

## Engineering of a charged incoherent BiFeO<sub>3</sub>/SrTiO<sub>3</sub> interface

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**[Ques] This study engineered a charged incoherent BiFeO<sub>3</sub>/SrTiO<sub>3</sub> interface by inserting a monolayer of FeO via shuttered oxide-MBE, which disrupted lattice coherence, stabilized a tetragonal BFO phase with downward polarization, and induced free electron accumulation and conductivity at the interface.**

**[关键问题]** 该研究通过在 BFO/STO 界面插入单层 FeO 破坏晶格相干性，从而稳定向下极化的四方相 BFO，并诱导界面处自由电子积累与导电行为。

**[Sum]** The authors successfully created a charged incoherent BFO/STO interface through precise shutter-controlled oxide-MBE, demonstrating that breaking lattice coherence can stabilize novel phases and induce interfacial conductivity via polarization-driven charge accumulation.

**[亮点 1]** 研究通过精确调控 MBE 快门序列，在界面插入单原子层 FeO，实现了相干→非相干界面的可控转换，为应变/界面工程提供了可复制的方法路径。

**[亮点 2]** 非相干界面诱导 BFO 由菱方相转为四方相，极化方向指向界面，导致自由电子在界面处积累形成导电通道，而体相仍保持绝缘，实现了典型的“界面导电—体相绝缘”分离效应。

**[思考]** 非相干界面的结构与电性在热循环、电场加载或长时间运行下是否稳定？此外，类似的“界面插入层”策略是否能扩展到 PTO/STO、BFO/LAO 等体系，以实现广义的相稳定调控与界面导电调控？

**[拓展阅读 1]** 非相干界面的结构本质与电子效应

**[拓展阅读 1]** 传统外延强调相干界面的应变保持，但本研究指出破坏相干性也能产生有益的相稳定与电荷重构。非相干界面通常具有松弛位错、台阶结构及局域应变不均匀分布，会改变局域晶体场、氧八面体旋转模式与极化方向，从而引发新电子

态的形成。例如自由电子的界面束缚态或二维电子气（2DEG）效应，类似 LAO/STO 体系。理解非相干界面的微结构演化、其对铁电/磁性/氧八面体调控的影响，是未来进一步工程化应用的关键。

## [拓展阅读 2] 从界面工程到功能化外延：可推广策略与器件前景

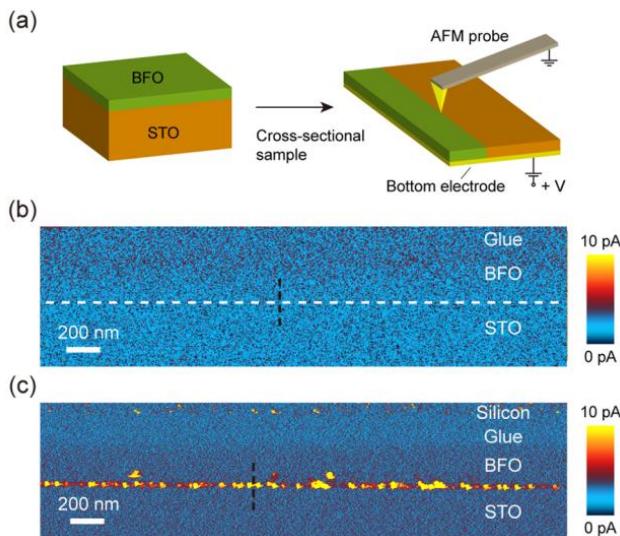
[拓展阅读 2] 插入原子层是一种可扩展的界面工程手段，可用于调控应变、极化方向、价态分布与局域导电性。若将该方法推广到更多钙钛矿体系（如 PTO、LNO、CFO 等），有望实现界面电导、铁电翻转势垒、交换偏置甚至拓扑态的精准调控。此外，界面导电通道结合铁电极化可能构建可写/可擦存储单元、铁电整流器或新型可控二维电子态器件。挑战仍包括原子级插层精度、热稳定性与重复性，以及与大面积工艺的兼容性。

[introduction] Perovskite oxide heterostructures have attracted intense interest in both fundamental research and device applications due to their wide range of fascinating properties and functionalities, such as high temperature superconductivity, colossal magnetoresistance, and multiferroics.<sup>1–5</sup> These phenomena originate from the intricate interplay between charge, spin, orbital, and lattice degrees of freedom.<sup>6</sup> By incorporating the effects of local symmetry breaking, reduced dimensionality, charge transfer, epitaxial strain, and other factors, even more exotic behaviors emerge at the interfaces between different perovskite oxides.<sup>7–9</sup> Remarkable examples include the discovery of a nontrivial two-dimensional electron gas (2DEG) with ferromagnetic and superconducting properties at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface,<sup>10–12</sup> and a switchable 2DEG at several ferroelectric oxide interfaces.<sup>13–15</sup> Furthermore, the macroscopic properties of the overlying thin film in an oxide heterostructure can be effectively modulated through atomic-scale interface engineering.<sup>16,17</sup>

Recent technological advancements in complex oxide thin film epitaxy enable atomic-scale interface engineering, facilitating the creation of artificial oxide heterostructures with chemically abrupt interfaces. In typical heteroepitaxy of perovskite oxides on substrates with a small lattice mismatch, the crystal lattice is typically coherent across the interface, where the A-site (B-site) columns of ABO<sub>3</sub> perovskite thin films align precisely with the corresponding A-site (B-site) columns of substrates. With an increasing mismatch in lattice parameters or film thickness surpassing a critical value, microstructural defects, such as dislocations, form to release misfit strain, resulting in a

semi-coherent or incoherent oxide interface.<sup>18,19</sup> Disruption of the oxygen octahedral networks, chemical bonding, and electromagnetic interactions across the interface could result in significant property changes, including enhanced ionic conductivity, stabilized electrical polarization, and the emergence of novel ferroelectric domain structures.<sup>20–23</sup> However, the controlled engineering of perovskite oxide heterostructures beyond coherent interfaces and the investigation of their potential functionalities remain to be explored.

In this work, we designed a new method for oxide thin film deposition using oxide molecular beam epitaxy (oxide-MBE) to engineer two types of perovskite oxide heterointerfaces with distinct lattice coherence and properties. During the growth of BiFeO<sub>3</sub> (BFO) thin films on a SrTiO<sub>3</sub> (STO) substrate, we achieved not only a normally coherent interface but also an incoherent BFO/STO interface by precisely controlling the shutter sequence of bismuth and iron sources. The incoherent BFO/STO interface exhibits distinctive properties compared to its coherent counterpart. It stabilizes the adjacent BFO layers in the tetragonal phase (T-phase) with an enhanced ferroelectric polarization pointing toward the interface, facilitating the accumulation of free electrons at the interface.



## Unleashing Electrocatalytic Oxygen Evolution Activity: Engineering Spin States in Strained Correlated Oxides for Enhanced Performance

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**[Ques] Perovskite oxides have emerged as compelling contenders for catalyzing the oxygen evolution reaction (OER) due to their low cost, high efficiency, and structural flexibility. Nevertheless, unraveling the intricate structure–activity relationships within correlated oxides remains challenging, impeding the rational design of efficient catalysts.**

**[关键问题] 如何揭示钙钛矿强关联体系中“结构—电子态—催化活性”之间的本质关联并用于提升 OER 性能？**

[Sum] Here, using LaCoO<sub>3</sub> epitaxial thin films as a model system, we illustrate a direct correlation between the spin state and OER activity. Through comprehensive investigations via X-ray absorption spectroscopy, scanning transmission electron microscopy, and first-principles calculations, we pinpoint that the enhanced OER activity observed in the tensile-strained films originates from lattice oxygen oxidation triggered by strain-engineered high-spin Co<sup>3+</sup>. Particularly, the high-spin sites correlated oxygen vacancies during OER lead the reaction into a new pathway, facilitating both the deprotonation of OH\* at the metal site and the formation of O–O bonds at the oxygen redox center.

**[亮点 1]** 工作直接揭示 Co<sup>3+</sup> 自旋态与 OER 机制之间的因果关联，证明高自旋态能激活晶格氧参与反应，从而显著提升催化效率。

**[亮点 2]** 通过应变调控实现对自旋态与氧空位形成的精准控制，展示了利用薄膜工程策略切换 OER 反应路径的可行性。

**[思考]** 是否能通过电场、光场或界面极化进一步调控 Co<sup>3+</sup> 自旋态，从而在无需应变工程的情况下提升晶格氧活性？

[思考] 若将 LCO 与其他过渡金属氧化物构成异质结，自旋态调控能否诱导更高效的双中心氧氧键生成机制？

[拓展阅读 1] （主编问题：高自旋态（HS）和低自旋态（LS）如何影响催化效率？应变如何调控自旋态？）

[拓展阅读 1] 过渡金属离子的自旋态决定其 d 轨道电子排布，直接影响金属–氧配位键强度与电子跃迁能力。低自旋态（LS）通常具有更满的  $t_{2g}$  轨道与较弱的 eg 电子参与度，使金属–氧键更强、更难打破，因此限制了中间体脱附及氧空位形成。而高自旋态（HS）中 eg 电子占据增加，使 Co–O 键更易伸长、断裂或发生杂化变化，从而促进  $\text{OH}^*$  去质子化及晶格氧参与反应，使反应路径更为活跃。应变工程通过改变晶格常数与八面体畸变来调节 d 轨道能级分裂。例如，拉伸应变降低晶场能，使  $\text{Co}^{3+}$  更易从 LS 跃迁至 HS；压缩应变则相反。因此，应变可视为一种非化学方式的“能级调节器”，通过控制电子结构实现对催化活性的精准调控。

[拓展阅读 2] （主编问题：晶格氧氧化机制（LOM）与吸附物演化机制（AEM）有何核心差异？各自优劣如何？）

[拓展阅读 2] AEM 是传统观点，认为反应仅发生在金属活性位点上，通过  $\text{OH}^* \rightarrow \text{O}^* \rightarrow \text{OOH}^*$  的逐步吸附和转化完成氧生成，其优势是机理明确、结构稳定，但其速率一般受  $\text{OOH}^*$  形成步骤限制，因此效率常受瓶颈制约。相比之下，LOM 允许晶格氧直接参与形成 O–O 键，从而绕过 AEM 中最慢的步骤，因而常表现出更高的 OER 活性；其活化来源于较弱的金属–氧键和可迁移的晶格氧。然而，LOM 的缺点是可能引发晶格氧损失、结构不稳定或表面重构，因此对材料的电子结构要求更高。简言之，AEM 稳定但慢，LOM 高效但风险大；如何通过自旋态、应变、缺陷控制等手段在二者之间寻求最佳平衡，是当前 OER 设计的重要科学前沿。

[introduction] Clean and renewable energy obtained through electrochemical conversion (such as water splitting and fuel cells) is a key to alleviating the energy crisis and environmental issues. Hydrogen gas produced by water electrolysis stands out as a promising clean energy source. Nevertheless, the efficiency of water splitting is hindered by the sluggish kinetics of the oxygen evolution reaction (OER), which can be circumvented to a great extent by the introduction of efficient OER electrocatalysts. Traditional precious metal oxides, including  $\text{RuO}_2$  and  $\text{IrO}_2$ , have shown excellent OER

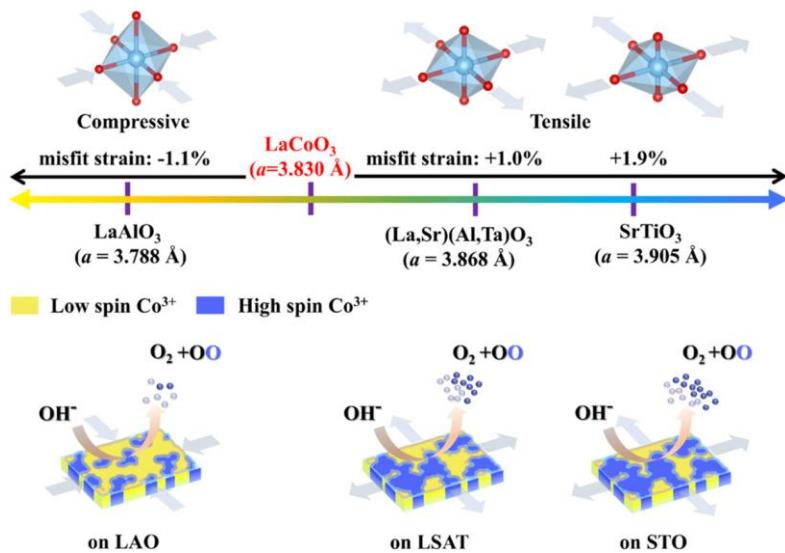
activity. However, their high prices, limited natural abundances, and stability concerns pose significant challenges to mass-producing them as durable electrocatalysts. In contrast, low-cost perovskite oxides, characterized as strongly correlated electron systems, exhibit considerable potential in OER electrocatalysis with tunable crystal and electronic structures. Consequently, extensive research efforts have been devoted to exploring perovskite oxide electrocatalysts with excellent OER performance.

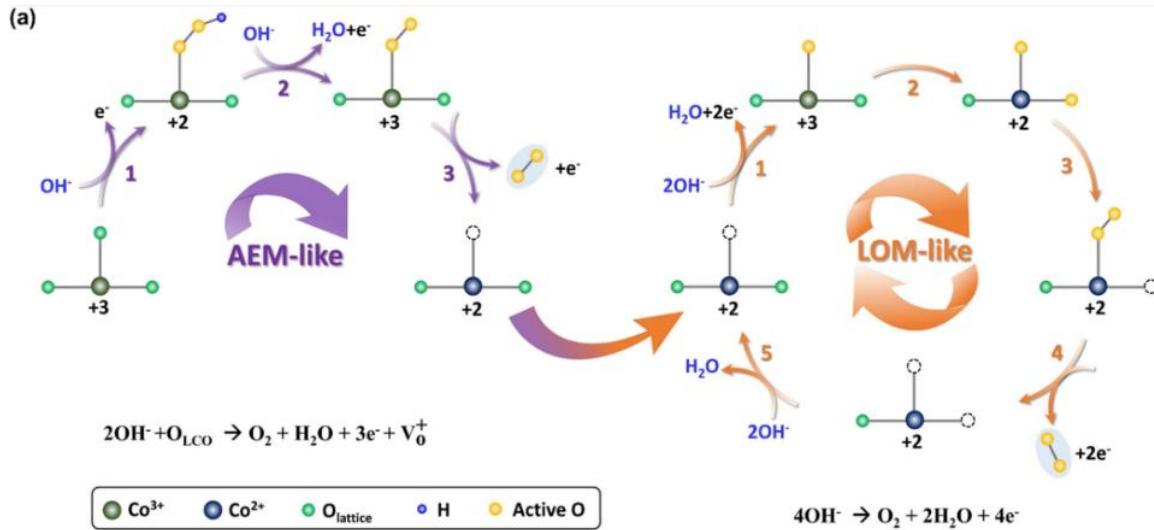
The adsorbate evolution mechanism (AEM) is the prevailing OER mechanism, which considers only the redox activity of the transition-metal sites, and the lattice oxygen oxidation mechanism (LOM) in OER has received widespread attention in recent years. The AEM involves the transformation of a series of reaction intermediates ( $\text{OH}^*$ ,  $\text{O}^*$ , and  $\text{OOH}^*$ ) adsorbed on metal active centers at surface, and it is considered as a pH-independent mechanism. In contrast, the LOM involves the direct participation of oxygen anions from the lattice of catalyst oxides as an active intermediate in the oxygen evolution, and it is considered to have pH-dependent activity. In addition, the LOM challenges the traditional view that OER is a surface reaction. The key advantage of a LOM-based OER lies in its ability to directly form an O–O bond by bypassing the rate-determining step of AEM (i.e. the formation of  $\text{OOH}^*$ ). This renders the LOM-based electrocatalyst usually more effective to enhance the OER activity. Therefore, an increasing number of researchers have delved into the nature of LOM and endeavored to optimize electrocatalytic performance. However, a comprehensive understanding of the nature of LOM, such as the electronic structure during the OER process, is still lacking. So far, most investigations have been based on polycrystalline powder systems, making the elucidation of the exact structure–activity relationship for heterogeneous electrocatalysts quite challenging. In order to circumvent multiple variations between different transition-metal elements, it is particularly important to probe the correlation between the electronic structure and catalytic activity in a single material with controlled parameters (e.g., crystal orientation, thickness, and surface roughness). Perovskite cobaltite  $\text{LaCoO}_3$  (LCO) is a classic strongly correlated oxide and has been considered as an efficient electrocatalysts because of its high OER activity and durability. The  $\text{Co}^{3+}$  undergoes a spin-state transition when subjected to external disturbances such as temperature and strain. In this case, two distinct primary spin states may occur, namely, low spin (LS,  $t_{2g}6eg0$ ) and high spin (HS,  $t_{2g}4eg2$ ). Different spin states of  $\text{Co}^{3+}$  can lead to changes in the hybridization of the Co–O bond, thereby altering the OER activity.

Although researchers generally understand that the spin state of  $\text{Co}^{3+}$  has an impact on OER activity, but the direct correlation between the spin state of  $\text{Co}^{3+}$  and the OER mechanism is still unclear. In consequence, deciphering the elusive impact of the spin states of transition-metal cations on the OER catalysis necessitates a comprehensive understanding of electronic structures, along with electrocatalytic mechanisms. This understanding is crucial for advancing catalyst design and optimizing performance.

In this work, we employ LCO single-crystalline thin films as a model system. Utilizing a diverse set of techniques, including X-ray absorption spectroscopy (XAS) and X-ray linear dichroism spectroscopy (XLD) together with configuration interaction (CI) cluster calculation, aberration-corrected scanning transmission electron microscopy (STEM), and density functional theory (DFT) calculations, we showcase our ability to tune the spin state (HS or LS) and even the OER mechanisms of LCO films under different strains. Noteworthy are the electrochemical measurements, revealing a strain dependence wherein LCO films under tensile strain (with a higher content in HS  $\text{Co}^{3+}$ ) exhibit superior OER performance (Figure 1). A pivotal aspect of our investigation indicates that, in comparison to LS  $\text{Co}^{3+}$  coordinated oxygen, HS  $\text{Co}^{3+}$  coordinated oxygen is more inclined to facile ligand dissociation, leading to the formation of oxygen vacancies during the OER. Consequently, HS  $\text{Co}^{3+}$  is more readily reduced to  $\text{Co}^{2+}$ , resulting in the weakening of the Co–O bond. This cascade facilitates the involvement of lattice oxygen as a redox site, further enhancing the OER activity. As evidence, with an increase in the proportion of HS  $\text{Co}^{3+}$  under tensile strain, the OER activity exhibits significant pH dependence. These findings underscore the close correlation between the spin state and the OER mechanism of LCO, emphasizing the crucial role of the high spin state in activating the oxidation of lattice oxygen, thereby enhancing the OER activity.

[相关图片]





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