level can now achieve comparable performance with earth-abundant materials, reducing reliance on expensive metals such as platinum or palladium.

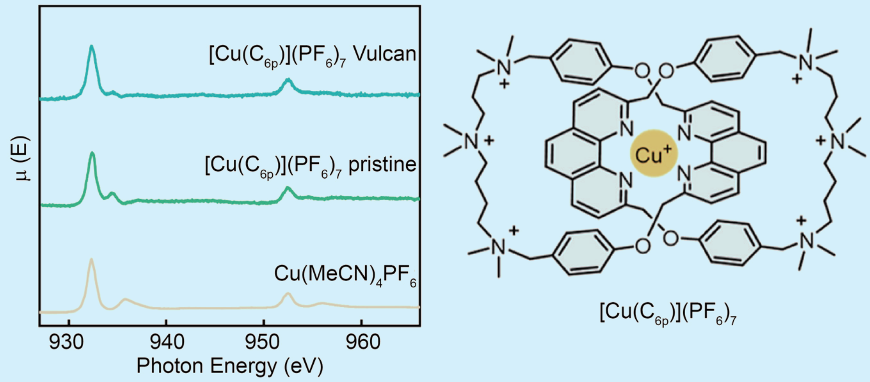

Fig. 3: Cu L$_3$-edge XAS of Cu(MeCN)$_4$(PF$_6$) reference (orange), [Cu(C$_{6p}$)](PF$_6$)$_7$ pristine (green), and [Cu(C$_{6p}$)](PF$_6$)$_7$ supported on Vulcan (blue). XAS spectra were collected in total electron yield mode. [Reproduced from Ref. 1]

As Tse explained, the interlocked copper system "demonstrates that precision molecular design can solve long-standing challenges in catalysis—stability, selectivity, and efficiency—without relying on rare metals." The team plans to expand this approach to other catalytic reactions. They also aim to integrate their catalysts into scalable devices that could convert wastewater pollutants into useful resources on an industrial scale. According to Au-Yeung, "Mechanically interlocked ligands offer a powerful platform for tailoring catalysts at the molecular level. This work provides a blueprint for developing robust, efficient systems for sustainable chemical transformations."

Through innovative molecular design, Au-Yeung and Tse's team at HKU transformed an environmental challenge into an opportunity for clean chemical production. Their copper catenane catalysts convert nitrate pollution into useful ammonia and demonstrate how mechanical chemistry can redefine the future of sustainable catalysis. (Reported by Shu-Chih Haw)

TLS 20A1

- Soft X-ray Absorption Spectroscopy
- Energy-related Materials, Catalytic Materials, Electron-correlated Materials, Molecular Films, Biomaterials

Reference

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When Order Defies Nature: Hexagonal High-Entropy Nanocrystals for Accelerated Hydrogen Evolution

Atomic engineering characterized by in situ X-ray diffraction and X-ray absorption spectroscopy leads to the design of novel catalysts for hydrogen production.

In the world of nanoscience, order and chaos often coexist in strange harmony. Imagine arranging five precious metals—ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), and iridium (Ir)—into a single, nanosized crystal. Each atom competes for space, but they somehow settle into a balanced configuration, forming what scientists call a high-entropy alloy (HEA). These materials, composed of multiple metallic elements in nearly equal proportions, have attracted enormous interest because of their unusual stability, catalytic properties, and resistance to degradation. There are three key questions in this field. First, how do these atoms organize themselves at the smallest scales? Second, can they form unconventional structures that nature rarely favors? Third, what forces allow such structures to persist? These are the questions driving a recent study on Ru@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2}$ core–shell nanocrystals, where Tung-Han Yang (National Tsing Hua University) and his collaborators engineered a new type of high-entropy material with a hexagonal close-packed (HCP) shell, a crystal structure that is normally unstable for this combination of elements. Through cutting-edge X-ray experiments, this study offers a rare glimpse into how atomic architecture evolves and stabilizes under extreme conditions.

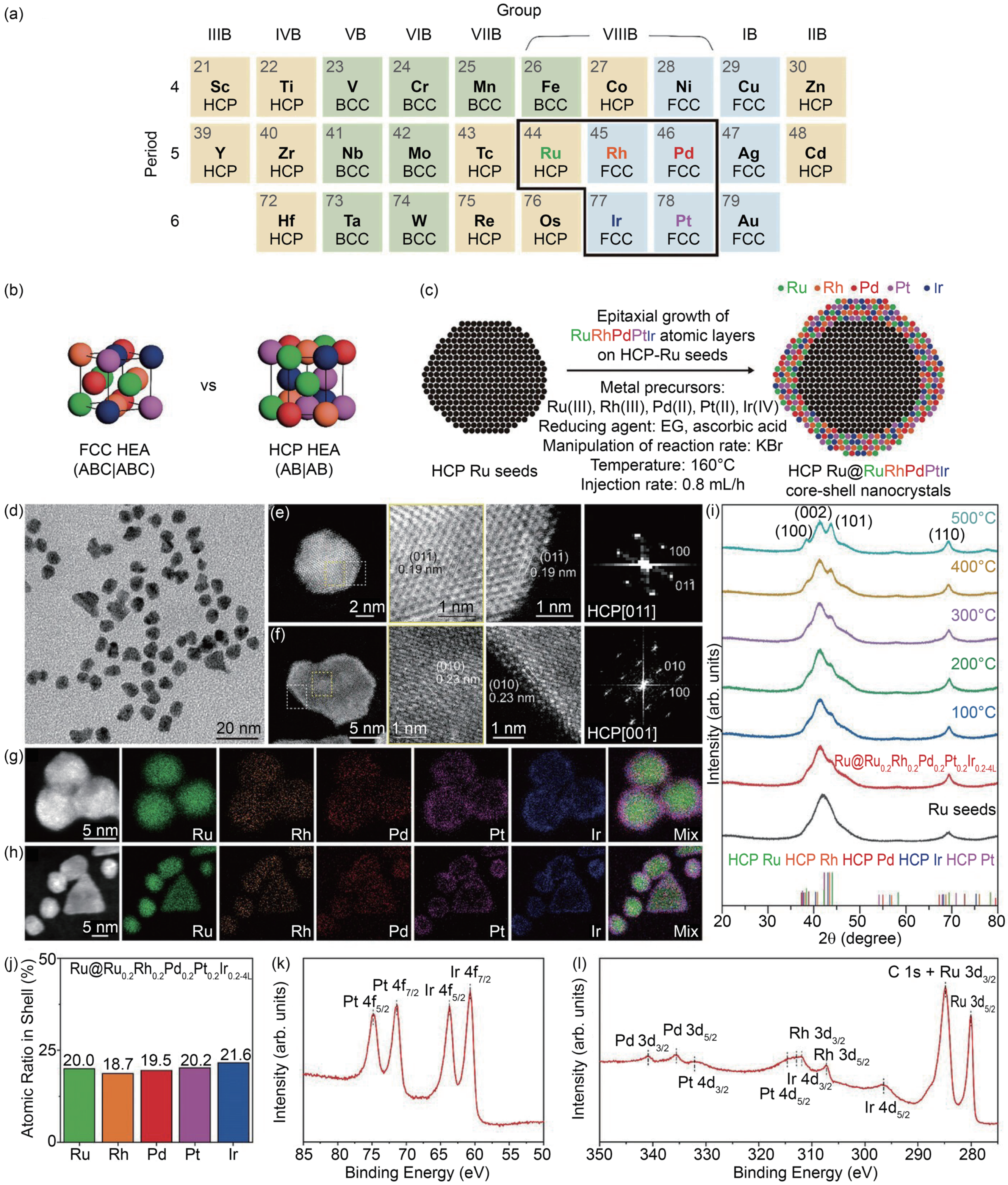

Fig. 1: Synthetic design and characterization of HCP Ru@RuRhPdPtIr core–shell nanocrystals. (a) The thermodynamically stable crystal structures of transition metals (HCP highlighted in orange, FCC highlighted in blue, and BCC highlighted in green). (b) The unit cells of FCC and HCP RuRhPdPtIr HEA. (c) Schematic of epitaxial growth to obtain HCP RuRhPdPtIr shells on Ru seeds. (d–h) TEM, HAADF-STEM, FFT, and EDS mapping analysis of Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ core–shell nanocrystals. (i) Synchrotron HRPXRD analysis of Ru seeds and Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ with *in situ* heating. (j) ICP-OES analysis of $Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ shells. (k,l) XPS spectra of Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ in the regions of (k) 50–85 eV and (l) 275–350 eV. [Reproduced from Ref. 1]

A core of Ru acts as the seed, guiding the growth of a shell made from five noble metals, each of which has its own atomic preferences in crystal structures. In most metals, nature favors the FCC structure, where atoms pack in a symmetrical cube. However, under the right conditions, the researchers discovered that the Ru core can coax its metallic neighbors into adopting the HCP structure, yielding a hexagonal arrangement rarely observed in high-entropy alloys. The team confirmed this transformation using *in situ* high-resolution powder X-ray diffraction (HRPXRD) at the synchrotron facility **TPS 19A** in the NSRRC. Unlike conventional XRD, which provides a static snapshot, *in situ* measurements capture the structural evolution of materials in real time as it is heated or cooled.

The diffraction patterns are shown in **Fig. 1**. At room temperature, two new peaks appearing around 38.5° and 43.9° emerged once the RuRhPdPtIr shell formed, corresponding to the HCP (100) and (101) planes. These signals confirmed that the newly grown shell adopted the same hexagonal structure as its Ru core, forming a coherent epitaxial layer. In other words, the atoms lined up in perfect registry with the underlying Ru lattice. When the temperature increased, the diffraction peaks remained sharp and well-defined up to 500 °C, proving the exceptional thermal stability of this structure. The results suggested that even though the alloy combined five different elements, each of which having its own preferred crystal symmetry, the overall configuration resisted collapse into a more common FCC phase. The researchers estimated that the shell comprises roughly four atomic layers (~1.7 nm thick), an arrangement so thin and precise that it could only exist under the stabilizing influence of the Ru template.

However, this structural harmony has limits. The study found that when the HEA shell grows beyond six atomic layers, the atoms begin to rebel against the Ru template. *In situ* and *ex situ* imaging revealed that the smooth, epitaxial layers gave way to rough, island-like growth. Eventually, the hexagonal order gave way to the thermodynamically favored FCC structure—a more relaxed, cubic packing typical of bulk metals. This delicate balance between epitaxial templating and atomic self-preference reflects a universal tension in materials science: structure versus freedom. Thin layers can be forced into unnatural arrangements by the substrate beneath them, but as the material thickens, the internal strain relaxes, and the atoms revert to their preferred configurations. In this case, maintaining the exotic HCP form required precise control of growth kinetics, keeping the rate of atomic diffusion higher than that of deposition to ensure ordered layering.

To move beyond geometry and uncover the electronic personality of these materials, the researchers turned to synchrotron-based X-ray absorption spectroscopy (XAS), as summarized in **Fig. 2**. This technique goes far deeper than traditional imaging, and it reveals how atoms bond and share electrons, offering clues about the forces that hold the alloy together. Two complementary modes of XAS were used. The first, X-ray absorption near-edge structure (XANES), identifies the oxidation state and local electronic environment of each element. The second, extended X-ray absorption fine structure (EXAFS), measures how atoms are spaced and coordinated. This essentially mapped the hidden geometry of atomic neighborhoods. The XAS-related measurements were conducted at **TLS 01C1** and **TPS 44A** in the NSRRC.

Comparing the HCP $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ structure with its FCC counterpart ($Pd@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$), the researchers observed striking differences. The valence state of Ir, for instance, followed a distinct order: metallic Ir^0 in pure foil < Ir in the FCC alloy < Ir in the HCP alloy < oxidized Ir^{4+} in IrO^2. This trend suggested that the hexagonal structure imposed a unique electronic environment, slightly oxidizing Ir compared to the FCC form. The EXAFS spectra further illuminated the atomic bonding within these alloys. For all five elements, alloy "doublet" peaks appeared between 1.8 and 2.7 Å. These are distinct signatures of interatomic bonding between different species. More importantly, the coordination numbers and bond lengths revealed subtle but meaningful differences: the Pt-Pt and Ir-Ir distances in the HCP phase (2.713 and 2.607 Å) were shorter than in their pure metallic foils (2.750 and 2.706 Å). This contraction hinted at stronger atomic interactions, likely due to the compressive strain imposed by the Ru core and the high degree of atomic mixing.

Electrochemical measurements revealed that the hexagonal high-entropy $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ nanocrystals exhibit remarkable activity for the alkaline hydrogen evolution reaction. The catalyst required a significantly lower overpotential to reach 10 mA cm^{-2} and demonstrated a smaller Tafel slope compared to its FCC-phase counterpart, indicating faster reaction kinetics and more favorable electron transfer. This superior activity originates from the synergistic interplay of the five noble metals, whose compressed interatomic distances and modified electronic structure—confirmed by XAS—enhance both water dissociation and hydrogen adsorption. The HCP configuration exposes a greater number of unsaturated active sites and optimizes hydrogen binding energy, bridging the gap between sluggish water activation and hydrogen desorption steps. Moreover, long-term stability tests showed negligible degradation over extended operation, highlighting the robustness of the epitaxially stabilized HCP structure. Together, these features make the Ru-based high-entropy nanocrystal a powerful candidate for next-generation electrocatalysts in sustainable hydrogen production. (Reported by Dun-Yen Kang, National Taiwan University)

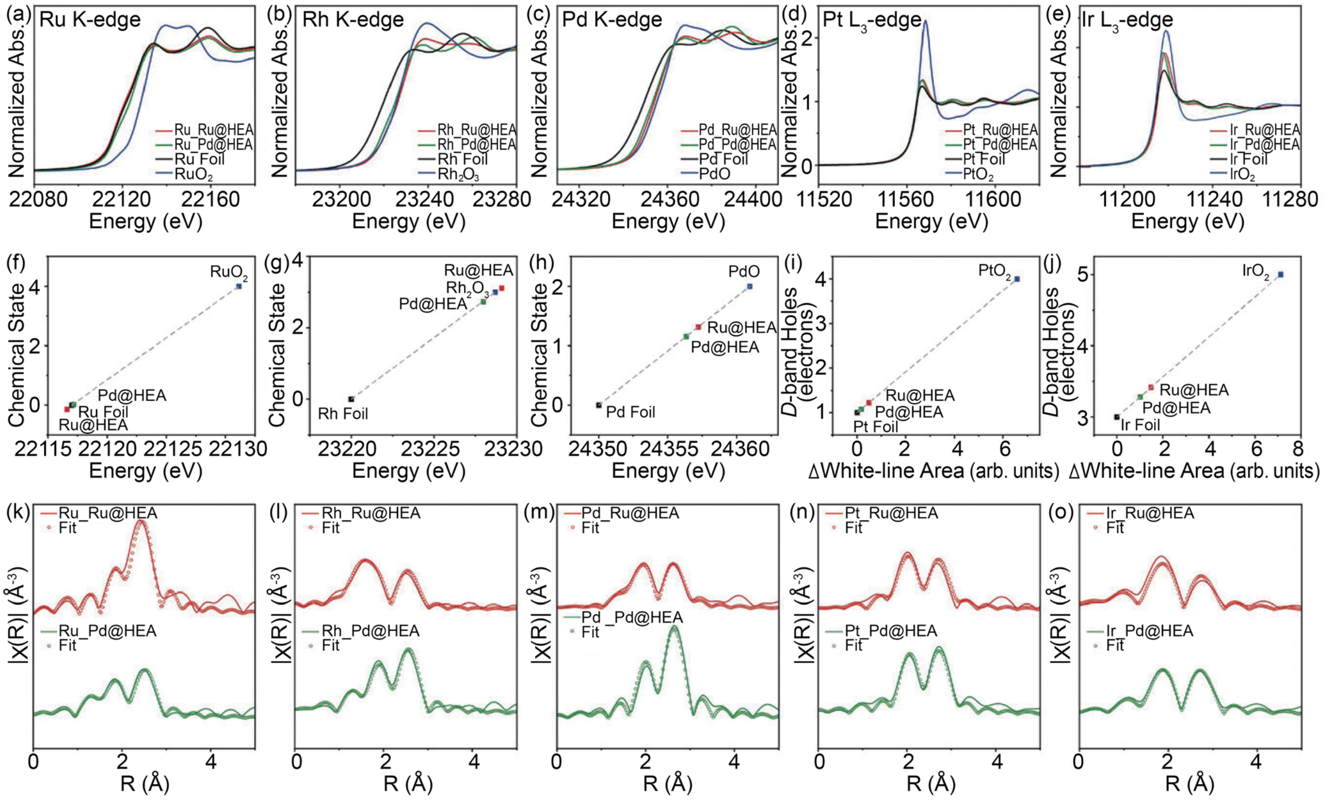

Fig. 2: Electronic structures and atomic coordination environments of HCP Ru@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$ and FCC Pd@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$ core–shell nanocrystals. (a–e) XANES spectra of HCP Ru@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$, FCC Pd@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$, and their corresponding metallic foils and oxidation states at the (a) Ru K-edge, (b) Rh K-edge, (c) Pd K-edge, (d) Pt L$_3$-edge, and (e) Ir L$_3$-edge. (f–j) Determination of chemical states and formal *d*-band hole count of Ru, Rh, Pd, Pt, and Ir elements for HCP Ru@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$ and FCC Pd@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$: (f–h) Absorption energy position versus chemical state of (f) Ru K-edge, (g) Rh K-edge, and (h) Pd K-edge; (i,j) White-line peak area difference versus formal *d*-band hole count of (i) Pt L$_3$-edge and (j) Ir L$_3$-edge. (k–o) FT-EXAFS spectra (lines) and curve fits (points) of HCP Ru@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$ and FCC Pd@Ru$_{0.2}$Rh$_{0.2}$Pd$_{0.2}$Pt$_{0.2}$Ir$_{0.2\text{-}4L}$ at the (k) Ru K-edge, (l) Rh K-edge, (m) Pd K-edge, (n) Pt L$_3$-edge, and (o) Ir L$_3$-edge. The data are k^2-weighted and without phase correction. [Reproduced from Ref. 1]

This report features the work of Tung-Han Yang and his collaborators published in Adv. Sci. ***12****, 2409023 (2025).*

TPS 19A High-resolution Powder X-ray Diffraction

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

TLS 01C1 EXAFS

- HRPXRD, XAS, XANES
- High-entropy Alloy, Hydrogen Evolution Reaction, Hexagonal Close-packed Structure

Reference

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