

# Energy Materials and Surface Sciences Unit

Professor Yabing Qi



## Abstract

The integration of solar energy harvesting devices with energy storage devices is essential in the effort to create a cleaner environment and move towards a zero-carbon society. The demand for renewable and sustainable energy is driving investigations into novel materials and technologies that can offer efficient, cost-effective, and eco-friendly solutions. Halide perovskite solar cells and modules have garnered significant attention in recent years due to their potential for high efficiency and low-cost manufacturing. In this report, we summarize our recent progresses on the fundamental aspects of perovskite surface decomposition (Section 3.1), developed fabrication strategies of perovskite solar cells and modules aiming at efficient solar energy conversion with prolonged lifetimes (Section 3.2). Additionally, we made progress on developing alternative cost-effective perovskite light-emitting diodes (LEDs) (Section 3.3). An essential area of research in solar energy harvesting pertains to uninterrupted utilization of electricity harvested from solar panels. The topics of Li-ion batteries with fast charging and 'beyond Li-ion battery' technologies were explored (Section 3.4). The future integration of non-intermittent solar energy harvesting-storage devices will heavily depend on the progress of cost-effective and high-performance electrical energy storage systems.

## 1. Staff

- Ms. Naoko Ogura-Gayler, Research Unit Administrator
- Dr. Luis K. Ono, Group Leader
- Dr. Chenfeng Ding, Researcher
- Dr. Tianhao Wu, Researcher
- Dr. Silvia Mariotti, Researcher

- Dr. Shuai Yuan, Researcher
- Dr. Penghui Ji, Researcher
- Dr. Tongtong Li, Researcher
- Mr. Jiahao Zhang, OIST Graduate Student
- Ms. Ilhem Nadia Rabehi, OIST Graduate Student
- Mr. Hengyuan Wang, Visiting Research Student
- Ms. Xiaomin Liu, Visiting Research Student
- Ms. Xiaomin Huo, Visiting Research Student
- Mr. Ting Guo, Visiting Research Student
- Mr. Zhong Xu, Visiting Research Student

## 2. Collaborations

### 2.1 Multiple-barrier design for light-heat stable perovskite solar cells

- Description: The stability issue of perovskite solar cells has been recognized as one of the major bottlenecks impeding their commercialization. In this joint research, a non-noble metal/metal oxide/polymer multiple-barrier was designed to contain the gaseous perovskite decomposition products release with the chemically inert bismuth electrode and Al<sub>2</sub>O<sub>3</sub>/parylene thin-film encapsulation. We provided the mass-spectrometry results confirming the efficacy of the multiple-barrier design. The results of the joint research can be found in *Nat. Commun.* **14**, 6120 (2023).
- Type of collaboration: Joint research
- Researchers:
  - Prof. Prof. Zhonghao Liu, Huazhong University of Science and Technology, China.
  - Prof. Wei Chen, Huazhong University of Science and Technology, China.

### 2.2 Perovskite solar cell efficiency improvements by reduction of bulk and surface defects

- Description: In this joint research, the strategy to improve the quality of both bulk and surface of FA<sub>0.98</sub>CS<sub>0.02</sub>PbI<sub>3</sub> perovskite films to enable high-performance inverted perovskite solar cells were proposed. The low-volatile dibutyl sulfoxide (DBSO) Lewis base additive has a strong coordination ability with PbI<sub>2</sub> (PbI<sub>2</sub>-DBSO) that improves the crystallinity, reduces the defect density and the internal residual strain of the perovskite bulk. The details of outcomes from the joint research can be found in *Nat. Energy* **8**, 839–849 (2023).
- Type of collaboration: Joint research
- Researchers:

- Prof. Wei Chen, Huazhong University of Science and Technology, China.

## 2.3 Semitransparent organic photovoltaic efficiency

### improvements via synergetic near-infrared light management

- Description: Semitransparent organic photovoltaics are considered as key technology to turn ubiquitous glass windows into active solar panels in buildings, vehicles, and greenhouses. One of the challenges consists in maximizing the optical absorption in the near-infrared (NIR) portion of sunlight that represents over 50% of solar energy. In this joint research, a strategy for enhanced NIR light management relying on plasmonic effects combined with optical coupling layers and anti-reflection coating was proposed. The details of outcomes from the joint research can be found in *Adv. Mater.* **36**, 2311305 (2024).
- Type of collaboration: Joint research
- Researchers:
  - Prof. Shenghao Wang, Shanghai University, China.
  - Prof. Mona Treguer-Delapierre, University of Bordeaux, France.

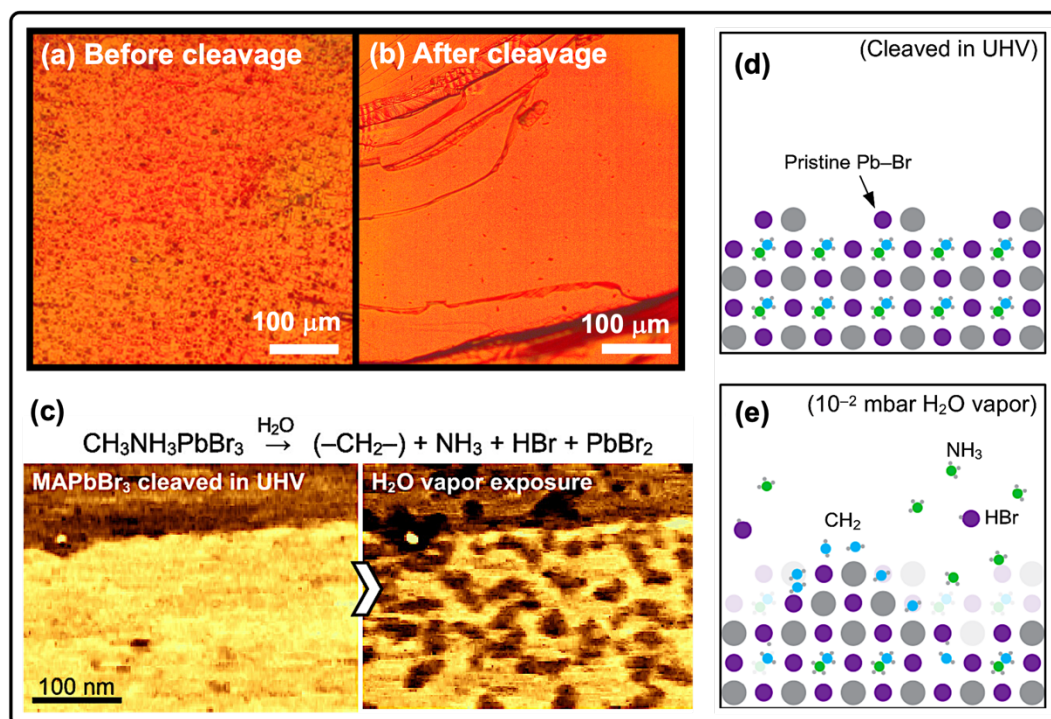
## 3. Activities and Findings

### 3.1 Fundamental mechanistic of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal surface decomposition by $\text{H}_2\text{O}$ molecules

Publication: Joong Il Jake Choi, Luis K Ono, Hunyoung Cho, Ki-Jeong Kim, Hyung-Been Kang, **Yabing Qi\***, Jeong Young Park\*, "Pathways of Water-Induced Lead-Halide Perovskite Surface Degradation: Insights from *In Situ* Atomic-Scale Analysis" *ACS Nano* **17**, 25679–25688 (2023). [Published before March 31st, 2024 corresponding to the end of FY2023 in the Japanese calendar.]

Description: While metal halide perovskites are emerging as promising materials for next-generation photovoltaic applications, the origins and pathways of perovskite instability remain speculative. Perovskites are susceptible to performance degradation under ambient conditions, and the interaction of perovskites and water is one of the most important factors in the instability of perovskite solar cells. In this study, the pristine surfaces of perovskites were prepared by cleavage of a  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  ( $\text{MAPbBr}_3$ ) single crystal under ultrahigh-vacuum (UHV) conditions [Fig. 1(a,b)]. By utilizing ambient pressure atomic force microscopy (AP-AFM), a comprehensive understanding of the degradation pathways of cleaved  $\text{MAPbBr}_3$  single crystal surfaces in controlled  $\text{H}_2\text{O}$  environments was attained at the atomic to molecular scale.  $\text{H}_2\text{O}$  molecules resulted in the dissociation of  $\text{CH}_3\text{NH}_3^+$  surface ligands followed by desorption of volatile species of  $\text{HBr}$  and  $\text{NH}_3$  under both low-pressure conditions ( $10^{-5}$  mbar regime) and high-pressure conditions (0.01 mbar) [Figs. 1(c–e)]. Furthermore, upon exposure to 0.01 mbar of  $\text{H}_2\text{O}$ , the perovskite surface was covered with hydrocarbon species [Fig. 1(e)]. This research provides valuable

insights for the future development of stable and efficient perovskite-based optoelectronic devices through molecular engineering.



**Figure 1.** Optical micrographs of a  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  (MAPbBr<sub>3</sub>) single crystal (a) before and (b) after the cleavage process. (c) Contact-mode ambient pressure atomic force microscopy (AP-AFM) topography of ultrahigh vacuum (UHV) cleaved MAPbBr<sub>3</sub> single crystal surface (left) and during exposure of H<sub>2</sub>O vapor ( $1.1 \times 10^{-5}$  mbar). (d,e) Schematic illustrations of a pristine Pb-Br-terminated surface (d) and growth of degraded patches in water vapor at  $10^{-2}$  mbar H<sub>2</sub>O with formation of PbBr<sub>2</sub> islands covered by hydrocarbon species (e).

## 3.2 Perovskite solar cells and modules: enhancing efficiency and operational stability

Two works are described in this section.

Publication 1: Guoqing Tong, Jiahao Zhang, Tongle Bu, Luis K Ono, Congyang Zhang, Yuqiang Liu, Chenfeng Ding, Tianhao Wu, Silvia Mariotti, Said Kazaoui, **Yabing Qi\***, "Holistic Strategies Lead to Enhanced Efficiency and Stability of Hybrid Chemical Vapor Deposition Based Perovskite Solar Cells and Modules" *Adv. Energy Mater.*, **13**, 2300153 (2023).

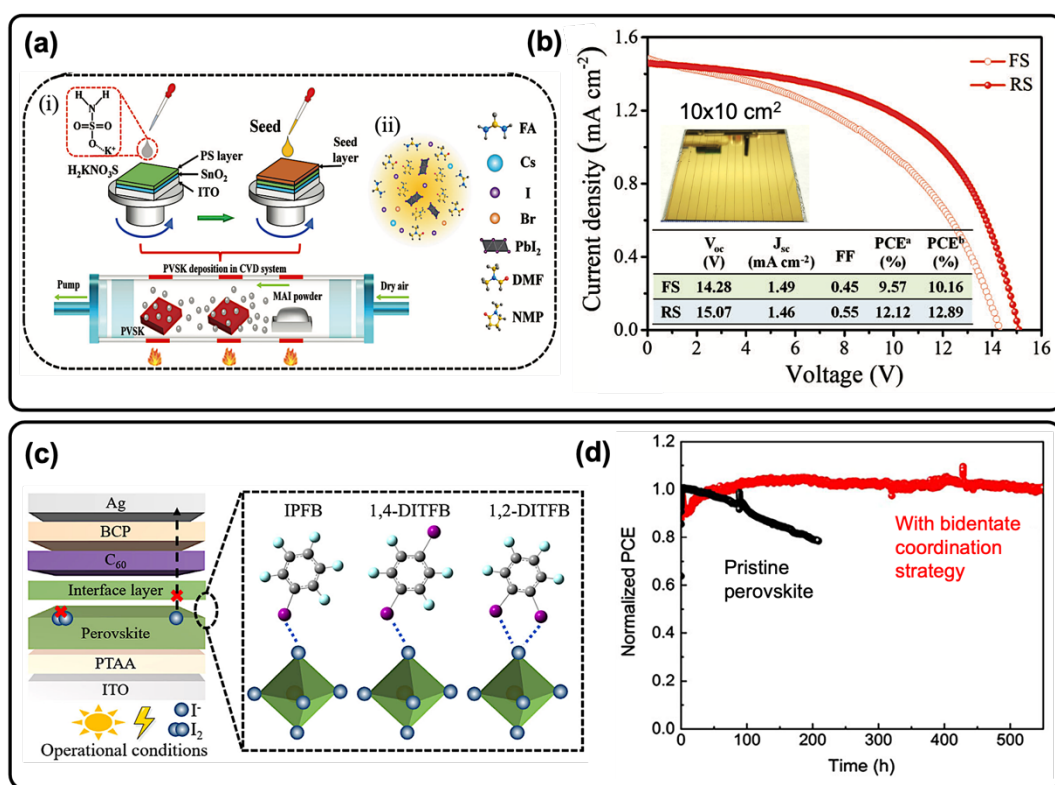
Description: The hybrid chemical vapor deposition (HCVD) method developed in my unit is a promising method for the up-scalable fabrication of perovskite solar cells/modules (PSCs/PSMs). However, the efficiency of the HCVD-based perovskite solar cells still lags behind the solution-processed PSCs/PSMs. In this work, the oxygen loss of the electron transport layer of SnO<sub>2</sub> in the HCVD process, which was found to have a negative impact on solar cell performance, was circumvented by using potassium sulfamate (H<sub>2</sub>KNO<sub>3</sub>S). H<sub>2</sub>KNO<sub>3</sub>S was introduced as the passivation layer to both mitigate the oxygen loss issue of SnO<sub>2</sub> and passivate the uncoordinated Pb<sup>2+</sup> in the perovskite film [Fig. 2(a)(i)]. In parallel, the use of N-methylpyrrolidone (NMP) solvent to dissolve PbI<sub>2</sub>,



formed a stable intermediate phase of  $\text{PbI}_2 \cdot \text{NMP}$ , which greatly improves the perovskite crystal nucleation in the HCVD process [Fig. 2(a)(ii)]. By applying the strategies above, perovskite solar cells with a champion power conversion efficiency (PCE) of 21.98% ( $0.09 \text{ cm}^2$ ) was achieved. In addition, these strategies were also suitable for scaling up perovskite solar modules leading to efficiencies of 16.16% ( $5 \times 5 \text{ cm}^2$ ) and 12.12% ( $10 \times 10 \text{ cm}^2$ ) [Fig. 2(b)].

Publication 2: Caiyi Zhang, Ting Guo, Luis K Ono, Shuai Yuan, Tianhao Wu, Hengyuan Wang, Jiahao Zhang, Xiaomin Liu, Xiaomin Huo, Congyang Zhang, Chenfeng Ding, Tongtong Li, Yanbo Wang, Liyuan Han\*, **Yabing Qi\***, "Constructing heterostructure through bidentate coordination toward operationally stable inverted perovskite solar cells" *Solar RRL* 2300253 (2023).

Description: In another work, aiming to enhance the operational stability of perovskite solar cells, 1,2-diiodotetrafluorobenzene (1,2-DITFB) molecule was employed. The rationale in this strategy was to form a strong halogen bonding with the undercoordinated iodine at the surface of the perovskite film, which was found possible employing 1,2-DITFB owing to the bidentate coordination nature [Fig. 2(c)]. We have learned that one of the influencing factors leading to stability issues in iodine-containing perovskite solar cells is the iodine loss from the perovskite. The stable heterostructure of perovskite/1,2-DITFB, formed through bidentate coordination, resulted in a prolonged operational stability retaining 96.15% of their initial PCE tested for  $\sim 550$  hours [Fig. 2(d)].



**Figure 2.** (a) Schematic illustration of the hybrid chemical vapor deposition (HCVD) method developed in my unit combined with the new strategies of (i) using potassium sulfamate ( $\text{H}_2\text{KNO}_3\text{S}$ ) to protect the  $\text{SnO}_2$  layer and (ii) N-methylpyrrolidone (NMP) solvent to enhance the perovskite crystal nucleation for the fabrication of solar cells and modules. (b) Perovskite solar modules with  $10 \times 10 \text{ cm}^2$  substrate size generates a power conversion efficiency (PCE) of 12.12% corresponding to an active area PCE of 12.89%. (c) Schematic of the device structure, the coordination mode between the perovskite and selected molecules (IPFB, 1,4-DITFB, and 1,2-DITFB). (d) Operational stability plot showing Normalized PCE vs. Time (h). The pristine perovskite (black) shows a sharp decline in PCE, while the device with bidentate coordination strategy (red) maintains a high PCE over 500 hours.

Operational stability of the unencapsulated perovskite solar cells in N<sub>2</sub> environment measured at room temperature (25 °C) with a fixed bias corresponding to the voltage at maximum power point (~1 to 1.5 V).

### 3.3 Metal halide perovskite materials in light-emitting diodes (LEDs)

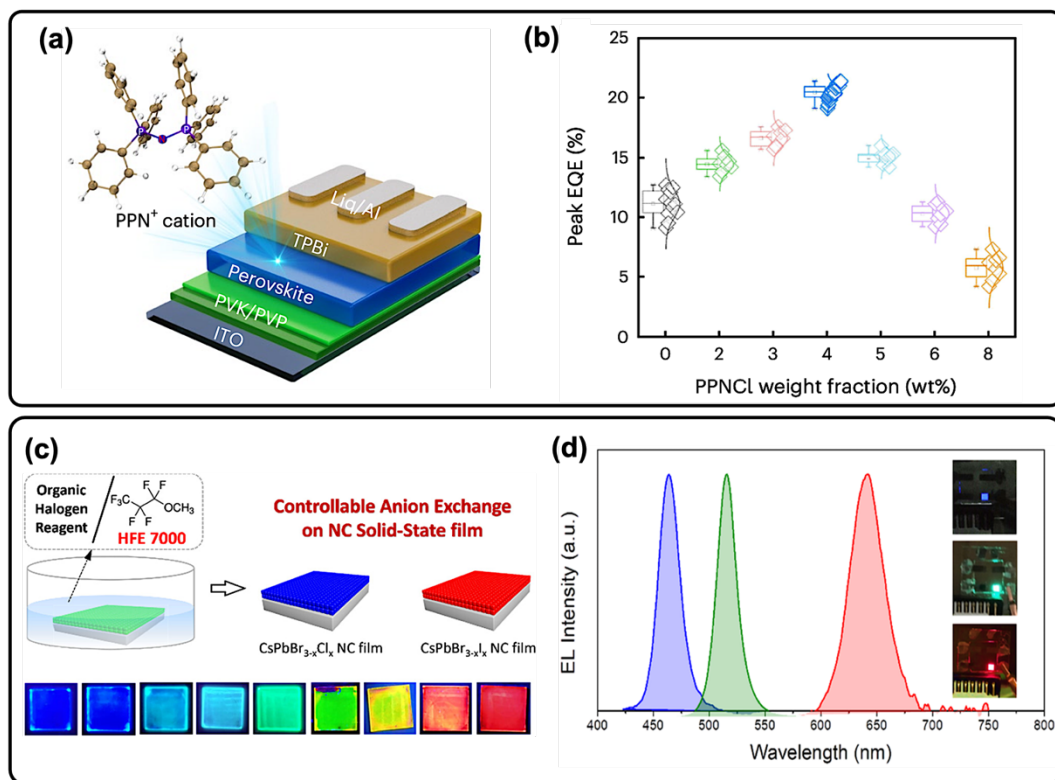
Two works are described in this section.

Publication 1: Shuai Yuan, Linjie Dai, Yuqi Sun, Florian Auras, Yu-Hang Zhou, Rui-Zhi An, Yun Liu, Chenfeng Ding, Cathal Cassidy, Xun Tang, Shou-Cheng Dong, Hyung-Been Kang, Kai Chen, Xiaomin Liu, Zhi-Feng Ye, Yixin Zhao, Chihaya Adachi, Liang-Sheng Liao, Neil C Greenham, **Yabing Qi**, Samuel D Stranks, Lin-Song Cui, Richard H Friend, "Efficient Blue Electroluminescence from Reduced-Dimensional Perovskites", *Nat. Photonics* **18**, 425–431 (2024).

Description: Metal halide perovskites are also promising materials for next generation display technologies as they combine low-cost and solution processability with outstanding luminescence properties. While significant advancements have been made in green- and red-emitting devices, the advancement of efficient blue perovskite light-emitting diodes (LEDs) is still lacking. Bis(triphenylphosphine)iminium chloride (PPNCl) [Fig. 3(a)], a multifunctional ionic additive, was identified as a substance that can improve the composition of perovskite films by facilitating the creation of highly emissive large-n perovskite phases and reducing non-radiative recombination losses associated with defects. Our developed approach enabled efficient and stable blue reduced-dimensional perovskite emitters for LEDs with a maximum external quantum efficiency (EQE) of 21.4% [Fig. 3(b)], close to state-of-the-art blue organic LEDs and inorganic quantum dot LEDs.

Publication 2: Congyang Zhang, Chenfeng Ding, Shuai Yuan, Luis K Ono, Caiyi Zhang, Tianhao Wu, Silvia Mariotti, Penghui Ji, Tongtong Li, Jiahao Zhang, **Yabing Qi\***, "Controllable Anion Exchange on Perovskite Nanocrystal Solid-State Thin Films" *J. Phys. Chem. C*, **127**, 9947–9956 (2023).

Description: In a second study, we proposed a facile method to tune the emission color of perovskite nanocrystal (NC) thin film-based LEDs through a controllable anion exchange. Our methodology is based on using hydrofluoroether (HFE) solvent media and it is achieved by directly immersing the perovskite NC thin films in the HFE solution with an organic halogen reagent. By tuning the halide composition of organic reagent and reaction time, mixed-halide perovskite NC films with precisely tunable emission colors and wavelengths can be achieved [Fig. 3(c)]. Importantly, benefiting from the chemically benign HFE solvent, the perovskite NC thin films are almost nondestructive during the anion-exchange reaction process. As a proof-of-concept, using these obtained colorful perovskite NC films, we fabricated red-green-blue (RGB) LEDs with a wide color gamut [Fig. 3(d)].



**Figure 3.** (a) Device architecture of the blue perovskite LED and molecular structure of bis(triphenylphosphine)iminium [PPN]<sup>+</sup> cation. (b) Statistics of peak external quantum efficiencies (EQEs) measured from 88 individual blue perovskite LEDs fabricated with various amounts of PPNCI additive. (c) Illustration of the anion-exchange reaction for blue and red emission perovskite NC thin films. (bottom) Photographs of the mixed-halide perovskite NC thin films under UV light excitation, which shows colorful emission across the visible spectra range. (d) Red, green, and blue EL spectra of the colorful perovskite NC thin film-based LEDs. Insets show photographs of these devices under operation.

### 3.4 Progress on efficient energy storage devices

Two works are described in this section.

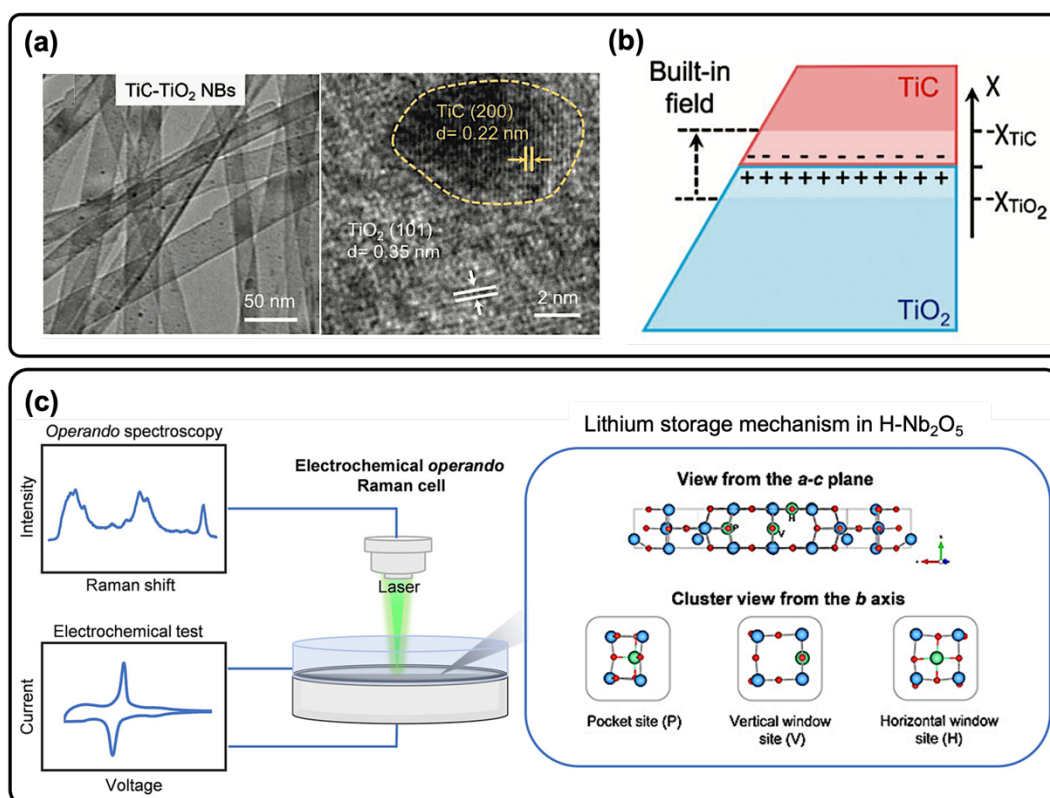
Publication 1: Chenfeng Ding, Mang Niu, Cathal Cassidy, Hyung-Been Kang, Luis K Ono, Hengyuan Wang, Guoqing Tong, Congyang Zhang, Yuan Liu, Jiahao Zhang, Silvia Mariotti, Tianhao Wu, **Yabing Qi\***, "Local Built-In Field at the Sub-nanometric Heterointerface Mediates Cascade Electrochemical Conversion of Lithium–sulfur Batteries" *Small*, 2301755 (2023).

Description: Lithium–sulfur (Li–S) batteries are regarded as one of the most promising candidates, owing to their high theoretical energy density (~2600 W h kg<sup>-1</sup>) and low cost (<US\$150/ton). However, the shuttling of lithium polysulfides during electrochemical reactions accelerate the capacity fading and lifetime. In this work, we proposed a heterogeneous catalysts composed of sub-nanometric clusters of titanium carbide (TiC) that are embedded into titanium dioxide nanobelts (TiO<sub>2</sub> NBs) [Fig. 4(a)]. The interfacial built-in electric field between TiC nano clusters and TiO<sub>2</sub> nanobelts ensured the rapid conversion from solid S<sub>8</sub> to soluble Li<sub>2</sub>S<sub>4</sub>. Furthermore, the preferential trapping of lithium polysulfides effectively inhibits the diffusion of sulfur intermediates into the

electrolyte ensuring the full utilization of active sulfur. The cathodes with catalytic mediators in Li–S cells yield a reversible capacity of 1412 mAh g<sup>-1</sup> at 0.1 C. Even under a sulfur loading of 8.0 mg cm<sup>-2</sup>, an areal capacity of 5.6 mAh cm<sup>-2</sup> is achieved with a fading rate of 0.093% per cycle over 330 cycles at 1 C. The above results showed that the cell with TiC–TiO<sub>2</sub> NBs exhibited a competitive performance compared with other Li–S batteries with other reported catalytic mediators.

Publication 2: Tongtong Li, Shengchi Huang, Nicholas Kane, Jeng-Han Wang\*, Zheyu Luo, Weilin Zhang, Gyutae Nam, Bote Zhao, **Yabing Qi\***, Meilin Liu\*, "Operando Raman and DFT Analysis of (De)lithiation in Fast-Charging, Shear-Phase H-Nb<sub>2</sub>O<sub>5</sub>" *ACS Energy Letters*, **8**, 7, 3131–3140 (2023).

Description: This study relates to fast-charging of Li-ion batteries. Li-ion batteries with fast charging capabilities have become increasingly popular in recent years due to the growing demand for quick and convenient charging solutions. Many niobium-based oxides exhibit rapid Li-ion diffusion. Unraveling the lithium storage mechanism in Nb-based oxides is especially important for the design of a new generation of storage materials with high power densities. In this study, vibrational modes of H-Nb<sub>2</sub>O<sub>5</sub> during lithiation/delithiation were analyzed by *in operando* Raman spectroscopy. Density functional theory (DFT) calculations were performed to complement the experimental results and explain the vibrational modes [Fig. 4(c)]. Our findings provide a detailed explanation of the lithiation mechanism in H-Nb<sub>2</sub>O<sub>5</sub>, highlighting the preference of lithium ions for specific sites and the corresponding lithium transport pathways. The methodologies outlined in this study can be utilized to investigate the storage properties of various materials, thereby further advancing the progress of developing Li-ion batteries that offer both efficient and safe fast-charging capabilities.



**Figure 4.** (a) Transmission electron microscopy (TEM) of TiC nanoclusters embedded in TiO<sub>2</sub> nanobelts. (b) Schematic diagram of built-in electric field at the interface of heterogenous TiC-TiO<sub>2</sub> nanobelts. (c) The evolution of vibrational bands was monitored by *in operando* Raman spectra of H-Nb<sub>2</sub>O<sub>5</sub> during lithiation in order to correlate the lithiation-induced structural variations of H-Nb<sub>2</sub>O<sub>5</sub> with the electrochemical properties. Complemented by DFT



calculations, the lithium storage mechanism was unraveled, including the preference for adsorption sites, the resultant electronic structure, and specific pathways for lithium transport.

### 3.5 Review articles

- Congyang Zhang, Luis K Ono, **Yabing Qi\***, "Color/Spectral Stability of Mixed Halide Perovskite Light-Emitting Diodes" *Adv. Funct. Mater.* **9947–9956** (2024).
- Tianpeng Li, Feifei He, Jia Liang, **Yabing Qi\***, "Functional Layers in Efficient and Stable Inverted Tin-based Perovskite Solar Cells" *Joule* **7**, 1966–1991 (2023).
- Wei Zhang, Xuan Zhang\*, Luis K. Ono, **Yabing Qi**, H. Oughaddou\* "Recent Advances in Phosphorene: Structure, Synthesis, and Properties" *Small* **2303115** (2023).
- Sanwan Liu, Vasudevan P. Biju\*, **Yabing Qi\***, Wei Chen, Zhonghao Liu\*, "Recent Progress in the Development of High-Efficiency Inverted Perovskite Solar Cells" *NPG Asia Mater.* **15**, 27 (2023).
- Zhifang Wu, Enbing Bi, Luis K. Ono, Dengbing Li, Osman M. Bakr\*, Yanfa Yan\*, **Yabing Qi\***, "Passivation Strategies for Enhancing Device Performance of Perovskite Solar Cells" *Nano Energy* **115**, 108731 (2023).

## 4. Publications

### 4.1 Journals

→[Please see our publications page for published journals](#)

### 4.2 Books and other one-time publications

Nothing to report.

## 5. Intellectual Property Rights and Other Specific Achievements

- Prof. Yabing Qi has received JSPS Prize from Japan Society for the Promotion of Science for his outstanding contributions to surface science and perovskite solar cells.
- Prof. Yabing Qi has been elected as of the American Vacuum Society (AVS) for his sustaining and outstanding contributions in the areas of interest to AVS.
- Prof. Yabing Qi has been elected as Fellow of the Materials Research Society (MRS) for his excellence in science and engineering and dedication to the advancement of materials research.
- Prof. Yabing Qi has been recognized as a Clarivate Highly Cited Researcher for his impactful research works.

- Dr. Luis K. Ono has been recognized as a Clarivate Highly Cited Researcher for his impactful research works.

## 6. Meetings and Events

### **Seminar: Provost Lecture**

**Title:** Surface sciences and perovskite solar cells

**Speaker:** Prof. Yabing Qi

**Date:** December 14, 2023

### **Symposium: The 20th "Next-Generation Photovoltaic Power Generation System" Symposium (The 3rd Annual Meeting of the Japan Photovoltaic Energy Society)**

**Title:** Surface and interface aspects in perovskite solar cells

**Speaker:** Dr. Luis K. Ono

**Date:** 2023 June 30

**Venue:** Kyoto TERRSA [[https://www.j-pvs.jp/symposium/events/pvsymp20/details\\_pvsymp20.html](https://www.j-pvs.jp/symposium/events/pvsymp20/details_pvsymp20.html)]

### **Event: New Technology Showcase event**

**Organizer:** JST (Japan Science and Technology Agency)

**Title:** Robust hole transport material with interface anchors enhances the efficiency and stability of inverted perovskite solar cells

**Speaker:** Dr. Luis K. Ono

**Date:** 2023 June 8

**Venue:** Zoom

### **Conference: International Summit on Organic and Hybrid Photovoltaics Stability (ISOS-14)**

**Title:** Piperazinium iodide as perovskite treatment for high-performance perovskite/silicon tandem solar cells

**Speaker:** Dr. Silvia Mariotti

**Date:** 2023 November 10

### **Seminar: Renewable Energy**

**Title:** Fabricating perovskite solar cells around the World: a toxic job

**Speaker:** Dr. Silvia Mariotti

**Date:** 2023 November 15

**Venue:** Stephenson Institute, University of Liverpool, UK (online)

### **Seminar: Invited by Prof. Annalisa Bruno**

**Title:** Perovskite solar cells: from tandem devices to module fabrication

**Speaker:** Dr. Silvia Mariotti

**Date:** 2024 January 29

**Venue:** Nanyang Technological University