

Operando TEM Investigation of Sintering Kinetics of Nanocatalysts on MoS₂ in Hydrogen Environment

Boao Song¹, Yifei Yuan¹, Soroosh Sharifi-Asl¹, Yuzi Liu² and Reza Shahbazian-Yassar^{1*}

¹. Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, IL, USA.

². Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA.

The possibility of synthesis and scale-up of two dimensional (2D) materials enable design of novel heterostructures for wide applications. As an example, 2D nanoflake assembled with metal nanoparticles can be used in catalyst, sensor, and energy storage devices. Among the 2D family, transition-metal dichalcogenides like MoS₂ is of great interests in catalyst field since its excellent hydrogen evolution reaction (HER) activity combined with good thermal and chemical stability [1]. The relatively inexpensive cost of MoS₂ is also beneficial of reducing the usage of noble metal particles. The heterostructure of MoS₂ combined with significant reduced amount of Pt is shown to have very exciting electrocatalytic activity [2]. However, degradation of nanocatalyst due to sintering decrease the active surface area resulting in a loss of catalytic activity strongly limits the application scope. Such degradation process of Pt on MoS₂, as well as methods to slow it down is not well studied and remains unclear. It has been shown in our earlier work that Au@Pt core-shell structure has better thermal stability compare to pristine Pt on MoS₂ surface in vacuum condition [3]. To investigate the thermal behavior of such nanocatalyst in real working conditions, we utilized *in situ* technique involving gas flow TEM to observe the sintering process under elevated temperature in combination with 1 atm H₂ gas environment. The Pt and Au@Pt nanocatalyst on MoS₂ were first synthesized by wet chemical reduction method and transferred onto Si microchips with SiN viewing windows. HAADF-STEM image in Figure 1a shows the morphology of synthesized Au@Pt core-shell nanostructures on MoS₂ substrate. The inset shows FFT of one representative Au@Pt core-shell with five-fold twin boundary. Both Pt and Au@Pt have a size distribution of 2-10 nm in diameter. EELS mapping in Figure 1b, as well as the EELS high-loss profiles (Figure 1c) corresponding to core and shell area in 1b confirm the existence of Au core and a thin Pt shell on MoS₂ substrate.

To capture the sintering behavior of Pt and Au@Pt, a gas flow TEM holder was assembled with two microchips isolated to form a flow cell environment. H₂ gas was introduced into the cell with a constant flow rate and after that local heating was triggered in the sample area. The temperature was increased from room temperature (RT) to 400 °C in 1.5 hr. TEM images were acquired after every 50 °C increment. The electron beam was blocked at all time except initial TEM alignment and during imaging period. Figure 2a shows the starting and ending morphology of Pt nanoparticles at RT and 400 °C in H₂ environment. A strong diffusion of smaller Pt towards the center larger Pt particle is observed, while the (200) surface orientation of center Pt remains unchanged. Figure 2b shows another example of three Pt particles coalescing behavior in H₂ as temperature increased from RT to 400 °C. The corresponding FFT show a change in both (200) and (111) surface orientations of these Pt particles, suggest that rotational movements of Pt particles are accompanied with diffusion behavior on MoS₂ (001) surface. In comparison, Au@Pt core-shell structures remain relatively stable (Figure 2c) with much less diffusion and rotational dynamics. These findings indicate that Au@Pt core-shell structure has better thermal stability compare to Pt nanoparticles on MoS₂ in H₂ environment at temperature of up to 400 °C. This work presents an applicable way to gain atomic-scale information of supported nanocatalysts behaviors at standard pressure, and help provide insights into design of novel catalysts that are robust to high temperature working conditions [4].

References:

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 [3] B Song et al., *Microscopy and Microanalysis* **24** (2018), p. 1892.
 [4] The authors acknowledge NSF Award No. DMR-1809439 and usage of Center for Nanoscale Materials at Argonne National Laboratory supported by U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

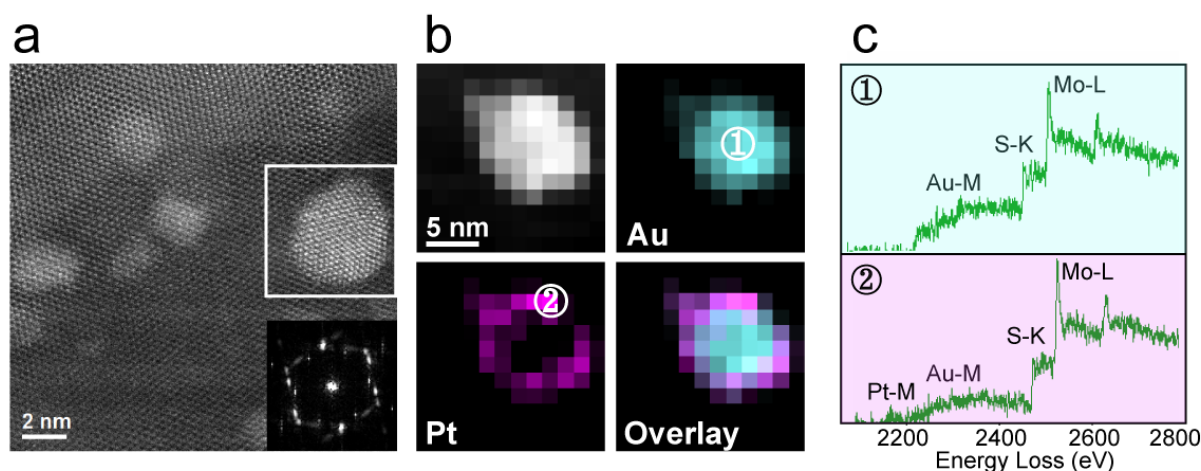


Figure 1. (a) HAADF-STEM image of Au@Pt core shell nanostructures on MoS₂ substrate. Inset is the FFT of white boxed area. (b) EELS mapping of an Au@Pt core shell nanostructure. (c) EELS profiles at the locations corresponding to b, showing the Au and Pt M edge, respectively, as well as Mo-L and S-K edge.

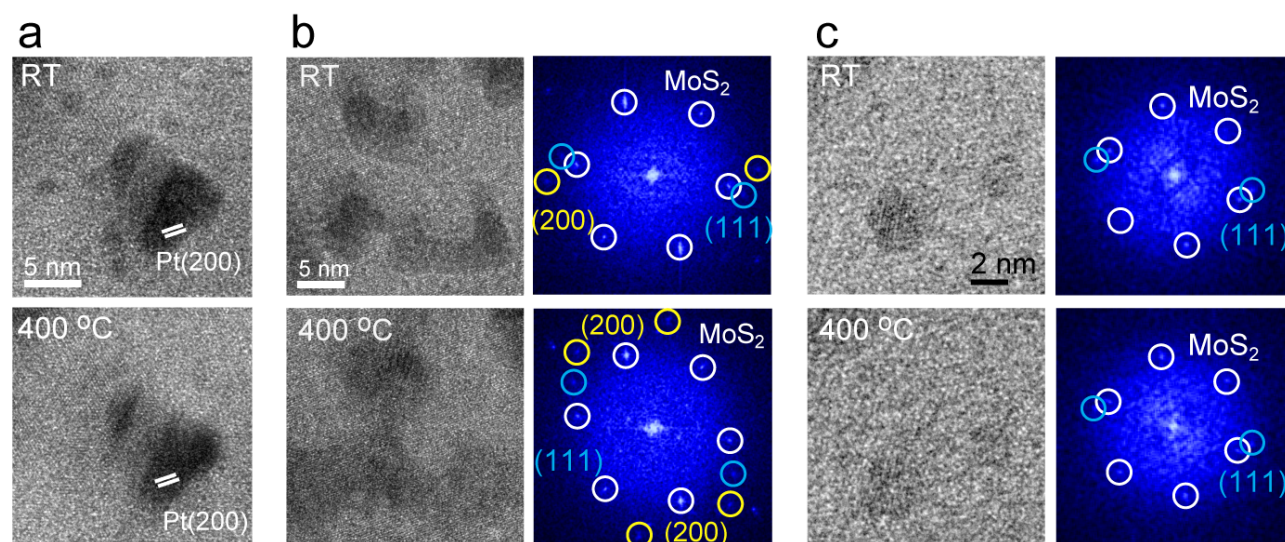


Figure 2. (a) HRTEM images of Pt nanoparticles on MoS₂ substrate at RT and after heated to 400 °C in H₂ environment. (b) HRTEM images and corresponding FFT of Pt on MoS₂ at RT and after heated to 400 °C in H₂, showing the rotation and diffusion of Pt nanoparticles. (c) HRTEM images and corresponding FFT of Au@Pt core-shell on MoS₂ at RT and after heated to 400 °C in H₂ environment.