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Two-dimensional Polycrystalline Co_3O_4 Supported High-Number-Density Metal Single Atoms and Clusters

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Two-dimensional (2D) materials have recently attracted strong interest because of their unique electronic structures and their potential applications in many technologies [1]. The high total surface area, the presence of many types of surface defects, and the potential quantum confinement effects of 2D materials make them especially appealing for applications in heterogeneous catalysis [2]. The recent rapid advance in synthesizing supported single-atom catalysts (SACs) has unambiguously demonstrated that SACs can be highly active and selective for a variety of catalytic reactions [3]. It is expected that unique catalytic properties can be achieved by dispersing single metal atoms onto high-surface-area 2D materials. In this work, we developed 2D Co_3O_4 supported Bi SACs and Ir single atom and cluster catalysts. Cobalt hydroxides and oxides supported Ir catalysts demonstrated highly efficient catalytic performance for oxygen evolution reaction [4] and Co_3O_4 supported Bi catalysts exhibited strong resistance to CO_2 for N_2O decomposition reaction [5]. Based on our previous work on the synthesis of ultrathin polycrystalline 2D Co_3O_4 nanosheets [6] we further developed synthesis protocols of dispersing high-number-density Bi single atoms and Ir single atoms and subnanometer clusters onto ultrathin polycrystalline 2D Co_3O_4 nanosheets. The synthesis approach is general and can be applied to different types of metals and 2D supports which enable the fundamental study of supported cluster catalysts with various atomicity.

The free-standing 2D Co_3O_4 flowers were produced via a modified solvothermal method [6]. Briefly, Ethylene glycol and deionized water were mixed with $Co(acac)_3$ under vigorous stirring at an ambient temperature. The resulting solution was then heated to 190˚C for a designated period of time in a Teflon-lined autoclave. The CoO_x flower-shaped precipitates were collected by centrifugation and thoroughly washed with deionized water and dehydration alcohol. The Bi or Ir metal precursor was then dropwise added into the CoO_x/ethanol solution and the corresponding metal species absorbed onto the surfaces of the 2D CoO_x nanosheets. The final transformation from CoO_x nanosheets to Co_3O_4 nanosheets was accomplished via a topotactic transformation by rapidly calcining the CoO_x flower powders. It is expected that during the topotatic transformation the metal species remain intact or do not sinter significantly. Aberration-corrected high-angle annular dark-field STEM (HAADF-STEM), indispensable for investigating the atomic structure of supported single metal atoms or clusters [7], was used to examine the dispersion and atomic configuration of the supported metal atoms and clusters.

A key challenge to practical applications of SACs is to anchoring high-number-density single metal atoms and keep them stable during a desired catalytic reaction [3]. However, with high levels of metal loading small metal clusters or even particles may be produced. Therefore, use of high-surface-area supports such as 2D materials and strong anchoring of single metal atoms onto the surface defect sites may provide a solution. Figure 1a shows a STEM-HAADF image of a typical example of 2D Co_3O_4 nanosheets supported Ir species: single atoms and subnanometer clusters. Detailed analyses of numerous STEM images revealed that the majority of the exposed Co_3O_4 surfaces are composed of Co_3O_4{112} planes [6].

Optimization of the synthesis procedures may eliminate the presence of the small metal clusters even though each specific metal and support combination requires a specific optimized synthesis protocol. Figure 1b shows an example of fabricating high-number-density Bi single atoms (indicated by the yellow arrows) supported on the ultrathin polycrystalline 2D Co_3O_4 nanosheets. Starting from these high metal loading SACs and with appropriate gas and temperature treatment, one can fabricate spatially uniform metal clusters with narrow size distributions. The availability of supported subnanometer metal clusters with different atomicity and relatively uniform size distributions provide ideal supported metal cluster catalysts for the fundamental study of structure-performance relationships of practical catalysts [8].

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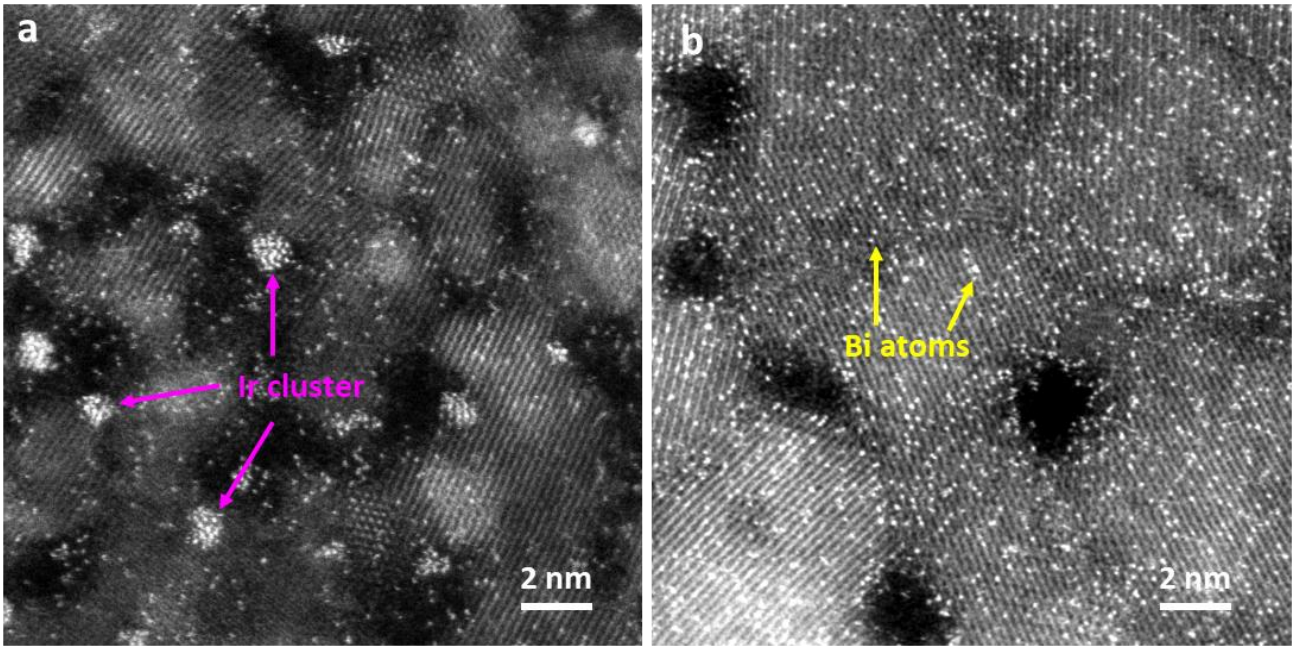

Figure 1. Aberration-corrected STEM-HAADF images of a typical ultrathin polycrystalline 2D Co_3O_4 supported Ir single atoms and clusters (a) and high-number-density Bi single atoms (b). The Ir clusters and Bi single atoms are indicated by the pink and yellow arrows, respectively. The majority of the exposed spinel Co_3O_4 surfaces are the Co_3O_4 {112} planes.

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