Facet Selective Growth of Iridium Chains/Wires of Single-Atom Width on the \{10-10\} Surfaces of ZnO Nanowires

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Self-assembly of individual atoms into ordered nanostructures is not only of fundamental interest but also provides unique electronic, magnetic or catalytic properties. Noble metal such as Pd or Ir were reported to form atomic chains on W (110) [1]. Recent work on fabricating Ir wires of atomic dimensions on Ge (001) surface suggests that electronic effects play a major role in stabilizing atomic size metal wires [2]. All the previous studies, however, focused on clean single crystal substrates and ultrahigh vacuum manipulation. We recently developed a unique process to synthesize high-surface area, ultra-clean ZnO nanowires (NWs) that primarily consist of ZnO \{10-10\} and \{11-20\} facets [3]. In this work, we report, for the first time, the synthesis and characterization of Ir chains/wires of single-atom width that selectively grow on the \{10-10\} nanofacets of ZnO NWs. More importantly, we achieved fabrication of Ir atomic chains by a scalable wet chemistry and post-synthesis treatment process. Aberration-corrected HAADF-STEM images reveal that all the \{10-10\} nanofacets of the ZnO NWs were decorated with single-atom wide Ir chains/wires or Ir atoms. The strong metal-support interaction is responsible for the growth and stabilization of such atomic wide Ir wires.

The ZnO NWs were prepared as reported previously [3]. The Ir/ZnO sample was synthesized by a modified adsorption method. Briefly, Ir precursors were dropwise added into the solution of pre-formed ZnO NWs. The resultant precipitate was filtered, washed with deionized water and dried. Then the Ir/ZnO NWs were calcined in air at 300°C - 500°C for 2-10 hrs. Aberration-corrected HAADF-STEM, indispensable for investigating the atomic structures of nanostructured materials [4], was used to examine the self-assembled Ir chains/wires of single-atom width.

Figure 1a shows a representative HAADF image of the synthesized Ir/ZnO NWs with the electron beam oriented close to the ZnO \{11-20\} zone axis. The bright dots (indicated by the yellow arrows) represent columns of Ir atoms decorating the ZnO \{10-10\} surfaces. Figure 1b shows an image of another ZnO NW with the \{10-10\} zone axis tilted toward the [0001] direction in order to reveal the Ir atoms on the different facets of the ZnO NW. It is clearly seen that atomic wide lines of Ir atoms (indicated by the dashed red lines) preferentially grew on the ZnO \{10-10\} but not on the \{11-20\} facets. Figure 1c shows an image of an Ir/ZnO NW oriented to the [0001] zone axis revealing the presence of individual Ir atoms without the occurrence of Ir chains on the ZnO \{0001\} surfaces. To clearly understand the structure of the Ir chains Fig. 1d and 1e show exactly the same region of a ZnO NW but with different tilting angles. When the electron beam was along the ZnO \{11-20\} zone axis the bright Ir atoms were perfectly aligned with respect to the electron beam (Fig. 1e). When the electron beam tilted away from the \{11-20\} zone axis the Ir chains were represented by the bright short lines (Fig. 1d). Figure 1f shows an image with the electron beam close to the \{10-10\} zone axis, clearly revealing the arrangement of the Ir atoms with respect to the Zn atoms on the ZnO \{10-10\} surface (see the schematic illustration). The growth processes of the atom-size Ir wires, their structures, and their catalytic properties have been investigated [5].

References:
Figure 1. HAADF images of a typical Ir/ZnO NW with electron beam close to [11-20] (a, d, e), [10-10] (b, f) and [0001] (c) zone, respectively. The bright dots and lines represent Ir atoms. The schematic models are shown below the HAADF images (d-f). The single-atom wide Ir chains preferentially grow on the \{10-10\} surfaces of the ZnO NWs.