

Golden Protection for a Ru-Pt Nanocatalyst

Gold clusters intercalated in nanocatalysts reduces carbon monoxide poisoning and improves durability of nanocatalysts for fuel cell applications.

Carbon monoxide (CO) is a poison for not only human beings but also for fuel cells. One of the biggest challenges for vehicles with hydrogen fuel cells is that CO in very small quantities present as an impurity in hydrogen can damage the platinum catalysts used in those fuel cells. Researchers have been trying hard to find ways to protect the platinum catalysts so as to improve the durability and lifetime of the fuel cells. A few years ago, Ru_{core}-Pt_{shell} nanocatalysts were found to be better than pure platinum catalysts,¹ but researchers are still working on how to improve their performance.

In this article, we discuss important work by Tsan-Yao Chen (National Tsing Hua University) *et al.* that shows that intercalating Ru_{core}-Pt_{shell} nanocatalysts with gold clusters (**Fig. 1**) results in significantly improved durability of Ru_{core}-Pt_{shell} nanocatalysts.² In a collaboration between National Tsing Hua University, National Chung Hsing University, National Taiwan Normal University and National Central University, the authors synthesized Ru_{core}-Pt_{shell} nanocatalysts in a sequence-controlled multistep polyol method. This was followed by intercalation of gold clusters of different sizes at the corner sites of Ru_{core}-Pt_{shell} nanocatalysts, because these corner sites are known to serve as nucleation sites to grow gold clusters. The synthesis was followed by several experiments to characterize the atomic structure, nanostructure and chemical properties of the gold intercalated Ru_{core}-Pt_{shell} nanocatalysts, including small-angle X-ray scattering (SAXS), high-resolution transmission electron microscopy (HRTEM), photoemission spectroscopy, CO voltammetric stripping and extended X-ray absorption fine structure (EXAFS) measurements. The experiments were followed by calculations using density-functional theory (DFT) to understand the observed behavior of gold intercalated Ru_{core}-Pt_{shell} nanocatalysts.

The nanostructure of the Ru_{core}-Pt_{shell} nanocatalysts was determined by small-angle X-ray scattering (SAXS) experiments; the results are shown in **Figs. 2(a) and 2(b)** for the pure Ru_{core}-Pt_{shell} nanocatalysts and Au-intercalated Ru_{core}-Pt_{shell} nanocatalysts (labeled Au-0, Au-5 and Au-15 for atomic ratios Au/Pt = 0, 0.05 and 0.15, respectively). The structural parameters (average diameter D_{avg} , so-called Schulz distribution of particle size P_R and shell thickness T_S) of pure

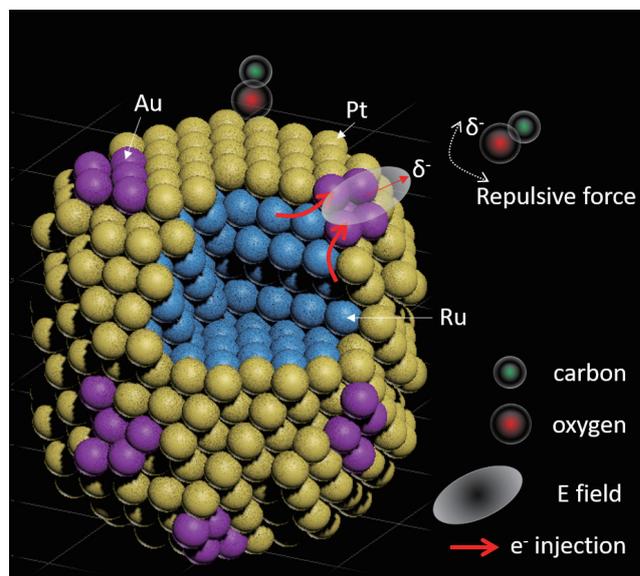


Fig. 1: Schematic rendering of Au-intercalated Ru_{core}-Pt_{shell} nanocatalysts. [Reproduced from Ref. 2]

and Au-intercalated Ru_{core}-Pt_{shell} nanocatalysts were obtained from analyses using the scattering scheme shown in **Fig. 2(c)**. The effects of the Au cluster size on the CO poisoning of the Ru_{core}-Pt_{shell} nanocatalysts were revealed by CO voltammetric stripping measurements. The results indicated that Au clusters drain electrons from Ru_{core}-Pt_{shell}, and the anti-CO poisoning factor of the nanocatalysts was doubled on increasing the Au/Pt ratio from 0 to 15 at %.

EXAFS measurements, **Fig. 3**, show features A, B and C due to contributions of chemisorbed oxygen (A and C) and metallic Pt atoms (B); the authors thereby found strong evidence for the shielding and local distortion of the Pt shell from the significantly reduced co-ordination number of Pt-O and Pt-Pt bond pairs. The valence-band photoemission spectra confirmed that the shielding effects are mainly due to charge donation from Pt to Au, driven by a localized interface strain and a strong negative charge dipole between Au clusters and the embedded Pt crystal. The distribution of charge density obtained from DFT calculations for a supercell of the Ru(0001)@Pt model intercalated with the Au cluster also provided evidence for the induced charge relocation.

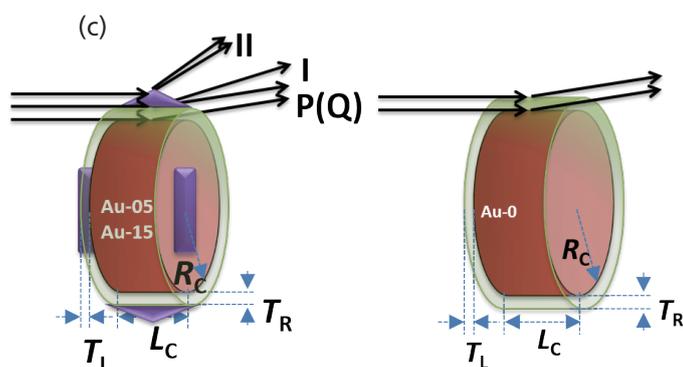
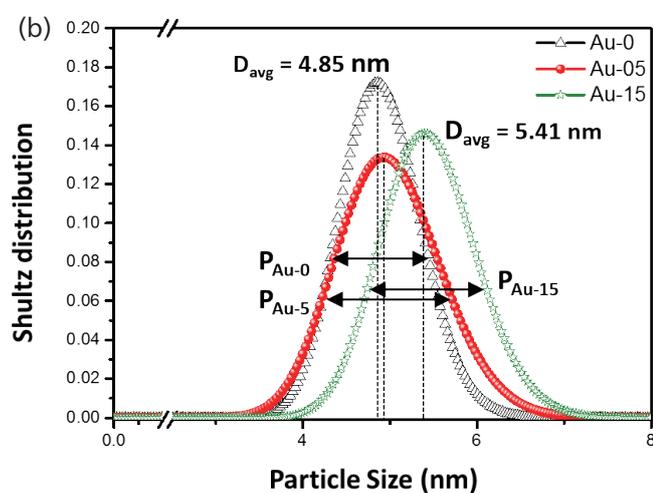
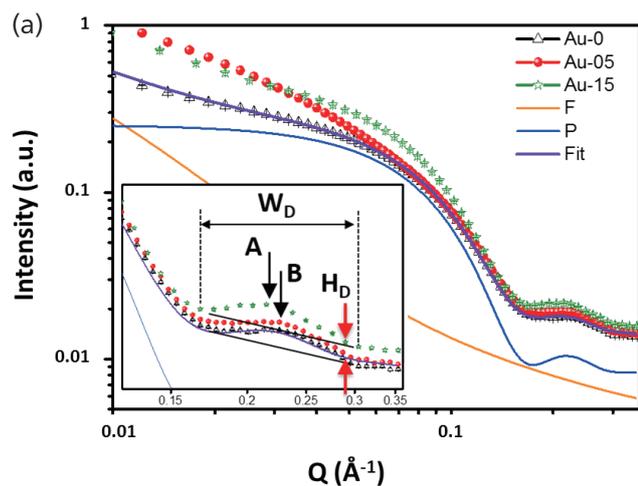


Fig. 2: (a) SAXS spectra of $\text{Ru}_{\text{core}}\text{-Pt}_{\text{shell}}$ nanocatalysts intercalated with Au clusters in Au/Pt ratios from 0 to 15 at %. (b) Corresponding distributions of particle size. (c) Scheme for scattering waveforms at core-shell nanoparticles (left) with and (right) without Au clusters atop. [Reproduced from Ref. 2]

The effects of atomic Au clusters intercalated in $\text{Ru}_{\text{core}}\text{-Pt}_{\text{shell}}$ nanocatalysts were thus elucidated from intensive investigation of their structure, electrochemical CO stripping, photoemission spectroscopy and DFT calculations. The significant improvement of the nanocatalysts is due to steric shielding and elec-

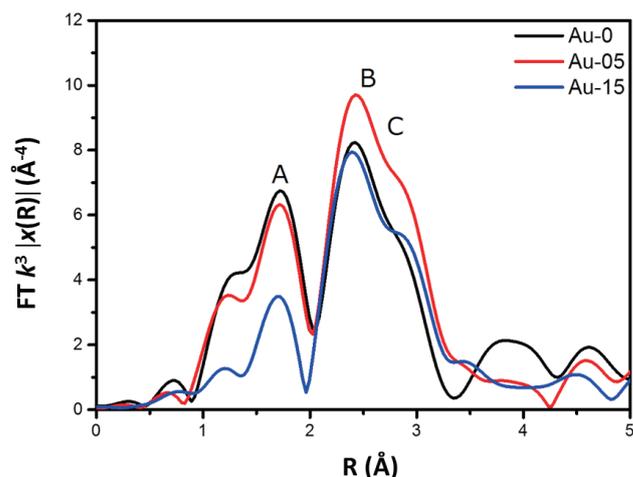


Fig. 3: Fourier-transformed EXAFS spectra (radial structure function, RSF) of $\text{Ru}_{\text{core}}\text{-Pt}_{\text{shell}}$ nanocatalysts intercalated with Au clusters in Au/Pt ratios 0, 5 and 15 at %. Features A, B, and C are contributions of chemisorbed oxygen (A and C) and metallic Pt atoms (B) around the Pt center, respectively. [Reproduced from Ref. 2]

tron injection from Pt to Au sites. The authors thus established valuable mechanistic insight for synthesis of new heterojunction nanocatalysts based on their study of Au-intercalated $\text{Ru}_{\text{core}}\text{-Pt}_{\text{shell}}$ nanocatalysts as chemically durable anodes for fuel-cell applications. (Reported by Ashish Chainani)

*This report features the work of Tsan-Yao Chen, Yu-Ting Liu and their co-workers published in J. Phys. Chem. C. **120**, 7621 (2016).*

TLS 01C1 SWLS – EXAFS
TLS 17C1 W200 – EXAFS
TLS 23A1 IASW – Small/Wide Angle X-ray Scattering
TLS 24A1 BM – (WR-SGM) XPS, UPS

- EXAFS, XANES, PES, SAXS, Core and Valence Band Photoemission Spectra
- Materials Science, Physical Chemistry, Condensed-matter Physics

| References |

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2. T.-Y. Chen, Y.-T. Liu, J. H. Wang, G.-W. Lee, P.-W. Yang, and K.-W. Wang, *J. Phys. Chem. C* **120**, 7621 (2016).