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2D oxides on metal materials: concepts, status, and perspectives

Giovanni Barcaro and Alessandro Fortunelli *

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Oxide materials at the two-dimensional limit, in particular in the form of ultrathin films of oxides (UTOx) grown on metal surfaces, represent promising materials in view of both fundamental science and technological applications. While the former aspect is widely recognized, these systems have not yet realized their full potential in terms of the latter (technological) aspect. In the present perspective, we review the field and its basic underlying concepts, and at the same time we provide an overview of the most promising future directions with a focus on their potential toward and relationships with real-world exploitation.

1. Introduction

After the completion of a coherent palette of surface science characterization techniques around the late 1970s, a systematic application of these techniques to and an exploration of a wide variety of systems began. Metal surfaces were the first material surfaces to be thoroughly studied, since they naturally satisfied the need to have a conducting substrate to avoid charging issues when using charged probe particles (electrons and ions). Next, ultrathin oxide-on-metal (UTOx) interfacial systems followed suit, and in the last 30 years a great deal of activity has been devoted to these materials – the topic of the present perspective. Oxides are often insulators or semi-conductors, but charging effects are circumvented by their ultrathin character, which enables charge transfer with the underlying metal. Starting with the early achievements,[1,2] great advances in both fabrication and characterization of hybrid metal/oxide interfacial systems have been realized and have rapidly accelerated in the last 2 decades or so, exploiting advances in microscopy and spectroscopy as applied to surface science, in conjunction with the pivotal role played by computational modelling.[3–6] Great efforts were devoted to the refinement of synthesis and characterization techniques (both experimental and theoretical), achieving a high degree of control over the obtained morphologies and in many cases clarification of their geometric structures down to atomic level.[7–13] This enabled the founding principles ruling the formation and properties of UTOx to be derived.[14]

The prevailing strategy in this field has traditionally been a fundamental and reductionist (typically physicochemical) approach. The key goal was to achieve a full structural and electronic characterization of model systems, including structural resolution reaching the atomic limit, resulting in the unprecedented possibility of precisely linking local atomic and electronic features of a single nano-object to its fundamental physicochemical properties. These model systems were deemed to provide the basic constituents into which a real system could be reduced.

Indeed, this strategy has been successful and the level of sophistication reached extremely high.[15] These studies soon realized that "small (UTOx) is different": although UTOx presented structural and electronic phenomena reminiscent of bulk oxides, these were realized in unique forms due to the effects of 2D confinement and UTOx/support interaction, leading to novel emergent phenomena. It was therefore clear that UTOx represented both models of bulk oxides and novel materials in their own right.

In terms of novel science and technological applications, UTOx systems present pros and cons. As an advantage/opportunity, the presence of a metal substrate, which can act as a reservoir of electrons, is beneficial when facile charge transfer is needed. As a drawback, the oxide film, being ultrathin, can be seen as a buffer layer, whose strong interaction with the substrate damps its specific features. For example, screening due to the metal reduces electrostatic interactions (potentially giving rise to strong and both scientifically and technologically appealing effects in charge-separated materials) up to metallization of the oxide (strong mixing of the oxide wave function with that of the metal, with oxide orbitals giving a significant contribution at the Fermi energy).[16]

Putting aside these intrinsic limitations, the link between fundamental studies and potential technological applications has not often been the primary objective in UTOx surface science studies. This is a pity since hybrid systems containing a metal-oxide interface can find a variety of chemical and physical applications. Indeed, the systems considered here belong to the wide class of 2D materials, which are the object of intense research activity and of several reviews and special issues, see *e.g.* ref. 17.

CNR-ICCOM & IPCF, Consiglio Nazionale delle Ricerche, Pisa, 56124, Italy. E-mail: alessandro.fortunelli@cnr.it

Clearly, the link between model systems and applications cannot be direct. Model systems are typically obtained under extreme or idealized conditions to get rid of perturbations and to achieve a complete understanding, but the link between materials under these conditions and real-world materials (which exhibit statistical fluctuations and local inhomogeneities) must be built piece-by-piece. Concepts and methods (and method validation) can be carried over, but specific results or predictions cannot be carried over straightforwardly.

Our aim in this perspective is to contribute to filling this gap. We will briefly review the status of the field, including the latest advances, and the main concepts thereby produced, and show which are the successes and which are the challenges, to build a link between the ideal and the real world, finally concluding by predicting possible (desirable) future developments.

The application and property we will use most to illustrate this link are chemical reactivity and catalysis. For reasons of space, the present perspective will not treat many aspects of UTOx science which are obviously important but also very promising for applications, such as spin/(opto)electronics. However, we are confident that the approach illustrated here can also be extended to these aspects and different fields.

Section 2 presents our main arguments, and for the convenience of the reader and for their intrinsic importance in potential technological applications it is split into 5 different topics: (i) structural motifs, (ii) robustness, (iii) catalysis, (iv) ternary oxides, and (v) surface nanopatterning. Coherently with our proposed goal, each topic is further divided into 4 sub-sections: (1) a brief introduction; (2) main concepts; (3) focused status review; (4) perspectives. Section 3 summarizes our conclusions.

Anticipating our main arguments and perspectives, when considering (i) structural motifs, apart from briefly reviewing the commonest UTOx motifs from the literature, we will outline a computational strategy to derive preferential growth modes according to a ''brick'' approach in conjunction with global optimization algorithms. We will also suggest that this general approach for structural prediction can be exploited to derive a general UTOx/metal catalogue and therefore general structure–property relationships, such as work-function or core-level shifts or chemical reactivity (catalysis), that can be checked and verified against experimental information.

A critical issue of such extreme nanostructured systems is related to their (ii) robustness, *i.e.* the stability/transformations of these materials from extreme synthesis/characterization conditions (very low pressures and high temperatures) to conditions closer to real-world technological applications. In this perspective we will briefly review ''naturally'' robust phases, mention coating and border passivation to avoid phenomena of aggressive oxidation, and discuss a strategy exploiting equivalence principles between the different thermodynamic conditions to link synthesis/characterization and applications.

UTOx materials can find potential applications in many technological fields. For reasons of space we limit ourselves to (iii) catalysis, where much progress has been achieved since the observation of the strong metal support interaction (SMSI) in the late 1970s. Both phase borders and the catalytic role of the metal support towards adsorbate species in relation to electrostatic polarization, metallization and work-function tuning effects will be discussed.

When at least two different metal cations are present, (iv) ternary oxides are obtained, which open the way to novel structural motifs and structure–property relationships. Grounded on the general principle that size-mismatch drives the formation of new structures, while energy-mismatch drives the tuning of reactivity, we will discuss segregation (resulting, for example, in layer-by-layer growth) or intermixing between the two components, the challenge represented by the associated combinatorial structural complexity, and suggest appropriate material design approaches to deal with such challenges (such as high-throughput screening).

Finally, we consider (v) surface nanopatterning, *i.e.*, the formation of regular nano-sized patterns on UTOx systems and their exploitation to induce supra-organization of adsorbed species. This phenomenon will be distinguished as being induced by morphological features (such as point defects or strain-relief patterns), electronic features (modulation of the work function), or entangled morphological/electronic features. After reviewing naturally nanopatterned UTOx phases, it will be shown how adsorbate species can have a feedback effect and create more complex metal/UTOx/adsorbate nanopatterned systems.

2. Review and discussion

Before discussing the 5 topics of this perspective, it is useful to repeat our aim and mention what will not be found in this article, topics which will be deferred to a future publication.

We will review the main concepts, and the successes and challenges – and thus the perspectives which will be useful for building a link between model systems and real-world applications, here mostly focused on catalytic function.

We will not deal, therefore, with UTOx synthesis and preparation, although these are obviously crucial for the development of the field. We mention only that impressive results have been achieved by combining surface chemistry and interface coupling and novel synthetic tools under the control of morphology or multilayer engineering (ternary or composite materials).[18–20] We refer to the several excellent reviews existing on these topics.[21–24]

We will also not treat fundamental methods, neither experimental nor theoretical. Methods can often be carried over almost directly from ideal to real-world systems and applications, naturally after augmenting, *e.g.* computational methods with appropriate statistical/stochastic approaches to face the greater complexity of real materials. Moreover, there are several excellent reviews devoted to methodological aspects.[16,25–28]

Finally, we will deal mostly with chemical reactivity and will not touch physics applications, such as electronics or solar cells,[29] although we believe that UTOx could make a significant contribution to these fields.[30,31]

2.1 Structural motifs

Introduction. An increasingly vast database of UTOx structures achieving atomic detail[32] is being provided to researchers in the UTOx field by the combined use of surface science characterization techniques and theoretical methods.[14,33] Experimentally, progress has been strictly connected to instrumental development, with microscopy characterization pre-eminent in this field,[3,34] and still currently advancing at great speed.[6,35,36] Fairly recent is the development of *in situ* characterization under environmental (*e.g.*, catalytic) conditions, from its early achievements[37,38] to its latest progress.[39,40] As mentioned above, characterization pushed to atomic limits on model systems has been triggered by the goal of deriving general principles ruling the formation of UTOx, and building structure–property relationships which link the local atomic structure of an individual nano-object to its physicochemical properties. Attention has, however, eventually often been focused on specific systems, so that a comprehensive review and understanding of UTOx structural motifs are still lacking.

Concepts. Defining/elucidating structural motifs (i) is useful, at a most basic level, as a classification scheme that allows one to synthetically describe a given UTOx structure, and catalogue it in a database. The ideal and more ambitious goal of such a classification is, however, to forge this information into a predictive tool. Clearly, this goal can be pursued at different levels of sophistication/accuracy, from (ii) using structural motifs as grounds for educated guesses, to (iii) deriving building principles ruling UTOx preferential growth modes, up to (iv) translating the structural motif analysis into operational computational protocols. Level (ii) pertains to experimental and/or qualitative thinking. Levels (iii) and (iv) pertain to the theoretical/computational realm. Computational modelling has indeed played a pivotal role in this topic. As an example of (iii) from our own work, we derived building principles of pseudomorphic UTOx grown on (111) metal surfaces, by taking TiO_x/Pt(111) phases as a prototypical example, and rationalized the interplay of morphology and stoichiometry in these phases.[41] Strikingly, these principles were found to apply to many (111)/(111) epitaxial systems, including oxides of radically different natures, such as reducible and non-reducible oxides which were found to exhibit unexpected similarities.[21] Hereafter, we will focus on how to extract and systematize structural motifs from given phases (i), and outline how to transfer these principles into a general approach for structural prediction (iv).

In Fig. 1 the extraction or decomposition of a given TiO_x/Pt(111) UTOx phase into its constituent structural motifs (i) is illustrated. The red circles define MO_3, rect-MO_4 and square-MO_4 motifs, which are then replicated to cover the 2D plane (tessellation); in the following the difference between rect-MO_4 and square-MO_4 bricks will be neglected, by using the general term MO_4 brick. Fig. 2 then shows how this definition can be pictorially schematized further and used to progressively decompose other TiO_x/Pt(111) UTOx phases,[42] together with an artistic decoration from the Pergamon museum recalling the same motif (Fig. 2d). A structural motif (or ‘‘brick’’) is then defined by its stoichiometry: MO_2, MO_3, MO_4,. . ., and by its epitaxial relationship with the underlying surface, as illustrated in Fig. 3 for the MO_2, MO_3, MO_4 motifs over the usual high-symmetry points: hollow, top, and bridge epitaxial sites and zero rotation angle. By combining bricks *via* vertex or side sharing, one can thus obtain a multitude of experimentally observed UTOx phases, with Fig. 4 showing a few examples.

The definition of structural motifs can be systematized (i) to build a general database or catalogue, which can also be tested against 2D material databases[43,44] to check the completeness of the approach. Let us consider as an illustrative example an fcc(111) surface, as depicted in Fig. 5a, with its usual high-symmetry epitaxial sites: hollow (H1, H2, H3), bridge (B1, B2, B3, B4) and top (T1, T2, T4, T4). The MO_2, MO_3, and MO_4 bricks discussed above can be defined and named according to a systematic nomenclature based on the population of stacking sequences: for example, MO_2 over a bridge site can be named as M(B3)//O(T3)–O(T4), where stacking sequences are separated by a ‘‘‖’’ symbol, M is the metal and O is the oxygen atom, and the

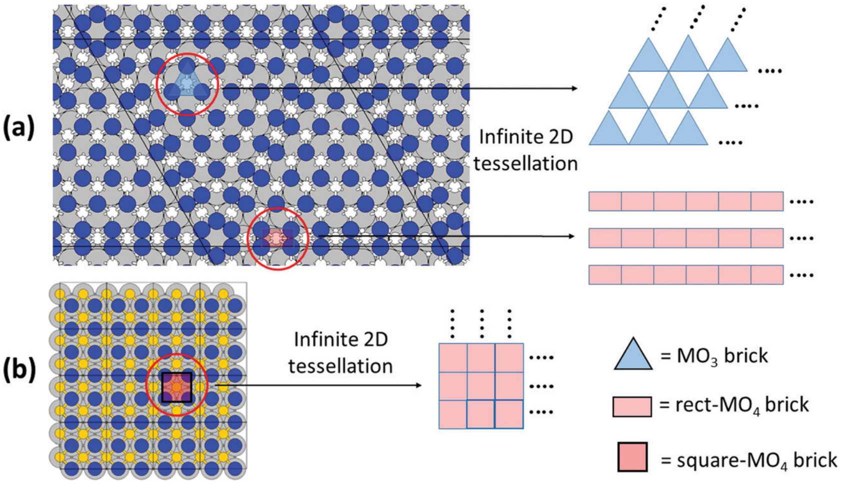

Fig. 1 (a) Left-hand side: hexagonal TiO_x (9 × 9) phase in which MO_3 bricks and deformed MO_4 bricks (rect-MO_4 bricks) are circled in red (hexagonal holes, not highlighted, also compose this phase); right-hand-side: MO_3 and rect-MO_4 bricks are replicated to cover (tessellate) the plane; (b) square NiO(100) phase in which regular MO_4 bricks (square-MO_4 bricks) are circled in red (left-hand side) and used to cover the plane (middle). Oxygen atoms are in blue, nickel atoms in yellow, titanium atoms in white, atoms of the support (platinum or silver) in gray.

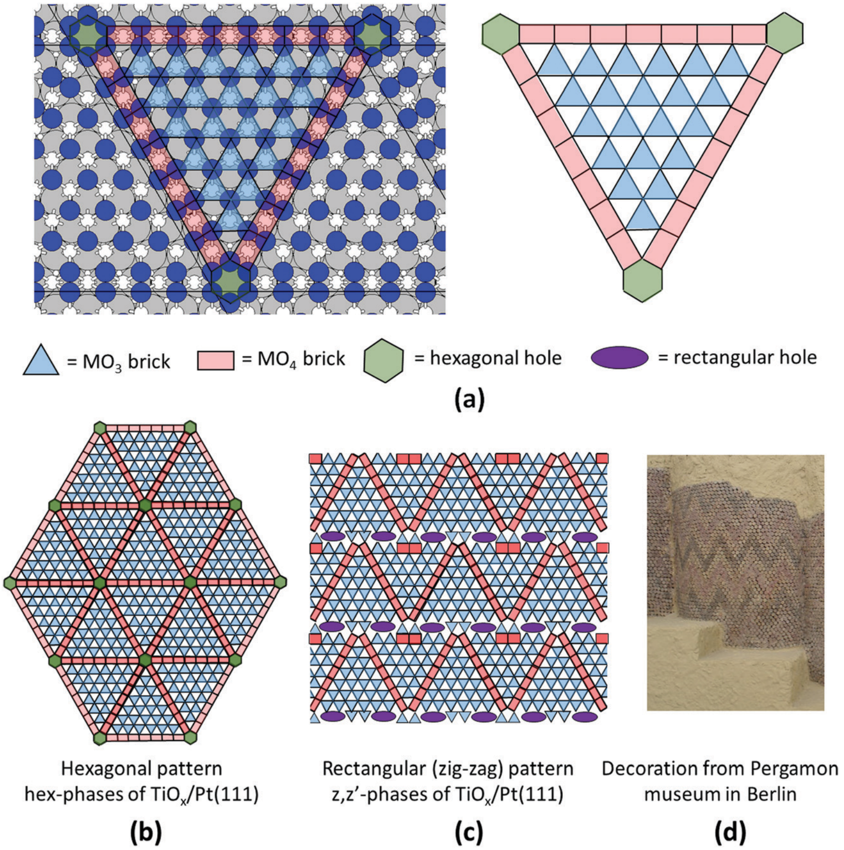

Fig. 2 (a) On the left, tessellation of the unit cell of a TiO_x (9 × 9) phase in terms of MO_3 and MO_4 bricks and hexagonal holes – on the right, the same unit cell without the atom depiction underneath; (b and c) the complex structural motif shown in the right panel of (a) is used to build hexagonal (b) or rectangular (c) UTOx TiO_x phases; (d) an artistic decoration from the Pergamon museum recalling the previous geometric motifs.

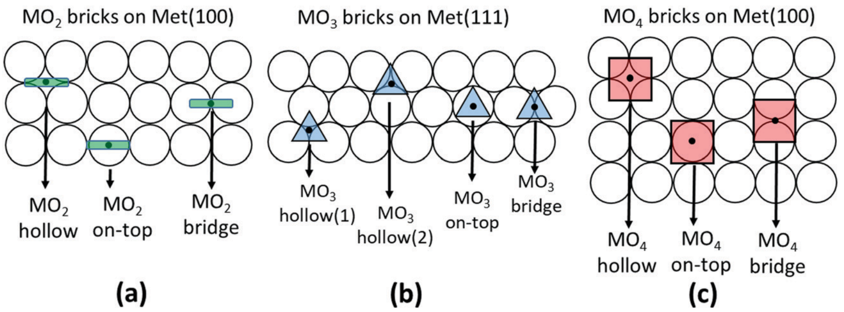

Fig. 3 Typical examples of epitaxy of: (a) MO_2 bricks on a (100) metal surface; (b) MO_3 bricks on a (111) metal surface; (c) MO_4 bricks on a (100) metal surface.

epitaxial sites are within parentheses. See Fig. 5b for MO_2(bridge), MO_3(hollow1, hollow2), MO_4(hollow) as examples. It is easy to generalize this procedure to multi-layer phases, pictorially illustrated for a few examples of UTOx bilayer systems in Fig. 6 (a previous discussion can be found in ref. 16 and the associated Fig. 2, 5 and 6).

Now, this knowledge can be exploited in structural prediction (iv).

First, at a basic level, structure databases can be exploited in a global optimization protocol as a source of configurations or moves.[16]

Second, we believe that this knowledge can be pushed further and translated into a general approach for structural prediction. The elementary action is to partition a system into a sum of known (recognized) pieces[45] or structural motifs, each extended and translated to cover the plane, as shown in Fig. 1a–c. This (which is the crucial point of this paragraph) allows one to associate to each structural motif a procedure to evaluate its energy. The next step is to calculate the structural motif energy as a function of a set of variables: stoichiometry (coordination, chemical environment), lattice parameters, charge state (which can be controlled and enforced in QM calculations as a

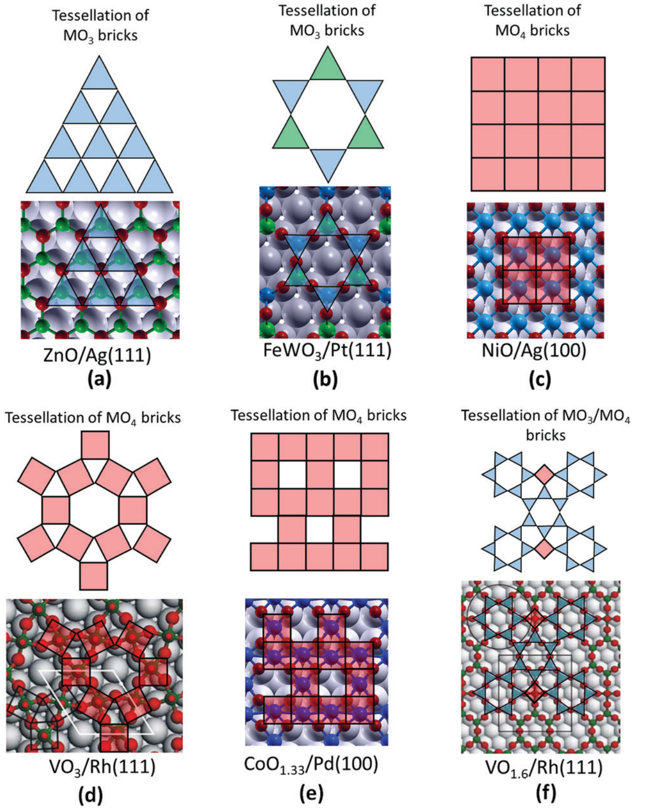

Fig. 4 Examples of single-layer UTOx phases and their 2D-tessellation using: (a) MO_3 bricks with a single orientation sharing vertexes – ZnO/Ag(111); (b) MO_3 bricks with two orientations sharing vertexes – $FeWO_3$/Pt(111); (c) MO_4 bricks sharing edges with a single orientation – NiO/Ag(100); (d) MO_4 bricks sharing vertexes with three orientations – VO_3/Rh(111); (e) MO_4 bricks sharing vertexes with a single orientation – Co_3O_4/Pd(100); (f) MO_4 and MO_3 bricks sharing vertexes with multiple orientations – $V_{13}O_{21}$/Rh(111).

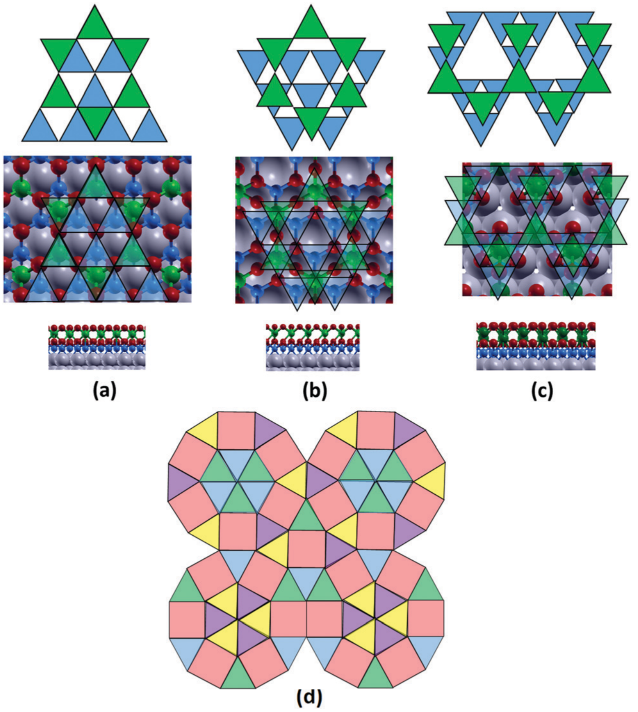

Fig. 6 Examples of double-layer ternary UTOx and their tessellation, with segregation of the metals in different layers: (a–c) illustrate three configurations of $FeWO_x$ with Fe in the lower layer and W in the upper layer; (d) the structure of a quasi-crystalline lattice of a $BaTiO_3$/Pt(111) UTOx phase.[178]

further degree of freedom), and epitaxial relationship with the substrate for any given oxide/metal combination. The so-calculated energy, the analytic or numerical function of these parameters, is the effective Hamiltonian (or force-field) providing the local quantity which, summed over all sections of any complex phase locally partitioned into structural motifs, finally gives the value of the global observable energy. Once the global energy of the system has been so defined, it can then be exploited in global optimization (GO) techniques to predict the structures of novel UTOx phases,[16] as well as the ideal dimension of the metal/oxide unit cell (see below), and the morphology and stoichiometry of the oxide layer under given conditions. Notably, we underline that not only can the energy be predicted or decomposed following this protocol, but equally well any property of the system, such as, for example, the local work function, which is a fundamental quantity,[14,46] or core-level shifts,[47] or structural dynamics (*i.e.*, catalysis). In fact, it is not only the lowest-energy configuration of the given model or structural motif, on the given unit cell and with the given stoichiometry, which is of interest, but one can also include in the structural database higher-energy configurations

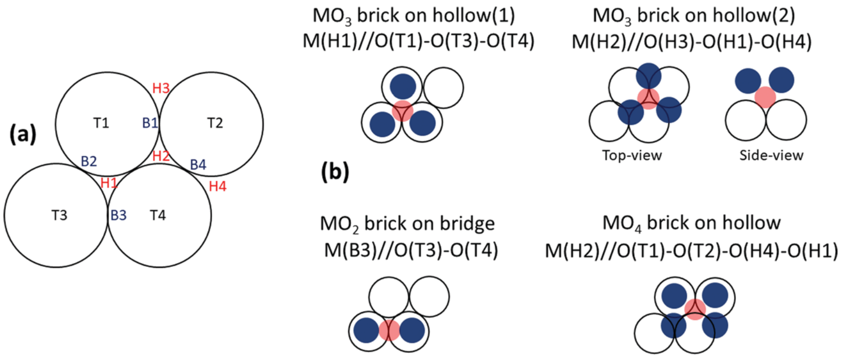

Fig. 5 (a) Epitaxy sites for bricks: hollow (H), top (T) or bridge (B) sites of a (111) metal surface; (b) corresponding examples of MO_2, MO_3 or MO_4 bricks on a (111) metal surface, named by specifying the sites of M and O atoms constituting the bricks.

of the motifs, and use them profitably in a structural prediction approach for the whole UTOx phase. This can be achieved by performing global optimization on the different models or structural motifs and extracting from the GO runs not simply the global minimum structures but also some low-energy configurations. Meta-stable higher-energy configurations are a natural outcome of a GO study – see, for example, the GO prediction of the structure of a $CuWO_4$/Cu(110) phase in ref. 48 – and the possibility of having such configurations is crucial for the success of global optimization schemes for global UTOx phases, in which constraints imposed by matching regions with varying stoichiometry and epitaxy impose a fraction of non-optimal local configurations. Moreover, such meta-stable higher-energy configurations can be used not simply to find global minimum structures, but also to explore saddle points in the potential energy surface (PES), and therefore energy barriers and hence reactivity and catalysis (see the discussion below).

We advocate this approach as a coherent and thorough implementation of the traditional reductionist or model-system approach, in which complexity is dissected into elementary building blocks, the basis of much surface science research.

Several partial but illustrative early implementations of the proposed approach exist.

A proof-of-principle example can be found in ref. 47 in which a joint experimental–computational investigation was carried out on an alumina $AlO_x/Ni_3Al(111)$ bilayer UTOx covered by a regular array of Ni nanoparticles pinned to nodes of the 4.2 nm superstructure (see Section 2.5 for further details of the oxide structure).[1,49] When exposed to oxygen, the oxide layer undergoes a thickening effect, while the metallic particle gets covered by an external layer of nickel oxide. In ref. 47 to model the thickened aluminum oxide, a further AlO layer has been added to the starting ABCA stacking, globally giving an ABCABC stacking and a composition of the top-layer of Al_3O_3. Using this structural model, a simulation of the Al 2p core level shifts of all the different Al atoms of the system brought the QM predictions into excellent agreement with the experimental XPS spectra.

As another example, the energy of extended structural motifs as a function of unit cell parameters has been used to define the intrinsic equilibrium lattice parameter and elastic moduli of ultrathin oxide-on-metal systems.[50] In this approach the energy difference between the two systems – supported UTOx and bare substrate – as a function of unit cell is defined as the intrinsic energy of the UTOx phase, whose minimum and curvature provide intrinsic equilibrium quantities. These considerations can be seen as an extension and generalization of the protocol for predicting Moiré patterns on the basis of elastic considerations.[51,52] They are akin to and eventually lead to the identification of generic sources of strain in heteroepitaxy (for example, in analogy with metal-on-metal systems[53] or in analogy to thicker films), then defining a thickness-dependent UTOx lattice constant,[54] and thus rationalizing inhomogeneous strain distribution in islands of $CeO_2(111)$ on Cu(111), for example. Our contention is that one cannot just identify these sources of strain, but can also turn this analysis into operative protocols for *a priori* structural prediction of nanopatterns (see Section 2.5).

As a further extension of this approach, a complete phase made up of a combination of structural motifs can be used as a 'complex brick', and its optimal epitaxy on a given substrate can be then studied. For example, assuming a hexagonal TiO_x/metal(111) phase, as illustrated in Fig. 2a, and assuming as a structural degree of freedom the dimension of this phase (the number of triangular units along each direction), one can ask for which dimension and angle rotation a perfect epitaxy (coincidence lattice) with a given underlying substrate is realized. This approach led us to predict the TiO_x/Pt(111) hex-(9 × 9) phase (with a rotation angle of 0°) discussed earlier[41] in advance of its experimental observation. Clearly, this approach can be further generalized using a finite rotation angle, to produce various TiO_x/Pt(111) wagon-wheel, pin-wheel, *etc.* phases.[55] It should be underlined that the theoretical or computational prediction of novel phases in advance of experiment includes other examples in the UTOx field (see *e.g.* ref. 56), thus demonstrating once more the pivotal role played by computational modelling in this field.

Additionally, the work function of an FeO_x/Pt(111) phase has been predicted by dissecting it into basic motifs with different epitaxial relationship to the substrate.[46]

Finally, polarity is also a key descriptor of energetics, see Fig. 7 for a schematic illustration of polar *vs.* non-polar UTOx phases, and has been investigated in depth.[26] We do not have space here to discuss in detail all the issues and results connected with polarity in UTOx systems, and we refer the reader to the excellent review by Goniakowski *et al.*.[57] A key concept in this topic is the competition between the tendency to adopt a depolarized *vs.* a polarized stacking, an effect which can give rise to unexpected morphologies in UTOx. A depolarized structure is preferred when the interaction with the underlying substrate is quite weak and the oxide adopts a flat structure in order to minimize its internal energy. As an example, this is the case of zinc oxide adsorbed on Ag(111): ZnO, which exhibits polar stacking along the (0001) planes in the bulk, but when adsorbed on the silver surface adopts a flat geometry modulated by a Moiré pattern due to the superposition of almost unperturbed metal and oxide patterns.[58] In contrast, the oxide prefers to retain a polarized stacking (associated with an energetically unfavourable surface dipole moment) when the interaction with the support is strong enough to prevail over the depolarization mechanism. This latter situation is often encountered in UTOx grown on 3rd-row transition metals, such as Pt, which form strong chemical bonds involving d orbitals with the UTOx overlayer. A classic example is the many phases of TiO_x grown on Pt(111)[59] where

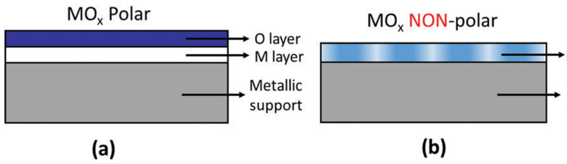

Fig. 7 Schematic depiction of: (a) polar and (b) non-polar UTOx.

polar structures exhibit Ti at the interface with the metal occupying hollow or bridge positions of the (111) metal lattice. A compromise between the two phenomena is found, interestingly, when considering the (9 × 2) structure of CoO grown on Pd(100), where the system adopts a mixed depolarized/polarized structure (in the form of "waves") managing to optimize at the same time the energy of the oxide and the interaction with the substrate.[60]

Review. Here we will not give a thorough review of UTOx structural families that have been classified up to now in the literature for which we refer to previous publications,[4,14] but rather we will illustrate few selected examples of how structural motif concepts can be used to analyse some prototypical metal-supported UTOx phases.

Let us consider first one of the several TiO_x phases grown on Pt(111).[41] With titania/platinum being a strong interaction, the TiO_x/Pt(111) film has a tendency to grow epitaxially (111)/(111). The most common motif is thus triangular TiO_3 bricks connected *via* vertexes (top red circles in Fig. 1a). Considering an optimal side of the TiO_3-brick/Pt-hollow-site of ≈ 3.12 Å, and the Pt lattice constant of 2.775 Å, we find that 8 TiO_3 bricks can be accommodated per 9 Pt atoms. However, the regions with TiO_3 bricks in bridge positions and especially on top of Pt atoms are highly stressed and the Ti:O stoichiometry is too low. Stress is reduced by removing the top brick, with the consequent creation of a hole (see hexagonal holes in Fig. 1a), while some TiO_3 bricks are replaced by TiO_4 bricks (bottom red circles in Fig. 1) that decrease the stress and, at the same time, increase the stoichiometry, thus predicting the experimentally observed phase.[41]

Further examples are nickel and cobalt UTOx grown on Ag(100) and Pd(100). Having a square symmetric metal substrate, MO_4 bricks sharing edges are the most common motifs. For NiO_x/Ag(100) this choice explains the experimentally known stable phase,[61] favoured by the 1 : 1 stoichiometry of the oxide and an excellent match between oxide/substrate lattice constants (see Fig. 4c). In contrast, for CoO_x/Pd(100) strain relief and a lower preferred stoichiometry (see the Co_3O_4 bulk spinel) lead to the formation of holes in a Co_3O_4 overlayer (see Fig. 4e).[62] Another well-known (100)/(100) UTOx phases is MgO/Ag(100), in view of its use in insulating layers in spintronic applications,[63] with the importance of after-growth treatments in the derivation of a given morphology of UTOx.[64]

A few more examples are given in Fig. 4.

In the case of ZnO grown on Ag(111), the UTOx can be described as a perfect tessellation by MO_3 bricks similar to the (111)-pseudomorphic islands discussed for TiO_x phases on Pt(111). However, in this case, given the stronger ionic character of the oxide with respect to titania, the film adopts a depolarized flat structure which interacts quite weakly with the underlying metal substrate, giving rise to a Moiré phase with a spacing of about 2.2 nm.[58] The absence of dislocation lines is justified by the fact that perfect tessellation corresponds to an ideal 1 : 1 ratio between metal and oxygen ions, which, in the case of zinc oxide (see Fig. 4a), corresponds to the thermodynamically preferred stoichiometry of both the bulk and the ML oxide. In the same figure, the structure of an $FeWO_3$ UTOx grown on Pt(111) provides another example of tessellation obtained by using only MO_3 bricks, rotating half of them at an angle of 180° (see the different colouring of the triangles in Fig. 4b) to produce a kagome-like pattern in which a larger number of oxygen ions is accommodated, thus achieving the desired stoichiometry.[65] Exotic patterns can also be realized by using MO_5 bricks (topologically analogous to the MO_4 bricks by adding a further oxygen ion on top of the central metal ion M), as shown in the structure of a VO_3 UTOx grown on Rh(111), see Fig. 4d,[66] obtained by linking the bricks *via* their vertexes. On the same metal surface, a phase with stoichiometry $V_{13}O_{21}$ can also be stabilized,[67] which can be described in terms of interconnected MO_3 and MO_5 bricks sharing their vertexes; see Fig. 4f. It is interesting to note that, in agreement with the basic principles of crystallography, phases characterized by a higher charge/oxidation state of the metal ion tend to increase the distance between positive cations by sharing vertexes more than sides. Side sharing is more often realized in the case of metal ions with lower positive charge, like NiO (+2.0) or Co_3O_4 (+2.7), in contrast to higher oxidation states (like +4 for W in $FeWO_3$ or +3.2 for V in $V_{13}O_{21}$) which present vertex sharing.

Not illustrated here, we finally note that other cases of tessellation by MO_3 bricks sharing vertexes can be found for FeO phases on both Ag(111) and on Ag(100),[68,69] where the 1 : 1 ratio between Fe and O ions is determined by the stabilization of the lower oxidation state of iron under reducing conditions. The morphology of ultrathin ceria on Pt(111) has also been investigated.[70–72]

Finally, (110) substrates have been much less studied, but are certainly of great interest, as more open surfaces will lead to a wider structural phenomenology, especially interesting in view of finding models of complex oxides. They have in fact been found in the oxidation of Ru surfaces.[73] They have also been studied in the case of ultrathin ceria on Cu(110),[74] where it was found that this more exotic substrate gives rise to and can in fact be described as a CeO_x/CuO_x/Cu(110) ternary system. Significantly, a ternary UTOx is also the $CuWO_4$/Cu(110) phase mentioned above.[48]

Perspectives. Referring to the extensive discussion given in the Concepts section for more details, we conclude that the two most promising perspectives in this topic are: (i) the rational construction of a database of UTOx structural motifs, and (ii) the development of predictive computational protocols which translate the reductionist idea founding UTOx science into a predictive tool for structural global optimization and dynamics. We believe that these two perspectives can be pursued by following the lines sketched above. Work is in progress in our lab to realize this perspective.

2.2 Robustness

Introduction. The issue of robustness (stability) is ubiquitous in nanoscience and nanotechnology. Nanomaterials are in fact intrinsically "frail" (meta-stable) because interfaces are energetically pricy. In the UTOx field, this issue is exacerbated by the extreme pressure conditions (typically ultra-high-vacuum, UHV) needed to apply surface science characterization tools, often accompanied by high temperatures to speed up growth and/or kinetics toward thermodynamic equilibrium. In other words, the robustness issue is ultimately related to the fundamental strategy and drive in this field toward idealized, model, but fully (atomistic-wise) characterized systems. In catalysis, this well-known issue goes under the name of pressure and materials gaps.[75] Such extreme pressures and temperatures correspond to strongly reducing or de-coordinating conditions. Therefore, the UTOx phases thus produced may not survive under milder, closer to real-world technological, (often oxidizing) conditions, due to the higher chemical potential of potentially reactive gas-phase species under these latter conditions and the abundance of low-coordinated sites in the 2D nanostructures. This poses an issue to which this sub-section is dedicated.

Concepts. From a thermodynamic point of view, every observed UTOx phase possesses a stability range as a function of temperature and pressure, *i.e.*, a range in which either it corresponds to the global minimum of the system under the given conditions and constraints, or it has kinetic barriers high enough to bring its lifetime up to macroscopic values and allow for its surface science characterization. By varying environmental conditions, phase transformations among different 2D oxide nanostructures can occur and have been observed. Therefore, phase diagrams as functions of environmental parameters can in principle be constructed, and have indeed been constructed for a few systems over a wide range of parameters, see *e.g.* ref. 76.

What is useful in this context is deriving equivalence principles, *i.e.*, mapping the position in the free-energy landscape of a given phase (stable under some conditions of temperature and chemical potential of constituent species) under the different conditions one is interested in (*e.g.*, room temperature). This translation exercise from ideal to real conditions is necessary to make information drawn from UTOx science meaningful to applications, and to make sensible predictions, *i.e.*, to carry over results, not simply methods and concepts.

Clearly, there are exceptions to the robustness issues and the need for a translation mapping, *i.e.*, UTOx phases exist that have been prepared under an extreme environment but are so stable as to survive under ambient conditions as well. Although not an oxide, graphene is a renowned example of a very stable 2D phase discovered by surface science,[77] and much later triggering the field of 2D materials.[17] Such exceptions also exist in the field of UTOx and some will be reviewed below.

In general, however, a major issue related to UTOx is frailty, *i.e.*, their high surface reactivity under realistic conditions. Thus we come to the crucial effects of adsorbates, leading to different stoichiometry and atomistic structures. Among the possible surface reactants, the most ubiquitous are oxygen and water/humidity (surface hydroxylation).[78,79] In recent years, the interface between water and oxides has started to be investigated thanks to the development of new instrumental techniques to derive information at the solid–liquid interface, such as synchrotron X-ray scattering,[80] X-ray photoelectron spectroscopy,[81] liquid-cell scanning tunnelling spectroscopy and microscopy,[82,83] and X-ray techniques coupled to cyclic voltammetry.[84,85] Water adsorption on thick oxides, which has been the object of many experimental and theoretical investigations,[86] can be used as an analogy to illustrate topics of investigation, such as: (1) the competition between molecular and dissociative adsorption with the consequent formation of hydroxylated surfaces (see the rich literature in the field of mineral–water interfaces[87]), and (2) how the presence of adsorbed water modifies surface reactivity and dielectric properties.

One approach to solving the issue of robustness is coating: when protected by a buffer layer, UTOx phases can be stable simply because the chemical potential of reactants at the buried interface is high.[88] One instructive example of an ultrathin buffer layer is that of a cobalt oxide CoO monolayer deposited on top of an Ni_3O_4 trilayer.[89] This pseudo-morphic overlayer allows for the growth of metal clusters onto the UTOx phase, still exploiting point defects in Ni_3O_4 to act as nucleation (nano-templating) centers for metal cluster growth, but without the undesirable reactivity of the bare Ni_3O_4 trilayer. Incidentally, it has been suggested for a long time[90] that, because of structural and chemical compatibility, thin films of Co_3O_4 may be useful as buffer layers for strongly oriented or epitaxial films of functional oxides, such as perovskite-type ferroelectrics and cuprate superconductors. In this connection, Liu *et al.*[91] offer an interesting example in which a decrease in size corresponds to enhanced resistance to oxidation, and in which a careful tuning of passivation techniques leads to the formation of stable 2D nanomaterials. A parallel may be established here with ligand-protected metallic nanoclusters in solution, where surface functionalization prevents particle coalescence/sintering and retains desirable (optical, magnetic) properties associated with nanoconfinement.[92]

Regardless of the possibility of finding stable UTOx phases, deriving equivalence or translation principles, as mentioned above, represents a powerful tool: for example, in catalysis to exploit UTOx science to reconstruct reaction free-energy diagrams. To illustrate this point, let us start with a well-known technique in this respect: that is reverse models, as illustrated in Fig. 8. Let us assume for definitiveness that the rate-determining step in the catalytic path of interest under given conditions corresponds to overcoming the "$\alpha \rightarrow \beta$" barrier *via* the "σ" saddle point, *i.e.*, the "$\alpha + B \rightarrow \beta$" reaction (where "$\alpha$" and "$\beta$" are given states of the surface and "B" is a gas-phase reactant), then followed by the "$\beta \rightarrow \gamma$" step, *i.e.*, the "$\beta + C \rightarrow \gamma$" reaction *via* the "$\sigma$*" saddle point (where "$\gamma$" is a state of the surface and "C" is a gas-phase reactant). Now, surface science can play a role in providing mechanistic information here. If the "β" state in fact represents a stable minimum along the path, one can prepare "β" under conditions of very low "C" pressure so as to increase the "$\beta + C \rightarrow \gamma$" free-energy barrier (as illustrated in Fig. 8 by the red box surrounding the modified energy profile in red) and make it larger than the "$\beta \rightarrow \alpha + B$" backward barrier, and perform a thermal kinetic study of "β" under these conditions, thus determining the free-energy difference between the "β" and "σ" states, which is a key piece of information to reconstruct the reaction free-energy diagram. A famous example of this approach outside the UTOx field is Ertl's studies of ammonia synthesis,[93] but reverse models can

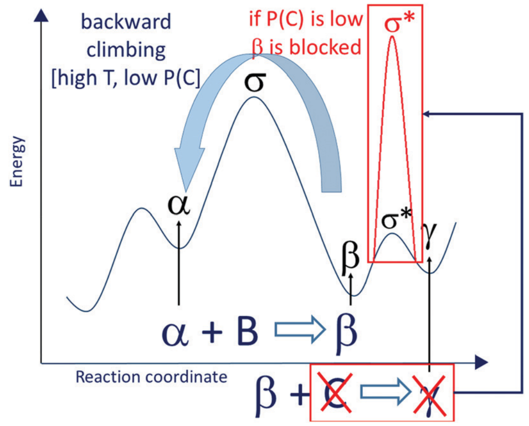

Fig. 8 Schematic reaction energy landscape in which α, β, and γ are local minima, and σ, σ* are transition states for the steps: "α + B → β" and "β + C → γ", respectively, where B and C are gas-phase reactant species. The energy profile under production conditions is in blue, while a non-reactive case is colored in red, in which the pressure of C – *i.e.*, *P*(C) – is damped to stop the reaction at β, thus allowing experimental investigation of the backward step "β → α + B".

equally well be applied to UTOx. We stress that this approach can be generalized and has a universal validity. The strategy is to analyze the given (assumed or predicted) catalytic reaction path, single out stable intermediates (*i.e.*, states occurring after a significant drop in free-energy, such as the "β" state in Fig. 8, but in general any state for which it is possible to find a UTOx phase which can be atomically characterized *via* surface science techniques), and manipulate these "β" states, punctuating the path to obtain information on their energetics, so as to quantitatively reconstruct portions of the reactive free-energy landscape which are as large as possible. To conclude, we add three notes. First, equivalence or mapping principles are obviously needed to make this translation quantitative. Second, one could extend the potentialities of this approach to their limits by combining it with the reductionist protocols of Section 2.1, *i.e.*, determine the energetics of a given phase *via* structural motif or elementary building block models. Third, the combination of surface science techniques with investigating systems *via ex ante* and *ex post* non-*in situ* characterization (before and after the catalytic process) is an approach which can be very usefully employed within the proposed framework.[94]

We believe that the approach just outlined is a powerful tool to simultaneously obtain quantitative information and qualitative insight into catalytic processes.

Finally, we note that a specific feature of ternary (multi-component) systems (discussed below in Section 2.4) in terms of robustness is the stability of a given chemical ordering with respect to fluctuations towards, for example, random distribution induced by the entropy driving force (thermal treatment). This feature is crucial for the exploitation of these oxide systems in applications.[95]

Review. It is useful to review briefly the most robust UTOx phases known so far.

In non-reducible oxides, variations in stoichiometry due to oxidation/reduction by species in the environment are not thermodynamically favored. This is the case of simple oxides that will be discussed at the end of this section. Reducible oxides in which the metal cation is in its highest oxidation state, often achieved under oxidizing conditions resembling those of real-world applications, are also robust to oxidation environments. An example which will be thoroughly discussed in the catalysis section is iron oxide, FeO_x. Iron oxide can be prepared in its lower oxidation state (FeO) at the nanoscale on Pt(111),[10] but generally, under ambient conditions, is converted to a trilayer with nominal stoichiometry of FeO_2.

Silica is an important material in many applications (it could perhaps be considered the most important oxide), and has SiO_2 stoichiometry in the bulk. When grown on Mo(112)[96] and on Ru(0001)[56] a single layer phase with nominal stoichiometry $SiO_{2.5}$ and crystalline-like structure can be stabilized. On Ru(0001) a bilayer phase can also be grown in crystalline-like, hydroxylated or amorphous structures.[97,98] It is interesting that all these phases are stable and have been produced, thus providing atomic models of widely different phases of a covalent oxide. Still considering Ru(0001), a (meta-)stable zig-zag-like phase has recently been singled out by Kuhness *et al.*,[99] characterized by a stoichiometry of $SiO_{2.17}$ and a thickness intermediate between the monolayer and the bilayer. Note that the hydroxyl termination achieved by subjecting the bilayer phase on Ru(0001) to electronic stimulation in the presence of an amorphous deposition of ice,[98] is technologically relevant, as all the surface dangling bonds are then saturated and robustness is remarkably improved. Although not within the scope of the present perspective, we note that fundamental insights into technologically relevant growth processes can also be provided by such UTOx studies.[100]

In the wide screening and resulting comprehensive phase diagram of TiO_x/Pt(111) phases,[41,76,101,102] the most robust phase turned out to be the react-one, generated at a relatively high value of oxygen pressure. Interestingly, its structural determination[103] demonstrated that it is formed by a stoichiometric TiO_2 bilayer with a lepidocrocite structure (formed by stacking of nanosheets in the form O–Ti–O···O–Ti–O···) which interacts quite weakly with the metal substrate.

Still in the class of transition-metal oxides, two other very stable UTOx phases have been found. One is WO_3 grown onto Pd(100).[104] This phase presents an oxidation state of the W atoms of 6+ and, importantly, tungstyl groups perpendicular to the surface so that it can be used as a good model for catalysis by WO_3. Another phase corresponds to a ternary UTOx: $CuWO_4$ on Cu(110),[48] which exhibits oxidation states of the W atoms of 6+ and of the Cu atom of 2+: its structure can be described as the stacking of WO_4 tetrahedra with two oxygens pointing towards the metallic substrate and with the other two oxygens pointing towards the top-most layer, where they are interconnected *via* [1−10] lines of Cu ions.

Finally, cerium oxide can be easily stabilized under ambient conditions in a CeO_2 bulk-like form both on Cu(111)[72,105] and on partially-oxidized Cu(110)[74] (for more details on these systems, see Section 2.4). Stoichiometric CeO_2 can also be grown on Ru(0001),[106] although this latter system corresponds to quite a thick deposition of oxide (from 7 to 10 nm).

Now considering simple oxides, we find the already-mentioned ZnO on Ag(111)[58,107] and the well-known MgO films supported on Ag or Mo(100), with MgO systems having been intensively investigated from the point of view of their structure and electronic properties.[33,64,108,109] Both Mg and Zn metals are stable in the 2+ oxidation state, giving rise to oxides with a strongly ionic character.

Although these phases have demonstrated stability under realistic oxygen pressure, only a few systems have been tested against the presence of water (humidity).[78,79] Note, in this connection, that some of the phases that are stable against oxygen can transform into hydroxylated phases in the presence of humidity or surface-adsorbed hydrogen, as in the case of an ML UTOx ZnO grown on Pd(111).[110] Another oxide which has been prepared in a crystalline-like form under UHV conditions, but which has been shown to undergo strong modifications when exposed to the environmental conditions of a real-world application, is Al_2O_3. UTOx bilayer alumina grown on either $Ni_3Al(111)$ or (110) surfaces has been present in the UTOx field since the beginning.[1,2] When subjected to O_2 these phases undergo thickening and surface oxidation (in the form of an Al_3O_3 tri-layer)[47] and when subjected to humidity they undergo amorphization/hydroxylation.[111]

More generally, we note that some attention has also been given to the effect of water on UTOx systems, and the first investigations have appeared on both reducible and non-reducible oxides, at both low water pressures (near to UHV conditions) and higher water pressures (nearer to realistic ambient conditions). In most cases, given the intrinsic complexity of these systems, joint experimental and computational investigations are needed to shed light on the interwoven effects taking place at the solid–liquid interface. To give some examples, it has been found by Sterrer *et al.*[79] that, under ambient conditions, water can dissociate on iron oxide UTOx, creating a super-structure where hydrogen bonding connects surface hydroxyl groups to water molecules from the first layer of the solvent, whereas the silica bilayer is less reactive towards water dissociation and only ion bombardment can induce the formation of surface silanol groups. Strongly basic ionic oxides (like CaO) can be morphologically altered by the presence of water, which determines the formation of the corresponding hydroxide and a consequent increase in the complexity of the system. Arble *et al.* have shown that in NiO(1 × 1) UTOx on Ag(100) a single water molecule (UHV conditions) is adsorbed in a molecular form, whereas, in presence of more than one molecule (higher vapour pressures) dissociation is induced thanks to stabilizing effects played by hydrogen bonding.[112] The same investigation carried out on UTOx of MgO supported on Ag(100) confirmed that at very low pressures and ambient temperature, water does not dissociate at flat terraces and the detected hydroxyl groups are probably due to dissociation taking place at the borders due to the active role of the metal substrate.[113] The role of surface defects in water adsorption has been investigated by Lackner *et al.*[78] in $ZrO_2(111)$ UTOx supported on a $Pt_3Zr(0001)$ substrate, finding that adsorption/desorption cycles can alter the surface morphology. As mentioned above, water attacks UTOx AlO_x surfaces, as first demonstrated by Maurice *et al.*[114] and quite recently confirmed by Shavorskiy *et al.*,[115] who both observed roughening and thickening effects due to the formation of a mixed oxy-hydroxide layer in the UTOx grown on NiAl(110) consequent to water attack of adsorbed OH and H_2O species and reaction with metallic Al from the underlying alloy.

Perspectives. The most straightforward perspective in this topic is to search for and widen the set of UTOx phases which are stable under ambient conditions in view of an easy technological transfer to real-world applications. In this search, computational global optimization approaches using structural motifs in conjunction with structure prediction protocols, as outlined in Section 2.1, could and should play a key role.

More generally, the most appealing perspective seems to us still pursuing the prevailing approach in UTOx science and completing it coherently and systematically by finding appropriate model systems for all phases of real-world interest. This seems especially promising in catalysis, as discussed above, since one can employ translation principles to derive crucial information (*e.g.*, quantitatively reconstruct portions of reaction free-energy diagrams that are as large as possible), but this strategy is completely general. In this connection, one most important and we believe actually most accessible perspective is to find model phases of hydroxylated surfaces. The importance of these systems is obvious, considering the ubiquitous presence of water/humidity under technological conditions. Although clearly more complicated than O-terminated phases, it is entirely possible that such models are not presently available simply because not enough effort has been dedicated to them. A similar goal for amorphous systems may be much more complicated, but would also be extremely rewarding, due to their connection to real-world systems.[16] We believe in fact that technological oxide substrates are both hydroxylated and amorphous.[111]

Finally, to conclude this robustness topic, we note that systems that are not robust enough to survive less extreme (realistic) conditions can still be relevant not only as models of meta-stable phases but also to study fundamental phenomena in an ideal setting. Moreover, in the future, along with technological developments, conditions which are presently extreme could become more accessible (less costly), and strongly reduced UTOx phases might be used directly in technology, *e.g.* in quantum technologies.[116]

2.3 Catalysis

Introduction. Most common catalysts consist of metallic particles deposited over an oxide support.[117] The different roles played by these actors in the catalytic process (metal particles and oxide support) have been controversial for a long time. Only in recent years, thanks to the development of sophisticated experimental characterization techniques[6] aided by theoretical modeling, have insights into the mechanistic steps of some (simple) catalytic processes become clearer.[12,118–122] Under typical working conditions and due to the ubiquitous presence of oxygen and/or humidity, the catalyst metallic particles are covered by a thin layer of oxide (usually mixed with hydroxyls and other ligand species), whose precise stoichiometry with respect to bulk phases depends on the specific reaction and reaction conditions. In this context, the study of model systems (such as metal-supported UTOx films) and of their multi-component variants (such as metal nanoclusters supported over UTOx) and of their transformations, can provide important insight into catalytically active species and reaction mechanisms of real-world processes, including 2D oxides as realistic catalysts.[123] Since the beginning of the field, the reactive properties of metal-supported UTOx have therefore been the subject of a growing number of investigations.[124–127] This is the topic of the present section.

Concepts. The basic point is that the reactive response of a metal-supported UTOx material is strongly influenced by the underlying metal surface, thus acquiring peculiar features.

Historically speaking, in an investigation of the catalytic properties of metal particles supported on oxide surfaces, a peculiar effect, consisting in the formation of a UTOx on the facets of the metallic particles, was recognized as being responsible for the abrupt reduction of the sticking coefficients on the oxide-encapsulated metallic particles with a consequent suppression of the catalytic activity.[128] This phenomenon, called SMSI – strong metal support interaction – contributed to opening the way to the study of the chemical properties of UTOx (oxide-on-metals ''inverse systems'' as catalysts). As will be shown in the review section, however, in some cases SMSI does not have a detrimental effect on the catalytic function of the system (and the opposite can even occur). Clearly, being able to predict this effect is the first step in controlling it, and energy descriptors can be useful for this purpose, such as the adhesion energy of the UTOx to the substrate.[129] Moreover, a distinction should be made between extended regions of UTOx and borders of UTOx islands, where the uncovered metal of the support can itself play a direct catalytic role.

In general, with regard to catalysis by UTOx, we can say that the proximity of the metallic substrate combined with the extremely reduced thickness of the oxide produces three main effects: (i) unique reaction (*e.g.*, oxidation–reduction) energetics related to the electrostatic polarization of the underlying metal support, especially when charge-separated species whose dipoles are oriented perpendicular to the surface are involved; (ii) UTOx metallization (closure of the band gap) due to the merging of the oxide wave function with that of the substrate, leading to various effects, among which is enhanced screening of dipoles oriented parallel to the surface; (iii) when the work function of the metallic support is low enough, electron tunneling thorough the oxide layer can take place from the support to adsorbed species. These aspects will be briefly discussed in the following review.

A concept that has been only very partially exploited so far in catalysis by UTOx is the connection with structural motifs and the associated predictive computational approaches discussed in Section 2.1. First, structural databases can be exploited in a global optimization protocol as a source of configurations or moves, not only in the unconstrained space of global optimization, but as actual reaction paths connecting two local minima. This possibility can be straightforwardly employed in computational approaches to catalysis such as the Reactive Glocal Optimization (RGO) algorithm.[130] Second and equally importantly, the rational design of catalysts by global optimization algorithms can relate not only to general surface properties (such as stability and work function) but also and crucially to specifically designed active sites. For example, active sites could be designed with a particular distribution of atomic and electronic features to selectively favor specific interactions among adsorbates to minimize transformation energy barriers.

Review. For reasons of space, we will limit the following review basically to the latest results achieved on the most investigated oxide materials in the field of catalysis. For a more exhaustive panorama of this topic, the reader is referred to the many existing excellent reviews and perspectives, such as ref. 124 and 131–135 to cite some among the most recent ones.

Reducible oxides: $\mathbf{FeO}_x$. Catalysis by FeO_x UTOx phases has been investigated by a large number of groups, as this oxide represents a prototypical case of a reducible oxide.

We start by recalling that, under extremely reducing conditions (very high temperatures between 700 and 1000 K and very low gas pressures), when using thick iron oxide as a substrate for metal cluster growth, the SMSI effect takes place, consisting in the full coverage (encapsulation) of the metallic particle by a monolayer-thick FeO deposit. In passing, we note that the process of reduction of Pt-supported FeO can be pushed even further, as shown by Knudsen *et al.*,[136] who exposed the supported FeO monolayer to atomic hydrogen at room temperature and produced a series of new phases containing only 2-fold-coordinated Fe atoms. Such phases are able to dissociate water and, if annealed at higher temperature in the presence of water, can be easily re-oxidized. However, later experimental and computational investigations showed that SMSI is not always detrimental to catalytic activity, and that the catalytic activity of SMSI systems can be restored, or even enhanced with respect to uncovered metal particles.[137] To mention the latest results, Xu *et al.*[138,139] have shown that a way to achieve an enhanced catalytic power by creating more active sites is to use incomplete covering by the oxide layer, exploiting the fact that the oxidation reaction can take place at the oxide island borders thanks to the so-called support–metal-interface-confinement (SMIC) effect.[11] Further confirmation of a ''reaction-at-border'' effect has come from Kudernatsch *et al.*,[140] who investigated at both experimental and computational level the CO oxidation reaction of Pt(111)/FeO islands, proposing that preferential catalytically active sites correspond to oxidized Fe edges. These results underlie a possible direct involvement of the supporting metal itself in the catalytic process, a phenomenon that can be realized when the metal is ''near'', *i.e.* when the oxide overlayer is ultrathin.

When the encapsulation of metal particles by the FeO bilayer is complete, a way to enhance the catalytic activity is to work under an oxygen-rich atmosphere and at lower temperatures, when an oxidized FeO_{2-x} overlayer can be formed, which can be catalytically active towards reactions like water dissociation.[141] The debate over the transformations and properties of Pt(111)/FeO_x is still open and very active,[142] and a recent review[135] discusses the most recent results on this system in an exhaustive way. Further results on this system come from Zhang *et al.*,[142] who suggested that both FeO and FeO_{2-x} overlayers play a role in CO oxidation, and that the reaction takes place at the interface between the reduced and the oxidized phase.

The use of metal supports other than Pt and ad-species other than CO has been taken into account by other groups. For example, Merte *et al.*[143] have investigated the adsorption of NO on an FeO bilayer by comparing two different metal supports: in the case of Pt(111), poor adsorption is observed (in agreement with the aforementioned tendency to inertness exhibited by the full FeO monolayer on Pt under reducing conditions), whereas a strong tendency towards adsorption is observed when FeO is grown on Ag(111). The authors have related the adsorption properties to the rumpling of the oxide layer induced by the underlying metal surface: in the case of Pt-supported FeO, the strong rumpling of the film passivates the oxide through steric hindrance, whereas this effect does not occur for the flatter and weakly interacting FeO on Ag(111).

Finally, to deal with issues related to the cost of expensive noble metals (like platinum or palladium) as catalysts, Guo *et al.*[144] proposed the deposition a single-atom (or very thin) noble-metal shell over a metallic NP made with a less expensive transition metal. In particular, the group investigated the catalytic performances in CO oxidation of an FeO UTOx grown on a Cu@Pt core–shell nanoparticle. The obtained conversion rates were similar to those obtained by using a thicker slab of noble metal and were supported by further studies of binary-alloy-supported UTOx materials.

Reducible oxides: TiO_x and CeO_x. In the first investigations of the SMSI effect[128] by Tauster in the late 1970, the formation of a UTOx TiO_x layer on Pt particles supported on TiO_2 surfaces was observed. As recently reported by Berko *et al.*,[145] the SMSI effect can also be encountered when considering Rh nanoclusters, but a possible way of avoiding complete encapsulation of the metallic particles is by using a combination of Rh and Au deposition, as TiO_x UTOx is not formed on the Au surfaces.

Analogous to the "inverse-effect" discussed for iron oxide, Boyle *et al.*[146] have shown that when TiO_2 particles are deposited on Au(111), it is the interface between the metal and the oxide which represents the active site for ethanol dissociative adsorption.

Another example of an efficient inverse-catalyst system is offered by Pt-supported ceria, investigated as a catalyst for methanol oxidation for clean hydrogen production. Ostroverkh *et al.*[147] have shown that the performances of pure Pt surfaces are greatly enhanced when an ad-layer of ceria is adsorbed, ascribing the catalytic efficiency at the interface to the synergic contribution of the oxide in exchanging oxygen and of the metallic species in anchoring the reactant species. Ceria on Ag particles has been proposed as a CO oxidation catalyst,[148] a system that also exhibits SERS resonant properties two orders of magnitude more pronounced than those of bare Ag particles. CeO_x on copper is also very interesting, as it has been advocated as an excellent catalyst for conversion of CO_2 to methanol.[149,150]

Reducible oxides: NiO_x and CoO_x. A pioneering exploration of the decoration of metallic step edges by metal oxides, which can exhibit peculiar catalytic properties due to low-coordinated sites, has been conducted by Surnev *et al.*[151] In particular, these authors experimentally and theoretically studied the formation of 1D NiO stripes grown on Rh(553) step edges and their reactive properties in promoting CO oxidation *via* an LH (Langmuir–Hinshelwood) mechanism involving CO and O co-adsorbed species.

An investigation related to the application of UTOx under electrochemical conditions for OER (oxygen evolution reaction) in water splitting[152] demonstrated that water molecules can cooperatively lead to water dissociation and hydrogen migration at the step edges of CoO_x nanoislands deposited on Au(111). This study had been anticipated by a previous investigation[153] on the interplay between CoO_x bilayer/trilayer phases in reducing/oxidative conditions analogous to that discussed in the case of FeO_x. CuO_x on Au surfaces has also been studied.[154]

Reducible oxides: VO_x. Reactive behaviour can also be associated with morphological changes, as demonstrated by von Boehn *et al.*,[155,156] who observed structural evolutions of VO_x depositions on rhodium surfaces accompanying reactions like the oxidation of CO, methanol and ammonia. In the case of vanadia, V can be probably reduced up to the metallic state during reaction cycles and alloy with Rh(110), giving rise to a profound transformation of the metal-oxide interface.

Reducible oxides: MnO_x. Although related to growth dynamics rather than catalysis, investigations on UTOx MnO_x have revealed that meta-stable kinetically stabilized phases can also be obtained with the proper choice of the metal substrate on which to deposit the oxide layer. As shown in ref. 157 there is symmetry breaking in the formation of MnO_x on Ag(100), due to a strong diffusional anisotropy of the Mn adatoms along the borders of the growing UTOx. This effect, which determines the stabilization of the (2×1) phase instead of the thermodynamically favoured (100) phase, demonstrates how energy barriers affect not only catalytic properties, but also structural properties, and this issue should be kept in mind in the search for structural motifs when using the GO tools provided in Section 2.1.

So far the discussion has been focused on the use of reducible oxides. We now switch to non-reducible oxides (like Al_2O_3, ZnO or MgO, among the most common) which, in recent years, have been the subject of several synergic experimental/computational investigations, with important findings on new mechanisms ruling electronic effects in this class of systems and indications that non-reducible UTOx materials can also represent novel catalytic systems.

Non-reducible oxides: MgO. In the MgO/Mo(100) system the low work-function of the metal and the charge compression effect played by oxide deposition can induce charge transfer[158] from the metal through the oxide layer[108,159] and promote the activation of adsorbed chemical species.[160]

The charge-transfer effect can in principle be used to induce surface reactions, such as from CO_2 to carboxylate/carbonate.[118,161,162] A recent study has investigated the possibility of using the same system for methanol dissociation.[163] Experimentally, Calaza *et al.*[164] have deposited CO_2 on small Au clusters grown on UTOx MgO/Ag(100) and succeeded in (reversibly) inducing the formation of oxalate ions by electron tunnelling from the metal substrate through UTOx and the adsorbed gold clusters.

It should be added that a less investigated but possibly important phenomenon is charge transfer occurring directly on UTOx if this possesses incompletely filled d-orbitals which are able to receive electron donation from the metal support.[165] Clearly, control over the charge transfer effect can be of great importance in several applications, and much effort has been expended to enhance[166] or reduce[167] it, and exploit it in catalysis.[168]

Non-reducible oxides: ZnO. For long time the $Cu/Al_2O_3/ZnO$ catalyst has been industrially employed for methanol synthesis and the water gas shift reaction. Nevertheless, no atomic detail about this system was available and only recently have investigations on the Cu/ZnO system[169,170] pointed to the formation of a wetting thin overlayer of zinc oxide on copper surfaces under reducing conditions. Computational modelling suggested that it is also possible that charge-transfer effects can in fact take place in this system,[107] and that electron tunnelling through a ZnO bilayer supported on a coinage metal surface (Cu, Ag or Au) can lead to the charging of species like Au, NO_2 or O_2. An analogy with UTOx MgO[164] led to a hypothesis that cooperative effects involving Au_1 or Au_2 could promote the formation of oxalate ions and that this could be connected with the facile methanol synthesis[170] in real catalysts.

Perspectives. As can be seen from the partial review above, a considerable body of knowledge has accumulated on the chemical properties of UTOx systems. However, in our view the present status presents a somewhat fragmentary picture. In terms of perspectives, then, we believe that a unifying framework is most necessary. To this purpose, we also believe that a coherent implementation of (i) the structural motifs (reductionistic or model-system) idea, as illustrated in Fig. 1 (Section 2.1), combined with (ii) the systematic derivation and exploitation of reverse models, as illustrated in Fig. 8 (Section 2.2), is the most promising avenue to be trodden in the future. In other words, key steps along the catalytic path can be associated with and unveiled by appropriate experiments and computations. This strategy corresponds (i) to punctuating the free-energy landscape with atomic-level-characterized intermediates (low-lying states on the potential free-energy surface), stable under appropriately chosen conditions, and (ii) to using these states as starting points for kinetic studies, such as the classic studies conducted by Ertl on ammonia synthesis, and a forward/backward search for reaction mechanisms ($4N \leftrightarrow 2N + N_2$),[93] with the final target of reconstructing *via* synergic experimental/theoretical tools and data as wide a portion of the catalytic path as possible. We expect that implementation of this approach and its systematic application to important catalytic reactions could lead to significant progress. Actually, it would be interesting to re-read previous literature in the light of this fundamental scheme and fill in missing information with further experiments or computations where necessary. As further steps, anticipated in the concepts sub-section, we mention: (iii) the exploitation of databases not simply of structural motifs but of dynamic reaction paths connecting two local minima as a source of moves in reactive global optimization (RGO) algorithms, and (iv) the rational design of catalytically active sites exhibiting atomic and electronic features that selectively favor specific interactions among adsorbates so as to minimize reaction energy barriers.

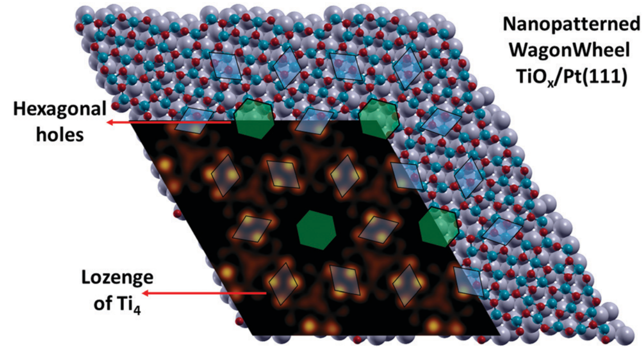

Fig. 9 A naturally nanopatterned wagon-wheel TiO_x/Pt(111) phase, where the simulated STM superimposed on a portion of the picture highlights the presence of a regular array of hexagonal holes (green hexagons) and lozenge regions where Ti atoms are locally four-coordinated. In the atomistic structure, oxygen atoms are in red, Ti atoms in blue, and Pt atoms in grey.

A further possibility, which to the best of our knowledge has not been fully exploited so far, although it seems appealing to us in perspective, is to combine catalysis with surface nanopatterning/templating phenomena, *i.e.*, to investigate metal particles grown on templates (see Section 2.5 and Fig. 9). Such systems exhibit much narrower size distributions and controlled inter-particle distances, and thus seem ideal for analysis of both size-dependent properties and transport and interconnection among particles.[47]

Clearly, further advances in experimental techniques and systematic studies, such as *ex ante* and *ex post* characterization studies of catalytic systems,[94] would be an ideal complement to modellistic investigations.

2.4 Ternary oxides

Introduction. The vast landscape offered by UTOx constituted by two different metal ions has up to now been only marginally unveiled and relatively few studies exist in the literature.[31,171] In fact, the preparation, characterization and interpretation of ternary oxides pose new challenges due to the intrinsically greater complexity associated with the controlled preparation of a multi-component system, its precise atomic characterization and predictive computational modelling. A synergic contribution of advanced experimental and computational tools is thus all the more desirable and necessary here to shed light on the properties of this novel class of materials, as demonstrated in the few available examples. See, for example, the preparation and first full atomic characterization of a mixed $CuWO_4$ UTOx phase grown on Cu(110).[48]

Concepts. The basic goal of studies on this class of systems lies in the possibility of achieving new structural motifs and new structure–property relationships *via* the added degrees of freedom provided by tuning the stoichiometry of the oxide.

Their greater complexity, however, makes reaching this goal challenging. Previous experience on and analogy with nanostructured multi-component metals (or nanoalloys[172]) can be usefully recalled,[16] with its three basic concepts.

First, in ternary oxides the additional metal element brings about an additional length and energy scales. This poses an issue for experimental and theoretical characterization, in that accuracy in dealing with each element must be homogeneous to achieve reliable data/predictions. As an example, given that relativistic effects are more sizeable in 3rd-row than in 2nd-row transition metals, a computational approach missing these will mismatch a 3rd-row/2nd-row TM ternary oxide description. Note that the distinction between length and energy scales can facilitate a comprehension of structure–property relationships in these 2D-ternary systems, as, in general, size-mismatch (between the two separate oxide components) drives the formation of new structures, while energy-mismatch drives the tuning of the reactivity properties.

Second, even for a fixed structural framework, the distribution of two metals in the cation sites generates a combinatorial number (an exponential number, expressible as a binomial coefficient) of different configurations. (These configurations are called 'homotops' in the nanoalloy field.) Experimental and theoretical characterization should be able to distinguish these different realizations of the 'chemical ordering' or 'compositional order' of the ternary system, as a function of their relative stability.

Third, specific tools must be introduced to deal with the increased complexity of ternary UTOx. For example, to compare the stability of ternary UTOx with similar structures but different chemical composition, their formation energy as a function of the ratio between constituent metal elements can be expressed in terms of pure oxides, as proposed in ref. 48 in analogy with the mixing energy concept in the nanoalloy field.[16]

In discussing ternary oxides, a distinction can be made between systems resulting from (i) the layer-by-layer deposition in successive stages (see Fig. 10a) where a separation between two different oxides can be expected,[20] and (ii) oxides produced by co-deposition of the two metals, in which new structural and reactivity modes emerge from the strong intermixing between the two metal species (see Fig. 10b). This distinction has a bearing on the phenomenon of segregation/mixing in multicomponent systems.[173]

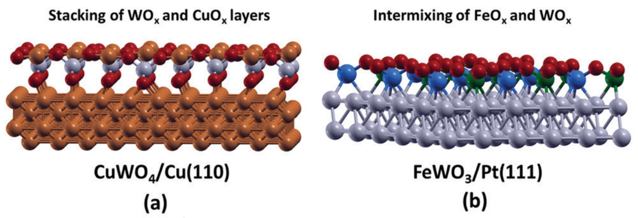

Fig. 10 Side view of atomistic models of: (a) a $CuWO_4$/Cu(110) phase where the CuO_x and WO_x planes are segregated at different heights in a double-layer UTOx; (b) a $FeWO_3$/Pt(111) phase where the Fe and W metal ions are intermixed in a single-layer UTOx.

Another relevant sub-class of ternary UTOx is obtained *via* doping a given oxide *via* post-deposition of a different metal undergoing local oxidation and the formation of a ternary system.[174] Following a well-known strategy in semi-conductor physics, it has been shown that proper doping UTOx with metal cations represents a way to enhance oxidative/reductive properties, even at a low concentration of doping species. The structure of the doped oxide is, in fact, often identical to the original matrix, with local perturbations caused by the doping agent. In the contrast, the electronic structure of the doped oxide is often remarkably altered, as will be demonstrated in the following.

Despite these unique features and the importance of multicomponent systems in perspective applications, which justify the dedication of a separate section to these systems, it is clear that some of the structural and electronic concepts of monocomponent UTOx do carry over, and help us to understand the building blocks, energetics, *etc.* in this field.

Review. Starting from the distinction between layer-separated and intermixed oxides introduced above, to the former class we can add phases generated by depositing a metal species under oxidative conditions on an oxidizable metal surface, resulting in the formation of a double-layer oxide: the bottom given by the oxidation of the metallic surface and the top due to the deposition of the oxide of a different metal. For the latter class we recall the formation of an asymmetric CeO_2 layer grown on Cu(110), where the formation of an irregular (and partially disordered) copper oxide interlayer[74] is responsible for the unidirectional distortion of the hexagonal ceria lattice and the formation of strained lattice sites with altered chemical properties with respect to regular ceria surfaces.

Other examples of multi-layer ternary UTOx are $Ba_xTi_2O_3$ phases on Au(111), where tuning Ba deposition (from very low to high concentration) on a preformed Ti_2O_3 honeycomb network was investigated, with consequent tuning of the surface rumpling and work-function of the system.[175] The stoichiometric $BaTiO_3$ system has attracted particular attention in UTOx form for its connection to perovskite-based materials and their possible use in ferroelectric tunnel junctions. Meyerheim *et al.*[176] have shown that $BaTiO_3$/Fe(001) is formed by a TiO_2 interface with Fe(001) and a BaO surface termination and that only two oxide layers are sufficient for the onset of the polarization and stabilization of a (permanent) antiferromagnetic state. The behaviour of UTOx perovskite phases is, however, far from being fully unveiled, as demonstrated by the latest reports on this class of systems. Two years after their first publication, Meyerheim *et al.*[177] found that $BaTiO_3$ at the UTOx level can undergo significant structural modifications due to the growth on different metallic substrates and due to oxygen doping at the metal-oxide interface. In particular, when adsorbed on Pt(001), a complete reversal from a BaO-terminated to a TiO_2-terminated overlayer was observed. Finally, when considering both $BaTiO_3$ and $SrTiO_3$ under strong reducing conditions on Pt(111), the formation of a novel dodecagonal oxide quasicrystal interface structure with aperiodic ordering was observed.[178,179] Although the properties of this new overlayer have still to be clarified, it represents an interesting example of a potentially well-characterizable system to shed light on the growth of oxide materials exhibiting quasi-crystalline morphologies (see Fig. 6d). According to the proposed structural model, unlike the previous perovskite UTOx, in this case Ba and Ti oxides are strongly mixed in the interface structure.

This last system introduces a discussion of the second class of ternary oxides, where strong intermixing of the two metal components takes place and novel structural morphologies, novel stoichiometries (with no counterpart in bulk oxides) and reactive landscapes are often observed. As anticipated above, size-mismatch between the two metal oxide components is often the driving force determining the final morphology.

To cite some examples, Shao *et al.*[180] have shown that, CaO grown on Mo(001) is amorphous due to a severe lattice mismatch between oxide and metal surface. However, after annealing at high temperature, a ternary oxide, with stoichiometry Ca_3MoO_4 and a rock-salt structure, has negligible mismatch with respect to the substrate, and hence a crystalline-like structure is achieved.

Decomposition of a molecular precursor on a preformed UTOx can give rise to the formation of a ternary UTOx, as shown in the case of molecular $(WO_3)_3$ units adsorbed and decomposing on a pseudomorphic FeO(111) on Pt(111): when the system is annealed at high temperature (above 800 K) novel $FeWO_3$ phases appear with a stoichiometry different from that of bulk $FeWO_4$.[65] This phase is particularly interesting because W is stabilized in a rather uncommon low oxidation state, 4+, and because an uncommon ferromagnetic ground state (with respect to FeO UTOx on Pt(111) and to the bulk state) is observed with a high Curie temperature of 95 K. This finding can be connected with the observation that the stoichiometry is the same as that of perovskite materials, whose multi-ferroic states – stable down to the nanoscale regime – have found remarkable applications in ferroelectric tunnel junction and high-density information storage devices.

Another way to form a ternary oxide has been achieved in a recent investigation by Vari *et al.*,[105] who found that, when a large amount of metallic cobalt is adsorbed on top of UTOx CeO_x/Cu(111), a redox process takes place which determines the oxidation of (a significant fraction of) cobalt atoms (from Co^0 to Co^{2+}) and the simultaneous reduction of Ce ions (from Ce^{4+} to Ce^{3+}) of the oxide layer. At high temperature (above 800 K), migration of cobalt ions inside the ceria matrix (and also inside the copper substrate) takes place, determining the formation of a mixed (Ce,Co) oxide.

Research on the sub-class of doped oxides has been pioneered by Shao *et al.*,[181] who have shown that, when growing gold clusters on thick CaO(001), a transition from 3D to 2D morphologies is achieved and associated with doping of the oxide slab by Mo atoms, which promotes charge transfer to the adsorbate species. In general, when working with metal-supported UTOx, close proximity of the metallic layer can give rise to deactivation of oxidative doped oxides.[182] For example, for MgO grown on Mo(100) doped with Fe^{3+}, it has been shown that magnesium vacancies are created to compensate for the charge mismatch. As Fe^{2+} represents a more stable charge state for iron, oxidative properties of the doped oxides were expected. Experimental evidence of the opposite phenomenon (poor oxidative power) was explained by invoking Mo atom migration (at high enough temperature) from the underlying metallic layer to the magnesium vacancies, with a consequent reduction of Fe^{3+} by Mo atoms in a new charge-compensation scheme.

Another recent example of doped UTOx comes from Stetsovych *et al.*,[183] who investigated Ce_6WO_{12}/W(100), where the relatively low concentration of W atoms in the oxide justifies its classification as a dopant. The interest in this system comes from the presence of (quite uncommon) Ce^{3+} and W^{6+} cations in the oxide matrix that could therefore be used to study the catalytic performances of mixed WO_x/CeO_x oxides. A clear demonstration of the different adsorption properties of doped metal-supported UTOx comes from the results of Torres *et al.*,[184] who showed that an Ni-doped MgO UTOx deposited on Mo(100) can promote the migration of atomic H from the surface to the inside to the oxide/Mo interface thanks to the strong interaction of H (in the form of hydride) with both Mg and Mo sites.

Perspectives. Many perspectives and challenges await further study in this as yet little investigated field.

As in the case of metallic systems, it has been found that some ternary oxides have a tendency to intermix, whereas other tend to segregate: principles clarifying this different behaviour in analogy or in contrast to bulk ternary phases are only in their infancy.

Appealing perspectives of ternary UTOx oxides are clear in applications such as catalysis, in which the possibility of achieving new stoichiometries provides a way to produce novel oxide alloys of potential interest as both model (see Sections 2.1–2) and operative systems.

Computational modelling using the tools outlined in Sections 2.1–2 is even more necessary in this complex field and has ample room to play an important role. First, it is interesting to note that the building blocks discussed in the structural motif Section 2.1 here become composite or multi-elemental and thus hybrid bricks or ''hy-bricks''. To illustrate this concept, Fig. 6(a–c) shows three different structural motifs of an $FeWO_3$/Pt(111) UTOx phase[65] constituted of triangular bricks in two different layers giving rise to new hybrid bricks. A further example in Fig. 6(d) shows the structure of a quasi-crystalline lattice of a $BaTiO_3$/Pt(111) UTOx phase:[178] the composition of triangular and square bricks in this case gives rise to self-similar scaling, and we note that the operation of grouping smaller bricks to form self-similar larger bricks is another way of generating hy-bricks. Second, the use of high-throughput screening algorithms to predict rapidly and at the same time accurately the effect of doping (atom replacement) on the structural, catalytic,[185] opto-electronic, *etc.* properties of ternary and higher component UTOx represents a very promising, but so far completely unexplored, possibility. Clearly, the power of this approach could be further enhanced by combining it with some variants of alchemic transformation algorithms. Finally, a great challenge in multi-component systems is associated with robustness, for example, with respect to atomic exchange or diffusion (chemical ordering): will the cation atoms stay put?

Will the property of interest be stable against intrinsic fluctuations in compositional and/or structural order exacerbated at the nanoscale and for ternary UTOx due to the exponential (combinatorial) increase in degrees of freedom? Answers to these and other questions are necessary to make progress in this field.

2.5 Nanopatterning

Introduction. An important application of metal-supported UTOx is related to their use as templates for nanopatterning,[186] *i.e.*, to induce the supra-organization of adsorbed species (both inorganic, like metal or metal oxide nanoparticles, and organic, like bio-molecules) for use in applications as sensors or catalysts, *etc.*[187] This section is devoted to a brief discussion of this topic.

Concepts. A key aspect of UTOx which opens the way to surface nanopatterning is the possibility of creating surface features with long-range order, see, for example Fig. 9, thus enabling transfer of this order into the supra-organization of adsorbate species, following previous studies of metal-on-metal systems.[53,188,189] In general, the surface pinning of ad-species at specific sites of the 2D unit cell of a UTOx can be related[186] either (i) to a morphological feature, like a picohole exposing the underlying metallic substrate[49] or more extended structure modulations such as Moiré or strain-relief patterns[51,52] (see Section 2.1 for how to predict such nanopatterns), or (ii) to an electronic feature, like a local lowering of the work-function of the system which can facilitate charging for electronegative adsorbate species.[108,159] In passing we recall that a pioneering and non-trivial route to producing the former class of nanostructured templates has been demonstrated by a buried dislocation network due to a Moiré pattern in an ''inverse'' system, an ultrathin metallic deposition of Ag on MgO(100).[190] Often the two effects, morphological and electronic, are interwoven and difficult to disentangle, as will be shown in the following discussion. Due to the importance of nanopatterning in a multitude of applications, we discuss this phenomenon in a separate section, although it should be clear that the origins of this phenomenon are in many cases to be sought in the preceding sections. Indeed, morphological features such as nanoholes arise naturally *via* the arrangement of building blocks, as discussed in Section 2.1, while relief patterns and dislocations can be justified on the basis of intrinsic equilibrium lattice parameters and elastic moduli of UTOx phases, as discussed above.[50] The reader is invited to make links among the topics of this perspective to reconstruct from the elements provided here a broader section focusing on structure, superstructure, and emergent nanoscale characteristics.[14]

We will mostly deal in the following with ''naturally nanopatterned UTOx phases''. However, the possibility of physically altering (mainly thorough electron beams and scanning probes) UTOx surfaces by, for example, creating oxygen vacancies, and hence pinning centers for adsorbate species, has also been investigated.[191] Another way to induce nanopatterning is by exploiting the effect played by adsorbate species, as discussed, in a more general context, in ref. 192. Adsorbates can indeed have a feedback effect on nanopatterning, such as inducing an energy crossing between different phases. One paradigmatic example is discussed in ref. 42 and is illustrated in Fig. 11. In this work, it was shown that Au deposition and nucleation of Au clusters on the rectangular holes of a zig-zag TiO_x/Pt(111) phase followed by annealing lead to a phase reconstruction. In the resulting reconstructed metal-on-UTOx system, the metal clusters still retain their size, but the underlying substrate transforms into a homomorphic, still nanopatterned, hexagonal phase. This is because the picoholes in the hexagonal phase are bigger than those on the zig-zag phase and can therefore better accommodate the nucleated Au clusters. The experimental observation is then rationalized by first-principles modeling as an inversion of stability between the rectangular and hexagonal phases before and after metal deposition, as illustrated in Fig. 11. This cooperative effect is thus the result of the simultaneous action of metal adsorption and oxide phase transformation.

Review. The following review for space reasons is not comprehensive in terms of all the investigations carried out on this topic, but we concentrate on two prototypical systems for which nanopatterning and/or adsorption of adsorbate species have been investigated in detail: UTOx AlO_x (alumina) grown on NiAl(110) or $Ni_3Al(111)$, and UTOx TiO_x (titania) grown on different metal substrates.

Starting with AlO_x UTOx, in 2006 Hamm *et al.* succeeded in obtaining atomic insight into the structure of ultrathin alumina grown on $Ni_3Al(111)$.[193] It was already known that this UTOx was characterized by two lattices: a larger one with a spacing of 4.16 nm and a smaller one with a spacing of 2.4 nm[1]. Moreover, this UTOx had been already used for adsorbing metal clusters,[194] and it had been observed that the ''nodes'' of the two lattices were able to pin these clusters, but very little information was available at the time on the nature of the ''nodes''. These pioneering studies were followed by a joint experimental and computational investigation which succeeded in unveiling the detailed atomistic structure of the UTOx and its lattices.[49] In particular, it was found that the oxide surface exhibited hexagonal nanoholes, which exposed the underlying metal surface. As for the nanopatterning effect, it had previously been demonstrated[195] that bimetallic PdAu deposition on this UTOx gave rise to well-ordered nanopattern arrays of alloyed nanoclusters with a spacing of 4.16 nm. This information, combined with the atomic structural determination of the oxide, pointed towards the stabilization of the PdAu nanoclusters inside the nanoholes. It is worth mentioning in this connection that, in order to achieve the nanopatterning effect, a specific recipe based on a prior deposition of Pd followed by Au had to be followed, whereas, when the ordering of the deposition was reversed, no bimetallic clusters were produced. The explanation is that both Pd and Au are able to diffuse on the surface until they reach the nanoholes, but only Pd is able to nucleate on the nanoholes, creating Pd seed clusters, and, subsequently, capturing the gold atoms diffusing on the oxide surface, whereas Au atoms are unable to nucleate at the nanoholes in the absence of Pd due to their larger size. Very recently, Alyabyeva *et al.*[196,197] have investigated the

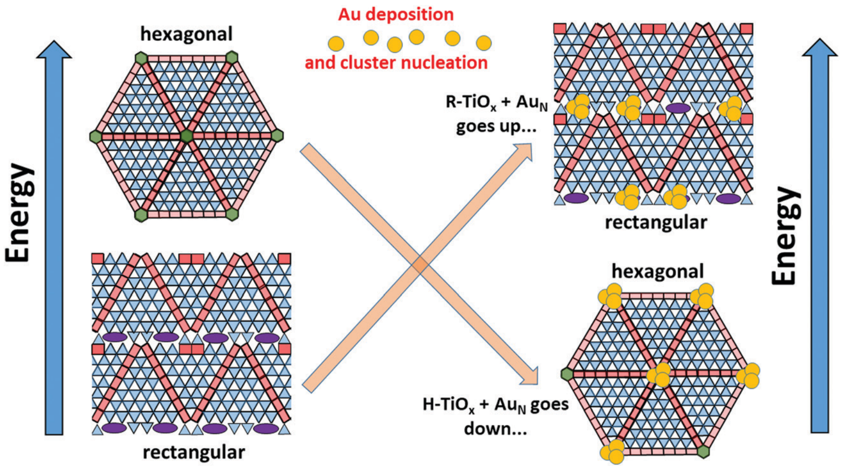

Fig. 11 Schematic representation of the energy crossing between hexagonal and rectangular TiO_x/Pt(111) UTOx phases induced by gold atom deposition and annealing (cooperative phase transformation). The metallic gold clusters are pinned at the UTOx holes exposing the underlying metal substrate.

optimal preparation temperature to obtain an ordered array of Pd pinned at the nodes of the dot structure and have found that slightly higher temperatures (of about 140 K) than those reported in the previous literature are required to obtain long-range ordered nanopatterned arrays.

In successive years, investigations have continued on the templating effects of this surface towards the adsorption of metal nanoclusters. Buchsbaum *et al.*[198] used Pd as nucleation pinning centers towards the adsorption of Fe and Co atoms on the oxide nanoholes and structurally characterized the obtained nanoparticles *via* a variety of microscopic techniques. Sitja *et al.*[199] were able to obtain a narrow distribution of increasing size of pure Pd particles on the nanoholes of the UTOx surface and to monitor the adsorption energy of CO molecules on them. From this investigation they were able to discriminate the chemical response of the Pd particles towards CO adsorption between a molecule-like regime (metal particles with fewer than 100 Pd atoms) and a bulk-like regime. Vlaic *et al.*[200] used the same template and a similar protocol as Sitja *et al.* to grow Fe particles by using Pd atoms as seeds and investigated the magnetic properties of the resulting Fe systems, in particular the coupling between the Fe nanoparticles and the Ni particles embedded in the underlying metal alloy. (In fact, the substrate in their studies resulted in there not being a uniform alloy between Al and Ni, but exhibited regions of Ni aggregation – probably a consequence of Al segregation upon annealing.) In an interesting study, the formation of Cu clusters was computationally investigated by Olmos-Asar *et al.*,[201] by finding that a single Cu is mobile on the oxide surface and becomes trapped inside the hexagonal nanohole, where up to six other Cu atoms can be accommodated, a result well in tune with the general understanding of this system and the previous experimental data on Cu cluster nucleation on this alumina UTOx.[202]

Once nucleation of metal particles on the nanopatterned template has been realized, the system can be further manipulated *via* a sequence of steps leading to a robust system while still preserving nanostructuring (see Section 2.2). A paradigmatic example is the nucleation of Ni nanoparticles onto a the AlO_x/Ni_3Al(111) bilayer system. This phase, subjected to oxidation (from a minimum quantity of 45 L to a maximum of 180 L) at 200 °C transforms into a nanopattern of NiO_x nanoparticles with the same density and nanopattern as the original system.[47] It is notable that exposure to O_2 does not unanchor the clusters from the support, but the UTOx alumina phase transforms from a bilayer into a trilayer, *i.e.*, there is thickening of the ultrathin oxide, as illustrated in Fig. 12a.

A different but related and instructive example is provided by the deposition of Pt clusters onto an analogous alumina ultrathin (bilayer) film grown on a single-crystal NiAl(110) surface.[2] When deposition of Pt_7 clusters is conducted at very low temperature, an array of these clusters is obtained.[203] In this case, the templating effect is given by domain boundary stripes (appearing as bright stripes in the STM images) onto which the clusters adsorb at low temperature. However, when increasing the temperature from RT the clusters become mobile and coalesce into large particles, as observed for other oxide surfaces.[204] Importantly, the nanopatterning effect can be retained *via* a different recipe: if subjected to realistic reaction conditions of CO oxidation (CoO_x), *i.e.*, the simultaneous presence of O_2 + CO (interestingly, with a likely but undisclosed amount of water or humidity) the systems evolve toward an amorphous but still ultrathin phase, in which the clusters do not coalesce but are robust even above RT.[111] The resulting UTOx alumina was not characterized in detail, and it is unknown whether it is a bilayer or a trilayer phase, but it is amorphous and with a hydroxylated surface; see Fig. 12b. Interestingly, the CoO_x catalytic properties of the resulting phase are very similar to those of an ultrathin (trilayer) alumina obtained *via* atomic layer deposition on a naturally oxidized B-doped silicon chip.[16] Clearly, geometric (morphologic) confinement effects and/or the presence of a shell of ligands surrounding the metal clusters and protecting them against disaggregation and diffusion[130,162,217] are the likely causes of the stabilization of the nanopattern; see Fig. 13.

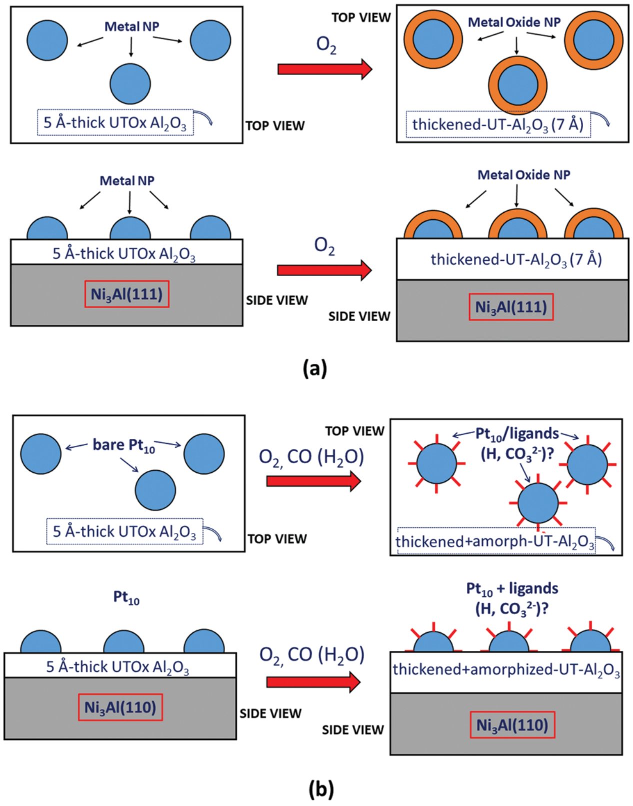

Fig. 12 (a) Schematic top (upper part) and side (lower part) views of nickel clusters deposited on an $AlO_x/Ni_3Al(111)$ UTOx phase before and after oxygen treatment: after exposure, the oxide thickens, while the metal clusters are partially oxidized with a shell of nickel oxide. (b) Schematic top (upper part) and side (lower part) views of Pt_{10} clusters deposited over an AlO_x/NiAl(110) UTOx phase before and after exposure to a gas mixture containing oxygen, carbon monoxide and traces of water. After exposure, the oxide thickens and becomes amorphous, while the metal clusters are covered by a variety of ligands, such as hydrogens, carbonate ions, *etc.*

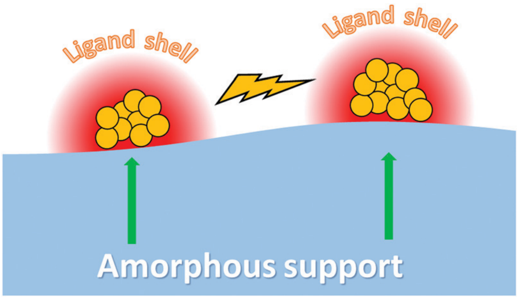

Fig. 13 Schematic idea of subnanometer (ultranano) cluster catalysis: the clusters reside on an amorphous support, are covered with a shell of ligand species, and may interact among themselves by exchanging mass or energy.

The case of TiO_x presents similarities but also differences with respect to the AlO_x system.[21] Titania is a reducible oxide, at variance with the simple oxide alumina. Both are characterized by oxygen surface terminations when titania is adsorbed on metals like Pd or Pt.

The first investigations on the growth of metallic clusters on TiO_x UTOx were performed using gold as a metal and two Pt-supported TiO_x phases, one with a zig-zag pattern and another with a wagon-wheel or pin-wheel pattern.[55] It was shown that on the zig-zag phases, Au clusters organize along parallel lines, whereas on the pin-wheel phase, nanopatterning was not achieved. A structural determination of the two phases[205] rationalized these findings, singling out the presence of defect lines in the case of the zig-zag phase where the underlying metal was exposed and therefore played a role in promoting the pinning of small gold clusters. The mobility of gold *vs.* iron atoms over the zig-zag titania phase was investigated at the computational[206] and experimental[207] level. It was found that Au has a high mobility and can easily enrich the defect lines on which it nucleates, whereas Fe atoms, being strongly oxidizable species, get adsorbed in hollow sites between the oxygen ions of the outer UTOx layer, as observed by Choi *et al.* in the case of electropositive metals on zirconia.[208] In this system, at variance with other UTOx or ultrathin dielectric supports,[108,158] Au does not receive an electron charge from the underlying metal surface, as the work-function of Pt is too high to allow for electron transfer to adsorbate species.

As a different case, a joint experimental–computational investigation of gold atoms adsorbed on a pinwheel-like TiO_x on Rh(111)[209] provides an example of a system in which the templating effect is a result of morphological and electronic features, in the absence of nanoholes. In this work, the authors showed that Au is pinned in specific top sites of the UTOx layer, where the adsorbate experiences an interaction almost as strong as that with the metal support. This stabilization effect, which is connected to a specific site of the surface, is attributed to a local relaxation of the oxide layer and to negative charging of the gold atom: in terms of geometric effects, the lattice strain plays the same role as nanoholes in favoring Au adsorption on specific sites of the UTOx, simultaneously modulating the work function. (These effects could be easily studied *via* the structural motif approach discussed in Sections 2.1–2.)

This work introduces the topic of adsorbate charging on UTOx. See ref. 108, 158 and 160 for a discussion. Charging, *i.e.*, adsorbate–adsorbate (electrostatic) interactions, can have an effect and even determine self-organization. Indeed, Sterrer *et al.*[108] have shown that Au atoms and small clusters can become negatively charged *via* tunneling from Ag(001) through a very thin (up to 3 ML) MgO deposition. As a consequence, charged gold atoms repel each other *via* Coulomb repulsion and this can lead to the formation of a regular long-range pattern at a very low temperature, although the order has already been lost at around 100 K because repulsion forces are overcome by thermal effects. Notably, self-organization does not occur in the case of Pd atoms, which do not have enough low-lying states to accommodate extra electrons. This effect has been investigated more extensively by Nilius *et al.*,[210] who found that small Au clusters on UT MgO on Ag(001) become negatively charged and therefore adopt a planar structure wetting the oxide, and exhibit electronic states with a good resemblance to those of a 2D free-electron quantum. Martinez *et al.*[211] used a DFT analysis to predict a similar effect in Li-doped SiO_2 UT grown on Mo(112): when interacting with the UTOx, Li donate one electron to the underlying metallic support and lower the work-function of the system – as a consequence, small gold clusters can become negatively charged when interacting with this system.

Finally, the adsorption properties of several noble and coinage metals on UTOx ZrO_2 on PdZr alloys have been studied[208] and a distinction has been made between electropositive metals (Ni and Pd), able to wet the surface by interacting with the negative oxygen ions of the surface, and Au, which, becoming negatively charged, is able to adsorb on top of the zirconia ions. Interestingly, switching between positively and negatively charged states remarkably reduces the mobility of gold with respect to the other metal species.

Perspectives. Exploiting the template effect of nanopatterned UTOx surfaces is in our opinion a very attractive path to novel findings in both fundamental science and applications. First, as mentioned above (Perspectives in Section 2.3), atomic metal deposition onto such systems produces intrinsically much narrower size distributions of the clusters[186] and thus a tool for the study of size-dependent properties.

Second, chemical and/or thermal treatment to test the robustness of the resulting nanoparticle arrays then provides a chance to observe cooperative phase transformations[42] and/or to single out magic clusters[212] or cluster transformations, such as oxidative processes.[47] Finally, third, the controlled inter-cluster distances offers a possibility to investigate mass transport and cluster–cluster interaction and interconnection phenomena; see Fig. 13. Among this wealth of possibilities, phenomena connected with ligand adsorption are the most promising in our view, starting with the interaction and template organization of simple molecules, such as water,[78,79] to controlled coating with surfactants,[92] up to more complex cases, such as those related to biological surface science.[213]

As a final note, we add that an appealing avenue could also be the use of nanopatterns as a path to layer stratification (3D patterning), a topic of recent interest in advanced preparation methods in materials science and applications.[18–20]

3. Summary and conclusions

The study of ultrathin oxide-on-metal films (UTOx) was born as an offspring of surface science: the need to avoid charging issues brought the thinness of oxides (semi-conductors or insulators in bulk form) to the extreme UTOx limit, down to the ultimate limit of single-atom or single-polyhedra-thick layers. The field has developed vigorously since then, fueled by the novelty of the structural and electronic phenomena thereby discovered. An excitingly rich set of concepts and methods has been derived, with a focus on ideal systems under extreme conditions, sometimes losing sight of technological applications. To fill this gap and trigger further developments, we have thus dedicated the present article to the existing and prospective links between UTOx and real-world systems.

Summarizing, we believe that UTOx surface science can provide a decisive and two-fold contribution to advanced technologies.

First, the UTOx field has produced a broad set of basic concepts, methods and procedures.

The contribution of the UTOx field in terms of basic concepts is paramount, and has been discussed extensively in dedicated subsections, both as a review and in perspective. We recall very briefly that, regarding structural motifs, a general computational protocol has been outlined aimed at unveiling new structures and novel structure–property relationships. This protocol can also be applied to ternary oxides, which opens the way to new structural motifs and new structure–property relationships and the design of new materials. Properties like catalysis have been discussed, including the possibility of exploiting synergic metal-oxide action at the phase borders and the indirect effect played by the underlying metal in altering adsorbate properties. The issue of robustness has been raised, also underlying the importance of equivalence or translation principles in linking the different thermodynamic conditions used in synthesis/characterization, on the one hand, and in real-world applications, on the other. Finally, nanopatterning cases have been demonstrated, providing a possible exploitation of these systems to induce the supra-organization of adsorbed species.

By choice, we have not included methodological aspects in this review, but it is well known that the availability of well-characterized systems has offered ideal test cases with which to calibrate and validate methodological approaches, both in theory and in experiment, as illustrated in several previous reviews, see *e.g.* ref. 16 and 25–28. The importance of UTOx to instrumental development is widely recognized.[124]

Less recognized and only hinted at in the present perspective, as by our choice it lies beyond its scope, but equally interesting is the contribution of UTOx in terms of protocols and procedures. To cite a couple of examples, we quote operative procedures, such as the conformal growth of protective or buffer layers (such as CoO onto NiO[89]) to modulate and attenuate the surface chemistry, a procedure that can also be used for technological perovskites. Or growth protocols optimized towards various forms of an oxide, and here the most thorough study is probably into SiO_2: crystalline[96] *vs.* amorphous (model of glasses),[97] or oxygen-[100] *vs.* hydroxyl-[98] *vs.* element-terminated.[214] Or the growth of strongly anisotropic structures due to symmetry breaking and diffusional anisotropy, which in the 2D case give rise to nanostripes,[157] but which is intrinsically equivalent to the growth of nanowires in materials science.[215] This aspect is less popular and more restricted to an academic audience than other contributions to the UTOx field (such as instrumental development), but we think in perspective it can give significant support to technology, including that involving analogous 2D materials.[30,216]

Second, apart from such fundamental contributions, we believe that UTOx operational results can also be of use in technology, albeit with caution and with appropriate translation protocols.

As reviewed in Section 2.2 (robustness), the extreme conditions typical in UTOx science are in fact far from real-world conditions, but robust UTOx systems do nevertheless exist (sometimes discovered by chance). Some known UTOx structures survive near-environmental conditions and thus already exist or potentially exist in nature (we recall that graphene was first obtained as a UT carbon phase) as reviewed above, such as $CuWO_4$,[48] NiO stripes,[151] WO_3/Pd(100),[104] TiO_2,[103] AlO_x,[47] and ultrathin SiO_2.[96–98] These phases have been shown to be robust mostly to O_2, whereas the interaction with water has scarcely been investigated as yet, but in our opinion can lead to very interesting findings.[111]

Even in those cases in which UTOx phases do not survive ambient conditions, they can be very useful as structural models in a reductionist approach to meta-stable or transient phases (see Section 2.1, structural motifs, and Section 2.3, catalysis). Indeed, there is much to be done in this connection, as real oxide supports (catalytic and non-catalytic) are invariably amorphous,[111] whereas so far we have good models basically only for a covalent amorphous oxide such as SiO_2, and we lack models for amorphous ionic oxides (both reducible and simple) such as alumina, zinca, ceria, *etc.*

Furthermore, UTOx can be useful as models of transient intermediates, *e.g.* in catalysis, and we have discussed in Section 2.3 how to build appropriate translation procedures/algorithms and a link between model studies and real systems, and how to extract from UTOx investigations important information on energy differences and reaction mechanisms which can then be relevant to, for example, catalytic technology.[93]

Concerning robustness, it should also be mentioned that, in the future, extreme conditions could become more accessible, thus enabling the direct use of UTOx phases, *e.g.*, in quantum technologies.[116]

In terms of operative results and UTOx contribution to technology, we finally recall that: (1) the structural motifs approach outlined in Section 2.1 can be translated into a method for structural prediction in materials science,[45] and (2) in our opinion great opportunities are offered by the combination of different oxide systems and/or surface nanopatterning (Sections 2.4 and 2.5).

In conclusion, it is to be expected that UTOx systems as well as their 2D analogues/variants on still-conducting or semi-conducting but less-screening substrates, such as dielectric ionic conductors (oxide memristor materials[216]) or non-oxide systems (such as transition metal dichalcogenides, their heterostructures, and the associated the electro-optical response),[30] will play a relevant role in the future, especially if the link between the novel phenomena hereby discovered and technology is systematically pursued. The contribution of fundamental understanding which has been offered by UTOx science thus corresponds not only to an intrinsic human need, but – as in the time-honored physico-chemical strategy here adopted – when thoroughly and profoundly achieved, it can lead to and trigger technological breakthroughs.

Conflicts of interest

There are no conflicts to declare.

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