

Manipulating Atomic Structures at the Au/TiO₂ Interface for O₂ Activation

Jiawei Huang, Shuai He, Justin L. Goodsell, Justin R. Mulcahy, Wenxiao Guo, Alexander Angerhofer, and Wei David Wei*



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ABSTRACT: The metal/oxide interface has been extensively studied due to its importance for heterogeneous catalysis. However, the exact role of interfacial atomic structures in governing catalytic processes still remains elusive. Herein, we demonstrate how the manipulation of atomic structures at the Au/TiO₂ interface significantly alters the interfacial electron distribution and prompts O₂ activation. It is discovered that at the defect-free Au/TiO₂ interface electrons transfer from Ti³⁺ species into Au nanoparticles (NPs) and further migrate into adsorbed perimeter O₂ molecules (i.e., in the form of Au–O–O–Ti), facilitating O₂ activation and leading to a ca. 34 times higher CO oxidation activity than that on the oxygen vacancy (V_o)-rich Au/TiO₂ interface, at which electrons from Ti³⁺ species are trapped by interfacial V_o on TiO₂ and hardly interact with perimeter O₂ molecules. We further reveal that the calcination releases those trapped electrons from interfacial V_o to facilitate O₂ activation. Collectively, our results establish an atomic-level description of the underlying mechanism regulating metal/oxide interfaces for the optimization of heterogeneous catalysis.

The integration of metal nanoparticles (NPs) with oxides offers unique opportunities for driving catalytic reactions as compared to their catalytically inaccessible single-component counterparts.^{1–16} However, an understanding of the exact functionality of atomic structures at metal/oxide interfaces in governing the catalytic activity and its implications for practical applications has not yet been established.^{17,18} For instance, interfacial atomic structures of Au/TiO₂ heterostructures are complicated when Au is nucleated at surface defects with various coordinated structures of different facets, surface structures, and grain boundaries of TiO₂ NPs.^{19–21} Another major limitation is the lack of strategies for constructing distinct atomic structures solely at the metal/oxide interface rather than adjusting atomic and electronic structures of whole oxides,^{22,23} making it challenging to correlate the interfacial-structure-dependent electron distribution with the catalytic activity.

In this contribution, we reported how interfacial atomic structures of metal/oxide were manipulated to alter the electron distribution and promote O₂ activation for CO oxidation. Using different fabrication strategies, we successfully fabricated two Au/TiO₂ heterostructures with distinct interfaces and revealed that for the defect-free Au/TiO₂ interface electrons originated from Ti³⁺ species were transferred from TiO₂ into Au NPs, while those electrons were trapped at V_o on TiO₂ at the V_o-rich interface. Further investigations showed that such divergent electron distributions on Au/TiO₂ heterostructures resulted in significantly different efficiencies for electron-driven O₂ activation. For Au/TiO₂ with the defect-free interface, electrons that transferred from Ti³⁺ species into Au NPs further migrated to O₂ molecules adsorbed on the perimeter (i.e., in the form of Au–O–O–Ti) to promote O₂ activation. This led to a ca. 34 times higher CO oxidation than that on Au/TiO₂ with the V_o-

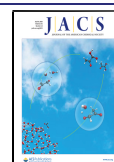
rich interface, where electrons were mainly trapped at interfacial V_o on TiO₂ and were inhibited from interacting with perimeter O₂ molecules. Moreover, we discovered that calcination at 320 °C significantly decreased the amount of V_o at the V_o-rich Au/TiO₂ interface, releasing electrons initially trapped at the interfacial V_o on TiO₂ for improving the efficiency of O₂ activation.

Two Au/TiO₂ heterostructures, with a defect-free interface or V_o-rich interface, were prepared (Figure 1A and B). Using the deposition–precipitation (DP) method,²⁴ chloroauric acid trihydrate (HAuCl₄·3H₂O) was directly reduced on the surface of TiO₂ NPs. The diffusion of Au atoms into surface V_o on TiO₂ mediated the formation of chemical bonds with Ti atoms²² and developed a defect-free interface (Figure S1A). Meanwhile, through a modified colloidal-deposition (CD) method,²⁵ presynthesized Au NPs were directly deposited onto TiO₂ NPs, maintaining V_o at the Au/TiO₂ interface (Figure S1B). X-ray photoelectron spectroscopy (XPS) proved that no observable citrate ions remained on Au NPs in Au/TiO₂ heterostructures with the V_o-rich interface (Figure S2A). It is noted that with the exception of different atomic structures, both defect-free and V_o-rich Au/TiO₂ interfaces contained well-defined nanoscale physical contacts to ensure the interfacial electron transfer (Figure 1C and D).^{24,26,27}

When compared to Au/SiO₂ heterostructures (i.e., 84.0 ± 0.1 eV in Figure S2B), high-resolution XPS showed that the Au

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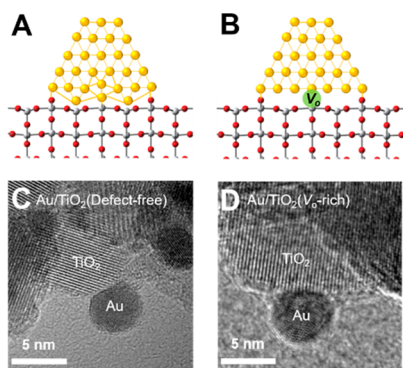


Figure 1. Au/TiO₂ heterostructures with distinct interfaces. Schematic of Au/TiO₂ heterostructures with (A) the defect-free interface and (B) the V₀-rich interface. The yellow, red, and silver dots represent gold, oxygen, and titanium atoms, respectively. The green dot stands for the interfacial V₀. High-resolution transmission electron microscopy (HRTEM) images of Au/TiO₂ heterostructures with (C) the defect-free interface and (D) the V₀-rich interface.

4f_{7/2} of both Au/TiO₂ heterostructures shifted to the lower binding energies (Figure 2A: 83.6 ± 0.1 eV for the defect-free

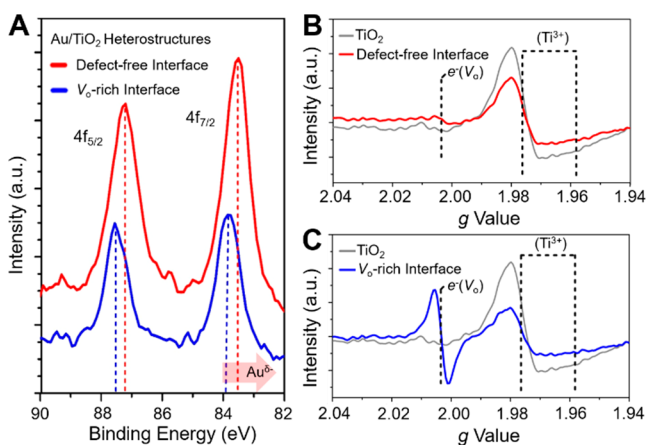


Figure 2. Electron distributions on Au/TiO₂ heterostructures with distinct interfaces. (A) High-resolution XPS spectra of the Au 4f orbital for Au/TiO₂ heterostructures with the defect-free interface (red curve) and Au/TiO₂ heterostructures with the V₀-rich interface (blue curve). Note: The energy resolution of XPS spectra is 0.1 eV. Different intensities of Au 4f spectra might come from the nonuniform distribution of Au/TiO₂ heterostructures on the Si wafer during the XPS sample preparation. (B) X-band EPR spectra of bare TiO₂ NPs (gray curve) and Au/TiO₂ heterostructures with the defect-free interface (red curve) at 90 K. (C) X-band EPR spectra of bare TiO₂ NPs (gray curve) and Au/TiO₂ heterostructures with the V₀-rich interface (blue curve) at 90 K. Note: EPR comparisons between bare TiO₂ and two Au/TiO₂ heterostructures were carried out using the same amount of samples (ca. 40 ± 2 mg). e[−](V₀) represents electrons trapped at V₀ on TiO₂, and Ti³⁺ stands for electrons accumulated at Ti centers of rutile TiO₂. The EPR background spectrum has been subtracted from the initial spectra of TiO₂ and two Au/TiO₂ heterostructures.

interface and 83.8 ± 0.1 eV for the V₀-rich interface). This indicated that electrons transferred from TiO₂ into Au NPs via the heterogeneous interface. Moreover, the lower binding energy of Au 4f_{7/2} (i.e., 83.6 ± 0.1 eV) strongly suggested that more electrons were transferred from TiO₂ to Au for Au/TiO₂ heterostructures with the defect-free interface.

Distinct electron distributions between those two Au/TiO₂ heterostructures were further verified using X-band electron paramagnetic resonance (EPR) spectroscopy. Compared to bare TiO₂ NPs, the EPR feature of electrons accumulated at Ti centers (i.e., Ti³⁺ species)^{28–30} significantly decreased on Au/TiO₂ heterostructures with the defect-free interface (Figure 2B and Figure S3A and B), suggesting that electrons transferred from Ti³⁺ species of TiO₂ into Au NPs (i.e., EPR silent) (Figure S4A). Additionally, no V₀-related EPR feature was observed at the defect-free Au/TiO₂ interface even with 5 wt % Au (Figure S5), demonstrating that the addition of Au NPs on TiO₂ did not affect the distribution of V₀ in TiO₂ to influence the electron distribution at the defect-free Au/TiO₂ interface. For Au/TiO₂ heterostructures with the V₀-rich interface, despite the observation of a similar decrease of Ti³⁺ species, a new EPR feature ($g = 2.003$) appeared and was assigned to electrons trapped at V₀ of TiO₂ (Figure 2C, blue curve, and Figure S3C).^{28–30} Interestingly, the intensity of this EPR feature continued to rise when the Au NP loading was increased (Figure S6), confirming that those V₀ must be placed exactly at the Au/TiO₂ interface. Thus, electrons originally from Ti³⁺ species would be trapped at the interfacial V₀ of TiO₂ rather than transferring into Au NPs (Figure S4B).

The electron distribution at the Au/TiO₂ interface has been reported to determine the activation of perimeter O₂ molecules, in which negatively charged Au NPs induced by the interfacial electron transfer from TiO₂ to Au exhibit a higher O₂ activation efficiency than that on neutral Au NPs.^{5,31,32} Meanwhile, it is known that the vibrational mode of adsorbed carbon monoxide molecules $\nu(\text{CO})$ is sensitive to the change of electron density of Au NPs,^{33,34} making CO an ideal molecular probe to spectroscopically study the electron-distribution-dependent O₂ activation on those two Au/TiO₂ heterostructures *in operando*.

For Au/TiO₂ heterostructures with the defect-free interface, two vibrational signatures were observed during O₂ activation (Figure 3A) that were distinct from the mode observed for adsorbed CO before O₂ activation (i.e., 2103 ± 2 cm^{−1} in Figure S7A and B). Interestingly, both CO vibrational modes blue-shifted ($\nu_1(\text{CO})_{\text{O}_2} = 2130 \pm 2 \text{ cm}^{-1}$ and $\nu_2(\text{CO})_{\text{O}_2} = 2118 \pm 2 \text{ cm}^{-1}$), suggesting a decrease of electron density on Au NPs during O₂ activation as the reduced electron density on Au weakened the Au–CO π -back-bonding.^{33,35} Furthermore, density functional theory (DFT) calculations found that during O₂ activation interfacial Au atoms near perimeter O₂ molecules were more electron-deficient than those away from the interface (Figure S8). Accordingly, we assigned $\nu_1(\text{CO})_{\text{O}_2}$ to CO molecules adsorbed at the Au/TiO₂ perimeter and $\nu_2(\text{CO})_{\text{O}_2}$ to CO molecules adsorbed on Au atoms away from the interface (Figure 3B). DFT calculations confirmed that once the electron density on Au NPs decreased, perimeter O₂ molecules became negatively charged (Figure S8), suggesting that electrons were transferred from Au NPs into perimeter O₂ molecules for O₂ activation (Figure 3B).

Vibrational modes of adsorbed CO molecules on Au/TiO₂ heterostructures with the V₀-rich interface ($\nu_1(\text{CO})_{\text{O}_2} = 2128 \pm 2 \text{ cm}^{-1}$ and $\nu_2(\text{CO})_{\text{O}_2} = 2116 \pm 2 \text{ cm}^{-1}$ in Figure 3C) were also found to blue-shift during O₂ activation compared to signals observed before O₂ activation (i.e., 2107 ± 2 cm^{−1} in Figure S7C and D). However, blue-shifts of both vibrational modes were less than those on Au/TiO₂ heterostructures with

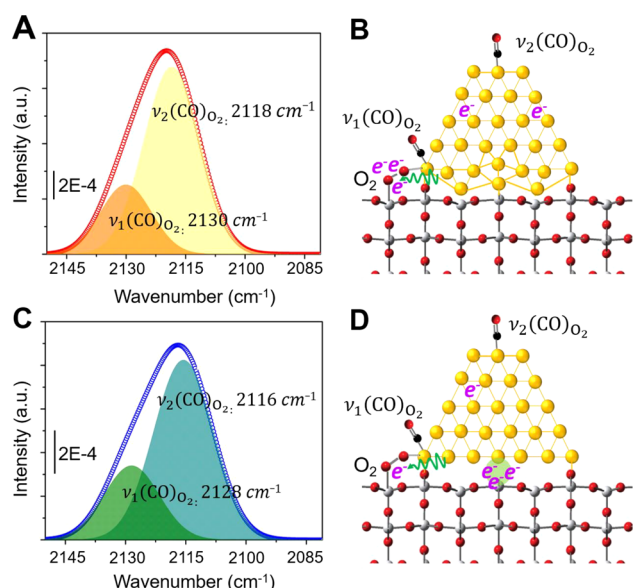


Figure 3. *In operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for O_2 activation on Au/TiO₂ heterostructures with distinct interfaces. (A) *In operando* DRIFTS spectra of $\nu(\text{CO})$ during O_2 activation on Au/TiO₂ heterostructures with the defect-free interface. $\nu_1(\text{CO})_{\text{O}_2}$ and $\nu_2(\text{CO})_{\text{O}_2}$ were observed at 2130 and 2118 cm^{-1} , respectively. (B) Schematic of O_2 activation on the defect-free Au/TiO₂ interface. The electron transfer from Au NPs into perimeter O_2 molecules resulted in less electron density within the interfacial Au-CO region than that of the area located away from the interface. (C) *In operando* DRIFTS spectra of $\nu(\text{CO})$ during O_2 activation on Au/TiO₂ heterostructures with the V_o -rich interface. $\nu_1(\text{CO})_{\text{O}_2}$ and $\nu_2(\text{CO})_{\text{O}_2}$ were observed at 2128 and 2116 cm^{-1} , respectively. (D) Schematic of O_2 activation on the V_o -rich Au/TiO₂ interface. The interfacial V_o trapped electrons and hindered the electron-driven O_2 activation, suppressing interfacial CO oxidation. Note: the resolution of DRIFTS spectra is 2 cm^{-1} , and CO molecules detected in the headspace have been removed from the spectra. Since DRIFTS spectra were collected during the O_2 activation, surface-adsorbed CO molecules kept being oxidized by perimeter O_2 molecules, resulting in weak CO vibrational signals.

the defect-free interface, suggesting that fewer electrons were transferred from Au NPs into perimeter O_2 molecules on the V_o -rich Au/TiO₂ interface. Further DFT calculations showed less of a decrease of electron density on the Au surface (Figure S9). This observation is consistent with that demonstrated in our XPS and EPR measurements of Au/TiO₂ heterostructures with the V_o -rich interface (Figure 2A and C): electrons were trapped at the interfacial V_o and, consequently, were hardly transferred into perimeter O_2 molecules (Figure 3D).

Different amounts of interfacial electrons transferred into perimeter O_2 molecules on these two Au/TiO₂ heterostructures led to discrete efficiencies for O_2 activation, which is the rate-determining step in CO oxidation.^{6,36,37} As shown in Figure S10A, the activation barrier of CO oxidation on Au/TiO₂ heterostructures with the defect-free interface (12.6 ± 1.9 kJ/mol) was much smaller than that on Au/TiO₂ heterostructures with the V_o -rich interface (34.6 ± 2.7 kJ/mol). This result confirmed that more electrons migrated from Au into perimeter O_2 molecules on the defect-free interface and significantly facilitated O_2 activation, eventually leading to a ca. 34 times higher activity of CO oxidation than that on Au/

TiO₂ heterostructures with the V_o -rich interface (Figure S10B).

High-temperature calcination has been used to reconstruct interfacial atomic structures between metal NPs and oxides.^{38,39} Figure S11 showed that, after treating Au/TiO₂ heterostructures with the V_o -rich interface at 320 °C for 3 h, calcination significantly decreased the amount of interfacial V_o , suggesting that electrons were released from interfacial V_o into perimeter O_2 molecules to promote O_2 activation for CO oxidation. Indeed, we observed a ca. 18.5 times higher activity of CO oxidation after the calcination (Figure S12).

In summary, we have successfully manipulated atomic structures at the Au/TiO₂ interface to alter the interfacial electron distribution and promote the catalytic activity. Compared to the V_o -rich interface, Au/TiO₂ heterostructures with the defect-free interface showed significantly higher efficiency for O_2 activation. Spectroscopic studies revealed that the defect-free interface permitted the electron transfer from TiO₂ into Au NPs to activate adsorbed perimeter O_2 molecules. By contrast, the V_o -rich interface trapped electrons at V_o on TiO₂ and prevented electrons from interacting with perimeter O_2 molecules. Moreover, we found that calcination significantly decreased the amount of interfacial V_o at the V_o -rich Au/TiO₂ interface and released electrons from interfacial V_o to promote O_2 activation, further illustrating the importance of manipulating interfacial atomic structures in facilitating heterogeneous catalysis. Taken together, our results not only establish an atomic-level understanding of the interfacial-structure-dependent catalytic activity on Au/TiO₂ heterostructures but also provide strategies to engineer metal/oxide interfaces for optimizing heterogeneous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b13453>.

Experimental details and additional data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Wei David Wei – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0002-3121-5798; Email: wei@chem.ufl.edu

Authors

Jiawei Huang – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0002-5184-2510

Shuai He – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States

Justin L. Goodsell – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States

Justin R. Mulcahy – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States

Wenxiao Guo – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0002-6674-9714

Alexander Angerhofer – Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0002-8580-6024

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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