

An Adaptive Ni–Si Layer to Drive Water Oxidation

An adaptive Ni–Si phase can serve an imperative role in the charge transfer of photocatalytic water oxidation.

In solar-driven water-splitting systems, the oxygen evolution reaction (OER) is driven by a four-charge carrier transfer path, while the hydrogen evolution occurs on the counter electrode. This OER reaction is regarded as a kinetic bottleneck for both artificial photosynthesis and overall water splitting because of the large energy requirements to drive the multi-electron transfers. To reveal the fundamental properties of the interfacial charge transfer, tracking techniques on an atomic scale that allow simultaneous realization of both the photo- and electrochemical behaviors are highly desirable. Several techniques *in situ* have been demonstrated to reveal the reaction intermediates at the material–liquid interface. Despite recent advances in techniques for characterization *in situ*, which have resulted in several new perspectives regarding the catalytic behavior of catalysts, detailed discussion of the photoinduced processes in metal and semiconductor (M–S) junctions remains largely inadequate.

Hao-Ming Chen (National Taiwan University) and his co-workers recently developed a Si microwire array with a nanoporous surface to act as a photoabsorber, on which Ni nanoparticles were inlaid with the textured surface of the wires with a tunable electrodeposition method, which allowed maximizing the interfacial contact of the M–S junction. Employing X-ray scattering/diffraction and absorption spectra *in situ* at **TLS 17C1**, **TLS 01C1** and **SP 12B1**,¹ the generation of a photoinduced adaptive NiSi structure was discovered at the interfacial M–S junction between a state-of-the-art porous Si wire and Ni electrocatalyst, at which oxygen evolution occurred under illumination. The contour plots and plots of current density as a function of applied potential under both dark and illuminated conditions highlight the different resulting behaviors of the M–S photoanode, as shown in **Fig. 1**. The newly identified features were proved to appear only during the photoinduced oxygen evolution, accompanied with the formation of α -Ni(OH)₂ and β -Ni(OH)₂. Furthermore, X-ray absorption spectra during (photo) electrochemical water oxidation were recorded *in situ* (**Fig. 2**), indicating the presence of the orthorhombic NiSi

phase. These results are the first direct demonstration through several methods *in situ* to verify the formation of an adaptive junction during photoinduced water oxidation; the observations of the photoinduced phases *in situ* were characteristic of the formation of a metal silicide from the parent metal and the silicon semiconductor.

In summary, the formation of an adaptive silicide phase during photoinduced water oxidation is the major factor causing a large barrier height. This photoinduced adaptive layer offers a new perspective regarding the catalytic behavior of catalysts, especially for the photocatalytic water-splitting system, and acting as a key aspect in the development of highly efficient photoelectrodes. (Reported by Yan-Gu Lin)

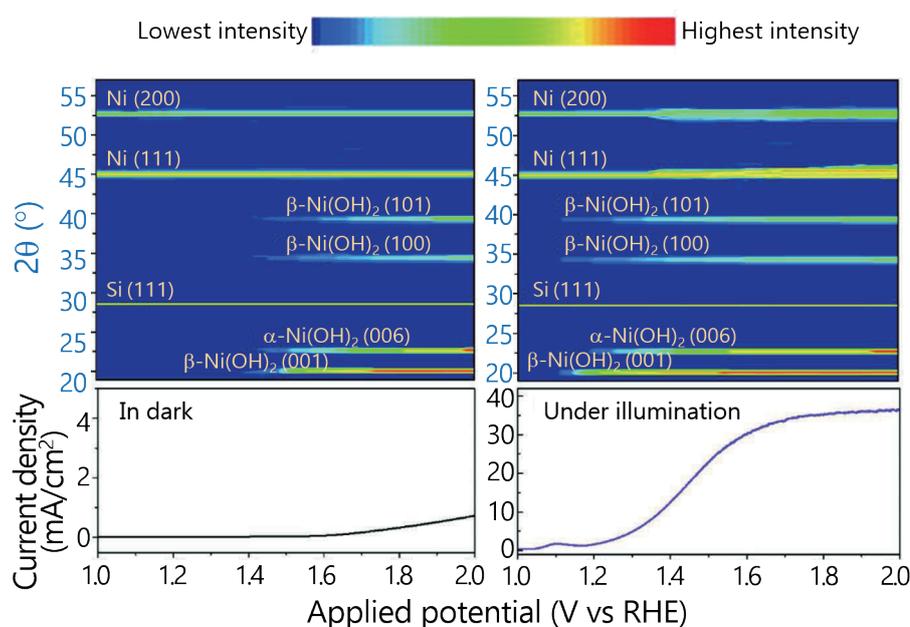


Fig. 1: Measurements *in situ* of grazing-angle X-ray scattering of a photoanode during (photo)electrochemical water oxidation: contour plots of grazing-angle X-ray diffraction signals of the photoanode *in situ* in solution (1 M KOH) under illumination and darkness. The upper images show the scattering intensity (color-coded) as a function of the voltage; the lower images show the measured current densities for both cases. [Reproduced from Ref. 1]

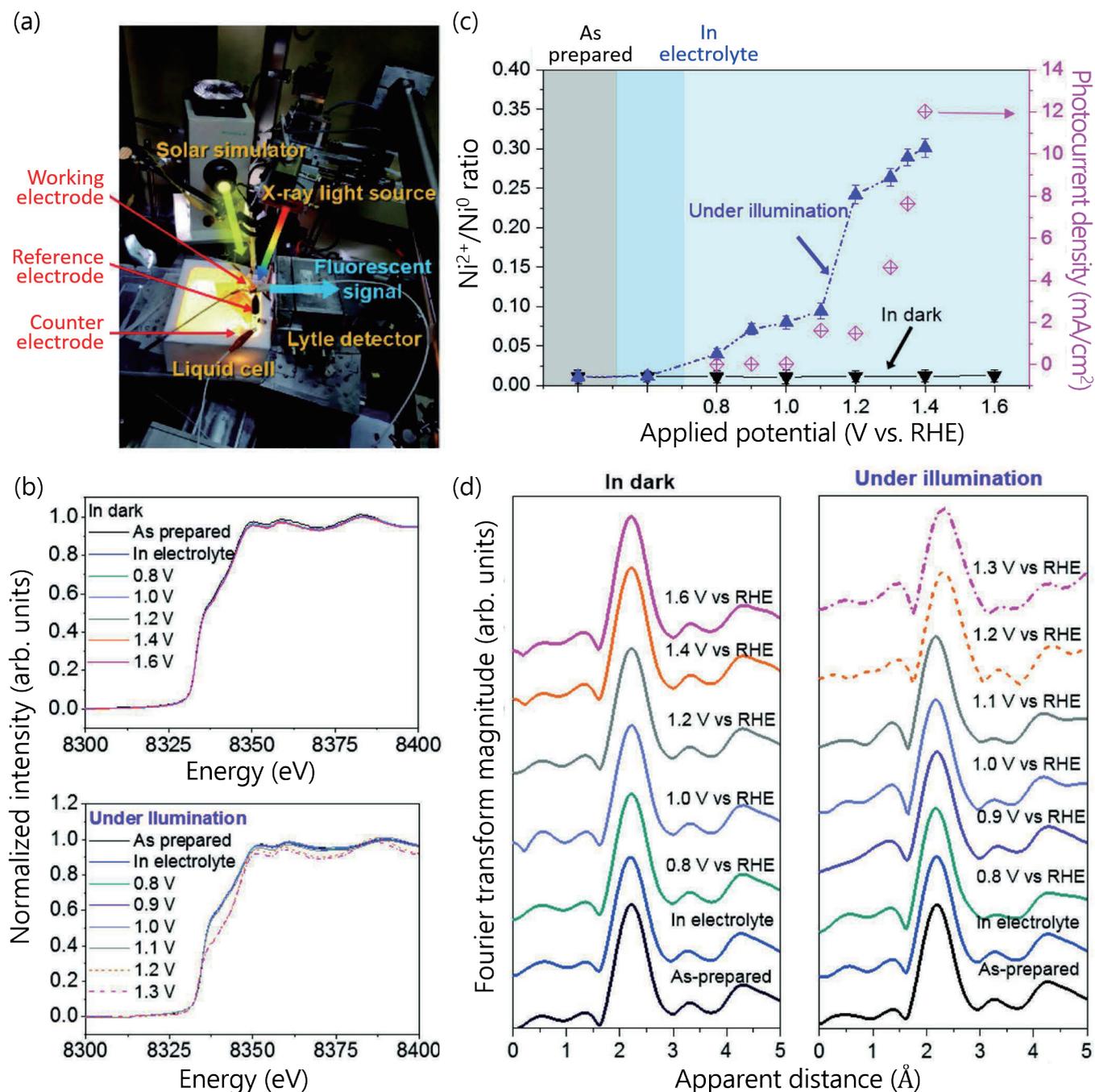


Fig. 2: X-ray absorption spectra of a photoanode recorded *in situ* during (photo)electrochemical water oxidation. (a) Digital photograph of customized cells used for the X-ray absorption measurements *in situ*. (b) Voltage-dependent XANES spectra under illumination and darkness. (c) $\text{Ni}^{2+}/\text{Ni}^0$ ratio and corresponding photocurrent density vs. control potentials. (d) Fourier-transform EXAFS spectra in aqueous solution containing KOH (1 M) under illumination and darkness at various bias voltages. [Reproduced from Ref. 1]

This report features the work of Hao-Ming Chen and his collaborators published in *Adv. Energy Mater.* **9**, 1901308 (2019).

TLS 01C1 SWLS – EXAFS

TLS 17C1 W200 – EXAFS

SP 12B1 BM – Materials X-ray Study

• XANES, EXAFS

• Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

Reference

1. C. W. Tung, T. R. Kuo, C. S. Hsu, Y. Chuang, H. C. Chen, C. K. Chang, C. Y. Chien, Y. J. Lu, T. S. Chan, J. F. Lee, J. Y. Li, H. M. Chen, *Adv. Energy Mater.* **9**, 1901308 (2019).