

Electric-field Control of Ionic Evolution in Complex Oxides

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ABSTRACT

Electric-field control of phase transformation with ion transfer is of great interest in materials science as it has enormous practical applications. Due to the strong electron-ion interactions, ionic evolution would naturally have a dramatic influence on a material's magnetic and electronic properties. In this article, we will review our recent progress on using electric field controlled ionic evolution to tune the functionalities of a couple of complex oxide model systems ($\text{SrCoO}_{2.5}$ and WO_3). Finally, we will provide an outlook for the related studies.

INTRODUCTION

Due to the strong correlations among the lattice, charge, orbital and spin degrees of freedom, complex oxides have demonstrated a rich spectrum of novel physical properties, such as superconductivity, colossal magnetoresistance, ferromagnetism, ferroelectricity and multiferroicity, etc. [1]. Conventionally, doping and strain form two essential pathways to manipulate these intriguing properties. For example, doping Sr into La_2CuO_4 or varying the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, lead to the discovery of the intriguing phase diagram of high temperature superconductors [2]. On the other hand, applying tensile strain in EuTiO_3 thin films during the growth triggers it from an antiferromagnetic-paraelectric into a multiferroic with both strong ferromagnetic and ferroelectric responses [3]. It is worth noting that both these two methods were generally applied during the sample's synthesis process, which would involve the harsh conditions of high temperature, high vacuum, high pressure,

etc. These disadvantages have inspired us to look for alternative pathways to design/manipulate the material properties, particularly after growth and at room temperature. When comparing the external perturbations (i.e. the electric field, temperature, magnetic field, and strain) and the energy scales of different interactions within solids, it can be found that the electric-field control covers a large range of energy windows, and forms a perfect candidate to realize such requirements [4, 5].

We note that realistically no material system can be “perfect crystalline” since thermodynamically the defect is an intrinsic property of materials. Therefore, the defect chemistry or ionic evolution within the material forms an essential controlling parameter to manipulate the corresponding material properties. In perovskite oxide, which has the chemical formula of ABO_3 with A and B representing alkaline (or rare earth) cations and transitional metal cations, respectively, the oxygen vacancy attracts extensive research interest due to its relatively low forming energy. The presence of oxygen vacancy would usually lead to degraded material performance, such as leakage current in the insulating ferroelectric or suppressed transition temperature in ferromagnetic and superconducting materials. Research has been focused mainly on how to avoid the formation of the oxygen vacancy. However, thinking from a different point of view, if we could find a way to delicately manipulate the oxy-

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gen content or oxygen vacancy within the materials, we would be able to find an effective and practical pathway to control the material properties. Due to the small formation energy, it would be possible to obtain such control at room temperature with an external perturbation, such as an electric field. Indeed, the electric field control of ionic evolution has already demonstrated its great potential for application in energy storage and conversion devices, in the form of batteries and in solid oxide fuel cells [6, 7].

Conventionally, thermal reduction and oxidation were widely employed to control oxygen ion evolution as well as the corresponding phase transformations [8, 9]. For instance, by reducing SrFeO_3 via CaH_2 , the oxygen ion can be extracted and finally SrFeO_2 phase with infinite planar crystalline structures can be formed [8]. Alternatively, in another model system LaSrCoO_4 , the oxygen ion is substituted by H^- to form a new phase of $\text{LaSrCoO}_3\text{H}_{0.7}$ when annealed with CaH_2 [9]. It has also been demonstrated that $\text{SrCoO}_{2.5}$ can be transformed into a perovskite SrCoO_3 through thermal annealing within ozone [10]. Clearly, those processes have their inevitable disadvantages due to their use of a high temperature environment and reactive agent, in addition to the uncontrollable reactions. In contrast, the aforementioned electric field controlled ionic evolution provides a practical and easily implemented pathway to control the material's properties with a large range of derived functionalities.

In recent years, ionic liquid gating (ILG) has emerged as an effective method to tune the carrier concentration through field effect transistor (FET) device geometry, which can reach around 10^{15} cm^{-2} carrier modulation, which is 1 to 2 orders of magnitude higher than conventional field effect transistors (Fig. 1a and 1b) [11, 12]. With this approach, many interesting results, such as

metal-insulator transitions, superconductivity, and ferromagnetism, have been realized [13-15]. However, during these studies, the researchers focused mainly on the electrostatic doping effect, while the electrochemical effects were intentionally avoided [16]. Actually, in most cases, both of these two effects would couple strongly together during the ILG, and the electrochemical effect can be equally (or even more) important as the electrostatic effect (Fig. 1c). In particular, the residual water exists ubiquitously within the ionic liquid, which can then facilitate the electrochemical reaction through the electrolysis process [17]. In this sense, if we can achieve good control of the electrochemical effect during ILG, then we would be able to make good usage of the H^+ and O^{2-} ionic evolution independently to modulate the physical properties of materials. Here we review our recent research progress on ILG induced ionic evolution in model systems of oxide materials $\text{SrCoO}_{2.5}$ and WO_3 , with the demonstration of a series of novel phase transformations and exotic physical properties [17-20].

PHASE TRANSFORMATIONS WITH IONIC EVOLUTION

We note that the electrolysis of water will lead to the formation of both positively and negatively charged ions (H^+ and HO^-). During the ILG, depending on the polarity of the applied gating bias, the corresponding ions will be accumulated at the sample surfaces. For negative voltage, the ILG can trigger the phase transformation from $\text{SrCoO}_{2.5}$ into $\text{SrCoO}_{3-\delta}$ through the electrochemical reaction induced oxidation process; the positive voltage can lead to the insertion of positively charged H^+ ions into the materials and then turn $\text{SrCoO}_{2.5}$ into a hitherto unexplored $\text{HSrCoO}_{2.5}$ phase through chemical reduction process. Furthermore, for $\text{SrCoO}_{3-\delta}$ or newly formed $\text{HSrCoO}_{2.5}$, when reversing gating voltage, they will

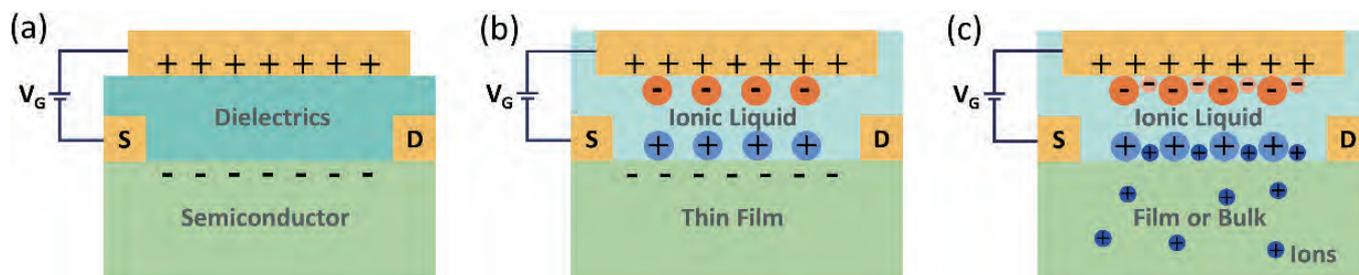


Fig. 1: Schematic diagram of three types of field effect transistors (FET). (a) Conventional FET with dielectric material as the electrolyte; (b) ILG controlled FET with the ionic liquid as the electrolyte. In this device, the induced carrier concentration through the electrostatic effect can reach up to 10^{15} cm^{-2} , which is about two orders of magnitude higher than conventional FET; (c) Ionic evolution induced reversible phase transformations through the electric-field controlled electrochemical effect during ILG.

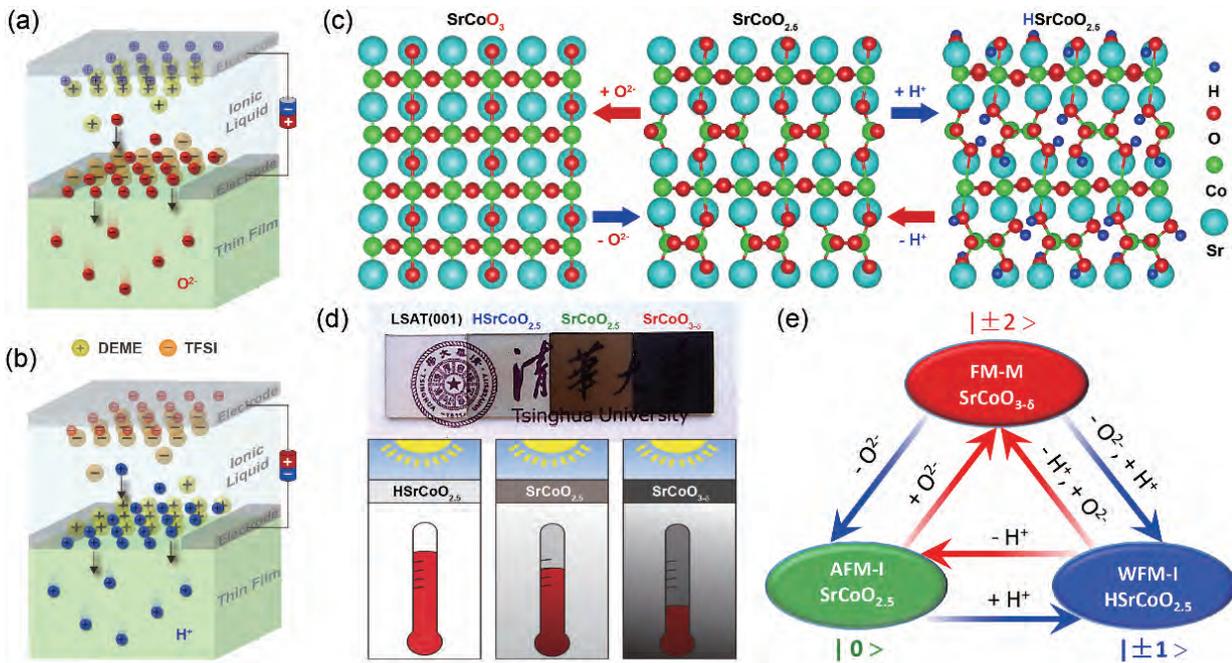


Fig. 2: Electric field controlled dual-ion evolutions and phase transformations. (a-c) Electric field control of O^{2-} and H^+ ion evolutions and tri-state reversible and nonvolatile phase transformations among the three extremely distinct $SrCoO_{3-\delta}$, $SrCoO_{2.5}$ and $HSrCoO_{2.5}$ phases. (d-e) Demonstration of novel dual-band (visible and infrared spectroscopic region) and tri-state electrochromic effects and multi-state electromagnetic coupling effects based on the electric field control of dual ion evolution (O^{2-} and H^+).

return back to the initial $SrCoO_{2.5}$ phase by extracting the relevant ions. Through a systematic study of the relationship between the phase transformations and gating voltages among the three distinct phases, we realized a reversible electric-field control of tri-state phase transformation with the selective dual-ions switch of O^{2-} and H^+ (Fig. 2a-c).

More importantly, the discovered phase transformation is non-volatile, meaning the newly formed phases remain robust even after removing the gating voltage and washing out the ionic liquid. These interesting properties provided the foundation to design a series of novel functionalities associated with the phase transformations. For instance, based on the different band structures among these three phases, we demonstrated the electric-field controlled nonvolatile dual-band and tri-state electrochromic effect (Fig. 2d). Similarly, due to the distinct magnetism ground states, i.e., ferromagnetic metal $SrCoO_{3-\delta}$, antiferromagnetic insulator $SrCoO_{2.5}$ and weak ferromagnetic insulator $HSrCoO_{2.5}$, the phase transformation can also host a new concept of multi-state electromagnetic couplings based on the dual ionic evolution of O^{2-} and H^+ (Fig. 2e).

We note that electric field controlled ionic evolution has great impact in a large range of exotic physical properties. For instance, using WO_3 (a $5d^0$ band insulator) as the model system, we have demonstrated that ILG induced hydrogen evolution can trigger the reversible control of insulator to metal transitions through gating (Fig. 3) [19]. It is interesting to note that extra oxygen ions cannot be intercalated into the crystalline lattice of WO_3 because of the difficulty to further increase the valance state of W^{6+} . Unlike the previous studies of $SrCoO_{2.5}$, in which the modulation of the electronic state is strongly coupled with the structure phase transformation, the studies in WO_3 reveals that with the application of a relatively small gating voltage of 1.5 V, the thin film WO_3 can turn readily into a metallic state without the structure phase transformation. By further increasing the gating voltage up to 3.5 V, the intercalated H^+ ion will trigger the structure phase transformation as well as the further increased carrier density. Therefore, one can conclude that the H^+ ionic adsorption at the sample surface can be equally important as that of the ionic intercalation to manipulate the electronic properties. We note that the carrier modulation induced by the H^+ absorption is in the order of $10^{16}/cm^2$, which is about one order of mag-

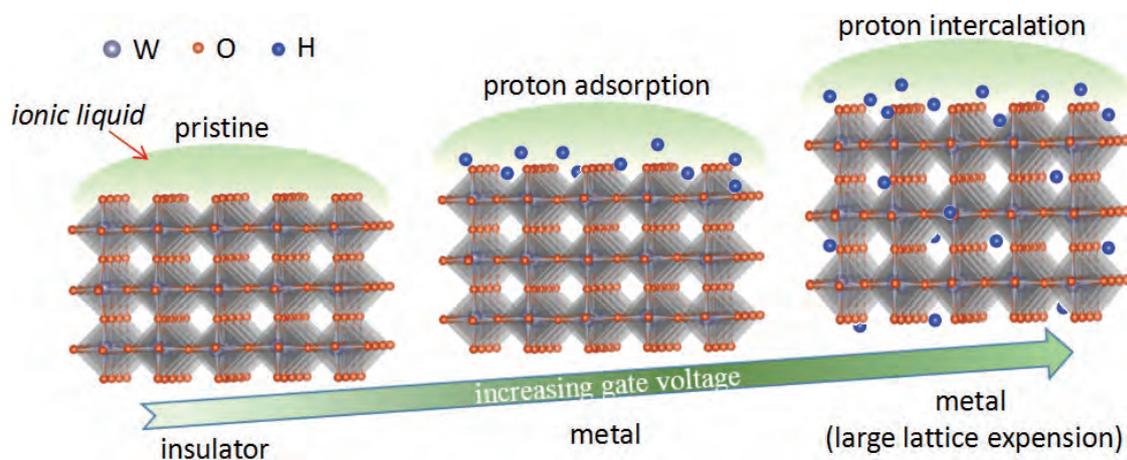


Fig. 3: Schematic illustration of electric field controlled electrical and structural transitions in WO_3 through hydrogen ion evolution. With increasing gate voltage, the hydrogen ions accumulate at the sample surface to induce the insulator to metal transition with electron doping. With further increase of the gating voltage, the hydrogens ion intercalate into the lattice to trigger the structural phase transformation with further modulation of the carrier density.

nitude larger than the conventional ILG, demonstrating its strong capability to tune the electronic state without triggering structural phase transformation.

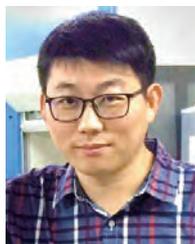
SUMMARY AND OUTLOOK

It is interesting to note that electric field controlled ionic evolution is a generic method to manipulate material functionalities, which will cover a large range of candidate ions and material systems. For instance, using the ILG induced protonation process, our recent studies have demonstrated nonvolatile electron doping into a series of Fe-based superconductors with dramatically enhanced transition temperatures [21]. Clearly, besides O^{2-} and H^+ ions, other ions such as Li^+ , Cu^{2+} , H^- , N^{3-} can also be employed to manipulate the materials' properties through ionic evolution [22-26]. While electric field controlled ionic evolution has already demonstrated its unique capability to tune material properties, a few fundamental questions call for immediate attention. For instance, what is the driving force for the hydrogen and oxygen ion evolutions? How are the ions intercalated into the lattice? Is this approach a generic method or are there any guidelines to make the material selection? To answer these questions, interdisciplinary research efforts from the fields of condensed matter physics, solid state chemistry and materials science are highly desired. With more research, we envision that this simple method will lead to a plethora of novel physical phases and interesting physical properties.

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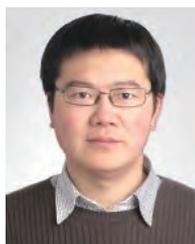
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