

Control of Electronic Conduction at an Oxide Heterointerface using Uniaxially Polar Adsorbates

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We study the effect of the surface adsorption of a variety of common laboratory solvents on the conductivity at the interface between LaAlO_3 and SrTiO_3 . This interface possesses a range of intriguing physics, notably a proposed connection between the surface state of the LaAlO_3 and the conductivity buried in the SrTiO_3 . We show that the application of chemicals such as acetone, ethanol, and water can induce a large change (factor of three) in the conductivity. This phenomenon is observed only for polar solvents. These data provide experimental evidence for a general polarization-facilitated electronic transfer mechanism.

The transfer of electrons between a solid surface and adsorbed atomic or molecular species is fundamental in natural and synthetic processes, being at the heart of most catalytic reactions and many sensors. In special cases, metallic conduction can be induced at the surface of, for example, Si-terminated SiC¹, or mixed-terminated ZnO², in the presence of a hydrogen adlayer. Generally, only the surface atoms are significantly affected by adsorbates. However, remotely changing electronic states far from the adsorbed layer is possible if these states are electrostatically coupled to the surface. Here we show that the surface adsorption of common solvents such as acetone, ethanol, and water can induce a large change (factor of three) in the conductivity at the buried interface between SrTiO₃ substrates and LaAlO₃ thin films³⁻⁸. This phenomenon is observed only for polar solvents. Our result provides experimental evidence that adsorbates at the LaAlO₃ surface induce accumulation of electrons at the LaAlO₃/SrTiO₃ interface, suggesting a general polarization-facilitated electronic transfer mechanism, which can be adapted for use in a range of oxide-based devices.

The intense interest in the LaAlO₃/SrTiO₃ interface³⁻²² has led to several recent experimental observations which suggest a close relationship between the interface and the LaAlO₃ surface. These include the use of conducting atomic force microscopy probes to toggle a metal insulator transition¹⁰⁻¹² through the writing of surface charge^{12,13}, and the use of capping layers of SrTiO₃¹⁴ or SrCuO₂¹⁵ to alter the interface conductivity. The origin of these effects, and indeed the interface conductivity itself, remains in debate^{4, 16-22}. The transfer of electrons from the surface to the interface, to reconcile the polar discontinuity between the neutral {100} layers in SrTiO₃ and the charged layers in {100} LaAlO₃, is one model that naturally connects the electronic states of the interface and LaAlO₃ surface^{4,18-22}. However, despite these concepts and recent experimental progress, the effect of the surface adsorbate has not been investigated. This

issue is addressed in the present work. We have found that the exposure of $\text{LaAlO}_3/\text{SrTiO}_3$ samples to a polar solvent can increase the sheet carrier density, n_{2d} , by more than $2 \times 10^{13} \text{ cm}^{-2}$, representing a change of the same order as the total charge density typical in this system⁴⁻⁸. Compared with the strong perturbations associated with other surface processes, *i.e.*, the extremely strong local electric field produced by the conducting atomic force microscopy probes¹⁰⁻¹³, or the structural variation by introducing capping layers grown at high temperatures^{14,15}, the changes associated with room temperature treatment using these solvents would naively be expected to be small. However, such processes result in a surprisingly large modulation of n_{2d} , revealing a dramatic surface-interface coupling.

Results

Transport characterization. The fabrication of the conducting $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces and the surface adsorption process (SAP) are described in the Methods. As shown in Fig. 1a, labels 1 & 2, a SAP using acetone increased n_{2d} from $\sim 1 \times 10^{13} \text{ cm}^{-2}$ to more than $3 \times 10^{13} \text{ cm}^{-2}$, over a wide temperature range ($2 \text{ K} \leq T \leq 300 \text{ K}$). This remarkable modulation suggests that the acetone molecules have been adsorbed on the LaAlO_3 surface and in turn change the electronic states at the buried interface. Heating the sample at 380 K in a moderate vacuum ($< 10^3 \text{ Pa}$, with a helium background) for several hours produced negligible conduction change (not shown). However, the original sample state was recovered after heating at an elevated temperature of 653 K, evidenced by the decrease in n_{2d} (Fig. 1a, label 3) and the subsequent increase after another SAP using water (Fig. 1a, label 4). These facts indicate that the surface adsorption is reversible but strong, not a physical adsorption driven by the relatively weak van der Waals force, and thus likely involves electron transfer. We note that as a function of n_{2d} , the qualitative shape of the $n_{2d}(T)$ data at low temperatures is quite different. Although unclear at this time, this may be associated

with the complex temperature and electric field dependencies of SrTiO₃, leading to a non-trivial variation of the confining potential as a function of n_{2d} , as discussed elsewhere²³.

Accompanying the n_{2d} increase, a striking reduction in the Hall mobility, μ_H , from 3,000 cm²V⁻¹s⁻¹ to 600 cm²V⁻¹s⁻¹ ($T = 2$ K) is observed after the acetone SAP (Fig. 1b). μ_H decreases quickly with increasing temperature, with a relatively small room temperature value of $\mu_H \sim 6$ cm²V⁻¹s⁻¹ due to the dominance of phonon scattering. At this temperature μ_H also has a very weak dependence on n_{2d} , thus the conductivity $1/R_{sheet}$ is a reasonable and convenient index of n_{2d} (Figs. 1a & c), and we will use it hereafter to characterize the effect of the SAP process on n_{2d} for a variety of common solvents. To study the repeatability of the adsorption / desorption processes, we repeatedly performed water SAP on a LaAlO₃/SrTiO₃ sample followed by a heating step at 573 K in an oxygen flow, to reset the system (Fig. 1d). The sample switches reproducibly between a high-conductivity state after SAP and a low-conductivity state after heating.

Effect of SAP using different solvents. To explore the origin of the SAP induced n_{2d} , we have studied the effect of SAP using a variety of solvents. These solvents can be classified into three categories: non-polar, polar aprotic (no dissociable H⁺), and polar protic (dissociable H⁺). The results are summarized in Fig. 2. Clearly, SAP using non-polar solvents produces no significant modulation in $1/R_{sheet}$ and by extension, n_{2d} . SAP using a relatively weak polar solvent, such as ethyl acetate, produces a slight increase in n_{2d} , while using more polar solvents produces a much larger increase, independent of whether the solvents are aprotic or protic. In Fig. 2 we also show that $\Delta(1/R_{sheet})$ is well scaled with the molecular dipole moment divided by the molecular volume. These results suggest that the polar nature of solvents plays a key role in determining the magnitude of the observed changes for the different solvents. In the context of an

electrostatic mechanism, the scaling of the change with the dipole moment density would be reasonable, since the strength of the effect should be related to not only the molecular dipole moment, but also the areal density of the molecules on the surface.

Comparison between the effect of SAP and the effect of adsorption of solvent vapor.

Additional insights into the origin of the SAP induced n_{2d} can be made by comparing the effect of SAP with the effect of adsorption from a solvent vapor. It is well known that a thin layer of water coats all hydrophilic surfaces under ambient conditions²⁴. Until now the adsorption of water on LaAlO₃, particularly on the AlO₂-terminated LaAlO₃ surface, has been scarcely studied. A water-dipping study showed that, while La₂O₃ is highly hygroscopic, LaAlO₃ only reacts weakly with water²⁵. In contrast, the adsorption of water on Al₂O₃ is well understood. It is known that Al₂O₃ adsorbs one monolayer of water when the relative humidity (RH) is ~35%, and more than five monolayers for RH > 70%^{26,27}. Thus, although these studies cannot be trivially extrapolated to the current heterostructures, we expect a thin layer of water with full coverage will coat the AlO₂-terminated LaAlO₃ surface when the LaAlO₃/SrTiO₃ sample is exposed to RH > 70% air at room temperature. Such a surface layer has also been inferred from charge writing experiments²⁸. Nonetheless, despite the existing water layer, we can still modulate the conductivity using the macroscopically large volumes of solvent in the SAP process.

Fig. 3a clearly shows that the conductivity of LaAlO₃/SrTiO₃ is still sensitive to water SAP using liquid even after exposing it to water saturated atmosphere for several hours. A similar result was found when acetone was used (Fig. 3b). From these results we can conclude that the thickness of adsorbate layer also plays an important role in the SAP effect, since the SAP with liquid is expected to produce a thicker adsorbed solvent film compared to the vapor experiments.

Thickness dependence. A key feature of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is that there exists a critical LaAlO_3 thickness, $d_{\text{LAO}} \sim 3\text{-}4$ unit cells (uc), below which the interface is insulating. It is instructive to see the dependence of the effect of SAP on the LaAlO_3 thickness. As shown in Fig. 4a, for $d_{\text{LAO}} = 2$ uc sample and bare SrTiO_3 substrate, no modulation in the conductivity is observed. For $d_{\text{LAO}} = 3$ uc, the as-grown sample is insulating and the acetone SAP drives the sample from an insulating state to a conducting state. In this case the absolute modulation in the carrier density, as indexed by $\Delta(1/R_{\text{Sheet}})$, is smaller than that in the thicker samples, but the sensitivity, defined as the ratio of the conductivity change with respect to that of the as-grown sample, is much larger. We speculate that with suitable optimization, this large sensitivity may be exploited for sensor applications. Interestingly, as shown in Fig. 4b, as d_{LAO} decreases, $1/R_{\text{Sheet}}$ tends to relax more quickly after the SAP, possibly associated with solvent desorption. This observation suggests that the surface adsorption is directly related to the nature of LaAlO_3 surface, or its polar character. We note that somewhat analogous observation has previously been found for the charge stability on the LaAlO_3 surface in the same system¹².

Discussion

Next we discuss the possible mechanisms that may explain these data. We exclude electrostatic attraction since the polar adsorbates themselves are charge-neutral as a whole and will not change the electrostatic boundary condition of $\text{LaAlO}_3/\text{SrTiO}_3$ without the transfer of electrons²⁹. Oxygen vacancies in the SrTiO_3 ¹⁶, atomic interdiffusion¹⁷, and an electronic reconstruction^{4,18-20} have all been suggested to be the origin of the interfacial conductivity in the $\text{LaAlO}_3/\text{SrTiO}_3$ system. In the case of the SAP experiments, we exclude the first two of these since we assume that a SAP at room temperature does not cause significant atomic structure changes at the interface, and we focus on the electronic reconstruction mechanism.

As discussed in several papers^{19,20}, and illustrated in Fig. 5a, for an idealized LaAlO₃ surface free from surface states, the valence band of LaAlO₃, E_V^{LAO} , is the electron source for the interface electrons. Here we assume no conductivity in the LaAlO₃ film itself, and for simplicity do not consider other processes that do not affect the electrostatic state of the LaAlO₃. An uncompensated potential, V_{Uncom} , across the LaAlO₃ film of the order of the band gap of SrTiO₃, E_g^{STO} , is needed to align the Fermi level, E_F , over the whole structure. A simple electrostatic consideration shows that $V_{Uncom} = \frac{e \left(\frac{\sigma_0}{2} - \sigma_{Inter} \right)}{\epsilon_{LAO}} d_{LAO}$, where σ_0 is the charge density of one atomic layer, σ_{Inter} is the total sheet electron density at interface, e is the unit charge, and ϵ_{LAO} is the dielectric constant of LaAlO₃. In reality σ_{Inter} is larger than n_{2d} due to the trapping of some electrons at the interface¹⁹. Immediately, we find that

$$\sigma_{Inter} = \frac{\sigma_0}{2} - \frac{\epsilon_{LAO}}{e d_{LAO}} V_{Uncom} \quad (1).$$

This simple relationship predicts the same thickness dependence of σ_{Inter} as several more detailed theoretical calculations^{20,31}, noting that V_{Uncom} is fixed for an ideal surface. In the work presented here, d_{LAO} is fixed, and the SAP induced change in n_{2d} is thus associated with a reduction in V_{Uncom} .

We note that there are several possibilities of reduction of V_{Uncom} . In practice, all samples have surface states associated with inevitable defects, surface reconstructions, surface adsorbates, and so on. If these surface states are within the bandgap of LaAlO₃ they can replace E_V^{LAO} as more energetically favorable electron sources, where a relatively smaller V_{Uncom} is required to dope electrons into the SrTiO₃. As far as surface adsorbates are concerned, they may interact with surface atoms or oxygen defects and cause complex surface states. Two recent theoretical papers have suggested that the dissociation of hydrogen²¹ and redox reactions²² on the LaAlO₃ surface

as possible electron sources. In both cases V_{Uncom} is reduced compared with that of the idealized surface. The role of water on the LaAlO_3 surface has also been recently stressed by S. Hellberg³⁰. However, we caution that the observed accumulation of electrons by SAP cannot be fully explained by the adsorbates induced surface states alone, since the polar character of the adsorbates and their thickness were found to play a vital role in our experimental results.

With the above picture in mind, we can interpret our results as follows. The strong polarization in the LaAlO_3 layer aligns to a degree the polar adsorbates nearest the surface, with a decaying trend as we move away into the adsorbate layer. As shown schematically in Fig. 5b, this leads to an electrostatic potential across the adsorbate layer, V_{ad} , quite similar to the built-in potential in the polar LaAlO_3 . As a result, electrons flow from adsorbates instead of the E_V^{LAO} of the surface LaAlO_3 to the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, and the V_{Uncom} across the LaAlO_3 is effectively decreased. The σ_{Inter} increases according to equation (1), consistently explaining the observed SAP induced accumulation of electrons at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. In this picture the change in σ_{Inter} is proportional to the value of V_{ad} and the areal density of adsorbates. If we assume that the thickness of the adsorbate layer is the same for all solvents, and that all solvents are equally likely to transfer electrons, it is simple to show that $\Delta\sigma_{Inter}$ will be proportional to D/V_m , consistent with the experimentally observed scaling relation between $\Delta(1/R_{Sheet})$ and D/V_m (Fig.2).

Our present observation is quite distinct from the proposed water-cycle mechanism that accounts for the modulation of interface conductivity by biased conductive scanning probe, since we achieve conductivity changes without actively dissociating water molecules²⁸. We note that in principle the biased scanning probe will also change the physical distribution of adsorbates,

(*e.g.* water), in addition to chemical changes, which may also contribute to the modulation in the interface conductivity in the charge writing experiments¹⁰⁻¹³.

The observed close coupling between polar surface adsorbates and interface conductivity provides new insights into the origin of electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, and demonstrates a new tuning parameter in controlling this exotic electron gas, which has the potential to be applied broadly in a wide range of novel oxide-based devices. These data also suggest that many of the conflicting (and often contradictory) studies of this popular system can be explained by this observation – *i.e.* whether measurements are made *in-situ*³², or after various surface exposures (*e.g.* atmospheric water, or solvent cleaning)^{33,34}, the sensitive electronic structure of the interface may be dramatically altered. For example, the predicted electric field across the LaAlO_3 layer¹⁸⁻²⁰ was not observed in X-ray photoemission studies³³, which may be explained consistently since the surface adsorbates (in particular atmospheric water) induced by the *ex-situ* processing reduce V_{Uncom} , or equally, the electrical field across LaAlO_3 layer. In contrast, in the $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices of multiple interfaces, the interfaces relatively far away from the surface may not be significantly affected by adsorbates³⁴.

Methods

Sample fabrication. Using optical lithography and lift-off, a six contact Hall bar (central bar length 50 μm , width 10 μm) with amorphous AlO_x as a hard mask was patterned onto the atomically flat TiO_2 -terminated SrTiO_3 (100) substrates. The LaAlO_3 thin films were grown on the patterned substrates by pulsed laser deposition with the growth monitored by *in-situ* reflection high-energy electron diffraction. The conducting interfaces are confined within the Hall bar region. For the samples shown in this Article, the growth was at 923 K in an O_2

pressure of 1.33×10^{-3} Pa, after a pre annealing at 1223 K in an O₂ pressure of 6.67×10^{-4} Pa for half an hour. After deposition there followed a post annealing step at 873 K in an O₂ pressure of 4×10^{-4} Pa for one hour. During deposition the laser repetition was 1 Hz and the laser energy density was 0.6 Jcm^{-2} . The same phenomenology is found for samples grown in a variety of temperatures, oxygen pressures and LaAlO₃ thicknesses.

Electrical contact and measurement. The conducting interface was contacted by ultrasonic bonding with Al wire. The temperature-dependent sheet resistance, sheet carrier density and mobility were deduced from standard transport measurements using the patterned Hall bar. All transport measurements were carried out using a standard four-probe method. To test for the possibility of parallel conductivity through the adsorbate layer itself, contacts were made directly to the surface using silver epoxy. No significant surface conduction was detected both before and after SAP, clearly demonstrating that the conduction is at all times dominated by the LaAlO₃/SrTiO₃ interface.

Surface adsorption process. SAP was achieved by placing a drop of the liquid solvent on the sample surface at room temperature and blowing off all visible solvent within less than ten seconds using dry nitrogen gas. Contacts were either left on the samples during the SAP, or reconnected afterwards, no significant difference in the conduction was observed by using either method.

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Author contributions

Y.W.X. performed sample fabrication, measurements, and data analysis. Y.H., C.B. and H.Y.H. assisted with the planning, measurements, and analysis.

Additional Information

The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to H.Y.H. (email: hyhwang@stanford.edu).

Figure legends

Figure 1 | Transport characterization. Temperature dependence of **a**, Sheet carrier density, n_{2d} , **b**, Hall mobility, μ_H , and **c**, Sheet resistance, R_{Sheet} , in different states of a $d_{LAO} = 10$ uc $\text{LaAlO}_3/\text{SrTiO}_3$ sample. The measurement sequence follows the labeled order. “As grown” corresponds to the sample before experiencing any SAP. “Acetone” (“water”) corresponds to the sample after an acetone (water) SAP process. “Heating” corresponds to $T = 663$ K in an O_2 pressure of 1.33×10^{-2} Pa for 5 hours. **d**, Room-temperature conductivity, $1/R_{Sheet}$, of a $d_{LAO} = 10$ uc $\text{LaAlO}_3/\text{SrTiO}_3$ sample which was repeatedly processed by water SAP and recovered by heating at 573 K in an oxygen flow for 3 hours.

Figure 2 | Effect of SAP using different solvents. The difference in $1/R_{Sheet}$ after and before SAP, $\Delta(1/R_{Sheet})$, reflects the change in n_{2d} at room temperature. A clear increase in $\Delta(1/R_{Sheet})$ is observed after SAP using polar solvents, independent of their aprotic or protic character. $\Delta(1/R_{Sheet})$ is reasonably scaled with the molecular dipole moment (D) of each solvent divided by the corresponding molecular volume (V_m) (crosses). The line is a guide to the eye. In each category the solvents are ordered from left to right by increasing polarizability. At least two samples were used for each solvent and all samples were $d_{LAO} = 10$ uc and in the “as grown” state before SAP.

Figure 3 | Comparison between the effect of SAP and the effect of adsorption of solvent vapor. Conductivity versus time plots for samples exposed to **a**, Water, **b**, Acetone vapours near the saturation point, followed by SAP. Note that surface adsorption of, e.g. water, would have already taken place when the sample was kept in normal air. The exposure to the nearly saturated water (acetone) vapour for many hours should achieve a full and thicker coverage of adsorbates on the LaAlO_3 surface. The samples are $d_{LAO} = 10$ uc and the measurements were performed at

room temperature. The irregular perturbations in Fig. 3a were caused by fluctuations in the local illumination and ambient temperature.

Figure 4 | Thickness dependence. **a**, The effect of SAP on samples of different LaAlO_3 thicknesses. Sensitivity was defined as a ratio between $\Delta(1/R_{sheet})$ and $1/R_{sheet}$ (as grown). The $d_{LAO} = 0$ uc sample is a bare SrTiO_3 substrate. The acetone SAP triggers a transition from an insulating state to a conducting state for a $d_{LAO} = 3$ uc sample. **b**, The time dependence of $1/R_{sheet}$ after acetone SAP for $d_{LAO} = 3, 5$, and 10 uc samples. Lines are guides for eyes. The green arrow indicates the measurement limit. The small perturbations in the data, notably on the 3 uc curve, were caused by small fluctuations in the ambient temperature.

Figure 5 | Sketches of band diagrams and electron transfer mechanisms. **a**, Idealized surface. Electrons transfer from E_V^{LAO} of surface LaAlO_3 to the conduction band of SrTiO_3 , E_C^{STO} , near the interface. eV_{Uncom} roughly equals to E_g^{STO} . **b**, Surface with aligned polar adsorbates. Electrons transfer from the surface adsorbates to E_C^{STO} near the interface. The built-in potential across the adsorbates, V_{ad} , effectively reduces V_{Uncom} across the LaAlO_3 layer. In both **a** and **b**, bulk stoichiometry and valences are shown for simplicity.

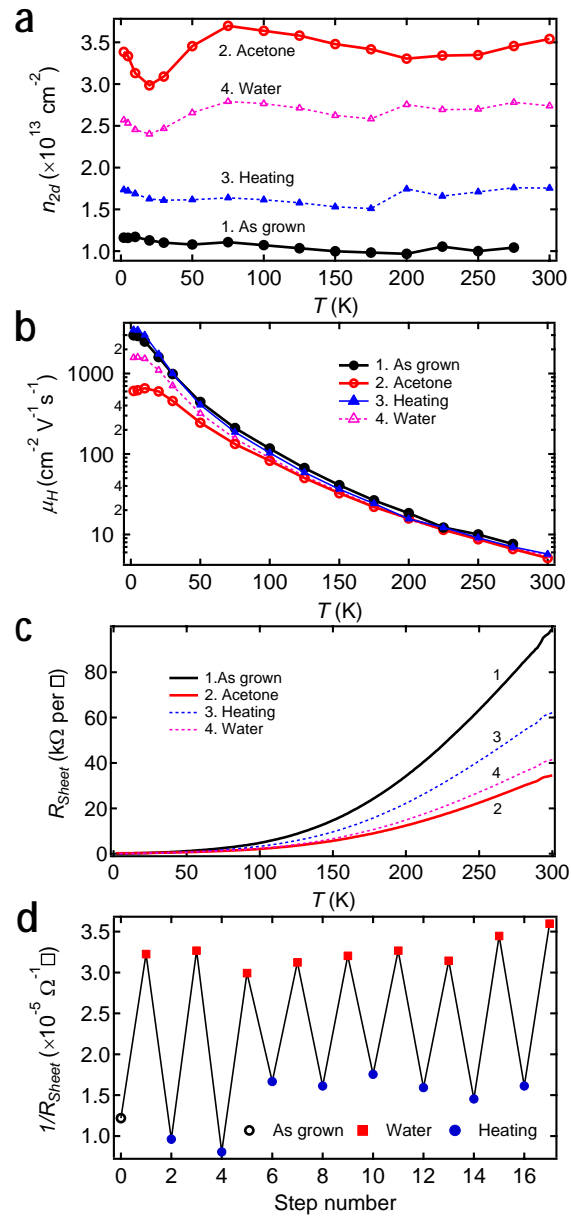


Figure 1 Y. W. Xie *et al.*

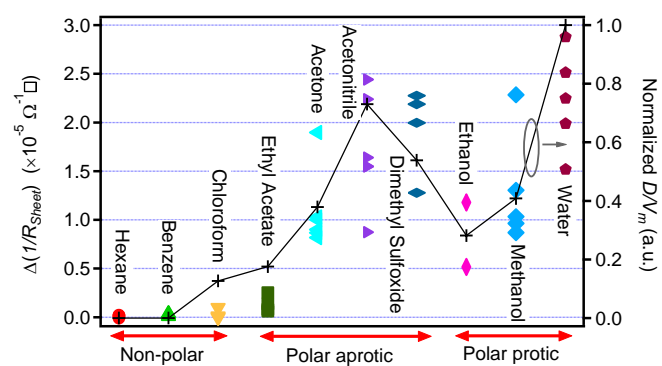


Figure 2 Y. W. Xie *et al.*

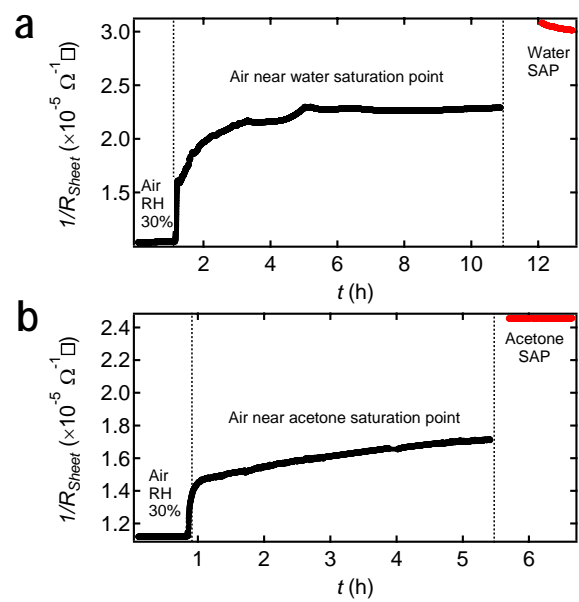


Figure 3 Y. W. Xie *et al.*

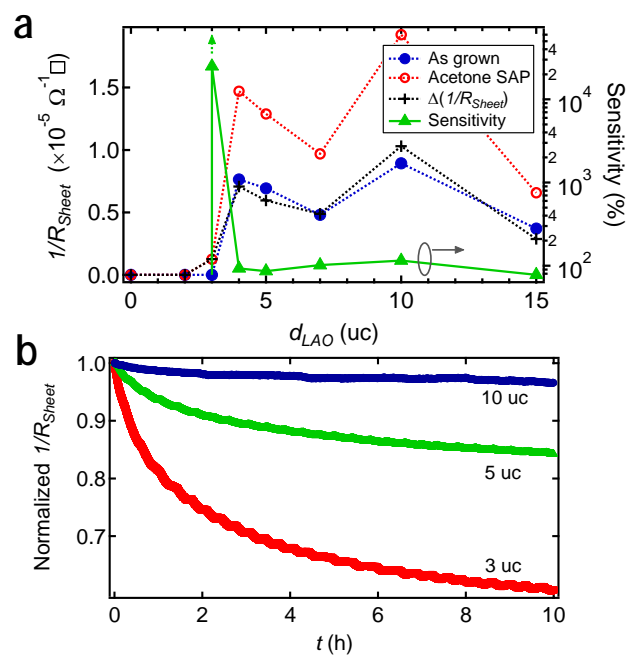


Figure 4 Y. W. Xie *et al.*

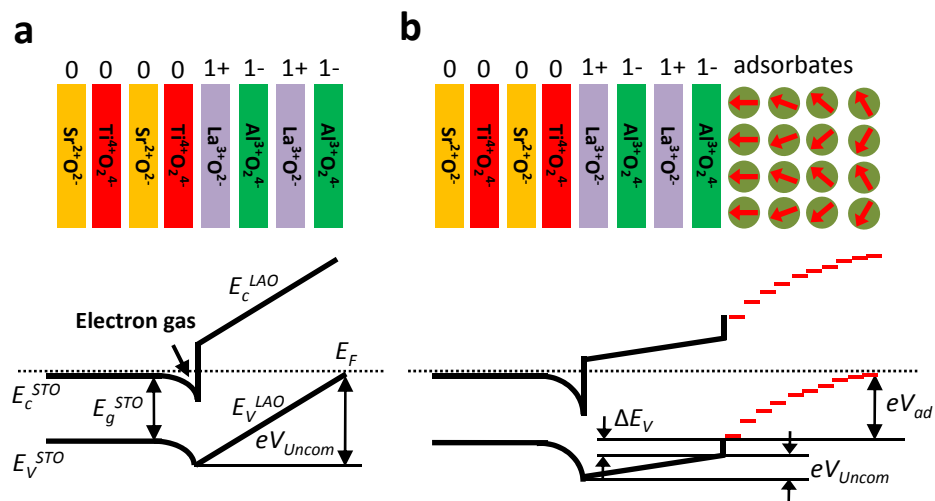


Figure 5 Y. W. Xie *et al.*