Ultrafast proton-assisted tunneling through ZrO$_2$ in dye-sensitized SnO$_2$-core/ZrO$_2$-shell films

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Core–shell architectures are used to modulate injection and recombination in dye-sensitized photoelectrochemical cells. Here, we demonstrate that exposing SnO$_2$-core/ZrO$_2$-shell films to acid permits photoinduced electron transfer through ZrO$_2$-shells at least 4 nm thick. A novel mechanism of charge transfer is proposed where protonic defects permit ultrafast trap-assisted tunneling of electrons.

A paramount challenge in all photoelectrochemical systems for solar energy conversion is facilitating desired charge transfer events while suppressing undesired charge transfer pathways. One highly successful strategy for charge management is the use of thin, conformal surface coatings, typically deposited via atomic layer deposition (ALD). In the case of water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs), conformal metal oxide shells can retard recombination of injected electrons and surface-bound holes.

We recently explored the ultrafast injection dynamics of a dye-sensitized SnO$_2$-core/TiO$_2$-shell architecture for use in WS-DSPECs.$^7$ The TiO$_2$-shells were prepared on SnO$_2$ nanoparticles using ALD. We used time resolved terahertz spectroscopy (TRTS) to observe either: (A) tunneling from the dye excited state directly into the SnO$_2$ core when the TiO$_2$ thickness was 6 Å or less, or (B) electron injection into the TiO$_2$ layer followed by trapping, and then followed by relaxation into the SnO$_2$ core when the TiO$_2$ thickness exceeded 6 Å. TRTS probes changes in oxide conductivity by monitoring ultrafast (fs–ns) photoinduced changes in THz radiation. Mobile conduction band electrons attenuate THz radiation, and thus, an increase in conductivity related to free-carrier generation manifests as a decrease in transmitted THz radiation, while a loss of mobile carriers by trapping or recombination results in an increase of transmitted THz light. Dempsey and coworkers$^8$ as well as Papanikolas and coworkers$^9$ observed similar behavior using nanosecond and ultrafast transient absorption, respectively, and also confirmed that recombination slowed with increasing shell thickness.

During our studies of SnO$_2$/TiO$_2$ films, we prepared SnO$_2$-core/ZrO$_2$-shell films as a control to distinguish between direct tunneling to the core and injection into the shell-material conduction band. Unlike TiO$_2$, the conduction band minimum (CBM) of ZrO$_2$ lies significantly above the S$_1$ and T$_1$-excited states of Ru(II)phos (bis-(2,2’-bipyridine)(4,4’-diphosphonato-2,2’-bipyridine)ruthenium(II)-bromide) (vide infra), which prohibits electron transfer via the ZrO$_2$ conduction band.$^{10}$ Contrary to our expectations, using TRTS, at pH 1 (0.1 M HClO$_4$) we observed photoinduced electron transfer into the SnO$_2$-core through ZrO$_2$-shell thicknesses of at least 40 Å (Fig. 1). As expected, we observed rapid injection into

![Fig. 1](image-url)
bare SnO$_2$, as well as with 1 and 2 Å of ZrO$_2$ where tunneling is expected. The increase in injection amplitude with thin layers of ZrO$_2$ is consistent with our previous observations, which we ascribe to passivation of non-mobile SnO$_2$ surface states.\cite{5,11} Beyond 2 Å of ZrO$_2$, however, we continue to observe significant electron injection into SnO$_2$, despite direct tunneling through the ZrO$_2$ being unrealistic (vide infra). We also cannot distinguish ultrafast features that can be ascribed to mobile electrons in the ZrO$_2$. This suggests that electron transport through the ZrO$_2$ must occur through non-mobile, localized states within the ZrO$_2$.

To gain a better sense of the manner in which electron transfer dynamics change with increasing ZrO$_2$ shell thickness, the TRTS traces were fit using a triple-exponential function (eqn (S1), ESI$^\dagger$) shown in red in Fig. 1, and the fitting parameters are summarized in Table S1 (ESI$^\dagger$). Surprisingly, in all cases, the fast (~2 ps) and intermediate (15–20 ps) injection components are nearly unaffected by film thicknesses. The ZrO$_2$ shell seems to primarily affect the slowest injection component, increasing its lifetime by about a factor of 2. Overall, the average weighted time constant for the electron to transit through the ZrO$_2$ shell increases by only a factor of ~3 for the thickest ZrO$_2$ shells relative to the thinnest ones. In comparison, a 25 Å thick TiO$_2$ layer slows the electron transport time by an order of magnitude.\cite{5}

ALD has been widely utilized to deposit uniform, conformal coatings of various oxides materials, including ZrO$_2$ on high surface area supports.\cite{12} Fig. S1 (ESI$^\dagger$) clearly shows that the ZrO$_2$ shell is intact and approximately 40 Å thick after the TRTS measurements, which eliminates the possibility of ZrO$_2$ dissolution and dye redeposition playing roles in the electron transfer. Dye desorption is also not observed. Additionally, ALD is well established as a conformal technique, and with 40 pulses of Zr, pinholes are not expected and are highly unlikely to account for the significant injection amplitude. The TRTS traces in Fig. S2 (ESI$^\dagger$) also demonstrate that mobile electrons in the SnO$_2$ are not photogenerated in the absence of Ru(II)phos, ruling out a contribution from direct above-band gap excitation of SnO$_2$ or ZrO$_2$.

The simplest model for the injection process from the photoexcited dye through the ZrO$_2$ shell to the SnO$_2$ core is tunneling, but is shown here to be implausible. Using a band gap estimate for monoclinic ZrO$_2$ of 5.4 eV and a valence band offset with silicon of 3.5 eV, we can infer that the CBM of ZrO$_2$ lies at ~1.35 V vs. NHE at pH 1.\cite{13} The structurally relaxed excited states T$_1$ and S$_1$ of Ru(II)phos have calculated potentials of 1.71 and 2.10 eV above the ground state, respectively, whereas without structural relaxation, the potentials are 1.88 and 2.25 eV, respectively. The calculated ground-state oxidation potential in CH$_3$CN is 1.45 V vs. NHE, and the experimentally measured potential is 1.33 V vs. NHE.\cite{14} Based on these potentials, the barrier for tunneling through ZrO$_2$ can vary between 1.08 eV for the structurally relaxed T$_1$ and 0.55 for the non-relaxed S$_1$. Using the WKB approximation (eqn (S2), ESI$^\dagger$), this yields tunneling transmission probabilities as a function of ZrO$_2$ thickness (Fig. 2). This figure also includes the calculated transmission for the experimental estimate of the barrier, as well as for a hypothetical tunneling barrier of 0.01 eV that would result in the high injection rate close to what we actually observe. This clearly demonstrates that direct tunneling does not contribute significantly except for the two thinnest ZrO$_2$ layers of ~2.04 Å.

Given that tunneling from the dye excited state into the SnO$_2$ conduction band is unlikely, a different mechanism of charge transport must exist. We note that in the absence of acid exposure (Fig. S3, ESI$^\dagger$), electron transport through the ZrO$_2$ is impeded, offering insight into the mechanism of charge transport. A possible mechanism involves trap-assisted tunneling facilitated by protonic defects (Fig. 1B). Houssa and coworkers describe a protonic trap energy that lies 0.77 eV below the CBM,\cite{15} which would be appropriately positioned to accept an electron from the S$_1$ state of Ru(II)phos and may be close in energy to the T$_1$. Transport through this defect level is consistent with our TRTS results that show the fastest injection components (possibly related to the S$_1$ state)\cite{16} are only marginally slowed by varying thicknesses of ZrO$_2$, while the slowest component (possibly related to the T$_1$) is significantly more sensitive to ZrO$_2$ thickness. Additionally, leakage current from sub-band gap charge hopping has been observed in ZrO$_2$ capacitors.\cite{17}

In an effort to gain a better understanding of how the acid treatment specifically affects the ZrO$_2$ layers, XPS measurements were carried out on high surface area SnO$_2$ nanoparticle films coated with 40 Å of ZrO$_2$. We investigated an as-prepared SnO$_2$/ZrO$_2$ film, a SnO$_2$/ZrO$_2$ film soaked overnight in anhydrous ethanol, and a SnO$_2$/ZrO$_2$ film soaked overnight in 0.1 M HClO$_4$. We also studied an uncoated, sintered SnO$_2$ film to identify any possible changes to the SnO$_2$ induced by soaking in solvent. Finally, as reference materials, we characterized commercial ZrO$_2$ and SnO$_2$ nanopowders. Survey scans of all films showed the presence of C, O, Zr and/or Sn, respectively. No nitrogen or chlorine was observed with high-resolution XPS scans of the N 1s and Cl 2p region.

Fig. S5a and b (ESI$^\dagger$) show high-resolution XPS scans of the Zr 3d and O 1s edge regions, respectively. Fig. S6 (ESI$^\dagger$) shows high-resolution scans of the C 1s and Sn 3d regions. All of the XPS peaks were referenced to adventitious carbon at 284.4 eV (Fig. S6c, ESI$^\dagger$). For the SnO$_2$ and ZrO$_2$ reference samples, we
observed a broad peak in the C 1s region related to adventitious
carbon that can be fit with two components, while the four
samples prepared from doctor-bladed pastes displayed an
additional peak at 288.4 to 288.6 eV, suggesting the sintering
process fails to remove all the carbon from these films. Importantly,
we do not observe any extra C 1s peaks for the acid-treated SnO2/
ZrO2 samples, which is an indication that carbon is not doping
the ZrO2 films.

In the Zr 3d region (Fig. S5a, ESI†), there is no evidence of Zr
in the SnO2 reference and sintered SnO2 samples. For the other
samples, Zr 3d\(_{3/2}\) and Zr 3d\(_{5/2}\) peaks are clearly seen, and there
is an additional feature at 186.7 eV in the ZrO2 reference
sample. This feature is most likely related to surface suboxide
species.\(^\text{18}\) The Zr 3d\(_{3/2}\) peaks at 184.1–184.5 eV and Zr 3d\(_{5/2}\)
peaks at 181.6–182.1 eV are related to crystalline ZrO2 species.\(^\text{19}\)
The X-ray diffraction pattern in Fig. S7 (ESI†) demonstrates that
the ZrO2 reference sample is the monoclinic phase, which is the
most stable polymorph at room temperature.\(^\text{20}\) It is clear from
Fig. S5a (ESI†) that the Zr 3d peaks at 184.4 and 182.0 eV for the
ZrO2 reference, as-prepared, and ethanol-treated SnO2/ZrO2
samples line up well, suggesting the as-prepared ZrO2 ALD
films are monoclinic after heating.

In Fig. S5a (ESI†) it is also apparent that the Zr peaks in
the HClO4-treated sample shift to higher binding energies of
184.6 and 182.2 eV. It is unlikely that a phase change has
occurred because, in the presence of strong acid and/or strain,
the tetragonal phase of ZrO2 undergoes a spontaneous phase
transformation to monoclinic at room temperature.\(^\text{21,22}\) Instead we
assign this shift to the incorporation of protons into the ZrO2 shell.
Chen et al.\(^\text{23}\) observed a shift in the Nb 3d spectrum to higher
binding energies upon hydrogen incorporation into Nb\(_2\)O\(_5\) while
electrochromic Nb2O5 films charged with Li\(^+\) exhibit a similar shift
in the Nb 3d spectrum.\(^\text{24}\) Shim and coworkers have found that
hydrogen impurities introduced during the ALD deposition of
yttria-stabilized zirconia results in a shift to higher energy of the
Y 3d peaks.\(^\text{25}\)

This assignment is further supported by the O 1s spectra
(Fig. S5c, ESI†). The O 1s XPS spectrum for monoclinic ZrO2 is
composed of two components: bridging oxygen (530.1 eV) and
–OH groups (~531 eV).\(^\text{26}\) For the as-prepared and ethanol-
treated SnO2/ZrO2 samples we find that the ratio of –OH groups
to bridging oxygen is about 0.52, while in the HClO4-treated
sample the ratio is 0.7 (Fig. S5c, ESI†). Introduction of protons
into ZrO2 is thought to induce breaking of bridging oxygen
bonds to form ZrOH,\(^\text{27}\) consistent with our results.

To gain further insight into the mechanisms of transport,
and 20 nm films of ZrO2 were deposited on planar Al2O3 and
patterned with gold electrodes. As shown in Fig. 3A and Fig. S8
(ESI†) (inset), the current–voltage (I–V) curve for the as-prepared
ZrO2 thin film exhibits an extremely small current response on
the order of femtoamps and hysteresis consistent with a large RC
time constant. This originates from the high dielectric constant
and resistivity of native ZrO2. Direct exposure to 0.1 M HClO4
(Fig. 3B) results in a ~10 order of magnitude increase in
conductivity after just three hours. A similar increase in con-
ductivity is also observed in 4 nm films after overnight exposure
to acid (Fig. S8a, ESI†).

To understand whether acid treatment primarily affects the
surface or bulk material, we fabricated three devices in series
on a single 20 nm ZrO2 film by depositing patterned gold
electrodes (Fig. 3C), leaving exposed ZrO2 “troughs” between
each of the evaporated gold films. Without any acid treatment,
the current across all three devices was on the order of ten
femtoamps (Fig. 3A), indicative of the high resistivity of the
as-prepared ZrO2 films. Device 1 was treated with 0.1 M HClO4
for three hours by adding the acid to the first device well. This
allowed us to expose a single partition of the ZrO2 film to HClO4
without exposing the other areas. The acid was subsequently
removed, and the current across all three devices was measured.
The current in device 1 reproducibly increased by ~10 orders of
magnitude, consistent with a substantial increase in conductivity.
The current in device 2 was also observed to reproducibly increase
by two orders of magnitude. After three hours, there was no
increase in the current in device 3, however, after 9 hours of acid
treatment of device 1, we did observe a factor of 20 increase in the
current across device 3. The fact that the current increased in
devices 2 and 3 despite not being directly exposed to acid is an
indication that the conductivity in this system is not a surface
property but rather a bulk property. These results are consistent
with proton incorporation into the film and subsequent diffusion
through the bulk of the ZrO2. We note that the increases in the
conductivity of devices 2 and 3 are unlikely to be related to

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**Fig. 3** (A) Current–voltage responses before acid treatment for 20 nm ZrO2 films patterned with gold into devices 1 (black circles), 2 (blue squares), and 3 (red triangles). (B) Current–voltage response for the same three devices after acid-treatment of device 1 for 3 hours. (C) Cartoon schematic of arrangement of devices 1, 2, and 3.
gaseous HClO₄ as the vapor pressure of pure HClO₄ is only 6.8 mmHg. In addition, Leng et al. observed a similar effect during the insulator to metal transition in tungsten oxide. 28

In summary, we have demonstrated a novel pathway for photoinduced electron transfer through wide band gap ZrO₂. Despite direct tunneling being unphysical, our TRTS measurements demonstrate that efficient, rapid electron transport is possible through thick ZrO₂ layers. We suggest a trap-assisted tunneling mechanism via mid-gap protonic defects. Furthermore, XPS measurements demonstrate that exposure to acid results in a shift of the Zr 3d peaks consistent with proton incorporation, while the O 1s spectrum of acid-treated samples shows an increase in the relative ratio of hydroxyl oxygen to bridging oxides due to the formation of ZrOH. Exposure to acid results in at least a six order of magnitude increase in DC conductivity. Using multiple devices patterned on the same film, we present evidence of proton incorporation and transport throughout the bulk film. The results of this study offer new insights into development of functional thin films for solar energy conversion and potential strategies for inducing conductivity.

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Conflicts of interest
There are no conflicts to declare.

Notes and references