Synthesis of Silver Sulfide Quantum Dots Via the Liquid–Liquid Interface Reaction in a Rotating Packed Bed Reactor

Qing Liu^{1,2} · Yuan Pu^{1,2} · Zhijian Zhao^{1,2} · Jiexin Wang^{1,2} · Dan Wang^{1,2}

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Abstract

We developed the high-gravity coupled liquid–liquid interface reaction technique on the basis of the rotating packed bed (RPB) reactor for the continuous and ultrafast synthesis of silver sulfide (Ag_2S) quantum dots (QDs) with near-infrared (NIR) luminescence. The formation of Ag_2S QDs occurs at the interface of microdroplets, and the average size of Ag_2S QDs was 4.5 nm with a narrow size distribution. Ag_2S QDs can disperse well in various organic solvents and exhibit NIR luminescence with a peak wavelength at 1270 nm under 980-nm laser excitation. The mechanism of the process intensification was revealed by both the computational fluid dynamics simulation and fluorescence imaging, and the mechanism is attributed to the small and uniform droplet formation in the RPB reactor. This study provides a novel approach for the continuous and ultrafast synthesis of NIR Ag_2S QDs for potential scale-up.

Keywords Ag_2S quantum dots · Near-infrared luminescence · Rotating packed bed · Liquid–liquid interface reaction · Process intensification

Introduction

In the last decades, quantum dots (QDs) have been used in biomedical imaging [1], television displays [2] and photovoltaic devices [3]. Among various QDs, Ag_2S QDs with a tunable emission from visible light to near-infrared light have attracted considerable attention [4–9]. Up to now, different methods have been developed to synthesize Ag_2S nanocrystals (NCs). For example, using $\text{Ag}(\text{DDTC})$ [$(\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Ag}$] as a single source of silver and sulfur, Du and co-workers pioneered the preparation of Ag_2S QDs with a fluorescence emission peak of 1058 nm at 200 °C [8]. Jiang et al. [10] have reported water-soluble Ag_2S QDs terminated with a carboxylic acid group and used AgNO_3 and 3-mercaptopropionic acid (3-MPA) as silver and sulfur sources, respectively. However, the abovementioned

methods have some inherent disadvantages for scale-up such as harsh reaction conditions, high toxicity of the reagents, complicated reaction environment and difficulty in amplifying the yield [11]. Therefore, there has been a trend of future development to develop continuous synthesis methods and to realize industrialized production of ultrafine Ag_2S QDs with a uniform size distribution [12].

As one of the cutting-edge process intensification technologies, the high-gravity technology on the basis of a rotating packed bed (RPB) has been proven to be an effective platform for the preparation of various inorganic and organic nanoparticles with ultrasmall sizes and uniform distribution [13–19]. The large shear force generated in RPB reactors can break the fluids into nanoscale or microscale membranes, wires and droplets, which results in the large and rapidly updated interface, which increases the mass transfer efficiency of the liquids by 10–1000 times compared with that in a conventional stirred tank reactor (STR) [15, 20]. In addition, as a type of continuous reactor, the reactants pumped into the RPB are continuously added, followed by the continuous flow of products. The quality of the products is more stable than that obtained in batch reactors [21]. Therefore, high-gravity RPB reactors are promising candidates for the continuous production of high-quality QDs [22].

✉ Dan Wang
wangdan@mail.buct.edu.cn

¹ State Key Laboratory of Organic Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

² Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, China

The liquid–liquid interfacial reaction technique has been intensively investigated for the synthesis of QDs [23–25]. Researches have shown that the droplets formed in the two-phase emulsified solution can significantly increase the two interphase contact areas to increase the specific surface area, which accelerates the reaction rate [26]. In general, the size of nanoparticles is indirectly controlled by the size of droplets. In this study, by combining the advantages of microchemical technology and high-gravity technology, we developed a high-gravity coupled liquid–liquid interface reaction technique on the basis of RPB reactors for the continuous and ultrafast synthesis of NIR Ag₂S QDs. The entire reaction process can be carried out at room temperature and protective gas. The effects of high-gravity levels, liquid flow rates and circulation time were investigated in detail to determine the proper technological conditions, and then, the synthesized products were compared with those synthesized by the STR route. The mechanism of the process intensification was revealed by both the computational fluid dynamics (CFD) simulation and fluorescence imaging.

Experimental Section

Materials

Silver acetate (AgAc, 99.5%), sodium sulfide nonahydrate (Na₂S·9H₂O), Tween 20, oleic acid (OAc, 85%), oleyl amine (OAm, 85%), 1-octadecene (ODE, 90%) and hexane were purchased from Aladdin Biochemical Reagent Co. Ltd. All chemicals were used without any additional purification unless otherwise mentioned. Deionized water prepared by a Hitech Laboratory Water Purification System DW100 (Shanghai Hitech Instruments Co., Ltd.) was used for all experiments.

Synthesis of Ag₂S QDs by the Conventional STR Route

For the synthesis of Ag₂S QDs in the conventional STR, 168 mg (20 mmol/L, 50 mL) of silver acetate was added into the mixed solution containing 40 mL of octadecene, 5 mL of oleyl amine and 5 mL of oleic acid, and then, the mixture was stirred at room temperature to achieve homogeneous mixing (25 °C). The resulting solution was in a colorless clarified state and formed a silver precursor solution (solution A). The sulfur precursor solution (solution B) with 120 mg of Na₂S·9H₂O (10 mmol/L, 50 mL) in 50 mL of deionized water and 2 wt% Tween-20 was prepared by the ultrasonic treatment. By adding solution B to solution A under stirring, the two phases were mixed to form a turbid brown solution. After stirring at room temperature for 5 min, the reaction solution was transferred to a centrifuge

tube, and a certain amount of ethanol was added before centrifugation. Then, the Ag₂S nanodispersion was obtained by redispersing the pastes in organic solvents (e.g., chloroform, toluene, cyclohexane and hexane) under the ultrasonic treatment. For the synthesis of Ag₂S QDs in a conventional STR, the total amount of 1 mmol Ag⁺ and 0.5 mmol S^{2−} were used in one experiment, and approximately 30–50 mg of Ag₂S was obtained, which corresponds to the product yield of 25%–40%.

Synthesis of Ag₂S QDs by the RPB Route

The preparation of solutions A and B was the same as mentioned above. For the synthesis of Ag₂S QDs in the RPB reactors, both solutions A and B were pumped into the reactor via two liquid inlets. The reactants were immediately collected after the reactions were performed in the RPB for several seconds [27]. The post-treatment processes of the solutions obtained by the RPB route were similar to those produced by the STR route. The yield of the products obtained by the RPB was similar to that by the STR route. The loss of products during the centrifugal purification stage is the main reason for the low and fluctuating yield. In our experiment, the effects of different high-gravity levels, liquid flow rate and circulation time on the product morphology and dispersion were investigated. The high-gravity level β of the RPB reactor is determined by $\beta = \omega^2 r / g$, where ω is the angular velocity of the RPB reactor; r is the geometric average radius of the rotator; and g represents the speed of gravity acceleration (i.e., 9.8 m/s²). The core component of the RPB reactor is a rotator with a 2.5-cm thick stainless packing. The detailed setup information on the RPB reactor can be found in our previous study [28].

Characterization

The crystallization phase of the sample was analyzed by X-ray diffraction (XRD) using a Shimadzu XRD-6000 diffractometer with a Cu-K α radiation. The scanning range was 5°–90°, and the scanning rate was 5°/min. The mixture of the Ag₂S QD powder and KBr was compressed at 10 MPa, and the PerkinElmer GX FTIR spectroscopy system was used to collect the FTIR spectra within the range of 400–4000 cm^{−1}. A Hitachi H-7700 transmission electron microscopy (TEM) instrument was used to investigate the morphology of the samples, and 100 particles in the TEM image were measured to obtain the average particle size of the sample. High-resolution transmission electron microscopy (HRTEM) images were obtained by a Tecnai G² F20 S-Twin HRTEM at an accelerating voltage of 200 kV. The valence states of silver and sulfur were confirmed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The photoluminescence (PL) emission spectrum of the sample was measured using the

Horiba FLS980 spectrometer with a 980-nm wavelength laser as the excitation light. The absorption of the Ag₂S QD dispersion at different wavelengths was characterized by a PerkinElmer Lambda 950 UV/VIS spectrometer. The size and morphology of droplets were observed by a LEICA SP8 confocal laser scanning microscope.

CFD Model

The volume of fluid (VOF) model proposed by Hirt and Nichols [29] was used to simulate the multiphase flow in RPB. Because this model is generally used to compute a time-dependent solution, our simulation was calculated using the time-dependent formulation. In addition, the processes were assumed to be at a steady temperature; therefore, the energy equation was not considered. The equation of mass conservation for the volume fraction function can be written as:

$$\frac{\partial \rho_q \alpha_q}{\partial t} + \frac{\partial \rho_q U_i \alpha_q}{\partial x_i} = S_m$$

where q represents the gas or liquid phase; and α_q is the volume fraction for the q phase. Because the simulation involves mass transfer between phases, the source S_m , which is the mass transfer from liquid to gas, is nonzero.

The use of the VOF model results in only a single momentum equation to be solved throughout the domain, and the resulting velocity field is shared between the two phases. The momentum equation in a steady zone can be expressed as:

$$\frac{\partial U_i}{\partial t} + \frac{\partial \rho U_i U_j}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \mu \frac{\partial^2 U_i}{\partial x_i \partial x_i} + \frac{\partial (-\rho \overline{u'_i u'_j})}{\partial x_i} + \rho S_F$$

where the density ρ and viscosity μ can be calculated as:

$$\rho = \sum \alpha_q \rho_q$$

$$\mu = \sum \alpha_q \mu_q$$

Results and Discussion

The schematic diagram of the preparation of Ag₂S QDs by high-gravity coupled liquid–liquid interface reaction technique is shown in Fig. 1. Solutions A and B were pumped into the RPB reactor via two liquid inlets, and then, the two phases were rapidly emulsified to form many droplets after the impact. The hydrophilic ends of Ag⁺ passivated by the coordination of oleic acid and oleyl amine were arranged to the aqueous phase side and then immediately reacted with S²⁻ in the aqueous phase at the interface. The Ag₂S crystal nuclei were generated at the oil–water interface. The crystal nuclei further collided with the remaining precursors and continued to grow and eventually grew to form ligand-coated Ag₂S NCs. Here, it is noted that the mixing of the two-phase solution in the RPB reactor differs from the mechanical mixing in STR [30]. Normally, the mixing in STR is macromixing, while that in the RPB reactor is micromixing. These two types of mixing clearly affect the size and distribution of nanoparticles. The grown crystal nuclei in the environment with a uniform concentration distribution will have a uniform size distribution, which can only be achieved by strong microscopic mixing [30].

The changes in the particle size of Ag₂S QDs under different operating conditions by RPB route were studied. To our knowledge, the liquid flow rate (V_L) influences not only the relative velocity between liquid elements but the liquid

Fig. 1 Schematic illustration of the preparation process of Ag₂S QDs by the high-gravity coupled liquid–liquid interface reaction technique

Fig. 2 TEM images of Ag₂S QDs prepared by the RPB reactor with V_L of **a** 1 mL/s, **b** 2 mL/s, **c** 5 mL/s, **d** 7 mL/s and **e** 10 mL/s. **f** Effect of V_L on the average particle size of Ag₂S QDs ($\beta=25$, $t=1$ s, $T=25$ °C)

turbulence degree in the RPB reactor [31]. Figure 2 shows the TEM images of Ag₂S QDs prepared in the RPB reactor at different V_L . As can be seen from Fig. 2f, with an increase in V_L from 2 to 7 mL/s, the average particle size decreases from 6.8 to 4.7 nm and the particle size distribution becomes narrower. Thereafter, with a further increase in V_L , the particle size remains unchanged. The abovementioned results indicate that within limits, with an increase in V_L , the liquid injection speed is accelerated and the collision reaction between the two phases is more intense, and at the same time, with an increase in the feed flow, the number of material cut by packing increases. The droplets continue to gather and disperse rapidly, which enhances the microscopic mixing in the RPB reactor and is conducive to the formation of smaller nanoparticles. However, when V_L is below 2 mL/s, the nanoparticles agglomerate, and the morphology becomes irregular. This occurs because V_L is smaller than that of the two phases that pack without collision and mixing to form droplets; the two phases will react during the processes of cutting and stirring. The reaction process will not be controllable to cause agglomeration. Therefore, V_L needs to remain within an appropriate range.

The high-gravity level (β) directly affects the microscopic mixing of reactants in the RPB reactor. The TEM images of Ag₂S QDs prepared at different high-gravity levels are shown in Fig. 3. When the high-gravity level is increased from 5 to 25, the average particle size of the nanoparticles decreased from 6.9 to 5.0 nm. Then, with a further increase

in the high-gravity level, the particle size did not considerably change. Because the higher the high-gravity level is, the greater the shear force is in the RPB reactor. The fluid in the porous packing will be split into smaller droplets and thinner films. The final particle size of the product is determined by the volume of microdroplets. Therefore, smaller and more uniform nanoparticles can be obtained with an increase in the high-gravity level of RPB. However, when the high-gravity level increases to a certain degree, its influence on particle size is small. Therefore, the optimal process condition is chosen at the high-gravity level of 25 for reducing loss and saving cost.

Figure 4 shows the morphology and size of nanoparticles obtained at different circulation times. As can be seen from the images, the size of nanoparticles remained at approximately 5.2 nm, and the decrease in circulation time did not change the morphology and average size of the particles. Therefore, it can be concluded that the reaction rate in the RPB reactor was extremely fast. The nucleation and growth of crystals finished within seconds and then reached a stable state. The primary reason is the formation of many ultrafine droplets in the emulsification process of the RPB reactor and the continuous renewal of the phase interface during the reaction process, which increases the specific surface area and the mass transfer capacity of droplets [26].

On the basis of the abovementioned results, when the molar ratio of Ag/S was controlled at 2:1, the technological conditions for the preparation of Ag₂S QDs with a minimum

Fig. 3 TEM images of Ag_2S QDs prepared at high-gravity level of **a** 5, **b** 10, **c** 25, **d** 75 and **e** 150. **f** Effect of the high-gravity level on the average particle size of Ag_2S QDs ($V_L = 7 \text{ mL/s}$, $t = 1 \text{ s}$, $T = 25^\circ\text{C}$)

Fig. 4 TEM images of Ag_2S QDs prepared at circulation time of **a** 0 min and **b** 5 min ($V_L = 7 \text{ mL/s}$, $\beta = 25$, $T = 25^\circ\text{C}$)

Table 1 Technological conditions for the preparation of Ag_2S QDs by the RPB route

Precursor concentration (mmol/L)	Ag/S	Liquid flow rate (mL/s)	High-gravity level	Reaction time (min)	Temperature ($^\circ\text{C}$)
$c(\text{Ag}^+) = 20$ $c(\text{S}^{2-}) = 10$	2	1	5		25
		2	10	0	
		5	25		
		7	75	5	
		10	150		

particle size by the RPB reactor are summarized in Table 1. Furthermore, we compared the products prepared in the RPB reactor with those by the STR route under the same

conditions. Figure 5 shows the TEM images of Ag_2S QDs prepared in the STR and RPB reactors, as well as the photoluminescence emission spectra. Figure 5a shows that when the reaction time is shortened to 1 s, the product prepared in the RPB reactor has good dispersion, and the particle size is approximately 4.5 nm. For comparison, the counterpart of Ag_2S QDs prepared in STR reactor after a few seconds is shown in Fig. 5b, and the product is agglomerated into large areas without distinct particles. Because the uniformity of the concentration distribution is not obtained, and the local concentration is too high, the reaction process is uncontrollable in STR reactor within a short period of time. As shown in Fig. 5c, when the reaction time increases to 5 min in STR reactor, the product has uniform particles with particle sizes of approximately 7.5 nm, which is an increase of approximately 40% compared with that in the

Fig. 5 TEM images of Ag_2S QDs prepared within seconds in **a** RPB and **b** STR reactors. **c** Ag_2S QDs prepared within 5 min in STR reactor, **d** photoluminescence emission spectra of the Ag_2S QD nanodispersion prepared in different reactors under 980-nm laser excitation

RPB reactor. To our knowledge, large particle size is not conducive to the stability of nanoparticles in solvents and to the application as biomarkers. The photoluminescence emission spectra (Fig. 5d) show that, compared to STR, the smaller particle size prepared by the RPB reactor results in a clear blue shift in emission spectra, which confirms the results shown in Fig. 5a, c.

Figure 6 shows the morphology and structure of Ag_2S QDs prepared in the RPB reactor under the optimal operating conditions. The TEM image in Fig. 6a illustrates that the product is composed of monodispersed spherical nanoparticles, and the average particle size of the product is 4.5 nm. The HRTEM image in Fig. 6b indicates the distinct atomic planes with a d -spacing of 0.23 nm, which is assigned to the (-103) facets of monoclinic α - Ag_2S .

Fig. 6 **a** TEM image and **b** HRTEM image of Ag_2S QDs and **c** XRD pattern of Ag_2S QDs. **d** UV–VIS–NIR absorption and photoluminescence spectra of Ag_2S QDs under the 980 nm laser excitation

The diffraction peaks in the XRD spectrum in Fig. 6c match well with those of monoclinic α -Ag₂S (JCPDS 14-0072), which indicates that the prepared product is actually Ag₂S nanocrystals. Figure 6d shows the ultraviolet–visible–near-infrared (UV–VIS–NIR) absorption and photoluminescence emission spectra of Ag₂S QDs under the 980 nm laser excitation. The sample exhibits a broad absorption spectrum from the UV–VIS to NIR region [32]. The photoluminescence emission spectrum shows an emission peak at 1270 nm under 980 nm laser excitation, which is promising for the use as luminescent agents for deep imaging.

Surface binding molecules of Ag₂S QDs were determined by FTIR. In Fig. 7a, the FTIR spectrum of Ag₂S QDs shows two distinct absorption peaks located at 2921 cm⁻¹ and 2854 cm⁻¹, which are caused by the asymmetric and symmetric stretching vibrations of C–H. The peaks at 1560 cm⁻¹ and 1460 cm⁻¹ correspond to the C=O stretching mode of the carboxylic acid group. The wide peak at 1050 cm⁻¹ is attributed to the stretching vibration of the C–N bond. The XPS spectrum was used to characterize the composition of elements in nanocrystals. As shown in Fig. 7b, the survey spectrum shows that Ag₂S QDs are mainly composed of Ag and S. In the high-resolution spectrum of Ag 3d shown in Fig. 7c, there are two distinct peaks at the binding energies of 373.9 eV and 367.9 eV, which correspond to the characteristic signal peaks of Ag 3d_{3/2} and Ag 3d_{5/2}, respectively. On the basis of previous literature, the peak shift of Ag 3d_{5/2} from Ag⁰ (368.2 eV) confirms that silver ions with unit valence exist in Ag₂S QDs. As shown in Fig. 7d, the S-band

can be decomposed into two Gauss peaks, which correspond to Ag–S (161.2 eV) and S–H (163.5 eV), respectively [33]. These analytical results indicated that Ag₂S QDs can be successfully synthesized by the high-gravity liquid–liquid interface reaction technique.

To better understand the advantages of the RPB reactor for the rapid preparation of QDs with small particle sizes, the CFD simulation of the reaction process was carried out. The simulation result (e.g., volume fraction of liquid in packing) is used to confirm the credibility of our work based on the reported insight observation [34]. Figure 8a shows the distribution morphology of the liquid in the RPB reactor under different gravity levels simulated by CFD. The color area is closer to red when a smaller amount of liquid is present. Figure 8b shows the distribution of turbulent kinetic energy of the reactants at different high-gravity levels, for which the surface of liquid drops continuously changes owing to the turbulence of RPB. As the high-gravity level increases from 5 to 25, the number of droplets and turbulent kinetic energy considerably increases, especially near the packing; then, the high-gravity level further increases, and the change becomes smaller. Clearly, the higher the high-gravity level is, the greater the turbulent kinetic energy is, and the smaller the liquid is cut, which provides additional opportunities for the reactants [35].

The size and size distribution of the droplets in the emulsion affect the nanoparticles and reaction rate in the droplets. Therefore, we compared the morphology and size of the emulsion droplets prepared in RPB and STR reactors. As shown in Fig. 9a, we use an ordinary optical microscope

Fig. 7 **a** FTIR spectrum of Ag₂S QDs, **b** XPS survey spectrum and the corresponding high-resolution spectra of **c** Ag 3d and **d** S 2p of Ag₂S QDs

Fig. 8 **a** Liquid proportion distribution in the reactant mixture and **b** turbulent kinetic energy simulated by CFD at different high-gravity levels

Fig. 9 **a** Optical micrograph of droplets prepared in the STR reactor, and **b** laser confocal fluorescence image of droplets prepared in the RPB reactor

to characterize the morphology and size of the droplets obtained in the STR reactor. Figure 9a shows that the droplets are spherical, with an uneven size distribution, and the size is on the micron level. The size of the droplets obtained in the RPB reactor is small. To better characterize the droplet size, we used a confocal laser scanning microscope. Nile red, an oleophilic fluorescent dye, is used to label the droplets. When Nile red is combined with lipids, it exhibits a strong orange fluorescence at the excitation wavelength of 543 nm, while for nonlipids (water phase), it appears black. Thus, the emulsion in Fig. 9b is water-in-oil (O/W) type. The

size distribution of emulsion droplets obtained in the RPB reactor is uniform, and the size is approximately 650 nm.

For the liquid–liquid interface reactions, the droplets of smaller size prepared in the RPB reactor have a larger specific surface area, which makes the reaction rate faster and produces many products in a short period of time [26]. In theory, the particle size distribution mainly depends on the nucleation process, and the nucleation rate depends on the size of supersaturation and the uniformity of its distribution on the spatial molecular scale [30]. The larger the supersaturation is, the higher the nucleation number is and the

smaller the final particles are. The degree of supersaturation considerably depends on the reaction rate, while the distribution uniformity of spatial molecular scale depends on the molecular mixing rate. Therefore, the RPB reactor has considerable advantages for the rapid preparation of nanoparticles with small particle sizes and narrow particle size distribution.

Conclusion

We explored a simple and rapid strategy for the synthesis of NIR Ag₂S QDs via the liquid–liquid interface reaction in a high-gravity RPB reactor. Under optimized experimental conditions (i.e., when the molar ratio of Ag/S was controlled at 2:1), the high-gravity level was 25, the liquid flow rate was 7 mL/s, and the average particle size of the product was 4.5 nm. The structure of Ag₂S QDs was monoclinic, and the morphological characteristics were monodisperse spherical with NIR emission at 1270 nm under 980-nm laser excitation. The prepared Ag₂S QDs can be perfectly dispersed in organic solvents such as *n*-hexane, toluene and chloroform. The CFD simulation of the droplets confirmed the unique advantages of RPB for the rapid preparation of small and uniform nanoparticles. This work provides a new approach and a theoretical basis for the low-cost and scaled-up preparation of Ag₂S QDs and can be used in the future commercial production of QDs.

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Dr. Dan Wang is now a Professor at the State Key Laboratory of Organic–Inorganic Composites, College of Chemical Engineering in Beijing University of Chemical Technology, Beijing, China. His research interests focus on process intensification (especially high-gravity technology, rotating packed bed reactor technology), optical nanomaterials and devices. Dr. Wang has been honored as Distinguished Young Investigator of China Frontiers of Engineering from Chinese Academy of Engineering (2018). He has authored over 70 peer-reviewed articles in Engineering, *Angew Chem Int Ed*, *AIChE J*, etc., and serves as the associate editor of *Applied Nanoscience*, editorial board member of *Transactions of Tianjin University*, member of international cooperation committee at Chemical Industry and Engineering Society of China (CIESC) and senior member of American Institute of Chemical Engineers (AIChE).