

Synthesis of Luminescence L-Cysteine Capped Silver Sulfide Nanocrystals Via Positive Microemulsion Route

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Abstract

Well-monodisperse L-cysteine capped-Ag₂S nanocrystals with the capability of visible luminescence imaging were synthesized via a green and simple positive microemulsion (water/sodium dodecyl sulfate (SDS)/n-amyl-alcohol) method using thiacetamide as sulfur source and L-cysteine as capping agent. It has been found that the size and properties of the Ag₂S nanocrystals were influenced by concentration of microemulsion. L-cysteine replaced sulfate radical group by the thiol conjugated nanocrystals absorption the surface of nanocrystals. L-cysteine was an important capped-molecule to prevent nanocrystals from growing large nanoparticles. Free carboxyl group and amino group could react with other molecule for further applications. The L-cysteine capped-Ag₂S nanocrystals owned good stability and photoluminescence.

Keywords

Silver sulfide, Luminescence, Positive Microemulsion, Nanocrystalline materials.

1. Introduction

Over the past decades, nanoscale semiconductor metal chalcogenides have received considerable interest as IR detectors, luminescence devices, photo catalysis due to their unique optical properties.[1, 2] Among those materials, nanoscale silver chalcogenides with narrow band gap and superior biocompatibility over other heavily metal chalcogenides (such as CdTe, InAs, PbS) are promising candidates for optical devices.[3, 4] Silver sulfide(Ag₂S) has a narrow band gap energy of 0.9-1.1 e V and is stable in the α -phase with a monocline crystal structure.[5] In addition, Ag₂S is reported to have no significant toxicity because of their ultralow solubility product constant ($K_{sp}=6.3 \times 10^{-50}$) which enable the minimum release of Ag⁺ ion into environment[6, 7]. Because nanoscale materials might have some unique physical properties that rely on the size and morphology of the particles, it would be a great challenge to synthesis nanostructures of uniform size. To date, different methods have been developed for photoluminescence Ag₂S nanocrystals synthesis. [8-11] Motte et al. firstly synthesized monodisperse silver sulfide clusters in microemulsion.[12] Microemulsion is generally defined as thermodynamically stable colloidal dispersions in which two initially immiscible liquids (typical water and oil) coexist in one phase due to presence of a monolayer of surfactant molecules with balanced hydrophilic-lipophilic properties. [13] Dissolved in water at a concentration above the critical micelle concentration (CMC), the surfactant monomers form spheroidal aggregates called normal micelles. Because the W/O microemulsion reaction method has certain drawback that the use of large amounts of organic solvent. The attention was more focused on positive microemulsion, which is a more environmental and biocompatible procedure since it uses water as the main component. L-Cysteine (HSCH₂CH(NH₂)COOH) is an inexpensive, environmentally friendly thiol-containing amino acid, which has high-affinity metal-ligand complexes. [14] To the best of our knowledge, there is no report addressing Ag₂S nanocrystals in water-based positive microemulsion. Herein we demonstrate a new approach to synthesize Ag₂S

nanocrystals in a water / sodium dodecyl sulfate (SDS)/n-amyl-alcohol microemulsion using TAA as sulfur source and L-cysteine as stabilized agents. By changing the concentration of microemulsion, we can obtain well-monodisperse and luminescence silver sulfide nanocrystals.

2. Experimental

2.1 Materials

Silver nitrate (AgNO_3), sodium dodecyl sulfate (SDS), ethanol, L-cysteine hydrochloride, sodium hydroxide (NaOH), thiacetamide (TAA), n-amyl-alcohol ($\text{n-C}_5\text{H}_{11}\text{OH}$) were purchased from Sinopharm Chemical Reagent Co., Lid. All chemicals used in the experiments were of analytical grade.

2.2 Preparation of Ag₂S nanocrystals.

A positive microemulsion system, water/sodium dodecyl sulfate (SDS)/n-amyl-alcohol microemulsion, was selected for this study. A mixture of SDS and n-amyl-alcohol (mole ratio is 1:4) with different concentration were dissolved in 25ml deionized water in a three-neck flask with magnetic stirring at room temperature. After the solution become clear, 0.045mmol sodium hydroxide, 0.015mmol TAA, 0.03mmol silver nitrate and 0.1mmol L-cysteine hydrochloride were introduced into the solution (pH=6.7). The mixture was then heated to 334K under N₂ with 300r/min for one hour, changing from clear to light yellow clear and finally to green yellow. Then the nanocrystals was washed with water and ethanol three times to remove the non-reactive organic molecules and inorganic ions. The colloidal solution of the nanocrystals in water were stable for more than several weeks.

2.3 Characterization.

Transmission electron microscopy (TEM) images were record on JEOL JEM-1200EX electron microscope with accelerating voltage of 100 kV. The size distribution were analyzed using Dynamic Light Scattering Instruments (Microtrac Int.). X-ray powder diffraction (XRD) using Cu K α radiation was used to study the structure of Ag₂S nanocrystals. UV-vis absorbance of the samples was measured on Lambda750 UV-vis-NIR spectrophotometer (PerkinElmer, US). Fluorescence spectra of Ag₂S nanocrystals were collected by using Cary Eclipse fluorescence spectrophotometer with excitation wavelength at 386nm.

3. Results and discussion

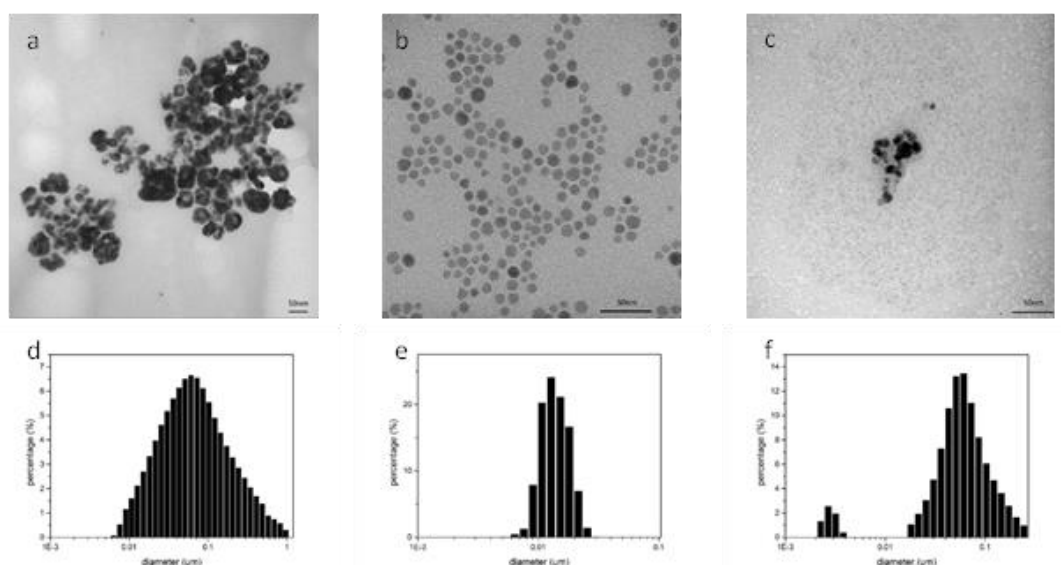


Fig.1. TEM image and size distribution of as-synthesized Ag₂S nanocrystals at different microemulsion concentration [(a, d) [SDS] = 8.6mM, (b, e) [SDS] = 60mM, (c, f) [SDS] = 100mM]

The TEM image (Fig.1a-c) and size distribution (Fig.1d-f) of as-synthesized Ag₂S nanocrystals is shown in Fig.1. It shows the size of as-synthesized Ag₂S nanocrystals are controlled by the microemulsion concentration. As the microemulsion concentration is 8.6mM (at the CMC), the size of Ag₂S nanocrystals is larger, and has a wide distribution (about 40-100nm, Fig.1a). By increasing microemulsion concentration to 60mM (7*CMC), the Ag₂S nanocrystals were monodisperse with a size of 12 ± 2nm (Fig.1b). But as microemulsion concentration become 100mM (12*CMC), the size of Ag₂S nanocrystals also has a wide distribution (Fig.1c). The size distribution histogram obtained by measuring the diameter of selected nanocrystals in TEM image are shown in Fig.1d-f. The diameter of the nanocrystals was in range of 40-100nm (Fig.1d), 10-20nm (Fig.1e), 20-50nm (Fig.1f), which agree with aforementioned TEM results respectively.

The changing size and distribution of Ag₂S nanocrystals with increasing surfactant concentration can be explained as follows: at low concentration, water was sufficiently available to dissolve the surfactant head group and counterion, so Ag₂S nanocrystals and surfactants coexist in water phase. The reaction are performed in the water phase and the particles would have wider distribution and irregular shape due to lack of the confinement of micelles.[15] With higher concentration, excessive sulfate radical and hydroxyl might quicken the crystal growth speed, so silver and sulfide atoms stack quickly in all space directions without selection, and nanocrystals were more absorbed around microemulsion interface.[16] The nanocrystals bond together in worm-like nano-materials in the aqueous phase. That's why those nanoparticles have no fluorescence. Therefore, the size of the crystal is determined by the suitable microemulsion concentration. The monodisperse sample is chosen for the followed characterization.

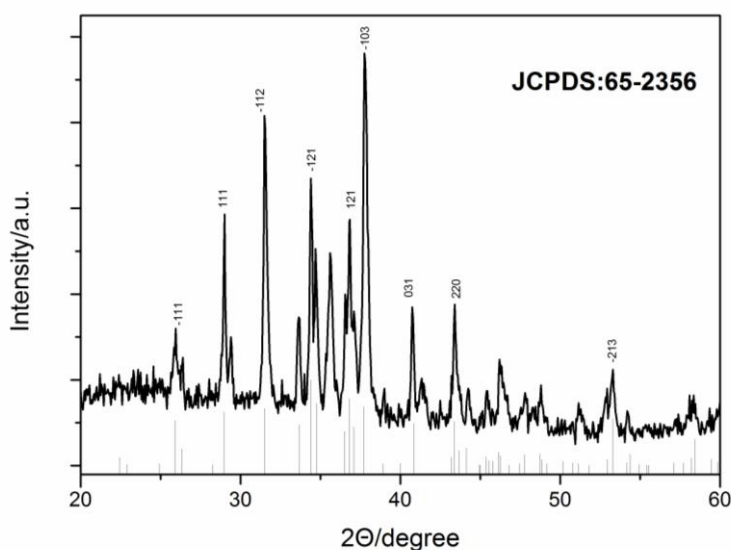


Fig.2. Powder X-ray diffraction (XRD) pattern of Ag₂S nanocrystals.

The X-ray diffraction (XRD) patterns of Ag₂S nanocrystals are shown Fig.2a. All of the peaks in the XRD patterns matched those of monoclinic Ag₂S, and the calculated lattice constants were $a=4.230\text{\AA}$, $b=6.910\text{\AA}$, $c=7.870\text{\AA}$ (JCPDS Card 65-2356). Fourier transform infrared (FTIR) spectroscopy of our synthetic product was shown in Fig.2. It was used to identify the chemical structure of L-cysteine capped Ag₂S nanocrystals.

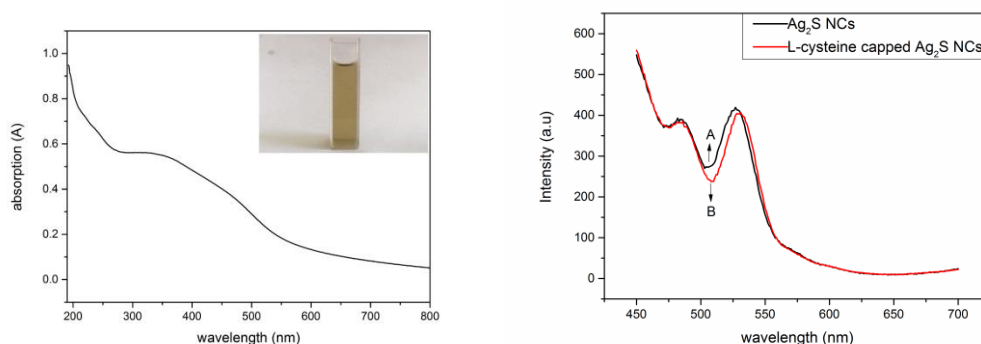


Fig.3. (a) UV-vis spectra of L-cysteine capped Ag_2S nanocrystals. (b) Room-temperature photoluminescence spectrum of Ag_2S nanocrystals (A) and L-cysteine capped Ag_2S nanocrystals (B). UV-vis spectrum of as-synthesized L-cysteine capped Ag_2S nanocrystals in deionized water was shown in Fig.3a (L-cysteine does not have UV-vis absorption). The colloid solution exhibited continuous absorption across the UV-vis wavelength range. A discernible absorption peak was detected at 323 nm. The band-gap energy is 3.84 eV that were blue-shifted compared with the band gap of bulk Ag_2S (0.9 eV -1.1 eV), which could be attributed to the quantum confinement effect. As shown in Fig.3b, the as-synthesized Ag_2S nanocrystals and L-cysteine capped Ag_2S nanocrystals both exhibit luminescence with similar emission peak around 528 nm with excitation wavelength at 386 nm. It could be seen that the capping material L-cysteine has little influence about the optical property of Ag_2S nanocrystals [14]. In addition, free carboxyl group and amino group give as-synthesized Ag_2S nanocrystals potential application in vivo detectors and luminescence devices.

4. Conclusion

To sum up, water soluble L-cysteine capped Ag_2S nanocrystals were synthesized via water-based positive microemulsion. By changing the concentration of microemulsion, we can obtain well-monodisperse luminescence Ag_2S nanocrystals. This method would be useful for the synthesis of other metal chalcogenides and metal nanoparticles. The monodisperse Ag_2S nanocrystals exhibit visible region emission 528 nm under 386 nm excitation. The Ag_2S nanocrystals hold great potential as vivo detectors and luminescence devices.

Acknowledgements

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