

Ambient Dependent Formation of Zn_2SiO_4 and SiO_2 from Core-shell $\text{ZnO}@ \text{SiO}_2$

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Hollow ZnO-based ternary phases nanostructures have gained popularity in various domains such as luminescent devices and selective metal ion adsorption. Literature reports usually demonstrate their fabrication from a $\text{ZnO}@ \text{SiO}_2$ core-shell structure prepared by costly non-scalable physical processes [1-3]. Moreover, owing to almost stationary nature of SiO_2 in terms of diffusion, very often they use precious metal catalyst like Au nanoparticles, which facilitate the interfacial diffusion in $\text{ZnO}@ \text{SiO}_2$ structure by melting at a low temperature [3].

Herein, we report a scalable, noble-metal free facile synthesis of Zn_2SiO_4 nanotubes using a two-step process consisting of a wet-chemical benchtop synthesis of core-shell $\text{ZnO}@ \text{SiO}_2$ nanorods followed by thermal annealing [4]. Owing to the porous nature of the wet-chemically fabricated silica shell (Figure 1 (a)), hollow silicate phase was formed at temperatures much lower than the ones reported in the literature (Figure 1 (b) and (c)).

Furthermore, to probe the course of the Kirkendall diffusion, we have observed void nucleation and growth at the $\text{ZnO}-\text{SiO}_2$ interface through *in-situ* heating experiments in transmission electron microscope (TEM), as shown in Figure 2. The ex-situ experiments carried out at different temperatures are also in agreement with the in-situ observations. As can be seen from Figure 2 (g), at 650° C, a diffraction spot corresponding to the willemite Zn_2SiO_4 is observed, indicating the nucleation of the silicate phase. Also, upon heating upto 800° C, the void growth is observed, as shown in Figure 2 (e-g). Figure 2 (h) shows high resolution transmission electron (HRTEM) image showing a large void grown in course of the Kirkendall diffusion. However, at very high temperatures, owing to the beam damage of silicate phase, the in-situ formation of the nanotube could not be observed.

Interestingly, annealing the $\text{ZnO}@ \text{SiO}_2$ precursor under reducing atmosphere leads to the formation of SiO_2 nanotubes (95% Ar + 5% H_2). This is intriguing because such hollow structure formation means leaching of Zn_2SiO_4 (formed by heating of $\text{ZnO}@ \text{SiO}_2$ structure) or ZnO from the core-shell precursor. Interestingly, both of these processes are thermodynamically unfavourable in bulk. Also, thorough scanning transmission electron microscopic studies coupled with energy dispersive spectroscopy (STEM-EDS) and TEM studies with heating for lesser time show that there is no formation of silicate indicating that ZnO is etched out by H_2 in the reducing gas. In order to prove the accessibility of the ZnO through SiO_2 shell, we conducted control experiments of etching in acid solution, thus confirming the porosity and accessibility of ZnO for evaporation.

Both the hollow structures, *viz.* silica and silicate nanotubes, exhibit good uranium adsorption at different ranges of pH making them possible candidates for nuclear waste management. The adsorption mechanism is largely driven by surface charge of the material, which, in turn depends on the pH of the solution [5].

References:

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[5] The authors acknowledge the financial support from Department of Science and Technology and also the Advanced Facility for Microscopy and Microanalysis, Indian Institute of Science, Bangalore, India for providing all the TEM facilities.

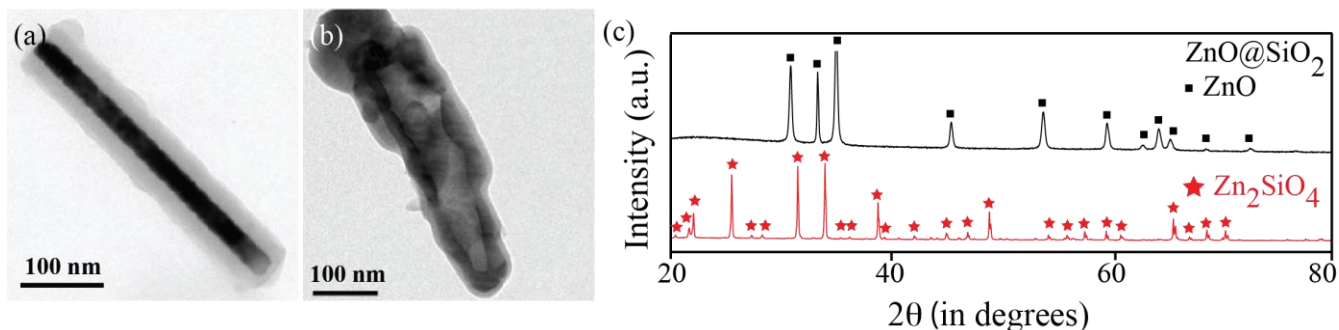


Figure 1. (a) Core-shell $\text{ZnO}@SiO_2$ nanorod precursor; (b) Formed Zn_2SiO_4 nanotube upon annealing the precursor in air; (c) X-ray diffraction pattern of the precursor and final silicate phase.

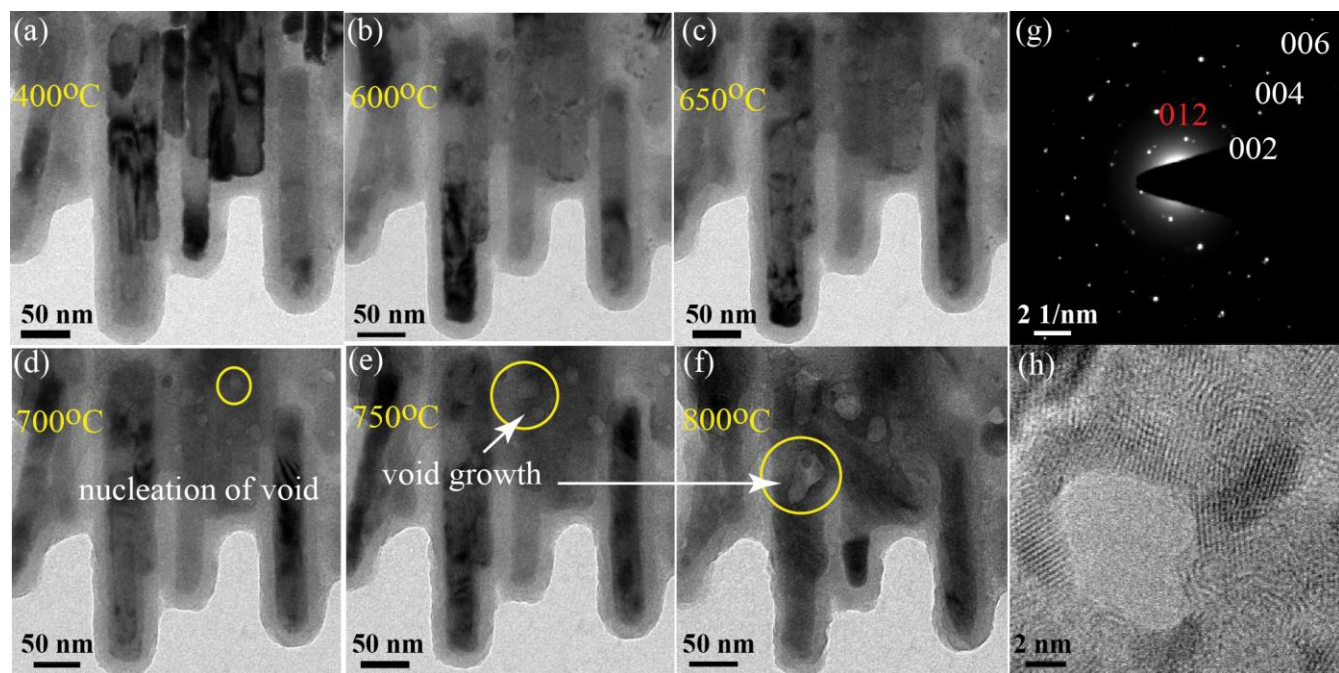


Figure 2. (a-f) are results of in-situ heating showing the hollow structure formation; (g) is selected area diffraction pattern of intermediate showing mixed phase of silicate (marked in red) and ZnO; (h) HRTEM showing Kirkendall void.