Bifunctional Superparticles Achieved by Assembling Fluorescent CuInS2@ZnS Quantum Dots and Amphibious Fe3O4 Nanocrystals

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Supporting Information

ABSTRACT: Monodispersed superparticles (SPs) consisting of hydrophobic CuInS2@ZnS quantum dots (QDs) were prepared through a self-assembling process induced by introducing ethanol into the cyclohexane solution of the QDs stabilized by 1-dodecanethiol. The solvent polarity-dependent size and size distribution of the resultant SPs were carefully characterized by using scanning electron microscopy, transmission electron microscopy, and dynamic light scattering. The formation and the growth mechanism of the SPs were investigated. By manipulating the nucleation and the growth kinetics through the addition rate of ethanol, the size was effectively tuned without broadening the size distribution of the SPs. By overcoating the SPs with amphibious Fe3O4 nanocrystals (NCs) stabilized by poly(4-vinylpyrollidone), aqueous dispersible SPs were obtained. Inheriting the fluorescent and magnetic properties from the corresponding mother particles, the resultant SPs presented excellent fluorescent and magnetic properties and, thus, may potentially be useful for bioseparation, detection, etc.

INTRODUCTION

Owing to the remarkable size-dependent electrical, optical, magnetic, and catalytic properties, inorganic nanocrystals (NCs) are often used as “artificial atoms” for fabricating superparticles (SPs) to magnify the physical properties of single NCs and, on the other hand, to integrate the unique properties of the subunits. Therefore, assembling NCs into uniform SPs has become a novel approach for achieving advanced materials potentially useful for photonics, sensors, catalysis, and bioanalysis.1−7

The preparations of SPs can roughly be classified into two groups, i.e., self-assembly of NCs formed in situ2,9−11 and self-assembly of NCs preformed.5,3,12−34 Contrasting the former approach, the latter one offers the opportunity to tailor the properties of the SPs by using NCs with clearly defined physical properties. In addition, it holds the flexibility to achieve SPs through different approaches, e.g., soft-template directed assembly and interparticle interaction guided assembly.

The soft-template approach generally consists of two steps, i.e., the formation of microemulsions containing hydrophobic NCs and the subsequent removal of the oil phase therein, which gives rise to SPs of the NCs glued together.12−14 Through this strategy, SPs of quantum dots (QDs),5,15 NaLnF4 NCs,16,17 magnetic iron oxide NCs,18,19 noble metal NCs,5,20 and multicomponent NCs21,22 have been fabricated. Nevertheless, to achieve SPs with controllable size and narrow size distribution remains difficult due to the complex thermodynamic and kinetic behaviors of the template. Furthermore, removing the oil phase also affects the morphology of the resultant SPs.14

The interparticle interaction guided self-assembly of preformed NCs, however, provides an alternative approach with better control over the morphology of the resultant SPs. The main driving forces include hydrogen-bonding,23 electrostatic interaction,24,25 and dipolar interaction,26 apart from multidentate molecule-mediated interactions.27 The sizes and size distributions of the SPs can normally be tuned by varying the ratio of particle surface ligands to the core NCs or mediator to nanoparticles. Recently, by partially removing the detergent molecules overcoated on hydrophobic Fe3O4 nanoparticle in aqueous system, Cao and co-workers reported supercrystals of Fe3O4 NCs with different shapes through the solvophobic interaction;28,29 the sizes of the SPs were successfully controlled by the ratio of the detergent to Fe3O4 NCs.

The hydrophobic−hydrophobic interactions between NCs can also be used for preparing SPs of preformed NCs. For example, by introducing a bad solvent into a thermodynamically stable dispersion of hydrophobic NCs, the stability of the dispersion is disturbed, which leads to coagulation of the preformed NCs.30 If the coagulation is induced in a controlled manner, SPs can consequently be obtained upon the hydrophobic−hydrophobic interactions. Very recently, Liz-Marzán and co-workers demonstrated the solvent-induced self-assembly of Au NCs coated with polystyrene by using an amphiphilic block copolymer (PS-b-PAA) to terminate the particle aggregation and obtained Au SPs with narrow size distribution.31 Although the solvent-induced self-assembly provides the possibility to fabricate differently sized SPs by controlling the kinetics of the self-assembling process,31−34 the content of inorganic NCs in SPs is limited by the thick polymer corona.
around the NC cores. Moreover, the complexity of solvent-induced conformation variation of the polymer coating layer, interactions between polymers from different particles, and interactions between polymer and solvent makes it difficult to control the size and size distribution of the resultant SPs.

In comparison with the polymer-coated NCs, the small molecule-coated ones are more sensitive to the changes of the dispersion media. On the other hand, the inorganic content of the NCs in SPs can largely be increased by using the latter ones as a building block. To show the solvent-induced self-assembly of NCs capped by small molecular ligands, we herein report SPs of CuInS$_2$@ZnS quantum dots (QDs) capped by 1-dodecanethiol. The effect of the solvent polarity on the self-assembly process of the hydrophobic QDs was investigated. On the basis of the kinetic studies, size tunable SPs with narrow size distribution were obtained. In addition, amphibious Fe$_3$O$_4$ NCs stabilized by poly(4-vinylpyrrollidone) (PVP) were used to overcoat the hydrophobic SPs so as to achieve water-dispersible fluorescent/magnetic bifunctional SPs, as depicted by Scheme 1.

Scheme 1. General Procedures for Preparing Hydrophobic SPs of CuInS$_2$@ZnS QDs and the Water-Dispersible SPs Coated with Amphibious Fe$_3$O$_4$ Nanocrystals

EXPERIMENTAL SECTION

Chemicals. Iron(III) acetylacetonate (Fe(acac)$_3$, Aldrich, 97%) was used after recrystallization two times. 1-Vinyl-2-pyrrolidone (NVP, Jiaozuo Meida Fine Chemical Co., Ltd., medical grade) was purified by distillation under reduced pressure in the presence of phenothiazine. Indium(III) acetate (In(OAc)$_3$, Alfa Aesar, 99.99%), 1-dodecanethiol (Sigma-Aldrich, 97%), copper(I) iodide (CuI, Aladdin, 99.995%), and zinc stearate (ZnSt$_2$, Aladdin, 90%) in the current investigations were used as received. Analytical grade chemicals such as ethanol and cyclohexane were obtained from Sinopharm Chemical Reagents, Beijing, Co., Ltd. and used as received.

Synthesis of CuInS$_2$@ZnS QDs. CuInS$_2@$ZnS QDs were synthesized as follows. Typically, In(OAc)$_3$ (0.5 mmol) and CuI (0.5 mmol) were added to a flask containing 1-dodecanethiol (30 mL) under vigorous stirring at room temperature. After being purged with N$_2$ at room temperature for 30 min, the mixture was heated to 200 °C and kept for 2 h under nitrogen to form CuInS$_2$ nanocrystal core. After the solution was cooled to room temperature, ZnSt$_2$ (1 mmol) was added to the flask. The mixture was stirred for 30 min under nitrogen and then heated to 230 °C. After maintaining at 230 °C for 1 h under nitrogen protection, ZnS-coated CuInS$_2$ (CuInS$_2@$ZnS) QDs were precipitated by ethanol, washed with ethanol for 3 times, and finally dissolved in cyclohexane for further experiments. The ZnS-coating was carried out herein for enhancing the fluorescence efficiency of the CuInS$_2$ nanocrystal core. In addition, the current QDs are more environmentally friendly than QDs of cadmium chalcogenides, though they are simply used as model particles in the current investigations.

Synthesis of Amphibious Fe$_3$O$_4$ NCs. The amphibious Fe$_3$O$_4$ NCs stabilized by PVP were synthesized according to a previous report. Typically, Fe(acac)$_3$ (1.2 mmol) was first dissolved in NVP (30 mL). The resultant solution was purged with nitrogen for 30 min at room temperature to remove oxygen, and then heated to 200 °C. After the reaction took place for 2 h, 30 mL of ethanol was introduced at room temperature, followed by 150 mL of ether as precipitant. The resultant black precipitates were isolated by a permanent magnet and redissolved in 30 mL of ethanol, followed by a precipitation process using 150 mL of ether. The above-mentioned purification procedures were repeated for 3 times to obtain amphibious Fe$_3$O$_4$ NCs.

Preparation of SPs of CuInS$_2@$ZnS QDs. In brief, a certain amount of ethanol was introduced by using a peristaltic pump into a cyclohexane solution of CuInS$_2@$ZnS QDs under vigorous stirring. With addition of ethanol, the solution turned from transparent red to turbid pink. After the addition of ethanol, the mixture was kept under stirring for 30 min. After that, the as-prepared SPs of QDs were collected by centrifugation and then washed 4 times with ethanol.

Coating the Hydrophobic SPs with Amphibious Fe$_3$O$_4$. The as-prepared SPs were first dispersed in ethanol, and then a certain amount of ethanol solution of the amphiphic Fe$_3$O$_4$ NCs was added dropwise under stirring. The molar ratio between the Fe$_3$O$_4$ NCs and CuInS$_2@$ZnS QDs was around 0.14:1. The resultant SPs@Fe$_3$O$_4$ particles were collected by centrifugation, washed by ethanol and deionized water, and then redispersed in deionized water for further characterizations.

Characterizations. Fluorescence and UV–vis absorption spectra were recorded with a Cary Eclipse fluorescence spectrometer and a Cary 50 UV–vis spectrometer, respectively. The transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were recorded with a JEM-100CXII microscope operating at an accelerating voltage of 100 kV. The scanning electron microscope (SEM) images were recorded with a Hitachi S4800 SEM operating at a beam energy of 5 kV. The hydrodynamic size of SPs was determined with the help of a Malvern Zetasizer Nano ZS. The CuInS$_2@$ZnS QDs concentration was determined by using inductively coupled plasma atomic emission spectroscopy (ICP-ABS) produced by Jiangsu Skyray Instrument Co., Ltd. The concentration of Fe was determined by the 1,10-phenanthroline spectrophotometric method. The addition rate of ethanol was controlled by a peristaltic pump produced by LongerPump (BT100-1J), China Co., Ltd.

RESULTS AND DISCUSSION

The representative TEM images and particle size histograms of CuInS$_2@$ZnS QDs and Fe$_3$O$_4$ NCs are shown in Figure 1. The as-prepared CuInS$_2@$ZnS QDs shown in Figure 1a are of 2.9 ± 0.6 nm. The SAED pattern shown as the inset of Figure 1a
indicates that the QDs possess a chalcopyrite (JCPDS Card No. 32-0339) crystalline structure. The ICP-AES analysis revealed that the ratio of Cu/In/Zn was 0.48:0.62:1. The as-prepared amphiphilic Fe₃O₄ NCs shown in Figure 1b are of 5.5 ± 0.6 nm. The SAED pattern placed aside suggests that the resultant particles are magnetite nanocrystals.

In fact, the long alkyl chain of 1-dodecanthiol enables the cyclohexane to be a good solvent and ethanol to be a bad solvent for the 1-dodecanthiol-capped QDs. Consequently, 1-dodecanthiol-capped QDs present a long-term colloidal solubility in cyclohexane or even in an ethanol/cyclohexane mixture with the $R_{EC}$ ratio (ethanol-to-cyclohexane v/v ratio) below 1:1. However, when the $R_{EC}$ ratio was increased to 1.25:1, QDs precipitates appeared in the solution with a small fraction of QDs remaining suspended in the supernatant within 24 h, which suggests that ethanol can effectively decrease the energy barrier between QDs to induce the coagulation of QDs. To disclose the solvent polarity-dependent self-assembling process of the hydrophobic QDs, a series of ethanol/cyclohexane mixtures with different $R_{EC}$ ratios were prepared and the cyclohexane solutions containing equal amounts of CuInS₂/ZnS QDs were injected into the above systems. The final $R_{EC}$ ratios were set as 1.5:1, 1.75:1, 2:1, 2.5:1, and 4:1, respectively.

It was observed that when the $R_{EC}$ ratio was higher than 1.5:1, the QDs quickly aggregated in the mixed solvents. To show the temporal evolutions of the self-assembling process of the QDs, dynamic light scattering (DLS) was used to continuously monitor the hydrodynamic size of the resultant SPs. As shown in Figure 2, the hydrodynamic size of the initially formed SPs and their growth tendency are inversely correlated to the $R_{EC}$ ratio. When the $R_{EC}$ was set as 2.5:1, the SPs reach their equilibrium size of 165.3 nm in 24 h. In contrast, 10 min of aging gives rise to SPs of 96.2 nm when the $R_{EC}$ was set as 4:1, while 24 h of aging slightly increases the size of SPs to 1115.2 nm. It should be mentioned that the results shown in Figure 2 were obtained by quickly injecting QDs solution into premixed solvents in order to disclose the self-assembling process of the hydrophobic QDs in media with defined polarities.

Since spherical SPs dominate the aggregated QDs when the $R_{EC}$ ratio was higher than 1.5:1, as shown in Figure S1 in the Supporting Information (SI), the classic LaMer model can principally be used for discussing the growth of the SPs. According to the LaMer model, the nucleation process of colloidal particles is determined by the supersaturation degree of the system. Higher supersaturation degree is in favor of fast nucleation, leading to a larger number of nuclei, followed by a particle growth process without further nucleation. According to the results shown in Figure 2, the size of the initially formed SPs is inversely correlated to the $R_{EC}$ ratio, which strongly supports that the nucleation of the SPs process is determined by the supersaturation degree of the QDs in the mixed solvent. With respect to SPs formed by $R_{EC}$ ratios higher than 2.5:1, the following growth of SPs is greatly suppressed, which implies that the solubility of hydrophobic QDs becomes rather limited. However, the SPs particles formed by $R_{EC}$ ratios below 2:1 did not reach equilibrium sizes within 5 days. Therefore, it can be deduced that the solubility of the hydrophobic QDs remains high. Consequently, Ostwald ripening drives the SPs to further grow in size.

To further disclose the growth kinetics of the SPs, the following samples were prepared. First, an ethanol/cyclohexane solution was prepared, into which a cyclohexane solution of QDs was quickly injected and the final $R_{EC}$ ratio was set to 1.5:1. Then, the resultant solution of the primary SPs was divided into three portions. In 2 min, an ethanol/cyclohexane mixture with the $R_{EC}$ ratio of 1.5:1 was injected into the first portion to achieve sample A. In parallel, an equal volume of ethanol was injected either quickly into the second portion to prepare sample B or slowly into the third portion to generate sample C. The final $R_{EC}$ ratio of the mixed solvent for samples B and C was of 4:1.

The DLS results of samples A–C are shown in Figure 3. Sample A presents a single scattering peak at 348.7 nm with a PDI (polydispersity index) value of 0.18. In difference, the fast addition of ethanol into the solution of the primary SPs greatly increased the particle size to 1115.2 nm; in the meantime, a big portion of smaller SPs of 114.7 nm in sample B were generated, which strongly suggests that the fast increase of the solution polarity quickly decreases the solubility of the hydrophobic QDs. Consequently, part of the free QDs chooses to grow on the primary SPs, and the rest is consumed by repetition nucleation. In difference, slow addition of ethanol into the solution of the primary SPs did not lead to repetition nucleation. Consequently, the hydrodynamic size of sample C was remarkably increased to 795.5 nm. Meanwhile, the PDI
value of sample C was slightly decreased to 0.12 in comparison with that for sample A. Even though sample B and sample C were eventually formed in the mixed solvent with identical R_EC ratio, the addition rate of the bad solvent strongly determines the particle size and PDI values of the resultant SPs. These results together with those shown in Figure 2 strongly suggest that the formation and the following growth of the SPs obey the classic LaMer model established for colloidal particles. If this deduction holds, the size and size distribution of the SPs should be controllable by manipulating the supersaturation degree of the QDs in the mixed solvent.

To verify this hypothesis, in combination with all aforementioned results, the SPs were prepared in the following experiments by introducing ethanol into the cyclohexane solution of the hydrophobic QDs. In this way, the supersaturation degree of QDs can better be controlled by the introduction rate of ethanol so as to suppress the repetition nucleation for achieving differently size SPs with narrow particle size distributions. In detail, three ethanol addition rates were adopted, i.e., 46.3 mL min⁻¹, 2.67 mL min⁻¹, and 0.27 mL min⁻¹, for producing SPs at an optimized R_EC ratio of 3.4:1. As shown in Figure 4, the addition rate of ethanol is very effective for achieving differently sized hydrophobic SPs, i.e., 183.0 ± 25.0 nm (46.3 mL min⁻¹), 496.7 ± 41.8 nm (2.67 mL min⁻¹), and 1024.1 ± 107.7 nm (0.27 mL min⁻¹). The SPs are fairly monodispersed and structurally stable. They slightly decreased in size by less than 12% over 6 months, as shown in Figure S3, revealed that the hydrodynamic sizes of the SPs obtained by R_EC ratios of 1.5:1 (sample A) and 4:1 (sample B and C), respectively. The scale bars correspond to 2 μm. The size histograms of the resultant SPs are placed aside.

Water-dispersibility is essentially required for the biological applications of functional particles. Different from the classic methods for transferring the hydrophobic nanoparticles into an aqueous system by using detergents, amphiphilic Fe₃O₄ NCs were used to overcoat the hydrophobic SPs shown in Figure 4, on the one hand for achieving water-dispersible SPs, and on the other hand for forming magnetic/fluorescent bifunctional SPs. The SEM results provided in Figure 5 suggest that the surface coating procedures did not alter the particle shape. But the particle sizes are slightly decreased to 169.8 ± 21.4 nm, 489.9 ± 32.4 nm, and 990.5 ± 127.1 nm, respectively, which is probably caused by the compression of the loosely packed hydrophobic QDs within the SP core induced by the surface tension at the particle/water interface. Further DLS results, as provided in SI Figure S3, revealed that the hydrodynamic sizes of the SPs shown in Figure 5 were of 214.3 nm, 598.2 nm, and 1023.0 nm, respectively, rather in consistence with SEM results, which suggests that the resultant SPs@Fe₃O₄ particles can well be dispersed in aqueous media.

Apart from the excellent water-dispersibility, the SPs@Fe₃O₄ particles also exhibit excellent colloidal stability, as shown in Figure 6a. Most importantly, they inherited both fluorescent and magnetic properties of the corresponding mother nanocrystals.

As demonstrated by the results shown in Figure 6b, the SPs@Fe₃O₄ particles are highly fluorescent and can be magnetically collected by a permanent magnet.

To further characterize the optical properties of the SPs, the fluorescence spectra of SPs (in ethanol) and SPs@Fe₃O₄ (in either ethanol or water) were recorded for comparing with that of the mother QDs. As shown in Figure 7, the emission peak of the SPs shifts from 620 nm for the mother QDs to 661 nm, partly be attributed to the stronger reabsorption of the photoemission at the shorter wavelength side by Fe₃O₄ NCs. In contrast, the following surface coating of the amphiphobic Fe₃O₄ NCs slightly shifts the emission peak further to 670 nm, which can partly be attributed to the stronger reabsorption of the photoemission at the shorter wavelength side by Fe₃O₄ NCs.

By using Rhodamine 6G as a fluorescence standard, the fluorescence quantum yield (QY) of the CuInS₂@ZnS QDs

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Figure 3. Hydrodynamic size profiles of SPs obtained by R_EC ratios of 1.5:1 (sample A) and 4:1 (sample B and C), respectively.

Figure 4. SEM images of the SPs prepared through addition of ethanol into the cyclohexane solutions of CuInS₂@ZnS QDs by rates of 46.3 mL min⁻¹ (a), 2.67 mL min⁻¹ (b), and 0.27 mL min⁻¹ (c), respectively. The scale bars correspond to 2 μm. The size histograms of the resultant SPs are placed aside.
was estimated to be around 23% based on a literature method. Due to the interference of the scattering effect, the conversion rate of the QDs for forming SPs was determined by the ICP-AES method. In combination with the fluorescence results shown in Figure 7, the fluorescence QY of SPs was estimated to be around 13% in ethanol, while it drops to ∼9% for SPs@Fe₃O₄ in ethanol and to ∼7% for SPs@Fe₃O₄ in water. Although the fluorescence QY drops by approximately 60% after the QDs are assembled into the final SPs@Fe₃O₄ particles, the fluorescence brightness remains high, since each SP contains approximately 10⁶−10⁸ QDs.

### CONCLUSIONS

In summary, superparticles of fluorescent CuInS₂@ZnS QDs have successfully been prepared through a facile approach by introducing bad solvent into the solution of QDs in good solvent. Systematic investigations reveal that the formation and the following growth of the SPs follows the LaMer model developed for conventional colloidal particles. Consequently, the ratio of bad solvent to good solvent plays an important role in determining the supersaturation degree of the system. Therefore, by manipulating the supersaturation degree through the controlled addition rate of the bad solvent, the SPs with narrow size distributions are obtained in the size range of 180−1000 nm. By overcoating the SPs with amphibious Fe₃O₄ NCs instead of conventional detergent, aqueous dispersible SPs are prepared. Since both the magnetism and fluorescence of the mother nanocrystals are largely preserved, magnetic field responsive fluorescent SPs are obtained in aqueous media. From a large perspective, the current investigations may offer a facile and universal approach for developing functional superparticles by integrating the unique properties of different kinds of preformed nanocrystals.

### ASSOCIATED CONTENT

#### Supporting Information
SEM images of the hydrophobic SPs formed in the ethanol/cyclohexane mixed solvents with different Rₑₑₑ ratios; SEM images of the hydrophobic SPs captured 6 months after they were prepared; and hydrodynamic size profiles of differently sized SPs@Fe₃O₄ particles in deionized water. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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