

Anchoring Au Nanoparticles onto ZnO Nanowires by Heteroepitaxy

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Supported Au nanoparticles (NPs) with sizes < 5 nm have been proved to be highly active for many important catalytic reactions [1]. The development of thermally stable supported Au NP catalysts, however, is challenging. Unlike other noble metals, Au NPs or clusters sinter rapidly during catalytic reactions at elevated temperatures or even under long-term storage [2]. There are many approaches to stabilizing supported metal NPs or clusters [3]. Our approach to developing sintering-resistant supported metal nanocatalysts is to anchor the active metal NPs to well-defined support surfaces by heteroepitaxial growth. We report here the synthesis of stable Au/ZnO nanostructured catalysts by epitaxially growing Au NPs onto the flat and clean surfaces of ZnO nanowires (NWs), the detailed atomic scale characterization of the fabricated catalysts, and their stability during the CO oxidation reaction.

ZnO NWs were fabricated by a thermal evaporation-condensation method in a high-temperature tube furnace. The 2wt% Au/ZnO nanocatalysts were prepared by a deposition-precipitation method. The ZnO NW and powder supported Au catalysts are labeled as Au/ZnO-NW and Au/ZnO-P, respectively. The final catalysts were obtained by calcining the precursors at 400°C for 4 hours. The 5wt% Au/ZnO nanocatalysts calcined at 600°C were synthesized for XRD analysis. The catalytic performances of the prepared samples for CO oxidation were evaluated in a fixed-bed plug-flow reactor. Powder X-ray diffraction (XRD) patterns were taken on a PANalytical X'pert PRO MRD X-ray diffractometer using Cu K α radiation. The JEOL JEM-ARM200F aberration-corrected scanning transmission electron microscope (STEM), with a nominal image resolution of 0.08 nm in the high-angle annular dark-field (HAADF) imaging mode, was used to investigate the structure of the Au/ZnO catalysts.

The XRD pattern for the 5wt% Au/ZnO-NW-600 catalyst (Fig. 1) showed that the ZnO NWs possess a wurtzite structure. Diffraction peaks from the Au NPs were visible and no alloy phases were found. Fig. 2a, a HAADF image of a representative ZnO NW in the Au/ZnO NW-400 catalyst, shows 2-4 nm gold NPs epitaxially grown onto the ZnO {10-10} nanoscale facets. The digital diffractogram (the inset in Fig. 2a) displays spots for both the Au NPs (indicated by the white circles) and the ZnO NW, oriented close to the [11-20] zone axis. The Au NPs grew epitaxially onto the ZnO {10-10} surfaces with an epitaxial relationship as ZnO [11-20] (-1101) // Au [110] (1-1-1). Fig. 2b shows a high magnification HAADF image, clearly revealing the atomic arrangement of the Au atoms and the interfacial structures between the Au NPs and the ZnO NW support. The Au NPs are highly faceted exposing predominantly {111} facets and some {100} facets. In order to understand the observed epitaxial growth of Au NPs on ZnO NWs, we adapted the model of domain-matching epitaxy [4]. The Au (111) planes matches with ZnO (0001) with about 10% misfit and a tilt angle of about 6° between the Au (111) and the ZnO (0001) planes. However, if we consider a domain containing five layers of Au atoms and four layers of Zn atoms of ZnO, the mismatch becomes much smaller, favoring epitaxial growth with the addition of a dislocation. Such epitaxially anchored Au NPs should exhibit high structural stability during catalytic reactions. A 20-hour test for CO oxidation at 150 °C was used to evaluate the stability of the Au/ZnO-NW-400 catalyst (Fig. 3). A similarly synthesized Au/ZnO-P-400 was also tested as a control. Fig. 3 clearly demonstrates that the

Au/ZnO-NW-400 catalyst is much more stable than the Au/ZnO-P-400 catalyst, illustrating the anchoring of Au nanoparticles by epitaxial growth. It is expected that the stability of the epitaxially grown Au NPs will become more prominent at higher reaction temperatures. Optimization of the catalyst synthesis processes and applications to other types of catalytic reactions will be discussed [5].

References:

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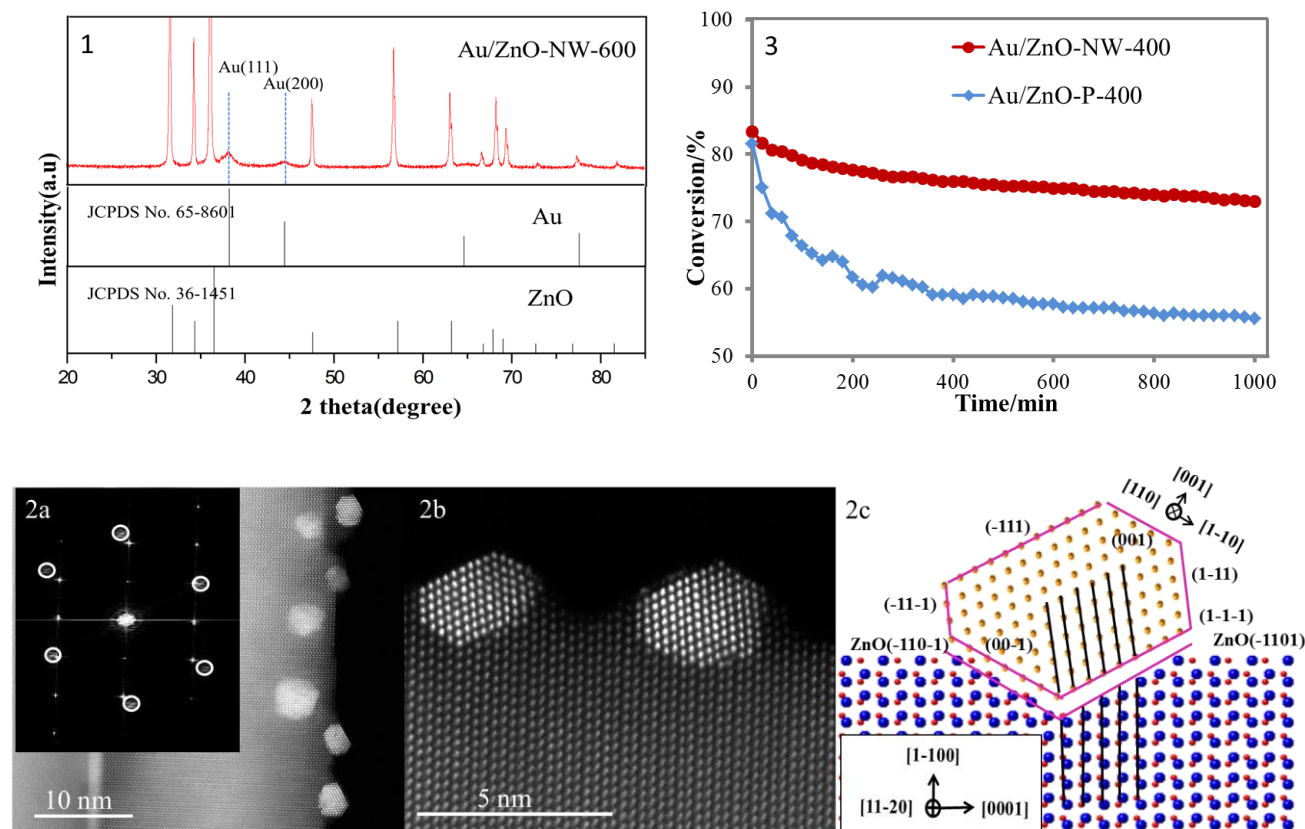


Figure 1. XRD pattern of 5wt% Au/ZnO NW after 4h@600°C in air shows Au and wurtzite ZnO.

Figure 2. Low (a) and high (b) magnification HAADF images of 2wt% Au/ZnO NW catalyst and (c) schematic diagram illustrating the relationship between the faceted Au NPs and the ZnO NW.

Figure 3. CO conversion as a function of time at 150°C on 2wt% Au/ZnO-NW and 2wt% Au/ZnO-P catalysts for CO oxidation reaction (1vol% CO + 1vol% O₂ and He balance, gas hourly space velocity of ~40,000 ml g⁻¹_{cat} h⁻¹).