

## Development of Two-Dimensional Polycrystalline $\text{Co}_3\text{O}_4$ Hierarchical Structures and $\text{Pt}_1/2\text{D-Co}_3\text{O}_4$ Single-atom Catalysts

Jingyue Liu<sup>1</sup>, Yafeng Cai<sup>1,2</sup> and Yun Guo<sup>2</sup>.

<sup>1</sup>. Department of Physics, Arizona State University, Tempe, Arizona, USA.

<sup>2</sup>. Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai, China.

Two-dimensional (2D) materials not only possess high specific surface area but also can have unique electronic, optical or catalytic properties. Cobalt oxides and their derivatives have attracted increasing interest because of their potential applications in energy conversion/storage, catalysis, sensing, etc. The recent successful synthesis of ultrathin 2D  $\text{Co}_3\text{O}_4$  demonstrated promising applications of these unique materials [1-3]. The specific nucleation/growth processes, which control the fine-tuning of synthesizing desirable  $\text{Co}_3\text{O}_4$  nanostructures, however, have not been clearly elucidated yet. In order to develop 2D  $\text{Co}_3\text{O}_4$  nanostructures with desirable properties we investigated the nucleation and growth processes of 2D  $\text{Co}_3\text{O}_4$  and developed unique hierarchical, porous 2D  $\text{Co}_3\text{O}_4$  nanostructures that can strongly anchor metal nanoclusters or single atoms. We further dispersed noble metal single atoms onto the synthesized hierarchical polycrystalline 2D  $\text{Co}_3\text{O}_4$  to produce  $\text{M}_1/2\text{D-Co}_3\text{O}_4$  single-atom catalysts (SACs). Noble metal based SACs have broad applications in catalytic transformations of important molecules [4].

The 2D  $\text{Co}_3\text{O}_4$  was synthesized by a modified hydrothermal method [1]. Briefly, ethylene glycol (EG) and water (volume ratio of 5:1) were mixed with 100 mg of  $\text{Co}(\text{acac})_3$  under vigorous stirring for 2h. The resulting green liquid was heated at 190° C for a designated period of time in a 50 ml Teflon-lined autoclave. After cooling down to room temperature,  $\text{CoO}_x$  precipitates were collected, thoroughly washed, and then dried at 60° C for 12h. The final 2D  $\text{Co}_3\text{O}_4$  were produced by a rapid calcination of the dried  $\text{CoO}_x$  precipitates for 5 min at a temperature between 200° C - 500° C. The  $\text{Pt}_1/2\text{D-Co}_3\text{O}_4$  SACs were prepared by a modified adsorption method. Briefly, the as-prepared 2D- $\text{Co}_3\text{O}_4$  powders were mixed with a selected amount of Pt salt precursor under vigorous stirring. The resultant precipitates were collected, thoroughly washed and then dried at 60° C for 12h. Field-emission SEM and aberration-corrected high-angle annular dark-field (HAADF) STEM were used to examine the morphology and the atomic structures of the as-synthesized 2D  $\text{Co}_3\text{O}_4$  and the  $\text{Pt}_1/2\text{D-Co}_3\text{O}_4$  SACs.

Figure 1a displays an atomic resolution HAADF image of a sample that was taken from the autoclave after only 1h of hydrothermal reaction. Both Co-containing monomers and  $\text{CoO}_x$  clusters coexisted in the mother solution. These  $\text{CoO}_x$  clusters, presumably encapsulated by EG molecules, self-assembled to form layers of 2D  $\text{CoO}_x$  which further grew hierarchically to form a final flower-like structure (Fig. 1b). Depending on the synthesis conditions, the self-assemble of the  $\text{CoO}_x$  layers may not be crystallographically aligned, resulting in polycrystalline 2D  $\text{CoO}_x$ . After a rapid calcination at 300° C for 5 min the  $\text{CoO}_x$  layers topotactically transformed into 2D polycrystalline  $\text{Co}_3\text{O}_4$  (Fig. 1c). The 2D  $\text{Co}_3\text{O}_4$  layers possess many types of surface defects including grain boundaries, vacancies, steps and kinks. When the rapid calcination temperature was set at 400° C well-crystallized and thin  $\text{Co}_3\text{O}_4$  layers were formed (Fig. 1d). Noble metal single atoms can be easily anchored onto the surface defects of the synthesized 2D  $\text{Co}_3\text{O}_4$  to produce noble metal based SACs. For example, the well-isolated Pt single atoms are clearly revealed in atomic resolution HAADF images (indicated by the yellow arrows in Fig. 1d) of a  $\text{Pt}_1/2\text{D-Co}_3\text{O}_4$  SACs. The thicknesses of the synthesized 2D  $\text{Co}_3\text{O}_4$  layers can be determined in edge-on HAADF

images (Fig. 2). Detailed analyses of many such atomic resolution images showed that the exposed surfaces of the 2D  $\text{Co}_3\text{O}_4$  hierarchical structures consist of predominantly  $\text{Co}_3\text{O}_4$  {211} and {100} planes. The surface steps on these exposed planes may have a height ranging from  $\sim 0.4$  nm to 0.5 nm, depending on the specific exposed surfaces [5].

#### References:

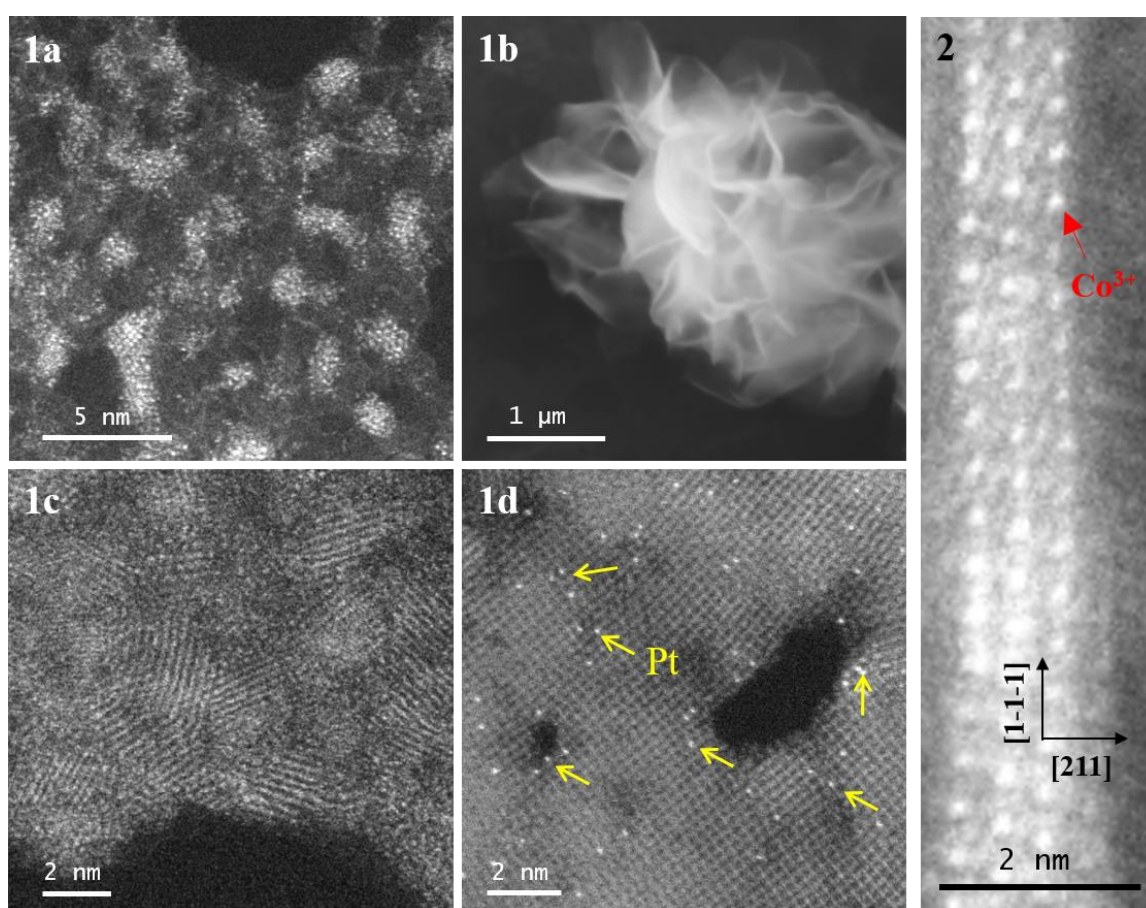
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**Figure 1.** Small  $\text{CoO}_x$  clusters in the mother solution after 1h of hydrothermal reaction (1a); SEM image of flower-like structure after hydrothermal reaction for 48h (1b); self-assembled 2D  $\text{Co}_3\text{O}_4$  grains after 5 min calcination at 300°C (1c) and Pt single atoms anchored onto the surface defect sites of ultrathin  $\text{Co}_3\text{O}_4$  layers in a  $\text{Pt}_1/2\text{D-Co}_3\text{O}_4$  SAC (1d).

**Figure 2.** Atomic resolution HAADF image of an ultrathin  $\text{Co}_3\text{O}_4$  flake with the electron beam oriented close to the [0-11] zone axis reveals the thickness of the 2D  $\text{Co}_3\text{O}_4$  layer  $< 1$  nm along the [211] direction. The bright dots (indicated by the red arrow) represent columns of the  $\text{Co}^{3+}$  in the octahedral sites.