# Emergent Monolayer Oxides $MnO_2$

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## Motivation

Since the discovery of two-dimensional electron gas (2DEG) at the interface between insulating $LaAlO_3$ (LAO) and $SrTiO_3$ (STO), the origin of 2DEG at such interfaces, eg. "polar catastrophe" and "atomic mixing", has been a topic of debate. In latest two years, we have reported that the band bending in the interfacial STO layers generated by a local electric field is the key to 2DEG at (110) and (001) LAO/STO interfaces, which is expected to end the decade-old controversy (Han, Phys. Rev. B, 2015). During conducting the study, we realized that an anisotropic 2DEG at freestanding (110) STO surface was observed (Wang, PNAS, 2014) and Jin-Feng Jia's group at SJTU discovered an extremely high temperature superconductor FeSe at doped STO interfaces, these fascinating phenomena motivate us to employ STO-based interfaces to engineer the monolayer 3*d* transition metal oxides (Fig. 1).

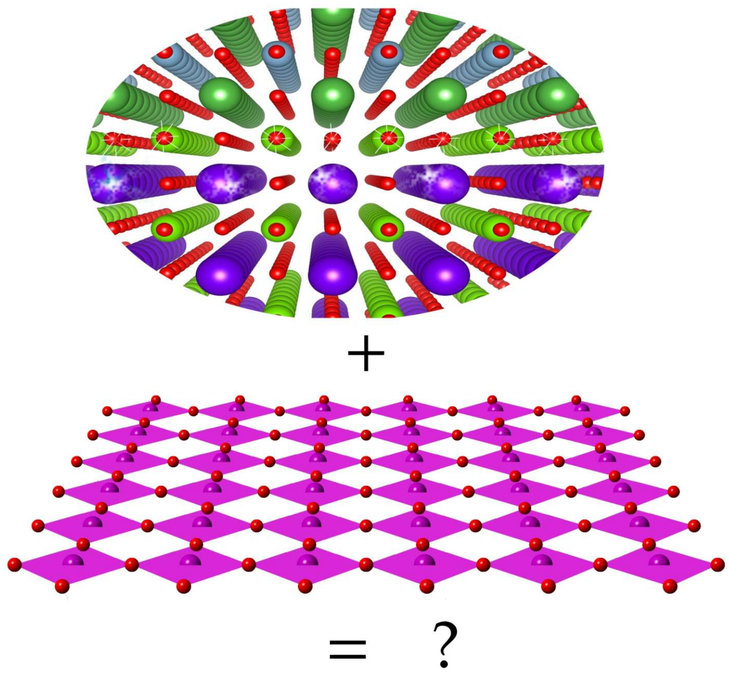
## Models

In order to study the $MnO_2$ monolayer at different STO interfaces, we constructed 3 interfaces: $SrTiO_3$-SrO-$MnO_2$-SrO-$SrTiO_3$, $SrTiO_3$-SrO-$MnO_2$-LaO-$SrTiO_3$ and $SrTiO_3$-LaO-$MnO_2$-LaO-$SrTiO_3$. Here, for convenience, we name them Case-1, Case-2 and Case-3, respectively. Fig. 2 shows the $\sqrt{2} \times \sqrt{2} \times 13$ slab models separated by 15 Å vacuum layers for Case-(1-3).

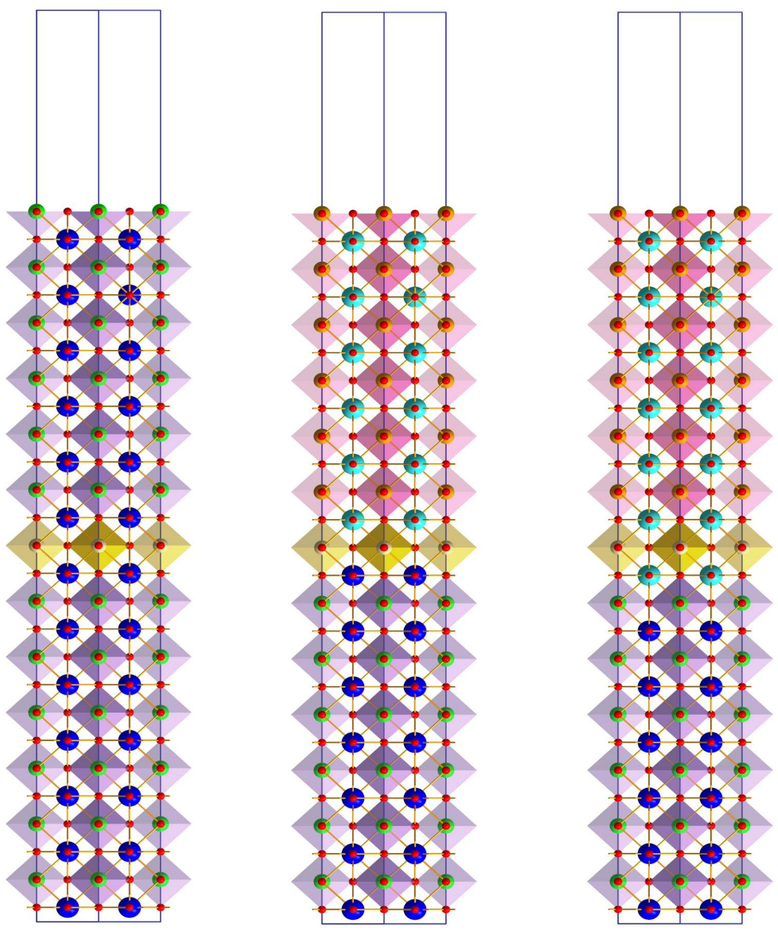
In the optimization for the three cases, we fixed the in-plane lattice constant of the supercells at the optimized lattice constant of bulk STO and performed relaxation of all the coordinates of atomic positions along the *c*-direction until the Hellmann-Feynman forces on each atom were less than 1 meV/Å.

## Figure 1

Figure: What could be induced if we combine STO-based interfaces and $MnO_2$ monolayer?




## Figure 2



## Magnetic order in theory

$SrMnO_3$ (SMO) is a band insulator and has a paraelectric cubic perovskites structure with G-type antiferromagnetism (AFM) ordering in the high-spin $Mn^{4+}t_{2g}^3e_g^0$ configuration below the Néel temperature of 233-260 K. Stochiometric bulk $LaMnO_3$ (LMO) with nominally $Mn^{4+}t_{2g}^3e_g^1$ occupancy, is a Mott insulator with strong Mott-Hubbard/charge-transfer Coulomb correlations in a half-filled $e_g$ band and has an A-type antiferromagnetism with a Néel temperature of 140 K caused by active Jahn-Teller effect. Then what's the magnetic order of monolayer $MnO_2$ in current study?

To address this question, we performed total-energy calculations for the heterostructures and acquired the energy differences on a per formula unit basis of $MnO_2$ between FM order and AFM order for each case as seen from Table 1. The energy differences in Tab. 1 are defined as $E_{FM}$-$E_{AFM}$ with energy unit of meV/formular unit.

## Table 1

Table: Energy differences (meV/f.u.) between FM order and AFM order.

| Case | $U_{Mn}^{eff}$=2 eV | $U_{Mn}^{eff}$=4 eV | $U_{Mn}^{eff}$=4.5 eV | $U_{Mn}^{eff}$=7 eV |
|---|---|---|---|---|
| 1 | 114.431 | 51.712 | 38.558 | 70.395 |
| 2 | -12.044 | -59.205 | -57.386 | 35.332 |
| 3 | -242.299 | -217.163 | -189.457 | -189.457 |

## Discussions and Conclusions

Discussions:

(1) As shown in Fig. 3, one easily finds that $MnO_2$ in Case-1 is a insulator and $MnO_2$ layer in Case-3 is a metal. Unexpectedly, $MnO_2$ monolayer in Case-2 indicates a half-metallic conductivity.

(2) In the non spin-polarized calculations for the models as presented in Fig. 4, $MnO_2$ monolayer in each case becomes metal, which indicates that metal-insulator transition of $MnO_2$ monolayer is induced by the magnetic order in the corresponding cases.

(3) By charge analysis, we find that the valence states of Mn in the three cases obey the rule Case-1 > Case-2 > Case-3

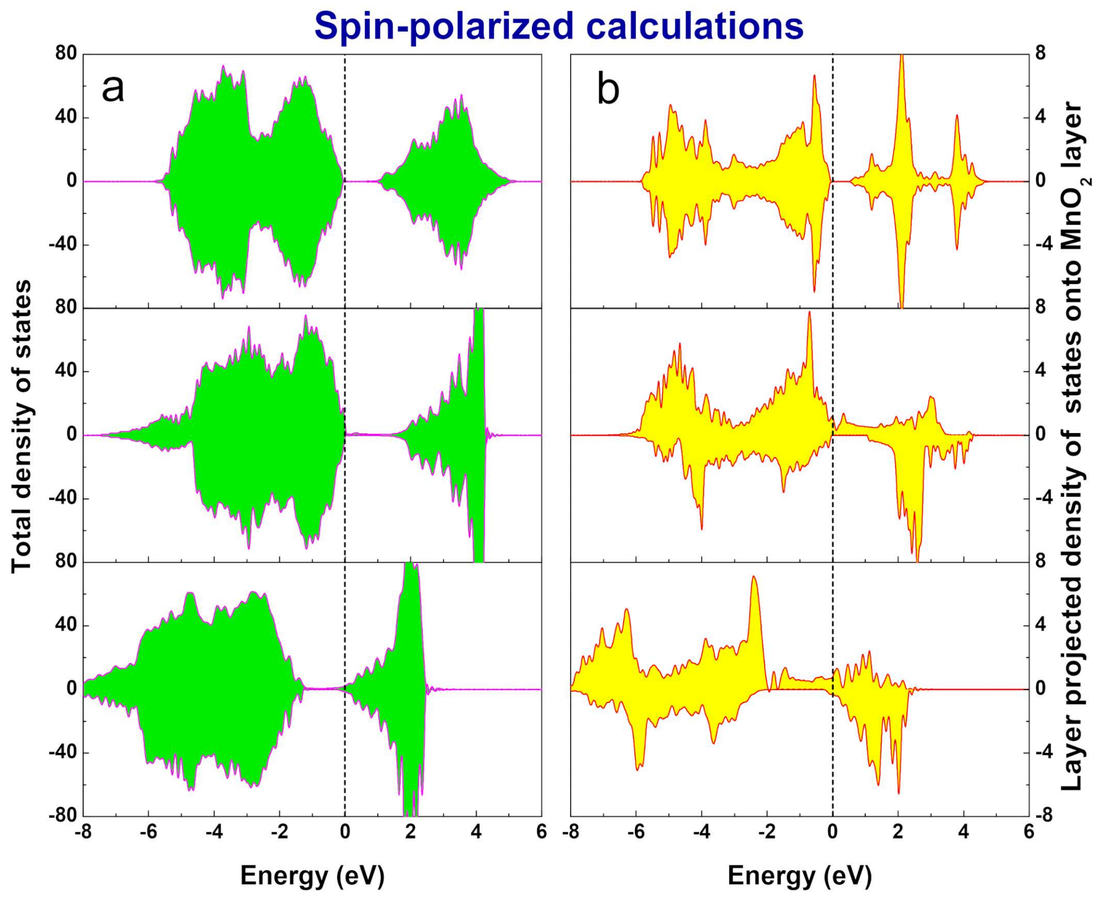
Conclusions:

Employing first-principles calculations for STO-based oxide interfaces, we propose a method to engineer the monolayer $MnO_2$ by using different terminations. Our predictions show that the magnetic structures of monolayer $MnO_2$ vary with the terminations and is thought to induce metal-insulator transitions at the interfaces. One of our collaborators Prof. Ying-Hao Chu at Academia Sinica (Taiwan) have proved our predictions in his experiments, indicating our method is a a very practical way to modify the physical properties of transition metal oxide interfaces.

## Spin-polarized electronic structures

We computed the electronic structures for the heterostructures and presented the obtained density states (DOS) extracted from spin-polarized calculations with $U_{Mn}^{eff}$=4.5 eV in Fig. 3a. One may find that it is not easy to determine the conductivity of Case-1 and Case-2 because of the large energy scale from -80 to 80 eV though actually we can use relatively smaller energy scale. Hence we are driven to analyse the layer projected DOS onto $MnO_2$ layer in each case, as shown in Fig. 3b.

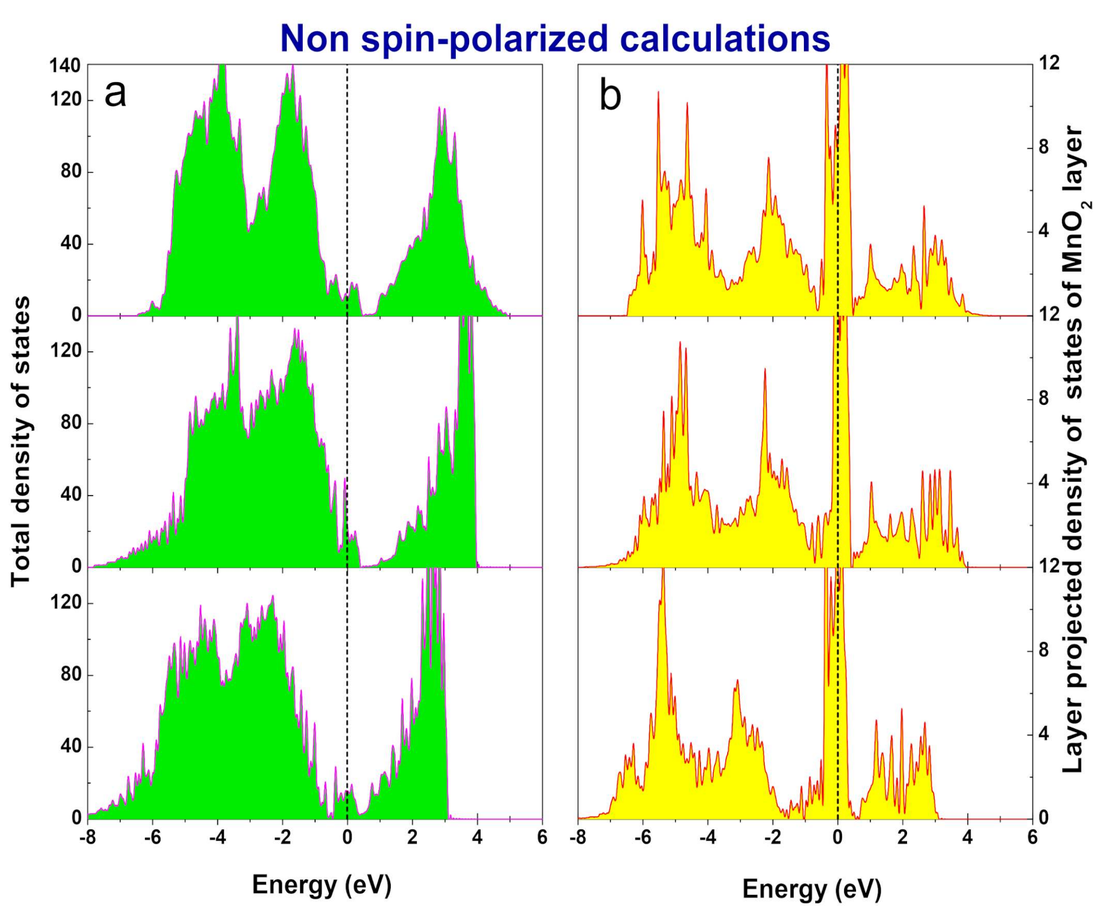
## Figure 3




## Non spin-polarized electronic structures

To elucidate the correlation between the magnetism and the electronic structures. We plotted the non-spin-polarized total DOS and layer projected DOS in Fig. 4. Different from the electronic structures given in Fig. 3, all the $MnO_2$ layers become metallic and the profiles of the projected DOS in each case illustrates no marked variances.

## Figure 4

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