

## **Hetero-Epitaxial Anion Exchange Yields Single-Crystalline Hollow Nanoparticles**

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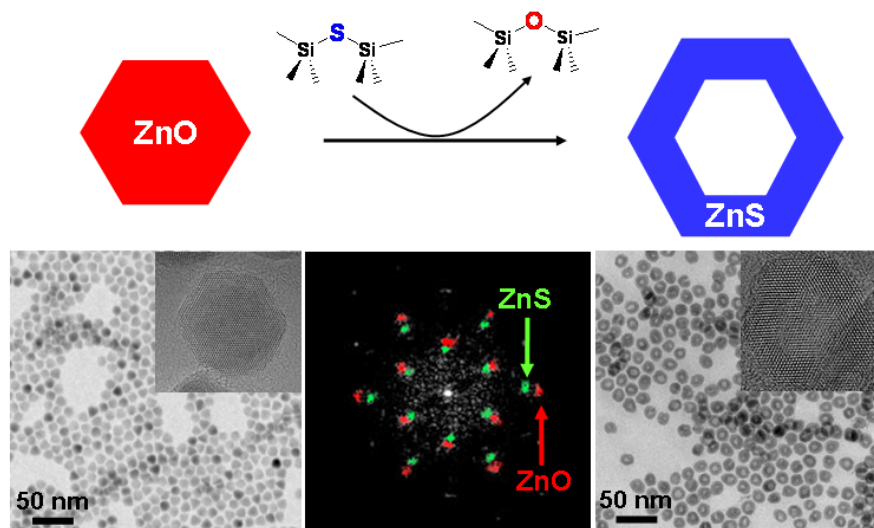
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**<Abstract for web publication>**

Anion exchange with S was performed on ZnO colloidal nanoparticles. The resulting hollow ZnS nanoparticles are crystal whose shape is dictated by the initial ZnO. Crystallographic and elemental analysis provides insight into the mechanism of the anion exchange.

**<TOC>**



In recent years, chemical transformation of inorganic solids has emerged as an attractive approach for nanostructure synthesis.<sup>1,2</sup> In addition to its utility in generating various nanoparticle materials - ranging from metal to semiconductor and to magnetic nanoparticles, this method has enabled the fabrication of new types of nanostructures with high compositional and structural complexity. For example, thermodynamically unfavorable hollow particles have been synthesized using chemical transformations, by exploiting the nanoscale Kirkendall effect<sup>2-5</sup> and non-equivalent stoichiometry<sup>6-8</sup> between solid ‘precursor’ nanoparticles and the incoming molecular species. Moreover, ion exchange of inorganic solids has proven an effective tool for chemical transformation of nanoparticles.<sup>9-11</sup> For example, we recently reported that the addition of cations into a binary semiconductor nanoparticle solution induces conversion of the initial nanoparticle into another chemical species.<sup>9,12,13</sup> The resulting nanoparticles are both highly crystalline and are characterized by size and shape monodispersity. Nanoscale heterojunctions<sup>12</sup> and ‘barcodes’<sup>13</sup> could further be fabricated by varying the ion concentration.

In the examples mentioned above, rapid cation motion strongly influences the final composition and geometry. In the present work, we examine a case of anion rather

than cation exchange. The most prominent example of anion exchange in a nanoscale system is for the ZnO/ZnS system. Schaak *et al.* have recently examined the case as well as Dloczik and Konenkamp.<sup>10,14</sup> We study the anion exchange of ZnO nanoparticles with molecular sulfur precursors to form high quality ZnS nanoparticles. Although there have been reports on anion exchange reactions of binary compound semiconductor nanoparticles (including Cu<sub>7</sub>S<sub>4</sub>,<sup>15</sup> ZnSe,<sup>16</sup> and AlN<sup>17</sup>), our study can be differentiated from previous research in the following regards: *i*) We find that the anion exchange of ZnO with sulfur molecules is accompanied by the nanoscale Kirkendall effect, yielding hollow structures rather than solid nanoparticles. Interestingly, the overall transformed morphology mimics the initial nanoparticle shape. *ii*) The resulting ZnS nanoparticles are single crystalline and preserve the crystal symmetry and orientation of the initial ZnO nanoparticles. Note that chemical transformation of nanoparticles accompanied by the Kirkendall effect often results in poly-crystalline nanoparticle products; single-crystalline hollow structures are rarely obtained.<sup>10,18,19</sup> In a recent study, intermetallic hollow nanorods including Ni<sub>3</sub>Sn<sub>4</sub> and PtSn have been produced by using Sn nanoparticles as a template.<sup>20</sup> Highly crystalline ZnAl<sub>2</sub>O<sub>4</sub> nanotubes were also fabricated *via* a thermal annealing process of ZnO-Al<sub>2</sub>O<sub>3</sub> coaxial nanowires.<sup>21</sup> However, this method required relatively high temperatures (~700°C) and

the fabricated nanotubes still exhibited crystallographically random orientations and grain boundaries. *iii*) We use both crystallographic and compositional analysis of partially-converted ZnO@ZnS yolk-shell particles to understand the shape and crystallographic retention properties of our ZnS hollow nanoparticles. This analysis yields further insight into the mechanisms of the chemical transformations.

Anion exchange of ZnO nanoparticles was performed using the following procedure: single-crystalline, hexagonal pyramid shaped ZnO nanoparticles (the diagonal distance of the hexagonal surface is 14 nm) (Figure 1a, c) were mixed with 5g of trioctylphosphine oxide under Ar gas and heated to 235°C. 26mg of hexamethyldisialthiane in 2g of trioctylphosphine was added drop-wise for 240 min. After 20 min, the reaction flask was cooled to room temperature, washed with acetone, and centrifuged several times to generate nanoparticles in white precipitate form. Additional details can be found in the Supporting Information.

When ion exchange of binary semiconductors is initiated on the surface, further exchange reaction requires diffusion of ionic reactants. Two possible scenarios may be identified: *i*) New ions diffuse inward to the parent nanoparticle continuously,

resulting in a directional migration of the reaction interface toward the core. Cation exchange reaction is such an example. *ii*) Inward ion diffusion is limited and core species diffuse outward, generating a void space inside the nanoparticle. Interestingly, unlike cation exchange reactions, the anion exchange of ZnO nanoparticles with molecular sulfur precursors follows the latter case, described in detail below.

Figure 1b shows a TEM image of the ZnS nanoparticles obtained. Similar to the parent ZnO nanoparticles, ZnS nanoparticles exhibit hexagonal pyramid geometry (see Supporting Information), but each nanoparticle has a single pore in its interior. So far, we have seen many cases where cation diffusion is much faster than anion diffusion.<sup>3,6,9,12,13</sup> The present case is also of this type where  $\text{Zn}^{2+}$  cations diffuse faster than incoming  $\text{S}^{2-}$ , so that even though anion exchange is taking place, it is the cation diffusion that controls the final morphology. In addition to fast diffusion of  $\text{Zn}^{2+}$ , faster diffusion of  $\text{O}^{2-}$  than incoming  $\text{S}^{2-}$  leads to the formation of a hollow structure from the anion exchange reaction. High-resolution transmission electron microscopy (TEM) and energy filtered TEM (Figure 1, see Supporting Information) experiments support the complete conversion of the initial nanoparticles into ZnS hollow nanoparticles. Most notably, the ZnS nanoparticle shells are single-crystalline wurtzite structures, identical

to the crystal structure of the initial ZnO nanoparticles.

Structural analyses of partially exchanged nanoparticles (ZnO@ZnS) provide important clues to the origin of the shape and crystallographic similarities of the ZnS nanoparticles with the initial ZnO. These partially-exchanged nanoparticles have voids between ZnO core and ZnS shell (Figure 2a). In addition, some nanoparticles have bridges inter-connecting the ZnO core with the outer ZnS. These bridges serve as transport pathways for the ZnO core (Figure 2a, inset).<sup>22</sup> HRTEM images (Figure 2b) indicate two sets of epitaxially aligned hexagonal fringes at the core and shell regions, corresponding to ZnO and ZnS lattice structures, respectively. Such hetero-epitaxial features are clearly confirmed by two well-aligned sets of hexagonal spots in the fast-Fourier transform (FFT) of the high resolution TEM image (Figure 2c). In addition, the reconstructed image from both sets of spots confirms epitaxially grown ZnO@ZnS yolk-shell particles (Figure 2d). These observations indicate that formation of single-crystalline ZnS is possible through hetero-epitaxial ZnO@ZnS intermediates during the anion exchange. It is noteworthy that bulk hetero-epitaxy between these two materials is not favored because of the high strain energy at the interface due to relatively large lattice mismatches.

We performed additional composition analyses of the ZnO@ZnS intermediates using energy filtered TEM (EF-TEM) analyses with oxygen and sulfur windows. The results provide insight about the release of lattice strain during the hetero-epitaxial anion exchange reaction. Color mapped EF-TEM images (Figure 3b) of the bright field TEM image (Figure 3a) and line profiles (Figure 3c) clearly show the presence of O and S at the core and shell, respectively. Interestingly, the oxygen signal also appears in the shell region. This observation supports the hypothesis that oxygen diffuses out of the core nanoparticles and is accumulated in the shell region before the anion exchange with sulfur precursors. Consistently, as the anion exchange reaction proceeds, a gradual shift of initial the ZnO x-ray diffraction (XRD) peaks to lower angles supports the presence of mixed  $\text{ZnO}_{1-x}\text{S}_x$  intermediate species (See also Supporting Information).

In fact, once the ZnS shell forms, outward oxygen diffusion spontaneously proceeds without the help of further anion exchange. Figure 4a shows a TEM image of nanoparticles obtained after thermal treatment of partially converted ZnO@ZnS without sulfur precursors. Core ZnO nanoparticles have disappeared in the TEM and EF-TEM



(Figure 4b) images, but oxygen signals now appear in the shell region. High resolution TEM images (Figure 4c) and their corresponding FFTs (blue spots in Figure 4d) indicate that the shell now forms  $\text{ZnO}_x\text{S}_{1-x}$  alloys as a result of ZnO diffusion into ZnS shells.

From our structural and composition analyses of partially and fully converted nanoparticles, we propose the following anion exchange reaction mechanism: initially, thin layers of ZnS grow epitaxially onto the ZnO core through the surface anion exchange reaction, which generate a highly strained interface between the ZnO core and the ZnS shell. To release this interface energy, the ZnO core spontaneously diffuses into the ZnS shell, which is finally exchanged with sulfur precursors at the outer shell surface, forming fully converted ZnS hollow nanoparticles.

In summary, we have demonstrated anion exchange of binary ZnO semiconductor nanoparticles. Unlike cation exchange, the anion exchange is accompanied by the nanoscale Kirkendall effect, yielding hollow nanoparticles. Parent-particle shape, single crystallinity, and orientation of the transformed particles are completely preserved through this hetero-epitaxial anion exchange reaction. Our anion

exchange can be extended to other binary or tertiary nanoparticles, to produce high quality, single crystalline hollow nanoparticles.

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**Supporting Information Available:** Experimental conditions, characterization methods, tilting TEM images, EFTEM images of ZnS, original images of figures discussed above, reconstruction process of FFT, and calculated alloy composition after thermal treatment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Figure 1. TEM images of initial ZnO nanoparticles (a) and ZnS hollow nanoparticles obtained (b) after anion exchange with HRTEM images (b, d, respectively). (e) XRD patterns before and after anion exchange.

Figure 2. (a) TEM image of partially exchanged ZnO@ZnS yolk shell nanoparticles with a magnified inset. (b) HRTEM image of a single ZnO@ZnS nanoparticle.

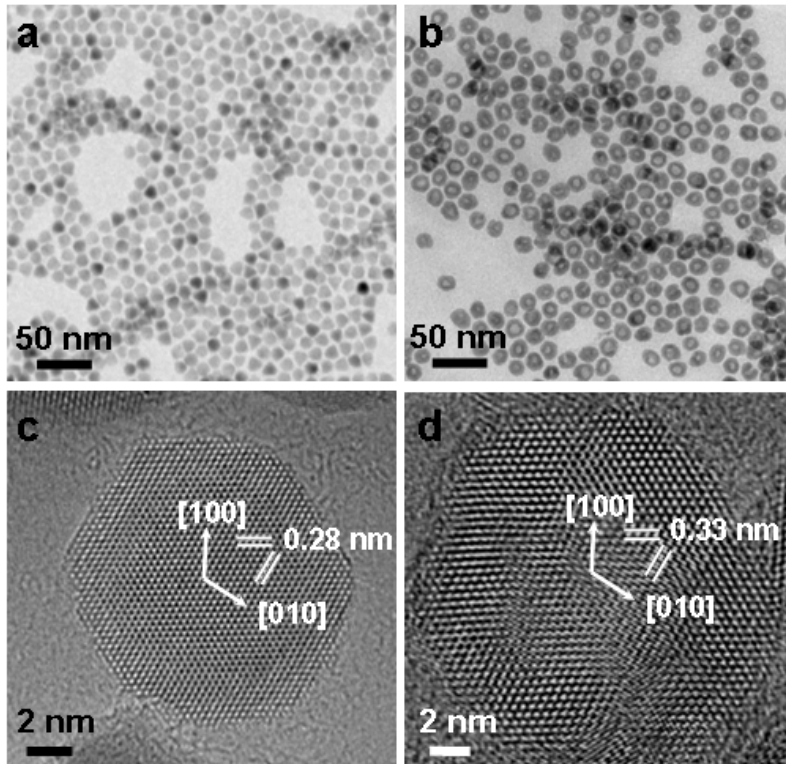
(c) FFT image of (b). (d) Reconstructed crystal structure from (c). (red: ZnO, green: ZnS, see Supporting Information for original images)

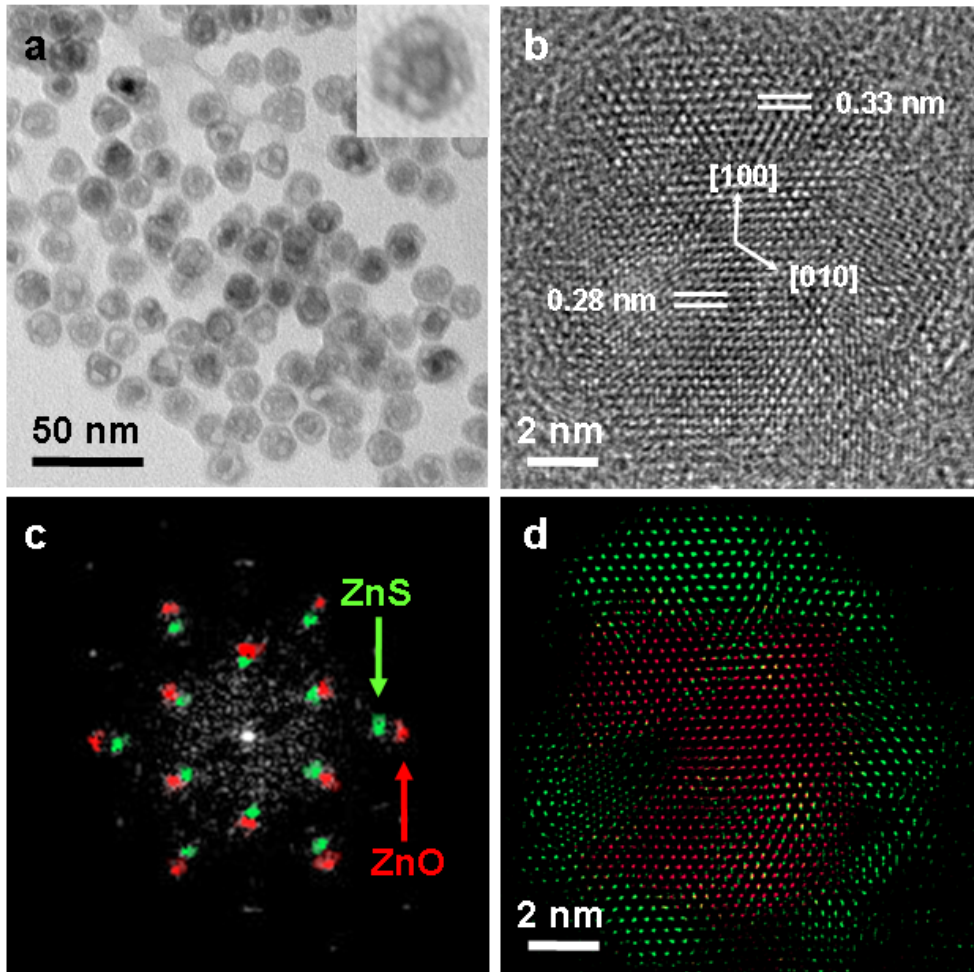
Figure 3. TEM image (a) and EF-TEM image (b) for the partially exchanged ZnO@ZnS nanoparticles (red: ZnO, green: ZnS, see Supporting Information for original images). (c) Oxygen and sulfur line profiles along the cross-section in (b). (d) XRD patterns of different stages of anion exchange reaction from initial ZnO (red) to final ZnS hollow (green) with the magnified and normalized inset from  $2\theta = 38.5^\circ$  to  $44.5^\circ$ .

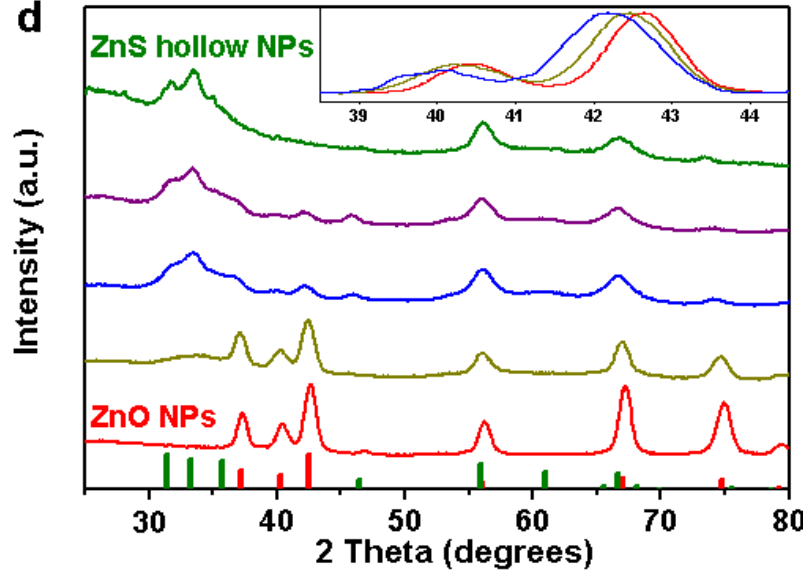
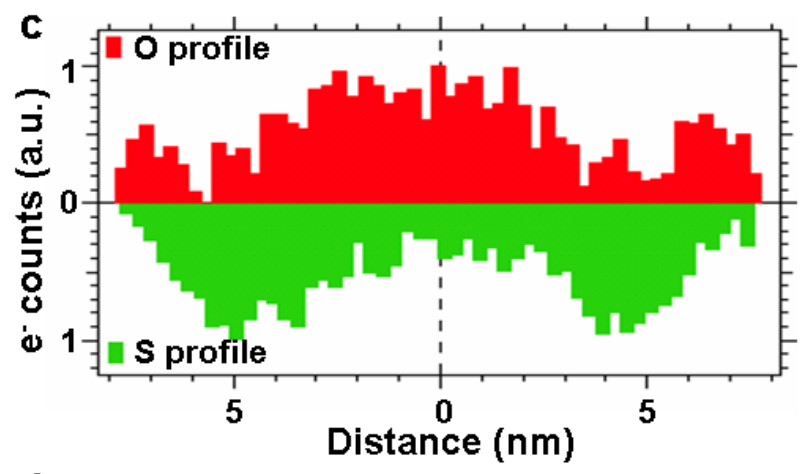
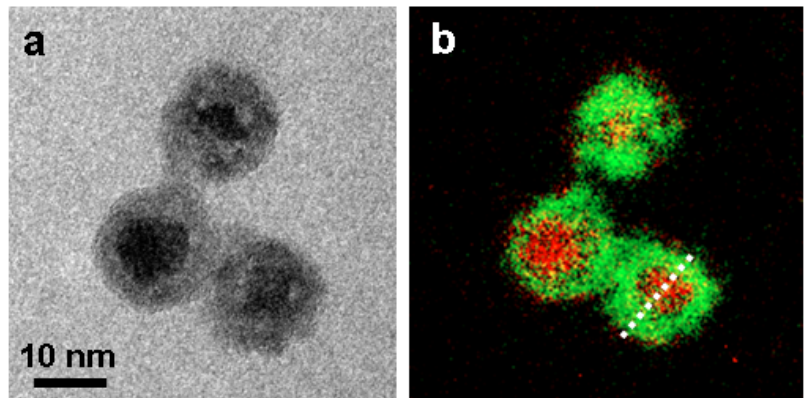
Figure 4. TEM image (a), EF-TEM image (b) with a magnified inset, and HRTEM image (c) for thermally annealed ZnO@ZnS nanoparticles. (d) FFT image overlaid on Figure 2(c). (red: ZnO, green: ZnS, blue: ZnO<sub>x</sub>S<sub>1-x</sub>, see Supporting Information for original images)

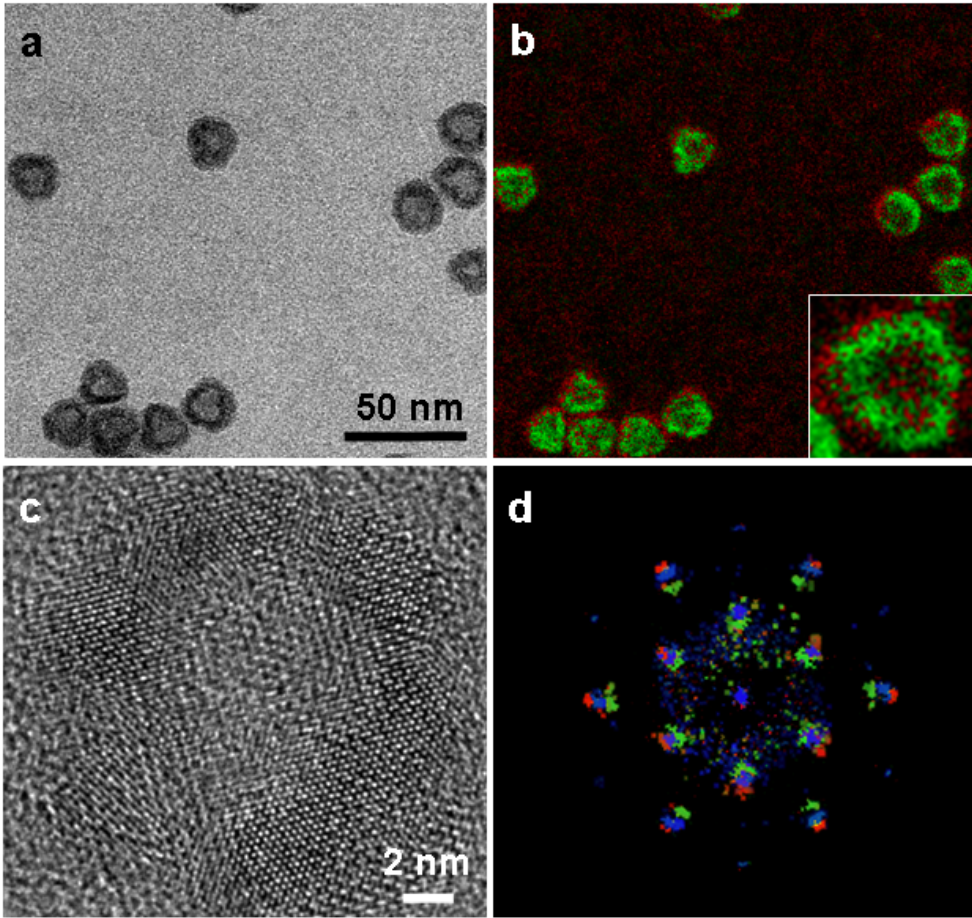
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