Two-Dimensional Iron Tungstate: A Ternary Oxide Layer With Honeycomb Geometry

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ABSTRACT: The exceptional physical properties of graphene have sparked tremendous interests toward two-dimensional (2D) materials with honeycomb structure. We report here the successful fabrication of 2D iron tungstate (FeWO₃) layers with honeycomb geometry on a Pt(111) surface, using the solid-state reaction of (WO₃)₃ clusters with a FeO(111) monolayer on Pt(111). The formation process and the atomic structure of two commensurate FeWO₃ phases, with (2 × 2) and (6 × 6) periodicities, have been characterized experimentally by combination of scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD) and understood theoretically by density functional theory (DFT) modeling. The thermodynamically most stable (2 × 2) phase has a formal FeWO₃ stoichiometry and corresponds to a buckled Fe²⁺/W⁴⁺ layer arranged in a honeycomb lattice, terminated by oxygen atoms in Fe–W bridging positions. This 2D FeWO₃ layer has a novel structure and stoichiometry and has no analogues to known bulk iron tungstate phases. It is theoretically predicted to exhibit a ferromagnetic electronic ground state with a Curie temperature of 95 K, as opposed to the antiferromagnetic behavior of bulk FeWO₃ materials.

INTRODUCTION

Inspired by the discovery of graphene and its promising prospects in both fundamental and applied science, in recent years an active and sustained search has developed for two-dimensional (2D) materials, some of which feature a honeycomb structure. Most of the 2D monolayers, like graphene, hexagonal boron nitride (h-BN), transition metal (TM) dichalcogenides (MoS₂), TM oxides (MoO₃), or the so-called MXenes (Ti₃C₂), have been generated from layered bulk crystalline solids with covalent intralayer bonding. An interesting aspect of 2D materials is the planar honeycomb geometry, which is at the origin of many of their fascinating properties, such as the linear electronic band dispersion at the Fermi level (Dirac cone), and as a consequence exceptional transport properties including ultrahigh carrier mobility and high electrical and thermal conductivities emerge, which create strong potential for future applications. Silicene and germanene have been considered as 2D allotropes of silicon and germanium, respectively, with a honeycomb structure and characteristic Dirac cone fingerprints. Unlike graphene, the honeycomb sp² configuration is not a structure element in the Si and Ge bulk crystals, and accordingly, silicene and germane exhibit a corrugated honeycomb structure with partial sp³ hybridization. The formation of 2D honeycomb materials is not limited to elements with p-electrons: one-atom-thick honeycomb layers have been also reported for transition metals with d-electrons, such as hafnium (hafnene) and tin (stanene). Recently, 2D honeycomb assemblies have been realized out of selenide nanocrystals as building blocks, which offers the possibility of tuning the material properties by tailoring the size and composition of the nanocrystals.

In a somewhat different perspective, the honeycomb lattice has been proposed to support topological insulator (TI) phases. In ternary ABO₃ oxides with the perovskite structure, the (111) plane can be viewed as a buckled honeycomb lattice, topologically equivalent to that of graphene. For this reason, ABO₃(111) surfaces have been regarded as potentially promising for realizing novel TI states. Recent theoretical work has predicted ferromagnetic and/or ferroelectric behavior of thin quantum wells of SrTiO₃(111).

Another interesting aspect of the honeycomb architecture can be encountered in ultrathin films of binary oxides, which expose polar surfaces in bulk crystals, such as, e.g., MgO(111) or ZnO(0001). Such surfaces are intrinsically unstable due to the presence of a nonzero dipole moment perpendicular to the surface, leading to a divergence of the electrostatic potential. It has been predicted theoretically and confirmed experimentally that, for a thickness of only few atomic layers, such

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oxide films adopt a hexagonal planar honeycomb structure as a means to cancel the polarity of oxide surfaces. Planar honeycomb lattices are also formed by metal-supported ultrathin silica films, such as in the SiOx,4 monolayer grown on Mo(112)25 and the SiOx bilayer on Ru(0001).26 Additionally, nonplanar honeycomb lattices have been observed in the so-called surface–V2O5 bilayer phase on Pd(111),27,28 and in TiO2 layers on Au(111),29 which form commensurate (2 × 2) overlayer structures with formally V3+ (Ti3+) species at the interface. The bonding to the metal surface, in conjunction with polarity compensation provided by the metal screening, stabilizes this honeycomb lattice.

In this paper, we report the first example of a 2D ternary oxide layer with a honeycomb geometry, which has been identified as FeWO3. 2D phases of ternary oxides have only recently been discovered, which feature fascinating structural behavior30–32 and show promise for nanocatalysis applications.33,34 The 2D iron tungstate phase described here is synthesized via a solid-state reaction of (WO3)3 clusters with a FeO monolayer on a Pt(111) surface and has been characterized by a variety of surface analytical techniques, including X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD), combined with first-principles density functional theory (DFT) analysis, thus achieving a thorough understanding of its structural and electronic properties. The bulk iron tungstate phase, ferberite (FeWO4), is the pure end member of natural wolframate (FeMn1−xWxO4) minerals, is a promising material with potential applications in photocatalysis, battery electrodes, photoluminescence, magnetism, and multiferrics.35–40

The preparation approach here employed has been proved successful for the fabrication of 2D CuWO4 nanolayers on the Cu(110) surface.31,41 Here, we utilize the reaction of cyclic (WO3)3 clusters on a well-defined FeO(111) monolayer on Pt(111), established by Li et al.,42 to create a 2D (2 × 2)-FeWO3 honeycomb structure, which has no similarity to bulk structure elements. This novel 2D ternary oxide layer consists of a mixed layer of Fe and W atoms, formally Fe2+ and W6+ species, sitting in face-centered cubic (fcc) and hexagonal close-packed (hcp) hollow sites, respectively, of the Pt(111) surface, and arranged in a (2 × 2) superstructure; this Fe2+/W6+ layer is terminated by oxygen atoms in Fe–W bridging positions, forming a buckled honeycomb lattice. DFT calculations also predict that the 2D FeWO3 layer exhibits a ferromagnetic order with a Curie temperature of 95 K, as opposed to the antiferromagnetic behavior in the bulk FeWO4 phase,43 and suggest a significant thermodynamic stability, as confirmed by the self-limiting character in agreement with the experimental observation of a self-limited growth, which is promising for advanced applications of this novel phase.

**Experimental and Computational Details**

The experiments have been conducted in three different ultrahigh vacuum (UHV) chambers, all with base pressures below 2 × 10−10 mbar, and equipped with LEED optics, electron-beam evaporators, quartz-crystal microbalances, and the typical facilities for sample manipulation and cleaning. Scanning tunneling microscopy experiments have been performed in a custom-designed UHV system, equipped with a variable-temperature STM (Oxford Instruments).27 In the present measurements, the STM was operated at room temperature in constant current mode using electrochemically etched tungsten tips. The tunneling conditions are given at the respective images, with the bias voltage applied to the sample, meaning that empty electronic states are imaged at positive bias voltage. XPS and TPD measurements have been performed in a second UHV chamber equipped with a dual X-ray source generating unfiltered Mg Kα or Al Kα radiation (XR 50, SPECS), a hemispherical electron analyzer (PHOIBOS 150, SPECS), and a mass spectrometer (QMG 220, Pfeiffer Vacuum). For the TPD measurements, the sample was positioned directly in front of the skimmer cone encapsulating the differentially pumped mass spectrometer and heated at a rate of 3 K/s. Ultraviolet photoemission spectra (UPS) have been taken in a third chamber equipped with a He I (21.2 eV) source (UVS 10/35, SPECS) and a hemispherical electron analyzer (PHOIBOS 100, SPECS). The sample work function has been measured from the low-energy secondary electron cutoff in the ultraviolet photoelectron spectra. The Pt(111) surface has been cleaned by cycles of Ar+ ion sputtering and annealing in UHV to 1173 K. In order to remove residual carbon contaminations the Pt crystal has been exposed to oxygen atmosphere (pressure of up to 1 × 10−8 mbar) at 973 K, followed by a brief flash to 1223 K in UHV. A well-ordered FeO(111) monolayer (ML) has been prepared by the deposition of 1 ML of Fe metal (1 ML is defined by the density of the surface atoms of Pt(111), i.e., 1.5 × 1015 atoms cm−2) in UHV onto the clean Pt(111) crystal held at room temperature, followed by an oxidation step at 973 K for 5 min in 2 × 10−6 mbar O2. For the experiments in the TPD chamber, the FeO monolayer has been prepared using isotopically labeled 18O2 (Sigma-Aldrich, 99%), whereas for the STM studies 16O2 was employed. The (WO3)3 clusters have been deposited onto the FeO(111) film via direct sublimation of WO3 powder, placed in a tantalum-coated Al2O3 crucible, and heated by electron bombardment. One monolayer of (WO3)3 is defined here by one WO3 unit per Pt surface atom. The Fe and WO3 deposition rates have been controlled by a quartz microbalance.

DFT calculations have been performed using the Quantum-Espresso computational code,44 employing a basis set of plane waves, ultrasoft pseudopotentials,35 and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-) functional.46 Values of 544 and 5442 eV are chosen as the energy cutoff for the selection of the plane waves for the description of the wave function and the electronic density, respectively. The first Brillouin zone is described by employing a (4,4,1) k grid in the case of the (2 × 2) phase and at the Γ point only in the case of the (6 × 6) phase. The electronic levels are broadened with a Gaussian smearing of about 27 meV, and all the calculations were performed spin-polarized. STM images were simulated applying the Tersoff–Hamann approach47 at a constant height of about 2 Å above the oxide surface. Along the z axis, a minimum empty space of 15 Å has been left to avoid interactions between replicated cells. A dipole correction48 has been applied to cancel spurious Coulombic interactions among replicated images. Core-electron energies of the W atoms were evaluated as in refs 36 and 49 by considering explicitly only the valence electrons and creating a core hole in the 4f levels, thus including both initial and final state effects into the calculations. Since a scalar relativistic approach has been applied in the present investigations, the theoretical values of core-level energies should be compared with the spin–orbit average of the 4f7/2 and 4f5/2 experimental peaks. Regarding the metal support, our DFT/PBE approach predicted an equilibrium value of the Pt lattice constant of 2.84 Å, in reasonable agreement with the experimental value of 2.77 Å. In the present calculations the DFT-predicted equilibrium parameter has been adopted, and the Pt(111) support is modeled via a slab made by four layers in fcc stacking.
frozen in the crystalline positions of bulk metal. All the Fe, W, and O atoms of the overlayer were optimized until the forces on the individual atoms were smaller than 10−3 eV Å−1.

To predict the geometric structure of the FeWO₃ phases, we perform a systematic search in the space of geometry and stoichiometry based on a novel global optimization (GO) protocol in which we use experimental input (the size of the unit cell=(2 × 2) or (6 × 6)—and the threefold symmetry), to restrict initial atomic positions into a lattice (or “sites”) and group atoms into equivalence sets so as to accelerate the geometric and configurational sampling. Figure S1 in the Supporting Information illustrates the steps of our GO approach with Figure S1b–e specified to the case of the (2 × 2) unit cell. (i) The system is composed of several layers starting from the (111) metal surface—Figure S1a (note that configurations with O atoms at the metal interface are unfavorable so that an M/O/M/O stacking is exemplified in the figure). (ii) On each layer of the (2 × 2) unit cell the following lattice sites are defined: top (T), fcc-hollow (F), and hcp-hollow (H)—Figure S1b (bridge sites are ignored as they are found from a preliminary sampling not to be significant). (iii) The lattice sites are populated according to three patterns which ensure that threefold symmetry is conserved: (111) pattern ≡ Figure S1c, kagomé pattern ≡ Figure S1d, and honeycomb pattern ≡ Figure S1e (with the two sites of honeycomb pattern populated by the same or different (as illustrated in Figure S1e) chemical elements).

By finally distributing the chemical elements (Fe, W, O) in the finite number of possibilities arising by the combination of different patterns in each layer, tentative structural models are generated as initial configurations which are then subjected to local energy minimization or a short (0.5 ps) run of DFT molecular dynamics at 800 K to check their stability.

## RESULTS AND DISCUSSION

Figure 1 shows a sequence of LEED pictures taken from the FeO(111) monolayer on Pt(111), after the deposition of 1 ML of (WO₃)₃ at room temperature, following the UHV annealing at (c) 823 K, (d) 1073 K, (e) 1173 K, and (f) 1223 K.

Figure 1. Sequence of LEED patterns (E = 60 eV) taken from (a) the pristine FeO monolayer on Pt(111), (b) after deposition of 1 ML of WO₃ at room temperature, and following the UHV annealing at (c) 823 K, (d) 1073 K, (e) 1173 K, and (f) 1223 K. consisting of six main diffraction spots surrounded by rosettes of satellite spots, which are caused by the 11% mismatch with respect to the Pt substrate. This lattice mismatch results in a Moiré pattern in the STM images with a periodicity of 25.4 Å, corresponding to a (√84 × √84)R10.9° superstructure (see Supporting Information, Figure S2). It is notable that the FeO forms a perfect wetting layer, providing a good template for the subsequent reaction. After the (WO₃)₃ cluster deposition at room temperature, the LEED pattern of the underlying FeO layer is completely attenuated and no new diffraction spots are visible (Figure 1b). This indicates that the (WO₃)₃ clusters form a continuous overlayer, which is disordered at room temperature. Annealing the sample above the reaction onset temperature of 823 K in UHV induces structural changes in the film. First, at 823 K (Figure 1c) the FeO diffraction spots reappear in the LEED pattern (although a bit blurry) and, in addition, weak reflections at the half-order positions are discernible, suggesting the formation of a (2 × 2) phase. On further increasing the annealing temperature to 1073 K, the FeO LEED spots fade away, whereas the (2 × 2) spots gain in intensity (Figure 1d), until at 1173 K only a sharp (2 × 2) pattern is present in the LEED (Figure 1e). The latter is replaced by a (6 × 6) pattern upon further annealing to 1223 K (Figure 1f). Eventually, heating above 1300 K in UHV recovers the (1 × 1) LEED pattern of the clean Pt(111) surface (not shown).

To identify the chemical nature of the ordered oxide phases presented above, the evolution of XPS core-level spectra (excited with Al Kα radiation hν = 1486.6 eV) has been monitored as a function of the annealing temperature. Figure 2 (top panels) shows a sequence of XPS spectra, which were taken in the Fe 2p₃/₂ (Figure 2a), O 1s (Figure 2b), and W 4f (Figure 2c) core-level regions for 1 ML (WO₃)₃ clusters deposited on the FeO/Pt(111) monolayer at 300 K and heated for 3 min to the indicated temperatures in UHV. For comparison, a similar sequence of spectra (without the W 4f) has been recorded after annealing of the pristine FeO(111) monolayer (see Supporting Information, Figure S3). In the bottom panels of Figure 2 the corresponding integrated core-level intensities (normalized to unity at room temperature) are plotted as a function of the
annealing temperature. The Fe 2p$_{3/2}$ and O 1s spectra of the pristine FeO(111) monolayer on Pt(111) (top curves) display peak maxima at binding energies of 709.8 and 529.7 eV, respectively, which are in good agreement with corresponding values in the literature.$^{52}$ The deposition of (WO$_3$)$_3$ clusters at room temperature causes some attenuation of the Fe 2p signal, but does not affect its peak position and spectral shape. The corresponding O 1s spectrum, however, exhibits a significantly broader line shape, which is peaked at a higher binding energy (BE) of 530.5 eV. For quantitative information, the W 4f spectra have been fitted with mixed Lorentzian and Gaussian profiles after subtracting a Shirley background.$^{53}$ The W 4f spectrum of the as-deposited (WO$_3$)$_3$ clusters could be fitted with a single W 4f$_{7/2}$–W 4f$_{5/2}$ doublet peak (marked “A”), with BEs of 35.6 and 37.8 eV, respectively, and a peak ratio of 4:3. These binding energies are compatible with an oxidation state 6+ of the W atoms, which is in line with results of previous studies.$^{31,42,54}$

On annealing to 823 K, the temperature at which the first structural changes are detected in LEED (Figure 1c), the Fe 2p spectrum recovers intensity and the O 1s spectrum remains unaffected, but the W 4f spectrum exhibits a weak shoulder at the lower binding energy side. To account for this change, an additional W 4f$_{7/2}$–W 4f$_{5/2}$ doublet component (marked “B”) with BEs of 33.9 and 36.1 eV, respectively, has been considered in the fitting analysis. This new component B can clearly be assigned to the (2 × 2) phase, which evolves at 823 K. It exhibits a much narrower line shape, with a full width at half-maximum (fwhm) of 1.0 eV, compared to that of the A component of the (WO$_3$)$_3$ clusters with fwhm = 1.7 eV, and this is attributed to the good structural order of the (2 × 2) phase (see STM images in Figure 3). The binding energy of the 4f$_{7/2}$ peak of the B component (33.9 eV) lies between the reported values for W$^{4+}$ (32.7 eV) and W$^{5+}$ (34.6 eV) species.$^{55}$ However, core-level binding energies of ultrathin oxide films on metal surfaces are difficult to compare to bulk values, due to the proximity of the underlying metal substrate.$^{56}$ For this reason, no clear

![Figure 2. Top panel: sequence of Fe 2p$_{3/2}$ (a), O 1s (b), and W 4f (c) core-level spectra taken from the pristine FeO monolayer on Pt(111) (top curves), after deposition of 1 ML of WO$_3$ at room temperature, and following the heating in UHV at the indicated temperatures. A Shirley background is subtracted from all spectra. Bottom panel: the corresponding integrated intensities (normalized to unity at 300 K) are plotted as a function of the annealing temperature. The solid curves correspond to the spectra of the (WO$_3$)$_3$ covered FeO layer, the dashed curves to the Fe 2p$_{3/2}$ and O 1s spectra of the FeO monolayer on Pt(111), displayed in Figure S3.](image)

![Figure 3. TPD spectra of oxygen from the (2 × 2)-FeWO$_3$ layer on Pt(111). The differently colored traces correspond to m/e = 32 (blue), 34 (red), and 36 (black). A heating rate of β = 3 K/s was used.](image)
assignment of the W oxidation state in the (2 × 2) phase should be made from the position of the W 4f peak. With further increasing the temperature, the B component progressively gains in intensity, whereas the A component decays linearly and completely vanishes at 1173 K (bottom panel in Figure 2c). At this temperature the (2 × 2) phase is fully established (see Figures 1e and 5c) and the W 4f spectrum contains only the B component. Its intensity is about one-fourth the intensity of the as-deposited (WO3)3 layer, which means that only a fraction of the (WO3)3 clusters reacts with the FeO layer to form the (2 × 2) phase; the rest sublimes into the gas phase. Further annealing to 1223 K, where the (6 × 6) structure is observed in LEED, causes no changes in the W 4f spectrum.

Turning to the Fe 2p3/2 and O 1s XPS spectra, it is instructive to examine first the corresponding spectra of the pristine FeO(111) monolayer (shown in Supporting Information, Figure S3) and the evolution of their intensities with temperature—see the dashed curves in the bottom panels of Figure 2, parts a and b. The latter remain constant up to 1023 K and then fall abruptly to zero at 1073 K, which is due to the thermal decomposition of the FeO layer: oxygen desorbs (see corresponding TPD spectrum in Supporting Information, Figure S4), whereas the Fe atoms diffuse into the Pt bulk, driven by the strong tendency of Fe–Pt alloying. The picture is significantly different for the (WO3)3 covered FeO layer. Here, the Fe 2p3/2 and O 1s intensities start decreasing already above 823 K, the onset temperature of the (WO3)3—FeO reaction, however, with a slower rate, reaching approximately one-fourth of their initial values at 1173 K. This rate decrease with respect to the pristine FeO monolayer is attributed to the process of incorporation of a fraction of the O and Fe atoms into the emerging (2 × 2) phase. This transformation into the (2 × 2) phase is completed at 1173 K, and the excess species desorb (O2) or diffuse into the Pt bulk (Fe). The (2 × 2) phase is characterized by Fe 2p3/2 and O 1s binding energies of 709.3 and 529.9 eV, respectively, which are different from those of the pristine FeO layer, indicating a similar chemical environment of the Fe and O atoms in the (2 × 2) phase. At 1223 K the (2 × 2) phase is replaced by the (6 × 6) phase, and this structure transformation is accompanied by a further loss of O and Fe species.

The thermal evolution of the Fe 2p, O 1s, and W 4f intensities shown in Figure 2 (bottom panels) allows us to estimate semiquantitatively the chemical composition of the (2 × 2) and (6 × 6) phases. A stoichiometric reaction between 1 ML of FeO and 1 ML of WO3 would ideally (without any material loss) lead to a layer with a FeWO4 composition. In the (2 × 2) phase, however, the initial Fe and W coverages are reduced to ~0.25 ML, which means that the (2 × 2) unit cell contains one W and one Fe atom. The oxygen coverage is 0.20 ML, yielding approximately three O atoms per (2 × 2) unit cell. This suggests that the (2 × 2) phase corresponds to a ternary oxide layer with a formal FeWO4 stoichiometry, as indeed confirmed by the DFT analysis presented below. It is noted in passing that the growth of the (2 × 2) layer is self-limited: deposition of more than the ideal coverage of 0.25 ML of (WO3)3 results in no further growth—the excess (WO3)3 amount desorbs. This is confirmed by comparing XPS spectra of the (2 × 2) phase prepared with 0.6 and 1.0 ML of (WO3)3, which are virtually identical (see Supporting Information, Figure S5). In the (6 × 6) phase, the Fe content has dropped to ~50% of its value in the (2 × 2) phase, whereas the W and O coverages have decreased less strongly, indicating that the (6 × 6) phase corresponds to an iron-deficient ternary oxide Fe1–xWO3 layer. Details of a possible atomic structure are disclosed by the DFT calculations (see Figure 8).

Further evidence for the formation of a 2D ternary oxide phase comes from TPD experiments where different oxygen isotope labeling of the precursor oxides has been employed. For this, (W16O34)3− has been deposited at 300 K onto a Fe18O monolayer and the (2 × 2) phase has been generated by annealing to 1173 K. Figure 3 shows oxygen TPD spectra from this (2 × 2) layer, where mass spectrometer (QMS) signals with m/e = 32, 34, and 36 corresponding to 16O2, 16O18O, and 18O2, respectively, are simultaneously recorded. The presence of all three molecular oxygen species in the TPD spectrum, and thus of 16O and 18O in the oxide layer, validates unambiguously the ternary nature of the (2 × 2) phase. Evaluation of the areas under the TPD traces reveals that ~60% of the oxygen in the (2 × 2) phase originates from the (W16O34)3− clusters, with the rest from the FeO substrate. This value varies with the (WO3)3 coverage, with a larger fraction of 16O atoms being incorporated into the (2 × 2) FeWO4 layer at higher (WO3)3 coverages (see Supporting Information, Figure S4d).

The surface morphology and structure evolution at different stages of the reaction between the FeO and (WO3)3 cluster layers on Pt(111) has been followed by STM. Figure 4a shows an STM image taken from a 1.0 ML FeO/Pt(111) surface covered with 0.2 ML of (WO3)3 deposited at 300 K and annealed at 673 K for 5 min (a), and after further annealing at 873 K for 5 min (b). The images in panels c and d are taken at higher resolution from the latter surface: (c) frame size, 50 × 50 nm2, U = 1.5 V, I = 0.1 nA; inset, 10 × 10 nm2, U = 0.8 V, I = 0.07 nA; (d) frame size, 20 × 20 nm2, U = 0.7 V, I = 1.0 nA.

Figure 4. STM images (100 × 100 nm2, U = 1.0 V, I = 0.1 nA) of 0.2 ML of (WO3)3 deposited at 300 K and annealed at 673 K for 5 min (a), and after further annealing at 873 K for 5 min (b). The images in panels c and d are taken at higher resolution from the latter surface: (c) frame size, 50 × 50 nm2, U = 1.5 V, I = 0.1 nA; inset, 10 × 10 nm2, U = 0.8 V, I = 0.07 nA; (d) frame size, 20 × 20 nm2, U = 0.7 V, I = 1.0 nA.
transformation of the FeO layer into the \((2 \times 2)\) phase, as exemplified in the STM images in Figure 4, part c and d. Here, the patches with the brightest contrast are ascribed to the remaining \((\text{WO}_3)_2\) islands, whereas the areas with intermediate and low contrast correspond to the FeO(111) and \((2 \times 2)\) phases, respectively. In the upper left corner of Figure 4c, a larger area covered by the \((2 \times 2)\) phase is visible, which coexists with the FeO layer, as evidenced by the high-resolution STM image in the inset of Figure 4a and \((\text{WO}_3)_2\) islands. In the middle part of the STM image shown in Figure 4c, the FeO layer is broken into several small triangular islands, which are surrounded by small domains of the \((2 \times 2)\) phase, as evidenced by the high-resolution STM image in Figure 4d.

The solid-state reaction is completed after annealing to 1173 K, as confirmed by the STM image in Figure 5a, showing the Pt(111) surface which is only partially covered by the \((2 \times 2)\) layer. The high-resolution image in Figure 5b confirms the good structural order of the \((2 \times 2)\) phase and allows us to measure its height with respect to the bare Pt(111) surface. On the latter, few triangular etch pits are visible, which is associated with the local distortion of the Pt surface caused by the Fe diffusion into thePt bulk, as detected in XPS (Figure 2a). The line profile in the inset of Figure 5b shows that the \((2 \times 2)\) layer features a corrugation of \(\sim 0.2\) Å and an apparent height of 1.0 Å, which is by \(\sim 0.5\) Å lower than the measured height of the FeO layer on Pt(111). A full \((2 \times 2)\) wetting layer could be prepared by depositing 1 ML of \((\text{WO}_3)_2\) onto the FeO monolayer at room temperature and annealing to 1173 K in UHV (Figure 5c). Here, two large Pt terraces separated by a monatomic step are displayed, which are completely covered by the \((2 \times 2)\) layer, with only few residual FeO islands present near the step edge. The STM image in Figure 5b reveals an ordered hexagonal array of triangular-shaped protrusions with a lattice constant of \(0.54 \pm 0.01\) nm, which defines the \((2 \times 2)\) periodicity. The origin of the experimental image contrast will be discussed below in connection with DFT modeling.

Raising the annealing temperature above 1173 K induces distortions in the \((2 \times 2)\) layer, where the initially homogeneous film separates into small \((2 \times 2)\) domains with an average size of about 7 nm (Figure 6a). On other areas of the same surface, the \((2 \times 2)\) phase is partially replaced by a new structure (top part of Figure 6b), which consists of rings with six protrusions and a hole in the center, arranged in a hexagonal \((6 \times 6)\) lattice. This is in line with the observation of a \((6 \times 6)\) LEED pattern in this temperature range (Figure 1f). Similar ringlike motifs (although with a different contrast than the \((6 \times 6)\) building units) can be spotted at the domain boundary regions in the \((2 \times 2)\) layer in Figure 6a (encircled with a solid black line) and may be considered as nucleation centers of the \((6 \times 6)\) phase. The transition from the compact \((2 \times 2)\) to the more open \((6 \times 6)\) phase appears to be quite smooth and continuous and is accompanied by a progressive loss of Fe and O species, as established in the XPS analysis. After final annealing at 1250 K, the \((2 \times 2)\) phase is completely converted into the \((6 \times 6)\) layer, which exhibits only moderate long-range structural order (Figure 6c). The high-resolution STM image in Figure 6d presents the \((6 \times 6)\) structure in greater detail: it consists of rings with six protrusions, arranged in a honeycomb lattice, and a hole in the middle. Line profiles (not shown) reveal an apparent height of 1.4 Å with respect to the Pt(111) surface.

DFT modeling is used to unveil structural and electronic properties of these unconventional \((2 \times 2)\) and \((6 \times 6)\) 2D
phases. To predict their geometric structure, we performed a systematic search in the space of geometry and stoichiometry, i.e., exploring different atomic arrangements and compositions,\textsuperscript{25,31} using as experimental input the size of the unit cell—$(2 \times 2)$ or $(6 \times 6)$—and threefold symmetry enforced within this cell. This search is based on a global optimization (GO) protocol in which, taking advantage of experimental input, the geometric and configurational sampling is accelerated by restricting initial atomic positions into a lattice (space volumes are merged into points or "sites") and by grouping atoms into equivalence sets or "orbits"\textsuperscript{47} (for more details see Supporting Information, Figure S1). This GO protocol has then been applied to two-layer and four-layer systems in the $(2 \times 2)$ unit cell. The Fe, W, and O chemical potentials\textsuperscript{59} needed to compare energies when the system's stoichiometry is changed in the random moves\textsuperscript{25,31} were taken from the Moiré FeO/Pt(111) phase, $(\text{WO}_3)_3$ clusters, and gas-phase O$_2$ molecules, respectively, where for O$_2$ the free energy obtained in the given conditions of temperature (673 K) and pressure (10$^{-13}$ atm) were used, while the use of an extended oxide phase such as FeO/Pt(111) or a gas-phase species such as the $(\text{WO}_3)_3$ cluster to define appropriate chemical potentials for the species involved in surface reactions follows the proposal given in formula 1 of ref\textsuperscript{31} in which such a procedure was successfully employed to study the CuWO$_4$ ternary ultrathin oxide phase.

Two major conclusions result from this systematic investigation. First, the lowest-free-energy structure of the two-layer system corresponds to a FeWO$_3$ stoichiometry where one Fe and one W atom per unit cell, arranged in the honeycomb pattern at the metal interface (Figure S1e, Supporting Information), are covered by a topmost O layer arranged in a kagomé pattern (Figure S1d, Supporting Information). The energetic, structural, and electronic features of the proposed model are in excellent agreement with experiment (vide infra). Second, both the enthalpy and the free energy of formation of all the four-layer systems are positive, implying that they are thermodynamically unfavorable in a wide range of experimental conditions. This result is consistent with the self-limited growth of the $(2 \times 2)$ phase observed experimentally and points to a fair robustness of the two-layer phase, thus making it interesting for applications. Indeed, despite its being a reduced phase—thus necessitating oxygen-poor and/or high-temperature conditions to be formed—its formation enthalpy from the FeO phase and $(\text{WO}_3)_3$ clusters is only slightly positive:

$$\text{FeO}(2 \times 2) + 1/3(\text{WO}_3)_3 \rightarrow \text{FeWO}_3 + 1/2\text{O}_2$$

while the formation free energy is strongly negative ($\Delta G = -7.62$ eV per unit cell) under the given experimental conditions.

The structure model of the $(2 \times 2)$ FeWO$_3$/Pt(111) phase is presented in Figure 7, parts a and b. All the O atoms in the upper plane are at the same height from the Pt(111) interface, whereas in the lower plane the W atom is located about 0.2 Å farther away from the interface than the Fe atom. Since the number of Fe atoms per $(2 \times 2)$ cell is about three in the pristine FeO/Pt(111) phase, the transformation into the $(2 \times 2)$ FeWO$_3$ phase (1 Fe per $(2 \times 2)$ unit cell) has to be accompanied by a loss of Fe atoms (presumably by dissolution into the Pt bulk), which is indeed observed experimentally (see Figure 2a). Furthermore, the experimentally determined saturation coverage of 0.25 ML for tungsten is in perfect agreement with the model structure. The simulated STM image of the $(2 \times 2)$ FeWO$_3$/Pt(111) phase, for bias voltage similar to the one used to obtain the STM image in Figure 5d, is shown in Figure 7c. The bright triangular contrast originates from the topmost O and the underlying W atoms. This triangular instead of honeycomb-like appearance is due to the weak contrast contributed by the Fe atoms and is in perfect agreement with the experimental STM image (Figure 5d). Additional agreement between experiment and the proposed
model is found for the work function and the W core-level binding energies: the predicted value of the system work function is 6.32 V, again in excellent agreement with the experimental value of 6.35 V (given the limitations of our DFT/PBE approach such a degree of agreement is of course in part coincidental). The DFT-predicted W 4f core-level binding energy is 35.7 eV for W atoms in gas-phase (WO₃)₃ clusters, and 34.6 eV in the (2 × 2) phase. This result is in qualitative agreement with the experimentally observed decrease of the W 4f₁/₂ binding energy from 35.4 eV for deposited clusters to 33.8 eV in the (2 × 2) phase.

In terms of magnetism, it should be stressed that the present DFT calculations predict a ferromagnetic electronic ground state, at variance with FeO which is an antiferromagnet in both bulk rock-salt structure ⁶⁰ and in its ultrathin FeO/Pt(111) state, at variance with FeO which is an antiferromagnet in both DFT calculations predict a ferromagnetic electronic ground phase.

The predicted value of the system work function of the (2 × 2) phase is 6.32 V, again in excellent agreement with the experimental value of 6.35 V (given the limitations of our DFT/PBE approach such a degree of agreement is of course in part coincidental). The DFT-predicted W 4f core-level binding energy is 35.7 eV for W atoms in gas-phase (WO₃)₃ clusters, and 34.6 eV in the (2 × 2) phase. This result is in qualitative agreement with the experimentally observed decrease of the W 4f₁/₂ binding energy from 35.4 eV for deposited clusters to 33.8 eV in the (2 × 2) phase.

In terms of magnetism, it should be stressed that the present DFT calculations predict a ferromagnetic electronic ground state, at variance with FeO which is an antiferromagnet in both bulk rock-salt structure ⁶⁰ and in its ultrathin FeO/Pt(111) form ⁶¹ (clearly due also to the different geometry of these systems). In Figure 7d the spin-resolved projected density of states (PDOS) of the (2 × 2) phase is reported, showing as interesting features a significant spin polarization on the d-orbitals of the Fe atoms (the d-spin-majority Lowdin population is 4.86 vs a d-spin-minority Lowdin population of 1.43) together with a significant ionic character (Lowdin charge is about +1.2 e on Fe), whereas the W atom is poorly spin-polarized and also scarcely ionic, due to a donation of 1.4 e from the W s-orbital; the latter is nearly compensated by a 1.2 e donation from the interfacial Pt atoms into the diffuse W p-orbitals according to a Lowdlin analysis (it should, however, be recalled that the Lowdlin analysis is not accurate for diffuse atomic orbitals, so the latter result should be taken with care). Stimulated by the finding of a ferromagnetic electronic ground state, we have calculated the energy difference between the ferromagnetic ground state and an antiferromagnetic state obtained by doubling the (2 × 2) unit cell and populating the Fe atoms of each primitive unit cell with opposite spins. This energy difference amounts to 0.01 eV, which, translated into an Ising model, gives rise to a Curie temperature of 95 K.

An analogous DFT investigation has been applied to the (6 × 6) phase, however, limiting the GO search to two-layer systems and a smaller set of possible configurations, thus a more focused sampling. Despite these limitations, the lowest-energy structure thus found, shown in Figure 8, parts a and b, is the only one with a negative value of free energy of formation (as detailed below). It exhibits a simulated STM pattern in fair agreement with the experimental one—see Figure 8c in comparison with Figure 6d. Moreover, the proposed stoichiometry Fe₃W₈O₂₁ corresponds to a further reduction in Fe coverage with respect to the (2 × 2) phase (which would contain nine Fe atoms in this unit cell), and analogously in O coverage (21 vs 27 O atoms), whereas the W content is basically kept (eight vs nine W atoms); this is in good agreement with the drop in the intensity of the Fe 2p and O 1s XPS peaks in going from the (2 × 2) to the (6 × 6) phase. The reaction energy for the transformation of the (2 × 2) into the (6 × 6) phase is

\[ \Delta E = -0.14 \text{ eV per } (6 \times 6) \text{ cell} \]

and in this case the reaction free energy \( \Delta G \) coincides with the reaction energy \( \Delta E \). The predicted value of \( \Delta E \) is close to zero, indicating that the (2 × 2) and the (6 × 6) phases are in competition and can coexist in the given conditions, as is indeed observed experimentally.

Clearly, the use of chemical potentials of the FeO phase and (WO₃)₃ clusters is an approximation, since in reality the excess Fe and W atoms will diffuse into the Pt bulk, whereas the excess O atoms will evolve as gas-phase O₂. The structural features of our predicted model are rather similar to those of the (2 × 2) phase, the two phases being composed of basically the same building blocks: each metal atom is tricoordinated by three O atoms in bridge sites between two metal atoms (a further discussion of STM images can be found in the Supporting Information). The predicted value of the work function of the (6 × 6) phase is 5.4 eV, slightly lower than the experimental value of 5.9 eV; this discrepancy can be attributed to the presence of some residual (2 × 2) patches in the preparation of the (6 × 6) phase, see Figure 6b, with their higher work function of 6.3 eV, which artificially increases the experimental estimate of the (6 × 6) work function. The predicted XPS BEs for all the W atoms in the unit cell are basically the same, despite the fact that there are two inequivalent W species, and amount to 34.8 eV, a value very similar to the corresponding quantity in the (2 × 2) phase, in agreement with experiment.

**CONCLUSIONS**

Two-dimensional iron tungstate phases with (2 × 2) and (6 × 6) honeycomb structures have been synthesized via a solid-state reaction of (WO₃)₃ clusters with a FeO monolayer on a Pt(111) surface and characterized by a variety of surface analytical techniques, including XPS, STM, LEED, and TPD, combined with first-principles DFT analysis. The DFT modeling clarifies the atomistic structure of both the (2 × 2) and (6 × 6) phases and allows us to rationalize their electronic properties. Particularly...
mixed Fe.  

neither of the iron tungstate bulk crystal phases has terms of electronic and magnetic behavior, which has no represents a structural phenomenon with wider implications in  

One-Dimensional Honeycomb Structures of Silicon and  

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