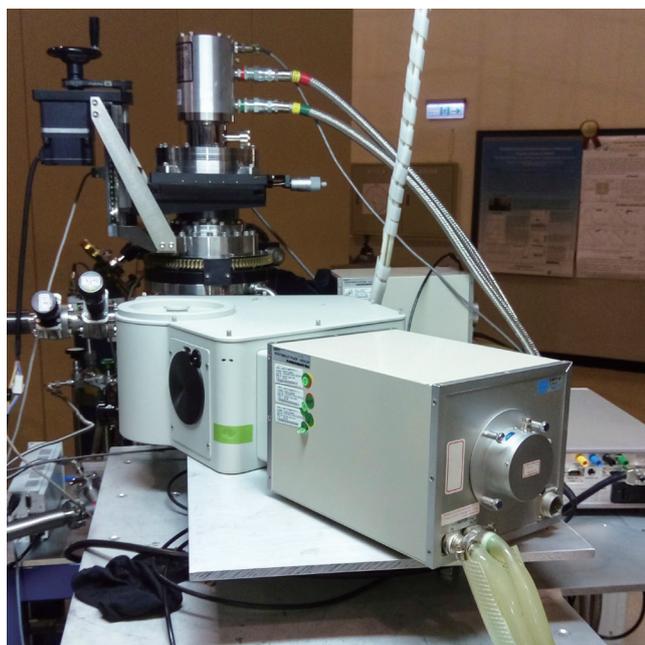


with energy of exciting radiation increasing from 254 to 147 nm; the blue transition concurrently grows in the opposite direction. Excitation energy increased from 254 to 211 nm leads to an enhanced probability of the excited electron to transfer to state 5D_3 on crossing the intersection between the $5d$ level and state 5D_3 . This mechanism is expected to be generally

applicable to Tb-doped phosphors and useful for the adjustment of the optical properties against well-known cross-relaxation processes on varying the ratio of the green and blue contributions. (Reported by Yu-Jong Wu)

This report features the work of Chun Che Lin, Ru-Shi Liu, and their co-workers published in Light-Sci. Appl. 5, e16066 (2016).



TLS 03A1 BM – (HF-CGM) – Photoabsorption/Photoluminescence

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- Photoluminescence
- Photochemistry, Materials Chemistry

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Plasmon-Enhanced Catalysis: Design of Nanocatalysts with a Combination of Catalytic and Plasmonic Metals

A successful one-step strategy to grow monodispersed Au-Pd alloy and core-shell nanocrystals for electrochemical and plasmon-enhanced catalysis.

Pd is a catalysts widely studied for its notable catalytic properties.¹ The catalytic activity of Pd becomes further enhanced with electronic and strain effects through blending with other metal partners.² Incorporating a localized surface-plasmon resonance (LSPR) effect in the Pd-M bimetallic nanostructures is also a promising strategy. In a recent study of a Au-Pd alloy and core-shell nanoicosahedra with terraced shells reported by Chun-Hong Kuo (Institute of Chemistry, Academia Sinica) and his co-workers, they utilized the LSPR effect of Au to enhance the catalytic activity of Pd, whereas Au helps to convert radiant energy to electronic energy and hence stimulates the catalytic activity of Pd.³ A one-step strategy selectively

to synthesize alloy or core-shell Au-Pd icosahedral (IH) nanocrystals was developed in one pot.⁴ The procedure involved HAuCl_4 , H_2PdCl_4 , sodium citrate, CTAC and CTAB in a hydrothermal synthesis at 90 °C. The rate of reduction of HAuCl_4 and H_2PdCl_4 was tuned on varying the ratio $[\text{Br}^-]/[\text{Cl}^-]$, which plays the major role in a selective formation of alloy and core-shell IH nanocrystals. These nanocrystals display more than twice the activity for the electrooxidation of ethanol than commercial Pd catalysts, and they exhibit superior SPR-enhanced reduction of 4-nitrophenol. **Figures 1(a) and 1(d)** display the high-angle annular dark-field (HAADF) images of nanocrystals with a scanning transmission electron microscope (STEM), prepared

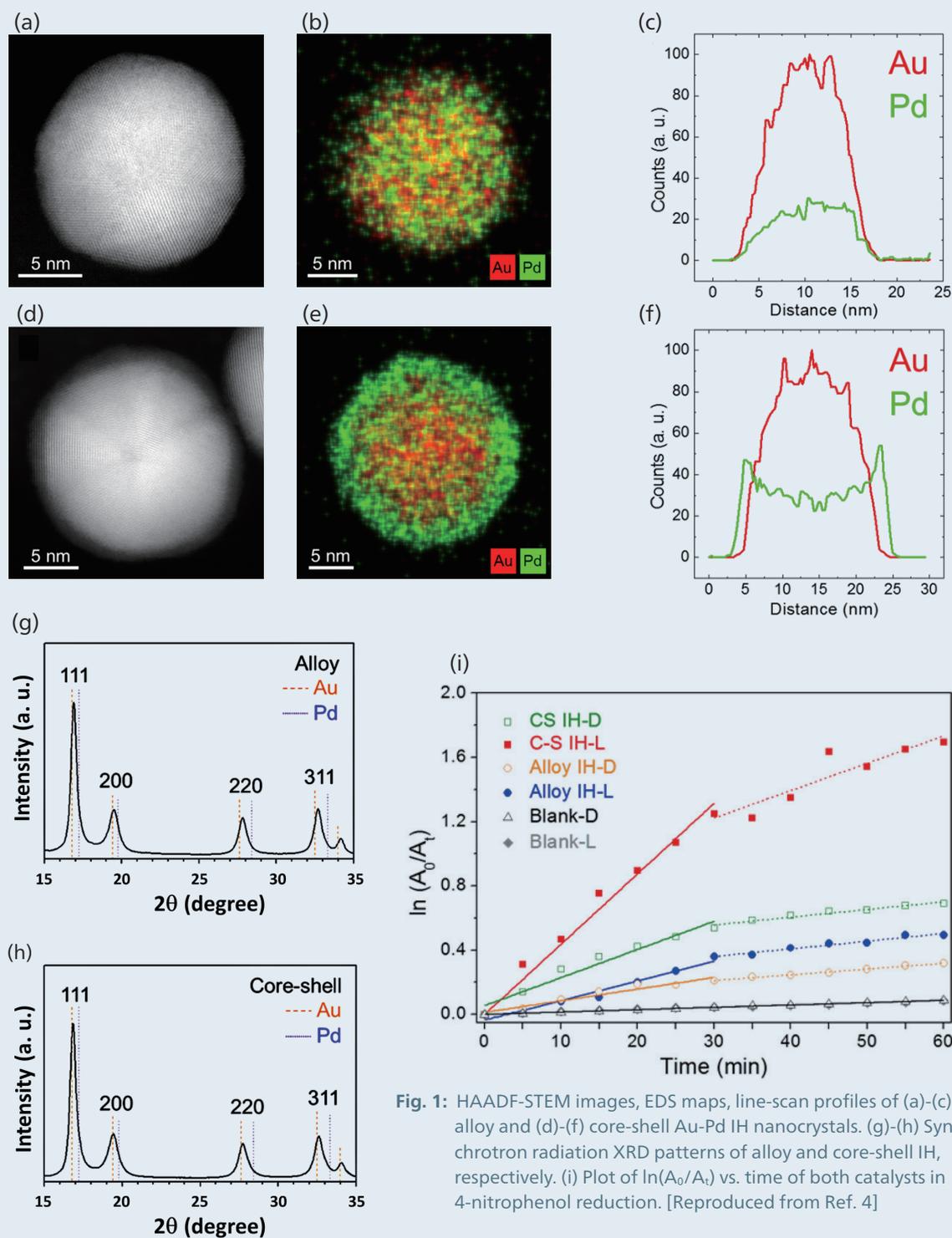


Fig. 1: HAADF-STEM images, EDS maps, line-scan profiles of (a)-(c) alloy and (d)-(f) core-shell Au-Pd IH nanocrystals. (g)-(h) Synchrotron radiation XRD patterns of alloy and core-shell IH, respectively. (i) Plot of $\ln(A_0/A_t)$ vs. time of both catalysts in 4-nitrophenol reduction. [Reproduced from Ref. 4]

with an enhanced molar content of CTAB (CTAB/CTAC = 9) and enhanced molar content of CTAC (CTAB/CTAC = 0.33), respectively. The dark-field images demonstrate that the increased CTAB content gave an alloy (Fig. 1(a)), whereas a core-shell IH (Fig. 1(d)) with greater CTAC content. The truth was confirmed with complimentary energy-dispersive X-ray spectra (EDS) in the mapping mode (Figs. 1(b) and 1(e)). Further analysis was performed in an EDS line-scanning mode, accompanied with an elemental line profile for

Au and Pd (Figs. 1(c) and 1(f)), confirming homogeneous and heterogeneous morphologies, respectively. The line-scan profile of a single core-shell IH (Fig. 1(f)) shows that Pd forms a thin shell (2 nm).

To understand their crystal structures, synchrotron X-ray diffraction on the two samples was conducted at NSRRC, Taiwan, as one of the most efficient tools for structural information; this measurement was performed with X-ray energy 18 keV. Au and Pd IH were

also measured as references for comparison with the alloy and core-shell IH. Diffraction signals were not, however, readily observable from the Pd shells of the core-shell nanocrystals because of a small Pd crystal domain in the core-shell IH nanocrystals. In **Figs. 1(g) and 1(h)**, signals 220 of alloy and core-shell IH appear at 27.83° and 27.73° , which are between standard Au (27.60°) and Pd (28.40°) signals. These broad signals indicate an alloy composition. The peak ratios for Au:Pd are 84/16 and 71/29 for the core of the core-shell and the alloy IH, respectively. ICP-OES provided, in contrast, a Au:Pd peak ratio 78.45/21.55 for core-shell and 79.44/20.56 for alloy IH nanocrystals. The greater Au content in the core of core-shell IH nanocrystals in XRD resulted from Pd atom segregation on the core surfaces of the core-shell IH or reduction of AuCl_4^- much more rapid than that of PdCl_4^{2-} complexes. The CTAB/CTAC ratio plays two major roles in the synthesis: the CTAB/CTAC mixing ratio controls the shape uniformity of IH nanocrystals, and the CTAB/CTAC ratio acts as a shape modulator from alloy to core-shell structures.

The catalytic activity of Pd was improved with Au consistent with the literature by Meng *et al.*⁵ This improvement resulted from two phenomena, a ligand effect and lattice strain resulting in upshifting of the Pd d-band center. The authors studied the reduction kinetics of 4-nitrophenol to 4-aminophenol (4-AP) in the presence of NaBH_4 , with and without irradiation with visible light (500 mW, Xe lamp) at 25°C . There is a negligible effect of light in the absence of catalyst (Blank-D, Blank-L, D: dark, L: light). **Figure 1(i)** shows the results of the core-shell and alloy IH nanocrystals in 4-nitrophenol (4-NP) reduction. The blank reduction reactions were conducted without catalysts. Upon adding the catalysts, the conversion of the

reaction increased substantially under irradiation of visible light relative to darkness (CS IH-D/C-S IH-L; and alloy IH-D/alloy IH-L). The conversion attained 81.6% with C-S IH-L, 40% greater than that with the alloy counterpart in the presence of light (Alloy IH-L). The Au-Pd core-shell nanocrystals are hence a kind of catalyst more effective for SPR-enhanced reduction reactions because of the greater Au content in the cores. (Reported by Yu-Chun Chuang)

This report features the work of Chun-Hong Kuo and his co-workers published in Nano. Lett. 16, 5514 (2016).

BL01C2 SWLS – X-ray Powder Diffraction

- PXRD
- Materials Sciences, Chemistry, Condensed-matter Physics, Soft Matter

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