Structural and electronic properties of Fe dopants in cobalt oxide nanoislands on Au(111) ³

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Jonathan Rodríguez-Fernández 🔟, Zhaozong Sun, Liang Zhang, Ting Tan, Anthony Curto ២, Jakob Fester, Aleksandra Vojvodic ២, and Jeppe V. Lauritsen ២

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Jonathan Rodríguez-Fernández,^{1,a)} D Zhaozong Sun,^{1,a)} Liang Zhang,² Ting Tan,² Anthony Curto,² Jakob Fester,¹ Aleksandra Vojvodic,^{2,b)} and Jeppe V. Lauritsen^{1,b)}

AFFILIATIONS

¹ Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark ² Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

^{a)}J. Rodríguez-Fernández and Z. Sun contributed equally to this work. ^{b)}Authors to whom correspondence should be addressed: jvang@inano.au.dk and alevoj@seas.upenn.edu

ABSTRACT

Mixed metal oxides of earth-abundant 3*d* transition metals are an interesting class of materials that show interesting magnetic properties and a significant synergistic effect as catalysts for electrochemical oxygen evolution compared to simple unary oxides. However, the exact atomic-scale nature of such mixed oxide phases and the link to their interesting physico-chemical properties are poorly understood. Here, a combination of scanning tunneling microscopy and x-ray photoemission spectroscopy reveals that Fe species embed in a facile way into CoO bilayers on Au(111) resulting in an Fe doped oxide. Density functional theory and the spectroscopic fingerprint from x-ray photoemission spectroscopy reveal that the Fe dopants in the cobalt oxide matrix assume a higher oxidation state than in the structurally corresponding unary bilayer oxide. Furthermore, the substituted Fe is structurally displaced further away from the Au than the metal in either of the corresponding pure unary oxides. Both O and to a smaller extent Co in the nearest coordination shell are also structurally and electronically perturbed. The interesting effects observed in the bilayer binary oxides may enable a better fundamental understanding of the nature of doping of metal oxides, in general, and promotion effects in catalytic applications.

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I. INTRODUCTION

Nanomaterials consisting of mixed oxides of 3*d* transition metals (Fe, Co, Ni, and Mn) exhibit very interesting physicochemical properties compared with the pure oxides.^{1–7} Recent reports have, for example, revealed a strong synergetic effect on the activity for the electrochemical oxygen evolution reaction (OER) when two metals are combined in binary oxides, e.g., FeNiO_x or FeCoO_x.^{8–14} The catalytically promoting effect of Fe was first discovered fortuitously as a result of Fe impurities in the electrolyte,¹⁵ but since then numerous mixed metal oxide phases and nanostructures have been investigated. The promotional effect is seen for unsupported mixed oxides, but recent studies have also shown that noble metal (e.g., Au) supported mixed oxides are promoted in the same way. It was recently shown that the Au support itself has a promoting effect, as it acts to stabilize Co oxide in the most active layered from as an oxyhydroxide phase,¹⁶ but the effect of Fe interaction with such layered Co oxide structures is at present unresolved. To shed light on this, we will here focus on the electronic and geometric properties of mixed Fe/Co oxide nanoislands on the Au support.^{10,17,18} It is generally hypothesized that Fe becomes embedded in the host metaloxide matrix; however, it is still an open question which type of atomic-scale site involving Fe, Co, or both metal atoms that leads to enhancement in catalytic activity.¹⁹ Both cobalt and iron can form different unary oxide phases, and when mixed together, several phases with different valences are possible, for example, spinel type CoFe₂O₄^{20,21} or mixed oxyhydroxides.^{22,23} For catalysis applications, previously proposed models for the active phase structure include structural effects, where bulk-like FeO_x and CoO_x phases interact directly or through the formation of composite nanostructures by surface/edge decoration, whereas other models consider Fe as a dopant (or promoter) directly substituted in the oxide.²⁴⁻²⁶ It is not currently clear whether both basal plane sites or the more directly accessible edge sites within the mixed platelet oxy-hydroxide nanostructures (CoOOH), which have been reported to develop under operating electrochemical conditions,²⁰ are expected to be affected. It is, however, clear that the presence of Fe promoted sites modifies the reactivity of the oxide towards different reactants, either in a direct way by interacting with the reactant or indirectly through the modification of the O or Co sites in the vicinity of the Fe dopant. Therefore, it is important to understand the chemical bonding nature surrounding the Fe sites within such mixed oxide phases, in order to enable the rational optimization of activity through the control of the mixed oxide nanostructures.^{19,27,28}

In this study, we use scanning tunneling microscopy (STM) to investigate the atomic-scale details of the Fe doped two-dimensional Co oxide phase that can be synthesized on a Au(111) surface. Metal oxide nanoislands of the pure metals (e.g., CoO_x or FeO_x) supported on noble metal surfaces have previously been extensively studied by us and others.²⁹⁻³⁷ In such studies, scanning tunneling microscopy (STM) has been an important technique to address the importance of heteroatoms, defects, cluster shapes, and adsorption, by imaging such materials directly on the atomic scale. Interesting catalytic properties pertaining to the bilayer oxides in contact with noble metal surfaces have been discovered.37-39 Specifically, improved OER activity has been reported to develop for unary oxides on Au.40-42 Here we find that mixed Fe doped Co oxide bilayers with a progressively varying concentration of Fe dopants may be formed starting from pristine CoO supported on Au(111). We show using Scanning Tunneling Microscopy (STM) that mixing preferentially leads to the incorporation of single Fe atoms substituted uniformly into the cobalt oxide host lattice. X-ray Photoelectron Spectroscopy (XPS) and Density Functional Theory (DFT) reveal that the single atom Fe sites influence the charge distribution on nearby oxygen atoms and distort the local geometry of the oxide matrix. Interestingly, we find that single atom Fe and the neighboring lattice O, and to small degree the nearest shell Co atoms, assume an oxidation state different from the ones in the corresponding pure unary oxides on Au(111).

II. EXPERIMENTAL

Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) measurements were carried out in a standard ultra-high vacuum (UHV) chamber, with a base pressure less than 1×10^{-10} mbar. Single Au(111) crystals were cleaned by standard repeated cycles of Ar⁺ ion sputtering for 30 min followed by annealing to 800 K for another 15 min. The UHV chamber has an Aarhus type STM. The STM images were acquired with a W tip at room temperature. The photoemission spectra were recorded using a hemisphere analyzer (SPECS Phoibos 100) with an Al K α X-ray source (SPECS XR50). Cobalt (purity 99.9%) and iron metals (purity 99.99%) (from



GoodFellow) were sublimated from an electron-beam evaporator with 4 pockets (Oxford Applied Research, EGCO4) using metals rods. The Au 4f, Co 2p, Fe 2p, and O 1s XP spectra were recorded at normal emission and at a photon energy of 1486.6 eV (Al K α X-ray source). The energy scale for all spectra is calibrated to Au4f_{7/2} = 83.98 eV. In the case of the O 1s, a polynomial background was used to subtract the background. For the rest of the peaks, a Shirley background was used. The different synthesis procedures have been described in Sec. III.

Spin polarized density functional theory calculations with Hubbard-U correction (DFT + U)⁴³ were performed using the implementation in the Vienna ab initio Simulation Package (VASP).44,45 Similar to previous studies, an effective Hubbard-U of 1 eV and 4.3 eV was applied to the d electrons of Co and Fe, respectively.^{30,46} Core electrons were described using the projector-augmented wave (PAW) method.47 Kohn-Sham single electron wave functions were expanded in a plane-wave basis with a kinetic energy cutoff of 500 eV to describe the valence electrons. The exchange-correlation energy was evaluated by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.⁴⁸ The basal planes of the Au supported CoO, FeO, and Fe–CoO nano-island were modeled using a $p(5 \times 5)$ unit with the metal-oxide layer placed in a FCC, HCP, and on top stacking relative to a commensurate 3-layer Au(111) lattice. A vacuum of 14 Å was added to all models to avoid the interaction between periodic images. A gamma-point sampling of the Brillouin zone was used. The bottom two Au(111) layers were kept frozen, while the metal oxide bilayer and the topmost Au(111) layer were set free to relax. Geometries were considered optimized when the force on each atom was <0.02 eV/Å.

III. RESULTS AND DISCUSSION

Figure 1(a) illustrates an STM image of a pristine cobalt oxide nanoisland grown on Au(111), which serves as the starting point in our synthesis of mixed oxides. The Co–O islands are grown by a pre-oxidation step consisting of reactive



FIG. 1. STM images of (a) a well-ordered pure unary Co–O bilayer nanoisland and (b) a mixed $Fe_xCo_{1-x}O(x \sim 0.1)$ nanoisland on Au(111). The bright lines crossing the bilayer island basal plane are oxygen ad-atom line defects.

physical vapor deposition of Co at 380 K in O₂ [p(O₂) = 10^{-6} mbar] and subsequent crystallization of the pre-oxidized Co in the same O₂ atmosphere at 523 K, as we reported in Ref. 46. The resulting cobalt oxide islands adopt a distorted rock-salt structure and consist of one Co-O bilayer terminated with the CoO(111) facet in parallel with the substrate and with the Co atoms forming a direct bond with the Au support. The bilayered nanoislands can readily be converted at slightly elevated O₂ pressures into hydroxylated O-Co-O trilayers, strongly resembling the cobalt oxyhydroxide phase.^{29,46} The bright lines crossing the basal planes of the nanoislands in Fig. 1(a) are well-known stacking fault lines of the O sublattice in the bilayer island reflecting the incorporation of excess oxygen.^{31,49}

We explored different synthesis procedures involving either Fe and Co co-deposition or post-deposition of Fe that all lead to Fe incorporation. More specifically, the formation of single-atom Fe species uniformly distributed in the CoO host oxide resulted from evaporating metal Fe onto the surface right after the formation of the pre-oxidized Co at 380 K, and subsequently crystallizing the structures by oxidation in O_2 at 523 K. The resulting crystalline islands in Fig. 1(b) retain the bilayer morphology known for both CoO⁴⁶ and FeO⁵⁰ on Au(111), respectively, but they now reflect a mixed bilayer, which we denote $Fe_xCo_{1-x}O$. The Fe fraction relative to the total metal content (denoted x) in the CoO nanoislands is readily quantified as the Fe sites are associated with perturbed contrast on the island basal plane in the STM images in Fig. 1(b) (further discussed below). We find that bilayers exhibiting a metal-oxide solid solution with a rather high Fe content of up to $x \sim 0.4$ could be formed, whereas higher Fe:Co ratios lead to phase segregation and formation of pure FeO islands as observed in STM. The original hexagonal shape of the pure unary CoO nanoislands is preserved upon Fe-modification, as

is the presence and appearance of oxygen line defects on the basal plane indicated by the bright lines crossing the island in both Figs. 1(a) and 1(b).

Before we discuss the atomistic structure details observed in STM images further, we present XPS data that confirm the formation of a mixed $Fe_xCo_{1-x}O$ phase and reveal the oxidation states of Fe and Co in the mixed-metal oxide. The lab-source XPS and STM data were recorded on a combined experimental setup allowing for reliable, consecutive characterization of the same samples. The first four XPS spectra in Fig. 2(a) compare the Co 2p contributions for metallic Co, CoO bilayers, and a low (x \approx 0.1) and high (x \approx 0.35) concentration of Fe in the $\mbox{Fe}_x\mbox{Co}_{1-x}\mbox{O}$ bilayers, all supported on Au(111). For pure bilayer CoO, the Co^{2+} state is reflected by a Co $2p_{3/2}$ and Co $2p_{1/2}$ doublet peak, with relatively broad components each shifted 0.5 eV from Co⁰, and characteristic satellites located at higher binding energies relative to the doublet components, in good agreement with previous studies.⁴⁶ Based on the Co2p XPS peak, core level shift of the Au4f⁴⁶ and DFT modelling,³¹ it was previously concluded that significant charge transfer takes place from the Au to the CoO layers. Upon formation of the Fe_xCo_{1-x}O bilayers with a low Fe content (x \sim 0.1), a 0.4 eV shift to higher binding energies of each of the Co 2p doublet peaks is observed together with a slight broadening of each peak. This trend is further enhanced for a higher Fe content (x \sim 0.35), where the peaks are shifted by 1 eV to higher binding energy relative to pure CoO. The characteristic shake-up satellites located at 787 eV from the main Co 2p_{3/2} peak indicates that cobalt is still in an oxidation state of 2+, although the peak position is changed from pure CoO. We attribute the shift to the gradually increasing influence of oxidized Fe species in contact with the CoO as a function of concentration. The corresponding XPS spectra of the Fe 2p [Fig. 2(b)] show a comparison between metallic Fe,



FIG. 2. XPS data illustrating the Co2p, Fe2p, O1s region for bilayer nanoislands of pure CoO, pure FeO, and $Fe_xCo_{1-x}O$ with a low (x ~ 0.1) and a high (x ~ 0.35) concentration of Fe. The spectra denoted "CoO + Fe" reflect metallic Fe deposited directly on CoO.

pure FeO, and the high Fe concentration $Fe_xCo_{1-x}O$ (x ~ 0.35) bilayers on Au(111), respectively. For the pure FeO reference, we find that the Fe $2p_{3/2}$ peak is at $E_b = 709.1$ eV and has a characteristic satellite peak at a higher binding energy at ~714 eV, which is in good agreement with previous studies assigning the Fe to the 2+ oxidation state.^{36,51-53} For the $Fe_xCo_{1-x}O$ bilayer with x \sim 0.35, the Fe 2p_{3/2} peak is distinctly different, the peak position is shifted around 1.8 eV higher than $E_{\rm b}$ = 710.9 eV and the spacing to the shake-up satellite is extended to 6-7 eV. The shift in binding energy and the shake-up satellite indicates that the Fe dopant within the $Fe_xCo_{1-x}O$ adopts a higher oxidation state than that in pure FeO, approaching the binding energy of Fe³⁺.^{22,51,54} This is surprising since the local O coordination of Fe is the same as in the pure FeO bilayers on Au(111), where Fe is in the 2+ state expected for FeO. Further charge transfer from the Au to Fe evidently does not explain this shift to a higher oxidation state, so instead, we attribute this to intrinsic charge transfer effects induced by the formation of a new higher oxidized Fe species within the Fe_xCo_{1-x}O phase (more details below). The O 1s spectra [Fig. 2(c)] show that the O 1s peak of the $Fe_xCo_{1-x}O$ bilayer (x = 0.35) is broadened and with a peak position located between the two pure unary oxides.

In a separate experiment, we investigated metal Fe deposition directly on top of the hexagonal CoO islands [Fig. 1(a)] at room temperature, without subsequent oxidation. Surprisingly, Fe deposition led to direct substitution of Fe into the CoO, leading to the same type of bilayer $Fe_xCo_{1-x}O$ structures observed in STM as in Fig. 1(b). The XPS data for a high Fe concentration sample synthesized in this manner (denoted CoO + Fe) in Fig. 2(a) also show the direct incorporation of Fe in the high oxidation state as before, together with metal Fe^0 which reflect unreacted metallic Fe from deposition on Au. The Co 2p peak (CoO + Fe sample) shows a peak structure at the high binding energy consistent with the assignment Co^{2+} in the $\text{Fe}_x\text{Co}_{1-x}\text{O}$ phase, with an additional peak structure at the position of metallic Co^0 . This evidences a facile process where Fe spontaneously exchanges with Co in the oxide structure, indicating a strong driving force for the formation of the mixed $\text{Fe}_x\text{Co}_{1-x}\text{O}$ phase from pure CoO. A similar effect is seen for the incorporation of transition metals (Co, Ni, etc.) into $\text{Fe}_3\text{O}_4(001)$ surfaces.⁵⁵ In our case, the exchange may be explained by the stronger metal to lattice O bonds in the pure bulk FeO phase compared with the CoO phase, based on the enthalpies of formation of the bulk phases.⁵⁶

Our atom-resolved STM images of the Fe_xCo_{1-x}O bilayer nanoislands reveal that single Fe atoms are embedded into the CoO islands. Figure 3 illustrates high-resolution STM images of an Fe_xCo_{1-x}O sample with a low Fe concentration (x \sim 0.1), where the locations of the Fe dopants are atomically resolved in the hexagonal lattice that compose the basal plane. It is generally observed for STM imaging, and in particular for oxides, that the contrast may be dependent strongly on the STM-tip state since the STM image is a convolution between electronic and geometric structure that may also depend on the tip termination.^{31,55,57,58} Therefore, we show two representative STM images of the same sample using two different imaging modes [Figs. 3(a) and 3(b)]. While the basal plane in both images is resolved as a hexagonal lattice reflecting the structure of CoO, the symmetry and corrugation associated with the Fe dopants are significantly different. In Fig. 3(a), the signatures of the Fe dopants are imaged as triangular features with a lower overall corrugation than the surrounding lattice. In Fig. 3(b), on the other hand, the same Fe dopant structures are imaged with a six-fold lattice distortion (flower shape) with a corrugation that protrudes from the surrounding lattice. The example included in the supplementary material (Fig. S1)



FIG. 3. Atom-resolved STM images showing the basal plane with a low Fe concentration of the $Fe_xCo_{1-x}O$ bilayer nanoisland on Au(111). Two complementary STM images are shown reflecting resolution of (a) the O sublattice and (b) the metal lattice. (c) Ball model illustrating the atom registry associated with the oxygen adatom line defects seen in both STM images. (d) Zoomed-in STM image of the Fe defect reflecting metal sublattice imaging. (e) The proposed ball model of the Fe dopant embedded in CoO. Co: blue, nearest neighbor Co: light blue, Fe: brown, and red: oxygen. (f) Zoomed-in STM image of the Fe defect reflecting oxygen sublattice imaging. STM imaging parameters: [(a) and (f)]: $V_t = -0.34$ V, $I_t = -0.45$ nA and [(b) and (d)]: $V_t = -0.20 \text{ V}$, $I_t = -0.50 \text{ nA}$.

shows the same $Fe_xCo_{1-x}O$ island in consecutively acquired images where the resolution switches between the O or metal sublattices, and they confirm that the defect sites have the same location and origin in both imaging modes. For CoO and FeO bilayers, it was previously shown that the change in the STM contrast may invert such that the hexagonally resolved lattice reflects the O sublattice or the corresponding metal lattice in the bilayer structure, respectively.^{31,57,58} Also, it was observed that the incorporation of transition metals (Co, Ni, etc.) at the $Fe_3O_4(001)$ surface modifies the STM contrast of the neighboring Fe atoms and the electronic structure of the surface.55 These two imaging modes thus allow us to resolve the location of the atoms surrounding the Fe dopants in the STM. To illustrate this, Fig. 3(c) shows a structural model for the O adatom line defect loop, which is present as a triangular loop in both STM images in Figs. 3(a) and 3(b). The O adatom line defect is a stacking fault of the O sublattice, which shifts the registry of the O lattice inside the loop relative to the one outside the loop.³¹ The Co lattice remains the same, and consequently a registry shift is observed only if the O positions are imaged in the STM image. By superimposing lines on the STM images, we can conclude that the O lattice indeed shifts in Fig. 3(a), whereas no shift is present in Fig. 3(b). Consequently, the triangular Fe dopant structure arises when the O lattice is imaged, whereas the six-fold feature arises when the metal lattice is resolved.

Figure 3(e) illustrates a ball model of the atomic structure of a single Fe dopant site which is constructed to be consistent with the symmetries on the metal and O lattice in the STM data. The proposed configuration consists of a single Fe atom placed substitutionally on the Co sublattice of CoO. In this geometry, the Fe dopant has three direct nearest neighboring (NN) O atoms [light red in Fig. 3(f)] arranged in a three-fold symmetry and six NN Co atoms [light blue in Fig. 3(d)]. Other Fe dopant positions or agglomerates of Fe atoms would not be consistent with the symmetry and size of the Fe induced site seen with STM in Fig. 3. The STM data do not allow us to conclude on the vertical position of atoms relative to the substrate because the atomic contrast in the STM images reflects a convolution of geometric effects and electronic effects resulting from charge transfer. We therefore used density functional theory (DFT) modelling of the Fe dopants in a CoO bilayer, not only to resolve the structural and geometric properties of the dopants but also to gain electronic structure information associated with them.

The pure unary CoO bilayer has a lattice mismatch of around 13.9% relative to the Au(111),²⁹ resulting in an alternating stacking of the CoO layer relative to the underlying Au(111) substrate. As a consequence, Co atoms within the bilayer oxide will be gradually shifted between the FCC, HCP, and TOP positions relative to the underlying Au(111) lattice leading to a topographic modulation that is reflected by a large-scale (~37 \pm 2 Å periodic) moiré superlattice, which can be seen in STM [Figs. 1(a) and 1(b)]. This morphology difference can be modelled in our DFT study by shifting the stacking of the complete oxide film in the computational supercell (see Sec. II and Fig. S2) as previously done for pure CoO and FeO.^{32,46} We find

that Fe can occupy substitutional lattice sites within the supported CoO bilayer, with an almost equal preference for Fe to be doped at sites where the metal sublattice is in the FCC and HCP stacking (within 0.01 eV), whereas the TOP stacking is only slightly less stable by 0.17 eV. This small variation in the energetics suggests that all Fe-dopant positions are possible, which agrees well with the experiment. The calculated structural parameters for Fe doped CoO, and the pure FeO and CoO bilayer films in the FCC stacking on Au(111) are compared in Fig. 4. For all systems, the metal atoms of the oxide are positioned between the Au support and the O of the oxide lattice forming a direct metal to Au bond. For the pure unary CoO basal plane in the FCC stacking [Fig. 4(a)], the average height (z distance from the Au substrate) of Co and O atoms is 2.16 Å (indicated by blue dashed line) and 2.94 Å, respectively. For the Fe-doped CoO [Fig. 4(b)], the optimized position of the Fe dopant atom is 2.35 Å above the Au surface, which is 0.19 Å higher than the Co atoms in the pure CoO and 0.09 Å higher than the Fe in the pure FeO. The Fe dopant also slightly elevates the six 1NN Co atoms of the CoO host lattice by 0.08 Å relative to the Co atoms of the pure CoO. Meanwhile, the position of 1NN O atoms along the z direction is much less influenced (~ 0.02 Å). The local geometric modification induced by the Fe dopant gives rise to a significant decrease in the oxygen distance in the pyramid formed by the metal atom and the upper O layer (denoted by h in Fig. 4) in the mixed Fe-CoO bilayer (h = 0.61 Å), to be compared with the pure FeO (h = 0.78 Å) and CoO (h = 0.83 Å), while the direct metaloxygen bond (denoted d_{M-O} in Fig. 4) remains almost constant. At the same time, the opening angle to the O lattice (θ_{O-M-O}) is augmented from 104.1° in the pure CoO to 109.8° in the CoO nanoisland when iron is incorporated. The observed elevated Au-Fe distance and the compression of the pyramid result, on one hand, in a weaker Au-Fe interaction compared to the one between Fe in the pure FeO bilayer [Fig. 4(c)], and on the other hand in a larger overlap between the Fe 3d states and the 2p states of its 1st nearest neighbor (NN) O atoms. Taken together, this leads to a significant change in the oxidation state of both the Fe and the NN oxygen as shown in the following discussion.

Table I summarizes the DFT calculated valence charges of pure CoO, pure FeO, and Fe-doped CoO supported on Au(111), as obtained from Bader analysis using the valence electron charge density from the optimized structures. We find that only the nearest neighboring atoms in the vicinity of the Fe dopant are affected with the NN O being affected the most while the Co atoms are only perturbed in a minor fashion, whereas atoms further away from the dopant are not, in agreement with the STM result where only the nearest shell atoms show a different contrast. Table I shows that the Fe dopant in the Fe_xCo_{1-x}O bilayer is significantly more oxidized than Fe in the pure FeO, which is consistent with our XPS results pointing to a Fe³⁺ character (Fig. 2). As we discussed above, such an increase in the oxidation states is a consequence of the weaker Au-Fe interaction and the stronger Fe-O hybridization. Meanwhile, we find that the nearby Co atoms (NN Co) are less affected with a minor shift to a higher



FIG. 4. Geometric structure of the CoO₃ triangle pyramid in pure unary CoO (a), FeO₃ triangle pyramid around the Fe-dopant in the Fe-CoO (b) and in the pure unary FeO (c) with FCC stacking on Au(111). Red, brown, blue, and gold balls represent O, Fe, Co, and Au, respectively. The two Co atoms (b) represent the geometric information on the six 1NN Co atoms surrounding the Fe-dopant. The blue dashed line indicates the height of Co atoms of the CoO basal plane.

oxidation state compared to pure CoO, which is consistent with the broadening and small shift to higher binding energy of the Co 2p peak in XPS [Fig. 2(a)] as a function of Fe content.

Based on the deconvoluted analysis of the DFT calculated geometry of Fe-doped CoO and its corresponding charge analysis, we conclude that the flower-like signature observed in STM for the metal sublattice can thus be explained by a central bright Fe dopant and the surrounding six 1NN Co

TABLE I. Calculated Bader charges of pure unary CoO, pure unary FeO, and Fedoped CoO in unit of electron. Positive and negative numbers correspond to the specified atom donating or accepting valance electrons, respectively.

Structure	Stacking domain	Bader charges (e ⁻)		
		Fe	Со	О
CoO	FCC HCP TOP	N/A N/A N/A	+1.04 +1.03 +0.91	$-0.82 \\ -0.84 \\ -0.82$
FeO	FCC HCP TOP	+1.09 +1.03 +1.01	N/A N/A N/A	$-0.85 \\ -0.86 \\ -0.87$
Fe-CoO	FCC HCP TOP	+1.43 +1.43 +1.23	+1.06 ^a +1.03 ^a +0.94 ^a	$-0.94^{\rm b} \\ -1.01^{\rm b} \\ -0.79^{\rm b}$

^a1st nearest neighbor (NN) Co atoms around the Fe dopant [see light blue Co in Fig. 4(b)].

^b1st nearest neighbor (NN) O atoms around the Fe dopant [see light red O in Fig. 4(b)].

atoms [light blue in Fig. 3(d)], which is elevated relative to the substrate compared with the regular CoO basal plane. Conversely, the three O atoms (NN) coordinated directly to the Fe dopant have a negligible change in z-distance from Au(111) but are more negatively charged as compared with the O in the pure unary oxides to accommodate the increase of oxidation states of Fe. In the STM image [Fig. 3(f)], the reduced contrast of the triangular feature is a reflection of this changed local density of states associated with the three NN O atoms surrounding the Fe rather than a geometric effect [light red atoms in Fig. 3(e)]. Table I furthermore shows that the charge transfer varies slightly between FCC, HCP, and TOP stacking relative to the gold. These changes are also reflected by the atom-resolved STM data, as we may observe qualitative variations in the appearance of the Fe defect structures depending on their location [Figs. 3(a) and 3(b)]. The calculated Density of States (DOS) and simulated STM images of an isolated Fedopant in the CoO bilayer matrix, FeCoO, are included in the supplementary material as Figs. S3 and S4, respectively. Figure S1(a) shows the clear differences in the projected DOS of the Fe dopant, the nearest neighbor Co to the Fe dopant, and compares these to the Co and Fe in their pure unary CoO and FeO, respectively, bilayer films supported on Au. The DOS of the oxygen atoms surrounding the metal atoms, either the Fe-dopant or the different Co atoms in the oxide framework [shown in Fig. S1(b)], shows significantly less variations in electronic structure. The simulated STM image of the FeCoO bilayer (Fig. S4) was performed using the Tersoff-Hamann scheme with a bias of -0.3 V. The STM for the Co plane shows clear differences between the Fe dopant and Co with some discrepancies as compared to the experimentally measured

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STM images which we attribute to the need to also explicitly include tip effects. Both the DOS and the STM images support the experimental findings; however, a more detailed analysis of the electronic structure is needed and will be performed in future work.

IV. CONCLUSIONS

In summary, we have used a combination of atomresolved microscopy, electron spectroscopy, and firstprinciple modelling to investigate the electronic and structural properties of Fe dopants in CoO bilayers on Au(111). Our study shows that Fe atoms occupy substitutional sites in the CoO and are present as single-atom dopants dispersed within the oxide phase. A distinctive structural and electronic character develops around these single Fe species embedded in the CoO bilayers reflected by a higher oxidation state of the Fe dopant and a distorted geometry develops around the site compared to the pure unary FeO and CoO. The observed higher oxidation state of the embedded Fe cannot be explained by charge transfer from the Au and is rather to be considered as an intrinsic effect of the mixed oxide that implies that bonding and redox properties of such sites may significantly differ from pure unary Fe oxide. We note that the active site in OER catalysis is generally expected to be specifically related to the presence of Fe in oxyhydroxides (CoOOH), rather than the bilayers studied here. The active oxyhydroxide phase develops directly by exposure to water and the electrolyte under electrochemical conditions,¹⁶ but it was not directly available in the studies here performed under well-controlled vacuum conditions. Future studies will be aimed at clarifying if the Fe position as singular dopants in the oxide matrix is stable when exposing to liquid water or electrochemical conditions. Such detailed atomistic information on the position of Fe dopants in precursor phases such as CoO or CoO₂ may help the rational synthesis of promoted mixed oxide nanostructures by intentional doping. We hypothesize that the synergistic catalytic properties may be unraveled by consideration of comparable single-atom Fe sites embedded in the Co sublattice in the oxyhydroxide phase and that a comparison to the reactivity of the single-atom Fe sites in CoO bilayers can reveal the importance of Fe embedded in Co-oxides with different crystal structures.

SUPPLEMENTARY MATERIAL

See supplementary material for details of STM images of different imaging modes in the same FeCoO nanoislands on Au(111) [pair distribution function (PDF)], DFT calculations of the different stacking of pure unary CoO and FeO, and mixed FeCoO bilayers supported on Au(111) (PDF), DFT calculated DOS of metal and oxygen sites in CoO, FeO, and FeCoO bilayers, and simulated STM image of FeCoO bilayers.

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