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Resolving the valence of Iron Oxides by Resonant photoemission spectroscopy

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Abstract

Precisely determining the oxidation states of metal cations within variable-valence transition metal oxides remains a significant challenge, yet it is crucial for understanding and predicting the properties of these technologically important materials. Iron oxides, in particular, exhibit a remarkable diversity of electronic structures due to the variable valence states of iron (Fe^{2+} and Fe^{3+}), however, quantitative analysis using conventional X-ray photoelectron spectroscopy (XPS) is challenging because of significant overlapping of the $\text{Fe}2p$ spectra among different oxidation states. In this study, we leverage the intriguing case of Pt supported FeO_2 phase of monolayer thickness (ML) as a model system and employ Resonant Photoemission Spectroscopy (ResPES) to directly quantify the cation valence states and compositional ratios in this complex Fe oxide. Our results reveal that this ultrathin FeO_2 film (Pt-O-Fe-O), contrary to the +3 valence predicted by density functional theory (DFT), consists of an equal mixture of Fe^{2+} and Fe^{3+} cations, yielding an average valence of +2.5. Structurally, FeO_2 is likely derived from the Fe_3O_4 sublattice, featuring an octahedral Fe layer (50% Fe^{3+} and 50% Fe^{2+}) bonded to upper and lower oxygen layers.

1 Introduction

Iron (Fe), the most common element on Earth by mass, is ubiquitous in nature and plays a crucial role in shaping our society[1]. The redox reactions between ferrous (Fe^{2+}) and ferric (Fe^{3+}) oxides are central to numerous processes, spanning biochemistry[2], geochemistry[3, 4], and heterogeneous catalysis[5, 6]. In the realm of heterogeneous catalysis, platinum (Pt) supported on iron oxides is frequently utilized[5-12]. Reduction treatments can partially reduce the iron oxide substrate, causing migration of ultrathin Fe oxide moieties and encapsulation of Pt nanoparticles[13-15], which can significantly boost catalytic reactivity compared to that of the noble metal alone[6], an effect known as strong metal support interactions[16].

Research on ultrathin Fe oxide films supported on Pt(111) substrates has been extensively conducted since the 1990s. Somorjai et al. initially identified the surface structure of FeO_x layers on Pt(111), revealing that it adopts an FeO (111)-(1 $\times$ 1) stoichiometry at monolayer thickness [17].

Using scanning tunneling microscopy (STM), Salmeron et al. found that FeO/Pt(111) forms a moiré pattern as a result from the lattice mismatch between the FeO (111) overlayer and the underlying Pt(111) substrate[18, 19]. This structure transforms into two distinct phases at higher coverages: a (2×2) structure and a ($\sqrt{3}\times\sqrt{3}$)-R30° structure, which were identified as an Fe-terminated surface of Fe₃O₄ (111) and α -Fe₂O₃[20], respectively. Additionally, partially reduced FeO films on Pt were observed by Besenbacher et al.[21-24], and other groups[6, 25-30], featuring ordered oxygen vacancy dislocations from coordinately unsaturated Fe atoms.

Recently, Freund et al. reported the formation of a new oxygen-rich phase of FeO, i.e., FeO₂, under severe oxidation conditions[31, 32]. This FeO₂ (O–Fe–O) phase was shown to catalyze CO oxidation on Pt(111) at 450 K, where the interfacial oxygen is reacted by CO and replenished by O₂ [31, 33, 34]. This new phase features an extra oxygen layer intercalated between Pt and FeO film of monolayer thickness (ML), transforming the FeO (Pt-Fe-O) to a FeO₂ (Pt-O-Fe-O) structure. Density functional theory (DFT) calculations suggest that Fe cations in the FeO₂ phase have a formal oxidation state of +3 because of electron back-donation to the Pt substrate[32, 35]. The FeO₂/Pt(111) structure was also confirmed by Bao et al. [26, 36, 37] and Wendt et al.[38]. However, apart from ambiguous results from Fe 2p X-ray photoelectron spectroscopy (XPS), due to the strong overlap of the peaks from various Fe oxidation states, an experimental measurement of the valence state of FeO₂ is still lacking[39].

In this study, we use resonant photoemission spectroscopy (ResPES) to identify the different iron oxides and present direct experimental evidence that the valence state of FeO₂ is +2.5, comprising equal amounts of Fe²⁺ and Fe³⁺ species, lower than the +3 valence state predicted by DFT. [32, 35] Our results also suggest that the FeO₂ phase originates from the Fe₃O₄ (111) sublattice, where the octahedral Fe layer is structurally bonded to the upper and bottom O layers. We highlight that ResPES enables precise determination of the ferrous and ferric composition ratio of Fe oxides directly under reaction conditions.

2 Methods

The experiments were carried out in two UHV systems. The first system is equipped with a low-temperature scanning tunneling microscope (LT-STM, Boson Instruments, Beijing) in a base pressure of less than 3×10^{-10} mbar and sample preparation chambers. The STM images were obtained at 78 K using a Pt-Ir tip. The second system, equipped with a Scienta R4000 HIPP analyzer, is located at beamline 9.3.2 of the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory) where X-ray photoelectron spectroscopy (XPS), Resonant photoemission spectroscopy (ResPES), and partial electron yield X-ray adsorption spectroscopy (PEY-XAS) measurements at 200 eV electron kinetic energy were performed, respectively. The Pt(111) single crystal was cleaned by cycles of Ar^+ ion sputtering (2 keV, 10 μA) and annealing at 1200 K. FeO_x films were deposited onto the Pt(111) surface at room temperature (RT) using an e-beam evaporator in a O_2 partial pressure of 1×10^{-7} Torr. Subsequent annealing at higher temperatures and O_2 pressures led to the formation of a well-ordered FeO_x film, with a coverage controlled by the deposition time.

3 Results and Discussion:

STM images of the FeO_x monolayer, the thin films of Fe_3O_4 and Fe_2O_3 prepared as described in the experimental section are shown in **Fig. 1**. The STM images of FeO overlayer display a moiré pattern with a periodicity of approximately 2.5 nm (**Fig. 1a, inset**) originated from the lattice mismatch between the Fe-O layer (3.1 Å) and Pt substrate (2.78 Å), showing three regions of different contrasts: HCP, FCC, and TOP.[18, 19] We then prepared $\text{Fe}_3\text{O}_4(111)$ thin film (~ 4.2 nm thickness) by cycles of iron deposition and oxidation at ~ 870 K in 1×10^{-6} Torr O_2 .[40] **Fig. 1c** shows STM images of as-prepared $\text{Fe}_3\text{O}_4(111)$ surface exhibits hexagonal lattice with a 5.8 Å spacing, i.e. (2×2) structure and the surface is terminated by the tetrahedral Fe layer [40, 41]. Increasing the oxygen pressure to 5×10^{-5} Torr while annealing at the same temperature results in further oxidation of the $\text{Fe}_3\text{O}_4(111)$ surface. This oxidation significantly decreases the films conductivity, hindering stable imaging at sample biased below 2.0 V (data not shown). It may suggest the formation of Fe_2O_3 phase as its lower conductivity compared with the Fe_3O_4 phase, which also agrees with the previous STM results. [20, 42] Accordingly, **Fig. 1e** displays an STM

image acquired at a positive bias of 3.0 V, revealing complex moiré patterns with a periodicity of approximately 3.3 nm. High-resolution imaging resolves atomic features with an interatomic spacing of 3.0 Å (**Fig. 1e inset**). These STM characteristics suggest the formation of a bi-phase $\text{Fe}_2\text{O}_3(0001)$ surface, although its precise termination remains to be fully elucidated. [43, 44]

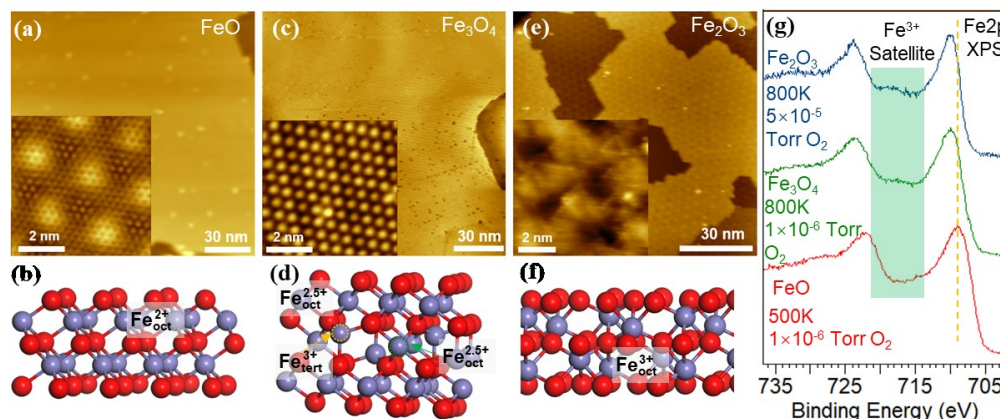


Fig. 1 STM and XPS of the $\text{FeO}_x/\text{Pt}(111)$. Large scale STM image and structural models showing the atomic flat terrace and side view of these Fe oxide films crystal structures: **(a-b)** FeO, **(c-d)** $\text{Fe}_3\text{O}_4(111)$ and **(e-f)** $\text{Fe}_2\text{O}_3(0001)$ film; **Insets:** zoom-in STM image with atomic resolution. **(g)** showing the Fe2p XP spectra of FeO (**red curve**), $\text{Fe}_3\text{O}_4(111)$ (**green curve**) and $\text{Fe}_2\text{O}_3(0001)$ (**blue curve**). The orange line marking the Fe2p 3/2 XPS peak position of FeO located at 709.0 eV and shadowed green box highlighting the satellite peak region. Scanning parameters: **(a)** inset: $V_s = +0.02$ V, $I_t = 6.02$ nA; **(c)** inset: $V_s = +0.9$ V, $I_t = 0.7$ nA; **(e)** inset: $V_s = +3.08$ V, $I_t = 5$ nA.

XPS experiments were performed to complement the above assignment of the FeO_x phase (**Fig. 1g**). The Fe2p XP spectra of ~ 15 ML FeO_x film after annealing at ~ 500 K under 1×10^{-6} Torr O_2 displays an asymmetric peak centered at 709.0 eV, characteristic of the FeO (**Fig. 1g, red curve**). After oxidation temperature further increased to ~ 800 K, the binding energy (BE) of this Fe2p 3/2 peak further shifted to 710.1 eV (**Fig. 1g, green curve**), in agreement with the that of Fe_3O_4 [39]. No further peak shift was observed as the O_2 pressure increased to 5×10^{-5} Torr except the emergence of a shake-up satellite peak at 718.5 eV (**Fig. 1g, blue curve**), indicative of the formation of Fe_2O_3 . [45] In summary, the FeO_x film evolves from FeO to Fe_3O_4 to Fe_2O_3 in response to the increasing O_2 chemical potential.

As demonstrated above, the accurate $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in mixed Fe oxide phases is difficult to determine due to the strong overlap of Fe 2p XP spectra among FeO_x [45]. Here, we utilize Resonant Photoemission Spectroscopy (ResPES) for this purpose. Usually the enhancement in the valence band (VB) signal in ResPES originates in a two-electron process[46-52], where the Fe 2p core-level electrons are first excited to the unoccupied 3d orbitals of the conduction band (CB), then decays back to the core level, simultaneously ejecting an occupied 3d electron from the VB (Fig. 2a). Thus, it combines X-ray absorption process and Auger decay process together. On the practical level, partial electron yield X-ray absorption spectra (PEY-XAS) were first conducted to identify the Fe L-edge region. Then, a series of valence band spectra (VBs) as a function of photon energy within this region were captured, creating a 2D heatmap of VBs. Fig. 2b-2c display Fe L-edge XAS and the 2D VBs heatmap of FeO and Fe_2O_3 films, respectively. It clearly shows that the highest resonant enhancement in VB for Fe^{2+} is at photon energy of 708.0 eV, while for Fe^{3+} , it is at 709.5 eV, accompanied by a secondary resonant feature at 708.0 eV. Fig. 2d-2e show the specific VBs of FeO and Fe_2O_3 at 709.5 eV (Fe^{3+} -resonance), 708.0 eV (Fe^{2+} -resonance), and 706.0 eV (off-resonance), respectively. For FeO, two resonant peaks were observed at ~ 4.5 eV and ~ 12 eV (Fig. 2d). For Fe_2O_3 , three resonant peaks were observed at ~ 2 eV, ~ 4.5 eV, and ~ 12 eV (Fig. 2e). The peak at ~ 21 eV showing in ResPES of both FeO and Fe_2O_3 responds to O 2s level.[53]

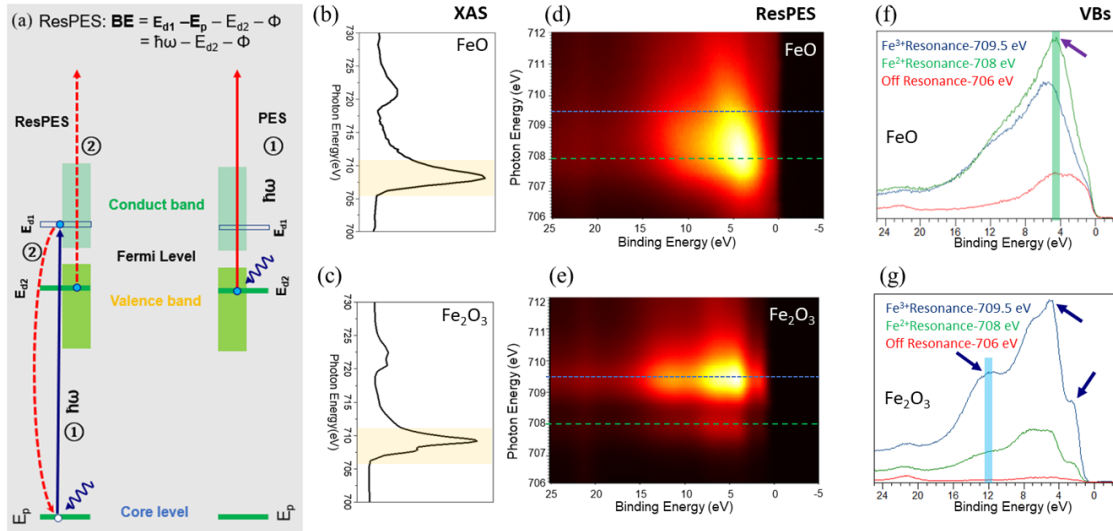


Fig. 2 ResPES of FeO and Fe_2O_3 film supported on Pt(111). (a) schematic illustration showing the two-electron process of the ResPES (left) and normal valence band spectra process (right). (b-e) XAS and 2D heat map of VBs of FeO and Fe_2O_3 , respectively. (f-g) Fe^{3+} -resonance (709.5 eV), Fe^{2+} -resonance (708.0

eV) and off-resonance VBs (706 eV) of FeO and Fe₂O₃, respectively. The arrows in the **(f)** and **(g)** mark the resonant peaks of Fe²⁺ and Fe³⁺ sites in FeO and Fe₂O₃, respectively. The stripes indicate the specific resonant peak positions of Fe²⁺ (4.5 eV) and Fe³⁺ (12 eV), which are used in the compositional analysis of the mixed FeO_x.

Next, we use a stoichiometric Fe₃O₄ film, where the Fe³⁺/Fe²⁺ concentration ratio is known as 2, to extract the linear factor (y) between resonant enhancement, $D(\text{Fe}^{n+})$, and concentration, $N(\text{Fe}^{n+})$. **Fig. 3a** displays the Fe L-edge PEY-XAS of Fe₃O₄, with pre-edge and main absorption peaks similar to those of Fe₂O₃, but with different peak ratios. The VBs heat map show similar strongest resonant features at 709.5 eV (**Fig. 3b**). Specifically, the Fe₃O₄ VBs features at Fe³⁺-resonance (709.5 eV) and Fe²⁺-resonance (708.0 eV) resemble those of Fe₂O₃, except for the missing of 2 eV peak at Fe³⁺-resonance (**Fig. 3c**). Accordingly, we use the 12 eV peak at 709.5 eV and the 4.5 eV peak at 708.0 eV as resonant signatures of Fe³⁺ and Fe²⁺ cations. Notably, VBs of FeO (pure Fe²⁺) in **Fig. 2d** exhibit a discernible peak intensity at 4.5 eV BE as photon energy set at 709.5 eV (Fe³⁺-resonance), which is 0.68 times that of the Fe²⁺ resonant peak intensity at 708.0 eV. Similarly, the VBs of Fe₂O₃ (pure Fe³⁺) in **Fig. 2e** also display a visible shoulder at 12 eV BE as photon energy set at 708.0 eV (Fe²⁺-resonance), which is 0.26 times that of the Fe³⁺ resonant peak at 709.5 eV. To achieve a more precise compositional Fe³⁺/Fe²⁺ ratio, we account for these residual effects rather than relying solely on the proportional relationship between the concentration ratio $N(\text{Fe}^{3+})/N(\text{Fe}^{2+})$ and the resonant enhancement ratio (RER), $D(\text{Fe}^{3+})/D(\text{Fe}^{2+})$ [48, 51]. The modified equations are listed:

$$\text{For Fe}^{3+}: D(\text{Fe}^{3+}) = y_1 * N(\text{Fe}^{3+}) + y_2 * N(\text{Fe}^{2+}) * 0.68 \text{ —— Equation (1)}$$

$$\text{For Fe}^{2+}: D(\text{Fe}^{2+}) = y_1 * N(\text{Fe}^{3+}) * 0.26 + y_2 * N(\text{Fe}^{2+}) \text{ ——Equation (2)}$$

Based on the known stoichiometric of Fe₃O₄ and measured value of resonant enhancement value, the y_1 (linear factor for Fe³⁺) and y_2 (linear factor for Fe²⁺) is determined as 0.55 and 0.46. According, these equations set changes to

$$\text{For Fe}^{3+}: D(\text{Fe}^{3+}) = 0.55 * N(\text{Fe}^{3+}) + 0.31 * N(\text{Fe}^{2+}) \text{ —— Equation (3)}$$

$$\text{For Fe}^{2+}: D(\text{Fe}^{2+}) = 0.14 * N(\text{Fe}^{3+}) + 0.46 * N(\text{Fe}^{2+}) \text{ —— Equation (4)}$$

Furthermore, for other nonstoichiometric FeO_x phase, the $N(\text{Fe}^{3+})/N(\text{Fe}^{2+})$ can be quantitatively determined with measured $D(\text{Fe}^{3+})$ and $D(\text{Fe}^{2+})$ through solving the system of linear equations with two variables.

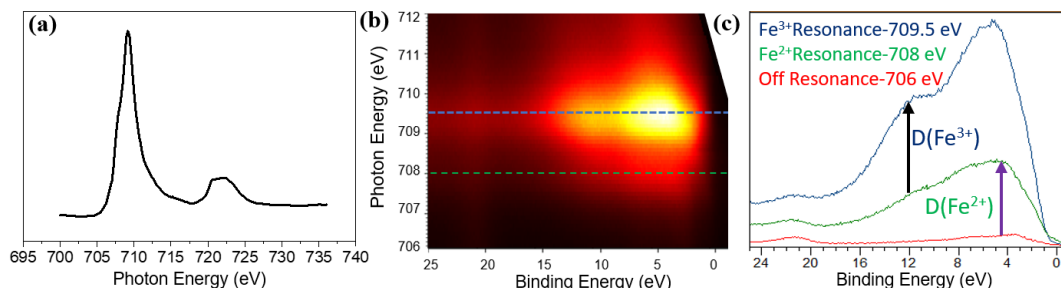


Fig. 3 ResPES of stoichiometric Fe_3O_4 supported on Pt(111). (a) Fe L-edge XAS of Fe_3O_4 . (b) 2D heat map of VBs of Fe_3O_4 . (c) Fe^{3+} -resonance (709.5 eV), Fe^{2+} -resonance (708.0 eV) and off-resonance VBs (706 eV) of Fe_3O_4 . Some data points near the Fermi level are absent for photon energies above 709.8 eV due to the setting of data acquisition parameters, but this does not affect the overall analysis.

Finally, we utilize ResPES to determine the valence state of the Pt supported 1ML FeO_2 film. The FeO_2 phase, first reported by the Freund group [31] and followed by other groups [26, 38, 54], forms after annealing monolayer-thick FeO at $\sim 450\text{K}$ in ~ 15 Torr O_2 because of extra oxygen layer intercalation at the Pt- FeO interface. The corresponding STM image displays a higher contrast and more corrugated surface compared to FeO [26, 38, 54]. This tri-layer FeO_2 (O-Fe-O) is believed to be the active phase for O_2 -rich CO oxidation via the Mars-van Krevelen (MvK) mechanism [31, 33, 34], where the intercalated oxygen layer can be reacted by CO and regenerated by O_2 . DFT simulations suggest that the oxidation state of FeO_2 is approximately 3+ rather than 4+ due to back-charge transfer from the Pt substrate to the oxide layer [35, 54]. However, experimental confirmation of this charge state has predominantly relied on Fe 2p XPS, which is ambiguous for mixed FeO_x phases due to overlap between Fe^{2+} and Fe^{3+} species [26, 39]. Moreover, the atomic structure of this tri-layer FeO_2 is primarily inferred from STM imaging and DFT simulations without extra experimental evidence [32]. As shown below, ResPES proves to be a powerful tool to determine the charge ratio and provide insights into the structural determination of FeO_2 .

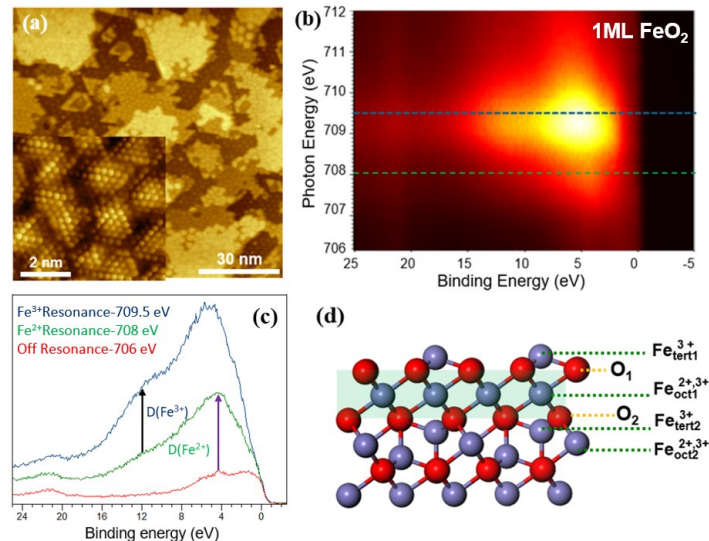


Fig. 4 ResPES of ML FeO₂ film supported on Pt(111). (a) STM image of the Pt(111) supported FeO₂ film. Inset showing the atomic resolution STM with 3.2 Å lattice spacing. (b) 2D heat map of VBs of FeO₂ film of monolayer thickness. (c) Fe³⁺-resonance (709.5 eV), Fe²⁺-resonance (708.0 eV) and off-resonance VBs (706 eV) of FeO₂. (d) structural model showing the side view of Fe₃O₄(111) with Fe_{tert1} layer termination. Scanning parameters: (a) inset: V_s = +1.0 V, I_t = 5.0 nA.

Fig. S1 displays the Fe 2p XPS spectra of a monolayer FeO (red curve), with a characteristic peak at 709.1 eV. After oxidation at 470K under 5×10^{-5} Torr O₂, the Fe 2p XPS remains unchanged. Increasing the pressure O₂ temperature to 100 mTorr and annealing at 540 K results in FeO₂ formation, indicated by a blue shift of Fe 2p_{3/2} peak to 710.1 eV, consistent with previous literature[26, 36]. **Fig. 4a** display the large scale STM image of the atomic flat FeO₂ film with 3.2 Å lattice spacing shown in the atomic resolution image (**inset**), agreeing with reported results[26, 32, 38]. Further Fe L-edge XAS (**Fig. S2**) and VB heat maps of this Pt (111) supported FeO₂ film show significant similarities to those of Fe₃O₄ phase in **Fig. 3b**, suggesting that the similarity between FeO₂ and the Fe₃O₄ (111) (sub)lattice. However, the corresponding Fe³⁺-ResPES displays a weaker peak intensity at 12 eV, indicating a lower Fe³⁺/Fe²⁺ ratio compared to Fe₃O₄. Based on the Equations (3)-(4), we determine the N(Fe³⁺)/N(Fe²⁺) ratio of FeO₂ film to be unit. This equal composition ratio of Fe³⁺ and Fe²⁺ species is also valid among the sub-monolayer FeO₂ film (**Fig. S3**).

To further elucidate the structural relationship between FeO_2 and Fe_3O_4 , the **Fig. 4d** shows the side view of $\text{Fe}_3\text{O}_4(111)$ terminated structures with stacking along the $[111]$ direction. From top to bottom, its unit cell consists of a tetrahedral Fe layer (Fe-tet1, Fe^{3+}), oxygen layer (O_1), octahedral Fe layer (Fe-oct1, 50% Fe^{3+} + 50% Fe^{2+}), oxygen layer (O_2), another tetrahedral Fe layer (Fe-tet2, Fe^{3+}), and another octahedral Fe layer (Fe-oct2, 50% Fe^{3+} + 50% Fe^{2+}).^[40] Given that previous theoretical calculations proposed an O-Fe-O stacking sequence for the FeO_2 structure [32, 35] and considering the 1:1 ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ experimentally resolved in RPES measurement, we propose that Pt(111)-supported FeO_2 structure is analogous to the $\text{O}_1\text{-Feoct1-O}_2$ sublattice within $\text{Fe}_3\text{O}_4(111)$ shown in **Fig. 4d**, where octahedral Fe cations are coordinated by upper (O_1) and lower (O_2) oxygen layers. This proposed FeO_2 structure ($\text{O}_1\text{-Feoct1-O}_2$ interfacial configuration) is in good agreement with the previous DFT simulations.

Conclusion

In summary, series of Fe oxides on Pt(111) were prepared after post annealing at different oxygen atmosphere and temperature, which serves as the standard stoichiometric oxides, i.e., FeO , Fe_2O_3 and Fe_3O_4 , to establish the ResPES methodology for nonstoichiometric FeO_x . Utilizing ResPES on catalytically active FeO_2 phase, we demonstrated that this FeO_2 is composed of equal amount of Fe^{3+} and Fe^{2+} species with an average +2.5 valence. Accordingly, this FeO_2 phase may evolve from the $\text{Fe}_3\text{O}_4(111)$ sublattice, consisting of the octahedral Fe1 layer bonded to upper (O_1) and lower oxygen (O_2) layers. This powerful ResPES method demonstrated here can be applied to practical Fe oxide nanoparticle systems to in-situ determine composition ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with high precision.

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Contributions

M.S. oversaw the project. H.C., conduct the X-ray spectroscopy experiment supported by the beamline scientists (S.N.). Y.L., X. Zhang, and S. Zhao., did the STM experiment. H.S.L D wrote the python code for the reading of 2D ResPES data. Data analysis were done by H.C., S.N. and M.S. The paper was written by H.C. with contributions from all authors. Y.L., S.N. and M.S. helped to review and edit the manuscript.

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