Anchored Pt/ZnO Nanowire Catalysts for Water-Gas Shift Reaction
Jiaxin Liu¹,², Yan Song¹, Yudong Huang³ and Jingyue (Jimmy) Liu*¹
¹Department of Physics, Arizona State University, Tempe, Arizona, 85287, (USA)
²College of Chem. Eng. & Technol., Harbin Institute of Technology, Harbin, 150001, (China)
*Jingyue.Liu@asu.edu

Introduction
The water-gas shift (WGS) reaction is a key chemical reaction for manufacturing many important chemical products such as hydrogen, ammonia, methanol, and hydrocarbons and can be used to purify hydrogen supplies for applications in proton exchange membrane fuel cells (PEMFC) [1]. Among many catalysts that have been studied, precious metals deposited on partially reducible metal oxides (e.g., CeO₂, TiO₂, Fe₂O₃, etc.) have been widely investigated. However, for WGS reaction catalyst deactivation is usually a major issue [2]. Here we report the development of anchoring Pt nanoparticles by epitaxial growth onto highly stable ZnO nanowires (NWs) which primarily consist of {10-10} nanoscale facets. The well-defined ZnO NWs with clean and flat nanofacets enable the systematic investigation of metal-support interactions and the study of epitaxial growth of metal nanoparticles onto metal oxide NWs. We found that the formation of PtZn nanoalloy increases the catalyst’s activity and that the epitaxial growth of these alloy nanoparticles into the ZnO {10-10} nanofacets stabilizes the Pt/ZnO catalysts during high temperature WGS (HT-WGS) reactions.

Materials and Methods
ZnO NWs were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace. The Pt/ZnO NW catalysts were prepared by a modified deposition-precipitation method. After being washed with deionized water, the resultant solid was dried at 60°C overnight and calcined at 400°C for 4 h in air. Prior to catalytic testing, the catalysts were reduced at different temperatures for 2 h in a flowing gas of 5% H₂/He. The final catalysts, reduced at different temperatures, were labeled as Pt/ZnO NW-X, where X represents the reduction temperature. The actual Pt loading determined by ICP method is 0.8wt%. The activity tests were conducted in a fixed-bed reactor with 50 mg of catalysts and the reaction feed gas composed of 2vol% CO/10vol% H₂O (0.18 ml/h in liquid) balanced with helium (36 ml/min). The gas hourly space velocity (GHSV) was 48,000 ml/gₚt/H. The reaction feed was preheated to 165°C to vaporize water. The effluent gas compositions were on-line analyzed by a gas chromatograph (HP 7890) equipped with a HayeSep DB column. The CO conversion was calculated based on the difference between inlet and outlet CO concentrations.

Results and Discussions
Figure 1a depicts CO conversion profile as a function of reaction temperature over Pt/ZnO NW catalysts after reduced at different temperatures. Although the particle sizes of the Pt/ZnO NW-300 catalyst are bigger than those of the Pt/ZnO NW-200 catalyst (Fig. 1c) it exhibited the highest CO conversion rate at all temperatures. Aberration-corrected electron microscopy analyses of the corresponding catalysts revealed that the Pt/ZnO NW-300 catalyst consisted of many small PtZn clusters and nanoparticles while such nanoalloys were rarely observed in the Pt/ZnO-NW-200 catalyst. It has been reported that PtZn alloy can form when the reduction temperatures were higher than 250°C [3]. We attribute the higher activity of the Pt/ZnO NW-300 catalyst to the formation of PtZn nanoalloys. The low CO conversion rate of the Pt/ZnO NW-500 is due to the larger particle size. The stability tests of the synthesized catalysts were conducted at a reaction temperature of 500°C for about 30 h (Fig. 1b). The deactivation slopes for both the Pt/ZnO NW-300 and the Pt/ZnO NW-200 catalysts were similar. On the other hand, the Pt/ZnO NW-500 catalyst was extremely stable. Figure 2 clearly shows that the PtZn alloy nanoparticles grew epitaxially and partially embedded into the ZnO {10-10} nanofacets. It is postulated that the stability of the Pt/ZnO NW-500 catalyst originated from the epitaxial anchoring and partial embedding of the PtZn nanoalloys.

Significance
Formation of PtZn nanoalloys improved the activity of Pt/ZnO NW catalyst system in the WGS reaction. The epitaxial growth of PtZn alloy nanoparticles into the ZnO{10-10} nanofacets stabilized the Pt/ZnO NW catalysts during the HT-WGS reaction. Such approach to stabilizing metal or alloy nanoparticles is general and can be extended to other supported metal catalysts for different catalytic reactions.

References
4. The authors acknowledge the College of Liberal Arts and Sciences of Arizona State University for funding and the use of the John M. Cowley CHREM facilities.