

# ZnSe Semiconductor Hollow Microspheres\*\*

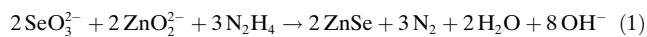
Qing Peng, Yajie Dong, and Yadong Li\*

Colloidal microspheres have been of continuous research interest ever since the beginning of the 20th century.<sup>[1–3]</sup> Traditionally, these systems have been regarded as ideal theoretical and practical objects of research because their intrinsic properties might be finely tuned by simply changing parameters, such as the diameter, the chemical composition, the bulk structure, and the crystallinity.<sup>[1–2]</sup> Recently, mono-dispersed silica and some polymer microspheres (e.g., polystyrene and poly(methyl methacrylate)) have been employed as fundamental building blocks in the fabrication of photonic bandgap (PBG) crystals,<sup>[3–7]</sup> 3D macroporous materials<sup>[8,9]</sup> and 3D crystalline arrays as optical sensors.<sup>[10]</sup> Although recent progress in this field has mostly concentrated on their potential optical application, the employed microspheres themselves do not exhibit any particularly interesting optical, nonlinear optical or electro-optical functionality.<sup>[3]</sup> To introduce particular optical properties into these systems, semiconductors<sup>[11]</sup> or metals<sup>[12]</sup> have been incorporated into silica or polymer colloids during the synthetic step, or coated onto polymer sphere templates to prepare TiO<sub>2</sub>, SnO<sub>2</sub>,<sup>[13]</sup> and ZnS<sup>[14]</sup> hollow spheres or core-shell structures.<sup>[15]</sup> However, until now, a simple template-free method to prepare semiconductor microspheres with intrinsic optical properties is much needed.

As an important group II–VI semiconductor with a room temperature bulk band gap of 2.67 eV (460 nm), ZnSe has long been a material of choice for blue diode lasers and photovoltaic solar cells. Efforts in the preparation of ZnSe usually focused on the synthesis of ZnSe nanocrystals with luminescent properties from single molecular precursors.<sup>[16–19]</sup> However, with a relatively high refractive index of 2.4 (at 300 K), ZnSe might also be ideal building blocks for materials with 3D PBG properties, but monodispersed ZnSe microspheres have not yet been reported. Recently, we reported the syntheses of a series of metal chalcogenides such as cubic  $\alpha$ -MnSe, MnSe<sub>2</sub> microcrystals,<sup>[20]</sup> and CdSe<sup>[21]</sup> nanorods. Herein, we report a novel and controllable method developed to prepare monodispersed ZnSe semiconductor microspheres. These microspheres were found to form through the aggre-

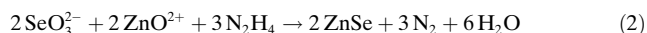
gation of small ZnSe nanocrystals sizes, which could be finely tuned by temperature control. Optical characterization showed that the microspheres have interesting photonic properties.

Salts of ZnO<sub>2</sub><sup>2–</sup> and SeO<sub>3</sub><sup>2–</sup> ions were chosen as the source of Zn<sup>2+</sup> and Se<sup>2–</sup> ions, respectively. The reaction process can be formulated as shown in Equation (1). After tuning the

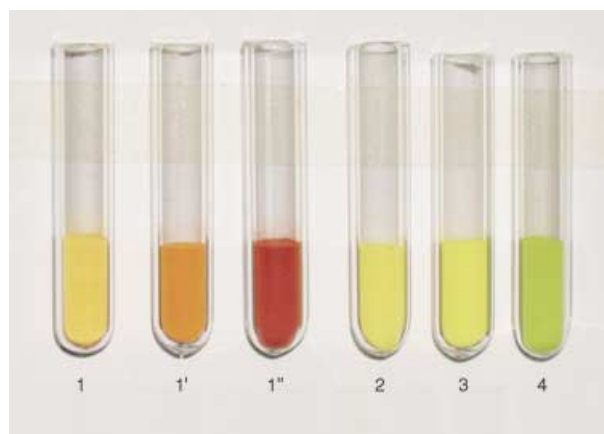


reaction temperature from 100°C to 180°C, and the products **1** (100°C), **2** (140°C), **3** (180°C) were obtained.

For comparison, control experiment has also been carried out under 180°C [Eq. (2)] and product **4** was thus obtained.



It is interesting to note two features of these products: First, they display gradient evolution in color from yellow to green from **1** to **4** (Figure 1), which implies that the intrinsic



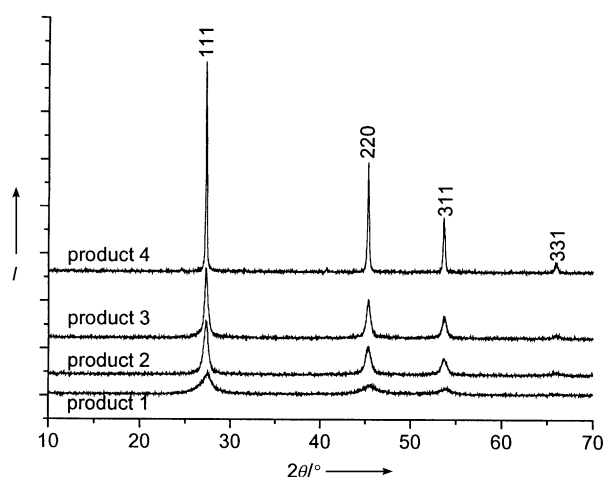
**Figure 1.** Color evolution of the as-obtained ZnSe products. Products **1**, **2**, and **3** are prepared by the route shown Equation (1) at 100°C, 140°C, and 180°C respectively. Product **4** is prepared through the route shown in Equation (2) at 180°C. Upon aging, the color of product **1** slowly changed from yellow to dark red (from **1** to **1'**, two weeks later, and finally to **1''**, one month later).

optical properties have changed. Secondly, upon aging, product **1** slowly changed from yellow to dark red (**1**, **1'**, **1''** in Figure 1), while all the others remained unchanged, which suggests a different stability in **1** compared with the other products.

The structures and morphologies of products were investigated by powder X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Figure 2 shows the evolution of the XRD patterns from **1** to **4**. From this figure, it is clear that all these products are pure-phase cubic ZnSe. With elevated reaction temperatures (100°C, 140°C, 180°C), the crystallinity of products becomes high, and the **4** obtained through Equation (2) shows the highest crystallinity. Based on the half-peak breadth of ZnSe(111) diffraction peak, the mean size of the products was calculated from the Scherrer equation and listed in Table 1. It is interesting to note that the color of ZnSe products is strongly dependent on their sizes.

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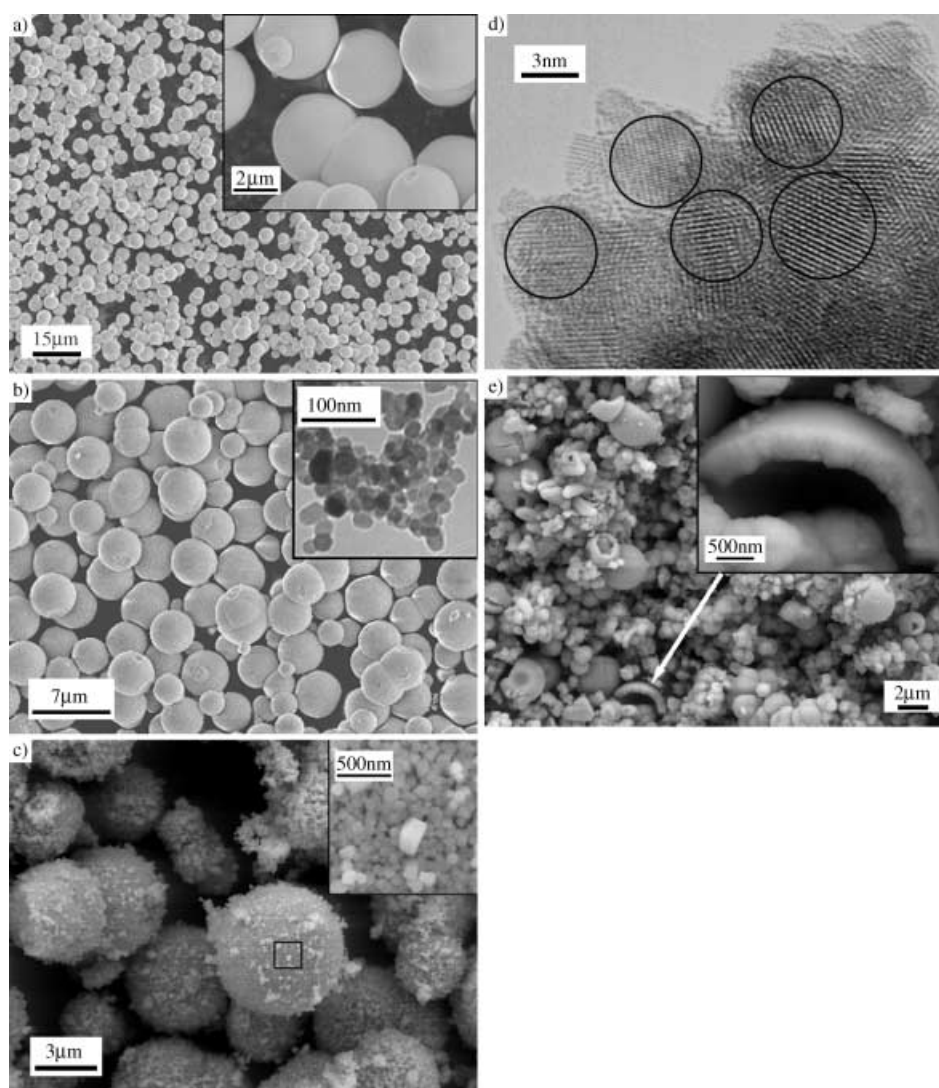


**Figure 2.** XRD patterns of products 1 (100°C), 2 (140°C), 3 (180°C). *I* = intensity, arbitrary units.

**Table 1:** Size of the interior nanocrystals in microspheres evaluated by XRD and TEM or HRTEM.

Reaction	Temperature	XRD (size)	TEM or HRTEM (size)
Eq. (1)	100°C	5.8 nm	5–6 nm
	140°C	14.2 nm	~15 nm
	180°C	19.1 nm	~20 nm
Eq. (2)	180°C	–	~100 nm

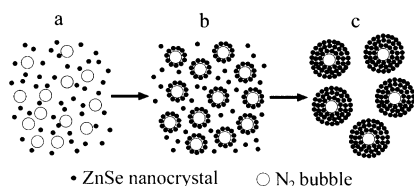
SEM images (Figure 3 a–c) show that these products are all microspheres with diameters of about 3  $\mu\text{m}$ . These microspheres are well dispersed with good monodispersity (Figure 3a and b), although a little portion of them have discrepant diameters. Product 1 to 3 through Equation (1) are usually of smooth surface (inset of Figure 3a, Figure 3b), whereas the surface of product 4 (Figure 3c) is relatively rough. The inset of Figure 3c shows that this sphere was aggregated from small nanocrystals of about 100 nm. To



**Figure 3.** From a) to c): SEM images of ZnSe microspheres, a) product 1, b) product 3, c) product 4. Inset of a) is the high magnification image of product 1. Inset of b) shows the interior small nanocrystals of product 3 after grinding. The size of them is about 20 nm. Inset of c) is the high magnification image taken from the highlighted section in c; d) HRTEM image of product 1 after grinding, which indicates that the microspheres are the aggregation of small nanocrystals with the size of about 5–6 nm. e) SEM image of the broken ZnSe microspheres (from product 3). Inset shows an individual broken shell, which indicates that these microspheres are hollow inside.

further investigate the interior structure of those smooth spheres, they were ground, dispersed in ethanol, dipped onto copper grids and characterized by transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM). Figure 3d and the inset of Figure 3b show that they were also aggregated from nanocrystals of smaller size but better monodispersity. The sizes of the nanocrystals measured from TEM, HRTEM are also listed in Table 1 and they agree with the XRD results very well. Acid treatment (3M citric acid solution was used, heating for 10–20 minutes) was also employed to break these spheres (see SEM image, Figure 3e). Most of the spheres have been destroyed, but there still many broken spheres present, which clearly show that they are hollow inside. The inset of Figure 3e shows an individual broken shell of one sphere and the shell thickness of the microsphere is about 300 nm.

Based on these observations, an aggregation mechanism to form ZnSe hollow microspheres is proposed, with reference to the preparation of monodispersed SiO<sub>2</sub> or TiO<sub>2</sub> microspheres.<sup>[22]</sup> In our reactions, the SeO<sub>3</sub><sup>2-</sup> ions are reduced first by hydrazine to Se atoms, which are further reduced or disproportionate in the alkaline solution to generate Se<sup>2-</sup> ions,<sup>[20,21]</sup> and these ions react with ZnO<sub>2</sub><sup>2-</sup> [Eq. (1)] or Zn<sup>2+</sup> ions [Eq. (2)] to form ZnSe monomers. As illustrated in Figure 4, after the initial nucleation, the monomers will grow



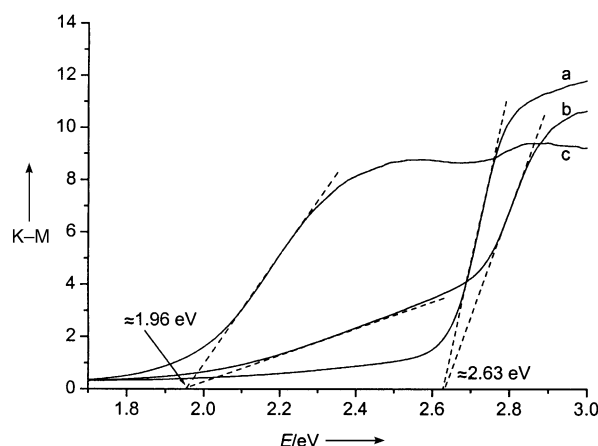
**Figure 4.** Schematic representation of the formation mechanism of ZnSe microspheres.

into nanocrystals (step a). These nanocrystals have a tendency to aggregate, and at the same time, lots of microbubbles of N<sub>2</sub> produced in the reaction provide the aggregation center (step b). Driven by the minimization of interfacial energy, small ZnSe nanocrystals may aggregate around the gas–liquid interface between N<sub>2</sub> and water (step b) and finally hollow ZnSe microspheres form (step c). In comparison, the direct reaction of Zn and Se under similar hydrothermal conditions, in which no microbubbles were introduced into the system, only led to ZnSe nanocrystals.<sup>[23,24]</sup>

The use of gas bubbles produced during the reaction to provide aggregation centers is a novel and effective method to fabricate hollow microspheres. Compared to the other template-synthetic methods, this soft-template method is very simple, convenient and avoids the introduction of impurities, and is therefore suitable for modern chemical synthesis. This idea might be extended to other solution systems in which easily aggregated monodispersed nanocrystals are produced during the reaction. The gas bubbles will help these nanocrystals to aggregate to form hollow microspheres. Our continuing studies are focusing on the development of improved techniques for improved control of

the spheres, such as the sphere size, shell thickness, and homogeneity of the spheres.

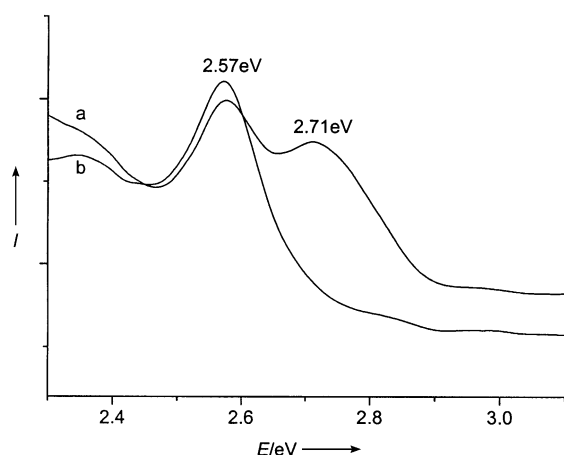
To further investigate the color change of ZnSe microspheres and their intrinsic optical properties, optical characterizations were carried out by optical diffuse reflectance and photoluminescence spectra. Based on the procedure described in the literature,<sup>[25,26]</sup> optical diffuse-reflectance spectra can be used to estimate the bandgap ( $E_g$ ) of semiconductors. The Kubelka–Munk function,<sup>[27]</sup> which is the ratio between the absorption and scattering factors, is used to plot the absorbance. In Figure 5, an absorption edge at 2.63 eV



**Figure 5.** Optical diffuse reflectance spectra (UV/Vis) of the products. a) A typical curve of stable samples (product 2, 3, and 4), which show an absorption edge at about 2.63 eV. b) Two absorption edges at 2.63 eV and 1.96 eV are observed in product 1' (two weeks later). c) Only the absorption edge of 1.96 eV can be observed in product 1'' (one month later). K–M = Kubelka–Munk function.

(trace a) is found for stable products (2, 3, and 4), which coincides very well with the  $E_g$  of bulk ZnSe. Trace b and c are from product 1' and 1'' respectively. Two absorption edges are observed at 2.63 eV and 1.96 eV ( $E_g$  of bulk selenium) in trace b, and only one absorption edge can be found at 1.96 eV in trace c. Further investigation suggests that this is because the Se<sup>2-</sup> ion on the surface of spheres in product 1 was oxidized in the air to amorphous Se and thus a ZnSe/Se core–shell structure was formed. Detailed study of this heterostructure will be presented in another report. On the basis of above results (see also Table 1), it can be found that the colloidal stability of ZnSe microspheres is strongly depended on the size of interior nanocrystals. Because of the high surface effect, ZnSe nanocrystals with size of about 5–6 nm are not stable in the air.

Figure 6 shows the photoluminescence spectra ( $\lambda_{exc.} = 290$  nm) of ZnSe microspheres. An emission maximum at 2.57 eV is found for product 2–4, which corresponds to the  $E_g$  of ZnSe. While for product 1', two emission peaks at 2.57 eV and 2.71 eV are observed. This may also be caused by the formation of core–shell structure of the sample. The little red shift ( $\sim 0.05$  eV) of photoluminescence peak (2.57 eV) with respect to the absorption spectrum (2.63 eV, Figure 5a) is caused by the Stokes shift, which is attributed to emission from a “dark exciton”.<sup>[19]</sup>



**Figure 6.** Photoluminescence spectra of as-obtained products. a) product 1' (two weeks later); b) stable samples (product 2, 3, and 4).  $I$  = intensity, arbitrary units.

In conclusion, ZnSe semiconductor microspheres have been successfully synthesized for the first time. The hollow nature together with the tunable interior nanocrystal size of these microspheres make them ideal entity for inter incorporation or surface modification, which might bring novel optical, electronic and magnetic properties.

### Experimental Section

For products 1–3 [Eq. (1)], analytical-grade  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.29 g, 0.001 mol) and  $\text{Na}_2\text{SeO}_3$  (0.17 g, 0.001 mol) were dissolved in NaOH (1M, 20 mL) and  $\text{H}_2\text{O}$  (10 mL) respectively to form clear solutions. These solutions were mixed together in a 50 mL Teflon-lined autoclave of and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (10 mL) was added into the mixture. After the mixture was stirred for five min, the autoclave was sealed and heated at one of three different temperatures: 100 °C, 140 °C, 180 °C for 2 h. The system was then allowed to cool to room temperature. The final product was collected by filtration, and washed with deionized water to remove any possible ionic remnants, then dried at 60 °C. For product 4 [Eq. (2)], no NaOH was added and all the other steps are the same as that of Equation (1).

The samples were characterized on a Bruker D8-advance X-ray powder diffractometer with  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The size and morphology of the ZnSe microspheres was determined at 20 kV by a JEOL JSM-6301F scanning electron microscope and at 200 kV by an Hitachi H-800 transmission electron microscope (TEM) and a JEOL JEM-2010F high-resolution transmission electron microscope. Optical diffuse reflectance of the samples was recorded on a Shimadzu UV-2100S spectrophotometer. Photoluminescence experiments were conducted in air on a Perkin-Elmer LS-50B fluorescence spectrophotometer.

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