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PERSPECTIVE

Transmission Electron Microscopy Finds Plenty of Room on the Surface

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The atomic features of materials surfaces are coming to have fundamental importance for applications in numerous fields, such as heterogeneous catalysis, energy conversion and thin-film growth. Now transmission electron microscopy (TEM) and affiliated techniques have thoroughly revolutionized many disciplines of the natural sciences, and is becoming one of the best solutions for surface exploration. In this Perspective, we try to summary the important progresses of surface elucidation by applying the state-of-the-art TEMs, which covers (1) from the essential features of oxides to the dynamic behaviors, and the interactions between surfaces and gases; (2) the visualization of emerging materials from zero-dimensional single atoms to two-dimensional materials, and the development towards an ultimate integration of three-dimensional surface. The plenty of room has been made for TEM exploration onto the materials surface, and the surface-integral frontiers are being pushed further.

1. Introduction

Since Ernst Ruska's pioneering study in electron optics, and designing the first transmission electron microscope (Nobel Prize in Physics 1986), [1, 2] this wonderful instrument and affiliated techniques have thoroughly revolutionized many disciplines of the natural sciences owing to its capacity to resolve the structure and chemistry of matter in real-space, diffraction-space and energy-space. [3] Visualization and probing were possible initially at the micrometer and later at the nanometer scale, and strides are currently being made into subangstrom and even picometer scales. [4, 5] Nowadays, the atomic features of materials surfaces are becoming fundamentally important for applications in numerous fields, such as heterogeneous catalysis, energy conversion and thin-film growth. [6-10] Unraveling of the chemical processes on solid surfaces has been receiving wide interest (Gerhard Ertl, Nobel Prize in Chemistry 2007). [7] Unlike low-energy electron diffraction, X-ray photoelectron spectroscopy, and other surface methods, techniques based on transmission electron microscopy (TEM) can supply precise information about individual nano-objects while effectively avoiding the averaging properties of materials. In particular, real-space TEM observation results in more straightforward analysis, thus enabling ultimate identification of surface characteristics and unique understanding of chemical processes.

As early as in the 1980s, the exploration of surface structure was already booming by applying the TEM techniques. For instance, Marks and Smith achieved the direct imaging of gold nanoparticle surfaces.[11, 12] Moreover, the surface termination of characteristic gold crystal planes was clarified combining with image simulation.[13-15] Yagi and Takayanagi made a series of important progresses in imaging the dynamic processes on the solid surfaces through *in situ* ultra-high vacuum (UHV) high-resolution electron microscopy.[16-18] Unraveling of these atomic surface features and reaction dynamics of metals has been directly benefited from the emergence of UHV systems.[19] Nowadays, TEM's potential reaches far beyond surface-science theory owing to the higher resolution. The last decade has witnessed the exciting and unprecedented development of the TEM application in surface exploration, thus enabling large segments of human knowledge to be updated.

In this Perspective, we summarize some important progress that has been made in surface exploration by using TEM-related techniques, firstly from the essential features of surfaces to the dynamic behaviours as well as the interactions between surfaces and gases; subsequently, we examine the visualization of emerging materials from 0D single atoms to 2D materials, and the TEM development towards the thorough identification of 3D surfaces.

2. Surface Features and Reaction Dynamics

2.1. Surface Termination of Oxides

One of the most fundamental scientific questions is the surface termination of metal oxides: termination with metal or oxygen atoms? The section addresses the real-space surface elucidation of the typical binary, ternary and large-unit-cell

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oxides, as well as oxide overlayers induced by strong metal-support interaction (SMSI).

By employing aberration-corrected high-resolution TEM (HRTEM) combined with first-principles calculations, Yu et al. explored the surface structure of the transition-metal-oxide spinel Co_3O_4. The surface structure and relaxation of the polar (111) surface were entirely unraveled to an accuracy of several picometers[20] while the (11-20) surface of hexagonal α-Fe_2O_3 is nonpolar. [21] Recently, through such a subangstrom measurement technique, the same research group observed the bonding rotations and contractions on the subsurface of (10-10) in ZnO nanowires, in agreement with the theoretical prediction for the relaxation of the ZnO surfaces. [22] They found that the {101} surfaces of zigzag SnO_2 nanobelts are dominatingly the reduced surface terminated by Sn atoms. [23]

Elucidating of the surface structure of design-shaped nanoparticles provides the crucial information in understanding crystal-plane-selective catalytic reactions. The Marks research group with aberration-corrected HRTEM showed that the atomic structures of the various surfaces in CeO_2 nanocubes were determined with identification of the oxygen atoms, [24] which was previously the experimental bottleneck. Moreover, they found that intricate surface reconstructions of ternary oxides depend largely on their synthetic process. The experimental observation and density functional theory (DFT) calculations were applied in illustrating the surface structure of the model $SrTiO_3$ nanocuboids: Oleic acid synthesis leads to a SrO termination while a TiO_2-rich reconstruction exists in acetic acid synthesis, and the mixed termination results from microwave-assisted acetic acid synthesis. [25]

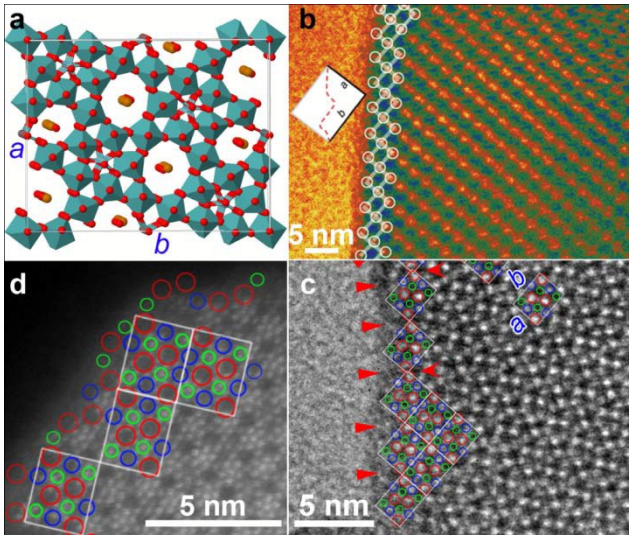

Figure 1. Surface structure of the complex M1 MoVTeNbOx catalyst. (a) Crystallographic model of the M1 phase. (b,c) HRTEM images of one M1 nanoparticle along the ⟨001⟩ direction far from (b) and near (c) the Scherzer focus. (d) STEM image. Copyright 2010 John Wiley and Sons.

Concerning the surface structure of large-unit-cell materials, a typical study is the elucidation of the surface termination of the orthorhombic $MoVTeNbO_x$ catalyst (M1 phase, 180 atoms in one unit-cell; **Figure 1**), the most important catalyst used for oxidizing propane to acrylic acid. Zhang et al. found by traditionally adjusting the focus in a standard LaB_6-filament TEM instrument that the lateral surface is terminated with the broken unit cells, which leads to exposure of the active hexagonal, heptagonal, and pentagonal channels. [26] This result demonstrates that the remarkable (001) plane is not the uniquely important surface and is thus consistent with a previous catalytic experiment. [27] Amorphous-like features along the ⟨001⟩ direction were ascribed to the random intricate surface termination through layer-by-layer growth, as verified by high-resolution scanning transmission electron microscopy (STEM) observation and image simulation. Following this work, the surface termination of the similar M2 phase was studied by using a probe-corrected STEM technique. [28] Very recently, through a chemical HRTEM analysis, Lunkenbein et al achieved a real-space observation of SMSI overlayer in an industrial catalyst $Cu/ZnO/Al_2O_3$. [29] The formation of graphite-like ZnO layers onto the Cu surface was probed, which may correlate to the synergistic effects between the two components towards methanol-synthesis.

In short, the surface termination of metal oxides corresponds to the solid-vacuum interfaces, which depends closely on their synthesis and processing history. In this sense, besides the advanced characterization, TEM has been updated to a toolbox for design and optimization of materials surface towards practical applications.

2.2. Dynamic Behavior of Surfaces

Not only the existing features of surfaces can be elucidated by TEM, but TEM can also be treated as a dynamic platform for *in situ* monitoring of surface evolution and for probing the instability of a surface under electronic stimulation. The aberration-corrected HRTEM can contribute effectively to explore the dynamic atomic configuration of surfaces. [30]

It was found that a reversible reconstruction between wurtzite and tetragonal phases can occur in ZnO(10-10) surfaces under electron beam (e-beam) irradiation on the basis of aberration-corrected HRTEM. Such surface bistability was confirmed by the DFT calculations. [31] Combining aberration-corrected HRTEM with a computational exit wavefunction restoration, the specific surface structure of CeO_2 nanoparticles was systematically monitored during a reversible e-beam-stimulated reaction. Such imaging of the active ceria surface can be possibly applicable to an individual facet/monolayer. The acquired information has an immediate industrial relevance, from which the future rationalization of the surface ions mobility of designed ceria will be benefited. [32]

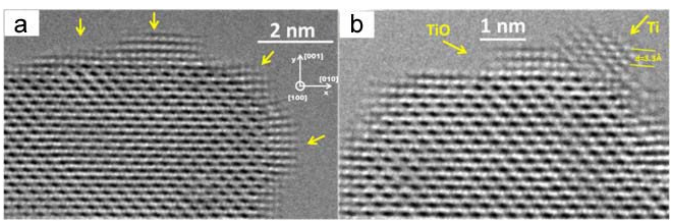

Figure 2. Real-space observation and comparison between TiO and Ti islands on a $SrTiO_3$ surface. (a) TEM image of TiO islands. (b) TEM image of a Ti island beside a TiO island. Copyright 2015 Elsevier.

For the ternary oxide $SrTiO_3$, it was demonstrated that surface segregation can occur, whereby TiO and Ti islands form on the Ti-rich (001) surface of $SrTiO_3$ nanocuboids as a result of intense e-beam irradiation (**Figure 2**). [33] The results are similar to those previous studies on $SrTiO_3$ single crystals subjected to high-temperature reducing conditions, and may be extended to the surfaces of other perovskite materials.

A focus of wide attention and great interest, gold has been developed into a very important heterogeneous catalyst since the verification of its high activity by Haruta. [34] Gold surface dynamics is a very hot topic. Under e-beam irradiation, the dynamic evolution of low-symmetry gold nanoparticles was observed. [35] Surface dislocation behaviors on gold terraces were dynamically probed by using *in situ* aberration-corrected HRTEM. At room-temperature, surface dislocations were formed when the (100) terraces with less than 4×5 atoms sink into the terrace below. At 77 K, no injected dislocations were observed. [36] Moreover, the surface self-diffusion on gold nanoparticles was quantitatively measured by applying aberration-corrected HRTEM. [37] By carefully measuring the temporal evolution of the surface atom column occupation, the diffusion coefficient of gold was estimated; under the imaging e-beam, a gold icosahedron shares a similar diffusion coefficient with a truncated gold octahedron. In short, the aforementioned studies are helpful for further understanding of the surface state of gold nanocatalysts.

Surface dynamic processes at the atomic scale, such as transitions of phase states activated by electron beam, provide a direct evidence of local evolution of characteristic structural features. Such merit enables us to reinvent nanoscale architecture chemistry on materials surface to search for the novel properties.

2.3. Gas-Surface Interactions

Molecules at surfaces have been a central topic in the elucidation of chemical processes on solid surfaces. [38] The three examples are given to illustrate the surface structure, modified from the interactions either with oxygen in a high-vacuum, or with carbon dioxide during the catalytic reaction, or even possibly with inert gases. The discoveries of these rich solid state phenomena were directly benefited from the powerful TEM-related techniques.

Through spectroscopic methods, Ertl and co-workers distinguished surface oxygen atoms on the Ag catalysts and subsurface oxygen atoms in the Ag catalysts. [39, 40] By means of a real-space observation, Su et al. showed that surface and subsurface oxygen atoms are positioned on the edges and steps of the Ag surfaces (**Figure 3**), on the basis of the analysis of aberration-corrected HRTEM; DFT calculations reveal that surface oxygen atoms is energetically unfavorable, provided if locating on or under perfect-latticed terraces. [41]

The reconstruction of the {100} facets of a ceria-supported gold nanoparticle was visualized with atomic resolution during CO oxidation at room-temperature, ascribed to the surface adsorption of CO molecules. [42] Aberration-corrected HRTEM and image simulation revealed that the adsorption occurs at the on-top sites of gold atoms; the reconstructed structure is energetically favorable, confirmed by *ab initio* calculations. These results are helpful in elucidating the reaction mechanisms.

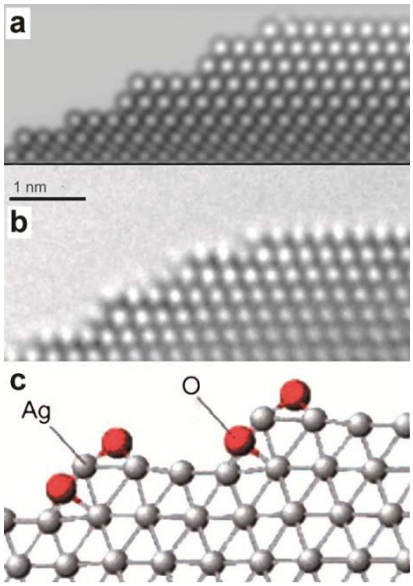

Figure 3. Surface elucidation of a Ag catalyst nanoparticle. (a) High-resolution simulated image. (b) HRTEM image. (c) Model representation. Copyright 2008 John Wiley and Sons.

By employing a 1 MeV JEM-ARM1000 TEM, it was found at room-temperature that the fluid Xeon gas has three well-defined surface layers in the faceted aluminum nanocavities. [43] The ordering demonstrated by the HRTEM observation indicates that nucleating nanoclusters of inert gases may occur in the nanocavities of selected materials. Thus the crystallographic features of the nanoclusters are correlated with the cavities geometry.

Resolving of surface structure interacted with the gas has been transformed from a challenge to the reality, thanks to the development of high-end TEM instruments. This helps to revisit some typical chemical processes including absorption and surface diffusion, previously accessible by those surface science methods.

3. Surface of Different Dimensional Materials

3.1. Single Atoms on Surfaces

The section covers the surface scenarios occurring with 0D single atoms. The two exciting progresses are the visualization of the emerging single-atom catalysts within a variety of supports, and the near-surfaced self-interstitials.

The surfaces of supported metal nanoparticles have been widely used in heterogeneous catalysis. For maximum catalytic efficiency, the synthesis of a single-atom catalyst has been a dream for chemists, which recently has become a reality. Gold nanoclusters supported by iron oxide have been demonstrated to be active and efficient for CO oxidation. [44] It is possible to determine the locations of individual iridium atoms and nanoclusters within the zeolite pores. [45] Recently, the Zhang research group successfully synthesized a single-atom catalyst: only isolated catalytically-active single Pt atoms are anchored to the iron oxide surfaces, as evidenced by STEM (**Figure 4**). [46] This single-atom catalyst has extremely high atom efficiency, ascribed to excellent stability and high activity for CO oxidation. DFT calculations showed that it is the partially vacant 5d orbitals, within the high-valent positively-charged Pt atoms, are responsible for the high catalytic activity. The partial vacancy of these orbitals facilitates reducing both the CO adsorption energy and the activation barriers for CO oxidation.

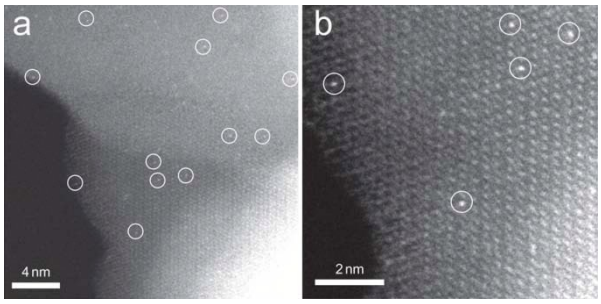

Figure 4. Atomic-resolution STEM images of platinum single-atom catalyst supported on an FeO_x surface. Pt single atoms, illustrated by white circles, are uniformly dispersed (a) on the support and (b) further exactly occupy the Fe-atom positions. Copyright 2011 Nature Publishing Group.

When the support was changed to TiO_2, the subangstrom resolution enabled the identification of five different Pt-atom adsorption sites on the TiO_2 (110) surface (**Figure 5**). [47] The combination of STEM with DFT calculations revealed that the most favorable Pt-adsorption sites are vacancy sites of basal subsurface oxygen atoms.

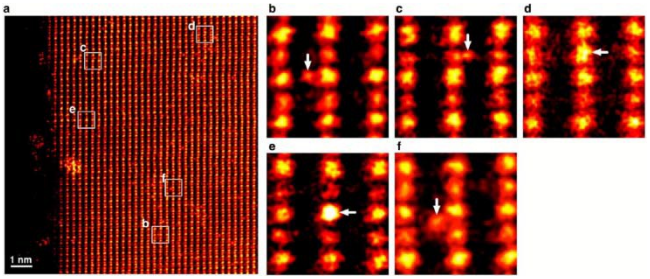

Figure 5. Atomic-resolution STEM images of platinum single atoms on a TiO_2 (110) surface. (a) The overview. (b-f) The local enlargement of five Pt single atoms located at various surface sites on the unit structure. Copyright 2014 American Chemical Society.

The combination of aberration-corrected HRTEM and phase contrast microscopy have made possible to achieve the 3D imaging of near-surfaced germanium self-interstitials with sub-nanometer precision. Confirmed by the first-principles calculations, a strong influence stems from the surface proximity as well as a positively charged interstitial. Thus the work can extend to directly visualize formation and migration of single defects. [48] Based on such imaging of the diffusing point defects, we may see the exciting atomic diffusion in the future, by utilizing defect stability and controlling electrically/thermally-induced diffusion. [49]

As a supplement to the traditional 2D projection in TEM, an aberration-corrected SEM may excel in a selective visualization to distinguish bulk atoms from surface atoms. [50] Thus the surfaced single atoms can be imagined as the sample was simultaneously probed through its whole thickness using transmitted electrons.

From a point view of nanoscience and nanotechnology, single-atoms are the ultimate cross-point linking bottom-up with top-down styles. Undoubtedly, direct visualization and physical characterization of single-atoms contributes more to understanding of properties of the targeting elements, which have positive implications for surface features of the relevant materials.

3.2. Surfaces of 2D Materials

The section covers the surface scenarios occurring with 0D single atoms. The two exciting progresses are the visualization of the emerging single-atom catalysts within a variety of supports, and the near-surfaced self-interstitials.

When studying the emergent 2D material graphene, it is necessary to decrease the high-tension of TEM from the traditional 300-200 kV to 80-60 kV. [51, 52] E-beam damage into the sample can be largely eliminated while the sacrificed spatial resolution can be compensated by the aberration correction. Thus low-voltage aberration-corrected HRTEM is one of the best choices for structural elucidation with atomic resolution. Recently, Kaiser et al. achieved a high spatial resolution of 0.2 nm even for single-layer graphene by using a surprisingly-low 20 kV TEM equipped with an electrostatic-monochromator and an aberration-corrector. [53] In fact, TEM has made key contributions to discover most types of nanocarbon forms. [54]

The Zettl research group investigated the stability at the atomic edge of a single-layer graphene and found that the armchair arrangement is less stable than the zigzag form. [55] A complete transformation process was recorded from graphene nanoribbons to single carbon chains under an e-beam irradiation. [56] Aberration-corrected HRTEM reveals a vivid transforming process from a graphene sheet to a fullerene, [57] which may reinvent formation mechanism of fullerene. Stimulated by e-beam, a solid-state transition was observed from a crystalline monolayer graphene into a 2D carbon glass in a transmission electron microscope. [58] Such order-to-disorder transformations greatly enrich our understanding of amorphous structures.

Probe-corrected STEM instrument enables visualizing how the single/isolated atoms are interacted with the surface. Recently, an interesting atomic-scale monitoring was reported to show how a rotary Si trimer was formed through silicon-graphene reactions in a graphene monolayer. The result further aids our understanding of chemical reactions towards the functionalization of graphene (**Figure 6**). [59] By manipulating a focused e-beam it was possible to control the local formation of mono- and divacancies in graphene. These vacancies were subsequently applicable to trap single dopant atoms to form covalently-bonded Fe/monovacancy and Fe/divacancy, as supported by DFT calculations. These dynamic configurations could facilitate distinguishing magnetic and nonmagnetic states in doped graphene. [60]

Great progress in surface exploration by TEM has not only been made in 2D graphene, but also in other emerging 2D materials. Through e-beam-irradiation, hexagonal boron nitride was demonstrated to be an un-supported quasi-2D material. [61] Combining first-principles atomistic simulations and HRTEM analysis, the behavior of catalytically important 2D transition-metal dichalcogenides under e-beam irradiation was recorded: Such atomically thin MoS_2 layers can be selectively doped through filling impurity atoms into the e-beam-induced vacancies. This has direct implication to engineering the electronic structure of the 2D material. [62]

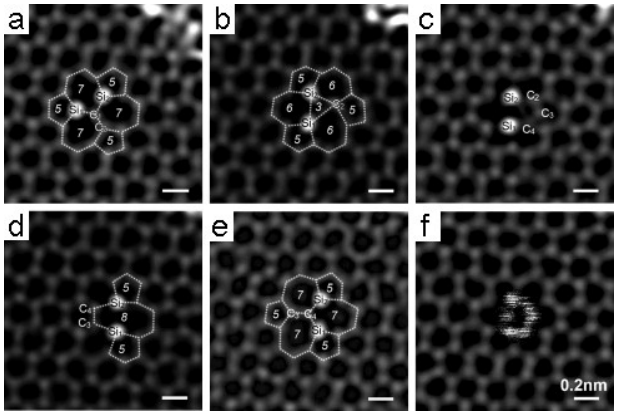

Figure 6. Formation of a silicon trimer at 80 kV was dynamically recorded in monolayer graphene with atomic resolution, showing the lattice dynamics process (a-f). Copyright 2014 John Wiley and Sons.

As all the atoms locate onto the surface for the 2D materials, TEM, thereof, will be one of the best choices to probe new performances of this emerging catalogue of material. This paradigm opens new horizon of understanding materials surface.

3.3. Towards the Integration of 3D Surfaces

Catalysis applications and nanoscale device require a determination of the 3D atomic arrangement of nanoparticles. [63] Real-space observation essentially gives 2D information of matters. Through electron tomography, the shape reconstruction of a nanoparticle can be made from a series of projection images. [64] The section targets the important progresses towards integrating 3D surfaces by applying TEM-related techniques.

By combining probe-corrected STEM, so-called statistical-parameter-estimation-theory and discrete-tomography, Van Aert et al. generated the first atomic-resolution 3D reconstruction of a complex Ag nanoparticle embedded in an aluminum matrix from only two images of the target. [63] Considering that an experimentally reconstructed exit wave consists of the superposition of the scattered spherical waves by the individual atoms in the object, Van Dyck et al. presented another electron tomography method that was employed to determine the position of individual atoms with subangstrom precision, from only one viewing direction. [65]

Following these events, new progress has been made towards a 3D surface elucidation. Chen et al. integrated 3D Fourier filtering with equal-slope-tomography-reconstruction in STEM mode and were able to observe nearly all atoms in a roughly 10 nm multiply twinned Pt nanoparticle. They revealed atomic steps at 3D twin boundaries and imaged the 3D core structure of edge and screw dislocations at atomic resolution. [66] Obtaining of the information is a leap towards the integration of the 3D surface of matter. [67] Very recently, aberration-corrected HRTEM combined with numerical-evaluation even allowed the 3D shape of a thin MgO crystal to be determined from only one single high-resolution image (**Figure 7**). [68, 69] The single-image method can facilitate a full visualization of radiation-sensitive materials by uncovering the whole surface at atomic resolution.

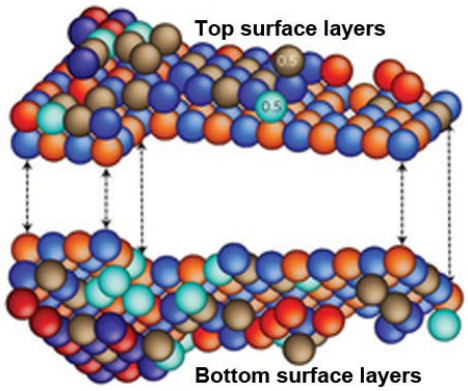

Figure 7. Overview of the two surface layers of a MgO crystal, as deduced from a dedicated aberration-corrected HRTEM image. The lattice sites, half-occupied sites, and Mg:O site ratio are clearly visualized. Copyright 2014 Nature Publishing Group.

As shown by the aforementioned surface exploration by TEM, imaging along a few zone axes of the targeted crystal can effectively exploit its translational symmetry, and determine the full atomic structure of 3D nano-objects. The careful choice of imaging conditions will help to provide a strong-localized-image contrast and an optimum signal-to-noise ratio. Thus, in order to determine the surface morphology of a crystal, information can be gathered on column positions, the atoms number in a column, and the species of the topmost atom. [69] The absence of a majority of

vacancies/impurities is essential in the targeted region. [68] Moreover, the reconstruction of a series of projected images is usually required for the extraction or encoding of the surface information, as TEM/STEM imaging gives projected 2D information about a nano-object. [64]

The integration of the whole surfaces, together with the essential resolving of materials bulk by using TEM, will lead ultimately to the complete understanding of matter structure and chemistry.

4. Complementary Techniques to TEM

Besides the real-space TEM observation itself, some complementary techniques to TEM enable aiding a lot for the surface exploration. This was already true in the early stage of surface investigations using TEM. A typical work was the structure elucidation of a reconstructed Si(111)-7×7 surface by using transmission electron diffraction pattern.[70] State-of-the-art reflection high-energy electron diffraction and reflection-electron-microscopy (RHEED-REM), which are extremely surface-sensitive, have been very useful in the exploration of materials surface. Yagi et al made a series of surface exploration by using RHEED and REM in the 1980s.[71] Some pioneering *in situ* REM investigations of surface dynamic processes include sublimation and atomic features of Si(111), the role of surface steps in phase transition and adsorption.[72-74] By combining TEM and RHEED as well as some other surface methods, it was confirmed that electronic decoupling exists among the non-Bernal-stacked multilayer epitaxial graphene synthesized with the laser method. [75] Moreover, REM-RHEED enables us to identify the more surface features, e.g. superstructures, domain boundaries and atomic steps. [76]

Nowadays, electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX) are two key analytical techniques that aid surface elucidation within the scope of TEM. A landmark in surface identification is the first atomic observation of the well-known SMSI in the famous Pt/Fe_3O_4 model catalyst by Willinger et al. [77] By dedicated HRTEM, STEM and EELS techniques, a SMSI monolayer of FeO was detected as the outmost covering of the 5 nm Pt particles supported by Fe_3O_4 (**Figure 8**), usually accessible by scanning tunneling microscopy.

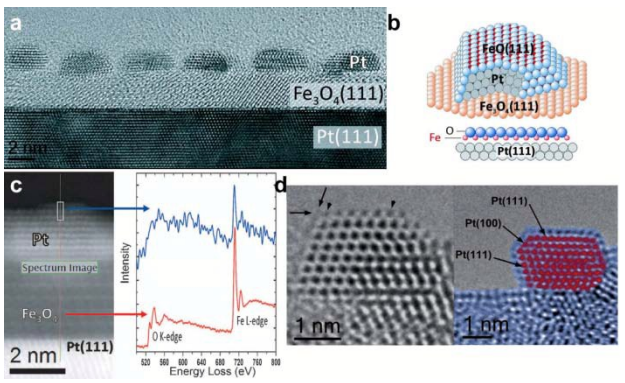

Figure 8. $Pt/Fe_3O_4(111)$ model catalyst. (a) The overview HRTEM image. (b) Model representation of the SMSI FeO(111) monolayer onto the Pt(111)surface. (c) EELS from the Fe_3O_4 to the Pt surface. (d) The magnified HRTEM image showing a SMSI FeO(111) monolayer. Copyright 2015 John Wiley and Sons.

The current possibilities of chemical analysis are approaching the single-atom limit. [78, 79] A combination of STEM, EELS, and *ab initio* or DFT calculations revealed that the single Si defect geometries on the graphene surface have a variety of electronic structure. [80, 81] By using probe-corrected STEM and EELS/EDX, one can exclusively identify the isolated impurity atoms (Si/Pt) in monolayer graphene. [82] However, the electrons number must be enough towards an optimum signal-to-noise ratio, in order to achieve the fine-structure EELS analysis of a single atom. This will bring forth the inevitable e-beam irradiation damage of the targeted area; on the other hand, the spatial resolution may be also lowered with the non-negligible EELS signal delocalization. [78] Luckily, the two problems can be tackled to the extent through decreasing the high-tension of TEM.

The synergistic effect of combining the analytical techniques with TEM will facilitate gaining fundamental insight into the investigated systems. They will play an increasingly important role in surface elucidation.

5. Concluding Remarks

Even though TEM is really powerful in surface exploration, there is another side to the coin: particular imaging conditions, a necessary assumption, or post-image analysis are sometimes indispensible for accurate elucidation of the surface structure. In TEM-related surface analysis, damage or modifications induced by the e-beam may be another concern for some investigated materials. [83-85]

Nevertheless, the significant progress made in the exploration of surface phenomena has been directly benefited from the advent and development of TEM-related techniques: From the invention of a transmission electron microscope in Germany with a voltage (due to primary electrons) of several tens of keV[86-88] to the establishment of an ultrahigh-voltage microscope (3 MeV) at Osaka University and the state-of-the-art Cs/Cc-corrected and monochromated TEAM0.5 instrument at the National Center for Electron Microscopy in Berkeley, from the first HRTEM image of $Ti_2Nb_{10}O_{29}$ by Iijima in 1971[89] to the first Cs-corrected image by Haider et al. [90] and the identification of atomic displacement by several picometers by Jia and Urban, [4, 5] we are seeing the exciting developments with TEM. The multidimensional electron microscopy[3, 91, 92] is now finding plenty of room on the surface. TEM and its development are becoming one of the best solutions to surface issues, in the fields ranging from heterogeneous catalysis and energy conversion to thin-film growth and more. Even larger room can be entered into if the unexpected barrier (of thermal magnetic-field noise[93, 94]) to better resolution in TEM can be overcome.

Acknowledgements

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