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Structural and Morphological Characterization of Catalytically-Active Co_3O_4 Powders

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Metal oxide micro- and nano-structures have received considerable attention due to their potential for applications in the field of catalysis, separations, microelectronic devices and biomaterial engineering [1,2]. In the recent years, these nanostructures have been synthesized using a variety of methods including thermal reduction, thermal oxidation, oriented aggregation, and self-assembly of building blocks through hydrophobic interactions, and template-assisted processes [3]. Recently, Richards and co-workers [4] developed a simple, template-free, and reliable synthetic method for producing hierarchically self-assembled architectures with tailored chemical compositions and controlled morphologies. Using this approach, a variety of transition-metal oxide (ZnO, TiO_2, NiO, and Cr_2O_3) powders have been synthesized. Here, we report the structural and morphological characterization of Co_3O_4 powders synthesized using this template-free process.

In our experiments, cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) was first dissolved in methanol, the solution transferred to an autoclave with 75000 Torr Ar, kept at ~260 ^oC for 5 h. After the supercritical fluid drying (via releasing the pressure on the autoclave), a grey colored powder was collected and subsequently calcined. Here, we examine, using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the morphologies and microstructures of as-synthesized powders and two sets of samples obtained one after calcination at 350 ^oC for 3 h and the other at 500 ^oC for 2 h. In addition, we also carried out *in situ* TEM observations of the calcination process. SEM images were obtained using a field-emission FEI Dual-Beam Nova Nano 600 operated at 10 kV. TEM images and selected area electron diffraction (SAED) patterns were acquired using both JEOL JEM-100CX, operated at 100 kV and a FEI S/TEM Titan operated at 300 kV. High-resolution TEM images and SAED patterns were processed using ImageJ software [5].

SEM images in Figures 1A and 1B show that the synthesized powders appear spherical, fully dispersed, and uniform in size and the microspheres are composed of sheets that are several nm thick. Figs. 1C and 1D show SEM images obtained after calcination at 500 ^oC for 2 hours. The overall morphology and the particle size do not change significantly, however, the sheets are now composed of pores. TEM and SAED analyses shown in Figs. 2 and 3 indicate that the sheets are single-crystalline, exhibit cubic Fd3m (227) (a=8.084 Å) spinel structure, and are oriented perpendicular to <111>. The crystal structure, orientation, do not change with calcination and we find that the pores are facetted with edges oriented mostly perpendicular to <112>.

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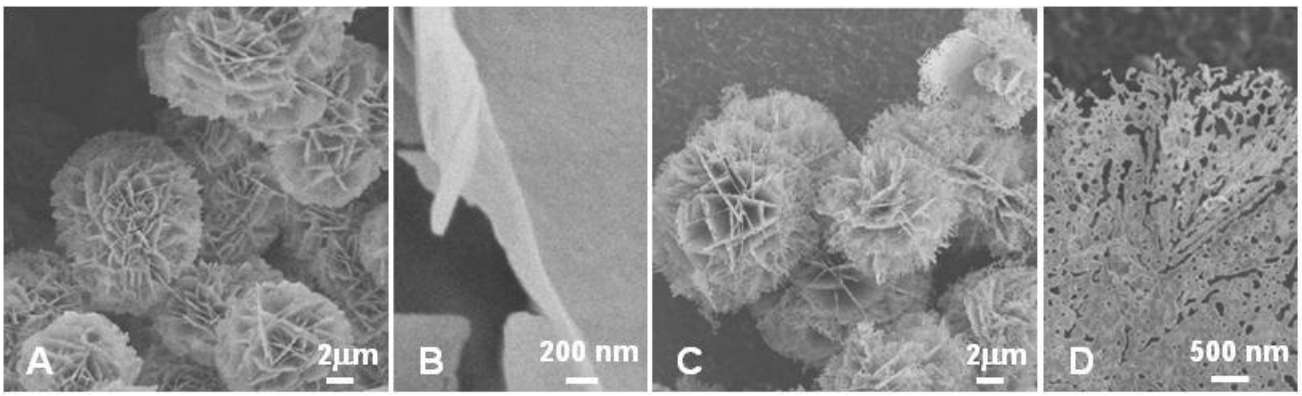

Figure 1. SEM images of the Co_3O_4 powders acquired at different magnifications from: (A, B) the as-synthesized samples and (C, D) after calcination at 500° C for 2 hours.

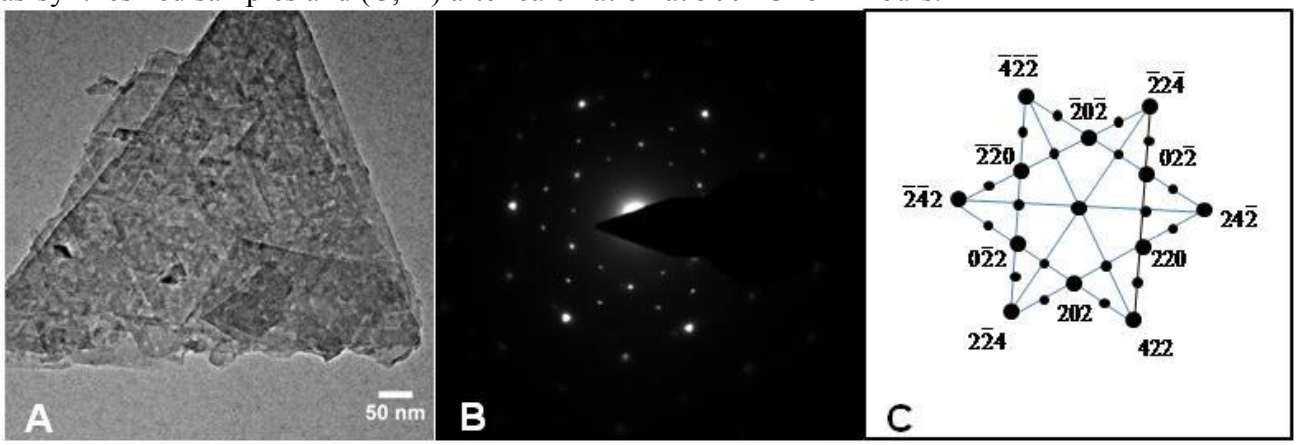

Figure 2. (A) Bright-field TEM image obtained from as-synthesized Co_3O_4 sheet. (B and C) Raw and indexed SAED patterns of the sheet shown in Fig. 2A. The results indicate that the sheet is <111>-oriented single crystalline Fd3m structure.

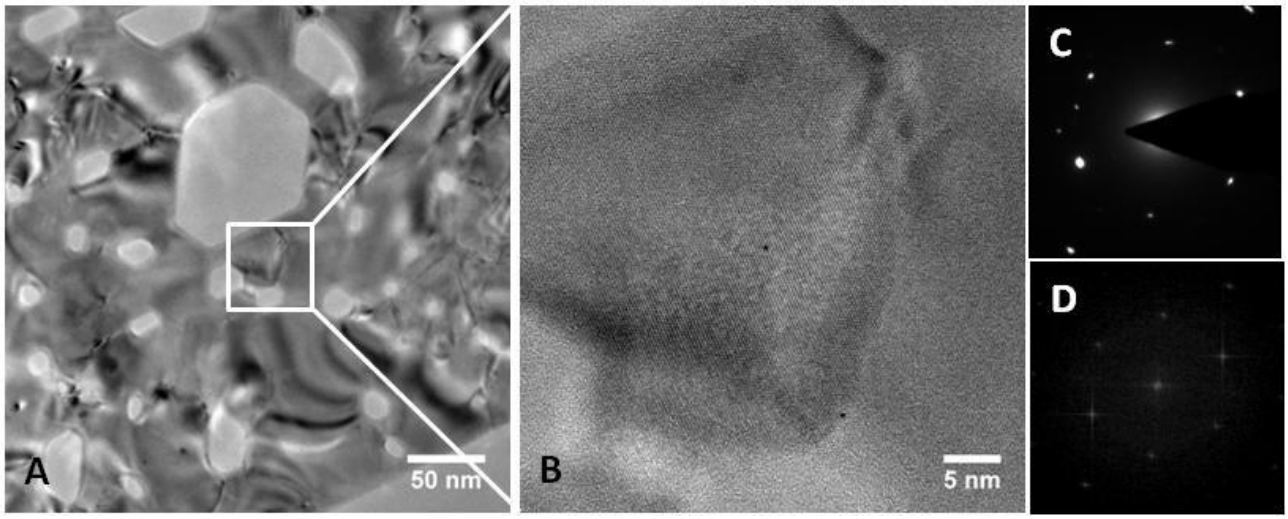

Fig. 3 (A, B) Bright-field TEM images showing a portion of the porous Co_3O_4 sheet structure obtained after calcination at 500 ^oC for 2 h. (C) SAED pattern of entire sheet in <111> zone axis (D) Fast Fourier transform of the higher-resolution TEM image in Fig. 3B. The pores are strongly faceted with most of their edges oriented perpendicular to <112> direction.

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