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Facile and controllable synthesis of molybdenum disulfide quantum dots for highly sensitive and selective sensing of copper ions*

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Molybdenum disulfide quantum dots (MoS_2QDs) were synthesized via a hydrothermal method using sodium molybdate and cysteine as molybdenum and sulfur sources, respectively. The optimal hydrothermal time was studied. Furthermore, the as synthesized water-soluble MoS_2 QDs were used as a fluorescence probe for the sensitive and selective detection of copper ions. The fluorescence of the MoS_2QDs was quenched after the addition of copper ions; the reason may be that the transfer of the excited electron from QDs to copper ions leads to the reduction of the radiative recombination. The fluorescence quenching of MoS_2 QDs is linearly dependent on the copper ions concentration ranging from 0.1 μM to 600 μM, the limit of detection is 0.098 μM, which is much lower than that of existing methods. Moreover, the MoS_2 QDs show highly selectivity towards the detection of copper ions.

Keywords: MoS_2 quantum dots, photoluminescence, fluorescent probe

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1. Introduction

Copper, as a common transition mental element, has high thermal conductivity and high electrical conductivity, therefore, it is widely used in electrical industry, light industry, construction industry, machinery manufacturing, national defense industry, and other fields.[1,2] In addition, copper ions play a critical role in the environmental and biological systems. Copper is a trace element in plants and animals including human body. Micro-copper can play a positive role in promoting the growth of plants, but when it accumulates to a certain quantity in the organism, the organism will suffer numerous symptoms including physiological block, failure to thrive, and even death. Excessive copper ions also have a harmful effect on human health.[3–7] The United States Environmental Protection Agency (US EPA) limits the maximum contaminant levels goals (MCLG) for copper in drinking water to 1.3 mg/L for the protection of public health.[8,9] Due to the vast outflow of copper ions from electroplating, metallurgy, and chemical industry, a low cost, effective, and highly sensitive method to detection copper ions in water is of great significance. In the past few years, quite a few methods for Cu^{2+} detection have been presented, including electrochemical methods, inductively coupled plasma mass spectroscopy (ICPMS), atomic absorption spectroscopy, etc.[6,10,11] Although these methods can detect Cu^{2+} precisely, the expensive cost and the characteristics of be incapable of carry-on limit their usage. Therefore, looking for a low price, high sensitivity, convenient, and fast tracking method is imminent.[12]

With the discovery of graphene, great attention has been paid to two-dimensional (2D) materials including transition metal dichalcogenides (TMDs) due to their high specific surface areas and excellent electronic properties, which render their applications in sensors, transistors, catalysis, energy storage, etc.[13–19] MoS_2 has a layered S–Mo–S structure and a weak van der waals force exists between the layers. For this reason, molybdenum disulfide is easy to form a quantum dot (QD) structure, whose size is less than 10 nm.[20–24] Due to the quantum confinement and small size effect, different from the molybdenum disulfide bulk material with indirect band gap, MoS_2 QDs have the characteristics of direct band gap, which leads to their high quantum efficiency.[25–28] According to the previous reports, the reduction in cell viability of HeLa is about 1% and 12% meanwhile the reduction in cell viability of HeLa cells is about 11% and 30% when the probe concentration is 250 $\mu g \cdot mL^{-1}$ and 2000 $\mu g \cdot mL^{-1}$, respectively, revealing that these quantum dots are harmless to cells.[29,30] Undoubtedly, these as-prepared MoS_2 quantum dots can be considered as promising, low toxic, biocompatible, and good cell-permeability probes for *in vitro* imaging.

So far, several methods have been developed for the synthesis of MoS_2 QDs, including electrochemical synthesis, sonication and solvothermal treatment of bulk MoS_2, electro-Fenton processing, liquid exfoliation, etc.[24,31] Most of them are top-down methods, which are generally more sensitive to the environment, or use expensive and toxic organic solvents, or need a complex pretreatment procedure, or are not under control.[31–38] Hydrothermal synthesis, a most widely-used bottom-up method, has significant advantages, such as simple, environmentally friendly, and energy-saving.[39,40] Recently, Gu *et al.* proposed a hydrothermal method using ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] as the precur-

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sor and hydrazine hydrate as the reducing agent for the synthesis of MoS_2 QDs with excellent properties.[41] Herein, MoS_2 QDs are synthesized via a hydrothermal method using sodium molybdate and cysteine as molybdenum and sulfur sources, respectively.[42] As-prepared MoS_2 QDs have highlighted photoluminescence due to the quantum confinement effect and edge effect. Moreover, the fluorescence can be quenched by introducing copper ions to MoS_2 QDs solution through a photoinduced electron transfer. Within a certain range, the concentration of the copper ion has a linear relation with the fluorescence intensity. Therefore, MoS_2 QDs, as a fluorescence probe to detect Cu^{2+}, has high sensitivity and selectivity. The detection limit is 0.098 μM, much lower than the detection limit of graphene quantum dots (∼ 0.226 μM) for detecting copper ions.[43]

2. Experimental section

2.1. Reagents and instrumentation

In this work, all the chemicals were purchased from commercial institutions and applied directly without additional purification. Aqueous solutions of Fe(III), Ni(II), Cl(I), Na(I), Zn(II), Ba(II), Al(III), and Ca(II) were prepared from their compound solutions. Deionized distilled water was used throughout experiment. Fluorescence spectra were characterized using a luminescence spectrometer (Fluorolog-3) with a standard 10 mm path length quartz cuvette. UV−vis spectra of MoS_2 QDs were characterized by a UV-3101 scanning spectrophotometer (Shimadzu, Japan) using a standard 10 mm path length quartz cuvette at room temperature. Transmission electron microscopy (TEM) image was obtained from a JEM-1400 operating at 120 kV. The x-ray photoelectron spectroscopy (XPS) measurement was carried on PHI Quantera (PHI, Japan), the binding energy was calibrated with C 1s = 284.8 eV.

2.2. Hydrothermal synthesis of MoS_2

MoS_2 QDs were produced using a hydrothermal synthesis method. Briefly, 0.3 g sodium molybdate and 0.6 g L-cysteine were added to 50 mL deionized water in a 100 mL beaker and sonicated in an ultrasonic cell disruptor (400 W) for 20 min. Then, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and reacted at 180 °C for 30 h. After the solution cooled naturally, the supernatant containing MoS_2 QDs was transferred to another test tube after being centrifuged for 10 min at the speed of 8000 rpm. After that, the supernatant was filtered with 220 nm diameter filter. Finally, the as-prepared MoS_2 QDs solution was preserved in the matte, low temperature sealed environment.

2.3. Procedures for detection of Cu^{2+} ions

The 1000 μM cooper ions solution was prepared by dissolving 0.1705 g $CuCl_2{\cdot}2H_2O$ in 1000 mL deionized water at a 1000-mL beaker. After that, the solution was further diluted to 0.2 μM/L, 0.4 μM/L, 0.6 μM/L, 0.8 μM/L, 1 μm/L, 2 μM/L, 4 μM/L, 6 μM/L, 10 μM/L, 20 μM/L, 100 μM/L, 500 μM/L, and 1000 μM/L, and then, different concentrations of copper ions were introduced to the MoS_2 QDs solution. Lastly, the fluorescent intensity of the mixture was obtained by the fluorescence spectrometer.

3. Results and discussion

3.1. Characterization of MoS_2 QDs

Figure 1(a) is the TEM image of MoS_2 QDs. A typical particle diameter distribution of the MoS_2 QDs (Fig. 1(b))

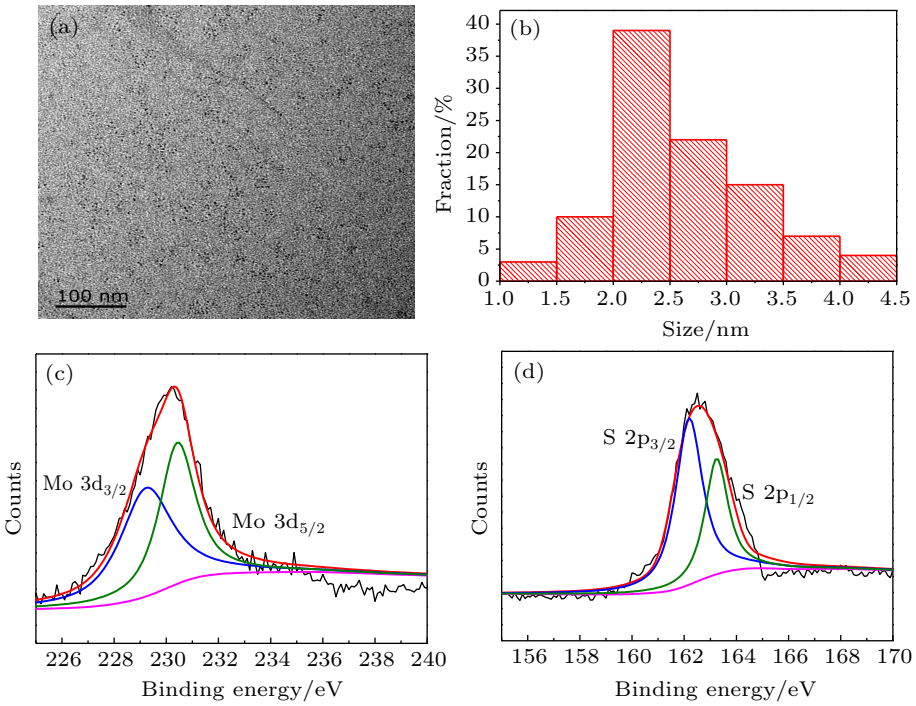


Fig. 1. (color online) (a) TEM image of MoS_2 QDs. (b) Size distribution histogram of MoS_2 QDs. (c) XPS Mo 3d state. (d) XPS S 2p state.

shows highly uniform and monodisperse nanocrystals about 2.25 nm diameter (the size is statistically calculated from more than 100 QDs in the TEM images). The x-ray photoelectron spectroscopy (XPS) measurements were carried out to survey the surface element composition and valence states of the MoS_2 QDs. As shown in Fig. 1(c), two characteristic peaks at 229.3 eV and 230.8 eV are the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ peaks from Mo^{4+} in MoS_2 QDs. Meanwhile the peaks at around 162.2 eV and 163.4 eV are corresponding to S $2p_{3/2}$ and S $2p_{1/2}$. The atomic ratio between Mo and S is close to 1:2, confirming the formation of MoS_2 QDs.

3.2. Optical features of MoS_2 QDs

The absorption (blue line) and fluorescence emission spectra (red line) of the MoS_2 QDs are presented in Fig. 2(a). The UV–vis spectrum shows a remarkable absorption peak at approximately 280 nm, which is similar to that reported previously,[42] and the typical band is attributed to the electronic transitions of the MoS_2 QDs. Moreover, when the excitation wavelength is 280 nm, the fluorescence emission spectrum has a conspicuous peak at 415 nm. As observed from the digital photo (the inset of Fig. 2(a)), the MoS_2 QDs solution has strong blue photoluminescence on exposure to a 365 nm UV lamp, and appears yellow under natural light. The normalized fluorescence spectra of the prepared MoS_2 QD dispersions were measured at room temperature under various excitation wavelengths from 320 nm to 400 nm. It shows that with the increasing excitation wavelength, the emission peak shifts to red, that is to say, the emission spectrum shows excitation wavelength dependence, which is the same as observed in MoS_2QDs from other synthesis methods.[13]

In order to study the optimal reaction conditions, hydrothermal reactions with different time were carried out prepare MoS_2 QDs. As shown in Figs. 2(c) and 2(d), the MoS_2 QDs' absorption and fluorescence emission spectra were acquired under 360 nm excition. Then, the fluorescence quantum efficiency can be measured according to

$$\frac{Y_X}{Y_S} = \frac{F_X}{F_S} \times \frac{A_S}{A_X},$$

where Y is the quantum yield, F is the integral area of the emission spectrum, and A is the UV absorbance at the excitation wavelength. The subscript "S" refers to quinine sulphate and the "X" denotes MoS_2 QDs.[15] According to this equation, the highest fluorescence quantum yield of MoS_2 QDs is 46.89% under 360 nm excitation, with hydrothermal time of 26 h.

3.3. Principle of the Cu^{2+} sensing system

As shown in Fig. 3, MoS_2 QDs were prepared via a facile hydrothermal process using sodium molybdate and cysteine as molybdenum and sulfur sources, respectively. The prepared MoS_2 QDs have photoluminescence of blue light under 360 nm excitation. With the introduction of copper ions to the MoS_2 QDs solution, the fluorescence intensity is decreasing. It may attribute to the transfer of excited electrons from MoS_2 QDs to copper ions.[18]

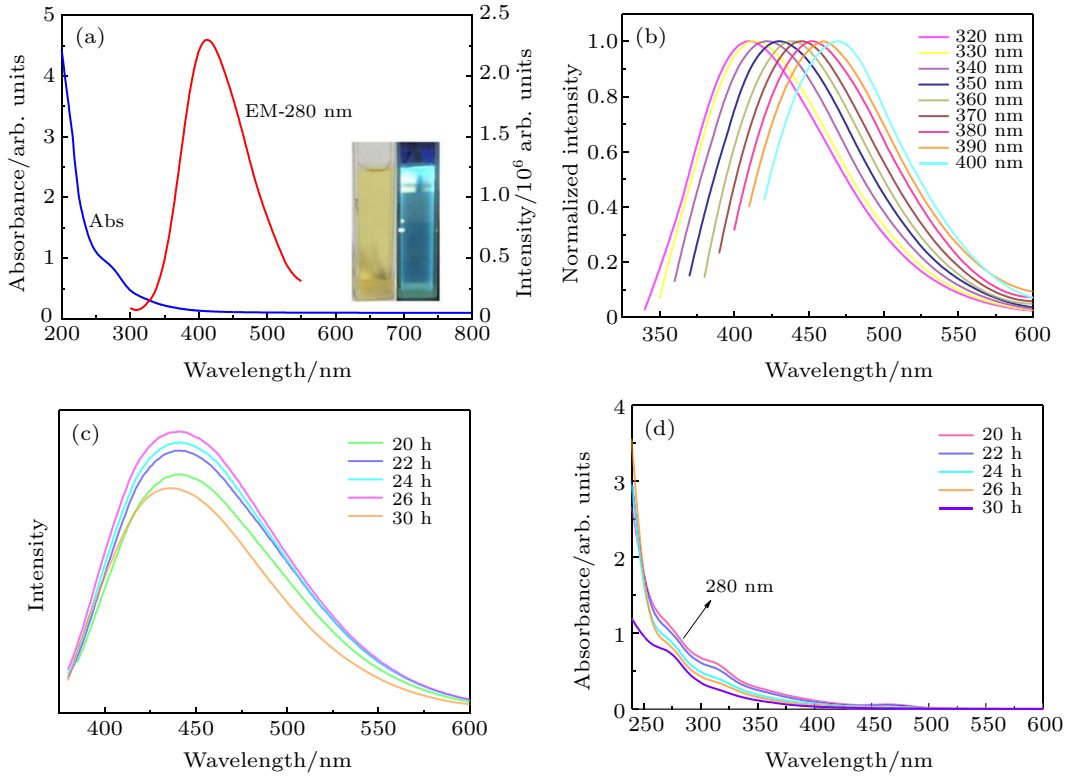


Fig. 2. (color online) (a) PL emission (red line) and absorption spectra (blue line) of MoS_2 QDs (inset: MoS_2 QDs are exposed under natural light and 365 nm UV light, respectively). (b) Normalized PL emission spectra of the MoS_2 QDs obtained under excitations of 320400 nm. (c) PL emission spectra of the MoS_2 QDs with different hydro-thermal synthesis time under 360 nm excitation. (d) Absorption spectra of the MoS_2 QDs with different hydro-thermal synthesis time under 360 nm excitation.

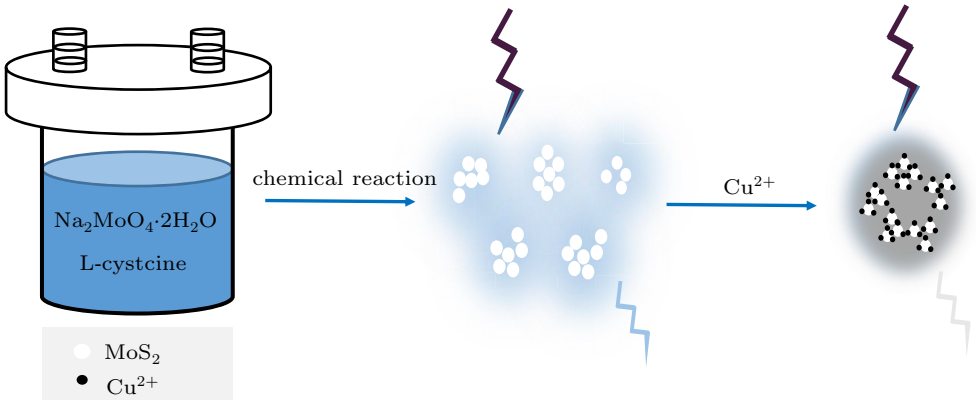


Fig. 3. (color online) Illustration of the preparation scheme of MoS_2 QDs and the detection of copper ions.

3.4. Performance analysis of the sensor

In order to develop applications of MoS_2 QDs in the field of sensor, we studied the detection of copper ions based on the on-off switching process. As described in Fig. 4(a), the emission intensity of the MoS_2 QDs significantly reduces in the presence of different concentrations of copper ions. The relationship between the copper ions concentration (from 0 μm to 600 μm) and $(F_0 - F)/F_0$ (the degree of quenching) is plotted in Fig. 4(b). The inset image (Fig. 4(b)) indicates that there is a linear relationship between the copper ions concentration and $(F_0 - F)/F_0$ in a range from 0 to 1.0 μm and the correlation coefficient is 0.986. The detection limit is 0.098 μm, which is much lower than the maximum level (20 μM) set by the US Environmental Protection Agency (EPA).[9]

In order to investigate the effect of pH on this process, the experiment was carried out by adjusting the pH value of the reagent. As shown in Fig. 4(c), the fluorescence intensity of mixture solutions (MoS_2 QDs with 100 μM copper ions) is not noticeable when the pH value increases from 2 to 11. Meanwhile, the MoS_2 QDs with no copper ions still have no obvious change (Fig. 4(d)). It suggests that the fluorescence intensity of the MoS_2 QDs and the mixture solution is insensitive to the pH, making the MoS_2 QDs a stable sensing platform in more complicated environment.

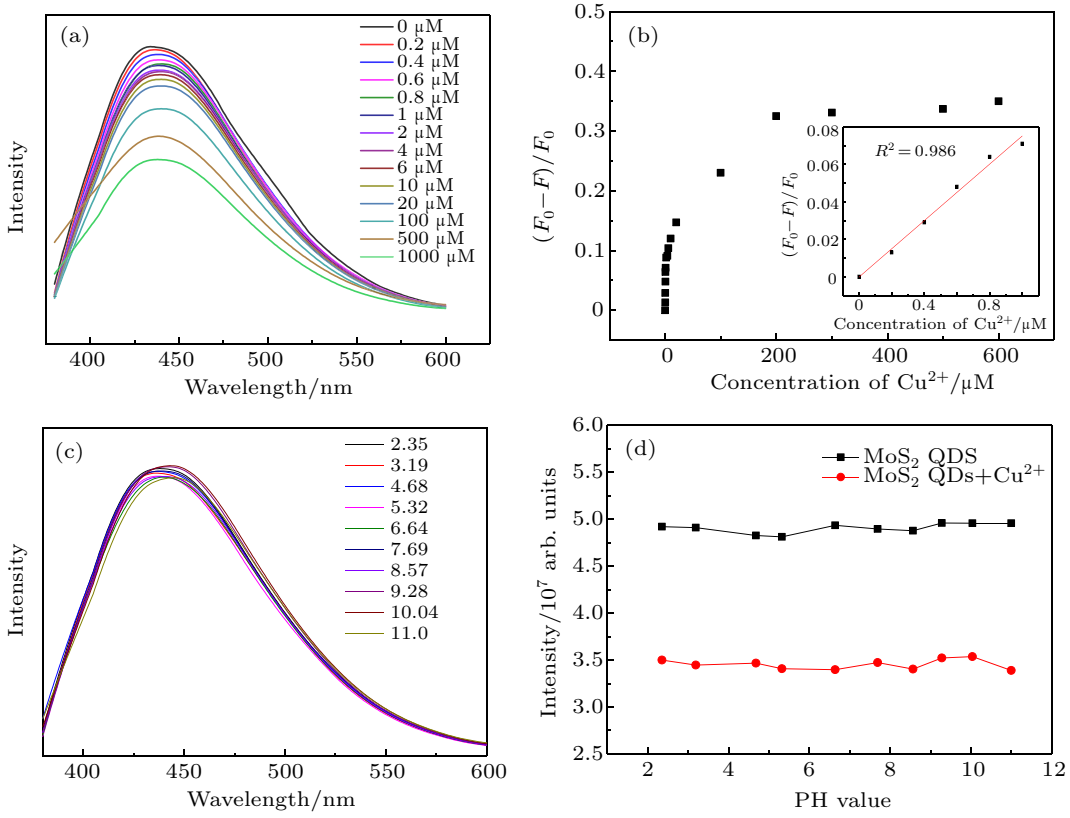


Fig. 4. (color online) (a) Emission spectra of MoS_2 QDs in the presence of Cu^{2+} with different concentrations in a range from 0 μM to 1000 μM. (b) The $(F_0 - F)/F_0$ plot of MoS_2 QDs with different concentrations of Cu^{2+}. (c) PL emission spectra of MoS_2 QDs with 100 μM Cu^{2+} under different PH values. (d) The relationship between the PH value and the fluorescence intensity.

3.5. Sensing selectivity of MoS_2 QDs

In order to assess the selectivity of the fluorescent probe established in this study, we investigated the influences of possible foreign substances (Cu^{2+}, Fe^{3+}, Ni^{2+}, Cl, Na^{+}, Zn^{2+}, Ba^{2+}, Al^{3+}, Ca^{2+}). As shown in Fig. 5, under the same conditions, the interfering ions show much less quenching effect on the fluorescence of the quantum dots, indicating high sensing selectivity of MoS_2 QDs towards Cu^{2+}.

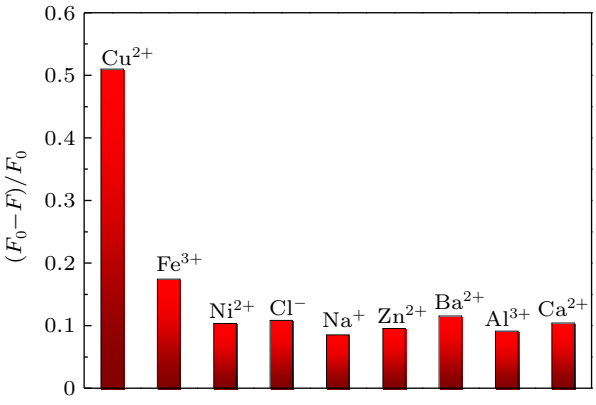


Fig. 5. (color online) Quenching efficiency of MoS_2 QDs toward different ions after addition of 1 mM of the ions solution under 365 nm excitation.

4. Conclusion

A facile and controllable method was used to synthesis molybdenum disulfide quantum dot. As-prepared MoS_2 QDs were utilized as a novel label-free sensor for detection of Cu^{2+} based on the fluorescence quenching effect causing by the excited electron transfer from MoS_2 QDs to copper ions. As a probe, it is insensitive to the pH change of the solution and highly sensitive and selective towards copper ions. Moreover, the detection limit is estimated to be 0.098 μM, which is much lower than the maximum level (∼20 μM) set by the US Environmental Protection Agency, representing a high-performance copper ion sensing platform.

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