

Surface Chemically Switchable Ultraviolet Luminescence from Interfacial Two-Dimensional Electron Gas

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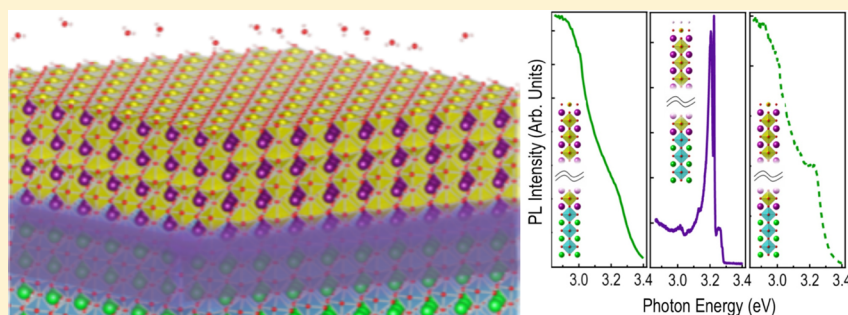
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Supporting Information



ABSTRACT: We report intense, narrow line-width, surface chemisorption-activated and reversible ultraviolet (UV) photoluminescence from radiative recombination of the two-dimensional electron gas (2DEG) with photoexcited holes at $\text{LaAlO}_3/\text{SrTiO}_3$. The switchable luminescence arises from an electron transfer-driven modification of the electronic structure via H-chemisorption onto the AlO_2 -terminated surface of LaAlO_3 , at least 2 nm away from the interface. The control of the onset of emission and its intensity are functionalities that go beyond the luminescence of compound semiconductor quantum wells. Connections between reversible chemisorption, fast electron transfer, and quantum-well luminescence suggest a new model for surface chemically reconfigurable solid-state UV optoelectronics and molecular sensing.

KEYWORDS: Two-dimensional electron gas, photoluminescence, $\text{LaAlO}_3/\text{SrTiO}_3$, chemisorption

The well-known *polar catastrophe* model^{1,2} explains the LaAlO_3 -thickness-dependent insulator-to-metal transition in $\text{LaAlO}_3/\text{SrTiO}_3$, with its electronic reconstruction consisting of holes at the surface and electrons at the interface, due to potential buildup across LaAlO_3 . The resulting conducting interfacial state is distinctly different from the 2DEG at a conventional semiconductor heterojunction located at an interface deep below the surface³ or at a semiconductor surface due to metal atom adsorption^{4,5} or intrinsic electron accumulation.^{6–8} The electronic structure and correlations in $\text{LaAlO}_3/\text{SrTiO}_3$ drive a host of unique features and findings in this interfacial 2DEG, including magnetic⁹ and superconducting ordering¹⁰ and room-temperature local surface-controlled switching of conductance¹¹ and of photoconductivity.¹² The interfacial conductance and functionality depend on the free surface. Capping the LaAlO_3 surface with metallic contacts,¹³

metal oxides,¹⁴ or polar solvents¹⁵ accommodates the electrostatics of the system, stabilizing the electronic reconstruction and increasing the electron density at the interface. This increment of the 2D electron density via surface modulation could advance light-emission technology involving these interfacial states. However, direct access to these conducting states is a remarkable challenge, since overlapping conduction and valence bands, internal electric fields within LaAlO_3 , low 2D electron density in bare $\text{LaAlO}_3/\text{SrTiO}_3$, and radiative recombination through O vacancies each contribute to preventing the observation of sharp optical transitions involving the interfacial states. The few photoluminescence (PL) studies on this system have mainly focused on the oxygen-deficient

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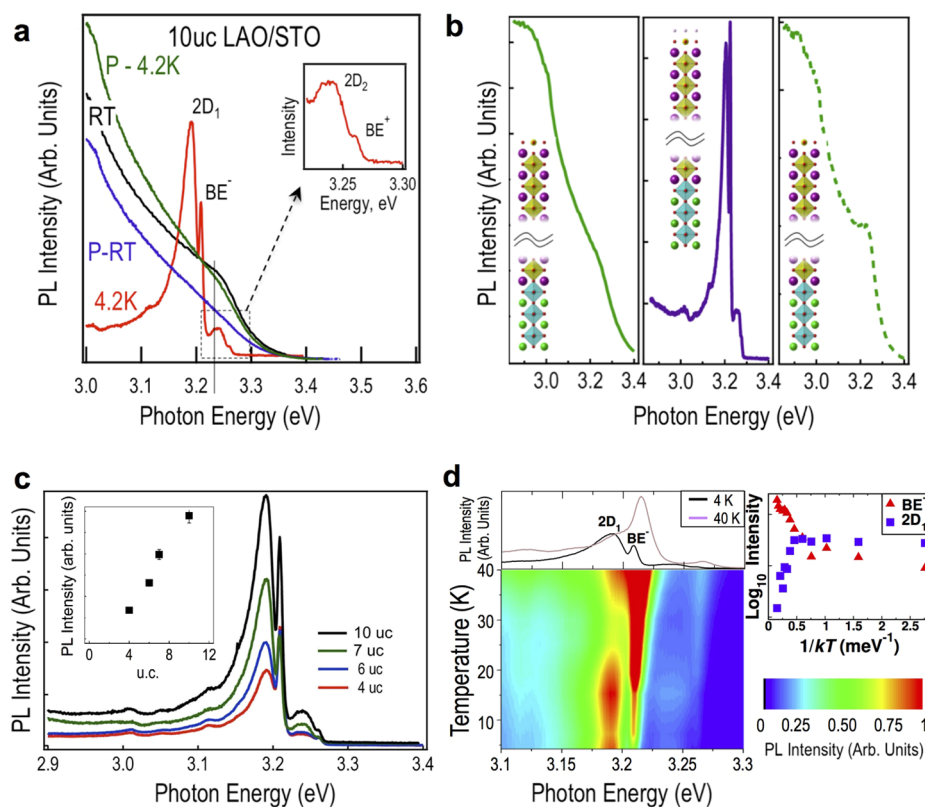


Figure 1. Absorption-induced optical transitions in complex oxide quantum well. (a) PL from a pristine (P) ten-unit-cell film of LaAlO₃ on SrTiO₃ bulk shows a broad feature (≈ 2.8 eV) attributed to recombination involving O vacancies. When the sample is exposed to water vapor in situ under vacuum, 300 K PL remains broad (black trace). Significantly, intense UV PL peaks emerge at 4.2 K (red trace). Peaks denoted 2D₁ and 2D₂ (inset) are assigned to different 2D quantized electronic energy level recombination with free holes. Peaks denoted zone boundary edge (BE⁻ and BE⁺, inset) are assigned to phonon-assisted interband transitions in SrTiO₃. (b) Reversibility of PL spectrum from a single LaAlO₃/SrTiO₃ film heterostructure as found (left), following H-chemisorption (center), and after annealing in O₂ and desorption of H (right), each collected at 4.2 K. (c) PL intensity collected at 4.2 K in LaAlO₃/SrTiO₃ samples exposed to water vapor in the same manner as described in the main text, with 4, 6, 7, and 10 unit cells (u. c.) of LaAlO₃, revealing a thickness dependence to the PL intensity. Shown in the inset are the integrated PL intensities for the 2D₁ peak at different unit cells thickness of LaAlO₃. (d) Temperature evolution of the PL from LaAlO₃/SrTiO₃ with the PL intensity legend on the side. Shown in the upper inset are the PL spectra at 4 and 40 K indicating the 2D₁ and BE⁻ peaks. In the side inset are the integrated intensities of the 2DEG and BE⁻ peaks plotted as functions of $1/kT$. Unlike the phonon-assisted PL peak, which decreases with decreasing T , cooling-induced onset and rise of the 2DEG peak is observed, followed by its saturation at lower T . This is a signature of the onset of spatial confinement of carriers, as found in classic III–V and III–N semiconductor heterojunction 2DEGs.

SrTiO₃ within the heterostructure,¹⁶ except for a recent report indicating broad PL signatures thought to arise from two-carrier radiative recombination of the interface induced electrons and photoexcited holes.¹⁷

In this Letter we demonstrate, through a combination of PL spectroscopy, density functional theory (DFT) simulations, Poisson-Schrödinger modeling, and thermodynamic analysis, a novel manifestation of PL properties from quantum well structures in oxide materials. We show that chemisorption-induced manipulation of the interfacial electronic structure can reversibly induce and suppress intense ultraviolet (UV) PL involving radiative recombination of electrons confined at the LaAlO₃/SrTiO₃ interface with photoinduced holes. Our studies reveal that the dissociated water fragments on the surface unentangle the interfacial electron density, allowing for direct optical examination of these states. DFT calculations elucidate the atomistic and electronic mechanism by which the H-chemisorption onto LaAlO₃/SrTiO₃ enables the system to reach potential and charge equilibrium. Chemisorption eliminates the average electric field in LaAlO₃ and increases the 2D carrier density in the quantized states at the interface, providing strong, accessible transitions in the near UV.

The PL measurements were performed on one set of 10 unit cells thick LaAlO₃ films, which were grown via reflection high-energy electron diffraction (RHEED)-monitored pulsed-laser deposition (PLD). The films were grown at a substrate temperature of 750 °C (this is the temperature of the Ag-paint used to provide thermal contact between the substrate and the heater plate, as measured via pyrometry), in an oxygen pressure of 1×10^{-3} Torr, with a laser repetition rate of 1 Hz, from a single crystal LaAlO₃ (001) target (Crystec, GmbH) on TiO₂-terminated SrTiO₃(001) substrates treated via standard methods. PL spectra were collected through a 0.3 m monochromator (Jobin Yvon U1000, Edison NJ), dispersed with 1200 grooves/mm gratings, and detected using a water-cooled photomultiplier tube (Hamamatsu). A 325 nm He–Cd laser (Kimmon-Khoa) was used as the excitation source, focused to a spot diameter of 1.15 μ m. The incident intensity was in the range of 1–22 W/cm². The samples were mounted in a cryostat (Janis ST-100) and held at 5×10^{-6} Torr (see [Supporting Information](#)).

The atomic and electronic structures of this system were computed via plane-wave basis set DFT using the local density approximation¹⁸ + Hubbard U method (LDA + U)¹⁹ as

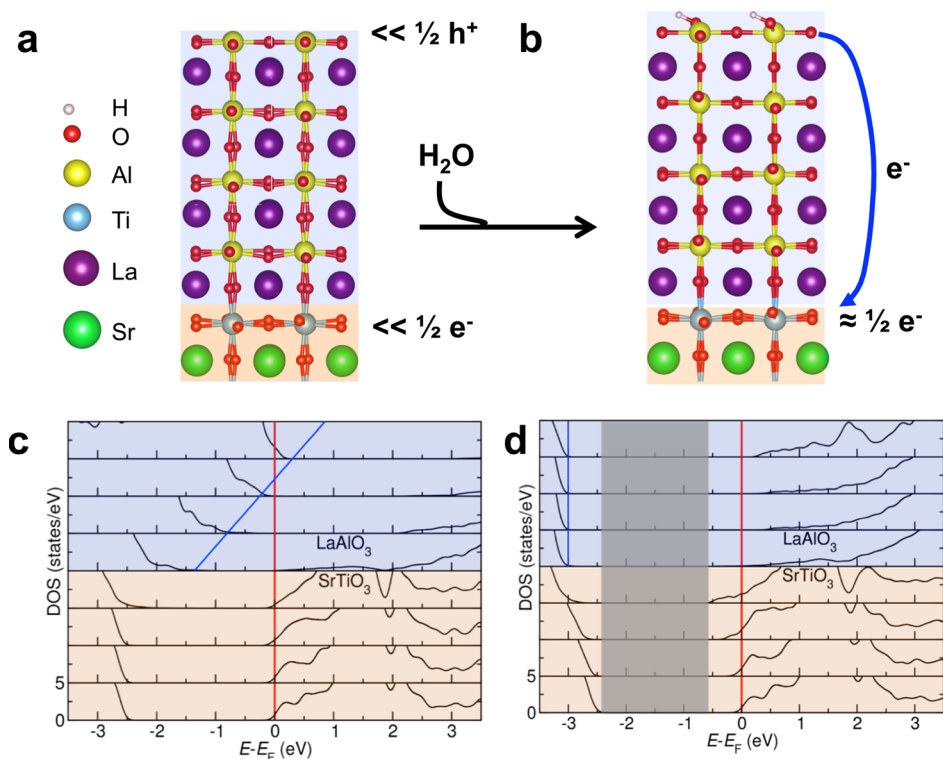


Figure 2. Access to optical transitions from the 2DEG. The atomic structure of the oxide heterostructure quantum well interface of (a) bare LaAlO₃/SrTiO₃, indicating that the hole density at the surface and the electron density at the interface are far smaller than the 1/2 hole/electron per surface unit cell at the infinite thickness limit, and (b) H-chemisorbed LaAlO₃/SrTiO₃, resulting in higher density of localized 2D confined electrons at the interface. Once the H atoms are chemisorbed on the surface, the holes are passivated, driving complete electron transfer to the interface, illustrated by the solid blue arrow. (c) Layer-resolved electronic density of states (DOS) for bare LaAlO₃/SrTiO₃ undergoing the polar catastrophe, with the blue line indicating the potential buildup. The potential buildup provides states that will inhibit sharp optical transitions. (d) Layer-resolved DOS after chemisorption of H onto LaAlO₃/SrTiO₃. The H atom transfers an electron to the LaAlO₃/SrTiO₃ interface at equilibrium, eliminating the potential build up and opening an energy gap, so that optical transitions can be accessed, indicated by the gray shaded area.

implemented in the Quantum Espresso²⁰ computer code. All atoms were represented by norm-conserving, optimized,²¹ designed nonlocal²² pseudopotentials generated with the Opium package²³ (see Supplementary).

To probe the optical properties of the interfacial electronic structure, a series of temperature-dependent PL measurements were performed under two distinct sample treatments. The PL spectra collected at both 4.2 K and room temperature (RT) from as-grown ten-unit-cell films of LaAlO₃ on SrTiO₃ bulk samples (Supplementary Figure S1) stored at 300 K and atmospheric pressure (denoted as “pristine”) reveal a peak near 2.8 eV with a broad PL feature (see Figure 1a). This signal is attributed to radiative recombination through oxygen vacancy defect levels.¹⁶ When the sample is briefly (1 s) exposed to water vapor in situ under vacuum at room temperature, the PL spectra collected still have the broad character.

However, the PL spectra at 4.2 K from identical samples collected immediately following 1 s exposure to water vapor, while under vacuum possess sharp UV features and nearly complete suppression of the broad lower-energy emission (Figure 1a). Peaks at 3.209 and 3.261 eV (BE⁻ and BE⁺, respectively) are assigned to interband transitions involving transverse optical phonon ($\omega_{\text{TO}} = 26$ meV) emission ($E_g - \hbar\omega_{\text{TO}}$) and absorption ($E_g + \hbar\omega_{\text{TO}}$) at the Brillouin zone boundary edge.²⁴ Phonon-assisted PL is commonly seen in indirect band gap materials like SrTiO₃, and the absence of excitons is consistent with its unusually high dielectric constant ($\approx 10,000$ at 4.2 K).²⁵ We thus estimate E_g of our SrTiO₃

samples to be 3.235 eV at 4.2 K, in agreement with previous reports.²⁶

We propose that the strong, sharp peak centered at 3.192 eV and the smaller peak at 3.240 eV (2D₁ and 2D₂, respectively, Figure 1a), originate from radiative recombination of two-dimensionally confined electrons at the LaAlO₃/SrTiO₃ interface with photoexcited holes. The strong 2D₁ and well-defined 2D₂ PL signals directly relate to the surface chemical state. After water exposure, the original broad 2.8 eV-centered PL can be recovered through ex situ O₂ annealing; subsequent exposure to water in situ again produces the identical strong 2D₁ and well-defined 2D₂, higher-energy PL features and suppresses the broad lower energy emission. This off-on-off process, driven by ex situ O₂ annealing, exposure to water, and further O₂ annealing, operates reproducibly in each sample tested (see Figure 1b). This strongly suggests that the PL associated with the 2DEG quantum wells is tuned by the strong coupling between the surface and interfacial electronic states.

There have been reports of changes in the electronic structure in conventional semiconductor heterostructure 2DEGs due to gating from distant surface adsorbates.³ In addition, irreversible changes in 2DEG electronic structure at surfaces due to metal⁴ or molecular^{27–30} adsorption have also been observed. Here we show, experimentally and theoretically, reversible changes in PL from the interface due to electrostatically accessible, but chemically inaccessible 2DEG. Tunability of the sharp 2DEG-photoexcited hole PL in our water-treated LaAlO₃/SrTiO₃ samples is achieved even at distances of ≈ 2 nm

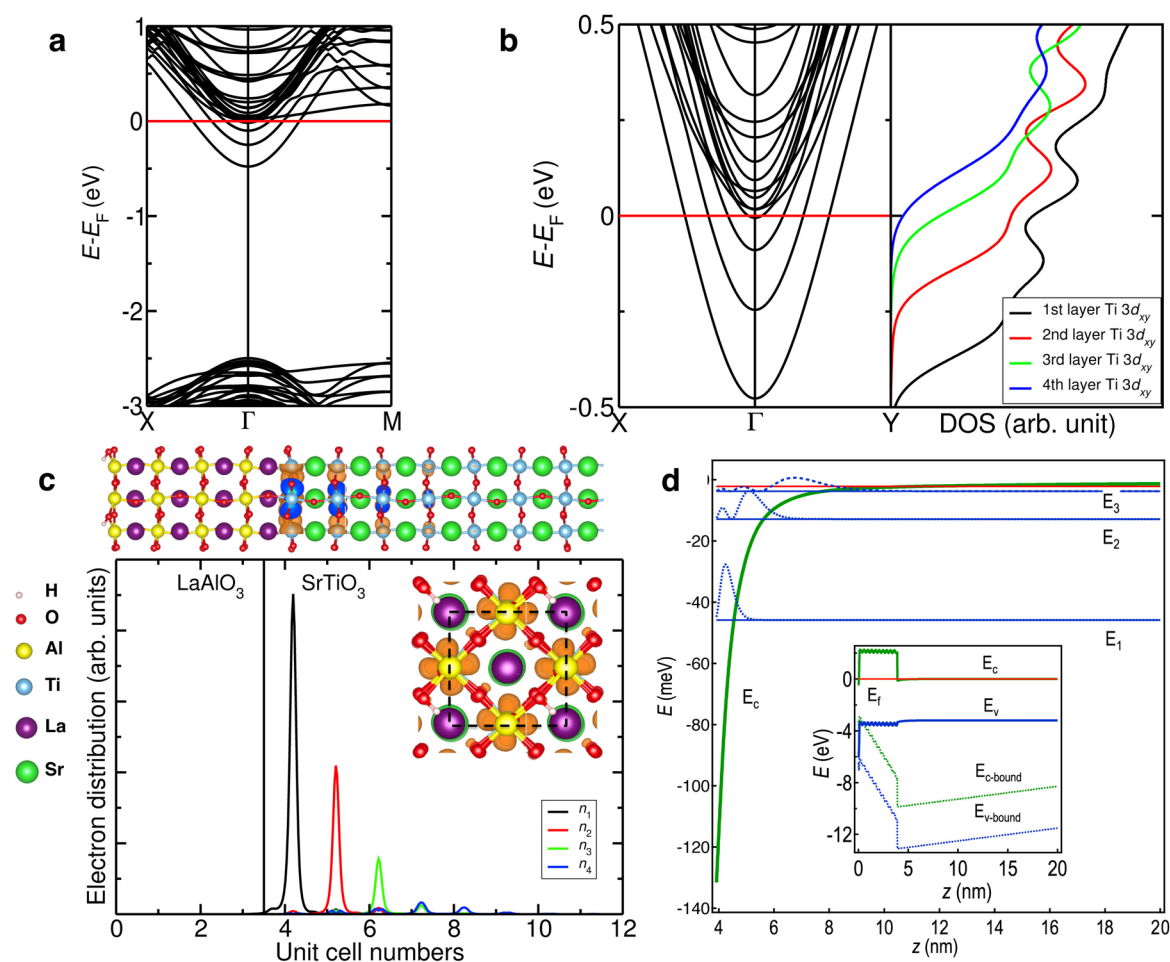


Figure 3. Influence of H^+ on electronic structure. (a) DFT calculated electronic band structure of H^+ surface-chemisorbed $\text{LaAlO}_3/\text{SrTiO}_3$ showing a large valence-conduction band gap. (b) Left panel: enlarged view of the conduction states in a; right panel: the projected DOS shows the contribution from the Ti $3d_{xy}$ orbitals in the layers near the interface. The red line indicates E_F . (c) Electron distribution of the conduction states. The atomic structure at the top of the graph shows a charge density isosurface for all the states within 0.5 eV below E_F , which consists of $n = 4$ bands. The graph below shows the planar-averaged filled state density of the conduction bands. The inset shows that the conduction electrons are strongly localized in Ti $3d_{xy}$ orbitals. (d) Self-consistent Poisson-Schrödinger model calculations show (inset) that passivation of AlO_2 -terminated $\text{LaAlO}_3/\text{SrTiO}_3$ by H^+ results in flattening of the conduction (solid green) and valence (solid blue) bands in LaAlO_3 ($0 < z < 4$ nm) compared with the bound potential (dashed green and blue, respectively) induced by AlO_2 and LaO , consistent with the DFT results in Figure 2c and d. Band bending (green), bound eigenstates (horizontal blue), and the modulus of the electronic eigenfunctions (blue) are shown and contribute to observed 2DEG-photoexcited hole PL.

between the free surface and the 2DEG interfacial quantum well. Figure 1c shows the quantum well PL signatures of the spectra collected at 4.2 K in $\text{LaAlO}_3/\text{SrTiO}_3$ samples with 4, 6, 7, and 10 unit cells of LaAlO_3 grown under the same conditions and exposed to water vapor. The fitted PL intensity increases for larger numbers of LaAlO_3 unit cells, along with the evolution of interfacial electronic reconstruction as a function of LaAlO_3 film thickness (see Supporting Information).

A distinctive signature of the two-dimensional origin of the PL is saturation of the 2DEG PL intensity at low T followed by thermally activated quenching at higher T .^{31,32} The $\text{LaAlO}_3/\text{SrTiO}_3$ 2DEG PL can be discerned in our spectra beginning at ≈ 40 K (Figure 1d). Its intensity rises for decreasing T with an activation energy of 8.06 meV, saturating at ≈ 23 K, which it is roughly constant (Figure 1d, inset). This activation and saturation signify thermally induced leakage of a critical density of carriers out of the interfacial quantum well into the bulk, and a 2D electron-photoexcited hole radiative recombination rate that exceeds the rate of carrier leakage, respectively. In stark

contrast, the intensities of the phonon-mediated PL peaks (BE^- , BE^+) exhibit a steady rise with T and are well-discerned even for $T > 200$ K.

The optical transitions from the 2DEG quantum well are controlled by the adsorbate dynamics on the AlO_2 surface layer. The H_2O molecules spontaneously dissociate into H^+ and OH^- when the AlO_2 -terminated $\text{LaAlO}_3/\text{SrTiO}_3$ system is exposed to water vapor, enabling the “water-cycle” mechanism.³³ The dissociated H_2O components can diffuse and influence the surface environment. Specifically, the dissociated OH^- can fill a surface O vacancy and become an adsorbed H^+ , reducing the number of O vacancies. However, dissociated H^+ has lower diffusion barriers than OH^- ,³⁴ leading to large surface regions populated mainly by H^+ . Our ab initio thermodynamic stability analysis of surfaces covered with either OH^- or H^+ shows that the H-chemisorbed system is much more stable than the OH-chemisorbed system (Supporting Figure S2). The relaxed atomic structures of the bare and H-chemisorbed $\text{LaAlO}_3/\text{SrTiO}_3$ systems are shown in Figure 2a and b, respectively.

Previous work on H-chemisorbed-LaAlO₃/SrTiO₃ indicates that the most stable coverage is one H per two surface unit cells,³⁵ and our DFT+U¹⁹ calculations show that this coverage leads to full elimination of the potential buildup which originally resides on the bare surface (Figure 2c and d). The calculated electronic structures for the four-layer LaAlO₃/eight-layer SrTiO₃ (001) system with chemisorbed H₂O and OH show typical metallic features, similar to bare LaAlO₃/SrTiO₃ (Supplementary Figure S3 and S4); however, the H-chemisorbed system is strikingly different. The electronic structure of the H-chemisorbed LaAlO₃/SrTiO₃ system differs from that of the bare system due to complete passivation of the surface charge. This translates into higher 2D electron density of 3.71×10^{14} electrons cm⁻² for the H-chemisorbed LaAlO₃/SrTiO₃ system, while the bare system shows 2.31×10^{13} electrons cm⁻² (Figure 2c and d). This occurs via electron transfer from the surface chemisorbed H to the interface, removing the “polar catastrophe”. Cancellation of the potential build up in LaAlO₃ unentangles the overlap between the conduction and valence bands, opening a gap in the spectrum (Figure 3a). This yields an isolated 2DEG, which consists of populating the Ti 3d states in the first few SrTiO₃ unit cells near the interface (Figures 3b, 3c). These states give a higher 2DEG density, enabling strong optical transitions at the interface and suppressing signals from deeper in the material, as observed experimentally. Though underestimated by DFT +U, the calculated $E_g \approx 2.1$ eV (Figure 3a, Supplementary Figure S5), taken together with the resulting high electron density, indicate that sharp radiative band-to-band transitions are due to H chemisorption.

The UV PL features arise from radiative recombination of electrons in quantized states with photoexcited holes. Our DFT calculations predict strongly localized 2DEG conducting states below E_F . These states mainly arise from Ti 3d_{xy} orbitals at and near the interface (Figure 3b). The spatially resolved electron distribution of these conducting states clearly shows that the 2DEG is distributed into four SrTiO₃ unit cells, strongly localized at the TiO₂ layers, with lower density farther from the LaAlO₃ interface (Figure 3c). These features indicate that the confining potential from the interfacial band bending has significant contributions from multiple quantum wells each spaced by an oxygen octahedral distance.

To further analyze the 2DEG-derived PL features, we consider how chemisorption of H⁺ on AlO₂ surfaces of LaAlO₃ alters the conduction and valence bands at and near the LaAlO₃/SrTiO₃ interface and induces changes in electron density, band bending, and formation of quantized 2D subbands at and near the interface. Self-consistent solutions of the coupled Poisson-Schrödinger eqs (Supporting Information) including band-bending³⁶ reveal H⁺ chemisorption-induced flattening of the potential gradient across the LaAlO₃ layer, and that the calculated $n = 1$ level is 42 meV below the bulk band edge (Figure 3d, Supplementary Figure S6), in excellent agreement with our measured value of 43 meV.

The removal of the electrostatic slope in the LaAlO₃ overlayer causes all of the transitions to have the same energy. In the absence of the H⁺ adsorption, radiative recombination of a photoexcited hole in the surface layer would result in a different photon energy than that for a hole in a subsurface LaAlO₃ layer. Following H⁺ adsorption, all LaAlO₃ layers provide equi-energetic holes. As the LaAlO₃ overlayer is made thicker, it gradually passivates the polar catastrophe, only completely doing so in the thick film limit. Here, by providing a

higher-energy source of electrons (thereby stabilizing surface holes) H allows the few layers of LaAlO₃-topped heterostructure to 100% passivate the polar catastrophe, making the potential flat and the PL sharp. This leads to our observation of a much more dramatic change in PL than one would see by thickening the LaAlO₃ incrementally.

This system provides a convenient external control of 2DEG properties that offers reversible switching between sharp UV and broad blue photoluminescence. This is fundamentally interesting physics, and this significant change in PL could be harnessed as a signal in a photonic circuit or relay, or as a sensitive new in operando probe of surface molecular adsorption since these results are observed in a non-UHV environment and water dissociated species are proxies for other electron-donating adsorbate species.¹⁵ Realization of these concepts in the UV and their strong dependence on the environment opens up new opportunities and challenges. Such a system could provide new optoelectronic devices that operate at short wavelengths.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b04461.

Film growth, photoluminescence of LaAlO₃/SrTiO₃ films; thermodynamic stability analysis of H⁺ and ⁻OH adsorption on the LaAlO₃/SrTiO₃ surface; density functional theory calculations of LaAlO₃/SrTiO₃; and self-consistent Poisson-Schrödinger model (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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