Anisotropic iron-doping patterns in two-dimensional cobalt oxide nanoislands on Au(111)

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ABSTRACT

An integrated approach combining density functional theory (DFT) calculations and atomic resolution scanning tunneling microscopy (STM) is used to study well-defined iron-doped cobalt oxide nanoislands supported on Au(111). The focus is on the structure and distribution of Fe dopants within these nanoislands of CoO as a function of Fe to Co ratio. The DFT and STM results agree strongly and complement each other to allow for a more complete understanding of the dopant structure trends on the nanoscale. Using Fe as a marker, we first find that the stacking sequence of the moiré structure of the host cobalt oxide nanoislands can be identified unambiguously through a combination of DFT and STM. Using the distinct contrast of the embedded Fe dopant atoms as observed with atom-resolved STM, we find correlations between Fe dopant position and the CoO/Au(111) moiré pattern at varying Fe dopant densities. Formation of Fe-dopant clusters within the nanoislands is investigated in detail through DFT and found to agree with the dopant patterns observed in STM. We find that the structural effects of Fe dopants throughout the nanoislands with the basal planes and the two types of edges—the oxygen and metal edges—have different nature. Both DFT calculations and STM images show a strong preference for Fe dopants to be located directly on or near the oxygen edge of the nanoislands as opposed to being directly on or near the metal edge. Taken together, our results illustrate that Fe dopant incorporation and distribution within CoO nanoislands are highly anisotropic and governed by both the moiré structure of the basal planes as well as nano-size effects present at the under-coordinated edges of different local geometry and chemistries.

KEYWORDS

scanning tunneling microscopy (STM), density functional theory (DFT), cobalt oxide, transition metal oxides, mixed transition metal oxides

1 Introduction

Unary, binary, ternary and mixed transition metal oxides (TMOs) in general have been shown to exhibit interesting physicochemical properties in terms of electronic, magnetic and catalytic properties [1, 2]. Therefore, some TMOs have been widely studied and have found applications in industry as catalysts, electrocatalysts, supports, lithium-ion batteries, electrochemical capacitors, metal-air batteries, fuel cells, sensors, micro-electromechanical systems (MEMS), metaloxide-semiconductor field-effect transistor (MOSFET), pigments and dyes etc. [3, 4]. However, the underlying physical and electronic properties of such mixed transition metal oxides are in many cases poorly understood. Herein, we focus on the properties of a class of mixed TMOs of relevance for catalysis. Several studies have shown that mixed TMOs exhibit better catalytic performance for the oxygen evolution reaction than their unary counterparts (oxygen evolution reaction (OER))[5-11]. Exploratory efforts have been made to develop high-performance TMO systems based on addition and mixing of different metal-components into the oxides [12, 13]. In particular earth-abundant mixed TMOs have gained attention as catalysts. For example, it was found that the catalytic activity of cobalt oxide, one of the most promising catalysts for OER and CO oxidation, can be

enhanced by orders of magnitude by addition of a small amount of other transition metals, e.g., Fe, Ni, Mn while excessive addition can suppress the activity and stability [14–21], hinting at an optimum ratio between the different metals in the mixed TMO for best performance.

Besides the chemical composition of the TMOs, their structure has been shown to have an influence on their catalytic performance. For example, studies have shown that mixed Fe-Co oxides can be synthesized as nanofilms, nanosheets, and nanoparticles [14, 15, 22-24]. These studies mainly discuss the potential relationship between the overall chemical performance and the different chemical components of the oxide taking a macroscopic viewpoint [14, 17, 24, 25]. Different oxide systems have been used to attempt to identify relations between the structure and activity, for example, the morphology of thin films of Co-Fe oxides has been shown to be dependent on the Co:Fe ratio or surface decoration, CoOx-FeOx composite oxides were used to study the surface species, while other models assumed Fe atoms to be incorporated into the host oxides lattice [26–29]. However, these studies rarely provide direct and detailed atomic structure information. In other words, the lack of structural information, i.e., the exact location of the Fe dopants in these systems and the lack of understanding of the potential synergistic effects, i.e., the interaction between the



Fe dopant atoms and the host Co-oxide structure make it hard to reach conclusions at the exact role(s) that these Fe dopants play in the chemistry of these oxides. Hence, it is clear that an understanding of the detailed structure of the mixed oxide is of uttermost importance to optimize the oxide structure to be able to improve the chemistry and catalytic activity.

A successful approach towards achieving a fundamental understanding of the chemistry of these complex metal oxide and other transition metal compound systems has involved studies of supported single metal TMO thin films or nanoisland model systems under vacuum conditions and more recently in-situ characterization has enabled study of these systems under environmental (e.g., catalytically relevant) conditions. One well-known example is the series of fundamental surface science characterization techniques and theoretical modeling studies on MoS2 nanoclusters with and without dopants which revealed both geometric, i.e., location of single and multiple dopants as well as electronic effects on their chemistry [30-35]. Similar approaches have been applied to TMOs to fully or partially reveal an atomic level understanding of the surface structure of doped oxides, e.g., Sn-doped In₂O₃, Mo-doped CaO, Li-doped MgO [36-39], as well as to gain understanding of the chemistries taking place on these nanomaterials, e.g., the reaction mechanism of CO oxidation on FeO/Pt(111) [40-45], CoO/Au(111) in OER [46-51], and adsorption of CO on TiO₂ and water on Fe₃O₄ [52, 53] to name a few. In a recent study of the initial growth of mixed Fe-Co oxide on Au(111), we examined how isolated single Fe dopant heteroatoms on the basal plane modify the geometric and electronic structure of pure cobalt oxide nanoislands [54]. It was found that Fe atoms get incorporated into the basal plane of the host CoO lattice occupying substitutional Co lattice sites resulting in a large electronic structure modification of the surrounding O lattice as well a smaller electronic perturbation of the nearest neighboring Co lattice atoms.

In this paper, we provide a complete picture of the Fe dopant structure including distribution and preferential incorporation sites within the host bilayer CoO nanoislands as a function of the Fe content. Combining, density functional theory (DFT) and scanning tunneling microscopy (STM), we are able to pinpoint the preferential locations of Fe dopants with atomic precision. In doing so, we unambiguously solve the epitaxial stacking of Fe and Co atoms of the Fe-doped CoO/Au(111) moiré superstructure present on the basal planes of the CoO nanoislands, which exists due to the lattice mismatch between CoO and the Au(111) support. At low Fe densities, we find that the Fe dopants present significant templated distribution towards two out of three specific moiré basal plane areas. Using DFT to study dopant clustering, we find that the basal plane distribution of dopants changes with Fe density and that Fe-dopant clusters within the CoO show no preferential shape pattern. Importantly, we find that different Fe incorporation patterns are present in the vicinity and at the O and Co edges of the nanoisland as compared to the basal planes. These distinct preferences of Fe incorporation suggest a high anisotropy of doping throughout the nanoisland.

2 Experimental and computational methods

The experiments were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of ~ 1×10^{-10} mbar. A Au(111) single crystal (MaTecK GmbH) was used as the support and cleaned by repeated cycles of Ar⁺ sputtering (2×10^{-7} mbar Ar, 1,500 eV, 30 min) and annealing (780 K, 15 min), which is proved by STM and X-ray photoelectron spectroscopy (XPS) to be sufficient to prepare a clean and crystalline Au(111) surface.

The Fe-Co oxide samples were prepared following the recipe previously reported in Ref. [54]. Briefly the procedure is as follows. With an e-beam evaporator (Oxford Applied Research, EGCO4), Co metal was deposited onto the Au(111) support in O₂ atmosphere

initially forming bilayer cobalt oxide nanoislands on Au(111). Next, Fe metal was evaporated at UHV conditions onto the CoO. Finally, a post-annealing treatment at 523 K was applied for crystallization and Fe mixing into the two-dimensional (2D)-layered oxides. Samples with different Co/Fe atomic ratios were prepared by varying the deposition time for Fe while keeping the Co coverage fixed. The STM images were recorded at room temperature (~ 300 K) using an Aarhus-type STM (SPECS, Aarhus 150).

DTF calculations with the Hubbard-U correction (DFT+U) were performed using the projector-augmented wave (PAW) method within the Vienna *ab initio* simulation package (VASP). The basal planes of the bilayered CoO, FeO, and Fe-doped CoO (CoFeO) nanoislands were studied using two different types of models: (1) a moiré model that includes the variation within the CoO to Au atomic stacking related to the lattice mismatch between the two materials which was observed in the experimental structure, and (2) a periodic boundary condition slab model. The moiré model was constructed using a (10×10) unit of CoO on a (11×11) unit of Au(111), which corresponds to a moiré superstructure of 31.680 Å. The large models were used to capture possible effects at present at the nm-scale which potentially could be omitted in the slab models as well as to identify the validity of the slab models (see discussion in results section below). The slab models utilized (6×6) , (5×5) and (4×4) units of thin bilayered films corresponding to each of the specific stacking modes of CoO, FeO, and Fe-doped CoO supported on Au(111) and strained to the lattice parameter of Au. For the edge calculations, we used stripe models of (2×4) , (2×5) , (2×6) CoO stripes exposing both the oxygen and the metal edge ontop of Au(111). In the following main text, we mainly focus on the results from the (6×6) slab models while the ones from the smaller models are included in the Electronic Supplementary Material (ESM). The thin film metal-oxide layer was placed in an face-centered cubic (FCC), hexagonal close-packed (HCP) or directly on top (TOP) stacking relative to the 3-layer thick Au(111) surface (the stackings refer to Co/Fe relative to Au, see Fig. S5 in the ESM), respectively. A cutoff energy of 400 eV was employed for the plane wave expansion. The k-point grid was set to $1 \times 1 \times 1$ for basal plane calculations and $4 \times 1 \times 1$ for stripe models. The bottom two layers of the Au(111) were frozen at their bulk positions while the metal-oxide layer and top layer of Au(111), unless otherwise specified, were allowed to relax until a maximum force threshold of 0.02 eV/Å was reached. The focus of this paper is to establish the favorable thermodynamics for Fe incorporation. Possible barriers associated with kinetic processes such as diffusion can probably be overcome with the energetic input from the annealing process since the thermodynamics of the final incorporated state is highly favorable as described below in the results section. The exact role of kinetics is beyond the scope of this paper.

It should be noted that determining the magnetic ordering for supported oxide films on Au can be challenging especially when an Fe dopant is present in the system. For the moiré model calculations we used a completely ferromagnetic (FM) magnetic ordering for both the CoO and Fe-doped CoO systems for simplicity due to the prohibitively high computational cost because of the system's size. Other magnetic configurations were investigated for the moiré models (see the ESM for details) and we found that the Fe doping preferences remained the same for all of them. For the (6×6) slab model calculations, we mapped out different magnetic configurations including FM, anti-FM (AFM) stripes and a ring/hexagonal pattern around the Fe dopant (see the ESM for more details) and reported the lowest energies in the main text. In addition, we found that the stripe models had a more well-defined magnetism and were all performed as zig-zag AFM [55] unless otherwise specified. For more details and discussion about magnetic ordering see the details in the ESM.

3 Results and discussion

3.1 Epitaxial properties and DFT model design of Fe-doped CoO nanoislands

Our prior experimental investigations of the CoO on Au(111) systems have elucidated that bilayer cobalt oxide (Co-O) synthesized under the conditions of the experiment performed here grows as hexagonally shaped nanoislands. In the bilayers, the Co is oriented towards the Au and with the O-terminated basal plane pointing away from the Au. In STM images of the basal plane, the Co oxide islands are thus seen to expose a perfect hexagonal atomic O lattice ($a_0 = \sim 3.3$ Å). Superimposed on this structure, a much larger superstructure $(a_{\text{moire}} = ~ 37 \text{ Å})$ related with the formation of a moiré pattern exists. The moiré pattern, well-known from many epitaxial monolayer systems, arises due to the lattice mismatch between Au(111) and CoO which leads to coexisting stacking modes of CoO and therefore differing interactions between the oxide and the metal support [48]. In the STM images, this shows up as long-range periodic height modulations across the basal plane. Figure 1(a) shows a representative STM image of cobalt oxide nanoislands with Fe dopants, where both the O atomic lattice and the much larger moiré structure (indicated by a white rhombic unit cell) are visible on the island. We find using STM that the moiré periodicity after incorporation of Fe dopants into the cobalt oxide nanoislands is 37 ± 2 Å and coincides with the periodicity observed of the pure cobalt oxide nanoislands (see also Fig. S1 in the ESM). This suggests that the Fe dopants have no significant effect on the lateral geometric structure of the pristine CoO lattice for the amounts of Fe incorporation investigated here. This is expected and in line with our earlier results which identified that individual Fe heteroatoms have substitutionally replaced the Co atoms of the oxide lattice while at the same time only modifying the local geometric and electronic structure of the neighboring lattice atoms [54]. As we previously reported in our initial study of Fe incorporation, the atomic triangular features resolved in the STM images on the basal planes of the nanoislands reflect the location of the Fe heteroatoms within the CoO (Fig. 1(a)) [54]. We do note that some amount of Fe could be intermixed with the Au support during the evaporation process in a similar manner as has been observed for other metals, for example, Ref. [56]. More details on the STM imaging parameters can be found in Ref. [54]. In the following, we will analyze the location of these Fe features in relation to their position relative to the moiré pattern and relative to the vicinity of the edge terminations of the CoO islands. We note that bright stripes protruding significantly from the basal plane observed in some parts of the CoO islands (e.g., in Figs. 1(c) and 1(d)) are not related with Fe incorporation and are instead identified as line defects related to the incorporation of excess O atoms into the nanoisland structure [48].

Interestingly, detailed analyses of the STM images show that the Fe dopants are not randomly distributed. On the basal planes, we find that the density of Fe heteroatoms differs significantly between light and dark areas of the moiré superstructure, with the lighter areas having a clear preference for a higher Fe density (see Figs. 1(a), 1(c) and 1(d)). The height modulation between bright and dark moiré sections reflect the fact that Co of the islands shift between being located at FCC, HCP and ontop (TOP) positions on the Au(111) substrate. Intuitively, it would be expected that the Co is pushed further away from the surface when located in the TOP positions on the Au and therefore taken to reflect the bright regions within the moiré structure in STM images. However, examples in the literature (e.g., graphene on Ir(111) and MoS₂/Au(111)) show that such an assignment of the moiré is not straightforward and can be imprecise, since electronic effects and relaxations can significantly affect the STM contrast [57, 58]. Instead, we use DFT to accurately determine the energetic preference for Fe dopants to be located at



Figure 1 (a) Representative atom-resolved STM image of a cobalt oxide nanoisland with Fe heteroatoms (Fe density 0.29 Fe /nm²). The contrast is adjusted to show the Fe heteroatoms and STM height modulations due to the moiré superstructure. The white rhomb indicates the moiré unit cell. (b) Theory model: a (10×10) CoO on (11×11) Au(111) atomic model representing a single rhombic moiré unit cell. The substitutional Fe-doping calculations are done with Fe in different positions (HCP, TOP, FCC indicated with different colors) corresponding to the presence of different local stacking of the oxide lattice. (c) and (d) STM images with different Fe densities, low 0.31 Fe /nm² (c) and high 0.60 Fe /nm² (d). ((a) $V_t = -0.44$ V, $I_t = -0.49$ nA. (c) $V_t = -0.20$ V, $I_t = -0.41$ nA. (d) $V_t = -1.06$ V, $I_t = -0.28$ nA.)

certain stacking positions, and in this way we can unambiguously assign the stacking of the moiré sections. To perform the calculations, we constructed an atomic model consisting of a (10×10) unit of CoO thin film ontop of an (11×11) unit of Au(111) (see Fig. 1(b)) to allow for representation of a full moiré structure and the different stacking domains which reflect placing Co at FCC, HCP or TOP position relative to the Au(111) surface. For computational reasons, the moiré superstructure model has a slightly smaller periodicity (~ 32 Å) than the measured moiré periodicity (~ 37 Å). Figure 1(b) shows the DFT model and indicates the specific locations of the FCC, HCP, and TOP stacking domains which all coexist within a single rhombic unit cell of the moiré structure. We use this moiré model and three different (6×6) unit periodic models, similar to those we used in previous studies [54], where each moiré domain is modeled separately as an FCC, HCP or TOP infinite film to capture the structure of the individual basal plane regions of the nanoislands and to determine the prefered Fe-doping incorporation in the different regions of the nanoisland. The moiré model is used to validate the smaller models in the restricted stackings and to justify their use moving forward to study the more complicated Fe incoproration patterns (see discussion in later sections). The computational resources required to run the full moiré model are significantly larger than the ones for the smaller models, hence showing the validity of the smaller models gives us the ability to explore more trends at a more reasonable computational cost.

3.2 Single Fe-atom doping in the basal planes of CoO nanoislands

Using DFT modeling combined with an elaborate stastical experimental analysis of the Fe position within nanoislands, we first determine the preferential and unfavored regions for Fe incorporation. We do this for a low Fe dopant density by using our models to study a single (isolated) Fe dopant in different regions. We calculate the incorporation energy of an Fe dopant using an undoped CoO model and an identical model with an Fe atom substituted for 1 Co atom. The incorporation energy per Fe dopant is defined as $(E_{\text{Fe-CoO}} - E_{\text{CoO}})/N$, where $E_{\text{Fe-CoO}}$ is the energy of the Fe-doped cobalt oxide bilayer system and E_{CoO} is the energy of the undoped CoO bilayer system divided by the number of dopants in the system (N is always 1 for single dopants which model the low Fe density situation, N varies from 1-3 for clustering and high Fe density situations). Figure 2(a) summarizes the Fe incorporation energies based on the full moiré model as well as the individual simplified stacking models. For low Fe density, we find that both the moiré model and the simplified models predict the most negative (most favored) Fe incorporation energy to occur in the HCP and TOP regions and that the least favored incorporation domain is in the FCC stacking. In the experiments, the Fe dopants rarely appear in the dark areas of islands in the STM images (see Figs. 1(a), 1(c) and 1(d)). Combining this with the DFT results discussed above and shown in Fig. 2(a), we can thus unambigously conclude that the dark moiré areas in the STM images reflect FCC regions. Having resolved and identified the FCC areas, our further analysis of STM images allows for complete mapping of the Fe distribution within the moiré pattern and assignment to different regions (FCC, HCP and TOP)(see Fig. S2 in the ESM for details of the assignment). STM images of nanoislands with different Fe densities, low (0.31 Fe /nm²) with mainly isolated Fe dopants and high (0.60 Fe /nm²) with clustering (to be discussed in more details below in section 3.3) are shown in Figs. 1(c) and 1(d), respectively. A distribution count, taken from 46 such images of different samples with various Fe densities, provides enough statistics and a quantitative measure of the Fe distribution (see histogram plots in Fig. 2(b)). Our statistical experimental analysis confirms that isolated Fe heteroatoms have unfavorable incorporation sites, which are located in the FCC regions (dark areas of the moiré pattern). The almost equal occupation on the two other regions in Fig. 2(b) also agrees well with the theoretical calculation, where Fe incorporation in the HCP and TOP regions are similarly favored (-0.73 eV vs. -0.68 eV) (see Fig. 2(a)).

To enrich our understanding of the Fe dopant properties and the structural relaxation induced by Fe, a structural analysis of the CoO without and with Fe dopants in different locations of the CoO moiré structure is provided in Fig. S3 in the ESM showing the relaxed average nearest neighbor distances in the x- and y-directions since it known that there is a change in the z position from our previous

(-) ·					(6) 50%		
(a)	Model	Domain	Inc. energy	Inc. energy relative to	(D) 2075		
			(ev)	FCC (eV)	ā 4070		
		FCC	-0.31	0.00	03		
	Moiré	HCP	-0.73	-0.42			
		TOP	-0.68	-0.37	- E		
		TCC	0.00	0.00	8 20%		
		FCC	-0.29	0.00			
	6×6	HCP	-0.51	-0.22	L		
		TOP	-0.67	-0.38	F 10/0		
•					0%		
					FCC H	CP TOP	
					Moir	Moiré area	

Figure 2 (a) DFT calculated incorporation energies for the 3 stacking regions (FCC, HCP and TOP) given both as the calculated incorporation energy and incorporation energies relative to the FCC stacking (most unfavorable) for Fe into CoO/Au(111). Note, a more negative value equates to more favored incorporation configuration. Results for the large moiré model and the (6×6) basal plane models are shown. (b) Histogram of Fe heteroatom distribution related to the different moiré regions as obtained from statistical STM analysis ((b) $V_t = -1.24$ V, $I_t = -0.33$ nA).

study [54]. We find that the distances between the metal atoms are indeed the shortest in the FCC stacking regions as compared to the HCP and TOP stackings for both the pure CoO as well as the Fe-doped CoO, which could be partly responsible for the FCC regions being the most unfavored for Fe dopant incorporation. Since the geometrical metal-metal distances between different domains remain consistent with and without Fe-dopants, we conclude that the structural effects due to Fe doping do not significantly affect the moiré periodicity, as in the experiment.

3.3 Clustering of Fe dopants in the basal planes of CoO nanoislands

We next map the incorporation of Fe at different dopant densities and discuss formation of different Fe dopant patterns. We define clustering as the existence of Fe dopants that have at least one or more nearest metal neighbor(s) that is(are) also Fe atom(s). We want to understand if there are unique changes in the incorporation energy of Fe as a function of Fe quantity, i.e., density. The Fe density is defined as the number of Fe dopants per area of the nanoisland. In particular, we want to know if the incorporation would cause any changes in clustering and/or preference for incorporation in the different regions of the basal plane.

First, we performed DFT calculations of Fe clustering arranged in a straight line to establish what the expected favorable patterns in each basal plane region (FCC, HCP and TOP) would be as a function of Fe dopant amount. Figure 3(a) shows the incorporation energies corresponding to the Fe line clustering of different sizes (Figs. 3(d)-3(g)) that we considered. As the Fe cluster size increases to 2 Fe dopants, we find a surprising change in the preferred incorporation region with FCC now being the favored region for a double Fe cluster as compared to the single Fe dopant where the FCC region was the least favorable (see discussion above in section 3.2). For larger linear clusters of Fe beyond 2 dopants, the difference in incorporation energy is smaller between the different regions and becomes negligible for an infinite linear chain of Fe dopants. Based on this thermodynamic data, we conclude that the Fe incorporation preference in the basal planes changes as a function of the Fe density with TOP and HCP regions incorporating single Fe dopants, then the preference for incorporation shifts from these regions to the FCC region in the form of single dopant followed by FCC double or multiple dopant incorporation. This was verified in the experiment. The ratio of Fe dopants identified in the STM images in the dark FCC regions various Fe densities of different samples is plotted in Fig. 3(b). At low Fe densities (less than 0.50 Fe /nm²), a very small amount (less than 13%) of Fe dopants are found in the FCC regions. The ratio of Fe dopants in the FCC region remains at a nearly constant value (11%-12%) as a function of Fe density for low densities (see Fig. 3(b)). As the Fe density increases above 0.50 Fe /nm², there is a strong increase in Fe dopants located in the FCC region (see Fig. 3(b)) which we attribute to favorable Fe incorporation energetics due to dopant clustering as predicted by our DFT calculations, which we next confirm with STM statistics.

By a direct counting of the triangular features, originating from the Fe dopants as explained above, in the atomic resolved STM images, we also perform an analysis to establish if the Fe dopants are isolated or clustered. As shown in Fig. 3(c), at low Fe densities $(0.31 / \text{nm}^2)$, a very small amount (~ 10%) of Fe dopants are clustered (as seen in Fig. 3(c), 1st column) and explained by the DFT results in Fig. 3(a). As the Fe density increases, however, clusters begin to form and at an Fe density of 1.10 / nm², the majority (more than 85%) of the Fe dopants are clustered (see Fig. 3(c), 3rd column). The transition at which ~ 40% of the Fe dopants are being clustered is observed to happen at an Fe density of 0.57 / nm² (see Fig. 3(c), 2nd column). This transition occurs at the Fe density where the percent of dopants in FCC increases (see Fig. 3(b)), which is in good agreement with our



Figure 3 (a) Incorporation energy of Fe dopants per Fe for 1, 2, 3 dopants and infinite chain for FCC, HCP, TOP stacking. (b) Histogram of ratio of Fe atoms in FCC vs. Fe density. (c) Counting data for Fe atoms in isolated or in a cluster for different Co/Fe ratios. (d)–(g) DFT stacking models: single, dimer, trimer-line, and infinite chain, respectively.

DFT calculation results showing that the Fe clustering is the driving force that causes an increase in dopants in FCC locations.

We performed further DFT analysis of Fe dopant clustering to understand if there is a driving force for Fe clustering with a specific favored Fe-Fe interaction that extends beyond the linear chain geometry and location in the nanoisland discussed above. Since we found that Fe clustering is likely to occur in all moiré regions, we here limited our investigation of these more complex Fe clusters by modeling the incorporation in a (6×6) FCC unit cell because it is the most stable stacking. In addition to 2 Fe-dopant clustered in a line (see Fig. 3(e)), we also investigated the distance and geometry dependence of the interaction between the two Fe dopants (see Fig. S12 and Table S2 in the ESM). There is an interaction between the two Fe dopants present even when they are positioned beyond nearest neighboring sites which is favorable over the Fe dopants being spread apart i.e. being isolated. This is one of the causes leading to Fe clustering even with apparently favorable Co sites in HCP and TOP regions that are available for substitution. For the 3 Fe dopant clusters, we found that Fe can dope in four unique 3 dopant (trimer) shapes, straight line, L-shape, triangle up, and triangle down (see Figs. 4(c)-4(f)). The line clustering pattern was found to be the most favored amongst the trimer shapes, however, the small energetic preference from DFT is not significant enough to make this the most dominant cluster shape and exclude existence of the other shapes. In agreement, a variation of 3 dopant large Fe clusters with the L-shape (Fig. 4(d)), triangle up (Fig. 4(e)) and triangle down (Fig. 4(f)) configurations are observed in the experiment, with no strong preference for any of these configurations. Experimentally, lager doping clusters (more than 3 Fe dopants), as can be seen in Figs. 4(b) and 4(h), do not show any particular shape preference. Computationally, larger doping clusters, besides the infinite chains discussed above, have not been considered since they would require significantly larger simulation models and increasing number of shapes, which is computationally prohibitive. We conclude that Fe incorporation into clusters consisting of 2 or more Fe dopants is highly driven by the CoO stacking on Au(111), preferring the FCC stacking, but show no significant shape preferences.

3.4 Fe-doping on edges of CoO nanoislands: edge sites preference

The STM image shown in Fig. 5(a) illustrates the full perimeter region

of a highly Fe-doped Co-oxide nanoisland. Interestingly, we observe a strong enrichment of the Fe content near the edges as indicated by the numerous triangular Fe features close to the perimeter of the island. Clearly, this suggests that there is a thermodynamically favorable effect for Fe doping incorporation at edge sites compared to the basal planes. Based on the crystal structure of CoO, a hexagonal Co oxide island and an Fe-doped CoO nanoisland, can be terminated by two types of edges: the O edge and the Co edge. We use DFT to establish a complete mapping of the Fe dopant incorporation thermodynamics at the two different edges present on the nanoislands. In order to perform this study, we use stripe models previously utilized to study reactivity of edges of CoO [49]. Here, we have modeled the edges using slightly wider CoO_x stripes (length of 6 instead of 4) in an FCC stacking. We examine the thermodynamically favored incorporation of Fe relative to the edge by positioning Fe throughout the stripe models. Figures 5(c)-5(e) show the atomic models and Fig. 5(b) summarizes the Fe incorporation energetics. Interestingly, we find that a single Fe dopant and an infinite linear Fe dopant chain are most stable at the oxygen edge (row 1) or right by it as compared to the Fe doping on the FCC basal plane (see Fig. 2(a)). This should be contrasted to a single Fe dopant and an infinite linear Fe dopant chain on the Co-edge which is less stable than the Fe doping on the FCC basal plane. In reality, the edges of a CoO nanoisland are not completely in an FCC stacking (or HCP or TOP stacking) like we have used in these models so far but rather a mixture of these stackings which leaves some room for further investigation of different types of edge effects for different stackings. We performed a series of calculations of single and infinite linear chain Fe doping in an HCP stacked stripe and found the same incorporation energetic trends as for the FCC stacked stripe, with an even more pronounced dopant incorporation preferences towards the oxygen edge vs. the metal edge and non-edge sites (see Fig. S10 in the ESM). This lends further evidence that the oxygen edge is the preferred site for Fe dopant incorporation.

Experimentally, one can distinguish between the two different edge type by means of the triangular features induced by the Fe dopants. Similar to the previous edge structure analysis of the pure cobalt oxide bilayer islands, parallel edges on opposite sides of an island display opposite edge structure and the sidelines of the triangular features are parallel to the O edge of an islands [50]. We note that the existence of O-defect lines adds complexity to the edge



Figure 4 (a), (h), and (i) Observed representative STM images containing some of the cluster shapes identified by DFT. (g) Table of DFT calculated incorporation energies per Fe for clusters consisting of 3 Fe dopants corresponding to the trimer dopant shapes in a (6×6) unit FCC DFT model. (b) Zoom in and atomic ball model overlay of some of the DFT probed 3 Fe dopant configurations: (c) line, (d) L-shape, (e) triangle up, and (f) triangle down.



Figure 5 (a) A representative STM images showing Fe dopant chains close to O edge and at the 3^{rd} row close to Co edge, indicated by red and blue lines, respectively ($V_t = -0.07 \text{ V}$, $I_t = -1.07 \text{ nA}$). (b) Fe incorporation energy throughout (2×6) CoO stripe edge models. Atomic representation of stripe model used to simulate Fe doping from a side view (c) and top view of example models showing a single dopant in row 1, i.e., O edge (c) and infinite Fe chain in row 6, i.e., metal edge. Examples of doping models, (d) single dopant row 1 (oxygen edge) and (e) infinite chain dopants row 6 (metal edge).

identification (see detailed discussion of the relations between Fe dopant features, O-defect lines and island edge types in Fig. S11 in the ESM and corresponding discussion). With this knowledge, the island edge type can, however, be easily identified as shown in Fig. 5(e) with red and blue lines indicating O and metal edges, respectively, allowing for a statistical quantification of Fe dopants at the two different edges vs. the basal plane. We find in the experiment that more Fe dopants are located at or close to the O edge areas. As can be seen from Fig. 5(a), almost all the O edges are decorated with Fe dopants while the metal edges seem to be Fe free. An extreme example can be found in the left bottom corner of Fig. 5(a), where there is a long Fe-dopant chain formed while there are no Fe dopants at the quite large area in the vicinity of the metal edge.

We can also investigate how the shape and location of the dopants in the nanoisland relative to the edges influence incorporation energies at higher Fe densities when Fe clustering occurs. We use stripe models to investigate the incorporation energy of some of the above studied Fe cluster sizes and shapes on the basal planes to now investigate if there is an effect of the oxygen and metal edges on the stability of these clusters. In order to avoid cluster interaction, we employ larger stripe models by doubling the size of the stripe in the x-direction making a wider stripe of (4×6) units CoO (see Fig. S9 in the ESM for examples). We have investigated the stability of 2 Fe dopant and 3 Fe dopant shapes (see Fig. S9 in the ESM) at different locations throughout these stripe models to simulate the position of the clusters at different proximities to the edges. Figures 6(a)-6(c)show the incorporation energies per Fe of the following configurations: a single Fe dopant, 2 Fe-dopant cluster, and 3 Fe-dopant shapes (L shape, triangle up, and triangle down) throughout the (4×6) stripe model. In general, we find the same trend as we identified for the single Fe dopant and infinite Fe chain, namely, Fe-dopant clusters prefer to form on or near the O edge. Overall, we find that the experimental data (see Fig. 5(e)) agrees with our DFT energy trends. To analyze the experimental data, we first define the edge area as the region from the outermost row to the 3^{rd} row in the metal lattice and the rest as basal plane. The ratios of Fe dopants at the basal plane and edge areas are counted from three representative STM samples with typical Fe densities. The statistical results are plotted



Figure 6 Calculated incorporation energy for clustering vs. the location of (a) single Fe dopant, (b) 2 Fe dopants, and (c) 3 Fe dopant shapes for the (6×4) stripe edge models. Single numbers mean that all dopants are in the same row, double numbers imply one in each row, and triple digits have a dopant distribution of as labeled. Example models and shapes are shown in Fig. S8 in the ESM. (d) Amount of Fe at edges vs. basal plane at different Co/Fe content based on statistical quantification of STM images (the edge area is defined as the outmost to 3rd rows in metal lattice and the rest is basal plane).

in a histogram (see Fig. 6(d)), which shows that Fe dopants tend to be incorporated at the edge area as the Fe density increases predominantly on the O edge. Combining this statistical information of dopants at the edges vs. the basal plane at different Fe contents and DFT calculations, we conclude that clusters prefer to form at the oxygen edges of the nanoislands. This leads to a higher ratio of Fe on the edges to Fe on the basal plane with increasing Fe content.

DFT results show that the Fe doping is primarily driven by the dopant location in the nanoisland in reference to both the location relative to the edges and location on the basal plane. The doping of Fe on the basal plane in TOP and HCP regions is competitive with that of the single Fe dopant on the FCC edges. At low Fe concentration there will be Fe primarily on/near the oxygen edge and in the TOP and HCP basal plane regions. At higher Fe densities HCP and TOP basal plane regions become unfavorable locations for Fe and clusters begin to form primarily near the oxygen edge and also in FCC regions. The oxygen edges are the most favored site for Fe incorporation, as seen in Fig. 5(e), and will therefore get the largest amount of Fe clusters. The full Fe dopant chains are the most preferred clusters at a given row when compared to single dopants or other non-linear shapes at the same locations. We conclude that at high Fe densities, the O edge and several rows in from the O edge of the nanoisland will be completely substituted with Fe. Fe incorporation on the metal edge is less favored than on the O edge but is competitive with the basal plane regions. Figure 7 indicates expected Fe percentage (assuming all regions have the same area) at different locations based on these incorporation energy trends.

4 Conclusions

A combination of complementary DFT calculations and STM images clearly elucidate the patterns of Fe incorporation into CoO nanoislands. DFT calculations predicted the unfavorable region for Fe doping at low Fe densities to be the FCC stacking region helping identify the different moiré domains in the STM images. The ratio of Fe dopants in the FCC regions increases dramatically at low Co/Fe ratios (high Fe content) which by DFT is attributed to clustering preferences of Fe in different regions. No dominant clustering shape preference was identified leading to the conclusion that doping on the basal plane is driven solely by the regions of the moiré pattern. In addition to the Fe dopant distribution within the moiré superstructure, the phenomena of doping near the edge was investigated through DFT and STM. DFT calculations indicated a clear Fe incorporation preference at or in the direct vicinity of the oxygen edge compared to the metal edge and basal plane regions. Presence of different Fe clusters were shown to be similarly driven by location relative to the edges regardless of shape or size. The combination of basal plane



Figure 7 Atomic-model of a high density Fe-doped CoO nanoisland illustrating the predicted Fe distribution and dopant clustering based on DFT and STM. A Boltzmann weight distribution graph (low and high Fe density correspond to DFT incorporation energetics of single Fe dopant and three Fe-dopant clusters, respectively) illustrates the anisotropic Fe incorporation throughout the nanoisland with the highly preferred Fe incorporation at the oxygen edge (O-edge) and how clustering changes the Fe incorporation preference in the basal plane regions.

distribution and an understanding of the edge preference for Fe incorporation provides a clear picture for predicting the Co/Fe nanostructure of the nanoislands, which is important for a complete understand of further studies of binary oxide systems. These results can be used to isolate the effects that Fe dopants have on other CoO and CoO_x nanoisland systems. Efforts are currently underway to examine if these unique modifications are capable of OER reactivity, and what cooperativity may exist between metal species in this Au(111) supported binary oxide system.

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References

- Rao, C. N. R. Transition metal oxides. *Annu. Rev. Phys. Chem.* 1989, 40, 291–326.
- [2] Barcaro, G.; Fortunelli, A. 2D oxides on metal materials: Concepts, status, and perspectives. *Phys. Chem. Chem. Phys.* 2019, 21, 11510–11536.
- [3] Galatsis, K.; Li, Y. X.; Wlodarski, W.; Comini, E.; Sberveglieri, G.; Cantalini, C.; Santucci, S.; Passacantando, M. Comparison of single and binary oxide MoO₃, TiO₂ and WO₃ sol-gel gas sensors. *Sen. Actuators B: Chem.* 2002, 83, 276–280.
- [4] Netzer, F. P. "Small and beautiful"—The novel structures and phases of nano-oxides. Surf. Sci. 2010, 604, 485–489.
- [5] Man, I. C.; Su, H. Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* 2011, *3*, 1159–1165.
- [6] Tahir, M.; Pan, L.; Idrees, F.; Zhang, X. W.; Wang, L.; Zou, J. J.; Wang, Z. L. Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review. *Nano Energy* 2017, *37*, 136–157.
- [7] Wang, J. H.; Cui, W.; Liu, Q.; Xing, Z. C.; Asiri, A. M.; Sun, X. P. Recent progress in cobalt-based heterogeneous catalysts for electrochemical water splitting. *Adv. Mater.* 2016, 28, 215–230.
- [8] Han, L.; Dong, S. J.; Wang, E. K. Transition-metal (Co, Ni, and Fe)-based electrocatalysts for the water oxidation reaction. *Adv. Mater.* 2016, *28*, 9266–9291.
- [9] Morales-Guio, C. G.; Liardet, L.; Hu, X. L. Oxidatively electrodeposited thin-film transition metal (oxy)hydroxides as oxygen evolution catalysts. *J. Am. Chem. Soc.* 2016, *138*, 8946–8957.
- [10] Hunter, B. M.; Gray, H. B.; Müller, A. M. Earth-abundant heterogeneous water oxidation catalysts. *Chem. Rev.* 2016, *116*, 14120–14136.
- [11] Zhang, B.; Zheng, X. L.; Voznyy, O.; Comin, R.; Bajdich, M.; García-Melchor, M.; Han, L. L.; Xu, J. X.; Liu, M.; Zheng, L. R. et al. Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* 2016, 352, 333–337.
- [12] Barsan, N.; Koziej, D.; Weimar, U. Metal oxide-based gas sensor research: How to? Sens. Actuators B: Chem. 2007, 121, 18–35.
- [13] Burke, M. S.; Enman, L. J.; Batchellor, A. S.; Zou, S. H.; Boettcher, S. W. Oxygen evolution reaction electrocatalysis on transition metal oxides and (oxy)hydroxides: Activity trends and design principles. *Chem. Mater.* 2015, 27, 7549–7558.
- [14] Zhuang, L. Z.; Ge, L.; Yang, Y. S.; Li, M. R.; Jia, Y.; Yao, X. D.; Zhu, Z. H. Ultrathin iron-cobalt oxide nanosheets with abundant oxygen vacancies for the oxygen evolution reaction. *Adv. Mater.* **2017**, *29*, 1606793.
- [15] Burke, M. S.; Kast, M. G.; Trotochaud, L.; Smith, A. M.; Boettcher, S. W. Cobalt-iron (oxy)hydroxide oxygen evolution electrocatalysts: The role of structure and composition on activity, stability, and mechanism. J. Am. Chem. Soc. 2015, 137, 3638–3648.
- [16] Yu, J.; Li, Q. Q.; Li, Y.; Xu, C. Y.; Zhen, L.; Dravid, V. P.; Wu, J. S. Ternary metal phosphide with triple-layered structure as a low-cost and efficient electrocatalyst for bifunctional water splitting. *Adv. Funct. Mater.* 2016, *26*, 7644–7651.
- [17] Du, P. W.; Eisenberg, R. Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges. *Energy Environ. Sci.* 2012, *5*, 6012–6021.
- [18] Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel–iron oxyhydroxide oxygen-evolution electrocatalysts: The role of intentional and incidental iron incorporation. J. Am. Chem. Soc. 2014, 136, 6744–6753.
- [19] Li, N.; Bediako, D. K.; Hadt, R. G.; Hayes, D.; Kempa, T. J.; von Cube, F.; Bell, D. C.; Chen, L. X.; Nocera, D. G. Influence of iron doping on tetravalent nickel content in catalytic oxygen evolving films. *Proc. Natl. Acad. Sci. USA* 2017, *114*, 1486–1491.
- [20] Batchellor, A. S.; Boettcher, S. W. Pulse-electrodeposited Ni-Fe (oxy)hydroxide oxygen evolution electrocatalysts with high geometric and intrinsic activities at large mass loadings. ACS Catal. 2015, 5, 6680–6689.

- [21] Song, F.; Hu, X. L. Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. *Nat. Commun.* 2014, *5*, 4477.
- [22] Deng, X. H.; Tüysüz, H. Cobalt-oxide-based materials as water oxidation catalyst: Recent progress and challenges. ACS Catal. 2014, 4, 3701–3714.
- [23] Smith, R. D. L.; Pasquini, C.; Loos, S.; Chernev, P.; Klingan, K.; Kubella, P.; Mohammadi, M. R.; Gonzalez-Flores, D.; Dau, H. Spectroscopic identification of active sites for the oxygen evolution reaction on iron-cobalt oxides. *Nat. Commun.* **2017**, *8*, 2022.
- [24] Yang, F. K.; Sliozberg, K.; Sinev, I.; Antoni, H.; Bähr, A.; Ollegott, K.; Xia, W.; Masa, J.; Grünert, W.; Cuenya, B. R. et al. Synergistic effect of cobalt and iron in layered double hydroxide catalysts for the oxygen evolution reaction. *ChemSusChem* **2017**, *10*, 156–165.
- [25] Heinz, K.; Müller, S.; Hammer, L. Crystallography of ultrathin iron, cobalt and nickel films grown epitaxially on copper. J. Phys.: Condens. Matter 1999, 11, 9437–9454.
- [26] Mountapmbeme Kouotou, P.; Vieker, H.; Tian, Z. Y.; Tchoua Ngamou, P. H.; El Kasmi, A.; Beyer, A.; Gölzhäuser, A.; Kohse-Höinghaus, K. Structure-activity relation of spinel-type Co-Fe oxides for low-temperature CO oxidation. *Catal. Sci. Technol.* **2014**, *4*, 3359–3367.
- [27] Haneda, M.; Kawaguchi, Y.; Towata, A. CoO_x–FeO_x composite oxide prepared by hydrothermal method as a highly active catalyst for lowtemperature CO oxidation. *J. Ceram. Soc. Jpn.* **2017**, *125*, 135–140.
- [28] Enman, L. J.; Burke Stevens, M.; Dahan, M. H.; Nellist, M. R.; Caspary Toroker, M.; Boettcher, S. W. Operando X-ray absorption spectroscopy shows iron oxidation is concurrent with oxygen evolution in cobalt-iron (oxy)hydroxide electrocatalysts. *Angew. Chem., Int. Ed.* **2018**, *57*, 12840– 12844.
- [29] Friebel, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M. J.; Sokaras, D.; Weng, T. C.; Alonso-Mori, R. et al. Identification of highly active Fe sites in (Ni,Fe)OOH for electrocatalytic water splitting. J. Am. Chem. Soc. 2015, 137, 1305–1313.
- [30] Walton, A. S.; Lauritsen, J. V.; Topsøe, H.; Besenbacher, F. MoS₂ nanoparticle morphologies in hydrodesulfurization catalysis studied by scanning tunneling microscopy. J. Catal. 2013, 308, 306–318.
- [31] Li, H. S.; Wang, S. S.; Sawada, H.; Han, G. G. D.; Samuels, T.; Allen, C. S.; Kirkland, A. I.; Grossman, J. C.; Warner, J. H. Atomic structure and dynamics of single platinum atom interactions with monolayer MoS₂. ACS Nano 2017, 11, 3392–3403.
- [32] Li, D.; Niu, Y.; Zhao, H. M.; Liang, C. J.; He, Z. Q. Electronic and magnetic properties of 3D-metal trioxides superhalogen cluster-doped monolayer MoS₂: A first-principles study. *Phys. Lett. A* 2014, 378, 1651–1656.
- [33] Zuriaga-Monroy, C.; Martínez-Magadán, J. M.; Ramos, E.; Gómez-Balderas, R. A DFT study of the electronic structure of cobalt and nickel mono-substituted MoS₂ triangular nanosized clusters. *J. Mol. Catal. A: Chem.* 2009, 313, 49–54.
- [34] Lauritsen, J. V.; Kibsgaard, J.; Olesen, G. H.; Moses, P. G.; Hinnemann, B.; Helveg, S.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Lægsgaard, E. et al. Location and coordination of promoter atoms in Co- and Ni-promoted MoS₂-based hydrotreating catalysts. *J. Catal.* **2007**, *249*, 220–233.
- [35] Robertson, A. W.; Lin, Y. C.; Wang, S. S.; Sawada, H.; Allen, C. S.; Chen, Q.; Lee, S.; Lee, G. D.; Lee, J.; Han, S. et al. Atomic structure and spectroscopy of single metal (Cr, V) substitutional dopants in monolayer MoS₂. ACS Nano 2016, 10, 10227–10236.
- [36] Morales, E. H.; He, Y. B.; Vinnichenko, M.; Delley, B.; Diebold, U. Surface structure of Sn-doped In₂O₃ (111) thin films by STM. *New J. Phys.* 2008, 10, 125030.
- [37] Myrach, P.; Nilius, N.; Levchenko, S. V.; Gonchar, A.; Risse, T.; Dinse, K. P.; Boatner, L. A.; Frandsen, W.; Horn, R.; Freund, H. J. et al. Temperature-dependent morphology, magnetic and optical properties of Li-doped MgO. *ChemCatChem* **2010**, *2*, 854–862.
- [38] Cui, Y.; Shao, X.; Prada, S.; Giordano, L.; Pacchioni, G.; Freund, H. J.; Nilius, N. Surface defects and their impact on the electronic structure of Mo-doped CaO films: An STM and DFT study. *Phys. Chem. Chem. Phys.* 2014, *16*, 12764–12772.
- [39] Walsh, A.; Catlow, C. R. A. Structure, stability and work functions of the low index surfaces of pure indium oxide and Sn-doped indium oxide (ITO) from density functional theory. J. Mater. Chem. 2010, 20, 10438–10444.
- [40] Fu, Q.; Li, W. X.; Yao, Y. X.; Liu, H. Y.; Su, H. Y.; Ma, D.; Gu, X. K.; Chen, L. M.; Wang, Z.; Zhang, H. et al. Interface-confined ferrous centers for catalytic oxidation. *Science* **2010**, *328*, 1141–1144.

- [41] Chen, H.; Liu, Y.; Yang, F.; Wei, M. M.; Zhao, X. F.; Ning, Y. X.; Liu, Q. F.; Zhang, Y.; Fu, Q.; Bao, X. H. Active phase of FeO_x/Pt catalysts in low-temperature CO oxidation and preferential oxidation of CO reaction. *J. Phys. Chem. C* **2017**, *121*, 10398–10405.
- [42] Giordano, L.; Lewandowski, M.; Groot, I. M. N.; Sun, Y. N.; Goniakowski, J.; Noguera, C.; Shaikhutdinov, S.; Pacchioni, G.; Freund, H. J. Oxygeninduced transformations of an FeO(111) film on Pt(111): A combined DFT and STM study. J. Phys. Chem. C 2010, 114, 21504–21509.
- [43] Zhang, K.; Li, L. F.; Shaikhutdinov, S.; Freund, H. J. Carbon monoxide oxidation on metal-supported monolayer oxide films: Establishing which interface is active. *Angew. Chem., Int. Ed.* 2018, *57*, 1261–1265.
- [44] Sun, Y. N.; Qin, Z. H.; Lewandowski, M.; Carrasco, E.; Sterrer, M.; Shaikhutdinov, S.; Freund, H. J. Monolayer iron oxide film on platinum promotes low temperature CO oxidation. *J. Catal.* 2009, 266, 359–368.
- [45] Merte, L. R.; Knudsen, J.; Eichhorn, F. M.; Porsgaard, S.; Zeuthen, H.; Grabow, L. C.; Lægsgaard, E.; Bluhm, H.; Salmeron, M.; Mavrikakis, M. et al. CO-induced embedding of Pt adatoms in a partially reduced FeO_x film on Pt(111). J. Am. Chem. Soc. 2011, 133, 10692–10695.
- [46] Li, M.; Altman, E. I. Shape, morphology, and phase transitions during Co oxide growth on Au(111). J. Phys. Chem. C 2014, 118, 12706–12716.
- [47] Fester, J.; Sun, Z. Z.; Rodríguez-Fernández, J.; Walton, A.; Lauritsen, J. V. Phase transitions of cobalt oxide bilayers on Au(111) and Pt(111): The role of edge sites and substrate interactions. *J. Phys. Chem. B* 2018, *122*, 561–571.
- [48] Walton, A. S.; Fester, J.; Bajdich, M.; Arman, M. A.; Osiecki, J.; Knudsen, J.; Vojvodic, A.; Lauritsen, J. V. Interface controlled oxidation states in layered cobalt oxide nanoislands on gold. ACS Nano 2015, 9, 2445–2453.
- [49] Fester, J.; García-Melchor, M.; Walton, A. S.; Bajdich, M.; Li, Z.; Lammich, L.; Vojvodic, A.; Lauritsen, J. V. Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. *Nat. Commun.* **2017**, *8*, 14169.

- [50] Fester, J.; Bajdich, M.; Walton, A. S.; Sun, Z.; Plessow, P. N.; Vojvodic, A.; Lauritsen, J. V. Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au(111), Pt(111) and Ag(111). *Top. Catal.* **2017**, *60*, 503–512.
- [51] Fester, J.; Makoveev, A.; Grumelli, D.; Gutzler, R.; Sun, Z. Z.; Rodríguez-Fernández, J.; Kern, K.; Lauritsen, J. V. The structure of the cobalt oxide/Au catalyst interface in electrochemical water splitting. *Angew. Chem., Int. Ed.* 2018, *57*, 11893–11897.
- [52] Reticcioli, M.; Sokolović, I.; Schmid, M.; Diebold, U.; Setvin, M.; Franchini, C. Interplay between adsorbates and polarons: CO on rutile TiO₂(110). *Phys. Rev. Lett.* **2019**, *122*, 016805.
- [53] Meier, M.; Hulva, J.; Jakub, Z.; Pavelec, J.; Setvin, M.; Bliem, R.; Schmid, M.; Diebold, U.; Franchini, C.; Parkinson, G. S. Water agglomerates on Fe₃O₄(001). *Proc. Natl. Acad. Sci. USA* **2018**, *115*, E5642–E5650.
- [54] Rodríguez-Fernández, J.; Sun, Z. Z.; Zhang, L.; Tan, T.; Curto, A.; Fester, J.; Vojvodic, A.; Lauritsen, J. V. Structural and electronic properties of Fe dopants in cobalt oxide nanoislands on Au(111). *J. Chem. Phys.* 2019, *150*, 041731.
- [55] Giordano, L.; Pacchioni, G.; Goniakowski, J.; Nilius, N.; Rienks, E. D. L.; Freund, H. J. Interplay between structural, magnetic, and electronic properties in a FeO/Pt (111) ultrathin film. *Phys. Rev. B* 2007, *76*, 075416.
- [56] Cullen, W. G.; First, P. N. Island shapes and intermixing for submonolayer nickel on Au(111). Surf. Sci. 1999, 420, 53–64.
- [57] Voloshina, E. N.; Fertitta, E.; Garhofer, A.; Mittendorfer, F.; Fonin, M.; Thissen, A.; Dedkov, Y. S. Electronic structure and imaging contrast of graphene moiré on metals. *Sci. Rep.* **2013**, *3*, 1072.
- [58] Bruix, A.; Miwa, J. A.; Hauptmann, N.; Wegner, D.; Ulstrup, S.; Grønborg, S. S.; Sanders, C. E.; Dendzik, M.; Grubišić Čabo, A.; Bianchi, M. et al. Single-layer MoS₂ on Au(111): Band gap renormalization and substrate interaction. *Phys. Rev. B* **2016**, *93*, 165422.