Mechanism of sulfdation of small zinc oxide nanoparticles

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ZnO has industrial utility as a solid sorbent for the removal of polluting sulfur compounds from petroleum-based fuels. Small ZnO nanoparticles may be more effective in terms of sorption capacity and ease of sulfdation as compared to bulk ZnO. Motivated by this promise, here, we study the sulfdation of ZnO NPs and uncover the solid-state mechanism of the process by crystallographic and optical absorbance characterization. The wurtzite-structure ZnO NPs undergo complete sulfdation to yield ZnS NPs with a drastically different zincblende structure. However, in the early stages, the ZnO NP lattice undergoes only substitutional doping by sulfur, while retaining its wurtzite structure. Above a threshold sulfur-doping level of 30 mol%, separate zincblende ZnS grains nucleate, which grow at the expense of the ZnO NPs, fnally yielding ZnS NPs. Thus, the full oxide to sulfdide transformation cannot be viewed simply as a topotactic place-exchange of anions. The product ZnS NPs formed by nucleation-growth share neither the crystallographic structure nor the size of the initial ZnO NPs. The reaction mechanism may inform the future design of nanostructured ZnO sorbents.

In this context, small few-nm size ZnO NPs can be expected to be particularly promising, but it is important to understand the manner in which these NPs undergo sulfdation. The structural mechanism of the sulfdation process may have critical differences compared to bulk ZnO powders or even larger NPs of tens of nm in size and may therefore influence sorbent design. In a seminal study, Park et al. studied the sulfdation of hexagonal-shaped 14 nm ZnO nanocrystals (NCS) at high temperature (235 °C) using hexamethyldisilathiane. The reaction was found to involve the anion exchange of O2− with S2− in the NC lattice. The overall shape and crystallography of ZnS NCS was templated by the initial ZnO NCS. However, due to the faster outward diffusion of Zn2+ as compared to the inward diffusion of S2−, the exchange reaction was accompanied by a nanoscale Kirkendall phenomenon, as a result of which the ZnS NCS formed were hollow.

Here, we track the step-wise sulfdation of smaller (ca. 5 nm) ZnO NPs using optical spectroscopy and X-ray crystallography. Prior to the onset of sulfdation, O2− in wurtzite ZnO NPs undergoes substitutional doping with S2− without any major change in its structure. Upon reaching a critical concentration of sulfur doping, separate zincblende ZnS grains form and grow into ZnS NPs. Thus, the sulfdation of these small ZnO NPs studied here is not simply a topotactic or templated place-exchange of anions; rather the nucleation and growth of a separate ZnS crystallite is involved in the latter stages.

Experimental methods

Synthesis of ZnO NPs

The synthesis of 4 nm ZnO NPs was based on a procedure from Kamat and coworkers with some changes. Briefly, 0.05 M of zinc acetate dihydrate (1.095 g) was added to 50 mL of ethanol
in a 100 mL three-necked round-bottom flask. The flask was put under Ar, heated to 80 °C, and refluxed for 2 h followed by gradual cooling down to room-temperature over the course of 1.5 h. The zinc precursor solution (0.05 M) was stored in a desiccator and used for a period of up to three months from the preparation date. Whenever needed, a batch of ZnO NP colloid was prepared by the hydrolysis of the zinc precursor using lithium hydroxide (LiOH) powder. Typically, 20 mg of LiOH was added directly to 3 mL of the precursor solution diluted with 12 mL of ethanol. The resulting reaction mixture was sonicated for 20 min without heating. The resulting colloid solution was washed by adding an equal volume of acetone and centripfuging at 10,000 rpm for 20 min. The precipitated colloid was redispersed in 25 mL of ethanol. The colloid was allowed to stand for 5 h or more to allow NP growth to stabilize before sulfidation studies or other measurements. The ZnO colloid was typically used up to a week from its preparation.

**Sulfidation of ZnO NPs**

The conversion from ZnO to ZnS NPs was carried out at a temperature of 45 °C. We started with a colloid of ZnO NPs dispersed in ethanol (at a concentration which yields an absorbance of ~1 at the ZnO excitonic peak maximum). The colloid was transferred to a 20 mL glass vial immersed in a water bath set at 45 °C. To this colloid, a solution of sodium sulfide (Na2S) in ethanol (3.1 mg mL−1) was added in aliquots of 10 µL with vigorous stirring. After each addition, the reaction was allowed to approach completion by waiting a duration of ~1.5 h. The zinc precursor solution (0.05 M) was stored in a glass bottle immersed in a 100 mL three-necked round-bottom flask under Ar, heated to 80 °C, and refluxed for 2 h followed by gradual cooling down to room-temperature over the course of 1.5 h. The zinc precursor solution (0.05 M) was stored in a desiccator and used for a period of up to three months from the preparation date. Whenever needed, a batch of ZnO NP colloid was prepared by the hydrolysis of the zinc precursor using lithium hydroxide (LiOH) powder. Typically, 20 mg of LiOH was added directly to 3 mL of the precursor solution diluted with 12 mL of ethanol. The resulting reaction mixture was sonicated for 20 min without heating. The resulting colloid solution was washed by adding an equal volume of acetone and centripfuging at 10,000 rpm for 20 min. The precipitated colloid was redispersed in 25 mL of ethanol. The colloid was allowed to stand for 5 h or more to allow NP growth to stabilize before sulfidation studies or other measurements. The ZnO colloid was typically used up to a week from its preparation.

**Elemental analysis**

The elemental composition of the NPs, specifically the molar ratio of S : Zn, was determined at three stages: the initial ZnO NPs before sulfidation, the intermediate stage obtained by the addition of 1.99 µmol of S2−, and the final ZnS NPs achieved by the addition of 11.9 µmol of S2− to the ZnO NPs. These samples were each purified of reagents and salts twice by washing with acetone and centrifugation. The washed precipitate was subsequently dried in quartz digestion tubes by flowing N2 gas. Samples were subject to inductively-coupled plasma atomic emission spectroscopy (ICP-AES) measurements, the results of which are presented in Table 1.

**Electron microscopy**

The initial ZnO NPs and final ZnS NPs were subject to TEM imaging. For ZnO NPs, 6 mL of ZnO colloid prepared as described above was treated with 0.3 mL of oleic acid and washed with 6 mL of acetone followed by centrifugation at 10,000 rpm for 20 min. Then the precipitated colloid was dispersed in ethanol. About 50 µL of the diluted ZnO NP colloid was drop cast onto an ultrathin carbon grid, which was then allowed to dry in a vacuum desiccator. ZnS NPs were prepared by complete sulfidation of 6 mL of ZnO colloid accomplished, as described above, by addition of S2−. The ZnS NP colloid was treated with 0.3 mL of oleic acid and washed with 6 mL of acetone followed by centrifugation at 10,000 rpm for 20 min. Then the precipitated colloid was dispersed in ethanol. The TEM grid, held by tweezers was dipped into the colloid once and then allowed to dry in a vacuum desiccator. TEM imaging was performed on a JEOL 2010-EFFEG instrument operating at 200 kV. NP size analysis was performed using the Fiji software. The diameter of each NP identified in a representative image was determined manually along three arbitrary directions across the NP and averaged.

**Structure factor simulations**

For the initial ZnO and the early-stage sulfur-doped ZnO NCs, pXRD patterns were simulated using the program PowderCell. The program performs a structure factor calculation using crystal symmetry, lattice parameters, atomic positions, site occupancies and Debye–Scherer broadening as input parameters. Input parameters for each simulated pattern are presented in Table 2. The X-ray wavelength was set to 1.54 Å corresponding to Cu Kα1 radiation. The starting model was ZnO in a wurtzite structure.

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**Table 1** Elemental composition of the NPs at key stages in the sulfidation

| Stage               | S/Zn, molar ratio |
|---------------------|-------------------|
| Initial (ZnO)       | 0                 |
| Intermediate (1.99 µmol of S2− added) | 0.27             |
| Final (ZnS)         | 1.06              |
The ZnO NPs, synthesized by a known procedure, had an average size of 4.7 nm (Fig. 1a and b) as found from TEM and a wurtzite structure as shown by their pXRD pattern of the wurtzite ZnO NPs. These lattice parameters, while close to the known parameters of bulk ZnO (a = 3.250 Å and c = 5.204 Å), are marginally smaller, which may be explained by a small degree of compressive strain in the NPs. A peak-dependent Debye–Scherer broadening (FWHM) of 0.79° was applied at a 2θ of 20°, along with a Lorentzian peak profile. The pXRD pattern simulated with these parameters matched the experimental pattern of the initial ZnO NPs, especially in terms of the (002):(101) peak intensity ratio. For sulfur-doped ZnO NCs, the structure was modeled by substitution of a fraction of the O²⁻ by S²⁻ in the 2b Wycoff positions. Four different S/Zn molar ratios of 0.1, 0.11, 0.24, and 0.29 were tested, simulated pXRD patterns of which matched experimental patterns (in terms of the (002):(101) peak intensity ratio) of the NPs at added S²⁻ amount of 0.4, 0.79, 1.99, and 2.78 µmol, respectively.

### Results and discussions

The ZnO NPs, synthesized by a known procedure, had an average size of 4.7 nm (Fig. 1a and b) as found from TEM and a wurtzite structure as shown by their pXRD pattern (Fig. 2a, dark purple curve). The NPs were subject to sulfidation with Na₂S in ethanol at 45 °C. The sulfidation was performed as a titration, wherein molar aliquots of Na₂S were added in a stepwise manner. Upon cumulative addition of 11.9 µmol of Na₂S or S²⁻, the ZnO NPs underwent complete sulfidation. This is evidenced by the complete loss of diffraction peaks of wurtzite ZnO and the appearance of the (111) and (220) reflections of zinc-blende ZnS in the pXRD pattern (Fig. 2a, brown curve). In the elemental analysis (Table 1) of the final-stage NPs, a S/Zn molar of ca. 1 was measured, which supports the complete sulfidation of ZnO NPs to form ZnS. TEM showed ZnS NPs with an average size of 2.7 nm, significantly smaller than the size of the starting ZnO NPs. The smaller grain size of the ZnS is also reflected in the greater Debye–Scherer broadening of the pXRD peaks of the final-stage ZnS NPs (Fig. 2a), which shed light on the manner of sulfidation.

At each step of the titration, the NP colloid was characterized by UV-vis extinction spectrophotometry (Fig. 1e) and pXRD (Fig. 2a), which shed light on the manner of sulfidation. The starting ZnO NPs exhibited an extinction spectrum with an exciton peak around 3.66 eV. This excitonic peak reflects the band-gap of these NPs, which is smaller than the bulk value of 3.37 eV due to the effect of quantum confinement. With the sequential addition of S²⁻ in the range of 0–1.99 µmol, the ZnO excitonic peak shifted to lower energies (Fig. 1f). This shift cannot be attributed to the formation of ZnS. ZnS has a higher band-gap than ZnO, so ZnS formation would have resulted in a shift to higher energies. Moreover, pXRD showed that, in the 0–1.99 µmol range of added S²⁻, the NPs maintain their wurtzite ZnO structure (Fig. 2a) and no diffraction peaks related to ZnS are observed. However, elemental analysis of the NPs obtained by treatment with 1.99 µmol of S²⁻ revealed a S/Zn molar ratio of 0.27 (Table 1). Thus, the ZnO NPs appear to be significantly sulfur-doped. Such sulfur doping can explain the red-shift of the exciton peak. Zinc oxysulfides, ZnOₓSᵧ, with x = 0–0.3 are known to have a lower band gap than ZnO due to the effect of band-bowing. If the sulfur-doping were to be limited to an outer shell of each NP, the resulting intermediate-stage NPs would consist of a shrunk ZnO core surrounded by...
a ZnS shell. Such NPs would exhibit a blue-shifted ZnO exciton peak as compared to the exciton peak of the initial ZnO NPs. On the other hand, we observe a red-shift of the ZnO exciton peak at the early stages in the sulfidation (Fig. 1f, bottom panel), which is consistent with the attainment of an oxysulfide composition. In other words, the sulfur-doping extends across the NP lattice.

Further confirmation of and insight into the sulfur-doping of the ZnO NPs at the early stages of the sulfidation (0–2.78 μmol of S\textsubscript{2}/C\textsubscript{0}) is obtained from a closer analysis of the pXRD findings. We performed pXRD simulations (Fig. 2d) of sulfur-doped ZnO lattices, where a fraction of the O\textsuperscript{2–} anions were replaced by S\textsuperscript{2–}, without any other modification of the wurtzite structure. The simulated pXRD patterns of sulfur-doped ZnO resemble the simulated pattern for wurtzite ZnO (Fig. 2d). However, there is one difference: the ratio of the \{002\}:\{111\} peak intensity is higher for the sulfur-doped ZnO NPs as compared to the undoped ZnO NPs. Larger the S/Zn molar ratio (Fig. 2d), greater is the ratio of the \{002\}:\{111\} peak intensity. This computed trend matches with the trend observed in the experimental pXRD, as shown in Fig. 2b. Thus, the pXRD analysis confirms that at the early stages of the sulfidation, the ZnO NPs undergo substitutional doping by sulfur. Simulations predict that NPs subject to 1.99 μmol S\textsuperscript{2–} have a S/Zn molar ratio of 0.24, which is close to the elemental analysis findings (Table 1).

At the point of 2.78 μmol added S\textsuperscript{2–}, a broad absorption peak emerged at higher energies, i.e., 4.6 eV. This peak can be attributed to newly formed ZnS NPs. After all, ZnS is known to have a higher band-gap than ZnO.\textsuperscript{44} Upon further addition of S\textsuperscript{2–}, the newly emerged excitonic peak increased in absorbance and shifted to lower energies (Fig. 1e and f). Alongside, the ZnO exciton peak decreased in strength until it was fully extinguished. These spectral trends can be explained by the following manner of sulfidation.

A small ZnS domain nucleates from the heavily sulfur-doped ZnO NPs. The considerably higher excitonic peak energy of 4.6 eV relative to the bulk ZnO band-gap\textsuperscript{35} of 3.72 eV suggests that the nucleated domain is ultrasmall. As more S\textsuperscript{2–} becomes available, the ZnS domains grow further, which is manifested in the red-shift of the ZnS excitonic peak and increase in its absorbance (Fig. 1e and f). Concomitantly, the ZnO domains, which serve as the source of Zn, shrink in volume, which is reflected in a small blue-shift of the ZnO excitonic peak along with a decrease in its absorbance beyond 3.57 μmol added S\textsuperscript{2–}. Eventually, the ZnO excitonic peak was fully extinguished. The final ZnS NPs exhibited a spectrum with a single excitonic peak at 3.94 eV, corresponding to small NPs.

The pXRD results provide further support to the above-described mechanism of sulfidation in the post-doping stages. At 4.37 μmol of added S\textsuperscript{2–}, a broad peak appeared at the position corresponding to the major (111) reflection of zincblende ZnS, which serves as a structural indicator of ZnS nucleation. This diffraction peak grew in relative intensity and also narrowed with increasing addition of S\textsuperscript{2–}, which would be consistent with a growth in ZnS domains. Alongside, with increasing addition of S\textsuperscript{2–}, the wurtzite ZnO diffraction peaks became...
gradually weaker in relative intensity, until they were fully extinguished. The final pXRD pattern is indicative of NPs in a single ZnS phase, as also confirmed by the elemental analysis (Table 1). The final ZnS NPs appear to have a broader size dispersion (Fig. 1d, standard deviation of 22%) as compared to that of the initial ZnO NPs (Fig. 1b, standard deviation of 11%). The final NPs are formed by sulfur-doping of ZnO NPs followed by nucleation and growth of separate ZnS domains, a process expected to be replete with inherent heterogeneities.

**Conclusion**

The scheme in Fig. 3 summarizes the mechanism of sulfidation that is drawn from the results taken as a whole. The sulfidation...
of ZnO NPs is preceded by a stage where the NPs undergo substitutional doping by $S^{2-}$. The wurtzite ZnO lattice remains otherwise unmodified in its structure. Above a concentration of ca. 30 mol% $S^{2-}$ dopants, ZnS nucleates from the ZnO. The threshold concentration probably corresponds to the solubility limit of $S^{2-}$ in ZnO. As more $S^{2-}$ becomes available, ZnS domains grow by supply of $Zn^{2+}$ from ZnO. The $O^{2-}$ diffuses into solution. Thus, the complete phase transformation of the NPs from ZnO to ZnS cannot be considered simply as a topotactic exchange of anions in analogy to cation exchange reactions.\unskip\textsuperscript{16–47} Rather the post-doping stage sulfidation is more akin to a dissolution-recrystallization process known in mineralogy,\unskip\textsuperscript{18} although the reprecipitation (nucleation-growth of ZnS) may occur in interfacial contact with the sulfur-doped ZnO NPs. The ZnS NPs formed from the nucleation-growth process share neither the crystallographic structure nor the morphology or size of the initial ZnO NPs. In topotactic sulfidation, the differences between the equilibrium unit cells of ZnO and ZnS would result in lattice strain and stress; in sulfidation occurring via the reprecipitation-like mechanism found here, such stresses and any resulting thermodynamic or kinetic bottlenecks in the solid-state transformation would be relieved. This mechanism of sulfidation must be taken into consideration when developing small ZnO NP-based sorbents for uptake of sulfur compounds from fuels. The major restructuring involved in going from the oxide to the sulfide can have major implications for the engineering design and operation of NP-based sorbent columns.

**Conflicts of interest**

P. K. J. is an inventor on two patents on nanostructured ZnO sorbents and has served in the past as a scientific consultant on nanostructured ZnO for desulfurization technologies.

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