

## Two-Dimensional Polycrystalline ZnO Hierarchical Structures as Single-atom Catalyst Supports

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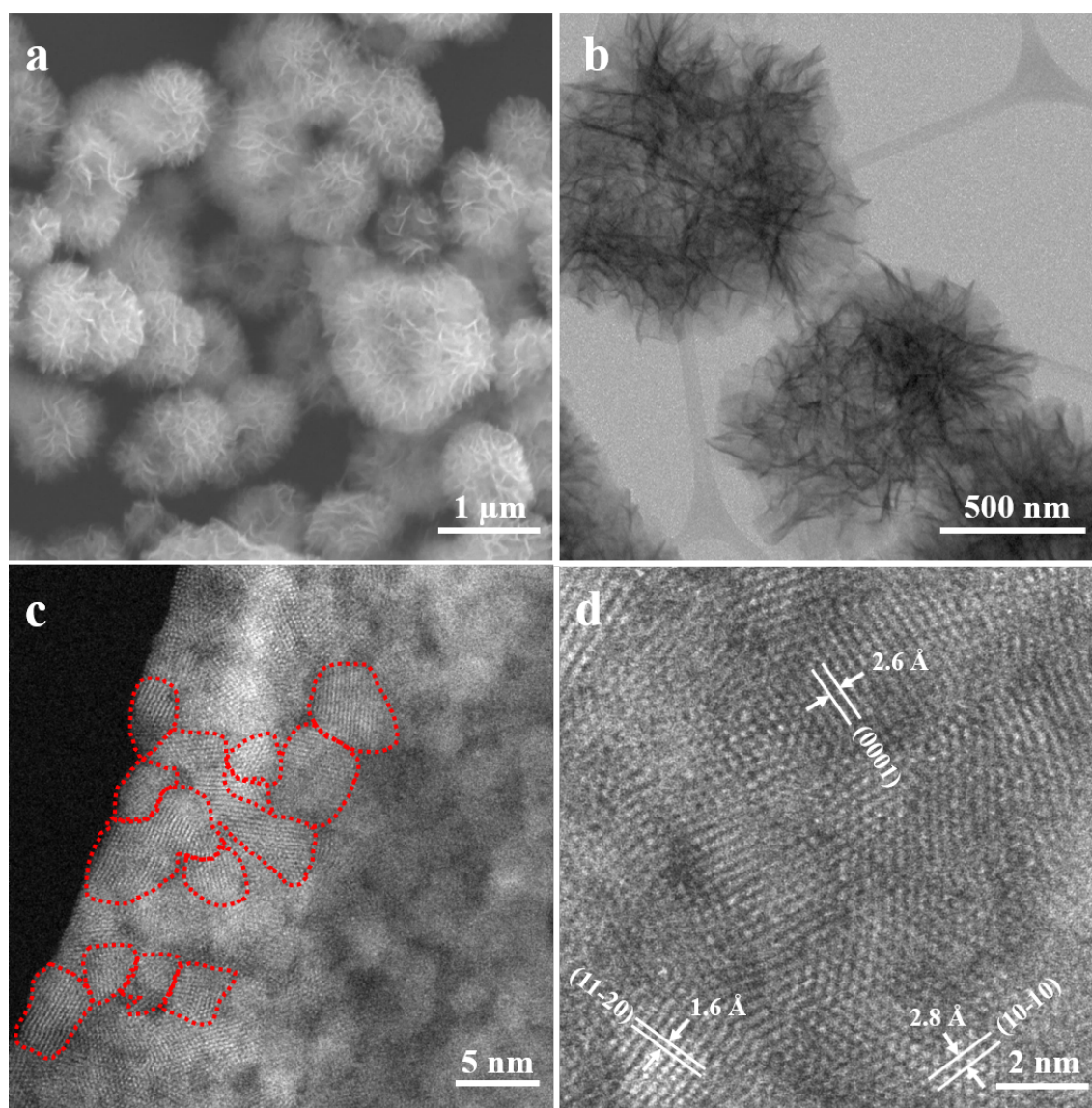
Free standing two-dimensional (2D) materials with confined thicknesses are of interest not only for their unique physicochemical properties but also their simplicity for fundamental research [1]. Zinc oxide, one of the most widely studied metal oxide semiconductors, has attracted increasing interest because of its potential applications in electronics, energy conversion/storage, catalysis, sensing, etc [2]. We have previously investigated the catalytic behavior of ZnO nanowire supported Pd<sub>1</sub> single-atom catalysts (SACs) for various catalytic reactions [3]. The total surface area of these single crystal ZnO nanowires is, however, limited to about 20 m<sup>2</sup>/g and it is difficult to load high levels of single metal atoms onto these single crystal nanowires. We report here the synthesis of high surface area and polycrystalline 2D ZnO hierarchical nanostructures as a catalyst support platform to anchor single metal atoms. Similar to the case of developing 2D Co<sub>3</sub>O<sub>4</sub> for anchoring noble metal atoms [4], our strategy is to fabricate high surface area 2D ZnO nanosheets with many defect sites (grain boundaries, surface steps, vacancies, etc.) to anchor metal atoms or clusters. Recent experiments have demonstrated the potential of SACs for broad applications in important chemical transformations [5]. But stabilizing high loading levels of single metal atoms onto appropriate support materials, especially during catalytic reactions at elevated temperatures, still poses a grand challenge.

The 2D ZnO was synthesized by a modified hydrothermal method. Briefly, a selected amount of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was dissolved in deionized water to make a clear solution and then sodium citrate and hexamethylenetetramine (HMTA) were added. The solution was vigorously stirred for 1h in air and the resultant transparent liquid was heated at 95° C for 3h in a Teflon-lined autoclave. After cooling down the autoclave to room temperature, 2D ZnO precipitates were collected, thoroughly washed, and dried at 60° C for 12h. Field-emission SEM and aberration-corrected STEM were used to examine the morphology and atomic structure of the as-synthesized 2D ZnO materials.

Figure 1a shows a typical SEM image of the as-synthesized 2D ZnO displaying a flowerlike morphology. Statistical analyses showed that the sizes of the ZnO flowers range from 0.5 μm to 3 μm. Figure 1b, a bright-field STEM image, shows that the ZnO flowers consist of hierarchically structured 2D ZnO nanolayers with thicknesses ranging from ~ 1 nm to ~ 5 nm. Atomic resolution HAADF-STEM images (Figure 1c and 1d) show that the 2D ZnO nanolayers are composed of many ZnO crystallites with an average size of ~ 4 nm. The presence of many grain boundaries and abundant surface defects such as atomic steps and vacancies provides desired sites for anchoring metal atoms. Detailed analyses of many such atomic resolution images showed that the exposed surfaces of the 2D ZnO nanolayers are predominantly ZnO {10-10} and {11-20} surfaces. Rapid calcination or reduction treatment can further modify the grain boundary structures without compromising the integrity of the 2D nanolayers. Noble metal atoms will be dispersed onto these high surface area polycrystalline 2D ZnO nanolayers and their catalytic performances for selected catalytic reactions will be discussed [6].

## References:

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[6] This work was supported by NSF under CHE-1465057. The authors acknowledge the use of facilities within the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University. Yafeng Cai gratefully acknowledges financial support from the China Scholarship Council.



**Figure 1.** SEM image of the as-synthesized 2D ZnO flowerlike nanostructures (a), a typical bright-field STEM image of individual 2D ZnO flowers, revealing ultrathin ZnO nanolayers (b), representative high resolution HAADF-STEM images showing the general grain morphology and sizes (c), and the grain boundary orientations and structures (d).