Engineering of Xianyang Normal University, Xianyang, 712000, PR China

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Tables

Due to technical limitations, table 1,2 is only available as a download in the Supplemental Files section.

Figures

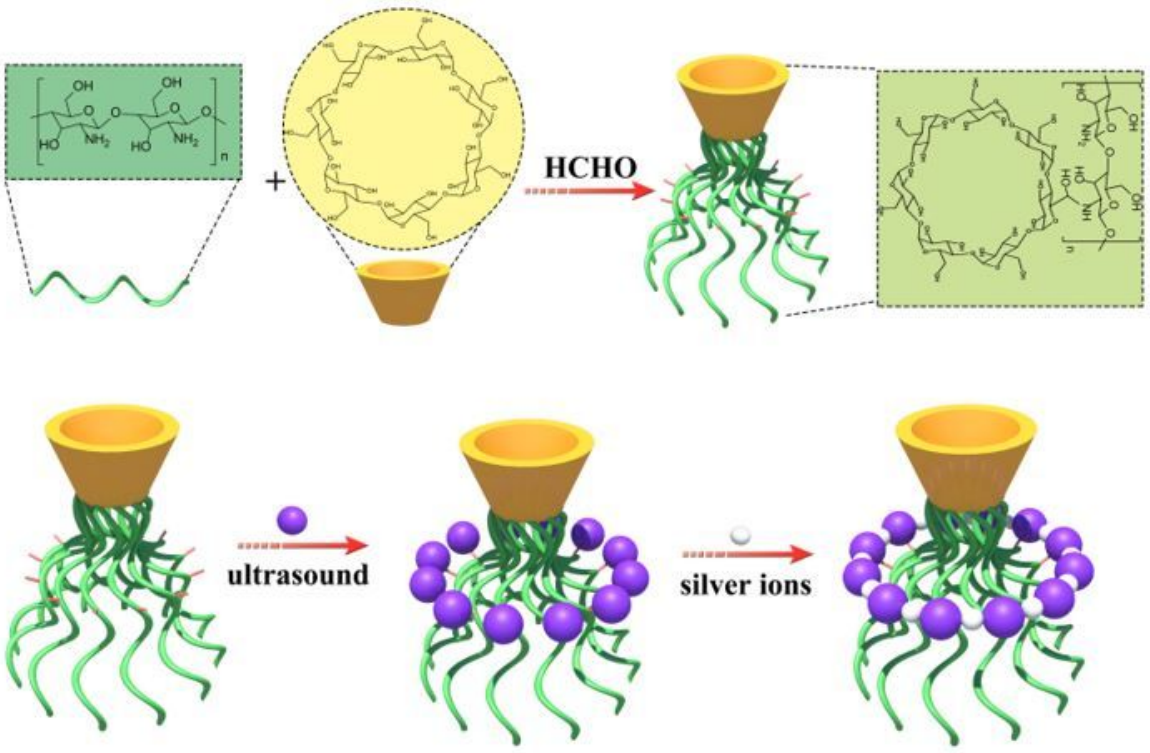

Figure 1

The possible mechanism of the novel sensor

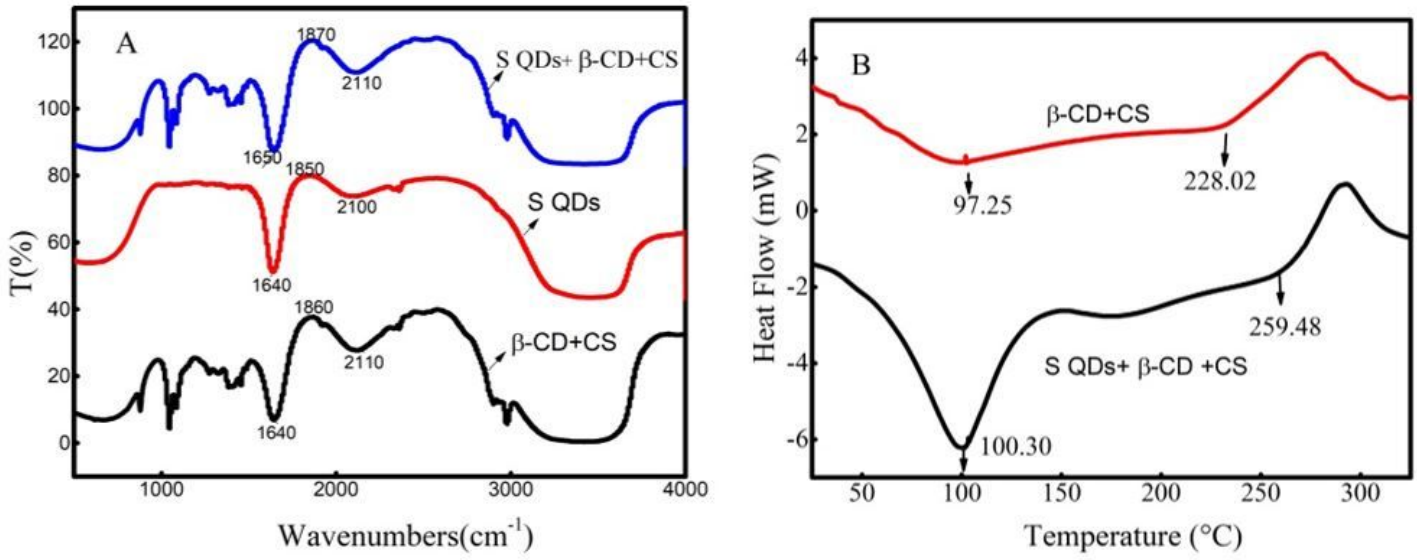

Figure 2

The FTIR (A) and DSC (B) of the S QDs/CTSCD nanocomposites

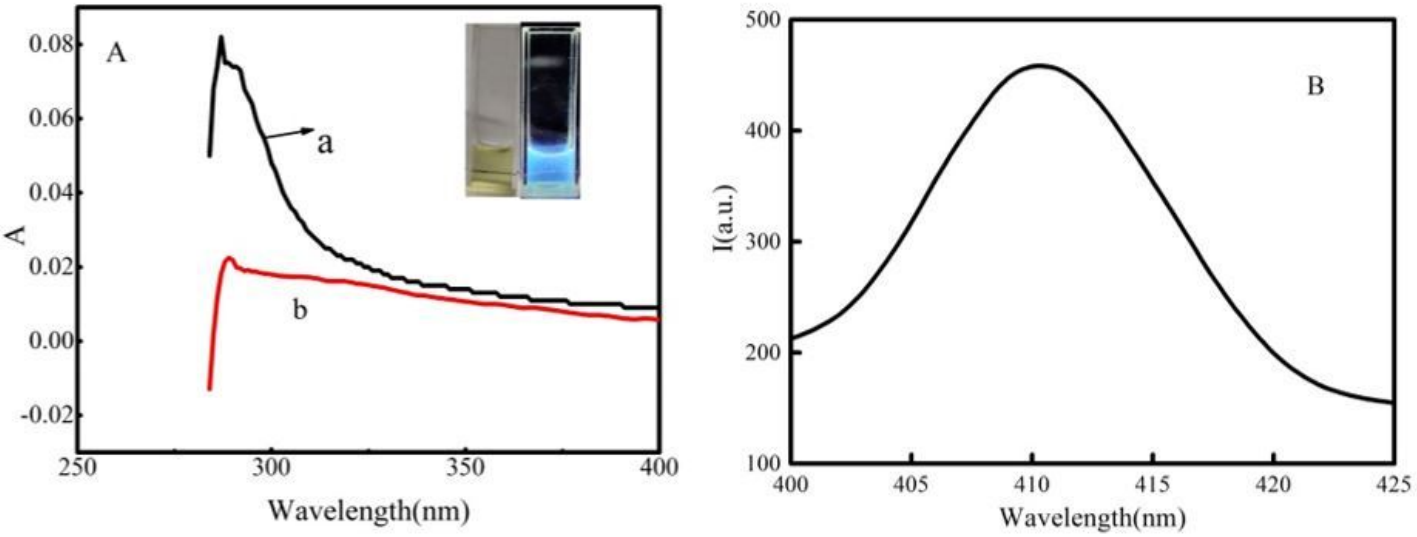

Figure 3

The UV/Vis spectra (A) and maximum fluorescence emission (B) of the S QDs/CTSCD nanocomposites

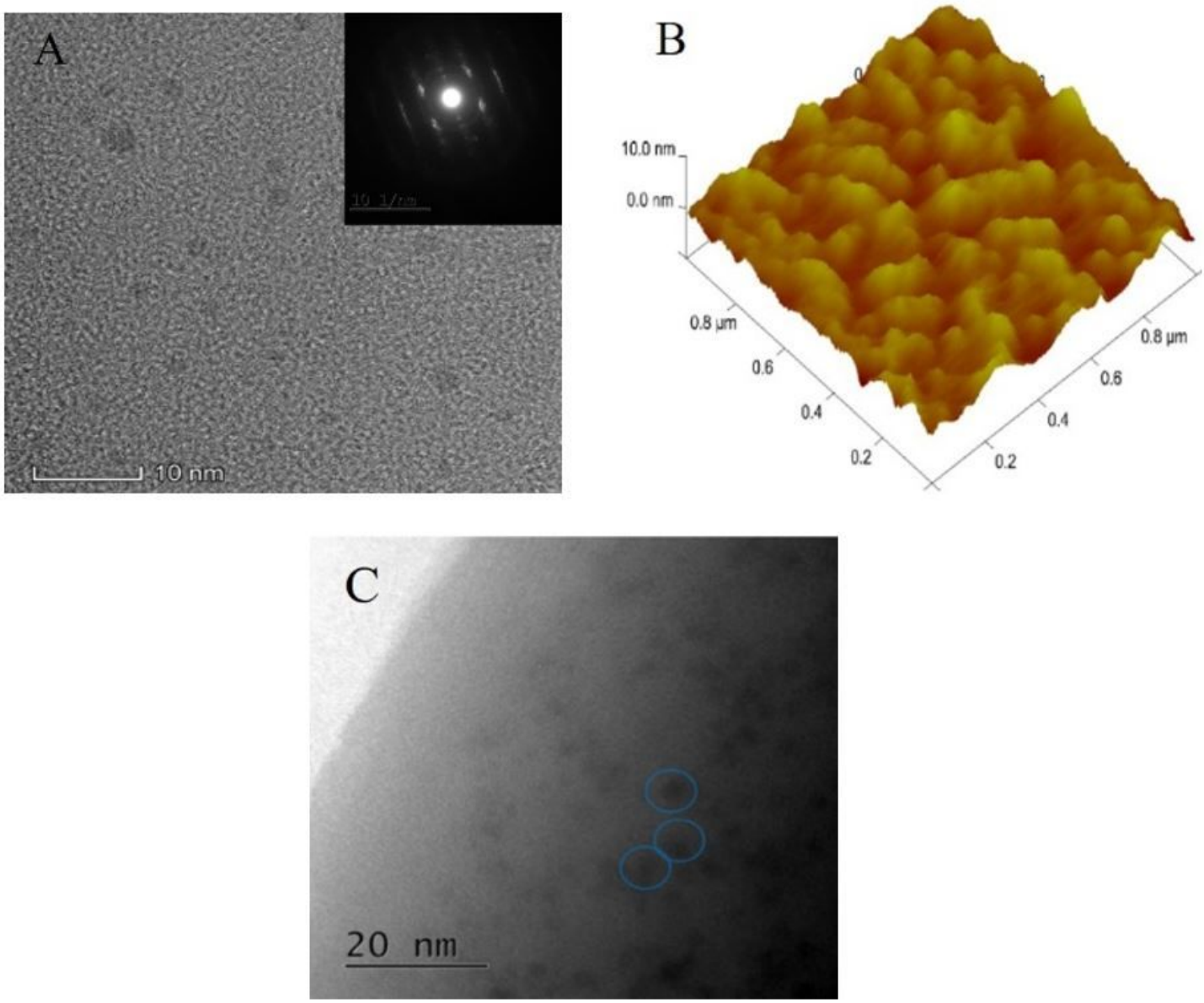

Figure 4

(A) TEM image of S QDs with diameter around 2-3 nm; (B) AFM representation of S QDs; and (C) The TEM of the S QDs/CTSCD nanocomposites.

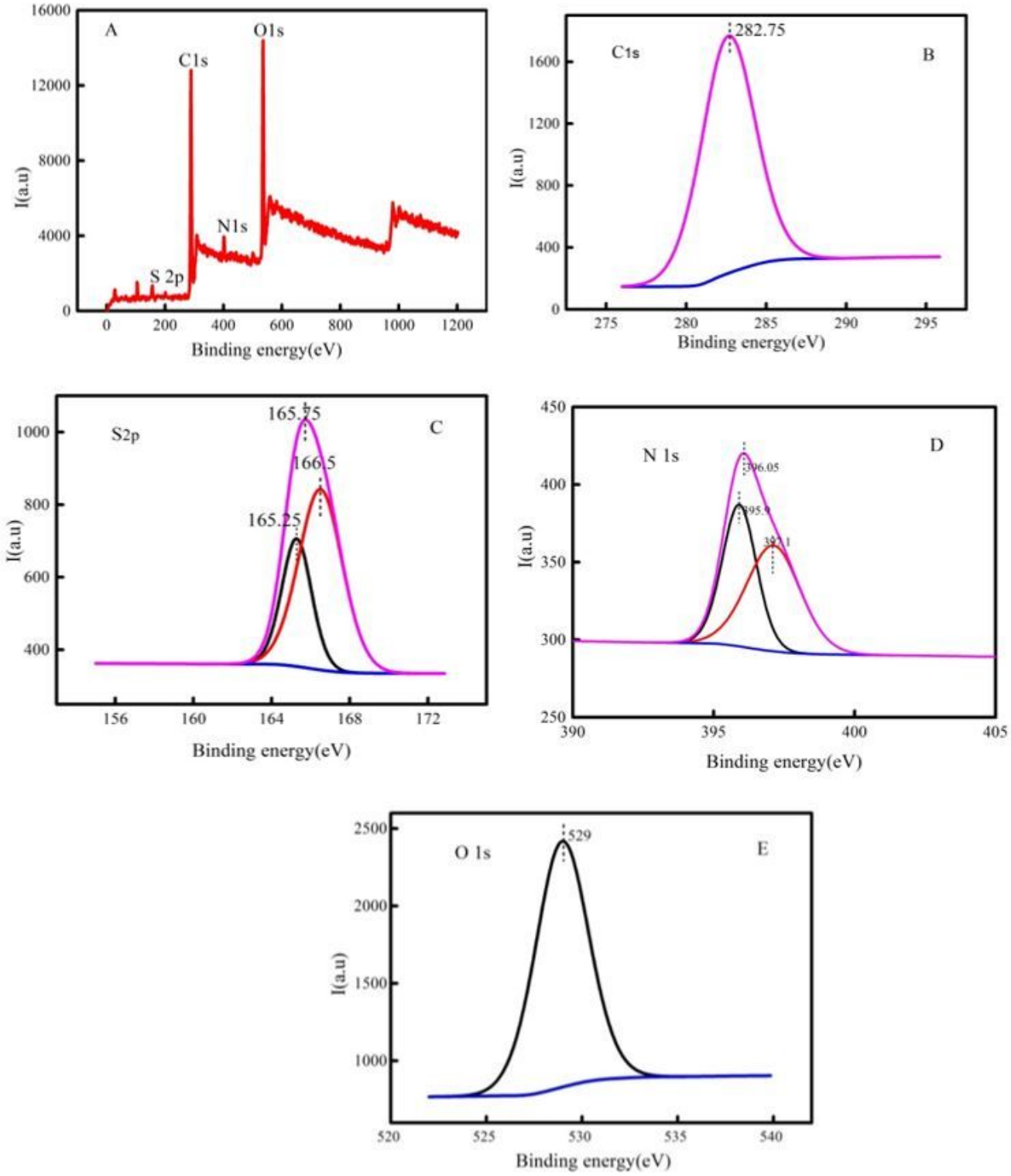

Figure 5

The XPS characterization of S QDs/CTSCD nanocomposites

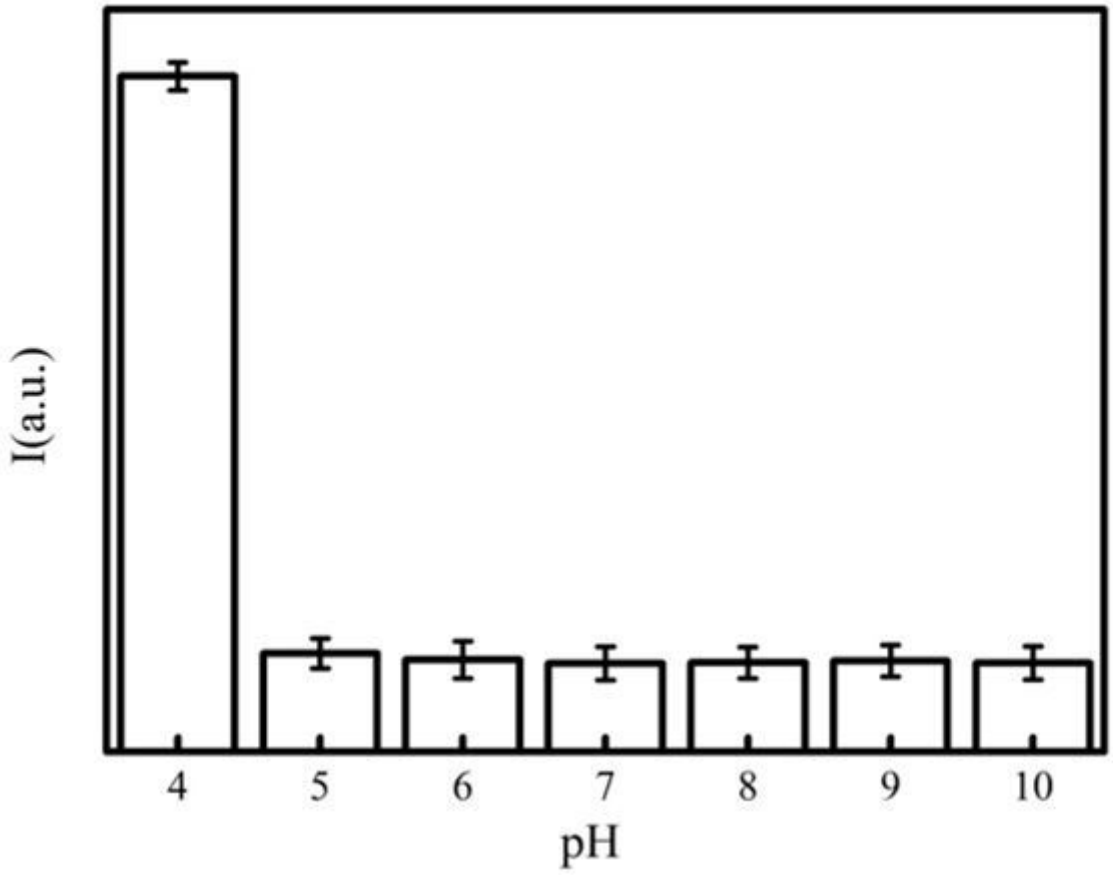

Figure 6

Effect of pH on the fluorescence properties of S QDs/ CTSCD nanocomposites

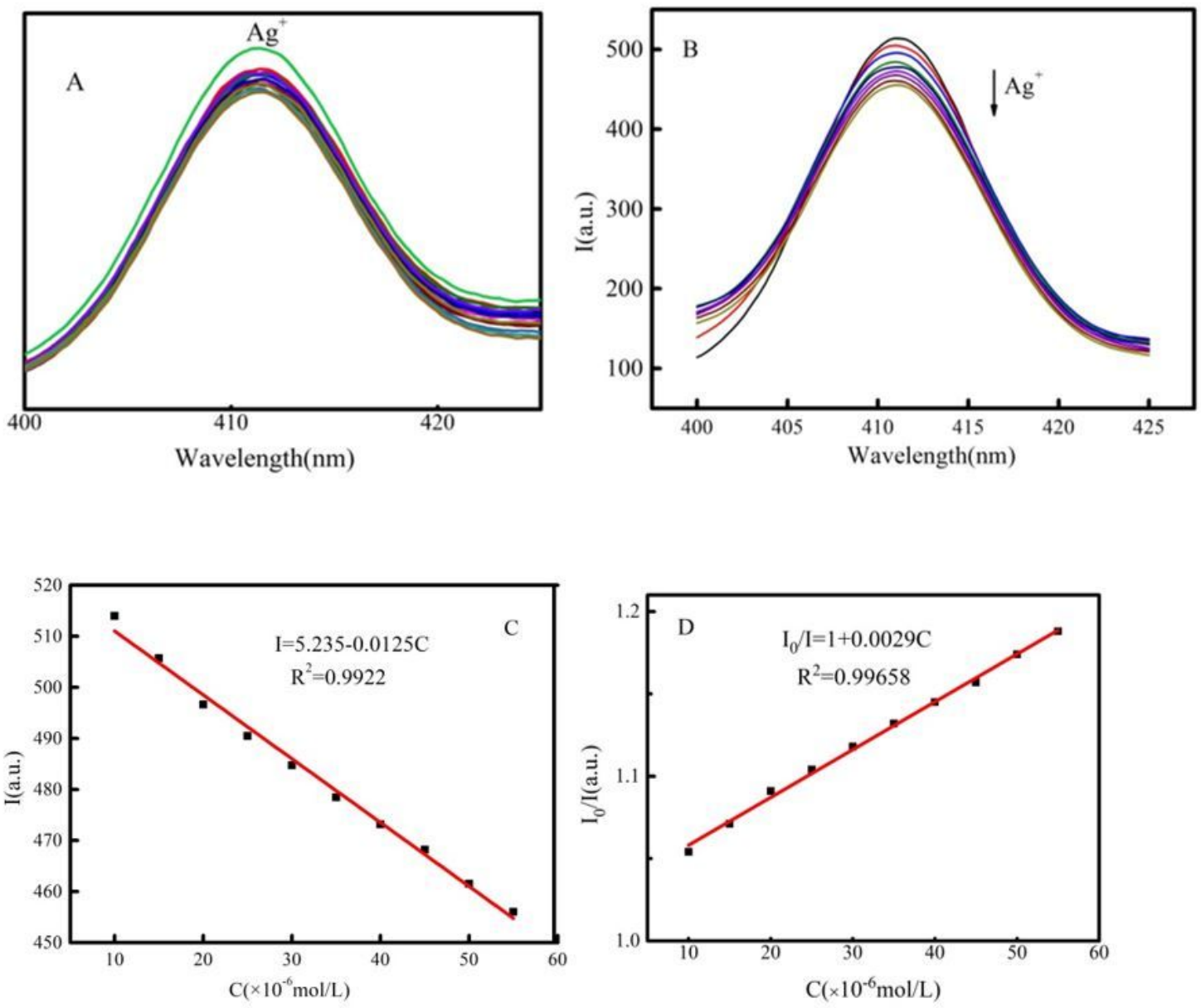

Figure 7

Study on the sensing properties of S QDs/CTSCD nanocomposites (A, Selectivity B, Sensing properties(Silver ion concentration from 1×10-5mol/L to 5.5×10-5 mol/L), C, Linear properties D, S-V equation) C Ag+:1, 1×10-5mol/L 2,1.5×10-5mol/L;3,2×10-5mol/L;4,2.5×10-5mol/L; 5,3×10-5mol/L; 6,3.5×10-5mol/L;7,4×10-5mol/L;8,4.5×10-5mol/L;9,5×10-5mol/L;10,5.5×10-5 mol/L)

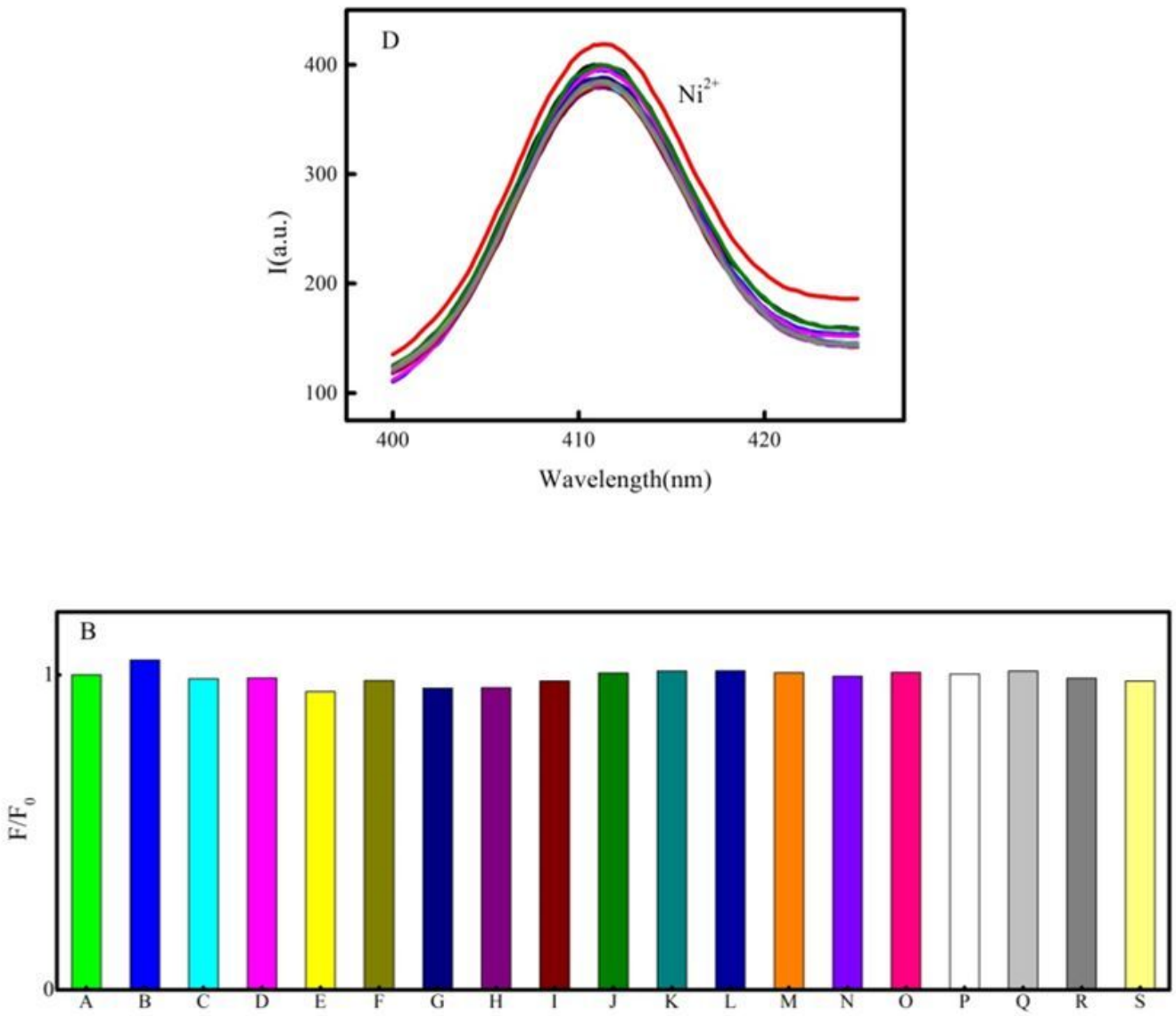

Figure 8

Interference of different inorganic metal ions in the sensing of silver ions by S QDs/CTSCD nanocomposites (A: Ag+, B: Ni2+, C: Mn2+, D: Fe2+, E: Mo6+, F: Cu2+, G: Fe3+, H: Ca2+, I: Pb2+,J: Na+, K: Cr3+, L: Bi3+,M: Zn2+, N: Mg2+,O: Ba2+,P: Cd2+, Q: Sr2+, R: Hg2+, S:Co2+)

Supplementary Files

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- Graph.docx
- Table1.jpg

- Table2.jpg