Au/SnO_2 core–shell structure nanoparticles synthesized by precipitation method and microwave–assisted hydrothermal synthesis method

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Carbon monoxide, CO, is highly toxic gas and notorious as the “invisible silent killer” since its colorless, tasteless and odorless nature. Sensors to detect CO have therefore been desired for the purpose of human safeties [1]. Transition–metal oxide semiconductors have been commercially available as the CO gas sensors because of their active sites to adsorb gas molecules and catalytic reactions [2]. In particular, tin oxide, SnO_2, a post–transition metal oxide and n–type semiconductor with relatively a wide band gap (3.62 eV), is recognized as a prominent sensing material due to its chemical stability, its high electron mobility, and the variation of donor density [3]. It has also been reported by several authors that the performances of gas sensors can be enhanced by increasing the specific surface area by way of achieving NPs and by incorporation of noble metals, such as platinum or gold [4]. These noble metals can support the formation of SnO_2 NPs and arrest their growth at high temperatures, which could therefore be a promising method to decrease the operating temperature of CO or increase the response transient to CO gas sensor [2].

Gold was selected as the core material in this study for CO oxidation under mild conditions and for the ease of the synthesis of uniform particles. Au/SnO_2 core–shell NPs were synthesized by a precipitation method (sample A) and by a conventional hydrothermal synthesis method (sample B), reported elsewhere [4].

The samples were dispersed in toluene by ultra–sonication and then loaded on formvar coated TEM copper grids. The structural and morphological information were observed by a TEM (TECNAI–F20, FEI, Eindhoven, The Netherlands) with a scanning–TEM high angle annular dark–field (STEM–HAADF) detector and a specially designed high–tilt holder (E.A. Fischione Instruments Inc., USA) for electron tomography. Tilt series of STEM–HAADF images were acquired from –70° to +70° recorded at every 2° giving a total of 71 images. The exposure time of individual STEM image acquisition was kept to a minimum (15 s) to reduce the irradiation damage. Once the acquisition of the tilt series was completed, the data were transferred to a PC for alignment and 3D reconstruction. Images were spatially aligned by a cross correlation algorithm using Inspect3D software (FEI, Einthoven), and 3D reconstructions were achieved using a simulated iterative reconstruction technique of consecutive 2D slices. Visualization was performed using AVIZO Fire 6.2 (Visualization Sciences Group).

Both samples show typical core–shell structures with their sizes ranging between 30 and 50 nm, as shown in Fig. 1(a) and 1(d), where large Au NPs are located at the center as core and densely decorated by SnO_2 NPs as shell. The thicknesses of SnO_2–shell layers were measured as 15.3 nm and 10.2 nm from sample A and B, respectively. The average grain sizes of SnO_2 NPs of sample A and sample B are also measured as 5.2 nm and 8.3 nm, respectively.

Reconstructed 3D voxels of both samples represent the presences of SnO_2–shell layers formed by aggregated SnO_2 NPs on Au–cores, shown in Fig. 1(b) and (c) of sample A and Fig. 1(e) and (f) of sample B, in which the contrast was optimized for viewing of SnO_2–shell layers. The reconstructed voxel of sample A, shown in Fig. 1(b), strongly suggests that Au NPs were densely covered by thick SnO_2–shell layers consist of small SnO_2 NPs. In addition, pores can be seen within SnO_2–shell layers from the sliced images with Au core of the similar field of view. On the other hand, the reconstructed voxel of sample B, shown in Fig. 1(e) and (f), indicates the high porosity of SnO_2–shell layers and the exposure of surface of Au NPs, as can be seen from sliced images with Au core. Both the porosity and the exposures of the surface of Au NPs was found enhancing the CO responses,

greatly.

References

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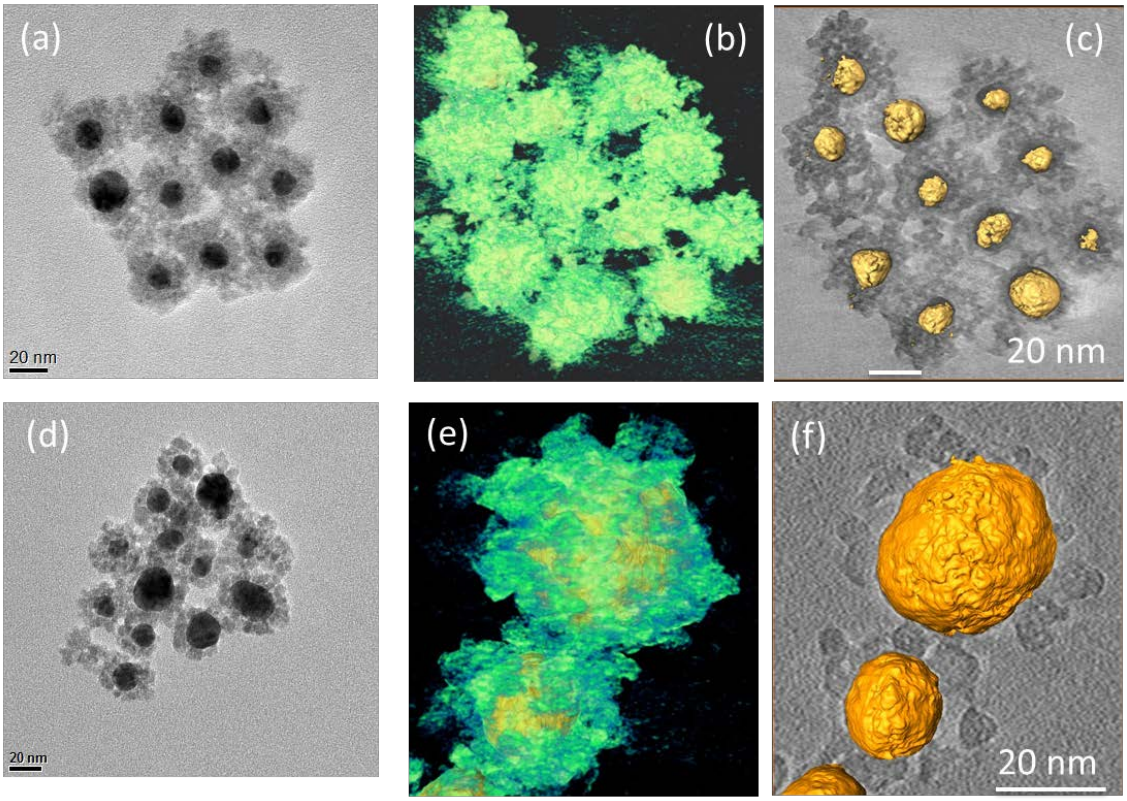

Figure 1*. (a) and (d) show a bright–field low-magnified TEM image of sample A, and sample B, respectively. 3D reconstructed volumes of sample A is shown in (b) and (c), and, those of sample B in (e) and (f), respectively.*