doi:10.1017/S143192762001925X
Microsc. Microanal. 26 (Suppl 2), 2020

EELS Analysis of Two-dimensional Co_3O_4 and Supported La Single Atoms

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Two-dimensional (2D) materials, with high surface area and high concentration of various types of surface defects, are of interest for applications in heterogeneous catalysis [1]. Recent advances in developing single-atom catalysts (SACs) have demonstrated that SACs can be highly active and selective for a variety of catalytic reactions [2]. We previously reported the growth of 2D polycrystalline Co_3O_4 flowers with numerous grain boundaries and surface defects that displayed superior activity in CO oxidation reaction [3]. In this work, we developed and optimized the synthesis protocol to prepare 2D Co_3O_4 supported atomically dispersed metal single atoms with controllable metal loading. In order to understand how the metal atoms interact with the various types of surface defects of the Co_3O_4 support we utilized the electron energy loss spectroscopy (EELS) in an aberration-corrected STEM instrument to explore the surface redox property of the Co_3O_4 support as well as the structural and chemical identification of the supported metal atoms. Such local probing of the chemical properties of active sites facilitates the fundamental understanding of supported metal atom and cluster catalysts.

The 2D Co_3O_4 flowers were produced via a modified solvothermal method [3]. Briefly, ethylene glycol and deionized water were mixed with $Co(acac)_3$ under vigorous stirring at ambient temperature. The resulting solution was then heated to 190˚C for a designated period of time in a Teflon-lined autoclave. CoO_x precipitates were collected by centrifugation and thoroughly washed with deionized water and dehydration alcohol. The CoO_x precipitates were toptactically transformed into Co_3O_4 by a rapid calcination process. The metal precursor was then dropwise-added into the Co_3O_4/ethanol solution and the metal species absorbed onto the surfaces of the 2D Co_3O_4 by electrostatic attraction. EELS analysis was conducted on a NION UltraSTEM 100 aberration-corrected microscope equipped with a monochromator and operated at 60 KV.

Typical HAADF images of La_1/Co_3O_4 SAC were acquired with 60 keV electron beam to minimize the damage of the ultra-thin 2D Co_3O_4 nano-sheets (Figure 1). The Co_3O_4 nano-sheets consist of numerous self-assembled nanocrystallites, generating numerous grain boundaries. The exposed surfaces of the Co_3O_4 nano-sheets primarily consist of $Co_3O_4\{112\}$ facets. The spatial distribution of Co^{3+}, which are proposed to be the active sites for CO oxidation on Co_3O_4, was obtained by collecting the Co L_3/L_2 signals to form images. Detailed analyses of many spectrum images showed that the fraction of Co^{3+} decreases with the increase of the number of Co_3O_4 layers, suggesting that the Co_3O_4 surfaces possess more Co^{3+} sites. Furthermore, we found that the Co^{3+} cations were enriched at grain boundaries among the Co_3O_4 nanocrystallites. The structural and chemical properties of the 2D Co_3O_4 supported La atoms were explored by monochromated EELS technique with the goal of identifying the valance state of the strongly anchored La atoms and small La clusters. The EELS spectrum in Figure 1 was acquired from a single La atom supported on a 2D Co_3O_4 nano-sheet, clearly revealing the La $M_{4,5}$ edges. The oxidation states of the surface anchored La atoms under different gas treatment will be evaluated. Detailed analysis of Co oxidation states from different exposed surfaces and the effects of single atom La doping will be discussed.

https://doi.org/10.1017/S143192762001925X Published online by Cambridge University Press

These electronic structural studies will be correlated with the catalytic performance of 2D Co_3O_4 supported SACs [4].

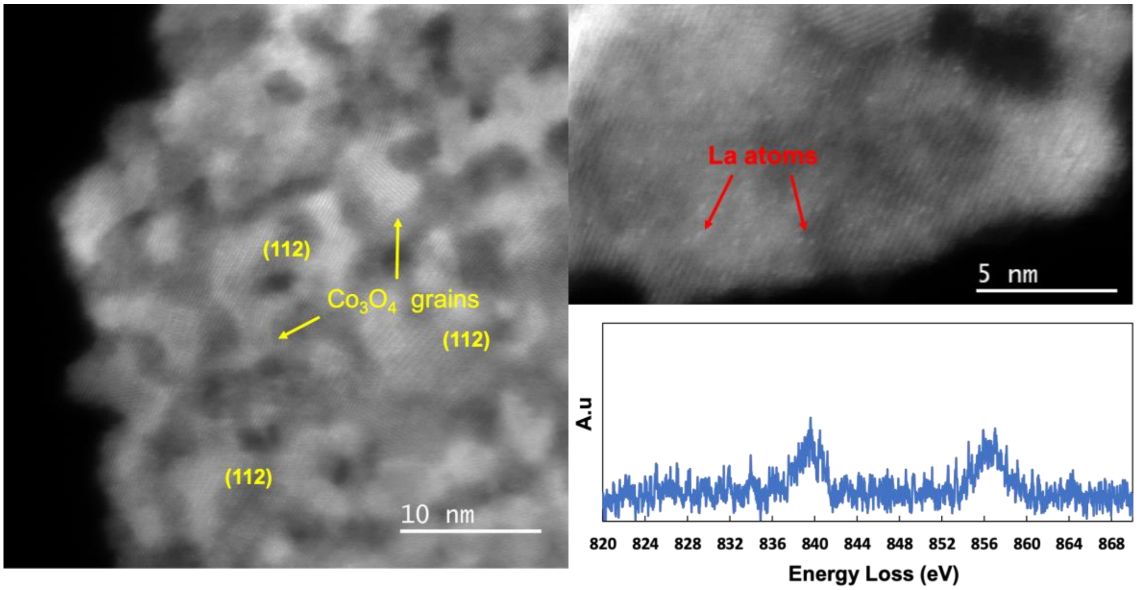

Figure 1. HAADF images of a typical 2D Co3O4 supported La single atom catalyst. Co3O4 nanocrytallites were marked by yellow arrows and supported La single atoms were marked by red arrows. The EELS spectrum was obtained from a supported single La atom.

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[4] We acknowledge the use of facilities within the Eyring Materials Center and the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.