

than for lattice oxygen atoms in FeOOH and NiFeOOH. The energy split in Ni–Fe–N–C is even smaller than that of $\text{Fe}(\text{NO}_3)_3$, probably due to a more asymmetric structure of the Ni–Fe units compared to $\text{Fe}(\text{NO}_3)_3$. All these results further support the formation of Ni–Fe double atoms.

In summary, the molecular nature of active sites in these double-atom catalysts facilitates the deduction of reaction mechanisms using data from XAS and electrokinetic measurements. In the future, the new molecular platform proposed by this team of researchers could be used to study heterogenous OER electrocatalysts in depth. For instance, it could help material scientists to understand better how an atomic configuration and chemical state of a catalyst affect its catalytic nature. (Reported by Yan-Gu Lin)

This report features the work of Xile Hu and Hao Ming Chen published in Nat. Energy 6, 1054 (2021).

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

TLS 01C1 EXAFS

SP 12B1 Materials X-ray Study

SP 12U1 Inelastic X-ray Scattering

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

Reference

1. L. Bai, C.-S. Hsu, D. T. L. Alexander, H. M. Chen, X. Hu, Nat. Energy 6, 1054 (2021).

Lighting the Path to Perovskite Photovoltaics

The time-resolved grazing-incidence wide-angle X-ray scattering technique is demonstrated to study the phase transition during the formation of perovskite quantum wells.

Perovskite quantum wells (PQW) exhibit greatly enhanced stability in contrast to the traditional 3D perovskite due to the long-organic-chain ligands. In contrast to cations of smaller size, the ligand molecules with a longer chain can form an interdigitating structure at an interface stabilized by the van der Waals force, resulting in an overall stabilization of the stacked perovskite hierarchy. The photovoltaic performance of pure 2D perovskite solar cells is, however, not at par with that of its 3D counterpart because of anisotropic charge-carrier transport. To combine the excellent efficiency of light to electricity of the 3D perovskite with the desired stability of the PQW, the hierarchy of building a low-dimensional perovskite layer on top of a 3D bulk perovskite layer has been introduced. Thus far, most studies on PQW/3D perovskite have focused on the photovoltaic performance (including stability) after the formation of the hierarchy; whereas the critical issue of determining how the coated ligand molecules convert the 3D perovskite lattice into the reduced-dimensional perovskite structure is rarely explored.

Gang Li (Hong Kong Polytechnic University, China) and his coworkers recently explored in detail the formation mechanism of PQW on top of a 3D perovskite bulk layer through the real-time tracking of crystal phase evolution. Employing grazing-incidence wide-angle scattering measurements (GIWAXS) *in situ* at beamline **TLS 23A1**,¹ the results revealed the formation *in situ* of PQW when hexyltrimethylammonium bromide (HTAB) was coated on top of the 3D perovskite layer. The time-resolved GIWAXS intensity map during the spin coating of HTAB on top of the pristine 3D perovskite layer is shown in **Fig. 1(a)** (see next page). Before the HTAB dripping, only the scattering rings from the 3D perovskite crystals at a large q regime appear, as shown in **Fig. 1(b)**. After the HTAB was coated on the 3D perovskite layer, a new ordered intermediate phase immediately emerged in the low q regime ($q = 0.31 \text{ \AA}^{-1}$), as indicated by the red arrow in **Fig. 1(c)**. Surprisingly, a strikingly strong ionic reaction between the 3D perovskite and the long-chain organic cation led to the rapid formation of an ordered intermediate phase within only a few seconds, as shown in **Fig. 1(d)**. The existence of this reaction sufficiently explained the decrease in the 3D perovskite (110) scattering signal when the 2D perovskite scattering signals in the small- q regime intensified as the HTAB concentration increased. The optimal PQW/3D architecture was achieved on controlling the HTAB casting, which was assisted by time-of-flight secondary-ion mass spectral characterization. On controlling the second ionic reaction during the long-chain cation coating, along with the fluorinated poly(triarylamine) as a hole-transport layer, the perovskite solar cells demonstrated efficiencies exceeding 22% along with greatly improved device stability.

In summary, to realize efficient and stable perovskite solar cells, the profound mechanism of PQW formation in the PQWs/3D heterostructure was explored. Time-resolved GIWAXS revealed a rapid ionic reaction immediately after HTAB casting, yielding

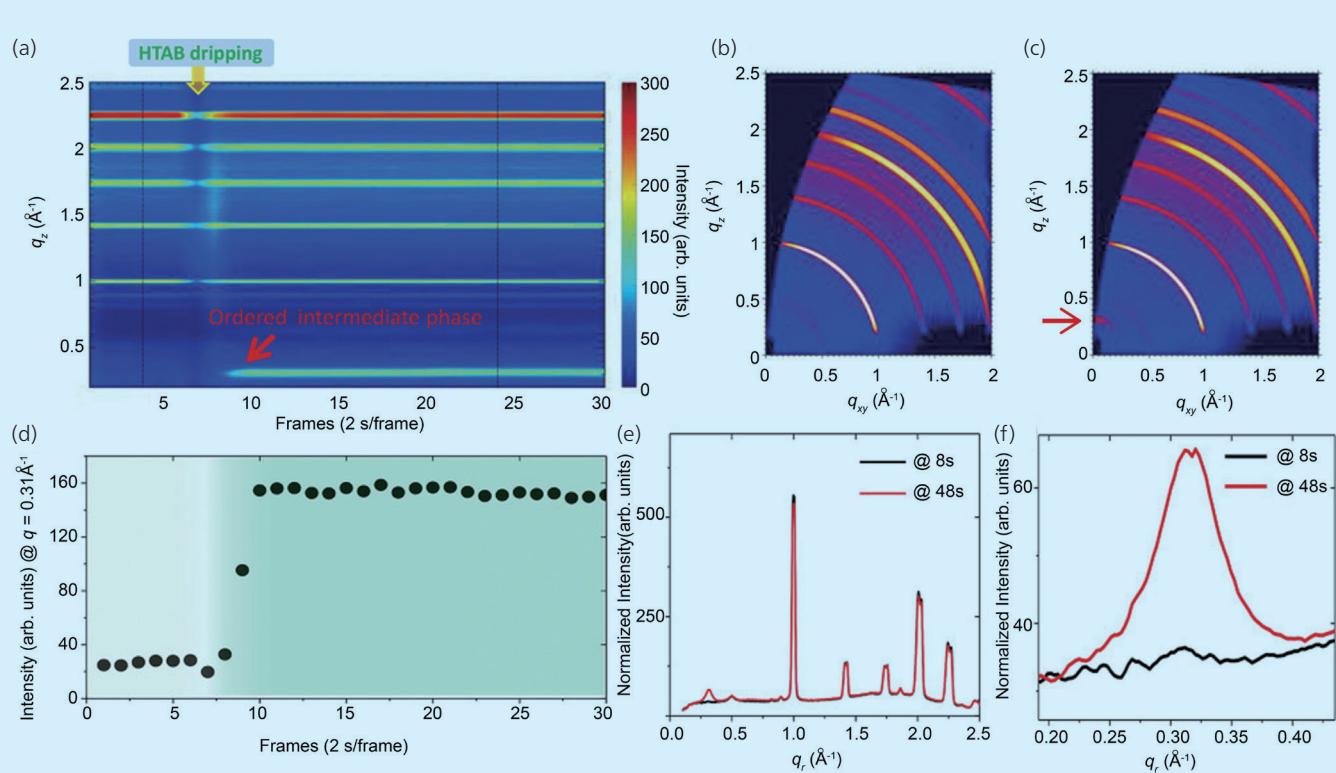


Fig. 1: (a) Time-resolved GIWAXS intensity maps showing the formation of an ordered intermediate phase during HTAB solution (10×10^{-3} M) spin coated on top of a pristine 3D perovskite layer. (b,c) 2D GIWAXS patterns for perovskite films before (@8 s) and after (@48 s) HTAB dripping, as indicated by the black dashed lines in (a). (d) Extracted intensity @ $q = 0.31 \text{ \AA}^{-1}$ (ordered intermediate phase, as indicated with a red arrow in (c)) as a function of time. (e) Integrated intensity versus q from 2D GIWAXS patterns at 8 s (black) and 48 s (red). (f) Magnification of the integrated intensity versus q in the low q regime. [Reproduced from Ref. 1]

a highly ordered intermediate phase within only a few seconds. Details regarding the mechanism of PQW formation and the relative phase transformation elucidated in this study would guide the control of chemical reactions toward the desired PQW/3D perovskite hierarchy, facilitating further improvements in both the optoelectronic property and stability, and ultimately benefiting the implementation of PQW modified with the 3D perovskite hierarchy in the near future. (Reported by Yan-Gu Lin)

This report features the work of Gang Li and his collaborators published in *Adv. Mater.* **33**, 2006238 (2021).

TLS 23A1 Small/Wide Angle X-ray Scattering

- SAXS, WAXS
- Soft Matter, Protein Crystallography, Materials Science, Atomic and Molecular Science

Reference

1. H. Hu, M. Qin, P. W. K. Fong, Z. Ren, X. Wan, M. Singh, C.-J. Su, U.-S. Jeng, L. Li, J. Zhu, M. Yuan, X. Lu, C.-W. Chu, G. Li, *Adv. Mater.* **33**, 2006238 (2021).