Fabrication of 50 to 1000 nm Monodisperse ZnS Colloids

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Monodisperse ZnS colloidal particles with precisely specified diameters over a broad size range were synthesized by controlled aggregation. Sub-10nm ZnS seed crystals were first nucleated at ambient temperature and then grown at an elevated temperature, which produced large polydisperse colloidal particles. Subsequent rapid thermal quenching and heating processes induced a number of secondary nucleations in addition to growing the large polydisperse microparticles which were finally removed by centrifugation and discarded at the completion of the reaction. The secondary nuclei were then aggregated further at elevated temperatures, resulting in colloidal particles which exhibited a nearly monodisperse size distribution. Particle diameters were controlled over a wide size range from 50 nm to 1 μm. Mie simulations of the experiment extinction spectra determined that the volume fraction of the ZnS is 0.66 in an aggregated colloidal particle and the colloidal particle effective refractive index is approximately 2.0 at 590 nm in water. The surface of the colloidal particles was subsequently coated with silica to produce ZnS@silica core-shell particles.

Key Words: ZnS, Colloid, Controlled precipitation, Mie scattering, Core-shell

Introduction

High dielectric constant materials (refractive index, $n \geq 2$) have attracted considerable attention in photonics due to their strong interaction with light.[1] Recent studies of a number of high dielectric nano- and micro-materials (e.g. GaN, InP, Si, CdS, ZnS, CdSe, ZnO, SnO_2, TiO_2) revealed interesting photonic properties, with applications including optical waveguides, lasing, and photonic crystals.[2-5] GaN nanorods and nanowires showed lasing behavior with a low lasing threshold in a Fabry-Pérot cavity mode.[2] Velikov et al. used ZnS microparticles for the fabrications of photonic crystal and microarrays by self-assembly and optical tweezers manipulation, respectively.[3,4]

Among the high dielectric materials, binary II-VI and III-V semiconductor compounds are good candidates for advanced optics because their bandgaps can be manipulated by both controlling their chemistry and through quantum confinement. II-VI semiconductors in particular have the distinct advantages of easy fabrication and facile size control by a chemical route, which has lead to numerous reports on II-IV semiconductor nano- and micro-materials. Previously reported synthesis of these materials typically yielded either small nanoparticles with a diameter of less than a few tens of nanometers[6] or large microparticles with a size greater than a few hundred nanometers.[3,7] However, there are few reports on the preparation of monodisperse dielectric particles in a mesoscopic size range of 50-200 nm,[8] principally due to the inherent challenges in precisely controlling particle size in this range. In this study, we report the fabrication and detailed structural and optical characterization of high dielectric ZnS (n_{ZnS}~2.36 at 589 nm for cubic phase[9]) colloidal particles. The ZnS colloid diameter is controllable over a wide size range of 50 nm to 1 μm.

Experimental Details

Preparation of ZnS colloidal particles. ZnS colloidal particles were prepared by the controlled aggregation of seed ZnS nanocrystals formed by the thermal decomposition of thioacetamide (the sulfur source), in the presence of nitric acid and zinc nitrate.[9,10] The reaction was performed in two steps. The first step is the formation of ZnS seed crystals at ambient temperature, followed by growth of colloidal particles at an elevated temperature. The detailed procedure is as follows.

In the first step, 2 mmol zinc nitrate (Acros organics, 98%) and 6 mmol nitric acid (Acros organics, 63%) were completely dissolved in 50 mL deionized water, and 10 mmol thioacetamide (Acros organics, 99%) was separately dissolved in 50 mL deionized water. The two aqueous solutions were filtered, mixed, and reacted for 4 h under mild stirring at 26 °C, yielding ZnS seed nanocrystals. In the second step, the solution was heated to 65-70 °C for 1-2 h and observed to turn cloudy, indicating the formation of larger particles (typical diameter > 500 nm). This was followed by cooling to room temperature, which induced secondary nucleation of colloid. Finally, the resulting solution was heated to 62-65 °C again for 5-60 minutes to precisely control the size of colloidal particles formed through secondary nucleation. The reaction was stopped at the desired particle size by rapid quenching to below 5 °C in an ice water bath. The resulting nearly monodisperse mesoscopic colloidal particles were separated from the initially grown larger microparticles by centrifugation (applied relative centrifugal forces were typically less than 300 g for the larger microparticles and 2,000-10,000 g for the mesoscopic colloids depending on their diameter) and stored in ethanol.

**Preparation of ZnS@silica core shell particles.** As-synthe-

sized ZnS colloidal particles were coated with silica using a modified Stöber method.[11] 15 μL of tetraethylorthosilicate (TEOS, Aldrich, 98%) was injected into 84 mL ZnS colloidal (diameter ~130 nm with a particle concentration n of ~10^{10} cm^{-3}) ethanol solution which also contained 1.0 M aqueous ammonium hydroxide and 1.0 M water. The reaction was carried out under sonication overnight.

Characterization. Imaging studies of the ZnS colloidal particles were performed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) operating at 10 kV and a transmission electron microscope (TEM, Philips CM-12) operating at 120 kV. The SEM was also equipped with an energy dispersive X-ray spectroscopy (EDX) system (FE-SEM/EDX, Hitachi SU-70) for elemental analysis. Extinction spectra were measured on a UV-Vis spectrophotometer (Shimadzu UV-1601PC). Theoretical extinction spectra for the dielectric ZnS particles were calculated from Mie theory using the MieCalc software (Simuloptics, GmbH).[12]

Results and Discussion

To monitor the formation of ZnS colloidal particles during the reaction, an aliquot of reaction solution at each stage was imaged by TEM. In the first step, the reaction performed at ambient temperature produced small ZnS nanocrystals with an average diameter of 7 nm, as presented in Figure 1a. In the second step, based on the TEM observations, the small ZnS seed nanocrystals aggregated into polydisperse particles (due to a range in nucleation onset time) at an elevated temperature of 62-65 $^{\circ}$C (Figure 1b). It has been suggested elsewhere in the literature that the aggregation is caused by liberal access to a sulfur source (H$_2$S) in the reaction solution, which acts as an adhesive to bind the seed nanocrystals together.[9,10] The small aggregated colloidal particles grew to larger sizes with continued reaction time, as shown in Figure 1c. In order to stop the reaction at the desired particle size, it was simply done by rapid thermal quenching the reaction solution to below 5 $^{\circ}$C in an ice water bath, which prevented generating H$_2$S adhesive. The formation mechanism is summarized in Figure 2. This is the first time the formation of ZnS colloidal particles through controlled aggregation route has been observed by direct TEM imaging.

For the production of monodisperse ZnS colloidal particles, simultaneous nucleation is a critical factor during reaction. To induce concurrent nucleation, the hot reaction solution including larger microparticles (typical diameter > 500 nm) is rapidly thermally quenched within a few seconds in ice water, then followed by heating to 62-65 $^{\circ}$C. This rapid thermal cycling generated a number of secondary nucleations in addition to growing the larger polydisperse microparticles which were finally removed by centrifugation and discarded at the completion of the reaction, leaving only the monodisperse secondary precipitated colloids in the solution. Depending on the secondary growing time, which ranged from 5-60 minutes, the diameter of the precipitated colloids is controlled from a few tens of nanometers up to a micrometer (Figure 3). We estimate the growth rate of the colloidal particles to be ~10 nm/min at 62-65 $^{\circ}$C. To the best of our knowledge, this is the first report on the precise control of high dielectric ZnS colloidal particles in a mesoscopic size regime (50 nm < d < 150 nm). The resulting colloidal particles show
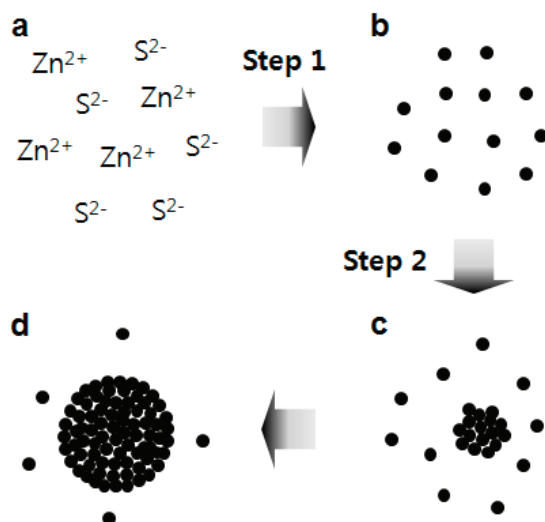
Figure 2. Growth mechanism of the ZnS colloidal particles performed in two steps, illustrating a) Zinc and sulfur sources and b) ZnS seed crystals in the first step, followed by c) nucleation of colloidal particle and d) controlled aggregation to a desired particle diameter.
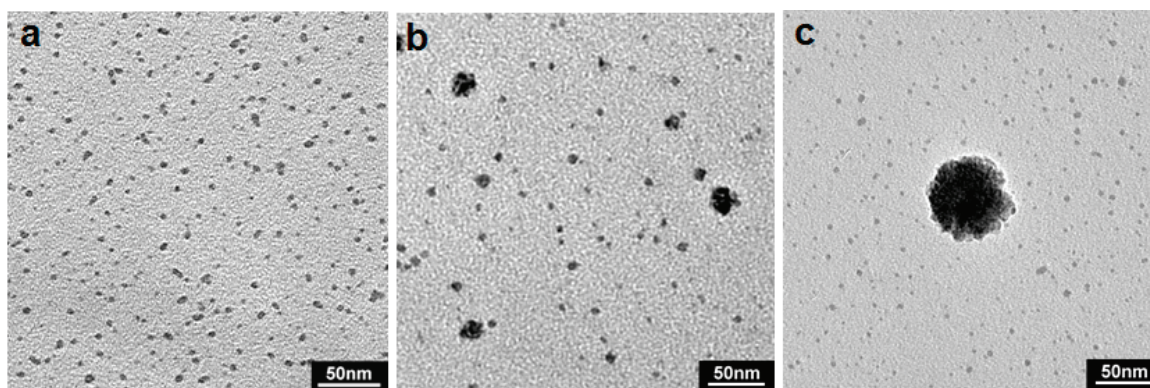
Figure 1. TEM images for the ZnS particles taken from different reaction stages; a) seed nanocrystals from the first step, b) small colloidal particles from the onset of the second step, and c) a larger colloidal particle grown during the second step reaction.
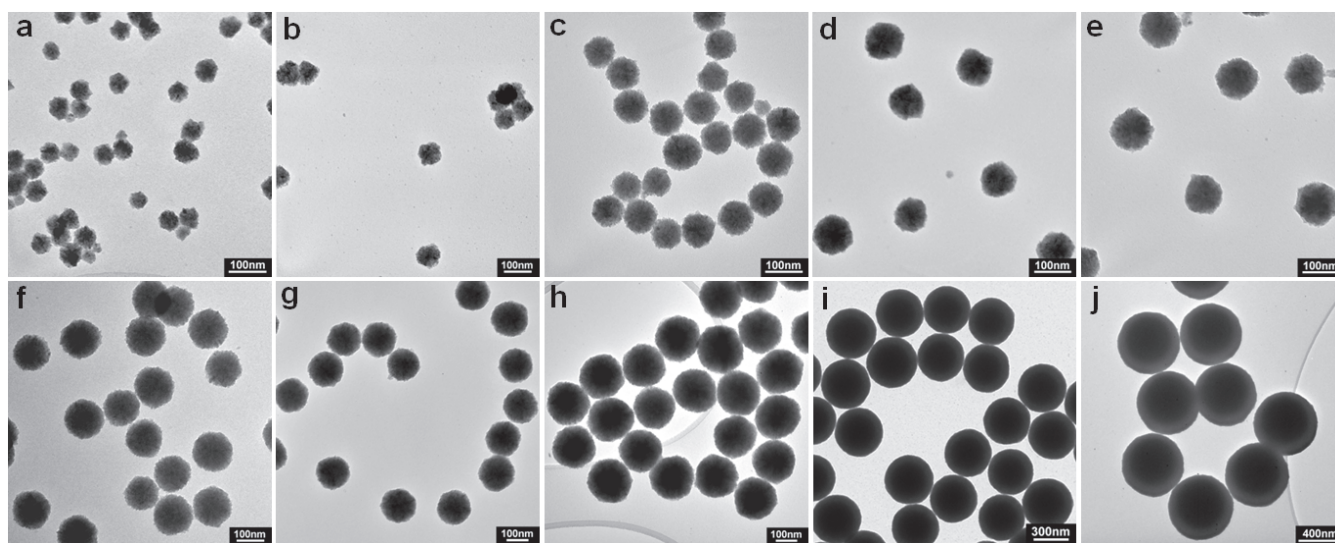
Figure 3. TEM images of the ZnS colloidal particles of different diameters: a) 58, b) 78, c) 92, d) 102, e) 120, f) 141, g) 160, h) 208, i) 415, and j) 595 nm.

a narrow particle size distribution with a polydispersity index of typically less than 5. EDX analysis confirmed that the elemental ratio of the colloidal particles is stoichiometric for the component zinc and sulfur atoms.

As colloidal particle size nears the wavelength of light (λ), a strong resonant coupling occurs, a characteristic pattern for

which can be observed in the extinction spectrum,[13] This is shown in Figure 4 for ZnS colloidal particles having a diame-
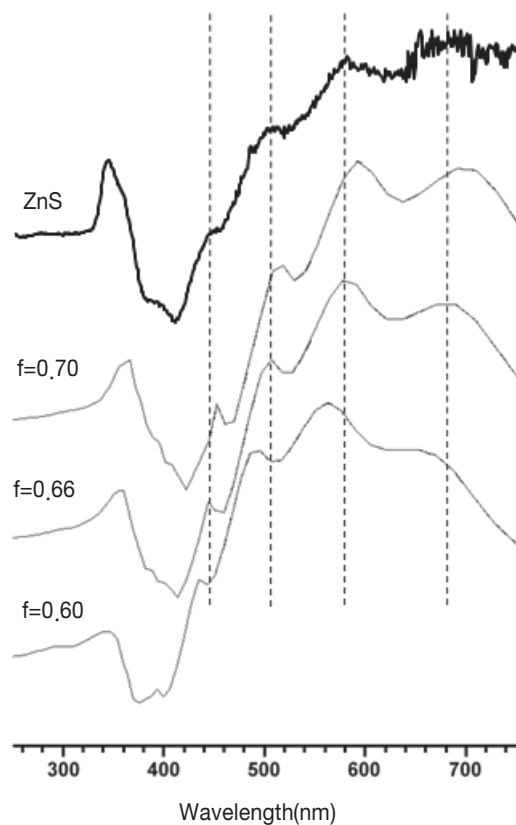
Figure 4. Extinction spectra of the ZnS (d = 595 nm) colloidal particle (top) and corresponding calculated theoretical extinction spectra from Mie theory. The packing fraction of ZnS seed crystals is varied from 0.6 to 0.7. The y-axis is in arbitrary units.
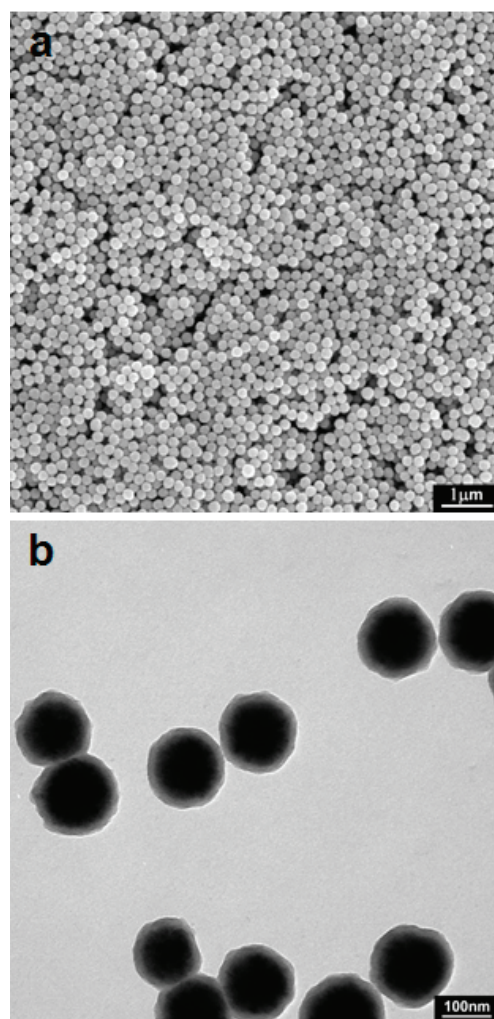
Figure 5. a) Representative SEM image of ZnS colloidal particles. b) TEM image of ZnS@silica core–shell particles.

ter of 595 nm, corresponding to a resonance in the visible regime. Here the extinction spectrum is the summation of absorption and scattering phenomena. According to the theory, in the cases of d $\ll \lambda$ or d $\gg \lambda$, Rayleigh scattering is predominantly responsible for the given spectrum. However, as the particle diameter approaches the wavelength of light (d $\approx \lambda$), Mie scattering dominates.[13,14] In order to calculate the theoretical extinction spectrum for the ZnS colloidal particle in water ($n_w \sim 1.33$), the particle diameter of 595 nm and a range of refractive indexes (real and imaginary parts) were used as input parameters to the MieCalc simulation. The resulting theoretical extinction spectra correlate reasonable well to the experimentally observed results. The spectra were also calculated as a function of packing fraction, f_{ZnS}, with the best fit occurring at a value of $f_{ZnS} = 0.66$ (Figure 4). This packing fraction indicates the volume of the colloidal particle occupied by the seed nanocrystals and is in good agreement with the packing fraction range of 0.60-0.75 reported previously for aggregated colloidal particles.[9,10] Based on the equation of $n_{eff} = f_{ZnS}n_{ZnS} + (1-f_{ZnS})n_w$, the effective refractive index (n_{eff}) is equal to 2.02 at 590 nm for the resulting ZnS colloidal particles in water. The synthesis reaction of the ZnS particles can easily be scaled up to increase the amount of monodisperse colloidal particles produced, as shown in Figure 5a. Since the ZnS particle surface is both highly charged (positively or negatively charged in acidic or basic media, respectively[15]) and water soluble, the straightforward Stöber method may be utilized to modify the surface with silica, thereby producing ZnS@silica core-shell particles (Figure 5b).

Conclusion

We prepared monodisperse ZnS colloidal particles through the controlled aggregation of seed nanocrystals. The particle diameter was controlled in a wide size range of 50 nm - 1 μm by simply adjusting growing time. Because the ZnS colloidal particles have a high refractive index (~2.0), chemically active surface, and interesting optical properties, they may potentially find broad applicability in the areas of photonics, phosphorescent coatings, and bioimaging.

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