Hydrogen Spillover-Driven Hydrogen Evolution Reaction *via* Heterointerface and Catalyst Phase Engineering

Tailoring materials that promote the hydrogen spillover effect is crucial for effectively controlling hydrogen atoms during the electrocatalytic hydrogen generation.

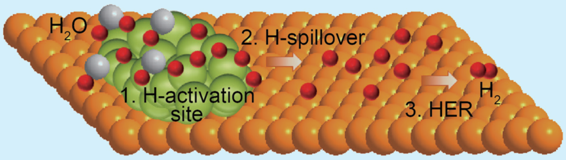

Fig. 1: The schematic diagram of the hydrogen spillover process.

Hydrogen spillover is an important interfacial phenomenon that regulates the behavior of hydrogen atoms in hydrogen-mediated catalytic conversion processes and hydrogen storage technologies. However, the hydrogen spillover effect (HSPE) is highly structure-dependent, and substrates with certain compositions are typically unfavorable. Therefore, selecting an appropriate substrate is crucial for effectively triggering hydrogen spillover. Qi Shao (Soochow University, China) and his team demonstrated that tuning the substrate's phase structure can transform spillover-inactive substrates into spillover-active ones.[1] Their work revealed that metastable hexagonal phase hafnium oxide (Hex-HfO_2) significantly enhances hydrogen spillover, whereas the conventional monoclinic phase (M-HfO_2) is spillover-inactive. The higher Gibbs free energy and distinct structural and bonding characteristics of metastable phases make them promising candidates for effectively triggering the HSPE. Their study systematically explored the hydrogen spillover phenomenon by uniformly dispersing ruthenium (Ru) nanoclusters on two types of 2D layered hafnium oxides, a metastable phase (Ru/Hex-HfO_2) and a stable phase (Ru/M-HfO_2). The occurrence of hydrogen spillover in these materials was assessed using multiple approaches, including colorimetric tests, hydrogen temperature-programmed desorption (H_2-TPD), and activity degradation evaluation with chemical probes. Electronic state characterization by X-ray photoelectron spectroscopy (XPS) revealed that Hex-HfO_2 has a higher Hf valence state than M-HfO_2. Additionally, the Hf 4f spectra of Ru/Hex-HfO_2 suggested electron transfer from Hex-HfO_2 to the Ru clusters. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements (**Fig. 2**) were conducted at the **TPS 44A** beamline of the NSRRC. The XANES spectra showed a stronger white-line peak at the Hf L-edge for Hex-HfO_2 compared to M-HfO_2, indicating a higher oxidation state of hafnium in the metastable phase. These

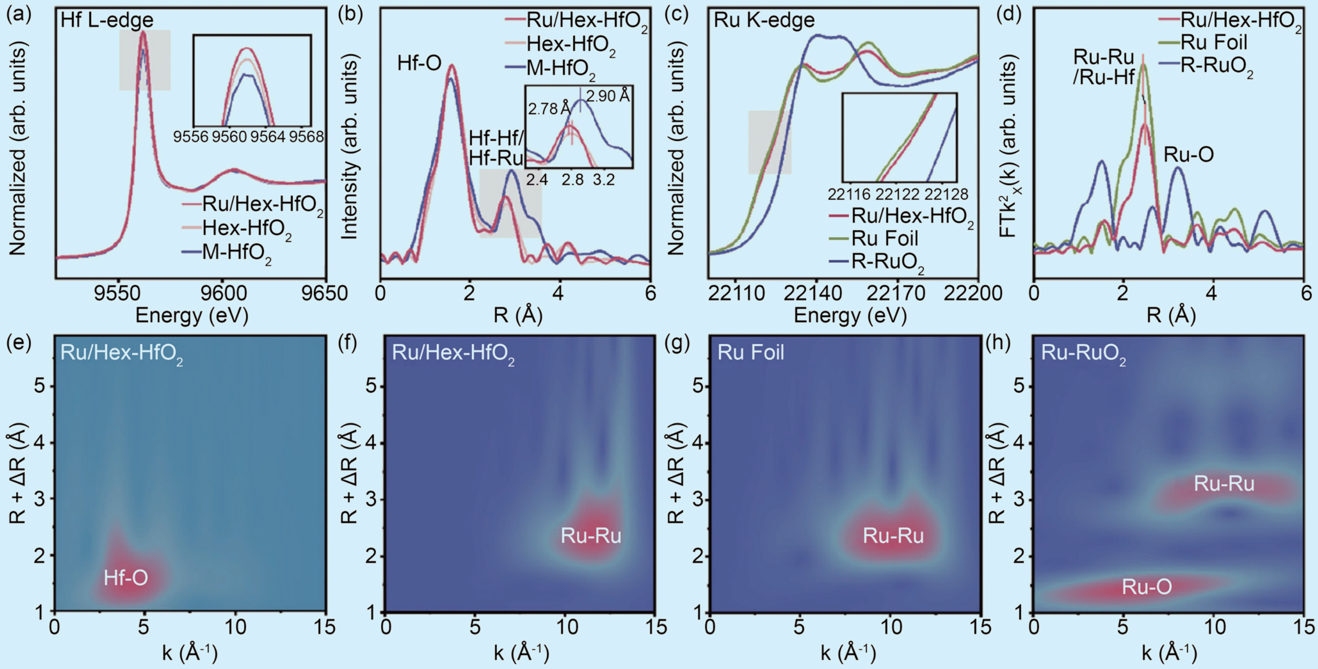

Fig. 2: (a) Hf L-edge spectra; (b) FT-EXAFS spectra; (c) Ru K-edge spectra; (d) FT-EXAFS spectra; (e) Hf L-edge WT-EXAFS; and (f–h) Ru K-edge WT-EXAFS of the materials. [Reproduced from Ref. 1]

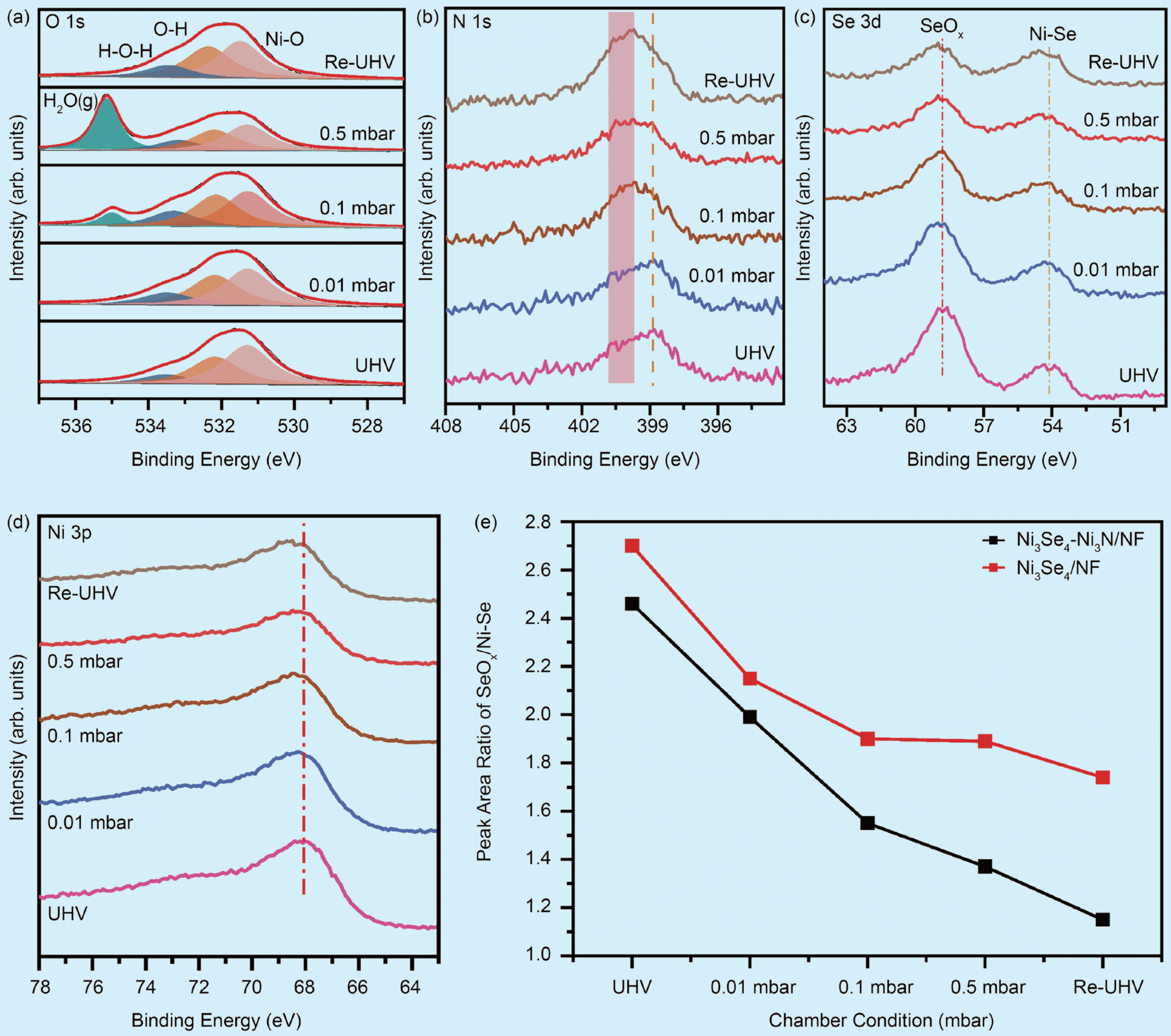

Fig. 3: Water adsorption characterization using NAP-XPS: high-resolution XPS (HR-XPS) of (a) O 1s, (b) N 1s, (c) Se 3d, and (d) Ni 3p for the Ni_3Se_4-Ni_3N catalyst at different water pressures, and (e) areal ratio of SeO_x/Ni-Se peaks, determined from Se 3d spectra at various surface water coverages. [Reproduced from Ref. 2]

analyses clearly demonstrated a pronounced HSPE on the metastable Ru/Hex-HfO_2 surface, while it was absent on the stable Ru/M-HfO_2 oxide. Due to this pronounced spillover activity, the metastable Ru/Hex-HfO_2 exhibited superior acidic hydrogen evolution reaction (HER) performance, achieving a high mass activity of 14.37 A mg_{Ru}^{-1} at an overpotential of 30 mV.

Recent studies have increasingly recognized the HSPE as a key design principle for accelerating HER kinetics. Bing Joe Hwang (National Taiwan University of Science and Technology) and his collaborators recently developed a dual-site Ni_3Se_4–Ni_3N catalyst with abundant heterointerfaces.[2] In this system, the Ni_3N substrate enhances water dissociation, increases hydrogen adsorption on the catalyst surface, and promotes hydrogen spillover to the Se sites of Ni_3Se_4, collectively boosting HER performance. This work demonstrates that the HSPE can be utilized to overcome the inherently sluggish water dissociation of transition metal selenides by integrating them with nitrides through heterointerface engineering while still leveraging the favorable electronic properties of these materials.

The electronic structure and atomic coordination of the materials were characterized using XPS and X-ray absorption spectroscopy (XAS) at beamlines **TLS 24A1** and **TLS 17C1** of the NSRRC. These analyses revealed strong interfacial charge transfer and an optimized electronic configuration in the tailored material. *In-situ* near ambient pressure XPS (NAP-XPS) measurements (**Fig. 3**) under varying water pressures further confirmed that the nitride surface exhibits enhanced water adsorption and dissociation, resulting in increased surface-adsorbed hydrogen atoms (H*). These H* species migrate to electron-rich Se sites, where they combine and release H_2 through a hydrogen spillover mechanism. The pronounced interfacial charge transfer and charge localization at the Se centers promote this spillover process. Consequently, the engineered catalyst demonstrates outstanding alkaline HER performance, requiring only ~60 mV overpotential to reach 10 mA cm^{-2} and maintaining stable operation at higher current densities.

Together, these studies provided compelling evidence that HSPE is highly structure-dependent and can be effectively activated through phase or interface engineering. Shao and his co-workers demonstrated that metastable Hex-HfO$_2$ serves as an efficient spillover-active substrate when combined with Ru nanoclusters, enabling exceptional acidic HER performance. By contrast, Hwang and his co-workers used a Ni$_3$N/Ni$_3$Se$_4$ heterointerface to facilitate hydrogen spillover, overcoming kinetic limitations of selenide materials and achieving outstanding alkaline HER activity. These findings suggest that HSPE is a promising strategy for controlling multiple intermediate steps in HER and other hydrogenation reactions. Incorporating HSPE into catalyst design allows researchers to optimize rate-limiting steps, improve catalytic efficiency, and reduce precious metal loading. Ultimately, these advances may accelerate the development of high-performance, cost-effective hydrogen production technologies, contributing to the realization of a sustainable hydrogen economy. (Reported by Dessalew Dagnew Alemayehu and Chia-Hsin Wang)

This report features the work of Qi Shao and his collaborators, published in Adv. Mater. ***37****, 2415978 (2025); and the work of Bing Joe Hwang and his collaborators published in J. Am. Chem. Soc.* ***147****, 16047 (2025).*

TPS 44A Quick-scanning X-ray Absorption Spectroscopy
TLS 17C1 EXAFS

- XANES, EXAFS
- Materials Science, Catalysts

TLS 24A1 XPS, UPS, XAS, APXPS

- HR-XPS, NAP-XPS
- Materials Science, Surface Science, Catalysts

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Projection X-ray Microscopy: Illuminating Pathways to the Future of Energy Storage

Projection X-ray Microscopy opens a window into the hidden architecture of all-solid-state batteries, decoding how microstructure shapes performance.

To reduce air pollution, including CO, CH$_4$, NO$_2$, SO$_2$, Pb, and PM particles, the development and production of electric vehicles has risen in prominence, with high-capacity and safe batteries being the most important priorities. All-solid-state batteries (ASSBs) using intrinsically nonflammable solid-state electrolytes (SSEs) show promise as an alternative energy-dense storage solution due to their achievable higher energy density and improved safety. In contrast to conventional lithium-ion batteries, which benefit from facile ion transport *via* infiltration of liquid electrolytes into porous electrodes, ASSBs require physical contact between solid materials to facilitate the electrochemical reaction. Ideally, all components in ASSBs should exhibit fully densified microstructures that lack any porosity to maximize volumetric energy density. However, in practice, the mismatch in particle sizes and mechanical properties of materials induces unavoidable porosity or nonideal tortuosity within ASSBs. Either formed in the initial fabrication process or during battery operation due to volume changes of cathode/anode materials, the pores and gaps in the microstructure can lead to contact loss and propagation of fractures/cracks. Contact loss of active material reduces utilization, thus leading to lower reversible capacity and capacity loss. Meanwhile, voids and fracture formation within the microstructure could also lead to structural degradation or cell failure due to the disruption of ion percolation pathways. Thus, scaled-up tomography techniques will improve the understanding of ASSBs, elevating the technology's potential commercially. To quantitatively investigate the internal microstructure and its evolution within ASSBs during fabrication and cycling, three-dimensional (3D) micro-computed tomography and reconstruction techniques are essential.[1–3]

Ying Shirley Meng (University of Chicago, University of California San Diego, and Argonne National Laboratory, USA) and her team utilized **TPS 31A** projection X-ray microscopy (PXM) 3D tomography