

Effect of  $\text{TiO}_x$  Substrate Interactions on the Electrocatalytic Oxygen Reduction Reaction at Au NanoparticlesAigerim Galyamova,<sup>\$</sup> Kihyun Shin,<sup>\$</sup> Graeme Henkelman,<sup>\*</sup> and Richard M. Crooks<sup>\*</sup>Cite This: *J. Phys. Chem. C* 2020, 124, 10045–10056

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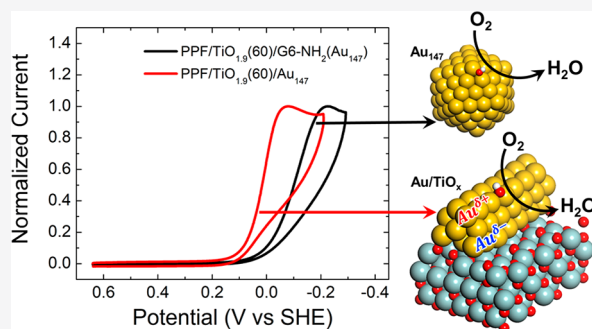
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**ABSTRACT:** In this article, we report a robust model for studying electrocatalytic reactions at metal nanoparticles (NPs) in contact with metal oxide surfaces. The metal oxide layer ( $\text{TiO}_x$ ) is prepared by atomic layer deposition, and it is sufficiently thin that it does not hinder electron transfer from the underlying conductive electrode to the supported AuNP electrocatalysts. In advance of the experiments, density functional theory (DFT) predicted that direct contact between AuNPs and  $\text{TiO}_x$  would lead to enhanced activity for the oxygen reduction reaction (ORR). DFT attributes the observed ORR enhancement to partial charge transfer from oxygen vacancies within the  $\text{TiO}_x$  film to the supported AuNPs and hence formation of anionic Au species. The experimental findings are in near quantitative agreement with the DFT results. Specifically, compared to isolated AuNPs, decreases of  $\sim 100$  and  $\sim 50$  mV in the ORR onset potential are observed experimentally for AuNPs supported on  $\text{TiO}_{1.9}$  and  $\text{TiO}_{2.0}$  films, respectively.



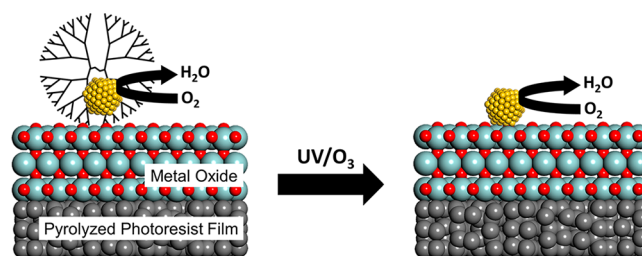
## INTRODUCTION

In this work, we report on a synergistic relationship between Au nanoparticles (NPs) and  $\text{TiO}_x$  ( $x = 1.9$  and  $2.0$ ) supports that leads to significantly improved electrocatalytic activity for the oxygen reduction reaction (ORR) compared to AuNPs in the absence of a support effect. Importantly, the electrocatalyst was selected by theoretical screening of different supports prior to the initiation of the experiments. Additionally, the findings discussed here build upon an earlier study from our groups in which density functional theory (DFT) was used to predict the nature of a different metal/support combination that would be beneficial for the ORR. The present study was undertaken to determine if the general principles that led to quantitative agreement between predictive theory and confirming experiments in this earlier work were fortuitous or if the approach used is robust. The results presented here suggest the latter.

As alluded to above, we previously reported a model that allowed us to study the effects of support interactions on the electrocatalytic response of metal NPs in the absence and presence of direct contact with metal oxide substrates.<sup>1–4</sup> In this model (Scheme 1), dendrimer encapsulated NPs (DENs)<sup>5–8</sup> are used as the principal catalyst.

Initially, the dendrimer prevents direct contact between the NPs and the underlying metal oxide support, and therefore electrocatalytic activity arises only from the metal NPs. Subsequent removal of the dendrimer by a  $\text{UV}/\text{O}_3$  treatment brings the NPs into direct contact with the oxide. Depending on the nature of the oxide, it might influence the electrocatalytic properties of the NPs. For example, we have shown that alumina substrates have no effect on the oxygen reduction

## Scheme 1



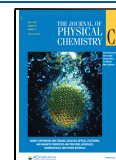
activity of PtNPs.<sup>1,2</sup> In contrast,  $\text{SnO}_x$  substrates significantly influence AuNPs for the same reaction.<sup>3</sup> Calculations, carried out prior to these latter experiments, predicted that this activity enhancement would exist due to a partial charge transfer from oxygen vacancies in the  $\text{SnO}_x$  support to the AuNPs. Furthermore, we have shown that the presence of the dendrimer around the NP has little to no effect on ORR activity.<sup>3,4</sup>

In addition to the aforementioned results from our group, Adzic and co-workers have also examined the effect of oxide supports on electrocatalytic reactions.<sup>9–11</sup> For example, they

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investigated the role of support interactions for the ethanol oxidation reaction at a  $\text{SnO}_x/\text{Pt}$  interface.<sup>9</sup> This interface was fabricated by depositing  $\text{SnO}_x$  nanoislands onto a Pt(111) surface, and it resulted in enhanced ethanol electrooxidation compared to Pt alone. The degree of activity enhancement was found to be highly dependent on  $\text{SnO}_x$  coverage, which clearly implicated the symbiotic relationship between  $\text{SnO}_x$  and Pt. In this case,  $\text{SnO}_x$  nanoislands were concluded to be actively promoting the removal of poisoning species, such as  $\text{Co}_{\text{ads}}$ , from the Pt surface.

In a related study, Wang and co-workers investigated the ORR at PdNPs supported on  $\text{TiO}_2$  monosheets with and without oxygen vacancies present.<sup>12</sup> The results showed that in the presence of oxygen vacancies, there was a small improvement in the onset potential for the ORR compared to commercially available carbon-supported PtNP catalysts. Interestingly, PdNPs supported on  $\text{TiO}_2$  having oxygen vacancies were found to be significantly more active for the ORR than when the vacancies were absent. As in our  $\text{SnO}_x$  study,<sup>3</sup> the enhancement was attributed to charge transfer from oxygen vacancies present in  $\text{TiO}_2$  to PdNPs.

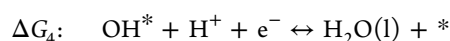
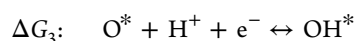
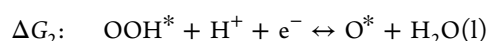
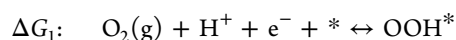
We began the present study by performing DFT calculations to identify possible synergy between AuNP catalysts and a rutile  $\text{TiO}_2(110)$  support. The calculations were carried out on isolated  $\text{Au}_{147}$  NPs, naked rutile  $\text{TiO}_2(110)$ , and an Au nanorod supported on  $\text{TiO}_2(110)$ . Reaction pathways were investigated by calculating the binding energy of reactants, products, and any intermediates. The predicted overpotential for the ORR was determined by the voltage required to make each elementary step exoergic. These calculations indicate that charge transfer between Au and  $\text{TiO}_2(110)$  influences the activity of the Au nanorod and lowers the ORR overpotential by  $\sim 100$  mV compared to unsupported AuNPs.

To evaluate the accuracy of the foregoing DFT calculations experimentally, we deposited  $\sim 2.8$  nm-thick  $\text{TiO}_x$  films ( $x = 1.9$  and  $2.0$ ), using atomic layer deposition (ALD), over pyrolyzed photoresist films (PPF).<sup>13</sup> Next, Au DENs composed of an average of 147 atoms ( $\text{Au}_{147}$ ) were immobilized onto this support. This construct (left side of Scheme 1) was evaluated for the ORR, and then the dendrimer was removed (right side of Scheme 1). As discussed earlier, this places the  $\text{Au}_{147}$  NPs into direct contact with the  $\text{TiO}_x$  support. In the latter case, a positive shift in the ORR onset potential of  $\sim 100$  mV is observed. Surface analysis by X-ray photoelectron spectroscopy (XPS) revealed the presence of increased electron density on the  $\text{Au}_{147}$  NPs when they are in direct contact with the  $\text{TiO}_x$  support. According to the DFT calculations, this accounts for the enhanced ORR activity.

## EXPERIMENTAL SECTION

**Computational Methods.** GGA-level, spin-polarized DFT calculations were performed with the Vienna ab initio simulation package (VASP) using a plane wave basis set with a cutoff energy of 400 eV. The Perdew–Wang (PW91) functional was used to describe electron exchange and correlation.<sup>14</sup> The DFT+U method was employed to treat localized Ti 3d orbitals with an effective U value of 4 eV, as reported in previous papers.<sup>15,16</sup> The Brillouin zone was sampled at the  $\gamma$  point, which was found to be sufficient given the large system size. The convergence criteria for electronic and geometric optimization were  $10^{-5}$  eV and 0.01 eV/Å, respectively.

Unsupported  $\text{Au}_{147}$  NPs were modeled as both icosahedral (Ih) and cuboctahedral (COh) structures. A  $\text{TiO}_2(110)$  slab and a Au nanorod supported on the  $\text{TiO}_2(110)$  slab ( $\text{TiO}_2(110)/\text{Au}$ ) were also modeled to determine if there are any synergistic effects between the Au nanocatalyst and the metal oxide support that might improve ORR activity. These atomic models are illustrated in Figure S1. The supported Au was modeled as a nanorod instead of an  $\text{Au}_{147}$  cluster to both capture the  $\text{TiO}_2(110)/\text{Au}$  interface and to minimize the computational cost. The  $\text{Au}_{147}$  NPs were isolated with a 10 Å vacuum gap in all directions, and all atoms were relaxed during the geometric optimization process. Both the  $\text{TiO}_2(110)$  and the  $\text{TiO}_2(110)/\text{Au}$  systems had a 20 Å vacuum gap in the  $z$ -direction; the bottom two  $\text{TiO}_2$  layers were fixed in their bulk positions. A surface Pourbaix diagram was calculated to identify the stable surface structures in the operating potential range of the ORR.<sup>17</sup> To calculate the ORR activity, the following four associative reaction steps were considered.



The ORR overpotential was found by a reaction energy diagram, drawn with the following eq 1.<sup>18</sup>

$$\Delta G(U) = \Delta E + \Delta \text{ZPE} - T\Delta S + neU \quad (1)$$

where  $\Delta E$  is the reaction energy,  $\Delta \text{ZPE}$  is the zero-point energy correction,  $\Delta S$  is the change in entropy,  $ne$  is the number of electrons, and  $U$  is the applied potential. The chemical potential of the solvated proton and electron pair ( $\text{H}^+ + \text{e}^-$ ) at standard conditions ( $p_{\text{H}_2} = 1$  bar,  $a_{\text{H}^+} = 1$ ,  $T = 298.15$  K) is calculated as  $0.5\mu_{\text{H}_2(\text{g})}^0 - eU$  by assuming equilibrium at the standard hydrogen electrode.<sup>19,20</sup> Solvation effects, modeled by surrounding the adsorbed species with water molecules, were included in the calculated reaction energy diagrams.<sup>21</sup>

**Chemicals and Materials.** The following chemicals were used as received: 1,1'-ferrocenedimethanol ( $\text{Fc}(\text{MeOH})_2$ , 98%, Acros Organics);  $\text{KNO}_3$  (99.994% trace metal basis, Alfa-Aesar);  $\text{AgNO}_3$  (99.85%, Acros Organics);  $\text{HClO}_4$  (+70%, ultrapure grade, J. T. Baker);  $\text{NaOH}$  (1 M, Fischer Scientific);  $\text{NaBH}_4$  (99.99% trace metals basis, Sigma-Aldrich); gold(III) chloride trihydrate (99.9% trace metals basis, Sigma-Aldrich); and tetrakis(dimethylamino)titanium(IV) (TDMAT, 99%, STREM Chemicals, Inc.). The following compressed gases were purchased from Praxair (Austin, TX): high-purity  $\text{N}_2$  (99.998%), high-purity  $\text{O}_2$  (99.995%), high-purity Ar (99.998%), and forming gas (5%  $\text{H}_2/95\%$   $\text{N}_2$ ).

Sixth-generation, amine-terminated, poly(amidoamine) dendrimers ( $\text{G6-NH}_2$ ) were purchased as a 9 wt % methanol solution from Dendritech, Inc. (Midland, MI). For the DENs synthesis, methanol was removed from the stock solution under vacuum and the dendrimers were reconstituted in water. UHPLC-grade water from Sigma-Aldrich was used to reconstitute the dendrimers, to synthesize DENs, and to prepare all aqueous solutions.

Fused quartz slides (GE 124, 3"  $\times$  1"  $\times$  1 mm) were purchased from Technical Glass Products, Inc. (Painesville

Twp, OH). Photoresist (AZ 1518) and photoresist developer (AZ 400 K, 1:4) were purchased from Integrated Micro Materials (Argyle, TX).

**Fabrication of Pyrolyzed Photoresist Film (PPF) Electrodes.** PPF electrodes were fabricated using a slightly modified version of a previously reported procedure.<sup>3</sup> Details can be found in the [Supporting Information](#).

**Deposition of TiO<sub>x</sub> (x = 1.9 and 2.0) Films on PPF Electrodes.** The metal oxide thin-films were deposited using a Savannah S100 Cambridge NanoTech ALD system (Ultratech, San Jose, CA). The titanium precursor, TDMAT, was heated to 75 °C, and the oxygen precursor (H<sub>2</sub>O) was maintained at room temperature (22–25 °C). The ultrathin TiO<sub>x</sub> films were deposited as follows. First, PPF electrodes were placed in the ALD chamber, which was then evacuated (<1 mmHg) and heated to 150 °C for 10 min under a constant N<sub>2</sub> flow (20 sccm). Second, the heated PPF electrodes were exposed to ten 0.015 s pulses of O<sub>3</sub>; each O<sub>3</sub> pulse was followed with a 20 s purge with N<sub>2</sub>. The purpose of this step was to introduce oxygen functionalities onto the PPF surface, thereby encouraging ALD. Third, an ALD cycle was carried as follows: (1) 0.10 s pulse of TDMAT; (2) 20.0 s purge with N<sub>2</sub>; (3) 0.015 s pulse of H<sub>2</sub>O; and (4) 20.0 s purge with N<sub>2</sub>. These four steps were repeated until the desired number of cycles were completed. This procedure results in formation of TiO<sub>x</sub> films having a Ti/O ratio of 1.0:1.9 (TiO<sub>1.9</sub>). To obtain stoichiometric TiO<sub>2.0</sub>, the as-deposited films were further oxidized by heating in a tube furnace at 200 °C for 2 h under a constant flow of O<sub>2</sub> (60 sccm).

**Synthesis of Au DENs.** G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs were synthesized using a previously published procedure.<sup>3</sup> Specifically, 10.0 mL of 2.0 μM G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs was prepared as follows. First, 200 μL of 100 μM of an aqueous G6-NH<sub>2</sub> dendrimer solution was added to 8.65 mL of vigorously stirred UHPLC water. Second, 147 μL of 20.0 mM HAuCl<sub>4</sub> was pipetted dropwise into the diluted dendrimer solution. Third, within 2 min after adding the first drop of the HAuCl<sub>4</sub> solution, a ~67-fold molar excess of NaBH<sub>4</sub> (in 1.0 mL of 0.30 M NaOH) was added. Fourth, the reaction mixture was stirred overnight in air to deactivate excess NaBH<sub>4</sub>. This synthesis has previously been shown to produce one AuNP (1.7 ± 0.2 nm) per dendrimer.<sup>22</sup>

Prior to immobilization of the G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs onto the PPF/TiO<sub>x</sub> supports, the pH of the G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs solution was adjusted to ~3.2 using 1 M HClO<sub>4</sub>. This did not change the size distribution of the AuNPs ([Figure S2](#)). The G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs were immobilized by immersing the PPF/TiO<sub>x</sub> supports in the G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs solution for 90 min. After immobilization, the modified supports (PPF/TiO<sub>x</sub>/G6-NH<sub>2</sub>(Au<sub>147</sub>)) were rinsed with a gentle flow of UHPLC water, dried under a flow of Ar, and then dried in air for at least 1 h prior to the use.

**UV/O<sub>3</sub> Method for Decomposition of G6-NH<sub>2</sub> Dendrimers.** The procedure for decomposing the dendrimers using UV/O<sub>3</sub> has been previously reported.<sup>3</sup> The resulting PPF/TiO<sub>x</sub>/Au<sub>147</sub> modified supports were left to equilibrate with the ambient lab atmosphere for at least 45 min before use.

**Structural Characterization.** XPS measurements were performed using a Kratos Axis Ultra DLD spectrometer (Chestnut Ridge, NY). Samples were mounted on Cu tape and grounded with carbon tape. Spectra were collected using an Al Kα source, 0.10 eV step size, and 20 eV band-pass energy. Charge neutralization was used during collection of each

spectrum. CasaXPS (version 2.3.19, Casa Software, Teignmouth, UK) was used for peak fitting and quantitative data analysis. Binding energies (BEs) were calibrated using the C 1s line of PPF (284.50 eV).<sup>23,24</sup> Symmetric line shapes were fitted using a mixed Gaussian/Lorentzian model, while asymmetric line shapes were fitted using an asymmetric Lorentzian model. The concentration of oxygen vacancies in the TiO<sub>x</sub> films were calculated using the ratio of atomic concentrations of O 1s and Ti 2p signals. Specifically, the O 1s signal was deconvoluted to obtain the fraction of oxygen bound to Ti, while the Ti 2p signal was used without additional processing. More details are provided in the [Supporting Information](#).

Ellipsometric thickness measurements were performed using a J. A. Woollam M-2000D spectroscopic ellipsometer (Lincoln, NE). Data were collected between 45° and 65° with 5° increments and a 10 s dwell time at each step. A three-layer model was used for data analysis: the first layer was 1.0 nm of SiO<sub>2</sub>, the second layer was 500 nm of PPF, and the third layer was amorphous TiO<sub>x</sub> films of varying thickness. The optical constants for the materials were either provided by the manufacturer (SiO<sub>2</sub>),<sup>25</sup> determined experimentally (PPF), or found in literature (TiO<sub>2</sub>).<sup>26</sup>

The topography of the PPF/TiO<sub>x</sub> thin films was determined using a Wyko NT9100 optical profilometer having a white light source and 0.1 nm vertical resolution. The data were collected using 20.0× magnification over an area of 237 μm × 316 μm.

The crystallinity of the PPF/TiO<sub>x</sub> thin films was studied using X-ray diffraction. For these measurements, the incident beam was scanned at 2°/min with a 0.05° step size and a 2.5° Soller slit.

Transmission electron microscope (TEM) images were collected using a JEOL-2010F TEM having a point-to-point resolution of 0.2 nm. A 2.0 μL portion of the G6-NH<sub>2</sub>(Au<sub>147</sub>) solution was pipetted onto a carbon-mesh-over-Cu TEM grid (Electron Microscopy Sciences, Hatfield, PA). The samples were left to dry in the laboratory ambient air for at least 5 h prior to analysis.

Scanning electron microscope (SEM) images were collected using a FEI Quanta 650 microscope with an accelerating voltage of 15 kV and a spot size of 3.0.

**Electrochemical Characterization.** A CHI 700D bipotentiostat and an Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode were used for all electrochemical measurements (CH Instruments Inc., Austin, TX). A Pt wire counter electrode was used for experiments in the flow cell and a glassy carbon rod counter electrode (Alfa Aesar, Tewksbury, MA) was used for all other electrochemical measurements. All potentials were converted to the standard hydrogen electrode to simplify comparison of experimental data and theoretical calculations.

The nonflow cyclic voltammetry experiments were performed in a Teflon electrochemical cell. The geometric area of the working electrode (12.4 mm<sup>2</sup>) was defined by a Viton O-ring. The extent of passivation and the stability of the PPF/TiO<sub>x</sub> supports were determined using a 1.0 mM Fc(MeOH)<sub>2</sub> redox probe in 0.10 M KNO<sub>3</sub>. For these experiments, the electrode potential was scanned between 0.14 and 0.83 V at 0.010 V/s.

Prior to ORR experiments, the PPF/TiO<sub>x</sub>/G6-NH<sub>2</sub>(Au<sub>147</sub>) or PPF/TiO<sub>x</sub>/Au<sub>147</sub> modified supports were electrochemically cleaned in an Ar-saturated, 0.10 M HClO<sub>4</sub> solution. During cleaning, the electrode potential was scanned ten times between 0.44 and 1.51 V at 0.050 V/s. Following electro-



chemical cleaning, ORR measurements were performed in an  $O_2$ -saturated, 0.10 M  $HClO_4$  solution. For these experiments, the electrode potential was scanned between 0.64 and  $-0.29$  V at 0.050 V/s. For the nonflow electrocatalytic measurements a glassy carbon rod counter electrode was used to avoid Pt contamination of the working electrode surface.

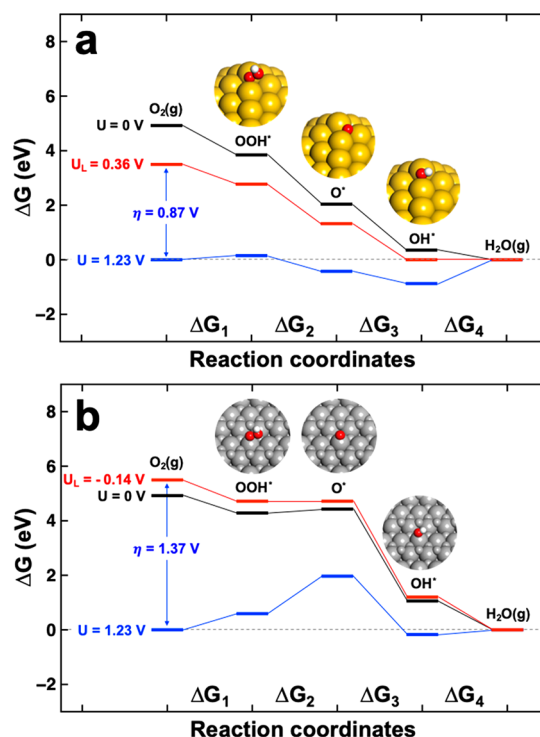
The kinetic measurements and the product-distribution experiments were performed using a flow cell and linear sweep voltammetry. The design and the characteristics of the flow cell have been previously reported.<sup>2</sup> Briefly, the flow cell has the following dimensions. The gap between the generator electrode (GE) and the collector electrode (CE) ranges from 10.1 to 11.5 mm, depending on the length of the quartz substrate on which the GE is patterned. The GE and CE lengths are 100  $\mu m$  and 7.6 mm, respectively, and the channel width is 500  $\mu m$ . For each surface modification, the electrocatalytic measurements were performed at volumetric flow rates of 10, 15, 20, 25, and 30  $\mu L/min$ . The system was allowed to equilibrate between each flow rate change for 10 min.

## RESULTS AND DISCUSSION

**Theoretical ORR Activity on  $Au_{147}$ .** Before discussing the  $TiO_2(110)/Au$  integrated system, we first consider the isolated  $Au_{147}$  NPs and the rutile  $TiO_2(110)$  surface to identify the ORR activity of each of the individual components. For the  $Au_{147}$  NPs, Ih and COh structures were considered, which are known to be stable for NPs having sizes on the order of 1–2 nm. Calculations of the relative energy of these two structures indicate that Ih is more stable than COh by 2.90 eV, which is in agreement with our previous combined theoretical and experimental EXAFS study of  $Au_{147}$  NPs.<sup>27</sup> Accordingly, the binding energies of the ORR intermediates ( $O^*$ ,  $OH^*$ , and  $OOH^*$ ) were calculated for the  $Au_{147}$  Ih NPs to determine the reaction energy profiles shown in Figure 1a.

For isolated  $Au_{147}$  Ih NPs, the ORR reaction intermediates are stabilized at the edge of the NP and not on the (111) facets. Figure 1a shows the most stable binding sites for each intermediate. For the ORR rate-determining step,  $\Delta G_4$ , the edge sites have an overpotential of  $\eta = 0.87$  V. This means a strong  $OH^*$  binding energy inhibits formation of  $H_2O$ . Following a review of ORR catalysts, we can construct a volcano plot with  $\Delta G_4$  and  $\Delta G_1$  using the  $OH^*$  binding energy as the descriptor.<sup>28,29</sup> On this volcano plot, Pt is positioned on the left side of the peak, indicating that a strong  $OH^*$  binding energy on Pt limits its ORR activity.<sup>28</sup> Specific to our case,  $Au_{147}$  Ih NP has a stronger  $OH^*$  binding energy than Pt by 0.47 eV, and therefore, it is necessary to reduce the  $OH^*$  binding energy to increase the ORR activity. The COh structure was also considered for the ORR, and an even higher overpotential (Figure S3,  $\eta = 1.06$  V,) was found compared to that of  $Au_{147}$  Ih ( $\eta = 0.87$  V). In summary, the Ih structure is both more stable and has a higher predicted activity than COh; we therefore use the Ih structure for subsequent modeling.

**ORR Activity on  $TiO_2(110)$ .** Calculations similar to those performed for the  $Au_{147}$  NPs were carried out for a rutile  $TiO_2(110)$  slab, and we found that the ORR intermediates bind strongly on the Ti atoms. Indeed, as shown in Figure 1b, rutile  $TiO_2(110)$  exhibits low ORR activity and a high overpotential:  $\eta = 1.37$  V, which is higher than that of isolated  $Au_{147}$  NPs. Specifically, a weak  $O^*$  binding energy results in  $\Delta G_2$  becoming rate determining for the ORR on the rutile  $TiO_2(110)$  slab. We conclude that the ORR is not likely to



**Figure 1.** Gibbs free energy diagrams for the ORR pathway and overpotential ( $\eta$ ) for (a)  $Au_{147}$  Ih NP and (b) rutile  $TiO_2(110)$ .  $\eta = 1.23 - U_L$  (limiting potential ( $U_L$ )).

proceed on  $TiO_2$  within the experimentally relevant potential window.

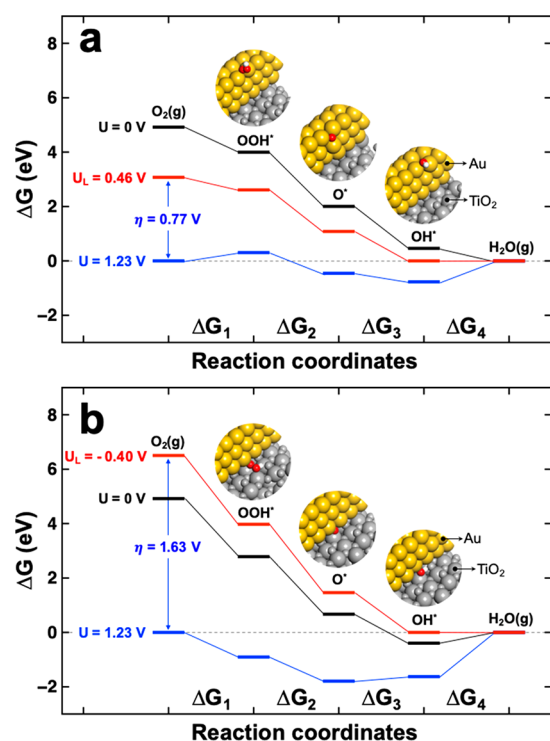
**Surface Pourbaix Diagram of  $TiO_2(110)/Au$ .** Under actual ORR operating conditions there are additional factors affecting the electrocatalytic activity of the  $TiO_2(110)/Au$  system including the applied potential and concentration of  $O_2$ . Accordingly, we calculated the surface Pourbaix diagram for this system to determine the most energetically favorable surface configuration for ORR activity. Specifically, oxygen coverages from 30% (with a structure labeled as 3O) to 90% (9O) and oxygen vacancy concentrations from 1 to 3 ( $1O_{vac}$ ,  $2O_{vac}$ , and  $3O_{vac}$  respectively), were considered. Each of these surface configurations (as shown in Figure S4) are stable within specific potential windows. In the case of oxygen vacancies, the  $3O_{vac}$  structure is stable at potentials lower than  $-0.24$  V and  $2O_{vac}$  is stable in a potential range of  $-0.24$  to  $-0.04$  V. In contrast, the stoichiometric  $TiO_2(110)/Au$  surface is stable in a lower potential range ( $-0.17$  to  $0.33$  V). In the case of oxygen surface coverage, the 4O structure is stable in an intermediate potential range ( $0.33$  to  $0.83$  V) and the 7O structure is stable at potentials above  $0.83$  V. Accordingly, we conclude that the stoichiometric  $TiO_2(110)/Au$  surface is the most stable configuration under the experimental ORR conditions.

As we discuss later, the ORR will commence at  $\sim 0.01$  V on the PPF/ $TiO_x$ /G6-NH $_2$ ( $Au_{147}$ ) modified supports. As shown in Figure S4, the most stable configuration at the potentials used in the experimental portion of this study is the stoichiometric  $TiO_2(110)/Au$  surface. Nevertheless, later in the discussion we also consider the effect the oxygen vacancies on the ORR activity.

**ORR Activity on Stoichiometric  $TiO_2(110)/Au$ .** In the previous section, we showed that stoichiometric  $TiO_2(110)/$

Au is stable under ORR operating conditions. We now focus on how the ORR activity changes when a Au nanorod is supported on the  $\text{TiO}_2(110)$  surface. To elucidate possible synergistic effects of the supported  $\text{TiO}_2(110)/\text{Au}$  system, two reaction sites are considered: (1) on top of the Au nanorod (top site) and (2) an interface site between the Au nanorod and the  $\text{TiO}_2(110)$  support.

Figure 2 shows Gibbs free energy diagrams for the ORR pathway and overpotential ( $\eta$ ) for  $\text{TiO}_2(110)/\text{Au}$  at the two different reaction sites.



**Figure 2.** Gibbs free energy diagrams for the ORR pathway and overpotential ( $\eta$ ) for  $\text{TiO}_2(110)/\text{Au}$  at different reaction sites (a) on the Au nanorod and (b) at the interface between Au and  $\text{TiO}_2$ .

Specifically, Figure 2a applies to the top site and Figure 2b to the interface site. For the top site, all ORR intermediates were adsorbed onto the top edge of the Au nanorod, which has a similar binding site to that of the  $\text{Au}_{147}$  1h NP. Our calculations show that the binding energies are similar to those on the  $\text{Au}_{147}$  1h NPs, with the  $\text{OH}^*$  binding energy being slightly weaker. For the interface site, all ORR intermediates bind between a Au atom in the bottom layer of the nanorod and a Ti atom with five neighboring oxygen atoms on the top layer of the  $\text{TiO}_2$  slab. The binding geometries are illustrated in Figure 2.

Our findings reveal that in the unsupported NP core, the Au atoms are slightly oxidized (average charge of  $-0.05 \text{ e}^-$ ), but they become more reduced (to  $+0.03 \text{ e}^-$ ) at the NP surface. The supported Au nanorod, however, exhibits a more complicated behavior. In this case, the first layer of the Au nanorod (closest to the  $\text{TiO}_2(110)$  surface) has, on average, fewer electrons ( $-0.07 \text{ e}^-$ ) than the unsupported Au nanorod. The other Au layers did not show a significant change. Looking more closely, however, the charge state of individual Au atoms on the  $\text{TiO}_2$  surface vary significantly depending on their position. Specifically, Au atoms atop surface oxygens are

significantly oxidized ( $-0.20 \text{ e}^-$ ), but Au atoms atop Ti are reduced ( $+0.10 \text{ e}^-$ ).

When  $\text{OH}^*$  binds at a Au top site of a nanorod, those Au atoms are slightly oxidized ( $-0.022$  and  $-0.008 \text{ e}^-$ ). Thus, a weaker binding energy of  $\text{OH}^*$  on the nanorod is due to a locally oxidized charge state compared to the unsupported  $\text{Au}_{147}$  1h NP. The important point is that this weak  $\text{OH}^*$  binding energy reduces the overpotential ( $\eta = 0.77 \text{ V}$ ) by  $\sim 100 \text{ mV}$  compared to the unsupported  $\text{Au}_{147}$  1h NP. In the case of the interface sites at the boundary between the Au nanorod and the  $\text{TiO}_2(110)$  slab, however, the intermediate binding energies are too strong (Figure 2), and this site, therefore, exhibits a high overpotential ( $\eta = 1.63 \text{ V}$ ).

The key point is that the top of the Au nanorod is predicted to have higher catalytic activity than the interface between  $\text{TiO}_2$  and Au due to charge transfer in the  $\text{TiO}_2(110)/\text{Au}$  supported catalyst system.

**ORR Activity on  $\text{TiO}_2(110)/\text{Au}$  with Oxygen Vacancies.** The  $\text{TiO}_2(110)/\text{Au}$  surface Pourbaix diagram (Figure S4) reveals that the presence of oxygen vacancies is unfavorable within rutile  $\text{TiO}_2$  at experimentally relevant potentials. The experimentally synthesized amorphous  $\text{TiO}_2$  thin-films are, however, more likely to have oxygen vacancies than the perfect rutile  $\text{TiO}_2$  modeled in our simulation cell.<sup>30</sup> Furthermore, as we show later in the experimental part of the discussion, we synthesized amorphous  $\text{TiO}_x$  thin-films (Figure S5) having two distinct oxidation states:  $x = 1.9$  and  $2.0$ . Thus, we also considered the ORR activity of the  $\text{TiO}_2(110)/\text{Au}$  system having different number of oxygen vacancies (structures labeled as  $1\text{O}_{\text{vac}}$ ,  $2\text{O}_{\text{vac}}$ , and  $3\text{O}_{\text{vac}}$ ).

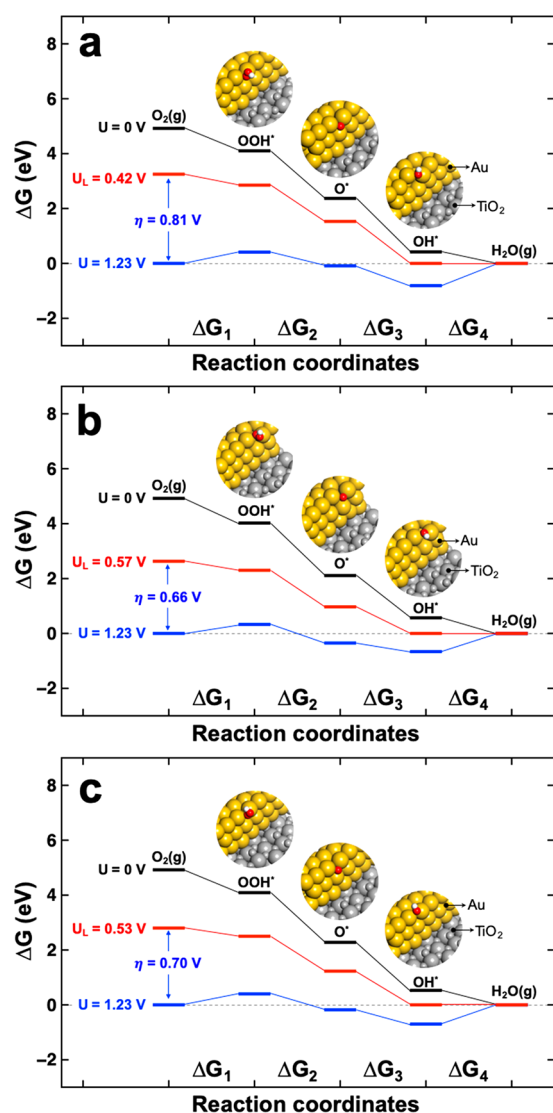
The top site (Figure 3) consistently exhibits higher ORR activity than the interface sites (Figure S6), regardless of the number of oxygen vacancies.

Specifically, the energy profiles in Figure 3 show that  $\text{TiO}_2(110)/\text{Au}$ , having  $1\text{O}_{\text{vac}}$ ,  $2\text{O}_{\text{vac}}$ , and  $3\text{O}_{\text{vac}}$  exhibit an enhanced ORR activity of  $\sim 60 \text{ mV}$ ,  $\sim 210 \text{ mV}$ , and  $\sim 170 \text{ mV}$ , respectively. Each of these surface configurations show similar energy profiles and the same limiting potential step ( $\Delta G_4$ ). This means the  $\text{OH}^*$  binding energy remains a key descriptor of the ORR activity. Strong  $\text{OH}^*$  binding energies remain problematic in the  $\text{TiO}_2(110)/\text{Au}$  system with oxygen vacancies, but they are weaker than that for the stoichiometric  $\text{TiO}_2(110)/\text{Au}$  system.

We performed a Bader charge analysis for the  $1\text{O}_{\text{vac}}$ ,  $2\text{O}_{\text{vac}}$ , and  $3\text{O}_{\text{vac}}$  structures to determine how electron transfer changes with the number of oxygen vacancies.<sup>31–34</sup> Both surface Ti and Au atoms (as shown in Figure S7) systematically obtain more electrons from oxygen vacancies. Even though surface Ti atoms become reduced with one or two oxygen vacancies, the Au nanorod remains in an oxidized charge state. Finally, Ti and Au atoms became reduced when  $3\text{O}_{\text{vac}}$  are present at the surface of  $\text{TiO}_2(110)$ . A similar trend was observed in our XPS results, as discussed later.

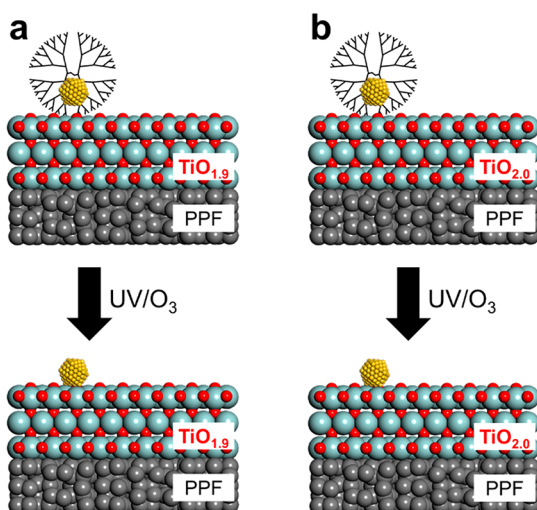
**Properties of  $\text{TiO}_x$  ( $x = 1.9$  and  $2.0$ ) Film.** We now turn our attention to experimental verification of the foregoing theoretical predictions. As discussed in the Introduction, the experimental model consists of PPF carbon electrodes coated with thin layers of  $\text{TiO}_{1.9}$  or  $\text{TiO}_{2.0}$  by ALD (Scheme 2, details provided in the Experimental Section and Supporting Information).

For the purposes of our electrocatalysis experiments, the thickness, uniformity, and stability of the  $\text{TiO}_x$  films are critical, and therefore, we address these points first.



**Figure 3.** Gibbs free energy diagrams for  $\text{TiO}_2(110)/\text{Au}$  at Au top sites with different number of oxygen vacancies: (a)  $1\text{O}_{\text{vac}}$ , (b)  $2\text{O}_{\text{vac}}$ , and (c)  $3\text{O}_{\text{vac}}$ .

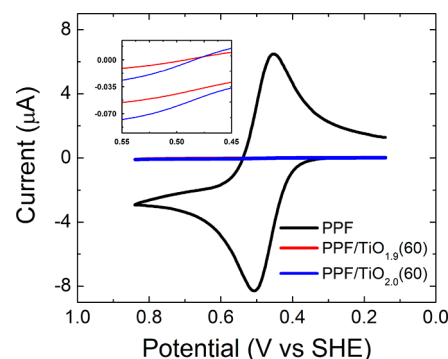
**Scheme 2**



Ellipsometry was used to measure the  $\text{TiO}_x$  film thickness as a function of the number of ALD cycles performed. The resulting calibration curve (Figure S8) reveals a linear growth rate of  $0.059 \pm 0.002$  nm/cycle with a nucleation delay of 12 ALD cycles. The nucleation delay is a well-known phenomenon in ALD in which several cycles are required before a detectable change in film thickness is observed.<sup>35</sup> Indeed, we have observed this behavior in our previous ALD-related studies.<sup>1–3</sup>

For electrocatalysis studies of the type described here, the optimal  $\text{TiO}_x$  thickness balances uniformity (no detectable pinholes) with sufficient thinness that electron transfer (eT) from PPF to the oxide-supported AuNPs is not inhibited.<sup>36–39</sup> As discussed next, we found this thickness to be  $\sim 2.8$  nm (equivalent to 60 ALD cycles).

Figure 4 shows cyclic voltammograms (CVs) comparing eT between PPF,  $\text{PPF}/\text{TiO}_{1.9}(60)$ , and  $\text{PPF}/\text{TiO}_{2.0}(60)$  working electrodes (the number in parentheses indicates the number of ALD cycles).



**Figure 4.** CVs obtained using the electrode configurations shown in the legend. The inset shows an expanded view of the voltage range over which the voltammetric peaks, if present, would be expected. The solutions contained aqueous 1.0 mM  $\text{Fc}(\text{MeOH})_2$  in 0.10 M  $\text{KNO}_3$  and the scan rate was 0.010 V/s. The geometric area of each electrode was 12.4  $\text{mm}^2$ . The experiments were carried out in triplicate for each surface modification.

Each CV was obtained using an aqueous solution containing 1.0 mM  $\text{Fc}(\text{MeOH})_2$  and 0.10 M  $\text{KNO}_3$ . The CV obtained using the naked PPF electrode (black) reveals well-defined oxidation and reduction peaks at 0.51 and 0.45 V, respectively. When the PPF electrode is coated with a  $\sim 2.8$  nm-thick  $\text{TiO}_{1.9}$  layer (red), however, eT is hindered and these peaks are absent. The result is the same for the  $\sim 2.8$  nm-thick  $\text{TiO}_{2.0}$ -modified PPF electrode (blue, note that the blue and red lines overlap in Figure 4). These results demonstrate that the  $\text{TiO}_x$  film, regardless of its oxidation state, passivates the PPF electrode against a common molecular redox molecule.

To further confirm the absence of pinholes that might be too small or two few to be revealed by the foregoing experiment, we used a previously reported electrodeposition method.<sup>1,40</sup> In this experiment, we attempted to electrodeposit Ag onto the  $\text{PPF}/\text{TiO}_x$  supports. If Ag islands are observed on the surface upon subsequent examination by SEM, then the location of a latent pinhole is revealed. Electrodeposition was performed by chronoamperometry in an aqueous solution containing 0.50 mM  $\text{AgNO}_3$  and 0.10 M  $\text{KNO}_3$ . The images shown in Figure S9a,b were obtained using  $\sim 2.6$  and  $\sim 2.8$  nm-thick  $\text{TiO}_{1.9}$ -modified PPF electrodes, respectively. The results show that



Ag islands (e.g., pinholes) are clearly present in the  $\sim 2.6$  nm-thick film, but they are absent in the  $\sim 2.8$  nm-thick  $\text{TiO}_{1.9}$  film. The same results is obtained for  $\text{TiO}_{2.0}$ -modified PPF electrodes (Figure S9c,d). We conclude that the  $\sim 2.8$  nm-thick  $\text{TiO}_x$  films (60 ALD cycles) are sufficiently free of pinholes to carry out the electrocatalysis experiments described later.

The stability of  $\sim 2.8$  nm-thick  $\text{TiO}_x$  films was tested under the same set of conditions used for the electrocatalysis described later. Specifically, a single PPF/ $\text{TiO}_x(60)$  support was sequentially subjected to the following conditions: immersion in a  $\sim \text{pH } 3.0$   $\text{HClO}_4$  solution for 90 min, exposure to the same  $\text{UV/O}_3$  process that is used during dendrimer removal, and then the same series of CV scans used for the ORR study. The latter included ten electrochemical cleaning scans and three ORR scans in  $0.10 \text{ M HClO}_4$  solution. The stability of the electrodes was gauged by determining their CV response to a solution containing  $1.0 \text{ mM Fc(MeOH)}_2$  and  $0.10 \text{ M KNO}_3$  (Figure S10a). The results show just a very slight increase in current for the treated electrode. Figure S10b shows analogous data for a PPF/ $\text{TiO}_{2.0}(60)$  electrode, and the results are the same: very little change in current. We conclude that the stability of the  $\sim 2.8$  nm-thick  $\text{TiO}_x$  films under electrocatalytic conditions is sufficient for subsequent electrocatalysis studies.

Optical profilometry was used to study the topography of  $\sim 2.8$  nm-thick  $\text{TiO}_x$ -modified PPF electrodes. These profilometry measurements were collected in phase-shifting mode and have a height resolution of  $0.1 \text{ nm}$ . Figure S11 shows representative topographic images over a  $237 \mu\text{m} \times 316 \mu\text{m}$  area. The average rms roughnesses of three independently prepared  $\text{TiO}_{1.9}$  and  $\text{TiO}_{2.0}$  films were  $0.67 \pm 0.06 \text{ nm}$  and  $0.60 \pm 0.06 \text{ nm}$ , respectively. These rms roughness values are in accord with other reports<sup>41–43</sup> as well as our own previous studies of  $\text{Al}_2\text{O}_3$  and  $\text{SnO}_x$  films having similar thicknesses.<sup>1,3</sup>

The foregoing discussion demonstrates that  $\text{TiO}_x$  films deposited onto PPF electrodes have well-defined thicknesses, good topographical uniformity, and sufficient stability for electrocatalysis experiments.

**Decomposition of G6-NH<sub>2</sub> Dendrimers.** An important aspect of our approach (Scheme 1) is that the electrocatalytic properties of NPs can be evaluated in the absence or presence of support effects. However, this requires effective removal of the dendrimer. In a previous study, XPS showed that most of the organic dendrimer framework can be removed from G6-NH<sub>2</sub>(Au<sub>147</sub>) DENs immobilized onto  $\text{SnO}_x$  films using  $\text{UV/O}_3$ .<sup>3</sup> In the present work, we applied this same methodology to DENs immobilized onto  $\text{TiO}_x$  films.

Figure S12a shows a high-resolution XPS spectrum in the N 1s region for a PPF/ $\text{TiO}_{1.9}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) modified support before  $\text{UV/O}_3$  treatment. Nitrogen is a marker for the G6-NH<sub>2</sub> dendrimers, and the observed signal can be deconvoluted into three individual peaks corresponding to the dendrimeric amine, amide, and protonated amine functionalities.<sup>44</sup> Figure S12b is an XPS spectrum for the same support after  $\text{UV/O}_3$  treatment, and it reveals an  $89 \pm 1\%$  decrease in the N 1s signal. We conclude that all but  $\sim 10\%$  of the dendrimer is removed and therefore the AuNPs reside on the  $\text{TiO}_{1.9}$  surface after  $\text{UV/O}_3$  treatment. Figure S12c,d provides analogous data for the PPF/ $\text{TiO}_{2.0}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) surface. In this case,  $78 \pm 4\%$  of the dendrimeric N is removed. Both values are in good agreement with our previous findings for dendrimer removal from  $\text{SnO}_x$ .<sup>3</sup>

**Effect of  $\text{UV/O}_3$  Treatment on the Oxidation States of  $\text{TiO}_x$  ( $x = 1.9$  and  $2.0$ ) Films.** According to the DFT calculations discussed earlier, oxygen vacancies (e.g., the oxidation state of  $\text{TiO}_x$ ) play a crucial role in controlling the ORR activity of supported AuNPs. Because it is known that  $\text{UV/O}_3$  can change the oxidation state of metal oxides,<sup>3,45</sup> we sought to determine the effect that the process of dendrimer removal exerts on the underlying oxide.

Figures S13 and S14 and Tables S1 and S2 summarize an XPS study of PPF/ $\text{TiO}_x$  electrodes before and after  $\text{UV/O}_3$  exposure. It consists of a quantitative analysis of the Ti 2p and O 1s signals arising from the as-prepared PPF/ $\text{TiO}_{1.9}(60)$  film before and after  $\text{UV/O}_3$  treatment. The results indicate that the Ti 2p/O 1s ratio remains at 1.9 even after exposure to  $\text{UV/O}_3$ . The same result is obtained for the PPF/ $\text{TiO}_{2.0}(60)$  film both before and after  $\text{UV/O}_3$ : the Ti 2p/O 1s ratio is 2.0 (Figure S14). We conclude, therefore, that the procedure used for decomposing the dendrimers does not measurably affect the oxidation state of the  $\text{TiO}_x$  films.

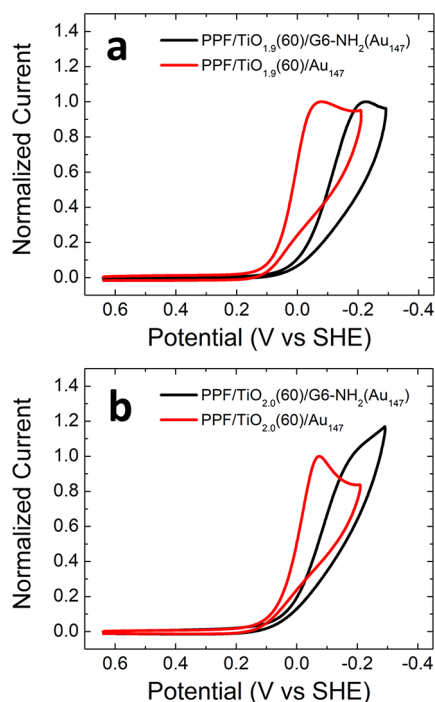
We want to emphasize that although the experimentally determined stoichiometric Ti 2p/O 1s ratio after oxidation of the as-prepared  $\text{TiO}_{1.9}$  films is 2.0, this value might be an overestimate due to the sensitivity limitation of XPS.<sup>23</sup> This means it is probably more appropriate to think of the  $\text{TiO}_{1.9}$  and  $\text{TiO}_{2.0}$  films as supports that have higher ( $\text{TiO}_{1.9}$ ) and lower ( $\text{TiO}_{2.0}$ ) concentration of oxygen vacancies.

**Evaluation of ORR Onset Potential in the Absence and Presence of Interactions between AuNPs and  $\text{TiO}_x$  ( $x = 1.9$  and  $2.0$ ) Supports.** We now turn our attention to electrocatalytic results obtained using CV. These experiments were performed in an aqueous solution containing  $\text{O}_2$ -saturated,  $0.10 \text{ M HClO}_4$ . A glassy carbon rod counter electrode was used for these measurements to avoid Pt contamination of the electrocatalysts.

Figure 5a presents ORR CVs obtained using PPF/ $\text{TiO}_{1.9}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) electrodes before (black) and after (red) removal of the dendrimer.

The results show that the onset of ORR activity, defined as the potential at which 10% of maximum ORR current is observed, occurs at  $0.01 \pm 0.01 \text{ V}$  and  $0.11 \pm 0.01 \text{ V}$  on PPF/ $\text{TiO}_{1.9}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) and PPF/ $\text{TiO}_{1.9}(60)$ /Au<sub>147</sub> supports, respectively. This means there is a positive shift of  $100 \pm 10 \text{ mV}$  in the ORR onset potential when the AuNPs are in direct contact with a  $\sim 2.8$  nm-thick  $\text{TiO}_{1.9}$  film compared to when they are fully encapsulated within the dendrimer. Clearly, there is a favorable interaction between the AuNPs when they are in contact with underlying  $\text{TiO}_{1.9}$  support. Figure 5b provides analogous results for the PPF/ $\text{TiO}_{2.0}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>)-coated electrode. In this case, the positive shift is smaller,  $50 \pm 10 \text{ mV}$ , but it is still unambiguous.

Importantly, the experimentally observed  $\sim 100 \text{ mV}$  (higher  $\text{O}_{\text{vac}}$  concentration,  $\text{TiO}_{1.9}$ ) and  $\sim 50 \text{ mV}$  (lower  $\text{O}_{\text{vac}}$  concentration,  $\text{TiO}_{2.0}$ ) shifts when the AuNPs are in direct with the  $\text{TiO}_x$  supports are in good agreement with DFT calculations. Recall that the corresponding DFT-predicted shifts were  $\sim 170 \text{ mV}$  and  $\sim 60 \text{ mV}$  for  $\text{TiO}_2(110)/\text{Au}$  having  $3\text{O}_{\text{vac}}$  and  $1\text{O}_{\text{vac}}$ , respectively. The deviation between the experimental and theoretical results at higher oxygen vacancies concentration ( $100$  vs  $170 \text{ mV}$ , respectively) may originate from differences between the simulation cell and the experimental model. Nevertheless, both experimental and theoretical results result in a higher degree of ORR activity when the  $\text{TiO}_x$  and AuNPs are in intimate contact. This



**Figure 5.** CVs obtained for the ORR using electrode with (a)  $\text{TiO}_{1.9}$  and (b)  $\text{TiO}_{2.0}$  ALD surfaces. The specific electrode modifications are given in the legends. The solutions contained aqueous,  $\text{O}_2$ -saturated 0.10 M  $\text{HClO}_4$ . A glassy carbon rod counter electrode was used to avoid contamination of the electrode surface. The scan rate was 0.050 V/s. The geometric area of each electrode was 12.4 mm<sup>2</sup>. The electrodes were electrochemically cleaned prior to each ORR experiment. The onset potential was defined as that potential corresponding to 10% of the ORR peak current. The currents for each CV were normalized to the corresponding ORR peak current. The experiments were carried out in triplicate for each electrode configuration.

indicates that the magnitude of charge transfer from oxygen vacancies in  $\text{TiO}_x$  to AuNPs plays a crucial role in the increase of ORR activity. This conclusion is confirmed by XPS results discussed later.

We carried out a few key control experiments to further confirm our conclusions. For example, no ORR activity is observed on PPF/ $\text{TiO}_{1.9}$ (60) (Figure S15, blue trace) or PPF/ $\text{TiO}_{2.0}$ (60) (Figure S16, blue trace) supports when AuNPs are absent in the system. This observation is consistent with the previously discussed theoretical model that predicted a high ORR overpotential (Figure 1b,  $\eta = 1.37$  V) for the  $\text{TiO}_2$  film alone (no AuNPs). Note, however, that the  $\text{TiO}_x$  films are active for the hydrogen evolution reaction at potentials higher than  $-0.20$  V (Figures S15 and S16).<sup>46</sup> This activity affects the shape of ORR CVs on PPF/ $\text{TiO}_x$ /G6- $\text{NH}_2$ ( $\text{Au}_{147}$ ) at high negative potentials. Consequently, the ORR current does not decay monotonically after reaching diffusion-limited conditions.

We carried out a second control experiment in which the ORR was investigated in the absence and presence of contact between AuNPs and the PPF electrode (no  $\text{TiO}_x$ ). These experiments were carried out exactly as described earlier for the case when the  $\text{TiO}_x$  support was present. PPF is a carbon electrode that is not known to affect electrocatalytic activity of supported metal NPs, and therefore, we expected that the ORR onset potential would be the same before and after

dendrimer removal.<sup>47</sup> The results in Figure S17 and Table S3 confirm this hypothesis.

The key conclusion of the ORR CV experiments is that there are shifts of  $\sim 100$  mV and  $\sim 50$  mV toward lower potentials when AuNPs are in direct contact with  $\text{TiO}_{1.9}$  and  $\text{TiO}_{2.0}$  supports, respectively. The control experiments cited above clearly implicate direct contact between the AuNPs and  $\text{TiO}_x$  as the cause of this shift. Finally, the experimental results are in rather good agreement with the DFT predictions.

**Evaluation of ORR Pathway in Absence and Presence of Interactions between AuNPs and  $\text{TiO}_x$  ( $x = 1.9$  and 2.0) Support.** In addition to the CV results, we also determined the number of electrons ( $n_{\text{eff}}$ ) transferred during the ORR for each of the electrocatalysts. These experiments were carried out using a custom-designed flow cell that we have described previously.<sup>2</sup> The principal virtue of the reported flow cell is that the working electrode can be easily removed and subsequently replaced. This flexibility makes it possible to obtain microelectrochemical measurements on exactly the same electrode before and after dendrimer removal, and to quantitatively measure the presence of electroactive products ( $\text{H}_2\text{O}_2$  in this case). Additionally, the flow cell can operate in generation or generation/collection mode, wherein the operating principle is the same as in the case of a rotating ring disk electrode.<sup>48,49</sup>

The following electrocatalysis experiments were obtained using a flowing, aqueous solution of  $\text{O}_2$ -saturated, 0.10 M  $\text{HClO}_4$ . The GE was a PPF modified with the electrocatalyst, while the CE was a quartz slide coated with a  $\sim 100$  nm-thick Pt film. The potential of the GE was scanned from 0.85 to  $-0.36$  V, while the potential of the CE was held constant at 1.34 V to oxidize  $\text{H}_2\text{O}_2$  formed at the upstream GE.

Figure 6a is a Levich plot showing the relationship between the current observed at the GE ( $i_{\text{GE}}$ ) at  $-0.16$  V (mass transport-limited region) and the cube root of the flow rate (representative ORR linear sweep voltammograms are provided in the Supporting Information: Figure S18 ( $\text{TiO}_{1.9}$ ) and Figure S19 ( $\text{TiO}_{2.0}$ )).

The Levich equation predicts a linear relationship between  $i_{\text{GE}}$  and (flow rate)<sup>1/3</sup> if the L  v  que approximation holds in the system.<sup>50,51</sup> This linear relationship is borne out for all four electrode modifications considered herein: PPF/ $\text{TiO}_x$ (60)/G6- $\text{NH}_2$ ( $\text{Au}_{147}$ ) and PPF/ $\text{TiO}_x$ (60)/ $\text{Au}_{147}$  ( $x = 1.9$  and 2.0);

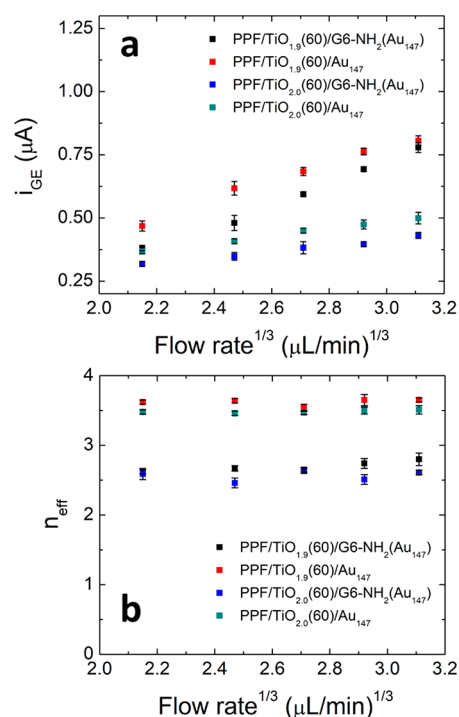
Next, we evaluated  $n_{\text{eff}}$  for each of the four electrode modifications using eq 2.<sup>52</sup>

$$n_{\text{eff}} = 4 \left( \frac{N i_{\text{GE}}}{N i_{\text{GE}} + i_{\text{CE}}} \right) \quad (2)$$

Here,  $N$  is collection coefficient ( $57 \pm 10\%$ )<sup>2</sup>, and  $i_{\text{ce}}$  is current at the CE. Figure 6b shows the relationship between  $n_{\text{eff}}$  and (flow rate)<sup>1/3</sup> with the GE potential set at  $-0.16$  V. For the PPF/ $\text{TiO}_x$ (60)/G6- $\text{NH}_2$ ( $\text{Au}_{147}$ ) electrode,  $n_{\text{eff}}$  is  $\sim 2.5$  (blue and black). This means that in the absence of direct interactions between AuNPs and  $\text{TiO}_x$  ( $x = 1.9$  and 2.0) supports, the ORR results primarily in  $\text{H}_2\text{O}_2$  as the product. In contrast, after removal of the dendrimer,  $n_{\text{eff}}$  is  $\sim 3.6$  and  $\sim 3.5$  on PPF/ $\text{TiO}_{1.9}$ (60)/ $\text{Au}_{147}$  (red) and PPF/ $\text{TiO}_{2.0}$ (60)/ $\text{Au}_{147}$  (green), respectively, indicating that in the presence of direct interactions between AuNPs and  $\text{TiO}_x$  supports,  $\text{H}_2\text{O}$  is the dominant product.

The key conclusion of this part of the study is that there are clear differences in the ORR pathway when AuNPs interact





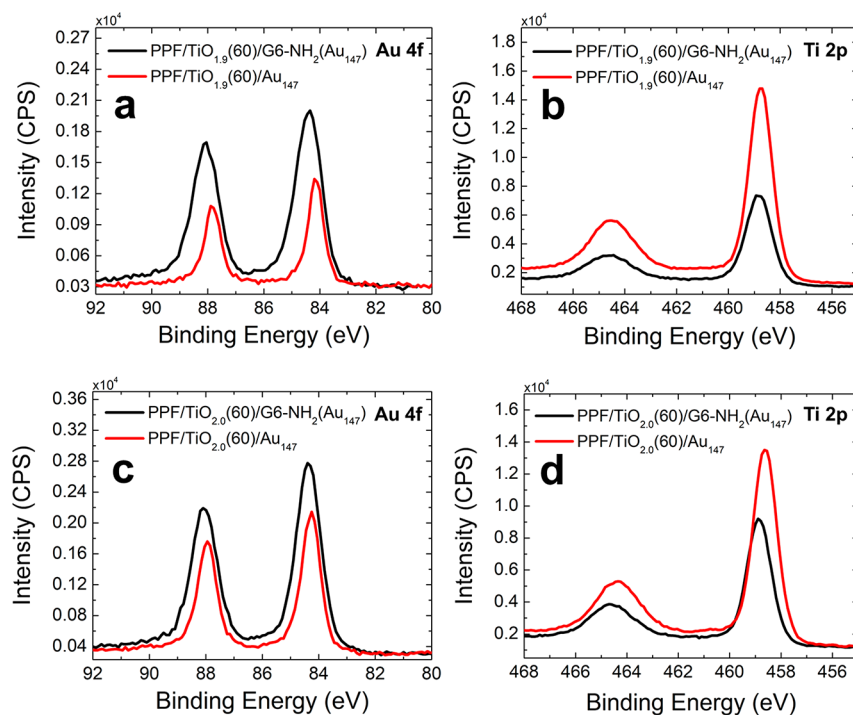
**Figure 6.** (a) Plot showing the relationship between  $i_{GE}$  and  $(\text{flow rate})^{1/3}$  for the GE compositions shown in the figure legend. (b) Plot showing the relationship between  $n_{eff}$  and  $(\text{flow rate})^{1/3}$  for the GE compositions shown in the legend. For both parts a and b, the GE was scanned from 0.85 to  $-0.36$  V at  $0.050$  V/s in  $O_2$ -saturated  $0.10$  M  $HClO_4$  and the Pt CE was held at  $1.35$  V. For each flow rate,  $i_{GE}$  and  $i_{CE}$  were extracted at  $-0.16$  V, which is in the mass transport-limited region. The error bars represent the standard deviation of the mean value for three independently prepared electrodes.

directly with the  $TiO_x$  films compared to the absence of such interactions. In other words, the  $TiO_x/Au$  interaction results in both a shift in the onset potential for the ORR and a shift in the product distribution. Additionally, the experiments represented in Figure 6 took  $\sim 3$  h to complete, indicating that the system is stable on this time scale.

**Electronic Interactions between  $TiO_x$  ( $x = 1.9$  and  $2.0$ ) Support and AuNPs.** DFT calculations presented earlier suggested that the enhanced ORR activity on  $TiO_x/Au$  electrocatalysts is observed due to partial charge transfer from the oxygen vacancies in  $TiO_x$  to the supported AuNPs. This in turn leads to a decrease in the  $OH^*$  binding energy on Au. We next aim to corroborate this theoretical hypothesis by investigating the electronic states of AuNPs and  $TiO_x$  films using experimental methods. Specifically, XPS was used to determine the BEs of Au 4f and Ti 2p before and after UV/ $O_3$  treatment of the PPF/ $TiO_x(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) supports. If the theoretical prediction is correct, and charge transfer occurs from the oxygen vacancies in  $TiO_x$  to the supported AuNPs (during direct contact), then we should observe a shift for Au toward lower BEs and a corresponding shift in the opposite direction for Ti.

The black traces in Figure 7a,b show the Au 4f and Ti 2p regions of PPF/ $TiO_{1.9}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>)-modified electrodes before UV/ $O_3$  treatment. The two Au peaks are present at  $84.36$  eV (Au 4f<sub>7/2</sub>) and  $88.03$  eV (Au 4f<sub>5/2</sub>), which correspond to zerovalent Au.<sup>3,23</sup> Two peaks are also present for Ti:  $458.84$  eV (Ti 2p<sub>3/2</sub>) and  $464.54$  eV (Ti 2p<sub>1/2</sub>). These peak positions and their separation suggest the dominance of the  $Ti^{4+}$  oxidation state.<sup>23,53,54</sup>

Following XPS analysis, the same PPF/ $TiO_{1.9}(60)$ /G6-NH<sub>2</sub>(Au<sub>147</sub>) electrode was exposed to UV/ $O_3$  to remove the dendrimer and place the AuNPs and the  $TiO_{1.9}$  film into direct contact. To ensure that Au oxides, which could be generated



**Figure 7.** High-resolution XPS spectra in the Au 4f and Ti 2p regions for the indicated electrode configurations. XPS peaks were referenced to the position of the PPF C 1s peak at  $284.50$  eV.<sup>23,24</sup> The analysis was performed on using three independently prepared electrodes.

by the UV/O<sub>3</sub> treatment, were removed, the supported NPs were electrochemically reduced back to metallic Au. The red spectra in Figure 7a,b correspond to these materials. In this case, the Au peaks occur at 84.15 eV (Au 4f<sub>7/2</sub>) and 87.82 eV (Au 4f<sub>5/2</sub>), which represent a shift of  $0.21 \pm 0.03$  eV toward lower BE when the AuNPs and TiO<sub>1.9</sub> are in direct contact. This indicates an increased electron density on the AuNPs compared to when they are encapsulated within the dendrimers.

Curiously, the Ti peaks shift in the same direction as the Au peaks following UV/O<sub>3</sub> treatment. Specifically, there is a shift of  $0.13 \pm 0.04$  eV toward lower BE for both Ti peaks when the AuNPs are in direct contact with TiO<sub>1.9</sub>. This is surprising, because we would anticipate that if electron density increases on the AuNPs, then it should decrease on TiO<sub>1.9</sub>. However, we observe the same trend for the stoichiometric PPF/TiO<sub>2.0</sub>(60)/G6-NH<sub>2</sub>(Au<sub>147</sub>) electrodes.

The black traces in Figure 7c,d show the Au 4f and Ti 2p regions of PPF/TiO<sub>2.0</sub>(60)/G6-NH<sub>2</sub>(Au<sub>147</sub>) before UV/O<sub>3</sub> treatment. Both the Au 4f and Ti 2p peaks appear at the same positions as those for the substoichiometric supports. The red traces in Figure 7c,d show the Au 4f and Ti 2p regions of PPF/TiO<sub>2.0</sub>(60)/Au<sub>147</sub>-electrodes after UV/O<sub>3</sub> and subsequent electrochemical reduction of oxides on the AuNPs. The data reveal a  $0.11 \pm 0.04$  eV shift toward lower BE for Au 4f and a  $0.21 \pm 0.03$  eV shift toward lower BE for Ti 2p when the AuNPs and TiO<sub>2.0</sub> films are in contact compared to those when they are separated.

The shape and separation of the Ti 2p peaks do not indicate an increased concentration of Ti<sup>3+</sup> in the lattice structure of either oxidation state of TiO<sub>x</sub> and therefore the observed negative BE shift does not seem to be related to the reduction of TiO<sub>x</sub>. A simultaneous shift toward lower BEs in both the Au 4f and Ti 2p peaks during direct contact has previously been attributed to formation of a Schottky barrier at the junction of AuNPs and TiO<sub>x</sub> films,<sup>55</sup> but we have no direct evidence of this in our system. There are several other studies in the literature that also report charge transfer from TiO<sub>2</sub> to Au and simultaneous negative BEs shifts for both TiO<sub>2</sub> and Au.<sup>53–58</sup> Similar behavior has been observed for Pt and TiO<sub>2</sub> too.<sup>59,60</sup> In any case, the XPS evidence suggests that charge transfer does proceed from oxygen vacancies within TiO<sub>x</sub> to AuNPs as predicted by DFT.

To further confirm our findings, we performed a set of control experiments, where XPS measurements were obtained for AuNPs in the absence and presence of direct contact with PPF electrodes (no TiO<sub>x</sub>). As stated earlier, PPF is not known to affect the electronic state of supported metal NPs.<sup>47</sup> Figure S20 shows XPS spectra of PPF/G6-NH<sub>2</sub>(Au<sub>147</sub>) before and after dendrimer removal and electrochemical reduction of Au oxides. Importantly, in this case, the Au 4f lines are consistent with metallic Au, and they do not shift after removal of the dendrimer.

## CONCLUSION

In summary, we have presented a model system for studying interactions between metal oxide supports, in this case TiO<sub>x</sub>, and AuNPs. DFT calculations predicted that when AuNPs are in direct contact with TiO<sub>x</sub>, a significant, favorable shift in the onset potential for the ORR should be observed (compared to the case when AuNPs are isolated from the support). This is a consequence of electron donation into the supported AuNPs

by oxygen vacancies. Experimental electrochemical and spectroscopic results confirm this prediction.

The results described here are fully consistent with our earlier findings of two different, but related, metal oxide/NP systems. Specifically, we showed that there is no change in the electrocatalytic activity of PtNPs for the ORR regardless of whether they are in contact with the nonreducible oxide Al<sub>2</sub>O<sub>3</sub>.<sup>2</sup> Additionally, as predicted by theory, a relatively large improvement in the onset potential of the ORR was observed when AuNPs were in contact with SnO<sub>x</sub>.<sup>3</sup> The key point is that we have developed a highly reliable experimental model that provides a means for testing first-principles calculations for rather complex electrocatalytic systems. We plan to continue challenging the calculations by examining smaller AuNPs, other oxide supports, and different electrocatalytic reactions. The results of those experiments will be reported in due course.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c02754>.

Atomic structures; fabrication of pyrolyzed photoresist films; TEM micrographs and particle-size distributions; Gibbs free-energy diagram for AuNPs; surface Pourbaix diagram; X-ray diffraction data; Gibbs free energy diagram for TiO<sub>2</sub>(110)/Au; Bader charge analysis; thickness analysis of ALD films; SEM images; stability test data; optical profilometry; high-resolution XPS spectra; ORR data (PDF)

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### Notes

The authors declare no competing financial interest.

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