



Cite this: *Chem. Commun.*, 2018, 54, 7971

Received 26th May 2018,
Accepted 22nd June 2018

DOI: 10.1039/c8cc04189j

rsc.li/chemcomm

Core-shell architectures are used to modulate injection and recombination in dye-sensitized photoelectrochemical cells. Here, we demonstrate that exposing SnO₂-core/ZrO₂-shell films to acid permits photoinduced electron transfer through ZrO₂-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).^{1–3} 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.^{4–6}

We recently explored the ultrafast injection dynamics of a dye-sensitized SnO₂-core/TiO₂-shell architecture for use in WS-DSPECS.⁷ The TiO₂-shells were prepared on SnO₂ nanoparticle films using ALD. We used time resolved terahertz spectroscopy (TRTS) to observe either: (A) tunneling from the dye excited state directly into the SnO₂ core when the TiO₂ thickness was 6 Å or less, or (B) electron injection into the TiO₂ layer followed by trapping, and then followed by relaxation into the SnO₂-core when the TiO₂ thickness exceeded 6 Å. TRTS probes changes in oxide conductivity by monitoring ultrafast (fs–ns) photoinduced

Ultrafast proton-assisted tunneling through ZrO₂ in dye-sensitized SnO₂-core/ZrO₂-shell films†

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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 coworkers⁸ as well as Papanikolas and coworkers⁹ observed similar behavior using nanosecond and ultrafast transient absorption, respectively, and also confirmed that recombination slowed with increasing shell thickness.

During our studies of SnO₂/TiO₂ films, we prepared SnO₂-core/ZrO₂-shell films as a control to distinguish between direct tunneling to the core and injection into the shell-material conduction band. Unlike TiO₂, the conduction band minimum (CBM) of ZrO₂ lies significantly above the S₁ and T₁-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 ZrO₂ conduction band.¹⁰ Contrary to our expectations, using TRTS, at pH 1 (0.1 M HClO₄) we observed photoinduced electron transfer into the SnO₂-core through ZrO₂-shell thicknesses of at least 40 Å (Fig. 1). As expected, we observed rapid injection into

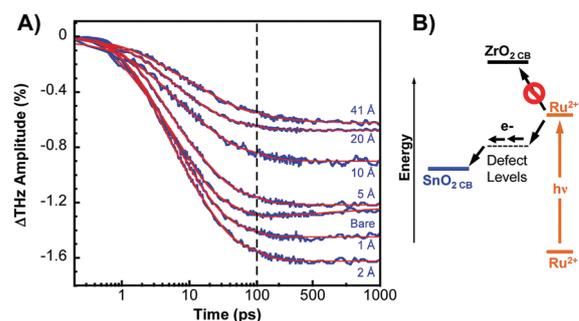


Fig. 1 (A) Time-resolved THz spectroscopy (TRTS) electron injection profiles monitored to 1000 ps following photoexcitation at 400 nm of Ru(II)phos-sensitized bare SnO₂ and SnO₂-core/ZrO₂-shell (1–41 Å) films in 0.1 M HClO₄ (aq). Solid red lines are fits of eqn (S2), ESI.† Dynamics from 0–100 ps are presented on an X-axis log scale while dynamics from 100–1000 ps are presented on a linear scale. (B) Schematic energy level scheme for dye-sensitized SnO₂-core/ZrO₂-shell films used in TRTS measurements.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cc04189j

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bare SnO₂, as well as with 1 and 2 Å of ZrO₂ where tunneling is expected. The increase in injection amplitude with thin layers of ZrO₂ is consistent with our previous observations, which we ascribe to passivation of non-mobile SnO₂ surface states.^{5,11} Beyond 2 Å of ZrO₂, however, we continue to observe significant electron injection into SnO₂, despite direct tunneling through the ZrO₂ being unrealistic (*vide infra*). We also cannot distinguish ultrafast features that can be ascribed to mobile electrons in the ZrO₂. This suggests that electron transport through the ZrO₂ must occur through non-mobile, localized states within the ZrO₂.

To gain a better sense of the manner in which electron transfer dynamics change with increasing ZrO₂ shell thickness, the TRTS traces were fit using a triple-exponential function (eqn (S1), ESI[†]) shown in red in Fig. 1, and the fitting parameters are summarized in Table S1 (ESI[†]). Surprisingly, in all cases, the fast (~2 ps) and intermediate (15–20 ps) injection components are nearly unaffected by film thicknesses. The ZrO₂ 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 ZrO₂ shell increases by only a factor of ~3 for the thickest ZrO₂ shells relative to the thinnest ones. In comparison, a 25 Å thick TiO₂ layer slows the electron transfer time by an order of magnitude.⁵

ALD has been widely utilized to deposit uniform, conformal coatings of various oxides materials, including ZrO₂ on high surface area supports.¹² Fig. S1 (ESI[†]) clearly shows that the ZrO₂ shell is intact and approximately 40 Å thick after the TRTS measurements, which eliminates the possibility of ZrO₂ 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[†]) also demonstrate that mobile electrons in the SnO₂ are not photogenerated in the absence of Ru(II)phos, ruling out a contribution from direct above-band gap excitation of SnO₂ or ZrO₂.

The simplest model for the injection process from the photoexcited dye through the ZrO₂ shell to the SnO₂ core is tunneling, but is shown here to be implausible. Using a band gap estimate for monoclinic ZrO₂ of 5.4 eV and a valence band offset with silicon of 3.5 eV, we can infer that the CBM of ZrO₂ lies at -1.35 V vs. NHE at pH 1.¹³ The structurally relaxed excited states T₁ and S₁ 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 CH₃CN is 1.45 V vs. NHE, and the experimentally measured potential is 1.33 V vs. NHE.¹⁴ Based on these potentials, the barrier for tunneling through ZrO₂ can vary between 1.08 eV for the structurally relaxed T₁ and 0.55 eV for the non-relaxed S₁. Using the WKB approximation (eqn (S2), ESI[†]), this yields tunneling transmission probabilities as a function of ZrO₂ thickness (Fig. 2). This figure also includes the calculated transmission for the experimental estimate of the barrier,

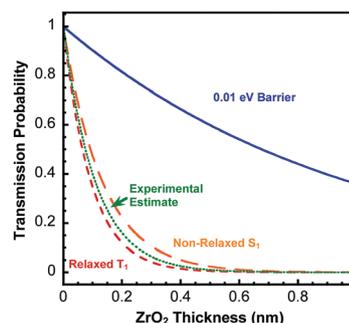


Fig. 2 Tunneling probability according to the WKB approximation, eqn (S2) (ESI[†]), using a barrier height corresponding to the difference between the ZrO₂ CBM and the excited state potential of Ru(II)phos. Also included is the largest hypothetical barrier (0.01 eV) that could allow for the tunneling through the ZrO₂.

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 ZrO₂ layers of ≤2.04 Å.

Given that tunneling from the dye excited state into the SnO₂ conduction band is unlikely, a different mechanism of charge transport must exist. We note that in the absence of acid exposure (Fig. S3, ESI[†]), electron transport through the ZrO₂ 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,¹⁵ which would be appropriately positioned to accept an electron from the S₁ state of Ru(II)phos and may be close in energy to the T₁. Transport through this defect level is consistent with our TRTS results that show the fastest injection components (possibly related to the S₁ state)¹⁶ are only marginally slowed by varying thicknesses of ZrO₂, while the slowest component (possibly related to the T₁) is significantly more sensitive to ZrO₂ thickness. Additionally, leakage current from sub-band gap charge hopping has been observed in ZrO₂ capacitors.¹⁷

In an effort to gain a better understanding of how the acid treatment specifically affects the ZrO₂ layers, XPS measurements were carried out on high surface area SnO₂ nanoparticle films coated with 40 Å of ZrO₂. We investigated an as-prepared SnO₂/ZrO₂ film, a SnO₂/ZrO₂ film soaked overnight in anhydrous ethanol, and a SnO₂/ZrO₂ film soaked overnight in 0.1 M HClO₄. We also studied an uncoated, sintered SnO₂ film to identify any possible changes to the SnO₂ induced by soaking in solvent. Finally, as reference materials, we characterized commercial ZrO₂ and SnO₂ 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[†]) show high-resolution XPS scans of the Zr 3d and O 1s edge regions, respectively. Fig. S6 (ESI[†]) 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[†]). For the SnO₂ and ZrO₂ 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.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.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.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.^{21,22} Instead we assign this shift to the incorporation of protons into the ZrO₂ shell. Chen *et al.*²³ observed a shift in the Nb 3d spectrum to higher binding energies upon hydrogen incorporation into Nb₂O₅, while electrochromic Nb₂O₅ films charged with Li⁺ exhibit a similar shift in the Nb 3d spectrum.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.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).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,²⁷ consistent with our results.

To gain further insight into the mechanisms of transport, 4 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 conductivity 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

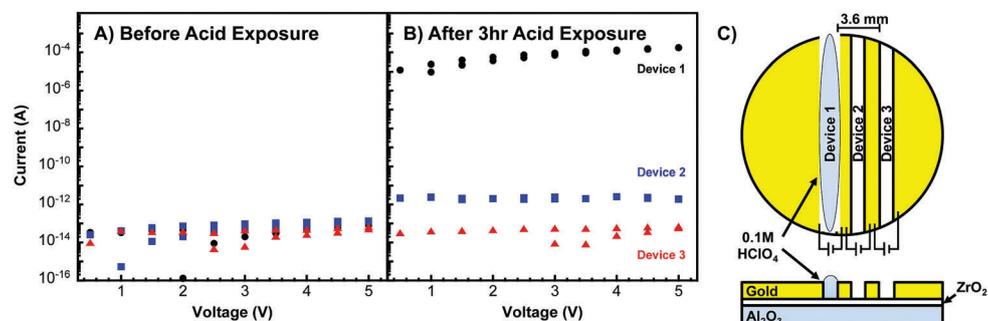


Fig. 3 (A) Current–voltage responses before acid treatment for 20 nm ZrO₂ films patterned with gold into devices 1 (black circles), 2 (blue squares), and 3 (red triangles). (B) Current–voltage response for the same three devices after acid-treatment of device 1 for 3 hours. (C) Cartoon schematic of arrangement of devices 1, 2, and 3.

gaseous HClO_4 as the vapor pressure of pure HClO_4 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 ZrO_2 . Despite direct tunneling being unphysical, our TRTS measurements demonstrate that efficient, rapid electron transport is possible through thick ZrO_2 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.

This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Energy Biosciences, Department of Energy, under contracts DE-FG02-07ER15911 and DE-FG02-07ER15909 as well as by a generous donation from the TomKat Charitable Trust. N. S. M. thanks the National Science Foundation for support as a graduate fellow under Grant DGE1255832. Instrumentation and facilities used in this project were supported by the Pennsylvania State University Materials Research Institute Nanofabrication Laboratory under National Science Foundation Cooperative Agreement ECS-0335765. The XPS analysis was performed at the Yale Materials Characterization Core.

Conflicts of interest

There are no conflicts to declare.

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