

***In situ* TEM Investigation of Anti-sintering Au@Pt Core-shell Nanostructures on MoS₂ at Elevated Temperatures**

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Since the discovery of graphene, two dimensional (2D) materials have opened wide possibility of fabricating novel heterostructures. For instance, 2D nanosheet decorated with metal nanoparticles can be of great application in catalyst, sensor, and energy storage. However, the nanoparticle stability on 2D materials is still a major concern in terms of industrial applications [1].

MoS₂, one of the transition-metal dichalcogenides in 2D family, is attracting tremendous attentions in catalyst field as its excellent hydrogen evolution reaction performance and good stability [2]. The heterostructure combined MoS₂ with Pt nanoparticles is shown to have further improved electrocatalytic efficiency [3]. However, decrease of active surface area due to Pt particle sintering during higher temperature processing strongly limits the application scope.

In situ TEM is an advance technique to study dynamic reactions during elevated temperatures. In this study we synthesized Pt nanoparticles and Au@Pt core-shell nanostructure supported with MoS₂ substrate. A heating holder is used to heat the sample to desired temperatures. The particle diffusion and aggregation on MoS₂ substrate is then captured. Our result suggests that Au@Pt core-shell structures help to reduce the diffusion and aggregation rate on MoS₂ substrate at temperature up to 400 °C.

HAADF-STEM images shown in Figure 1a and b show the exemplary synthesized Pt nanoparticles and Au@Pt core-shell nanostructures on MoS₂ substrate. Both two kinds of nanoparticles have a size range of 2-10 nm in diameter. It can be seen from Figure 1b that the outer fringe of Au@Pt has lower contrast in HAADF image, suggesting the existence of Pt shell. To further confirm this, EDS line scan across an Au@Pt core-shell (Figure 1c) is performed. The result shown in Figure 1d indicates a ~1 nm thick Pt shell in a single ~7 nm Au@Pt nanostructure.

To test and compare the anti-sintering property of Pt and Au@Pt core-shell on MoS₂, the samples were firstly dropped on Ni grid and then allow it to dry at room temperature. Gatan furnace-based heating holder was assembled with the sample and inserted into the microscope. A constant heating rate of 10 °C /min was used from room temperature to 400 °C. Images were taken at 100, 200, 300, 350 and 400 °C with 45 min interval. Electron beam was blocked during all heating process. The STEM images above 300 °C for Pt and Au@Pt are shown in Figure 2a-c, d-f respectively. It can be observed that Pt nanoparticles diffuse on MoS₂ more severely than Au@Pt core-shell, and aggregation happens between several nanoparticles. In contrast, Au@Pt core-shell structure remain relatively stable except several of the particles began to form “neck”. Figure 2g and h show distance and curvature between two particles with similar distance at the beginning for both Pt and Au@Pt, the results show that Au@Pt core-shell has a lower diffusion and aggregation rate compare to Pt nanoparticles on MoS₂. The better anti-sintering property of Au@Pt core-shell structures on MoS₂ may benefit future design of catalyst that require high temperature operations.

References:

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 [2] Voiry D *et al*, *Nano letters* **12** (2013), p. 6222.
 [3] Hou, Dongman *et al*, *Electrochimica Acta* **166** (2015), p. 26.

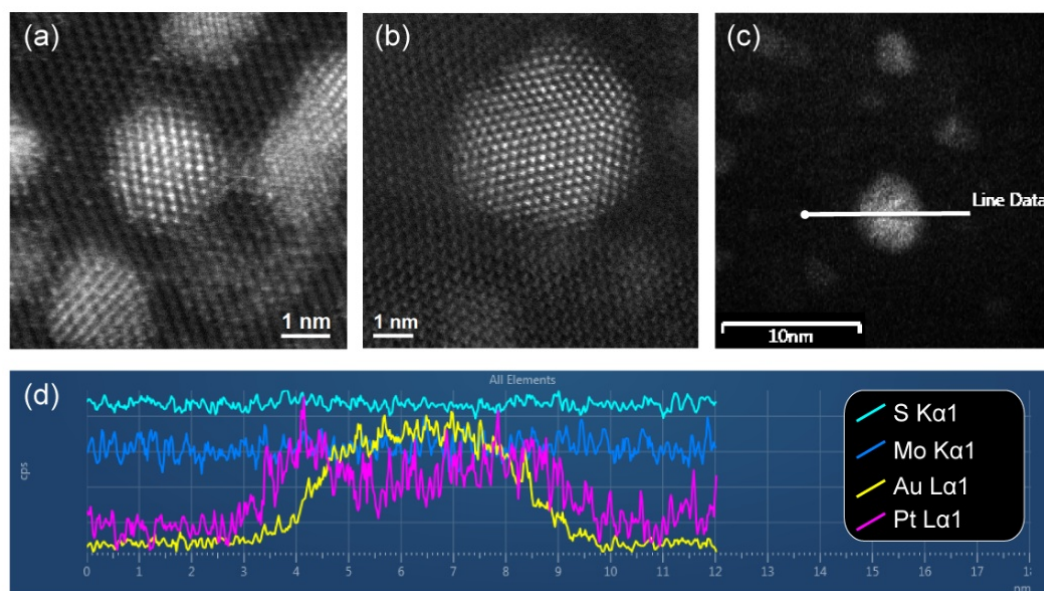


Figure 1. (a, b) HAADF-STEM images of Pt and Au@Pt core shell nanostructures on MoS₂ substrate, respectively. (c) EDS line scan pathway across an Au@Pt core shell nanostructure. (d) EDS line profile corresponding to c.

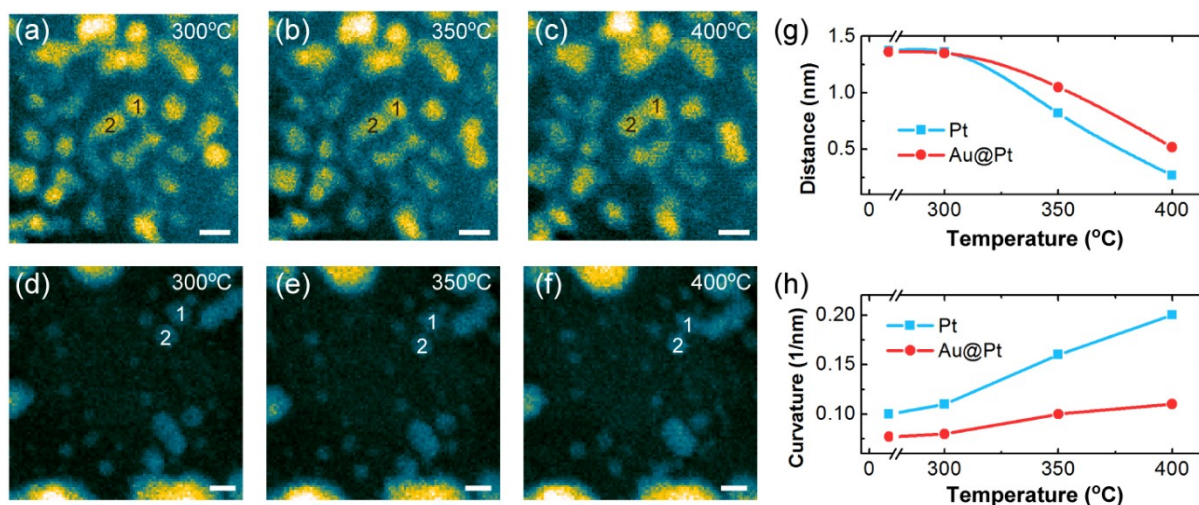


Figure 2. (a-c) HAADF-STEM images of Pt nanoparticles on MoS₂ substrate at elevated temperatures. (d-f) HAADF-STEM images of Au@Pt core shell nanostructures on MoS₂ substrate at elevated temperatures. (g, h) Distance and curvature between particles 1 and 2 as a function of temperature. All scale bars are 5 nm.