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Sulfidation-Oxidation Cycling of a H_2S Adsorbing Hollow Sphere Array

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Hydrogen sulfide (H_2S) is a toxic, corrosive, and flammable gas, occurring in various hydrocarbon sources such as natural gas and crude petroleum. The main industrial source of H_2S is in oil refineries, where gas streams are desulfurized upon treatment with hydrogen to create automobile and heating fuels with low sulfur content. Desulfurization process generates H_2S, which is a major contributor to acid rains, if released in to the atmosphere [1]. Therefore, adsorbents that can selectively remove H_2S from gaseous streams and can be re-used multiple times while maintaining their performance are needed. Herein, we report a novel Zn-Ce-Al hollow-sphere array and investigate the morphological changes by ex-situ HAADF-STEM imaging of the material (i) before exposure to H_2S, (ii) after exposure to H_2S and (iii) upon sequential oxidation.

Atomic-resolution HAADF-STEM imaging was performed at 200 kV with an incident semi-convergent angle of 21.4 mrad and detector collection angles of 58.5–200 mrad on an FEI Titan G2 60–300 STEM. Energy dispersive X-ray (EDX) spectrum imaging was performed in STEM operating mode using a Super-X system at 80 kV and 10-30 pA beam current with 24 mrad convergence angle.

Unit cell of the array was determined by imaging along three perpendicular directions and a three-dimensional model was created based on the observations (Figure 1a,b). This array was formed by inverse templating of colloidal silica spheres to yield hollow spheres (~100 nm diameter) connected by smaller nodes (~50 nm diameter) centered at the octahedral and tetrahedral voids of a FCC lattice, respectively. Elemental mapping showed that Zn, Ce and Al were distributed uniformly in a sphere as their respective oxides (Figure 1c). Atomic-resolution HAADF-STEM imaging further confirmed the presence of 5-10 nm sized ZnO and CeO_2 nano-crystallites (Figure 1d-f). This hollow-sphere array was then exposed to a stream of H_2S-containing gas flowing at 450 °C and 1 atm. STEM-EDX maps revealed that zinc oxide converts to zinc sulfides and migrates to form clusters upon sulfidation, while CeO_2 and Al_2O_3 maintain the structural integrity of the hollow sphere, thereby preventing it from collapsing (Figure 1a,b,d,e). Regeneration of the adsorbent resulted in removal of sulfur and formation of oxides, while Zn showed no further aggregation (Figure 1c,f). Conversion to sulfides and regeneration of oxides was corroborated by x-ray diffraction data (Figure 1g). Furthermore, we will discuss in detail the formation of hollow-sphere array, its sulfur-removal performance and the effect of electron beam on distribution of elements [3].

References:

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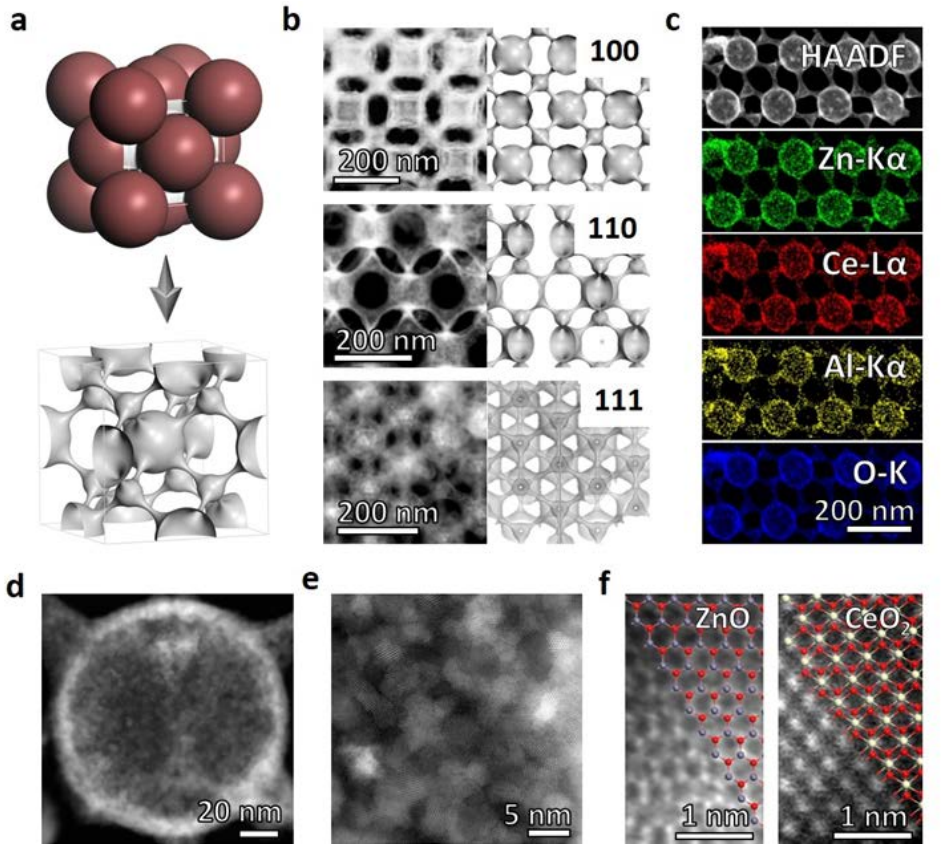

Figure 1 | a, FCC packing of colloidal silica spheres shown in brown color and the resulting hollow sphere morphology in gray formed by removal of silica spheres upon heating. **b,** HAADF-STEM images of three mutually perpendicular zone axes are shown with the corresponding models overlaid. **c**, STEM-EDX maps showing uniform distribution of Zn, Ce, Al and O across the array. **d-e**, HAADF-STEM images of a single hollow-sphere showing the individual grains of 5-10 nm size. **f**, Atomic-resolution images of ZnO and CeO_2 from the sphere shown in d, with the structural models overlaid.

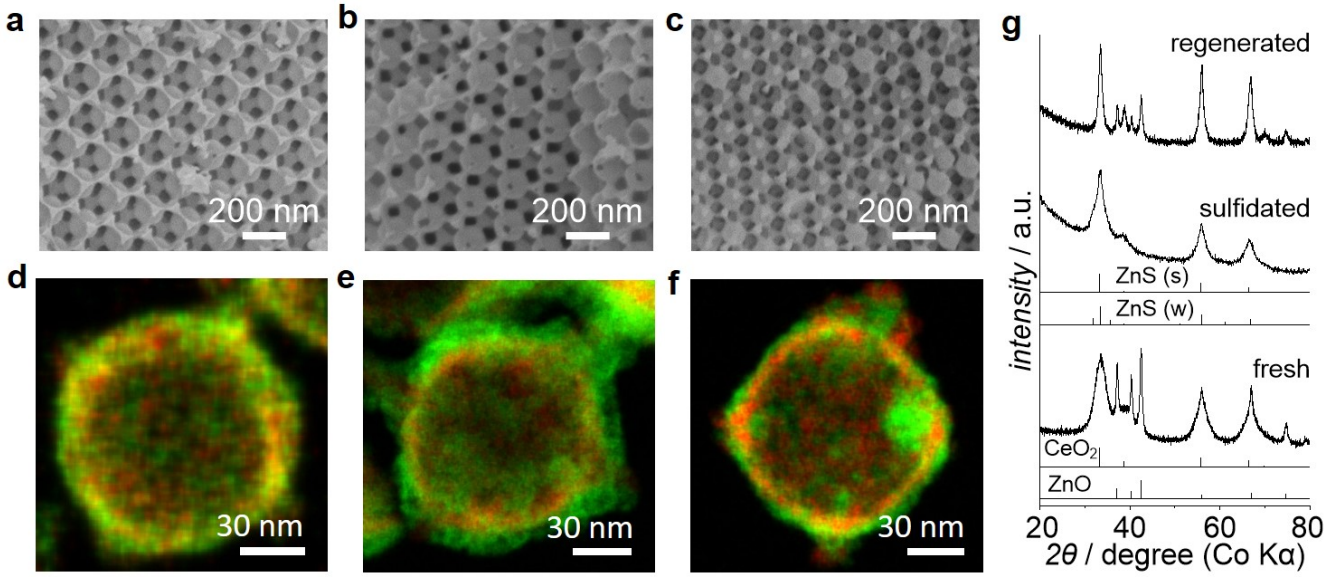

Figure 2 | Morphology and microstructure evolution of the hollow sphere arrays during sulfidation and regeneration. a- c, SEM images of the hollow sphere arrays before sulfidation, after sulfidation and after regeneration, respectively. **d-f,** STEM-EDX elemental maps showing the locations of the zinc and cerium species in a single hollow sphere in the hollow sphere of the arrays before sulfidation, after sulfidation and after regeneration, respectively. **g**, XRD patterns of the fresh, sulfidated, and regenerated hollow sphere arrays.

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