

## Probing the Active Sites of ZnO Nanowire Supported Ir Species for CO Oxidation

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The atomicity and configuration of metal nanoclusters play an important role in controlling their adsorption and catalytic behaviors. The recent rapid development of single-atom catalysis [1-2] has attracted intense interest in understanding heterogeneous catalysis by supported metal clusters [3]. For metal clusters with sizes in the subnanometer range, not only the total number of atoms but also the specific geometric arrangement of the individual atoms within the cluster and their interactions with the support surfaces become critical in controlling their reactivity. We have previously reported that under the appropriate gas treatment ZnO nanowire (NW) supported Ir clusters can be transformed into single-atom chains and furthermore the Ir atom chains can oxidize CO at moderate temperatures [4]. In this work, we developed a method to reversibly transform Ir single-atom chains to highly disordered subnanometer Ir clusters or well-crystallized Ir clusters. We further used CO oxidation as a probe to evaluate the catalytic properties of the different configurations of the ZnO NW supported Ir clusters. The correlation between cluster structure and catalytic performances demonstrates that well-crystallized clusters possess the highest activity for CO oxidation.

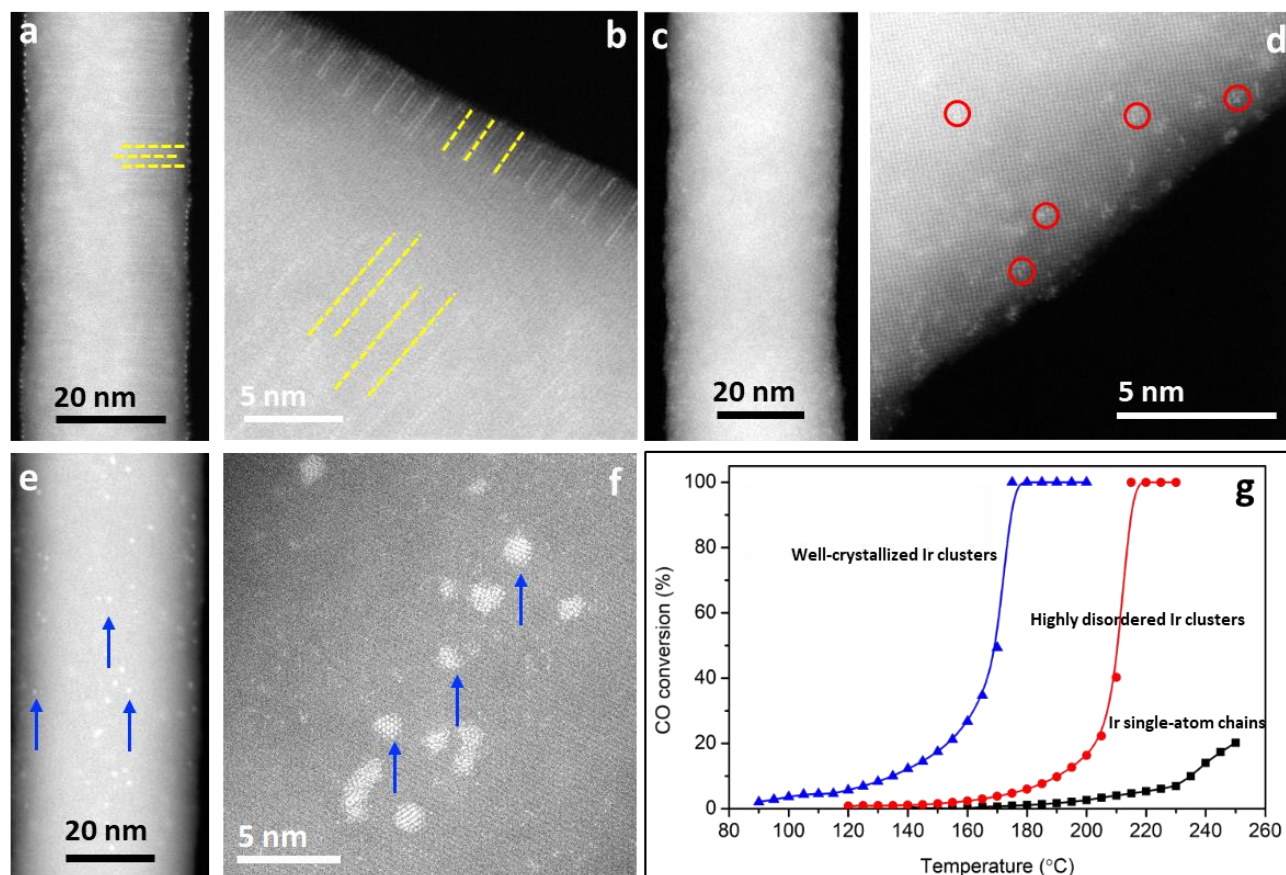
The Ir/ZnO sample was synthesized by a modified strong adsorption method. Briefly, Ir metal precursors were dropwise added into the solution of pre-formed ZnO NWs. The resultant precipitate was filtered, washed with deionized water and dried. The dried Ir/ZnO NWs were then calcined in air at 300°C - 500°C for 2-10 hrs to form single-atom Ir chains on ZnO NWs [4]. Post-treatment in CO and H<sub>2</sub> was carried out to transform the single-atom Ir chains into atomically dispersed, sub-nanometer Ir clusters (under 10 atoms) or well-crystallized Ir crystallites with an average size of ~1.3 nm. The Aberration-corrected HAADF-STEM, indispensable for investigating the active species in supported metal atom and cluster catalysts [5], was used to examine the self-assembled Ir single-atom chains, the highly disordered Ir clusters and the well-crystallized Ir nanoclusters.

Three pairs of low and high magnification STEM-HAADF images are shown in Figure 1 (a-b: Ir single-atom chains; c-d: Ir sub-nanometer clusters; and e-f: well-crystallized Ir clusters). The Ir single-atom chains preferentially grow on the ZnO {10-10} nanofacets (marked by the yellow dotted lines in Figure 1a-b) [4]. After treating the supported single-atom Ir chains in CO and H<sub>2</sub> at the selected temperatures, we transformed the single-atom Ir chains into subnanometer clusters (dimers, trimers, etc.) with various sizes and configurations including highly disordered sub-nanometer Ir clusters (indicated by the red circles in Figure 1c-d). Under a different post-treatment condition, the single-atom Ir chains were transformed into well-crystallized Ir clusters (indicated by the blue arrows in Figure 1e-f). These Ir crystallites are strongly anchored onto the ZnO {10-10} nanofacets, probably by an epitaxial relationship. Since the various configurations of the Ir clusters can be *in situ* transformed in a catalytic reactor we have conducted CO oxidation reaction on the same ZnO supported Ir catalyst but with different types of Ir configurations that

were accomplished by *in situ* gas treatment (Figure 1g). The experimental data unambiguously showed that the activity of CO oxidation depends on the atomicity and cluster structure: well-crystallized Ir clusters (blue plot)  $\gg$  highly disordered subnano Ir clusters (red plot)  $\gg$  Ir single-atom chains (black plot). This result demonstrates that the coordination number and bonding of Ir atoms as well as their interactions with the ZnO{10-10} surfaces may play an important role in determining their catalytic activity for CO oxidation [6].

#### References:

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**Figure 1.** HAADF images of ZnO supported: (a-b) single-atom Ir chains/ZnO NW, (c-d) highly disordered subnanometer Ir clusters and (e-f) well-crystallized Ir clusters. The yellow dotted lines, red circles and blue arrows indicate single-atom Ir chains, highly disordered small Ir clusters and well-crystallized Ir clusters. Figure 1g shows the conversion rates for CO oxidation on the corresponding catalysts. Reaction condition: 1vol% CO + 4vol% O<sub>2</sub> and balance with He, WHSV = 10,000mlg<sup>-1</sup>h<sup>-1</sup>.