Real-time observation of Ostwald ripening in an oxide-on-metal system: Understanding the mechanisms that drive the size and structure of oxide species in “inverse” catalysts

Natalia Michalak,1,2 Tomasz Ossowski,3 Zygmunt Miłosz,1 Mauricio J. Prieto,4 Ying Wang,1 Mirosław Werwiński,2 Visnja Babacic,1 Francesca Genuzio,5 Luca Vattuone,6,7 Adam Kiejna,3 Thomas Schmidt4 and Mikolaj Lewandowski1,*

1NanoBioMedical Centre, Adam Mickiewicz University, Wszechlnicy Piastowskiej 3, 61-614 Poznań, Poland
2Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland
3Institute of Experimental Physics, University of Wrocław, Pl. M. Borna 9, 50-204 Wrocław, Poland
4Department of Interface Science and Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany
5Elettra–Sincrotrone Trieste S.C.p.A., S.S. 14 - km 163, 5 in AREA Science Park, 34149 Basovizza, Trieste, Italy
6Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy
7IMEM-CNR, Via Dodecaneso 33, 16146 Genova, Italy
*Corresponding Author: E-mail: lewandowski@amu.edu.pl, Phone: +48618296710

ORCID: 0000-0002-0984-3456 (N.M.), 0000-0002-2301-8671 (T.O.), 0000-0002-4938-9331 (Z.M.), 0000-0002-5087-4545 (M.J.P.), 0000-0002-8905-0818 (Y.W.), 0000-0003-1934-4818 (M.W.), 0000-0002-6986-550X (V.B.), 0000-0003-0699-2525 (F.G.), 0000-0003-3718-6470 (L.V.), 0000-0002-0983-7953 (A.K.), 0000-0003-4389-2080 (T.S.), 0000-0002-1480-8516 (M.L.)

Author contributions
M.L. authored the original idea for the studies, performed (with the assistance of N.M.) STM/STS and LEED experiments in Poznań, prepared the figures (supported by T.O. and M.W.) and wrote the manuscript (supported by N.M., T.O., Y.W., M.W. and V.B.). N.M., Z.M., M.P., F.G., T.S. and M.L. performed LEEM/µLEED, XPEEM and XPS measurements at the BESSY-II synchrotron in Berlin. N.M., Z.M., Y.W. and V.B. analyzed the experimental data together with and under the supervision of M.L. T.O. and M.W. conducted the theoretical calculations and analyzed the results. N.M. and M.L. acquired the funds for the studies. L.V. and A.K., in addition to other Authors, contributed to the discussion.
ABSTRACT

Oxides-on-metals are the well-known “inverse” catalysts. Fundamental knowledge on the structural transformations that occur in such systems under oxidizing and reducing conditions is crucial for maximizing their catalytic activity. Sintering of oxide species is one of the effects that may, on one hand, lead to catalyst deactivation, but on the other constitutes a powerful means for fine-tuning their size and structure – which is one of the major challenges in the field. In this Letter, we show that the structure of well-dispersed bilayer iron monoxide (FeO) islands grown on Ru(0001), which constitutes a model “inverse” catalyst, can be optimized by thermally-driven sintering and phase transition. The structural transformation occurs via the Ostwald ripening mechanism, as observed in real time using in situ low energy electron microscopy (LEEM). The structure of the islands before and after the transformation is determined using ex situ experimental methods, as well as theoretical calculations.

TOC GRAPHICS

KEYWORDS

iron oxide; ruthenium; model system; inverse catalyst; structure; Ostwald ripening
Catalysts consisting of metals and oxides are among the most commonly used in chemical industry. In the “classical” form, the oxide acts as a support for the growth of well-dispersed metal particles, which are the active species in catalytic reactions (with possible contribution of the oxide and the metal-oxide interface). “Inverse” catalysts, on the other hand, utilize low-dimensional catalytically-active oxide species grown on an oxide or metal support (with possible contribution of the oxide-oxide or oxide-metal interface sites – see Ref. 3 and references therein). Under reaction conditions, such species can also appear on well-dispersed metal nanoparticles as a result of the so-called strong metal-support interaction (SMSI) and suppress or increase the catalytic activity of the system.

Depending on the reaction, it may be desirable to maximize the number of specific surface sites in a catalytic material, such as crystal facets, edges or exposed support regions. This is usually done by optimizing the catalyst preparation method. However, the structure of the catalyst may also evolve during the reaction. The precise control of the structure of metal-on-oxide catalysts is much more trivial than in the case of oxides-on-metals, as the mechanisms governing the growth and structural evolution of metals under oxidizing and reducing conditions are well-understood. However, the mechanisms that drive the size and structure of supported oxide species are not clear, with control over these parameters being one of the main challenges in the field.

Islands of metal oxides supported on metal single-crystal substrates constitute well-defined model systems for the studies on “inverse” catalysts. Such systems often exhibit unique catalytic activity on their own, thanks to their low-dimensionality and the associated lattice flexibility (which may lead to unusual structural arrangements not observed for the corresponding bulk oxides). From the point of view of catalytic reactions, the size and number of the islands, their perimeter length, number of internal defects and stoichiometry are the crucial structural parameters that drive the reactivity. For example, in the case of the CO oxidation reaction over FeO islands grown on Pt(111), one of the reaction steps (overoxidation of FeO) was found to take place only for islands of certain size, while the other (CO reaction with weakly-bound O atoms) to proceed from the islands edges. This shows the importance of the ability to precisely control the structural parameters of oxide islands in “inverse” catalysts.

In classical metal-on-oxide catalysts, thermal treatments may lead to particles sintering and, thus, the change in the ratio between the facet and edge sites. Sintering usually proceeds through one of the two mechanisms: coalescence, i.e. Brownian-like motion of particles and their merging upon collision, or Ostwald ripening, a process in which smaller particles decompose, the material diffuses across the surface and feeds bigger particles that grow in size. For oxide-on-metal catalysts, the situation is more complicated due to the non-trivial structure of oxide materials and their varying interaction with different supports. This motivates the studies on the structural evolution of such systems upon exposure to oxidizing and reducing conditions.

In our recent work, we have shown that ultrathin FeO islands grown on Ru(0001) undergo a transformation to an O-rich FeOx (1 < x < 2) phase when subjected to strongly oxidizing conditions (exposure to atomic oxygen). Here, using real time low energy electron microscopy
(LEEM), we show that reducing conditions, i.e. high-temperature annealing under ultra-high vacuum (UHV), leads to islands sintering and transformation of FeO into an O-poor FeₙO (1 < x ≤ 2) phase. The process proceeds via the Ostwald ripening mechanism, which is known to facilitate the wet chemistry growth of various oxide nanostructures,¹⁸,¹⁹ however, was not observed in an oxide-on-metal system so far.

Scanning tunneling microscopy (STM) image of pristine FeO islands grown on Ru(0001) by Fe deposition and post-oxidation in 1×10⁻⁶ mbar O₂ at 950 K is shown in Figure 1(a). The system after annealing at 950 K in UHV for 10 and 20 min is shown in Figures 1(b) and 1(c), respectively. Pristine islands are well-dispersed, have different sizes and grow both at the regular terrace sites and from the step edges of the substrate.²⁰,²¹ They are composed of two FeO layers and characterized by a Moiré superstructure with 21.6 Å periodicity (originating from the lattice mismatch between the oxide (aₐFeO(111)=3.1 Å) and the Ru(0001) support (2.71 Å) – Figure 1(d)). The observed growth mode and structure are characteristic for the preparation conditions used.²⁰,²¹ Bigger islands are formed through the coalescence of smaller ones, which results in the appearance of characteristic line defects within the islands.¹⁷,²⁰,²¹ (Figure 1(d)). Scanning tunneling spectroscopy (STS) dI/dV mapping (Figure 1(e)) reveals that such defects have the same electronic structure as island edges, indicating that they host highly catalytically-active coordinatively unsaturated ferrous sites (CUFs).²²,²³ Low energy electron diffraction (LEED) exhibits the characteristic “satellite”+(2×2) pattern (inset to Figure 1(d)) originating from the presence of the FeO Moiré superstructure,²⁰ the symmetry of the Ru(0001) substrate²⁴ and the presence of 3O-(2×1) domains²⁵ on the exposed substrate regions. Following annealing at 950 K in UHV for 10 min, the number of islands decreases, while the average island size increases (with the total coverage staying the same within an accuracy of 5%). Moreover, the island edges become sharper, running along the crystallographic directions of the ruthenium support. Annealing for additional 10 min at the same temperature leads to further growth of the bigger islands at the expense of the smaller ones and the visible change in the islands shape towards an equilibrium one, i.e. truncated triangle (or – ultimately – hexagonal). It is important to note, that the total edge length decreased by approx. 20% after the first annealing and stayed more or less the same after the second one. Even more significant decrease was found for the internal structural defects, ~80% of which vanished after the first annealing and almost none were left after the second one (Figure 1(f)). The diffraction pattern of the annealed sample (inset to Figure 1(f)) reveals better ordering of the structure (higher intensity of diffraction spots), with the arrangement of reflexes staying exactly the same.
Figure 1. STM images of pristine FeO/Ru(0001) (a) and the system after annealing at 950 K for 10 (b) and 20 min (c) in UHV. (d) and (e) show the structural defects within an extended island observed in STM and STS dI/dV mapping modes, respectively. (f) reveals the lack of defects following annealing at 950 K for 10 min. Inset in (c) shows the island height histogram, while those in (d) and (f) present LEED patterns obtained for pristine and annealed samples, respectively. STM: V_{sample} = +1.0 V; I_{t} = 0.7 nA (all images, including the STS dI/dV map); Image sizes: 500×500 nm^2 (a-c), 50×50 nm^2 (d-f). LEED: 64 eV.

The observed restructuring could be explained either by coalescence of the islands or by Ostwald ripening. To clarify this issue, we used low energy electron microscopy (LEEM) which allows real-time monitoring of structural changes that occur at solid surfaces during thermal or chemical treatments. Figure 2(a) shows pristine FeO islands on Ru(0001), while Figures 2(b) and 2(c) show the system after UHV annealing at 1050 K for 45 seconds and 2 minutes, respectively. The movie showing the process (with the speed adjusted to show the whole process in approx. 45 seconds) can be found in the online Supporting Information section. The higher temperature used in the case of LEEM studies was due to the slow dynamics of the process at 950 K. As can be seen, during annealing the smallest islands (marked with yellow and blue circles in Figures 2(a) and Figure 2(b), respectively) disappear and, after some time, the bigger ones start to grow laterally in size (Figures 2(d-f)). This kind of behavior is characteristic for Ostwald ripening and indicates that the smaller islands decompose, the material diffuses across the surface and feeds the encountered bigger islands. The growing parts show different contrast in LEEM when imaged with certain
instrument parameters (Figure 2(d)), which indicates that they are characterized by a different structure than the original islands. During prolonged annealing, the contrast within the islands equalizes towards that of the newly-grown part (Figures 2(h-i)).

**Figure 2.** LEEM images obtained for (a) pristine FeO/Ru(0001) and (d-i) the system at different time intervals of annealing at 1050 K. The observed structural evolution can be divided into three phases: (a-c) disappearance of smaller FeO islands, (d-f) growth of bigger islands, with new parts exhibiting different structure, and (g-i) unification of the structure towards that of the newly-grown parts. The scale bar in (a) corresponds to 500 nm. LEEM energy: 20 eV.

To determine the difference in the structure between pristine FeO and the phase formed following the annealing, we performed additional experimental and theoretical studies. As evident from Figures 1(d) and 1(f), as well as the insets to the figures, both structures appear virtually-
identical in STM and LEED (except for the degree of ordering). Indeed, no differences in the atomic or Moiré periodicities can be observed. However, the height profiles taken across STM images of both structures (Figure S1 in the Supporting Information file) reveals that the annealed islands are by ~0.5 Å lower than the pristine ones (4.45 +/- 0.15 Å (annealed) vs. 5.0 Å (pristine)). The structural evolution takes place gradually, as evidenced by the histogram shown in the inset to Figure 1(c). The acquired X-ray photoelectron emission microscopy (XPEEM) images, obtained for the energy range in which the Fe 3p photoelectron signal is expected to appear, allowed plotting local signal intensity curves from the original and growing parts of an exemplary island (Figure 3(a)). The results indicate that the growing parts host iron in a lower oxidation state than the original parts that did not fully decompose. The maximum of the signal recorded for the original structure, ~54.5 eV, lies in between the ones expected for Fe$^{2+}$ (53.7 eV) and Fe$^{3+}$ (55.6 eV). This is in agreement with our recent studies which indicated mixed valency of iron in bilayer FeO on Ru(0001). The signal recorded from the growing parts, on the other hand, consists of two components, with a dominant contribution from the one located at lower binding energies, i.e. corresponding to the Fe$^{2+}$ oxidation state. Similar trend was observed in the recorded X-ray photoelectron spectroscopy (XPS) Fe 3p (Figure S2(a)) and Fe 2p (Figure 2(b)) results, which showed gradual shift of both signals to lower binding energies following brief and prolonged annealing. Fe 3p and O 1s spectra (not shown) allowed determining the change in the Fe:O ratio before and after the complete annealing-induced structural transformation (Figure S2(c)). For this purpose, the total area under the signals was integrated and multiplied by the atomic sensitivity factors of the respective photoelectrons. Taking into account the initial and final FeO coverage (with their local fluctuations on different sample regions), as well as the fact that the remaining part of the surface is covered with chemisorbed oxygen in a 3O-(2×1) arrangement, the stoichiometry of the new phase was determined to be roughly Fe$_2$O. The precise stoichiometry could not be determined due to potential partial diffusion of iron into the substrate, local changes of oxygen concentration on Ru(0001) (partial transformation of the 3O-(2×1) structure into 2O-(2×2)) and the possibility that the transformation was not fully completed for all the investigated islands.

In order to address the structure of the newly-formed iron oxide phase, we performed density functional theory (DFT) calculations. The information obtained from the experiments, i.e. atomic and superstructure periodicities similar to pristine FeO(111) (deduced from STM and LEED), the ~0.5 Å lower height (from STM), the lower oxidation state of iron (from XPEEM and XPS) and the Fe:O ratio (from XPS), allowed us to limit the number of investigated systems to three differently stacked Fe$_2$O layers: Fe-O-Fe/Ru, Fe-Fe-O/Ru and O-Fe-Fe/Ru. The large size of the (7×7)FeO-(8×8)Ru Moiré superstructure unit cell and the necessity to include three atomic layers forming the oxide (two layers of Fe and one layer of O), as well as five layers of the Ru substrate, made the size of the computational cell challenging. To make computations feasible, separate calculations were carried out for different high-symmetry regions of the Moiré supercell, i.e. top, fcc and hcp. Such approach was found to reproduce the crucial structural features of FeO on different single-crystal substrate – Pt(111). Here, we discuss the results obtained for the fcc...
region and for Ru(0001) lattice constant (Figure 3(b)), which was found to be the most energetically-stable one, while the results obtained for other high-symmetry regions and the FeO lattice constant are presented in Figures S3 and S4. Analysis of the stability shows that the Fe-O-Fe/Ru and O-Fe-Fe/Ru stackings are the energetically most preferred ones and very close in total energy values, with the Fe-O-Fe/Ru being the most preferred one by 0.35 eV. The Fe-Fe-O/Ru system with oxygen atoms at the interface is energetically unfavored, as its total energy is by 13.11 eV higher than that of the most stable one. The calculations also reveal that following the relaxation the structure remains uncorrugated within a single high-symmetry region. The estimated layer thickness for the Fe-O-Fe/Ru configuration is 5.05 Å (Figure S3), which is only ~15% lower than the height of the most energetically-preferred FeO configuration, i.e. O-Fe-O-Fe/Ru (6.08 Å\textsuperscript{28}). It has to be noted that the Fe-O-Fe/Ru stacking is the natural stacking of bilayer FeO(111), with the top O layer removed. Even though the experimentally determined height difference between pristine FeO and Fe\textsubscript{2}O is only 10%, the Fe-O-Fe/Ru stacking of the Fe\textsubscript{2}O layers seems reasonable, as the height measured with STM may be altered by electronic effects, especially when measuring the height between the oxide and the metal. The calculations performed using the lattice constant of FeO resulted in an Fe\textsubscript{2}O layer height lower by approx. 0.5 Å (Figure S4). Notably, this height is again lower by ~15% compared to similarly calculated FeO structure (independently of the Moiré high symmetry region).

As Fe-O-Fe/Ru and O-Fe-Fe/Ru stackings are almost degenerate in energy, work function values of both structures were calculated to be used as fingerprints for their distinguishment (Table S1 in the SI). The Fe-O-Fe/Ru structure is characterized by a work function value (~4.65 eV) that is much lower than the one obtained for the O-Fe-Fe/Ru structure (~7.7 eV) and the one obtained for FeO/Ru in its most preferred layers stacking (~7.8 eV for O-Fe-O-Fe/Ru\textsuperscript{28}. From the recorded LEEM-IV curves (Figure 3(c)), it is evident that the work function of the newly-grown phase is lower than the one of pristine FeO (the work function difference can be determined from the characteristic signal intensity drop observed in between 2 and 5 eV). Determination of exact values is not trivial due to the appearance of intensity oscillations (peaks) in the transition region, however, a different of at least 1 eV is clearly visible. All this suggests that even though the Fe-O-Fe/Ru and O-Fe-Fe/Ru are very close in total energy, their calculated and measured work function values favor the former as the one observed experimentally.
Figure 3. (a) XPEEM-IV Fe 3p spectra obtained for different parts of iron oxide island formed following annealing FeO/Ru(0001) at ~1050 K in UHV: the part where the original big FeO island was present (black curve) and the part corresponding to the new iron oxide phase that grew (red); (b) side views of differently stacked iron oxide structures with Fe₂O stoichiometry on Ru(0001) structures obtained from DFT calculations. Gold spheres represent Fe atoms, red O atoms and silver Ru atoms. The energies are referred to the energy of the most stable system. The distances are given in Å. (c) LEEM-IV spectra obtained for FeO/Ru(0001) (black) and Fe₂O/Ru(0001) (red).

The origin of the FeO-to-Fe₂O transformation comes from the structural characteristics of the FeO/Ru(0001) system. First of all, the partial presence of Fe³⁺ iron ions in pristine FeO opens the route for its thermal reduction to structures with lower iron oxidation state (Fe²⁺ or metallic Fe). Secondly, the O atoms chemisorbed on Ru(0001) constitute an oxygen “reservoir”, making reoxidation of the diffusing material (most probably iron) possible, at least to a certain extent. The final structure is also partially dependent on the vicinity of pristine FeO with its original layers stacking, i.e. O-Fe-O-Fe/Ru, as well as atomic and Moiré periodicities.

The final puzzle to solve is the determination of the expected oxidation state of iron in the Fe₂O structure. Figure 4(a) shows the graphical representation of the distribution of calculated Bader charges (BCs) on Fe, O and Ru atoms in the relaxed pristine FeO/Ru, as well as in reduced Fe₂O/Ru system (numbers in brackets). In the case of FeO, each atom in the top oxygen layer gains 1.14e (electron), each iron atom in the layer underneath loses 1.83e, the oxygen atoms in the next layer gain 1.4e, the iron atoms at the interface with ruthenium lose 0.91e and each ruthenium atom gains 0.23e.
Figure 4. (a) Graphical representation of the distribution of charges on different atoms within the FeO bilayer and the most stable Fe$_2$O structure (numbers in brackets) on Ru(0001). (b) Density of states (DOS) of Fe 3p orbitals calculated for FeO (denoted as “Fe$_2$O”) and Fe$_2$O structures on Ru(0001) (the calculations were performed for U(Fe 3d) = 4 eV; the results obtained for different (0 and 2 eV) U values are presented in Figure S3).

Even though a direct correlation between the BCs and oxidation states is not trivial, a recent work by Posysaev et al. provides hints for this based on large data set analysis, using AFLOW database and machine learning algorithm. By analyzing a large number of binary oxide systems, the Authors concluded that there are certain BC intervals which define different oxidation states. Even though they did not find strict correlations for Fe$_x$O$_y$ binaries, our analysis of their data (Figure 10 in Ref. 30) indicates such correlations. The only single-valence iron oxide compound consisting of Fe$^{2+}$ ions is FeO (wüstite). This compound is (most probably – no AFLOW compound number provided) marked by a cross in the figure and represents the BC value of 1.38e. The single valence Fe$^{3+}$-based iron oxide compounds, such as α-Fe$_2$O$_3$ (hematite), are characterized by BCs that fall into an interval 1.43–1.84e. Mixed valency compounds “65338” and “98086” (the names correspond to the numbers in the AFLOW database) represent Fe$_3$O$_4$ (magnetite), which hosts a mixture of Fe$^{2+}$ and Fe$^{3+}$ ions. These compounds have ions with BC values below 1.38e and ions with BCs higher than 1.43e. Compound “87697” is also Fe$_3$O$_4$, but prepared at high pressures. Such pressure could results in the formation of a compound with the same crystal structure, but with Fe$^{3+}$ ions only (maghemite). That is why all the ions in this compound have BCs larger than 1.43e. Based on this analysis, one may conclude that a BC of less than 1.38e corresponds to the oxidation state 2+ (or lower), while the BC value that fall into an interval 1.43–1.84e indicates the presence of Fe$^{3+}$ ions. Adopting this interpretation to our results brings the conclusion, that the Fe atoms located at the interface with Ru are in the 2+ oxidation state (as they bear an 0.91e BC), while the atoms in the topmost Fe layer are in the 3+ oxidation state (with a charge of 1.83e falling into the 1.43–1.84e interval). The Authors of Ref. 30 also provide a general “rule of thumb” according to which the cations of the same element in binaries are in different oxidation state, if the maximal BC difference is more than 0.1e (which again supports our interpretation). Another rule applies to oxygen: if the BC falls into the interval 0.53–2.00e, then the oxygen is in the -2 oxidation state. Therefore, we may conclude that the oxygen atoms in both layers of our FeO film are in the -2 valence state (bearing BCs of 1.39 and 1.14e for
the top and bottom layers, respectively). For the reduced phase, i.e. Fe₂O, the BCs on Fe atoms in top and bottom layers are 0.64 and 0.96e, indicating that they are all in the 2+ oxidation states.

In order to gain insight into the DOS of Fe 3p orbitals of FeO and Fe₂O, and correlate it with the Fe 3p XPEEM and XPS spectra obtained experimentally, we performed core-level DFT calculations using a full-electron code. As can be seen from Figure 4(b), the Fe 3p states of the Fe₂O phase are more widely spaced and shifted towards lower binding energies compared to those of FeO (denoted as “Fe₂O₄” in the figure), which is in agreement with the experimental observations. The Fe 3p spectra of both structures consist of superimposed contributions originating from Fe atoms in both layers, i.e. top and bottom. Each Fe site provides six 3p states the configuration of which depends, inter alia, on spin-orbit coupling and spin polarization (see Figure S4). The chemical shift of the 3p states results from charge redistribution caused by the rearrangement of chemical bonds (reduction of iron oxide). The calculates magnetic moments and Mulliken charges on atoms are presented in Table S2 and reveal that the most significant changes are observed for the outer (top) iron layer. Moreover, the decrease in the value of the spin magnetic moment from -4.21 to -3.55 µB on Fe_top atoms causes a narrowing of the 3p spectrum. On the other hand, the decrease in the positive charge (from +0.96 to +0.39) leads to a shift of the spectrum towards lower binding energies, which in turn provides a route to widening of the total Fe 3p spectrum (Fe_top+Fe_bottom). The widening and shift in the Fe 3p spectra between Fe₂O and FeO is, thus, a consequence of the changes in charges, magnetic moments and DOS. Notably, the changes in Mulliken charges follow the trend seen in Bader analysis.

In summary, we have shown that UHV annealing is an efficient method for fine-tuning the structure of ultrathin FeO islands on Ru(0001): the average island size, perimeter length, number of internal defect and the stoichiometry of the oxide phase. These parameters are particularly important from the point of view of catalytic reactions over oxide-on-metal (“inverse”) catalysts, as shown in numerous published works. The morphological changes occurring during the annealing follow the Ostwald ripening mechanism, i.e. decomposition of smaller islands, diffusion of the material across the surface and feeding the larger ones. The process, shown here in real-time with in situ low energy electron microscopy, was not observed for an oxide-on-metal system so far. Annealing leads to irreversible morphological changes (formation of large islands instead of well-dispersed smaller ones) and, unfortunately, also to phase transition (FeO-to-Fe₂O). The latter could be, however, potentially reversed through reoxidation (regaining the FeO stoichiometry, while preserving the new morphology). Thus, the results not only contribute to the understanding of surface phenomena occurring on oxide-on-metal system, but also allow fine-tuning of their structure.

Experimental and computational methods

The experiments were performed in two different UHV chambers with base pressures in the 10⁻¹⁰ mbar range. The chambers were equipped with sample preparation (Ar sputter guns, e-beam heating stages, Fe evaporators, O₂ lines) and characterization facilities (STM/STS and LEED
in one chamber, LEEM/XPEEM and XPS with synchrotron radiation in the other (beamline UE49 SMART at BESSY II)). Ru(0001) single crystal was cleaned by repeated cycles of Ar\(^+\) sputtering, annealing in O\(_2\) and in UHV. Ultrathin FeO islands were grown by Fe deposition at room temperature and post-oxidation. The islands were annealed in UHV, with the monitored using infrared pyrometers. The structural changes were studied \textit{in situ} with LEEM and \textit{ex situ} using STM/STS, LEED, XPEEM and XPS.

Theoretical calculations on the structure of FeO and Fe\(_2\)O films were performed using spin-dependent DFT, as implemented in the Vienna ab initio simulation package (VASP).\(^{34-36}\) A 3×3 surface unit cell, projector-augmented-wave (PAW) potentials,\(^{37,38}\) spin-polarized generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional\(^{39}\) and Hubbard U correction were applied.\(^{40}\) The electron charges on atoms were determined using Bader analysis.\(^{41,42}\) Simulations of Fe 3p electronic states, magnetic moments and Mulliken charges on atoms were performed using a full-potential local-orbital scheme code (FPLO version 18.00-52).\(^{43}\) The relaxed geometries obtained from VASP constituted an input for FPLO18, while the use of a full-electron code allowed going beyond the limitations of VASP in describing the electronic core-levels. Detailed description of experimental and computational methods is provided in the Supporting Information file.

**Supporting Information**

Movie showing the structural transformation in real time (published online), detailed description of experimental and computational methods, additional STM images with height profiles taken over FeO and Fe\(_2\)O islands, XPS Fe 3p and 2p spectra, Fe:O ratios determined from XPS results, differently-stacked Fe\(_2\)O structures obtained from DFT calculations, calculated DOS of Fe 3p orbitals in FeO and Fe\(_2\)O structures, work function values, magnetic moments and Mulliken charges.

**Notes**

The results were partially presented at the NANOTECH Poland 2017 and 2018 conferences (Poznań, Poland), the Physics of Magnetism 2017 conference (Poznań, Poland) and DPG Berlin 2018 conference (Berlin, Germany).

The authors declare no competing financial interests.

**Acknowledgments**

The studies were financially supported by the National Science Centre of Poland (until 2017 through the SONATA 3 project No. 2012/05/D/ST3/02855 – granted to M.L. – and from 2017 to 2019 through the PRELUDIUM 11 project No. 2016/21/N/ST4/00302 – granted to N.M.) and the
Foundation for Polish Science (from 2019, through the First TEAM/2016-2/14 (POIR.04.04.00-00-28CE/16-00) project “Multifunctional ultrathin Fe(x)O(y), Fe(x)S(y) and Fe(x)N(y) films with unique electronic, catalytic and magnetic properties” co-financed by the European Union under the European Regional Development Fund – granted to M.L.). The authors thank the Helmholtz-Zentrum-Berlin for the allocation of a synchrotron radiation beamtime, as well as Gina Peschel and Feng Xiong for their assistance during the measurements. T.O. and A.K. acknowledge the computer time granted by the ICM of the Warsaw University (projects GB77-16 and GB82-9). The calculations performed by M.W. were partially carried out using the computational resources provided by the Poznań Supercomputing and Networking Center (PSNC).

References

1. Liu, L. & Corma, A. Metal Catalysts for Heterogeneous Catalysis: FromSingle Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **118**, 4981 (2018).

2. Munnik, P., de Jongh, P. E. & de Jong, K. P. Recent Developments in the Synthesis of Supported Catalysts. *Chem. Rev.* **115**, 6687–6718 (2015).

3. Rodríguez, J. A. *et al.* Inverse Oxide/Metal Catalysts in Fundamental Studies and Practical Applications: A Perspective of Recent Developments. *J. Phys. Chem. Lett.* **7**, 2627–2639 (2016).

4. Tauster, S. J., Fung, S. C. & Garten, R. L. Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide. *J. Am. Chem. Soc.* **100**, 170–175 (1978).

5. Qin, Z.-H., Lewandowski, M., Sun, Y.-N., Shaikhutdinov, S. & Freund, H.-J. Encapsulation of Pt nanoparticles as a result of strong metal-support interaction with Fe<inf>3</inf>O<inf>4</inf>(111). *J. Phys. Chem. C* **112**, (2008).

6. Lewandowski, M., Sun, Y. N., Qin, Z.-H., Shaikhutdinov, S. & Freund, H.-J. Promotional effect of metal encapsulation on reactivity of iron oxide supported Pt catalysts. *Appl. Catal. A Gen.* **391**, (2011).

7. Ni, B. & Wang, X. Face the Edges: Catalytic Active Sites of Nanomaterials. *Adv. Sci.* **2**, 1500085 (2015).

8. Hansen, T. W., DeLaRiva, A. T., Challa, S. R. & Datye, A. K. Sintering of Catalytic Nanoparticles: Particle Migration or Ostwald Ripening? *Acc. Chem. Res.* **46**, 1720–1730 (2013).

9. Freund, H.-J. J. Model Studies in Heterogeneous Catalysis. *Chem. - A Eur. J.* **16**, 9384–9397 (2010).

10. Sun, Y.-N. *et al.* Monolayer iron oxide film on platinum promotes low temperature CO oxidation. *J. Catal.* **266**, (2009).

11. Giordano, L. *et al.* Oxygen-induced transformations of an FeO(111) film on Pt(111): A combined DFT and STM study. *J. Phys. Chem. C* **114**, (2010).

12. Martynova, Y., Shaikhutdinov, S. & Freund, H.-J. CO Oxidation on Metal-Supported Ultrathin Oxide Films: What Makes Them Active? *ChemCatChem* **5**, 2162–2166 (2013).
13. Liu, Y. et al. Enhanced oxidation resistance of active nanostructures via dynamic size effect. *Nat. Commun.* **8**, 14459 (2017).
14. Zhang, K. et al. Size effect in two-dimensional oxide-on-metal catalysts of CO oxidation and its connection to oxygen bonding: An experimental and theoretical approach. *J. Catal.* **393**, 100–106 (2021).
15. Zhang, K., Li, L., Shaikhutdinov, S. & Freund, H.-J. Carbon Monoxide Oxidation on Metal-Supported Monolayer Oxide Films: Establishing Which Interface is Active. *Angew. Chemie Int. Ed.* **57**, 1261–1265 (2018).
16. Voorhees, P. W. The theory of Ostwald ripening. *J. Stat. Phys.* **38**, 231–252 (1985).
17. Wang, Y. et al. Reversible and irreversible structural changes in FeO/Ru(0 0 0 1) model catalyst subjected to atomic oxygen. *Appl. Surf. Sci.* **528**, 146032 (2020).
18. Yang, H. G. & Zeng, H. C. Preparation of hollow anatase TiO2 nanospheres via Ostwald ripening. *J. Phys. Chem. B* **108**, 3492–3495 (2004).
19. Tong, Y. et al. Growth of ZnO nanostructures with different morphologies by using hydrothermal technique. *J. Phys. Chem. B* **110**, 20263–20267 (2006).
20. Ketteler, G. & Ranke, W. Heteroepitaxial growth and nucleation of iron oxide films on Ru(0001). *J. Phys. Chem. B* **107**, 4320–4333 (2003).
21. Palacio, I., Monti, M., Marco, J. F., McCarty, K. F. & De La Figuera, J. Initial stages of FeO growth on Ru(0001). *J. Phys. Condens. Matter* **25**, 484001 (2013).
22. Fu, Q. et al. Interface-Confined Ferrous Centers for Catalytic Oxidation. *Science* (80-. ). **328**, 1141–1144 (2010).
23. Zeuthen, H. et al. Unraveling the Edge Structures of Platinum(111)-Supported Ultrathin FeO Islands: The Influence of Oxidation State. *ACS Nano* **9**, 573–583 (2015).
24. Michalak, N. et al. Symmetry-induced structuring of ultrathin FeO and Fe3 O4 films on Pt(111) and Ru(0001). *Nanomaterials* **8**, 719 (2018).
25. Kostov, K. L. et al. Observation of a novel high density 3O(2 × 2) structure on Ru(001). *J. Phys. Chem. B* **107**, L138–L144 (1997).
26. Yamashita, T. & Hayes, P. Analysis of XPS spectra of Fe2+ and Fe3+ ions in oxide materials. *Appl. Surf. Sci.* **254**, 2441–2449 (2008).
27. Giordano, L. et al. Interplay between structural, magnetic, and electronic properties in a Fe O/Pt ( 111 ) ultrathin film. *Phys. Rev. B* **76**, 075416 (2007).
28. Ossowski, T., Wang, Y., Kiejna, A., Lewandowski, M. (in preparation).
29. AFLOW. Available at: http://www.aflowlib.org/.
30. Posysaev, S., Miroshnichenko, O., Alatalo, M., Le, D. & Rahman, T. S. Oxidation states of binary oxides from data analytics of the electronic structure. *Comput. Mater. Sci.* **161**, 403–414 (2019).
31. Han, Y., Han, J., Choi, H. J., Shin, H.-J. & Hong, J. Microscopic and electronic roles of B in CoFeB-based magnetic tunnel junctions. *J. Mater. Chem.* **21**, 14967 (2011).
32. Bansmann, J., Lu, L., Meiwes-Broer, K. H., Schlathölter, T. & Braun, J. Relationship between magnetic circular and linear dichroism in photoemission from Fe 3 p core level: An experimental and theoretical investigation. *Phys. Rev. B* **60**, 13860–13868 (1999).

33. Pronin, I. I. *et al.* Magnetic ordering of the Fe/Si interface and its initial formation. *J. Appl. Phys.* **104**, 104914 (2008).

34. Kresse & Hafner. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B. Condens. Matter* **48**, 13115–13118 (1993).

35. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).

36. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).

37. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).

38. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).

39. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).

40. Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J. & Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **57**, 1505–1509 (1998).

41. Bader, R. F. W. *Atoms in molecules : a quantum theory.*

42. Henkelman, G., Arnaldsson, A. & Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **36**, 354–360 (2006).

43. Köpfernik, K. & Eschrig, H. Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme. *Phys. Rev. B* **59**, 1743–1757 (1999).
Supporting Information

Detailed description of experimental and computational methods

The experiments were performed in two different UHV chambers with base pressures in the $10^{-10}$ mbar range. Both chambers were equipped with in situ sample preparation (Ar sputter guns, e-beam heating stages, Fe evaporators, O$_2$ lines) and characterization facilities. One chamber (located in Poznań, Poland) was hosting STM and LEED (both from Omicron), while the other (located at the BESSY II synchrotron light source in Berlin, Germany) was equipped with a LEEM instrument allowing, in addition to basic imaging, recording μLEED patterns, as well as XPEEM images and XPS spectra using synchrotron light (beamline UE49 SMART). The Ru(0001) single crystal (purity ≥ 99.99%; from MaTeck) was cleaned by repeated cycles of Ar$^+$ (99.999%; Messer) sputtering followed by annealing in O$_2$ at 1000 K and at 1450 K in UHV. Fe was deposited from a 2 mm rod (99.999%; Alfa Aesar) using an electron beam evaporator and oxidized in $1 \times 10^{-6}$ mbar O$_2$ (>99.995%, Linde gas). The cleanliness of the crystals and the formation of well-ordered iron oxide films were confirmed by STM and LEED (in Poznań), as well as LEEM and μLEED (in Berlin). The samples were annealed in UHV at 950 (Poznań) and 1050 K (Berlin), with the temperature monitored using infrared pyrometers (LumaSense). The STM images were recorded at room temperature, in constant current mode, using electrochemically etched W tips. The images were processed using Gwydion computer software. The STS curves were collected using the lock-in technique (oscillation frequency: 6777 Hz, amplitude: 40 mV). XPEEM and XPS curves were recorded using photon energies of 120 (for recording Fe 3p spectra), 600 (O 1s) and 780 (Fe 2p) eV. The spectra were calibrated based on the position of the valence band, by taking into account the parameters of the spectrometer and the mutual position of the signals. The XPS results were analyzed using CasaXPS (Casa Software Ltd.) software. Shirley background subtraction and Gaussian-Lorentzian lineshape were used for the analysis. For presentation, all XPS and XPEEM spectra were normalized, with XPEEM spectra being additionally smoothed.

The theoretical calculations on the structure of FeO and Fe$_2$O films on Ru(0001) were performed using spin-dependent DFT, as implemented in the Vienna ab initio simulation package (VASP). The electron ion-core interactions were represented by the projector-augmented-wave (PAW) potentials. A plane wave basis set with a kinetic energy cutoff of 500 eV was applied. The exchange-correlation energy was treated at the spin-polarized generalized gradient approximation (GGA) level using the Perdew-Burke-Ernzerhof (PBE) functional. The realistic description of electronic structure of FeO requires consideration of strong correlations of Fe 3d electrons. This was realized by the Hubbard U correction within the rotationally invariant approach of Dudarev et al., with the effective parameter $U_{eff} = 4$ eV. The Brillouin zone was sampled using Γ-centered k-point meshes of 24×24×16 for bulk hcp Ru calculations. A Fermi surface broadening of 0.2 eV was applied to improve convergence of the solutions using the second order Methfessel-Paxton method. The calculated lattice constant of rock-salt FeO, 4.35 Å, is in agreement with
other theoretical calculations (4.35 Å$^9$), as well as experimental observations (4.35 Å$^{10}$). Analysis of the magnetic structure shows that the oxide is antiferromagnetic in the [111] direction, with a magnetic moment per Fe atom of 3.69 μB (which fits reasonably well the value determined experimentally at 4.2 K by the Author of Ref. $^{11}$, i.e. 3.32 μB). The calculated lattice parameters of bulk hcp ruthenium, a = 2.73 Å and c/a = 1.58, also agree with the published experimental data (a = 2.71 Å and c/a = 1.58).$^{12}$ Ru(0001) surface was modelled by an asymmetric slab consisting of five atomic layers and a 3×3 surface unit cell. The two bottom layers were frozen in their bulk positions, while the atomic positions of the remaining atoms were optimized until the residual Hellman-Feynman forces on atoms were smaller than 0.01 eV/Å. Iron oxide adlayers were placed on top of the substrate in fcc, top and hcp geometries, which aimed in reproduction of the three high-symmetry regions of the FeO/Ru(0001) Moiré supercell. The 3×3 surface unit cell is a good approximation, however, it requires to fit one geometry (FeO) to the other (Ru). From calculations, the interatomic distances within the iron and oxygen planes in FeO(111) equal to about 3.07 Å and in the Ru(0001) to about 2.73 Å. Thus, adjusting the structures requires either to compress the oxide or expand the substrate by about 10%. In order to get reliable results, two sets of calculations were performed: with the FeO (Fe$_2$O) lattice constant compressed to the one of Ru(0001) and with the Ru(0001) lattice constant expanded the meet the one of FeO. The electron charges on atoms were determined using the Bader analysis.$^{13,14}$ Simulations of Fe 3p electronic states were performed using a full-potential local-orbital scheme code (FPLO version 18.00-52).$^{15}$ The relaxed geometries obtained from VASP constituted an input for FPLO18, while the use of a full-electron code allowed going beyond the limitations of VASP in describing the electronic core-levels. The calculations were carried out with a spin-polarized fully relativistic approach (including spin-orbit coupling). For the exchange-correlation potential, GGA with PBE parameterization was used. The fully localized limit of the GGA+U (actually, local spin density approximation – LSDA+U) functional,$^{16}$ with the Hubbard U repulsion set to 0, 2 or 4 eV for Fe 3d orbitals, was used. An antiparallel configuration of magnetic moments on the two (top and bottom) Fe layers was assumed. The k-meshes equaled to 20×20×4 and the energy convergence criterion was set to 2.72×10$^{-5}$ eV (10$^{-6}$ Hartree). From the calculations, the density of states (DOS) of Fe 3p orbitals, the magnetic moments on iron atoms and the Mulliken charges on Fe and O atoms were determined.
Additional data

Figure S1. STM images of (a) pristine FeO/Ru(0001) and (b) the system after annealing at 950 K in UHV for 10 min. (c) shows height profiles drawn over iron oxide islands in (a) and (b) (the colors of the lines correspond to the colors of arrows on STM images). STM: $V_{\text{sample}} = +1.0 \text{ V}$; $I_t = 0.7 \text{ nA}$; Image sizes: $200 \times 200 \text{ nm}^2$.

Figure S2. XPS (a) Fe 3p and (b) Fe 2p spectra obtained for pristine FeO/Ru(0001) (black symbols), as well as the system after (red) brief and (blue) prolonged annealing at 1050 K in UHV. (c) shows the Fe-to-O ratios determined from Fe 3p and O 1s (not shown) XPS spectra obtained for pristine and annealed samples by taking the atomic sensitivity factors and local iron oxide coverage fluctuations into account.
Figure S3. Theoretically calculated structures of differently stacked iron oxide films with Fe$_2$O stoichiometry adsorbed on Ru(0001). The calculations were performed for the iron oxide adopting the lattice constant of the ruthenium substrate. Gold spheres represent Fe atoms, red O atoms and silver Ru atoms. All the layers were found to be uncorrugated after the relaxation. The total energy values are referred to the most stable system (fcc Fe-O-Fe/Ru). The distances are given in Å. The step heights range from 5.05 to 5.78 Å. The lowest heights are observed for systems with Fe-O-Fe/Ru stacking, which is the natural stacking of FeO. For O-Fe-Fe/Ru and Fe-Fe-O/Ru layers
arrangement, the step heights are larger by more than 0.2 Å. Analysis of the stability of Fe₂O layers on Ru(0001) shows that the system with oxygen atoms at the interface is energetically unfavored. It could be the case when two layers of Fe are adsorbed on an O precovered Ru(0001). The total energy of such configuration is by few eV higher than the one of the most stable configuration. The Fe-O-Fe/Ru and O-Fe-Fe/Ru stackings are very close in the total energy values. The latter can be considered as a monolayer of O adsorbed on two monolayers of Fe on Ru(0001).

Figure S4. Theoretically calculated structures of Fe-O-Fe stacks adsorbed at different high-symmetry sites (top, fcc, hcp) of the Ru(0001) substrate. The calculations were performed for the ruthenium substrate adopting the lattice constant of iron monoxide (FeO). Gold spheres represent Fe atoms, red O atoms and silver Ru atoms. All the layers were found to be uncorrugated after the relaxation. The total energy values are referred to the most stable system (fcc). The distances are given in Å. The step heights obtained for the fcc and hcp regions are roughly 0.5 Å lower compared to those obtained for the iron oxide adopting the lattice constant of the ruthenium substrate, while the one calculated for the top region is by approx. 0.2 Å lower (compared with Figure S1).
Figure S5. DOS of Fe 3p orbitals as a function of on-site repulsion $U_{3d}$ calculated for FeO/Ru and Fe$_2$O/Ru structures.
Figure S6. Spin-polarized DOS of Fe 3p orbitals calculated for (a) bilayer FeO/Ru (denoted as “Fe$_2$O$_2$” in the figure) and (b) Fe$_2$O/Ru structures.

Table S1. Calculated work function values of Fe$_2$O films with different layers stacking adsorbed on Ru(0001).

| Stacking | Fe-O-Fe-Ru | Fe-Fe-O-Ru | O-Fe-Fe-Ru |
|----------|------------|------------|------------|
| fcc      | 4.65       | 4.89       | 7.65       |
| hcp      | 4.47       | 4.35       | 7.67       |
| top      | 4.64       | 4.46       | 7.77       |

Table S2. Spin ($m_s$) and orbital ($m_l$) magnetic moments, as well as Mulliken atomic charges calculated for bilayer FeO/Ru and Fe$_2$O/Ru structures with an antiparallel configuration of magnetic moments on the two (top and bottom) Fe layers. The calculations were carried out using...
the FPLO18 code in a fully relativistic approach, with PBE+U (U(Fe 3d) = 4 eV) and for the quantization axis [001].

|                | FeO/Ru (pristine) | Fe2O/Ru (growing) |
|----------------|-------------------|-------------------|
|                | \(m_s (\mu_B)\) | \(m_l (\mu_B)\) | charge | \(m_s (\mu_B)\) | \(m_l (\mu_B)\) | Charge |
| Fe bottom      | 4.00              | 0.09              | +0.58  | 3.77              | 0.07              | +0.46  |
| O middle       | 0.05              | 0.00              | -0.87  | 0.04              | 0.00              | -0.84  |
| Fe top         | -4.21             | -0.06             | +0.96  | -3.55             | -0.20             | +0.39  |
| O top          | -0.31             | 0.00              | -0.63  |                   |                   |        |

**References**

1. Kresse & Hafner. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B. Condens. Matter* **48**, 13115–13118 (1993).
2. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
3. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
4. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
5. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
6. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
7. Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J. & Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **57**, 1505–1509 (1998).
8. Methfessel, M. & Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **40**, 3616–3621 (1989).
9. Wdowik, U. D., Piekarz, P., Jochym, P. T., Parlinski, K. & Oleś, A. M. Influence of isolated and clustered defects on electronic and dielectric properties of wüstite. *Phys. Rev. B* **91**, 195111 (2015).
10. Roth, W. L. Defects in the crystal and magnetic structures of ferrous oxide. *Acta Crystallogr.* **13**, 140–149 (1960).
11. Roth, W. L. Magnetic Structures of MnO, FeO, CoO, and NiO. *Phys. Rev.* **110**, 1333–1341 (1958).
12. Haynes, W. M. *CRC handbook of chemistry and physics : a ready-reference book of*
chemical and physical data. (CRC, 2012).

13. Bader, R. F. W. *Atoms in molecules: a quantum theory*.

14. Henkelman, G., Arnaldsson, A. & Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **36**, 354–360 (2006).

15. Koepernik, K. & Eschrig, H. Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme. *Phys. Rev. B* **59**, 1743–1757 (1999).

16. Czyżyk, M. T. & Sawatzky, G. A. Local-density functional and on-site correlations: The electronic structure of La$_2$CuO$_4$ and LaCuO$_3$. *Phys. Rev. B* **49**, 14211–14228 (1994).