

# Phosphorus Doping Enlarges Hydrogen Evolution

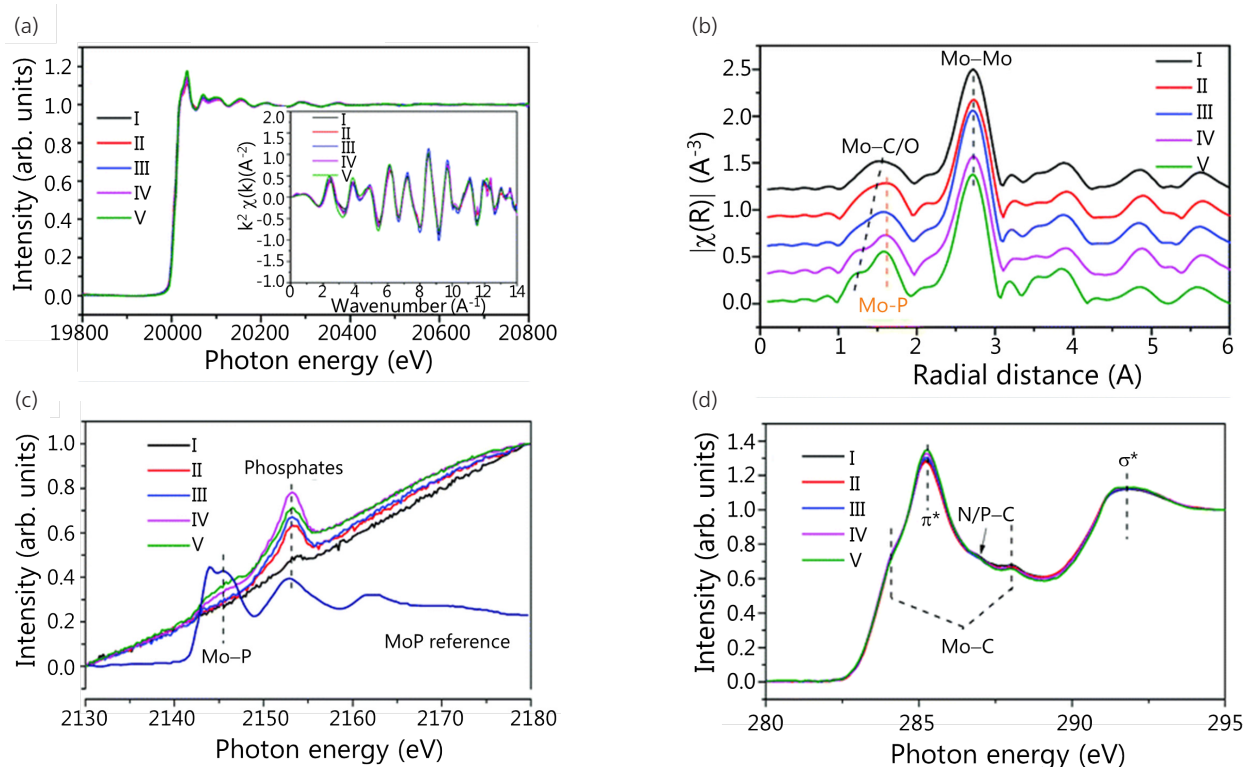
*Elucidating feasible electronic regulation and the remarkably enhanced catalysis associated with controlled P-doping has paved the way for developing efficient noble-metal-free catalysts via rational surface engineering.*

The hydrogen evolution reaction (HER) by water electrolysis can sustainably produce high-purity hydrogen, which is a promising solution to the energy crisis and several environmental issues. To this end, numerous efforts have been made to explore cost-effective electrocatalysts based on earth-abundant elements. Among them, molybdenum carbide ( $\text{MoC}_x$ ) has attracted intensive interest due to its low-cost, wide pH applicability, and tunable phase and composition. However, due to the unoccupied d-orbitals with large density, the strong Mo–H bonding restricts  $\text{H}_{\text{ads}}$  desorption and leads to an intrinsic limitation in activity.

In the work<sup>1</sup> done by Zhangping Shi (Fudan University) and his co-workers, a facile and universal approach was proposed to engineer P-doping in carbides, which can increase the electron density around the Fermi level of  $\text{Mo}_2\text{C}$  and introduce steric hindrance by P on the  $\text{Mo}_2\text{C}$  surface, resulting in weakened Mo–H

bonding toward promoted HER kinetics. Remarkably, the optimal P- $\text{Mo}_2\text{C}@\text{C}$  nanowires with controlled P-doping (P: 2.9 wt%) deliver a low overpotential of 89 mV at a current density of  $-10 \text{ mA cm}^{-2}$  and striking kinetic metrics (onset overpotential: 35 mV, Tafel slope:  $42 \text{ mV dec}^{-1}$ ) in acidic electrolyte. Furthermore, the authors performed synchrotron-based X-ray adsorption techniques at **TLS 20A1**, **TLS 16A1** and **TLS 01C1** to clarify the interactions between the dopant (P) and active sites ( $\text{Mo}_2\text{C}$ ).

The Mo K-edge spectra and K space oscillation curves in **Fig. 1(a)** show gradual changes with different P concentrations. **Figure 1(b)** gives the corresponding R space curves after  $k^2 [\chi(k)]$  functions Fourier transform, and two peaks at around 1.5 and 2.7 Å in  $\text{Mo}_2\text{C}@\text{C}$  are associated with Mo–C/O and Mo–Mo bonding, respectively. Notably, a shoulder emerges after P-doping at 1.7 Å, which can be assigned to Mo–P coordination. Visibly, with increased P-doping,



**Fig. 1:** (a) Mo K-edge extended XAFS spectra and K space  $k^2[\chi(k)]$  function oscillation (inset), (b) their corresponding R space spectra and (c) Mo K-edge X-ray absorption near edge structure (XANES) spectra of the compounds of (I)  $\text{Mo}_2\text{C}@\text{C}$ , (II)  $\text{P-Mo}_2\text{C}@\text{C-0.8}$ , (III)  $\text{P-Mo}_2\text{C}@\text{C-1.9}$ , (IV)  $\text{P-Mo}_2\text{C}@\text{C-2.9}$ , and (V)  $\text{P-Mo}_2\text{C}@\text{C-3.4}$ . [Reproduced from Ref. 1]

the intensity of Mo–P coordination increases, and the Mo–C/O bonds slightly shift to a lower radical distance. These observations should result from the lattice distortion by P incorporation. Indeed, they clearly confirm the presence of P–Mo bonds in P-Mo<sub>2</sub>C@C and the direct interaction between the dopant and carbide. Additionally, P K-edge and C K-edge X-ray absorption near edge structure (XANES) spectra are also recorded. **Figure 1(c)** depicts the P K-edge XANES spectra of P-Mo<sub>2</sub>C@C, and the XANES spectra of MoP is also replotted from the reference. Except for the sharp peak around 2153 eV related with phosphates, the broad feature at the pre-edge region (around 2145 eV) further indicates the formation of Mo–P species, showing the increasing trend corresponding to the enhanced Mo–P coordination (**Fig. 1(b)**). The C K-edge XANES results are presented in **Fig. 1(d)** in which pronounced C=C  $\pi^*$  and C–C  $\sigma^*$  resonances located at 285 and 292 eV can be observed, respectively. The additional peak and shoulder at 288 eV and 284 eV respectively should be assigned to typical features of Mo<sub>2</sub>C. Another shoulder around 287 eV is typically associated to carbon bonded with nitrogen and phosphorus, demonstrating the co-doping of N and P into the carbon matrix. Noticeably, the P-Mo<sub>2</sub>C@C and Mo<sub>2</sub>C@C samples display slight changes in the C K-edge XANES profiles, which indicates the negligible influence on the carbon matrix after varied P-doping.

In summary, controlled P-doping was developed to effectively optimize the electronic configuration and HER activity of Mo<sub>2</sub>C electrocatalysts. Remarkably, P-doping into Mo<sub>2</sub>C can increase the electron density around the Fermi level of Mo<sub>2</sub>C, leading to weakened Mo–H bonding promoting HER kinetics. The synergy of electron transfers into the anti-bonding orbitals of Mo–H and steric hindrance of H atoms on P-doped sites is responsible for the effectively weakened Mo–H. This work opens up a new opportunity to develop efficient noble-metal-free catalysts. (Reported by Yan-Gu Lin)

*This report features the work of Zhangping Shi and his co-workers published in Energy Environ. Sci. **10**, 1262 (2017).*

#### TLS 01C1 SWLS – EXAFS

#### TLS 16A1 BM – Tender X-ray Absorption, Diffraction

#### TLS 20A1 BM – (H-SGM) XAS

- XANES, EXAFS
- Materials Science, Chemistry, Condensed Matter Physics, Environmental and Earth Science

#### Reference

1. Z. Shi, K. Nie, Z.-J. Shao, B. Gao, Hu. Lin, H. Zhang, B. Liu, Y. Wang, Y. Zhang, X. Sun, X.-M. Cao, P. Hu, Q. Gao, and Y. Tang, *Energy Environ. Sci.* **10**, 1262 (2017).

## Voltammetric Enhancement of Li-ion Conduction in Al-Doped Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> Solid Electrolyte

*Cyclic voltammetry has served as a tool to accelerate the Li-ion mobility within a garnet-phase solid electrolyte, Al-doped Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>; the modification of the local ionic arrangements has been studied by refinement of neutron powder diffraction (NPD) ex situ and correlated with the results of X-ray absorption near-edge spectra (XANES).*

A cutting-edge Li-ion battery (LIB) utilizes liquid or organic-based electrolytes. Several challenges and safety issues restrict their use in high-temperature operation and small-scale devices. Solid-state Li-ion conductors are promising alternatives to liquid-based LIB electrolytes, mitigating the safety issues of dendritic Li growth.<sup>1</sup> Among Li-ion conducting materials, Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO), possessing a garnet-type crystal structure, is of particular interest for application as a solid LIB electrolyte because of its suitable ionic conductivity, chemical stability in a wide potential range and ease of scaling for industrial

applications.<sup>2</sup> LLZO can crystallize in cubic or tetragonal symmetry phases depending on the conditions of synthesis. Cubic LLZO possesses space group symmetry  $Im\bar{3}d$  with La, Zr and O atoms located at 24c, 16a and 96h sites, respectively, whereas Li occupies both 24d tetrahedral and 96h octahedral sites.<sup>3</sup> Tetragonal LLZO possesses space group symmetry  $I4_1/acd$  with La, Zr and O atoms located at 8b (and 16e), 16c and 32g sites, respectively. The conductivity of tetragonal LLZO is about 1/100 that of cubic LLZO; doping with Al, which preferably occupies the 24d site, provides a method to stabilize the more favorable cubic LLZO phase.