

# Reagents for ZnS Hierarchical and Non-Hierarchical Porous Self-Assembly

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**ABSTRACT** Monodispersed highly ordered and homogeneous ZnS microsphere with precisely controlled hierarchical and non-hierarchical surface structure was successfully fabricated in water–ethanol mixed solvent and in water without using any catalysts or templates in a hydrothermal process. The microsphere formation has been facilitated by self-assembly followed by Ostwald ripening process. The products were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectrometry (EDX). The XRD results indicated that the cubic phase ZnS formed in hydrothermal process at various reaction times. Introducing ethanol as a co-solvent with water facilitated hierarchical porous surface structure. The influences of various zinc and sulfur precursors, various alcohols as co-solvent, and solvent ratio on the formation of specific surface structured microsphere was investigated. The water–ethanol (1:1) solvent ratio is the minimum required to facilitate hierarchical porous surface structure. The by-products formed during the hydrothermal process are induced specific surface structure in ZnS microsphere. This is the first report on in situ generated by-products being used as a reagent to facilitate surface structured material fabrication. The formed by-products could be used as recyclable reagents to fabricate hierarchical porous ZnS in three consecutive cycles. A plausible growth mechanism of by-product-induced surface structure in different solvent was discussed. The research results may lay down new vistas for the in situ generated by-product-assisted specific surface structured ZnS fabrication.

**KEYWORDS:** ZnS • microsphere • hierarchical porous • surface structured materials

## INTRODUCTION

Controlled fabrication of nano/microstructured materials is of great importance in both fundamental and potential applications because of their unique properties that differ from those of their bulk counterparts. ZnS is one of the important II–VI semiconductor materials with wide band gap energy of 3.5–3.7 eV for cubic zinc blende structure and 3.7–3.8 eV for hexagonal wurtzite structure (1). Recently, much attention has been paid because of its application in the field of optoelectronics and catalysis (2–5). Precise surface structure controlled nano/micro materials fabrication by self-assembled process is immense important in nanotechnology research. Thus, such fabrication can create an opportunity for producing functional materials with new properties, which are of importance to applications in various fields (6–10). Therefore, there is a need to design materials with desired surface properties by using a simple methodology and such fabrication is big challenging task for chemists and material scientist. It is known that many reagents being used to facilitate specific reactions in organic chemistry and are well-documented in the literature (11–14). However, there are no such specific reagents reported for either nano/micro materials fabrication or specific surface

structured material fabrication. Therefore, there is a need to synthesis such type of reagents and invention of such common reagents for nano/microstructured materials fabrication may bring the nanotechnology research into a new milestone. Thus, an attempt has been made to synthesize reagents that can induce the specific surface structures. In this communication, we have first reported a new perspective on precisely controlled, specific surface structured materials fabrication by using in situ generated by-products. The in situ generated by-products were successfully used as reagents to induce hierarchical and non-hierarchical porous surface structure in a hydrothermal process in two different solvents.

## EXPERIMENTAL SECTION

Anhydrous zinc chloride, zinc nitrate hexahydrate, zinc acetate dihydrate, zinc sulfate hepta hydrate, potassium thiocyanate, diethyl sulfide, diethyl disulfide and ethanol, methanol, 1-propanol were obtained from Aldrich chemical Ltd. (Helsinki, Finland). Zinc chloride and potassium thiocyanate were used as sources for zinc and sulfur. These chemicals were used without further purification. For all experimental work Milli Q-Plus water (resistance = 18.2 M  $\Omega$ ) was used. In a typical experiment, 0.92 M of anhydrous ZnCl<sub>2</sub> was dissolved in 25 mL of water and then 50 mL of ethanol was added with constant stirring (solution 1); 2 M of potassium thiocyanate was separately dissolved in another 25 mL of water (solution 2). Under magnetic stirring, solution 2 was then added drop by drop into solution 1. The clear solution was stirred for another 30 min and then transferred into a 250 ml capacity Teflon cup for hydrother-

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mal reaction. The Teflon cup was covered by stainless steel and the autoclave set up was kept in 195 °C at desired time in an oven. The precipitate formed was harvested by filtration and washed several times with deionized water and ethanol to remove possible impurities before being dried in an oven at 120 °C for 2 h. For reaction carried out in water solvent, instead of ethanol we have added 50 mL of water and the same reaming procedure was followed in all reactions. The synthesized catalyst was characterized by using appropriate analytical techniques.

The by-products formed during the hydrothermal reaction were analyzed by using a GC-MS, Agilent Technologist (G1888), equipped with an auto-injector and inert mass selective detector (5975). The separation column was a DB-624 capillary column (Model Number-Agilent 122-1364) with 60 m in length and 250.00  $\mu\text{m}$  and filled with 1.40  $\mu\text{m}$  film thickness. Samples were injected by using Agilent G1888 headspace sampler into the GC for detection. The oven temperature was held at 50 °C, and the temperature was then ramped at 20 °C/min to 200 °C. The total run time for each sample was 40 min.

The X-ray diffraction (XRD) patterns were recorded using a X' Pert PRO PAN analytical diffractometer, scanned angle from 10° to 100°. The working voltage of TEM was 200 kV. The morphology of the catalyst was examined using a Hitachi S-4100 scanning electron microscope (SEM). Prior to SEM measurements, the samples were mounted on a carbon platform which was then coated by platinum using a magnetron sputter. The plate containing the sample was then placed in SEM for the analysis with desired magnifications. The X-ray photoelectron spectra were collected on an ESCA-1000 X-ray photoelectron spectrometer (XPS), using Mg K $\alpha$  X-ray as the excitation source. The nitrogen adsorption method was analyzed by using an Autosorp-1 Quantachrome instrument. Prior to analysis, 0.25 g of powder was degassed at 120 °C for 15 h.

## RESULTS AND DISCUSSION

The synthesized ZnS microspheres were characterized by using suitable analytical techniques. The EDX microanalysis demonstrates that the synthesized material consists of Zn and S elements. Moreover, according to the quantitative analysis of EDX, the Zn: S molar ratio is about 1:1.08, which is close to the stoichiometric ratio of ZnS. Figure 1 shows the typical XRD pattern of the zinc sulfide synthesized by hydrothermal process at 195 °C for various reaction times in water and water: ethanol (1:1) mixed solvents. The diffraction peaks of the synthesized ZnS in both solvent can be readily indexed as cubic ZnS (JCPDS card no. 77-2100) with lattice constant (3.820 and 6.257 Å). However, a peak appears at 27.3° that can be indexed as the (100) reflection of wurtzite, the hexagonal polytype. The percentage of (100) reflection in water solvents is higher than that of water-ethanol mixed solvents. Though, cubic phase is observed in both solvents, the peaks of the ZnS synthesized in water solvent are narrow and the peaks appeared in water-ethanol mixed solvent are wide as shown in Figure 1. These results clearly indicated that the particle size of the ZnS synthesized

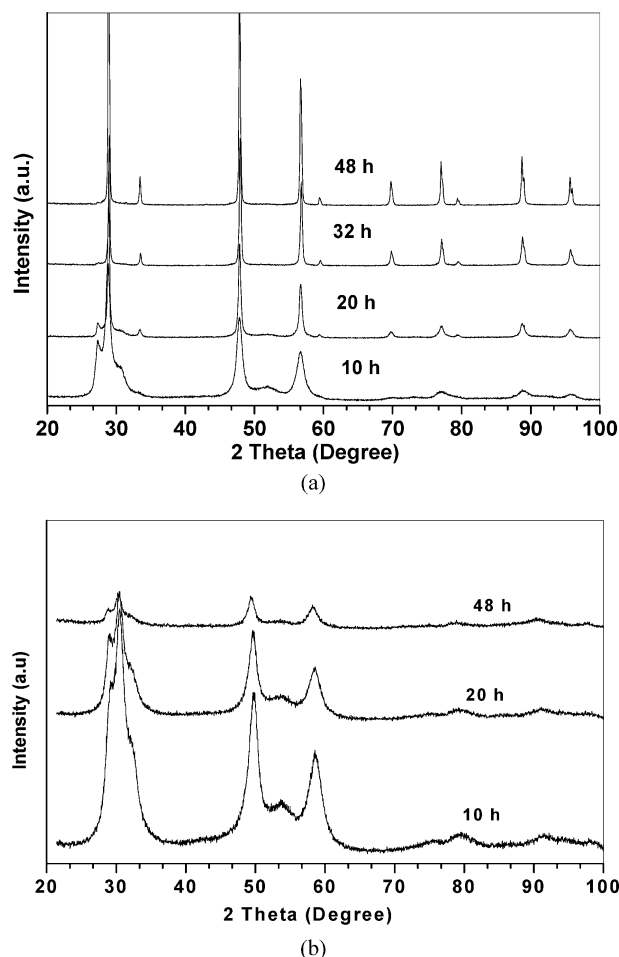


FIGURE 1. XRD of ZnS synthesized under hydrothermal process at 195 °C at various time in (a) water and (b) water-ethanol mixed solvents (1:1).

in ethanol-water solvent mixture is very small when compared to ZnS synthesized in water.

It is interesting to note the morphology of the ZnS synthesized under similar experimental conditions in both solvents at different reaction time. Smooth surface structured microsphere is formed in both solvents at 10 h as shown in Figure 2a. Moreover, the microspheres formed were aggregate-free and well-dispersed, and their surface structures were uniform with size ranging from 1 to 5  $\mu\text{m}$ . Nevertheless, further increase the hydrothermal reaction time, the ZnS formed in water and water-ethanol mixed solvent has different surface structures. In water solvent, increasing the reaction time from 10 to 20 h increases the surface roughness of the microsphere, as evident from Figure 2b. However, further increasing the reaction time (32 h), the microsphere starts to degrade and eventually generate various nanoparticles/plates from the microsphere surface. The microsphere surface is continuously grown as nanoplates when the reaction time in further increased to 48 h as shown in Figure S1 in the Supporting Information. Though nanoplates were generated from the microsphere, it was not well dispersed and well interconnected so it appeared as loosely bound aggregates. However, the results obtained in water-ethanol (1:1) mixed solvents are quite different from the results using water alone. Increasing the

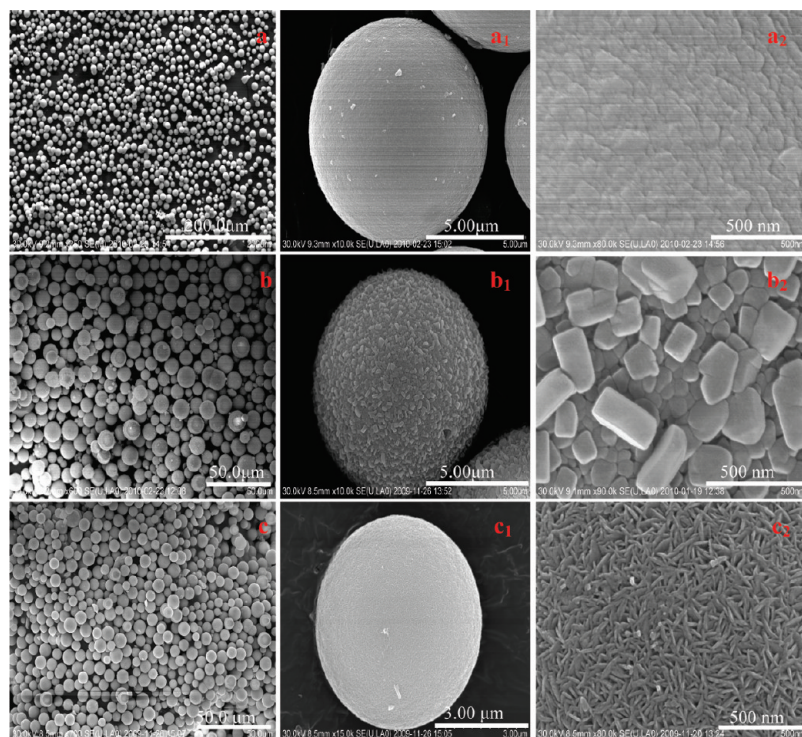


FIGURE 2. FESEM picture of ZnS prepared at 195 °C (a) in water solvent for 10 h, (b) in water solvent for 20 h, and (c) in water–ethanol mixed solvent for 20 h.

reaction time from 10 to 20 h results in hierarchical porous surface structured microsphere as shown in Figure 2c. Unlike the microsphere formed in water solvent, the hierarchical porous microsphere formed in water–ethanol solvent is highly stable during long reaction time (48 h), as presented in Figure S2 in the Supporting Information. However, after a prolong time (90 h) the hierarchical porous microsphere starts to degrade and its surface nanoparticles grown as nanoplates. Nevertheless, similar surface nanoparticle growth has not been observed in microspheres synthesized by using low precursor concentrations. Moreover, the aforementioned surface nanoparticles growth in both solvents is caused by the by-products formed during the hydrothermal process, and its influence is discussed in a later part of this manuscript. Though numbers of reports have been discussed on various aspects of ZnS microsphere synthesis, the nanoparticle growth on microsphere surface observed in our study is quite different from those reports (15–19). We have examined the formation of microspheres in repeated experiments under similar experimental conditions and the results indicated that the synthesis method is 100% reproducible. The surface properties of the synthesized microspheres in both solvents at different reaction time are shown in Table 1. The surface area of the synthesized ZnS decreases with increasing the hydrothermal reaction time, which may be due to the increase the particle size on the microsphere surface as the hydrothermal reaction time increases. However, hierarchical porous microspheres formed at 20 h poses higher surface area and further decrease when the hierarchical porous surfaces grown after prolong reaction time. Similarly, the pore size and pore volume increase in both

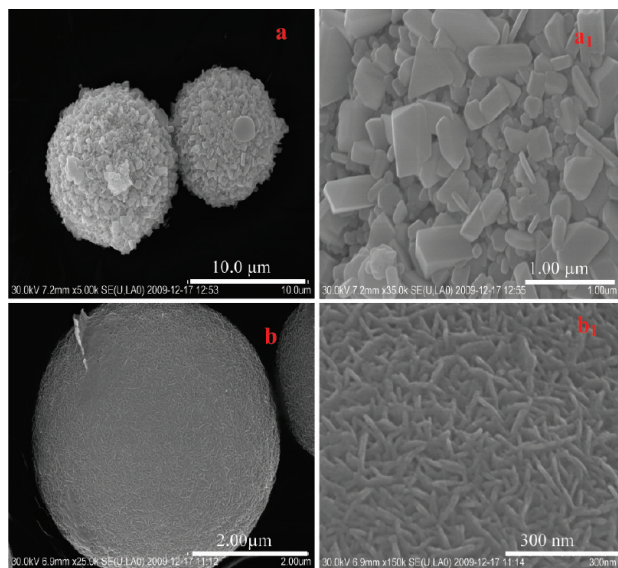
Table 1. Surface Properties of ZnS Prepared in Water and in Water–Ethanol (1:1) Solvent at 195 °C for Different Hydrothermal Times<sup>a</sup>

samples	BET surface area (m <sup>2</sup> /g)	pore size (nm)	pore volume (cm <sup>3</sup> /g)
S1	36	5.7	0.05
S2	11	38	0.10
S3	6	77	0.12
S5	28	3.3	0.23
S6	34	2.6	0.02
S7	4	104	0.11

<sup>a</sup> ZnS prepared in a hydrothermal process at 195 °C for different reaction times in water solvent, S1 = 10 h, S2 = 20 h, S3 = 32 h, and in water–ethanol (1:1) mixed solvent, S5 = 10 h, S6 = 20 h, S7 = 90 h.

solvents as the time increases due to increase the porous surface structure.

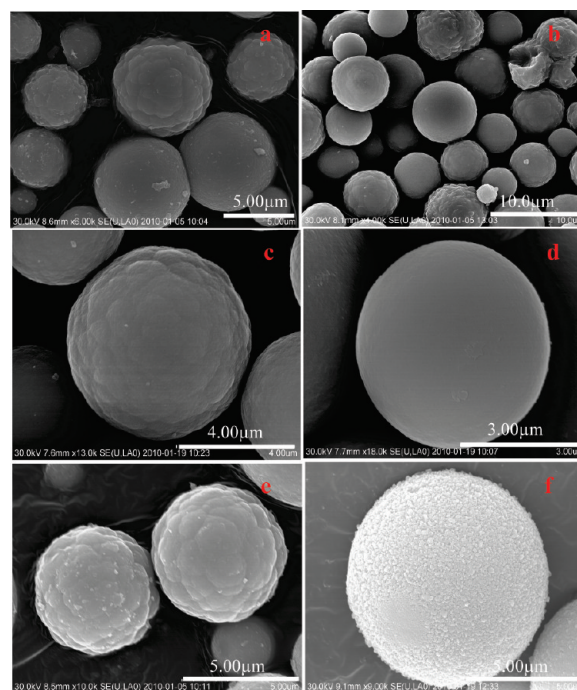
To understand the unusual growth of the ZnS microspheres, various controlled experiments have also been studied under different experimental conditions in both solvents. The influence of alcohol as a co-solvent on the formation of hierarchical porous surface structure has been investigated by changing the water to alcohol ratio (v/v) from 4:0, 3:1, 1:1 and 1:3 at 195 °C for 20 h. The results clearly indicated that the alcohol co-solvent played very important role on the formation of hierarchical porous surface structure. Moreover, water–ethanol 1:1 (v/v) ratio is the minimum required to facilitate hierarchical porous surface structure. Moreover, at a 3:1 water–ethanol ratio, the surface roughness of the microsphere increased when compare to one synthesized in water solvent, and as expected, the hierarchical surface structured microsphere is formed at a 1:3 water–ethanol ratio as evident from Figure 3. Thus,



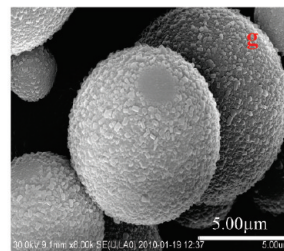
**FIGURE 3.** ZnS formed at 195 °C for 20 h at (a) water–ethanol (3:1) and (b) ethanol–water (3:1) mixed solvent.

experiments were also performed by replacing ethanol with methanol and n-propanol as co-solvent with water at 1:1 molar ratio and the formation of hierarchical porous surface structure was investigated at 195 °C for 20 h. The FESEM results in Figure S3 in the Supporting Information indicated that both methanol and n-propanol facilitated hierarchical surface structure and its morphology is quite similar to one formed in ethanol as co-solvent. Therefore, alcohol playing a common role during the synthesis and the importance of the alcohol as co-solvent is discussed in a later part of this manuscript on the basis of the by-products formed in the hydrothermal process.

Similarly, another important experimental parameter that influenced the microsphere surface structure is the initial concentration of the precursors. One of the unique differences between this investigation and the literature methodology is the initial concentration of precursor used for the synthesis (15–19). We have used quite a high concentration of the precursor, which yields unusual results. Therefore, the influence of initial concentration of the precursor on the formation of specific surface structured ZnS microsphere was studied in both solvents. About 0.92, 0.46, 0.23, and 0.092 M of the zinc chlorides with corresponding potassium thiocyanate at a 1:2 molar ratio was taken and the hydrothermal reaction was facilitated in water and water–ethanol (1:1) mixed solvent at 195 °C for 20 h. The FESEM pictures in Figure 4 clearly indicated that no hierarchical surface structured microsphere formed in mixed solvent except 0.92 M. However, the surface roughness of the microsphere has been facilitated from 0.23 M in water solvent. Interestingly, at low concentration (0.092 M), either hierarchical porous surface or surface roughness has not been facilitated in water–ethanol mixed solvents and in water, respectively. Moreover, the formed microsphere surface is not uniform when compared to one formed at high initial concentration.



**FIGURE 4.** ZnS formed under various initial concentrations of the precursors at 195 °C in water–ethanol (1:1) mixed solvents (a) 0.092 M at 10 h, (b) 0.092 M at 20 h, (c) 0.23 M at 20 h, (d) 0.46 M at 20 h, and in water solvents at (e) 0.092 M at 20 h, (f) 0.23 M at 20 h, (g) 0.46 M at 20 h.



Finally, on the basis of the aforementioned experimental results, we believed that the by-products formed during the hydrothermal reaction are playing a very important role to control the surface structures of microspheres in both aqueous and in water–ethanol mixed solvents. Thus, to the best of our knowledge, we have first proposed a new concept for precisely controlled specific surface structured ZnS synthesis by using in situ generated by-products. To confirm the influence of by-products, we also studied additional experiments. As we discussed earlier, no hierarchical structure is formed in water at any stages of the hydrothermal process and therefore the smooth surface structured microsphere formed at 195 °C for 10 h was used for control experiments. About 1 g of the above mentioned microspheres were taken in water and in water–ethanol (1:1) mixed solvents and hydrothermally treated for 195 °C for 10 h. The results in Figure S4 in the Supporting Information imply that the formed microspheres have no hierarchical surface structure in water–ethanol mixed solvents and no surface roughness noted in water solvent. Similar results were also noted in smooth surface structured microspheres formed in water–ethanol mixed solvents at 195 °C for 10 h as shown in Figure S5 in the Supporting Information.

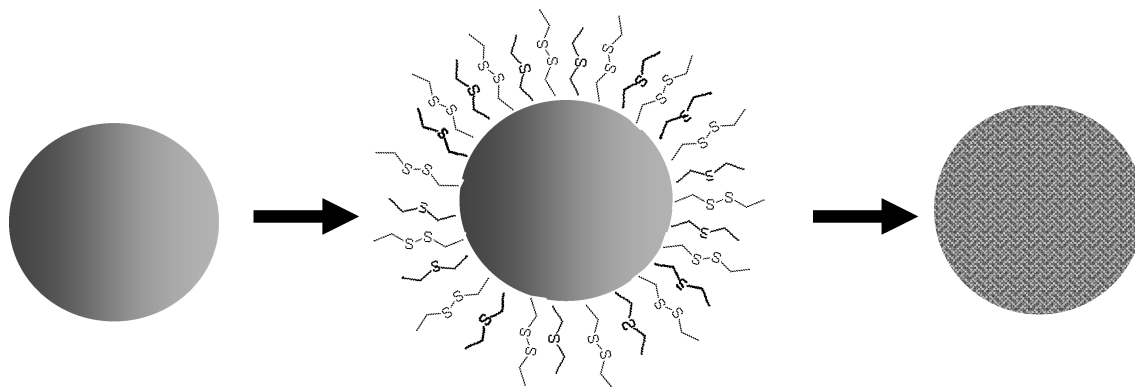
These experimental results confirmed that either hydrothermally generated pressure or microsphere surface itself did not induce surface nanoparticle growth during the hydrothermal process. Thus, we have also performed additional experiments with the mother liquor formed in water–ethanol mixed solvent (1:1) in a hydrothermal process at 195 °C for 10 h. About 100 mL of the mother liquor formed in the abovementioned process was added with 1 g of smooth surface ZnS microsphere (formed in water solvent) and treated hydrothermally at 195 °C for 10 h and the results are presented in Figure S6 in the Supporting Information. The FESEM result shows that the hierarchical porous surface structured microsphere formed and its sizes were not changed which revealed that the mother liquor specifically induces the hierarchical surface structure without affecting the microsphere morphology. The aforementioned results confirmed that the synthesized mother liquor could be used as “reagents” for the hierarchical porous surface structured ZnS fabrication. Hereafter, the mother liquor was denoted as reagents.

The applicability of the reagents for the formation of hierarchical surface structured ZnS has also been evaluated in three consecutive cycles. At the end of each cycle, the reagents were filtered and then mixed with fresh smooth surface structured microspheres and treated for 195 °C for 10 h. The results shown in Figure S6 in the Supporting Information imply that the reagents induced hierarchical surface structure in all three cycles without affecting microsphere morphology. However, in the third cycle, a small amount of aggregates were also noted. The reagent’s ability to induce hierarchical surface structure in other materials was not explored and is currently being studied in our laboratory. Beyond the doubt, we have confirmed that the by-products formed in water–ethanol and in water solvent during the hydrothermal process (195 °C for 10 h) are responsible for hierarchical surface structure growth in water–ethanol mixed solvent and surface roughness growth in water solvent, respectively. Nevertheless, we believed that the formed by-products in water–ethanol mixed solvent may differ from water solvent, which may induce different surface structure during the hydrothermal process. An attempt has been made to identify the constituents of the reagents formed during the hydrothermal method. Because

we have used high initial concentrations of zinc chloride and potassium thiocyanate as precursors, it could produce KCl as one of the by-products. These counter ions have no effect on the hierarchical porous structure fabrication, as confirmed by replacing zinc chloride with zinc acetate or zinc nitrate as precursors. The results showed that the counter ion has not been involving the hierarchical surface structure fabrication.

To identify other constituents of the reagents, we have performed GC-MS. The GC-MS analysis of reagents showed that the hydrothermal process at 195 °C results in two major by-products, namely, diethyl sulfide and diethyl disulfide in water–ethanol (1:1) mixed solvent. The formation of both by-products has been confirmed by comparing with standard samples of diethyl sulfide and diethyl disulfide (Aldrich) in the GC-MS analysis. Interestingly, both diethyl disulfide and diethyl sulfides were noted in 10 and 20 h and their concentrations are nearly equal (based on the GC peak area of the products). It should be mentioned here that the concentration of the both by-products formed at low initial concentration of the precursor is relatively very small when compared to one formed at higher initial concentration of the precursors (based on GC peak area). Because we didn’t add any foreign substance in the hydrothermal process, it is obvious that these by-products were generated from zinc thiocyanate complex. Therefore, the concentration of these by-products should depend on the initial concentration of the precursors. Therefore, it is reasonable to expect that the formed by-product concentration is not enough to facilitate hierarchical surface structure at low precursor concentration. These results explain why low precursor concentration didn’t facilitate hierarchical porous surface structured ZnS microspheres. However, it is hard to differentiate the role of either diethyl disulfide or diethyl sulfide on the formation of hierarchical surface structure. On the other hand, carbon disulfide was noted as the major by-product along with very small amount of diethyl disulfide in water solvent. Therefore, the abovementioned two different types of by-products in water and in water–ethanol solvent could facilitate different surface structured ZnS. Though diethyl disulfide is also noted in water solvent, its concentration is very small and therefore it did not facilitate hierarchical porous surface structure. Thus, we should also consider the solubility of both by-

### Scheme 1. Formation of Hierarchical Porous Surface Structured ZnS Microspheres by Interaction of In situ Generated By-Products with ZnS Surface



products in water solvent. Generally, diethyl disulfide is not soluble in water and may be very slightly soluble in water during the hydrothermal process because we have used 195 °C for hydrothermal reactions. However, it was unclear why hierarchical porous microspheres were not formed at 3:1 water–ethanol ratio.

It should also be noted that the microspheres formed were highly porous when compared to microspheres formed in water solvent. Therefore, on the basis of these results, we can conclude that the added ethanol amount at 3:1 ratio may not generate enough by-products (concentration required to facilitates hierarchical structure). However, it is assumed that the generated by-product concentration should be higher than that of the amount generated in water because of the presence of ethanol and that's why the microspheres formed at a 3:1 solvent ratio has a highly porous surface structure when compared to the one formed in water at 195 °C for 20 h. Because of the aforementioned reason, hierarchical porous surface structure is not formed in water solvent and implies the role of alcohol as a co-solvent during the hydrothermal synthesis. Therefore, the presence of alcohol as co-solvent may favor the formation and solubility of diethyl disulfide and diethyl sulfide and are playing an indirect role on the formation of hierarchical surface structure.

The mechanism of microsphere formation can be understood by time-dependent observation of the ZnS morphology. Because we did not use any templates or catalysts, the microspheres may form by self-assembly process followed by Oswald ripening process. Thus, after 2 h we have observed small size microspheres in both solvents and such small sizes were not noted after 10 h, which clearly confirmed the involvement of Oswald ripening process. One important and interesting subject to study is how the by-products induced hierarchical surface structures. The formed diethyl sulfides and diethyl disulfide could act as capping agents to facilitate hierarchical surface structure. Moreover, the interaction of either diethyl sulfide or diethyl disulfide with ZnS surface may induce thiol type bonding ( $-S-H-$ ) and such interactions: organic molecules capped or functionalized ZnS is reported in the literature (20–23). Wang et al. report mercaptopropyl acid functionalized core–shell ZnS quantum dots synthesis and their proposed mechanism is similar to our proposed mechanism (23, 24). Scheme 1 shows the by-product interaction with ZnS surface to facilitate hierarchical surface structure. The interactions of ZnS microspheres with the generated by-products have also been confirmed by XPS analysis of ZnS. The deconvoluted S 2p spectra reveals that in addition to the sulfide peaks at 162.5 eV, there is an additional peak appeared at 163.5 eV, which corresponds to the alkyl group peaks as shown in Figure 5. Thus, Mekhalif et al., reported unbound thiols ( $-SH-$ ) at 164 eV (25). These results confirmed that the thiols type surface structure present on the surface. Moreover, the Zn2p spectra showed intense peak at 1022 and 1045 eV, which corresponds to Zn2p<sub>3/2</sub> and Zn2p<sub>1/2</sub>, respectively.

In summary, we have first synthesized recyclable reagents that can induce hierarchical and non-hierarchical

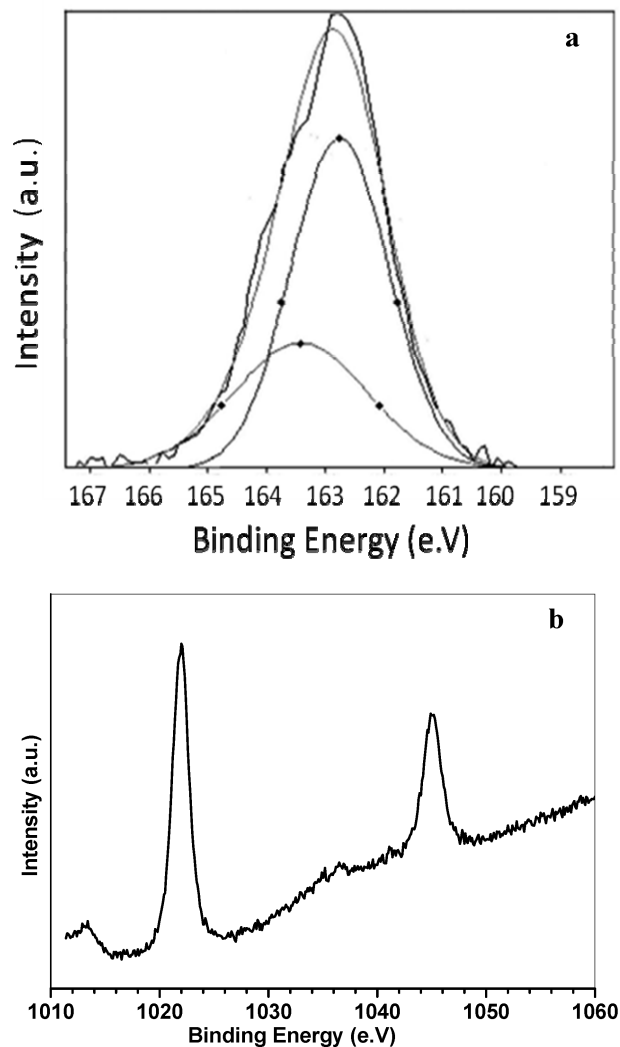


FIGURE 5. (a) S 2p core levels, (b) Zn 2p of ZnS prepared in water–ethanol (1:1) solvent at 195 °C for 10 h.

surface structure in different solvents by a simple hydrothermal process. The hydrothermal solvent played an important role in generating by-products and the alcohol co-solvent, and the initial precursor concentration played very important role in the formation of hierarchical porous microspheres. The research results may lay down new vistas for the in situ generated reagents induced specific surface structured material fabrication. Finally, the bottom-up self-assembly offers an attractive route for low-cost synthesis of precisely controlled surface structured ZnS.

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**Supporting Information Available:** FESEM pictures of microspheres prepared under various experimental conditions (PDF). This material is free of charge via the Internet at <http://pubs.acs.org>.

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