One-Step Synthesis of Water-Soluble CdS Quantum Dots for Silver-Ion Detection

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ABSTRACT: To realize fast synthesis of cadmium sulfide (CdS) quantum dots with a low-toxic material, a one-step synthesis method is investigated and conducted. Potato extract is used as a stabilizer and modifier, by which aqueous CdS quantum dots can be prepared at a lower temperature with a shorter time. Through systematic characterization and analysis, a green and fast synthesis mechanism is demonstrated in detail. And the nanoscale CdS quantum dots are uniform in size and dispersity. With low cost and high sensitivity, the prepared CdS quantum dots show promising application in silver-ion detection. This method shows great significance for an environmentally friendly and facile synthesis of CdS quantum dots.

1. INTRODUCTION

As an effective antibiosis component, silver ion (Ag⁺) is commonly applied in biochemical products. Despite its highly functional property, silver ion is a kind of poisonous heavy-metal ion that might lead to water pollution and health threats. Therefore, developing a detection technology of silver ion shows great significance for environmental protection. Characterized by high productivity and stable emission of fluorescence, quantum dots are widely investigated for heavy-metal detection.

Cadmium sulfide (CdS) quantum dots, the most important II–IV semiconductors, have a narrow band gap (2.42 eV), quantum confinement, and large surface area. Excellent electrochemical, optical, and fluorescence properties enable their valid utilization in pharmacological analysis and elements detection fields. It is well known that the performance of CdS nanomaterials greatly depends on the size and spatial structure. Therefore, much effort has been made to prepare CdS nanomaterials with desired sizes and structures. Conventional preparation methods include organic solvent method, hydrothermal method, sol–gel method, and microwave method. Peng et al. added a mixture containing CdO or Cd(AC)₂, 3,3-thiodipropionic acid (TDPA), and hydroxypropyl acrylate (HPA) to trioctylphosphine oxide (TOPO) to successfully prepare CdX (X is S, Se, Te) quantum dots with a high fluorescence quantum yield. Guo et al. used hydrophobic amino acids to synthesize stable CdS quantum dots under hydrothermal conditions. Bawendi et al. injected an organometallic precursor into a high-temperature ligand solution; the precursor pyrolyzed at a high temperature and rapidly nucleated, and then the crystal nucleus gradually formed quantum dots. Vossmeier et al. used Cd(ClO₄)₂· 6H₂O, H₂S, and thioglycolic acid as precursors in aqueous solution to synthesize CdS-sulfhydryl quantum dots with thioglycolic acid as a stabilizer. Fresco-Cala et al. utilized microwave radiation to fabricate graphene quantum dots with urea and glucose at 120 °C.

Due to the long preparation process, complicated steps, harmful raw materials, and high cost, more simplified and safer methods for the preparation of quantum dots are desired and attempted. Wang et al. used cucumber juice as stabilizer and dispersant, and hair as a carbon source for the synthesis of N, S, and P co-doped carbon quantum dots by one-step hydrothermal method, which was successfully applied for the detection of mercury ions. Liu et al. reported that grass extracts could be used as raw materials in the preparation of nanoquantum dots, which showed promising application in the detection of copper ions. Shivaji et al. investigated the waste tea extract as a biosurfactant for the synthesis of CdS quantum dots, which effectively inhibited the growth of breast cancer cells. Therefore, the synthesis of quantum dot materials now uses less toxic and easily obtained matters as raw materials. The extracts of starch-containing plant tubers (such as potato, sweet potato, purple potato, yam, and taro) having various
organic groups and starch, which can provide a colloid-like synthesis environment and modify the surface of the material. Therefore, starch-containing plant tubers show great potential in both the synthesis and surface modification of quantum dots.

Herein, we report a simple one-step preparation method for the synthesis of water-soluble CdS quantum dots. The potato extract contains various organic groups such as hydroxyl, carboxylic, carbonyl, and sulfhydryl, which enable the excellent water dispersion of the prepared samples. Besides, the starch from potato extract provides a stable environment for the synthesis of CdS quantum dots. And the CdS quantum dots are evaluated as a fluorescence detector for silver ions. The synthesis mechanism of quantum dots and the application in silver-ion detection were deeply explored based on the systematic characterizations.

2. RESULTS AND DISCUSSION

The morphology and phase of CdS samples were characterized by transmission electron microscopy (TEM). As shown in Figure 1a, the CdS quantum dots are uniform in size with good dispersion. And the diffraction fringes of (200) and (111) planes can be clearly observed in high-resolution mode (Figure 1b) with interplanar spacings of 0.29 and 0.33 nm, respectively. It indicates that the nanoscale CdS samples prepared from potato extract are well crystallized, and the particle size of cadmium sulfide quantum dots is about 5 nm.

Figure 2 shows that the prepared sample has different absorption ability in the band of 200−470 nm. A strong absorption band in the range of 300−400 nm can be observed. And the absorption intensity of water-soluble CdS quantum dots reaches maximum at $\lambda = 330$ nm, which is also determined as the excitation wavelength of the prepared CdS quantum dots. Meanwhile, the fluorescence spectrum test was performed on the prepared water-soluble CdS quantum dots with the excitation wavelength as $\lambda = 330$ nm, and the pure potato extract was used as the control group. It can be seen from Figure 2b that no obvious fluorescence excitation can be observed from pure potato extract solution in the test wavelength range, and the aqueous solution of CdS quantum dots using potato extract has a distinct emission peak at $\lambda = 490$ nm.

CdS quantum dots prepared using other starch-containing tubers such as sweet potatoes, yam, taro, and purple sweet potatoes were also compared. The prepared samples and their fluorescence emission spectra (excitation light $\lambda = 330$ nm) are displayed in Figure 3. Except the one using the purple potato group, all of the prepared samples are fluorescent yellow and have obvious fluorescence under the irradiation of ultraviolet light. The weak fluorescence effect of the purple potato group is mainly due to the existence of a large amount of purple anthocyanins. The fluorescence spectra in Figure 3 show that the light intensity excited by CdS quantum dots prepared using potato extract is the strongest and an obvious fluorescence excitation at $\lambda = 490$ nm is observed. It is worth noting that the other four groups have different extents of redshift, which is mainly due to the relationship between the fluorescence characteristics of CdS quantum dots and their particle sizes. Bawendi et al. used Se-tri-n-butyl phosphine and diethyl cadmium as the anion and cation precursors and quickly injected the anion and cation precursor mixture into the mixture of tri-n-butyl phosphine and tri-n-butyl phosphine oxide during the reaction. And by controlling the contents of the two, the reaction system presents different viscosities. Different viscosities have different binding abilities to cadmium atoms, which makes the content of cadmium atoms in the free
state different and finally leads to the different size of cadmium sulfide quantum. Peng et al. used octadecene as a noncoordinating flux, replaced flammable and explosive diethyl cadmium with metal carboxylate, and changed the viscosity of the reaction system by controlling different amounts of octadecene to obtain cadmium quantum dots of different particle sizes. Therefore, materials of different sizes can be obtained by controlling the viscosity of the reaction system. The potato extract is a colloidal solution, which is mainly starch, and other organic biomolecules can provide a small amount of reactive groups for overall functionality, such as aldehyde groups, hydroxyl groups, carboxyl groups, and amino groups. Similarly, the viscosity of the reaction system can be changed by controlling the concentration of the potato extract, and finally cadmium sulfide quantum dot of different sizes can be obtained. Different plant extracts have different components and viscosities; the size of CdS quantum dots and fluorescence emission peak intensity can be adjusted by adjusting the concentration of the extract solution.

The binding molecules and groups on the CdS quantum dots surface were explored based on the Fourier transform infrared (FT-IR) spectroscopy analysis (Figure 4). The infrared spectrum of CdS synthesized by 3CdSO₄·8H₂O and thioacetamide (TAA) under the same reaction conditions is shown in Figure 4a. The infrared spectrum of CdS dots synthesized by potato extract is shown in Figure 4b.

By comparison, we can find that the introduction of potato extract has a significant change in the number of functional groups on the surface of cadmium sulfide. The peaks at 2922, 1630, 1538, 1012, and 702 cm⁻¹ are significantly enhanced. Among them, the peak at 2922 cm⁻¹ is attributed to the stretching vibration of C–H; the enhancement is due to the symmetric (−CH₂) and antisymmetric vibration of the hydrocarbons present in vegetable protein and starch. The peaks at 1630 and 1538 cm⁻¹ are attributed to the carbonyl stretching vibration peaks of acetamido, the amide I (C=O) vibration and the amide II (NH) bending vibration, respectively. The amide peak is derived from the CN vibration in the O=C–N–H structure, which also corresponds to the carboxylate asymmetrical vibration of COO–. The enhancement is also due to the protein content in the potato extract. The peak at 1012 cm⁻¹ obviously enhances, which corresponds to the stretching vibration of the C–O bond and the bending vibration of the C–OH bond. The enhancement also proves that a large amount of organic matter in the potato extract is on the surface of the cadmium sulfide quantum dots.

The weak peak at 702 cm⁻¹ corresponding to the stretching vibration of the C–S bond also slightly enhances, indicating that the presence of potato extract can increase the number of sulfhydryl groups on the surface of cadmium sulfide quantum dots. Besides the positions mentioned above, Figure 4a,b shows obvious broad peaks in the range of 3500–3000 cm⁻¹. Figure 4a shows the O–H vibration in water molecules, and Figure 4b can be attributed to a typical stretching vibration of O–H in the carboxyl group.

It is worth noting that the N–H stretching vibration peaks of plant proteins, amino acids, and other substances often appear at 3500–3000 cm⁻¹, but they are not found in the spectrum, which may be hidden by the stronger O–H peaks. Smaller peaks appeared at 1372 cm⁻¹, which corresponds to the symmetrical contraction of the carboxylate anion. The bright intensity of the peak at 571 cm⁻¹ in Figure 4a is higher than that of Figure 4b, which corresponds to the vibration peak of metal sulfide. The increase in peak intensity is mainly due to the fact that cadmium sulfide is not covered by other substances in Figure 4a, resulting in a stronger vibration intensity.

Through FT-IR analysis, it can be determined that the chemicals (proteins, minerals, vitamins, amino acids, etc.) in the potato extract solution play a major role in the generation and stabilization of the quantum dots. This also demonstrates that during the synthesis of CdS quantum dots, the potato extracts have also simultaneously realized the surface modification of CdS quantum dots.

To further explore the chemical composition on the surface of water-soluble CdS quantum dots, a wide X-ray photoelectron spectroscopy (XPS) scan was conducted. As shown in Figure 5a, based on the main characteristic peaks detected, it can be judged that there are mainly O, Cd, C, and S elements on the surface of the sample, with corresponding peaks around 532, 410, 285, and 162 eV. Moreover, the narrow-scan spectra of the elements are displayed in Figure 5b–d. Two strong
peaks of Cd at 411.8 and 403.8 eV are corresponding to the binding energies of Cd 3d_{3/2} and Cd 3d_{5/2} (Figure 5b), which is consistent with the former research result.\(^\text{44-46}\) As shown in Figure 5c, the S 2p spectra are fitted into S 2p\(_{1/2}\) (162.4 eV) and S 2p\(_{3/2}\) (161.7 eV) peaks, while the peak at 161.7 eV is corresponding to sulfide,\(^\text{41}\) which further confirms the formation of CdS. The peak at 162.4 eV indicates the sulphydryl groups on the CdS surface,\(^\text{47}\) which is consistent with the results of FT-IR spectroscopy and also reveals the existence of excess sulfur on the CdS quantum dots surface. Figure 5d shows the narrow scanning spectrum of C 1s. The binding energy of 284.1 eV is attributed to the C–C peak, which is due to the large number of organic groups on the CdS surface. The binding energy of 285.4 eV is attributed to the C–O–R peak, mainly derived from the protein in the extract and proved the existence of a large number of O elements.\(^\text{47}\)

Based on the FTIR and XPS analyses, it can be preliminarily deduced that starch, protein, amino acids, minerals, and other substances in potato extracts play an important role in the synthesis and stabilization of the CdS quantum dots. Cd ions tend to combine with free groups or proteins during these processes, which suggests that free amine groups can be combined with metal ions.\(^\text{48}\) The sulfur element originating from thioacetamide does not exist as the free S\(^2^-\), and it bonds with the free group to form C–S and exists as a sulfur-containing group.\(^\text{32,49,50}\) The schematic diagram of the formation mechanism is shown in Figure 6. The whole reaction process is realized in the interaction between protein or organic substance and starch. In the reaction system, the cadmium atoms first interacted with the organic group to form the functional group A.\(^\text{32,49,50}\) The sulfur atom in the thioacetamide interacts with the organic group to form the functional group B.\(^\text{32,49,50}\) The stable reaction conditions provided by electronic autoclave ensure sufficient energy for bond formation and bond breaking. Under this condition, the cadmium atom in group A interacts with the sulfur atom in group B to form CdS, which is then wrapped by the organic group from the other end subsequently, stabilized in the colloidal environment created by starch, and the water-soluble CdS quantum dots are finally formed with a small particle size.

Silver-ion solution with a concentration of 1–100 mg/L was detected by the prepared water-soluble CdS quantum dots solution through the change of the fluorescence emission performance. The fluorescence intensity of the CdS quantum dots solution decreases with the increase of silver-ion concentration, and the quenching effect and redshift can be observed (Figure 7a). After fitting the fluorescence change value as a function of silver-ion concentration, a straight line with correlation coefficient (\(R^2\)) = 0.987 can be obtained.

![Figure 6. Formation mechanism of water-soluble CdS quantum dots.](https://dx.doi.org/10.1021/acsomega.1c00162)
(Figure 7b), which suggests the promising application of CdS quantum dots in the detection of silver ions.

It can be known from the above results that as the concentration of silver ions increases, the fluorescence value of the prepared water-soluble CdS quantum dots solution decreases and red-shifts accordingly; moreover, the fluorescence value has a good linear relationship with the concentration of silver ions.

At present, the following five ways are usually used to explain the mechanisms of fluorescence intensity of quantum dots quenched by metal ions, e.g., cation exchange, competition of ligands, electron transfer, binding with surface ligands and electron transfer, and inner filter effect. Electron transfer and competition of ligands may explain the phenomena in this study, i.e., the combination of silver ions with the surface of cadmium sulfide quantum dots results in a decrease of the ability of fluorescence emission.

Traditional-metal-ion detection methods include atomic fluorescence spectroscopy, atomic absorption spectroscopy, inductively coupled plasma-mass spectrometry (ICP-MS), ICP-atom emission spectroscopy (AES), etc. Shortcomings such as expensive instruments, expensive reagents, and complex detection process restrict the traditional detection method, make it difficult to apply to real-time detection on site, and ultimately reduce its practicality. Using the water-soluble CdS quantum dots, the solution prepared in this study as a detection system can easily obtain the corresponding silver-ion concentration with the help of a fluorescence spectrometer. Owing to the advantages of short detection time, convenience, low detection cost, and high practicability, it can be practically applied for the rapid detection of silver ions in water.

Since this study has only discussed the detection of silver ions, whether it can be applied to the concentration detection of other metal ions still needs further research; however, its ability to rapidly detect metal ions has a very broad application prospect.
3. CONCLUSIONS

The preparation and synthesis mechanism of water-soluble CdS quantum dots were studied in detail. Using typical starch-containing plant (potatoes, sweet potatoes, yam, taro, and purple potato) extracts as stabilizers and modifiers, water-soluble CdS quantum dots can be obtained by a green and fast process. Through systematic characterization, the synthesis mechanism of water-soluble CdS quantum dots is deduced. Chemicals (proteins, minerals, vitamins, amino acids, etc.) in the potato extract solution play a major role in the generation and stabilization of the quantum dots. Compared with the samples prepared using other plant extracts, the intensity of light excited by CdS quantum dots prepared from potato extract is the highest. And such a prepared CdS quantum dots solution is subjected to the fluorescence intensity test of Ag+, with a concentration of 1–100 mg/L, to observe a good fluorescence quenching effect, which suggests its promising application for the rapid detection of Ag+. This study confirms the significance of the green synthesis of CdS quantum dots and nanomaterials.

4. EXPERIMENTAL SECTION

4.1. Materials Synthesis. The chemical reagents used in the experiments are of analytical grade. Potatoes (200 g) produced in Keshan County (Heilongjiang Province, China) were peeled, cut, and then put into 500 mL of deionized water. After boiling for 30 min, the sample was cooled to room temperature and filtered through eight layers of gauze. With the supplement of deionized water, 1 L of potato extract solution can be obtained. Thioacetamide (TAA, 2.5 g) and 3CdSO\textsubscript{4}·8H\textsubscript{2}O (0.275 g, Cd\textsuperscript{2+}/S\textsuperscript{2−} = 1:30) were added into the potato extract; then, they were divided into several 150 mL conical bottles. The conical flask was sealed, placed in an electronic steam sterilizer, and reacted at 121 °C for 20 min (102 kPa). After cooling to room temperature, a uniformly dispersed water-soluble CdS quantum dot solution was obtained. The preparation process of water-soluble CdS quantum dots is displayed in Figure 8. Other starch-containing tubers, sweet potatoes, yam, taro, and purple sweet potatoes, were also investigated as raw materials for the preparation of CdS quantum dots through the same route.

4.2. Characterization and Test. Morphology, interplanar spacing, and dispersion of the sample were characterized by a high-resolution transmission electron microscope (HR-TEM, JEOL2100, 200 kV). Phase analysis of the sample was performed by X-ray diffraction (XRD, TongDa, TD-3500, 40 mA, 40 kV, Cu Ka radiation). Infrared spectrum (FT-IR, Bruker Tensor,\textsuperscript{27} with the scan range 4000–400 cm\textsuperscript{-1}) was applied in the surface group analysis and the synthesis mechanism exploration of CdS quantum dots. And the element distribution and chemical valence on the sample surface was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, with an Al Ka 300 W X-ray source).

The fluorescence property of the sample before and after addition of metal ions was evaluated by a fluorescence spectrometer (Hitachi Fluoro-7000, with 10 nm raster).

As for the silver-ion detection test, every 8 mL of the prepared aqueous CdS quantum dot solution was added into cuvettes, together with 2 mL of silver-ion solution with a concentration of 1–100 mg/L. After the solution stood for 30 min at room temperature, the pre-reaction fluorescence value (F\textsubscript{0}) and the post-reaction fluorescence value (F\textsubscript{t}) of the sample were recorded. Then, a relationship curve of fluorescence value (F\textsubscript{0} − F\textsubscript{t}) as a function of silver-ion concentration was constructed.

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### Notes

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