The cause of extremely long-lasting room-temperature persistent photoconductivity in complex oxides

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It has been recently revealed that complex oxides display persistent photoconductivity with unique characteristics: it occurs at room temperature and lasts over a very long period of time. Illumination of SrTiO\textsubscript{3} crystals at room temperature with sub-bandgap light reduces the electrical resistance by three orders of magnitude and persists for weeks or longer (Tarun \textit{et al.}, Phys. Rev. Lett. 111, 187403 (2013)). Experiments indicate that oxygen vacancy and hydrogen play important role, yet the microscopic mechanism responsible for this remarkable effect has remained unidentified. Using hybrid density functional theory calculations we show that an instability associated with substitutional hydrogen H\textsubscript{O} under illumination, which becomes doubly ionized and leaves the oxygen site, can explain the experimental observations. H\textsubscript{O} then turns into an interstitial hydrogen and an oxygen vacancy, leading to excess carriers in the conduction band. This phenomenon is not exclusive to SrTiO\textsubscript{3}, but it is also predicted to occur in other oxides. Interestingly, this phenomenon represents an elegant way of proving the existence of hydrogen substituting on an oxygen site (H\textsubscript{O}), forming an interesting, and rarely observed, type of three-center two-electron bond.

Photoconductivity is a fundamental physical process in semiconductors where excess charge carriers that are created under illumination lead to often dramatic enhancement in electrical conductivity\textsuperscript{[11]}. In general, the conductivity goes back to its original value after the termination of the exciting illumination. Interesting cases happen when the photogenerated increased conductivity persists for very long times after the exciting light has been switched off. In these cases, the excess charge carriers remain delocalized in the bands, due to some microscopic mechanism that hinders carrier recombination. Persistent photoconductivity (PPC) in semiconductors is typically observed at low temperatures\textsuperscript{[2]}, i.e. below about 77 K, meaning that recombination of the photogenerated carriers is obstructed by relatively low thermally activated energy barriers in real, configurational, or momentum spaces\textsuperscript{[11]}. Recent experiments by Tarun \textit{et al.}\textsuperscript{[3]} have shown that SrTiO\textsubscript{3}, with indirect (direct) band gap of 3.25 eV (3.75 eV)\textsuperscript{[4, 5]}, exhibits extremely long living PPC at room temperature upon exposure to light of energy 2.9 eV or higher. The microscopic mechanism behind this extraordinary effect observed at \textit{room temperature} remains unknown.

SrTiO\textsubscript{3} (STO) has the cubic perovskite crystal structure at room temperature (Fig. 1(a)) and is often used as substrate for the growth of other oxides, including superconducting thin films\textsuperscript{[6]}. The discovery of two-dimensional electron gas at the interface of STO with other complex oxides such as LaAlO\textsubscript{3}\textsuperscript{[7]} and GdTiO\textsubscript{3}\textsuperscript{[8]} has fueled interest in its application in oxide electronics. Through doping, the electrical properties of STO can be tuned from insulating to semiconducting, metallic, and even superconducting\textsuperscript{[9, 12]}. Experiments by Tarun \textit{et al.}\textsuperscript{[3, 14]} have shown that STO with specific annealing treatment exhibits PPC at room temperature upon exposure to sub-band gap light excitation; the conductivity increases by three orders of magnitude and lasts over a year. This makes STO unique since large PPC in semiconductors is normally observed only at low temperatures\textsuperscript{[2]}. A tentative model for the mechanisms behind PPC was proposed, in which hydrogen impurities seem to play critical role\textsuperscript{[13]}. Hydrogen is an ubiquitous impurity in oxides and can greatly affect their electrical properties\textsuperscript{[14, 17]}, making them electrically conductive. Experiments have demonstrated that H impurities can be easily incorporated into STO\textsuperscript{[18]}, with infrared (IR) spectroscopy measurements showing hydrogen-related local vibrational frequencies in the range of 3350-3600 cm\textsuperscript{-1}, associated with the stretching of O-H bonds. Density functional theory (DFT) and hybrid functional calculations have been performed to identify the H-related vibration frequencies\textsuperscript{[19, 20]}, and attributed the observed IR peaks to interstitial hydro-
Here we use first-principles calculations based on DFT and hybrid functional to investigate the role of hydrogen in the observed PPC in STO. We find that $H_2^+$ introduces a doubly occupied defect state near the valence-band maximum (VBM) of STO, as schematically shown in Fig. 2. Upon exposure to light with energy close to or higher than the band gap ($\hbar \omega \gtrsim 2.9$ eV), one electron from the $H_2^+$-related state is excited to the conduction band, transforming it into $H_2^{2+}$, which in turn is unstable at room temperature. The H atom then moves out from the O site, bonding to an adjacent O in the form of $HOO^+$, leaving an ionized vacancy $V_O$ behind, thus liberating electrons that contribute to the PPC. The $H_2^+$ can easily diffuse in the material, eventually finding a Sr vacancy. We find that these results also apply to other oxides, such as TiO$_2$ and BaTiO$_3$, and that the observed PPC is an interesting way to probe the existence of substitutional H$_2O$ which is often difficult to detect in conducting oxides using standard vibration spectroscopic techniques [21].

Our calculations are based on DFT [23, 24] in the generalized gradient approximation (GGA) [25] and the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) [26, 27] as implemented in the Vienna *ab initio* simulation package (VASP) code [28, 29]. The electron-ion interactions are described using the projector augmented wave (PAW) method [30, 31] with a plane-wave energy cutoff of 400 eV. For the defect calculations we used a 135-atom supercell, built out of the five-atom cubic primitive cell with calculated equilibrium lattice parameter of 3.913 Å. Brillouin zone sampling was restricted to the Γ-point, yet tests using a $2\times2\times2$ $k$-points mesh change formation energies by less than 0.1 eV. The calculated indirect band gap of 3.22 eV is in good agreement with the experimental value of 3.25 eV for the cubic phase of STO at room temperature [4, 5].

Hydrogen can incorporate into SrTiO$_3$ either as interstitial $H_i$, forming an H-O bond, or as substitutional ($H_O^+$), replacing an O atom. As $H_i$, H can be bonded to a regular O atom, in which case it acts as a donor, $H^{2+}$, or it can be bonded to an O atom neighboring a Sr or Ti vacancy [19], lowering the acceptor charge state of the vacancy. The electronic structure of $H_i^+$ can be understood as follows: a neutral $H$ forms a chemical bond with an O lone pair, resulting in a doubly occupied bonding state several electron volts below the VBM and an antibonding state well above the conduction-band minimum (CBM), which then lowers its energy by becoming a delocalized electron in the conduction band.

The electronic structure of substitutional $H_O^+$ can be described as follows: the H 1s state combines with the doubly occupied symmetric $a_1$ state of the neutral O vacancy ($V_O$), resulting in a bonding state near the VBM, and an antibonding state above the CBM, which also becomes a conduction-band electron, resulting in a single donor center $H_O^+$. The formation of the bonding state is schematically drawn in Fig. 2. This description is corroborated by inspecting the calculated orbital-projected density of states (DOS) of $H_O^+$ in STO shown in Fig. 3(c), where we compare the DOS of the perfect STO crystal and the supercell with one $H_O^+$ defect. The calculated $H_O^+$-Ti bond length is 2.00 Å, compared with the equilib-
rium Ti-O bond length of 1.96 Å in STO.

We note that $H^+_O$ has been predicted and subsequently observed in ZnO \cite{15, 21}, and predicted to occur in other oxides such as SnO$_2$ \cite{32}, In$_2$O$_3$ \cite{16}, and TiO$_2$ \cite{33}. The observation of $H^+_O$ in oxides other than ZnO has remained elusive.

In the experiments of Tarun et al. \cite{3}, the PPC occurs when the sample is exposed to light with photon energy of 2.9 eV or higher, which is slightly lower than the band gap of 3.25 eV. Our results shown that $H^+_O$ introduces a defect level near the VBM. One electron from this level can be excited to the conduction band when exposed to light with photons of sub-band gap energy.

Recent studies by Poole et al. \cite{13} reveal that the presence of hydrogen and oxygen during high temperature annealing plays a critical role in the observed PPC. Based on our results above, we propose the following model for the PPC mechanism:

$$H^+_O + (V_{Sr} - H)^- \rightarrow V^{2+}_O + (V_{Sr} - 2H)^0 + 2e^-.$$  \hspace{1cm} (1)

First, $H^+_O$ and $(V_{Sr} - H)^-$ defects are introduced during the high-temperature annealing process under the "hydrogen rich" condition, resulting in almost fully compensated samples with low electrical conductivity. Upon exposure to light, one electron from the $H^+_O$-related level is excited to the conduction band, resulting in $H^+_O$. The $H^+_O$ configuration in the doubly positive charge state is unstable, and the H atom easily leaves the substitutional site to become an interstitial hydrogen ($H^+_i$), which is stabilized by forming a H-O bond with a nearby oxygen atom. Then the $H^+_i$ diffuses in the material and eventually is trapped by a Sr vacancy turning $(V_{Sr} - H)^-$ into $(V_{Sr} - 2H)^0$. A large thermal barrier due to the repulsion of $H^+_i$ and $V^{2+}_O$ prevents H from returning to the original initial state. The resulting defects elevates the sample to a high conductivity state.

The process in Eq. 1 involves (a) hopping of the H from the O vacant site to the closest interstitial site and (b) the diffusion of $H^+_i$ until it becomes trapped by a Sr vacancy. Previous calculations have shown that the migration barrier for an $H^+_i$ in STO is only \~0.25 eV \cite{20}, indicating that $H^+_i$ is highly mobile at room temperature. They also found that $H^+_i$ tend to bind to $V^{2-}_O$ or $(V_{Sr} - H)^-$, which is consistent with the proposed model. Thus the bottleneck in the process represented by Eq. 1 seems to be the sub-process (a). Thus, we calculated the barrier for this step as discussed below.

In STO, each O atom has eight O neighbors. So when an $H^+_O$ moves away from the O site, becoming $H^+_i$, it moves towards one of the eight identical O atoms. The most stable structure for the $H^+_i$ is shown in Fig. 1, in which the H binds to one O atom near the vacancy site and points to another O. The diffusion length of H from the O site to this interstitial site is about 2 Å, much larger than the equilibrium O-H$_i$ distance of 1 Å \cite{20}. Without exposure to light, this process is represented by the following charge-conserving reaction:

$$H^+_O \rightarrow V^{0}_O + H^+_i,$$  \hspace{1cm} (2)

where $V^{0}_O$ represents two small polarons bound to the doubly positive O vacancy $V^{2+}_O$ forming a neutral complex \cite{22}. On the other hand, under exposure to near band gap light excitation, the initial defect is in $H^{2+}_O$, and the charge conserving reaction becomes:

$$H^{2+}_O \rightarrow V^{+}_O + H^+_i,$$  \hspace{1cm} (3)

where $V^{+}_O$ represents one small polaron bound to the doubly positive O vacancy $V^{2+}_O$ forming a singly positive complex \cite{22}. The reaction represented by Eq. 2 is endothermic with an energy barrier of \~3.7 eV, and therefore unlikely to occur at room temperature, indicating the $H^+_O$ strongly prefers to sit on the O site (see Fig. 4). On the other hand, the reaction in Eq. 3 which occurs after photo excitation, is exothermic with an energy drop of 1.5 eV. The result shown in Fig. 4 indicates that $H^{2+}_O$ is unstable, and the H atom is spontaneously displaced from the O site towards the interstitial region. It sees a very low barrier of only 0.4 eV to separate into $H^+_i$ and $V^{2+}_O$, and this process is very likely to occur at room temperature. The Coulomb repulsion between the $H^+_i$ and $V^{2+}_O$ then favor to drive them apart.

The reaction rate for processes in Eq. 2 and 3 can be estimated using:

$$\Gamma = \Gamma_0 e^{-\frac{\Delta a}{k_B T}},$$  \hspace{1cm} (4)

where $\Gamma_0$ is the reaction barrier, $k_B$ is the Boltzmann constant, $T$ is the temperature and $\Gamma_0$ can be approximated by the highest frequency of the local vibration mode (see

![Graph showing energy levels and transitions](image-url)
Infrared (IR) spectroscopy peaks of around 3500 cm\(^{-1}\) have been observed in hydrogen-doped STO samples. These peaks are associated with the local vibration modes associated with the H impurity. For the H\(^+\) case, we obtained a non-degenerate mode at 2.87 eV (not shown). Here too, we find that the H\(^+\) will not move out of the O site at room temperature, while, upon illumination, H\(^+\) turns into H\(^{2+}\), which is unstable and easily move out of the O site.

To aid in the experimental identification of H\(^{2+}\) in STO, we calculated the frequencies of the local vibration modes above discussed. If we take \(\Gamma_0 = 40\) THz, \(T = 300\) K, we obtain \(\Gamma = 7.9 \times 10^{-49}\) s\(^{-1}\) for \(E_a = 3.7\) eV, and \(\Gamma = 1.0 \times 10^5\) s\(^{-1}\) for \(E_a = 0.4\) eV, i.e., H\(^+\) will not move out of the O site at room temperature, while, upon illumination, H\(^+\) turns into H\(^{2+}\), which is unstable and easily move out of the O site.

In the case of H\(^{2+}\), H is bonded to two Ti atoms with H-Ti distances of 2 Å. We thus expect the frequencies of the H\(^{2+}\) local vibration modes to be much lower than those associated with O-H bond stretching. For the H\(^{2+}\) local vibration modes we obtained a non-degenerate mode at 1300 cm\(^{-1}\) and a twofold degenerate mode at 837 cm\(^{-1}\). Although these are much higher and outside the phonon spectrum of STO, we may be difficult to probe them due to possible overlap with absorption due to free-carriers.

Having discussed the role of H\(_O\) in the observed PPC in STO at room temperature, we then ask if this effect is exclusive to STO. We then explored if H\(_O\) would behave the same way in other oxides with similar band structure of STO, such as BaTiO\(_3\) and TiO\(_2\). These oxides have band gaps of 3.20 eV \([36]\) and 3.05 eV \([37]\), respectively, with upper valence bands derived mostly from O 2p orbitals and lower conduction bands derived from Ti 3d orbitals, similar to STO. The total DOS and the orbital projected DOS on H\(_O\) in BaTiO\(_3\) are shown in Fig. 5. This result shows that the H\(_O\)-related state resides near the VBM in BaTiO\(_3\), and electron from this state can be lifted to the conduction band using light with photons of near or higher energies than the band gap, as in STO.

The configuration coordinate diagram corresponding to the reaction path of Eqs. 2 and 3 for H\(_O\) in BaTiO\(_3\), displayed in Fig. 6, also shows that while H\(_O\) is stable at room temperature, with an energy barrier of 3.8 eV for dissociation into V\(_O^+\) and H\(_{O}^+\), upon illumination with photons of energy near or higher than the band gap, H\(_O\) is then transformed into H\(_{O}^{2+}\), which is unstable, with an energy barrier of only 0.3 eV to dissociate into V\(_O^+\) and H\(_{O}^+\), liberating electrons to the conduction band.

For TiO\(_2\), we find that H\(_O\) sees an energy barrier of 2.4 eV for dissociation, whereas H\(_O^+\) sees a barrier of only 0.5 eV (not shown). Here too, we find that the H\(_O\)-related state is near the top of the valence band. Therefore, we expect that once H\(_O\) is incorporated with concentrations that are much higher than the free electron concentration, due to compensation effects, we expect that illumination with photons with near band gap energies or higher will lead to long lasting PPC at room temperature.

In summary, our calculations show that hydrogen incorporated on oxygen site (H\(_O^+\)) can explain the observed long lasting PPC in STO. H\(_O\) is initially very stable at room temperature, but upon exposure to light with near band gap energy, one electron from the H\(_O\)-related state
is lifted to the conduction band; the resulting H$_2^{+}$O is unstable and leaves the O site, transforming into V$_O^+$ and H$_i^+$ with a barrier of only 0.4 eV. The reverse reaction is hindered by a larger barrier due to the Coulomb repulsion between the positively charged V$_O^+$ and H$_i^+$, which drives them apart. This effect is not exclusive to STO, but is also predicted to occur in BaTiO$_3$ and TiO$_2$ for example.

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