Observing Atoms at Work by Controlling Beam–Sample Interactions

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Functional behavior can be initiated and captured in series of images with previously unknown details using a successful effort to effectively control beam–sample interactions in high-resolution transmission electron microscopy. The approach uses tunable electron dose rates that can be chosen to be as low as attoamperes per square-Ångstrom to delay sample degradation to an unexplored end. Dose rates can be systematically increased to stimulate and observe dynamic object responses. Observations can be made in real time with deep sub-Ångstrom resolution and single-atom sensitivity, even if radiation-sensitive matter is probed and either pressure or temperature is raised in the electron microscope.

1. Introduction

Over the past decades, materials sciences and technology have evolved to a point where our knowledge and equipment allows us to understand the atomic structure of static matter atom-by-atom. These capabilities are exploited with great success at the Molecular Foundry, which includes now the National Center for Electron Microscopy (NCEM) see for example ref. [1–3]. They are complemented by a large variety of in situ experiments that are fueled by a rapidly growing collaboration between academia and industry designing a rich variety of customized sample holders and promoting environmental transmission electron microscopy (E-TEM). Remarkably, even functional behavior can already be captured in operando, using micrometer-size reactors that are inserted into electron microscopes[4] and by E-TEM.[5] Beyond these applications, research efforts now aim to synthesize systems of greater complexity to create previously unknown functionality or to mimic nature. Established programs to produce transportation fuel from sunlight are such attempts, where hybrid materials are used to fabricate artificial photosynthetic systems with the goal of establishing a more-sustainable energy solution on earth.[6] Such hybrid materials are synthesized and characterized at The Molecular Foundry, where theoretical guidance is provided.

However, our imagination is still challenged at a very fundamental level when it comes to predicting functional behavior, because functionality is intimately linked to atom and charge dynamics on surfaces and across interfaces. Bottlenecks exist because it is difficult to reliably access and understand time dependences at atomic resolution, without explicitly controlling beam–sample interactions over large time scales.[7] As a result, dynamic processes at the atomic scale tend to escape direct observations. The needed spatial resolution, time resolution, and single-atom sensitivity simply lie beyond existing experimental and computational skills, and further progress will demand that fresh ideas are adopted.[8]

These exciting scientific developments occur during a time of ground-breaking innovations in electron microscopy that were driven by projects such as TEAM, CREST, SALVE,[9] and others providing aberration-corrected electron optics. They enabled unprecedented experiments by establishing the ability to detect single atoms across the periodic table of elements at deep sub-Ångstrom resolution (ca. 0.5 Å) with electron beams of voltages in the range between 20 kV and 300 kV.[10,11] Clearly, the majority of advanced applications already benefits greatly from aberration-corrected electron microscopy by decoding the electronic and atomic structure of matter together with its chemical composition at the level of single atoms in broad-beam and scanning electron microscopy (see for example ref. [12], and they will steadily grow.

In the wake of these projects, however, it has also become clear that the intense radiation emitted from electron or X-ray sources sets limits to resolution, and further progress demands a suitable control of beam–sample interactions. Solutions to mediate undesired effects of radiation damage are sought worldwide, and they fall into two categories that can be labeled “hit and destroy”[13] and “divide and conquer”.[14] They are schematized in Figure 1.[15] In the “hit and destroy” approach (Figure 1a) a high-brightness particle or photon beam hits the molecule, which decomposes on a time scale of femtoseconds. However, the finite atom mass requires a finite amount of time for the atoms to escape from their equilibrium positions. During this brief time period, diffraction patterns are captured that are analyzed to reveal the initial structure of the molecule. Alternatively, one may deliver the probing particles or photons one-by-one (as shown in Figure 1b). In this case, a probing particle may also cause a distortion of the structure that remains irrelevant as long as the excitation is reversible and decays before the next probing particle hits the molecule. In such a situation, the excitation can be repeated over and over again to build up, in time, a static image of the molecule with a desired resolution.

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contrast. If the probing dose rate can be kept small enough to maintain the static structure, it can also obviously be increased to stimulate specific system excitations such as molecule conformations, as schematized in Figure 1c).

Here, existing capabilities are summarized, which address the control of beam–sample interactions, thereby gaining the capability to observe and stimulate structural changes on a single atom level in real time.

2. Low-Dose-Rate Electron Microscopy

New capabilities and concepts were recently developed to establish a “divide and conquer” approach for electron beams. This approach uses low electron dose rates, in analogy to best practices in biological research, and exploits reversible object excitations in real time that are captured in the amplitude and phase of in-line holograms.[15] The method opens the exciting perspective to observe genuine nanomaterials and interfaces in radiation-sensitive matter at increased resolution, and enables real-time studies of functional behavior. Technically, the approach utilizes a Nelsonian illumination scheme that bypasses the conventional collimator setup and delivers electrons in a controlled manner exclusively onto the imaged sample area. This method changes TEM illumination practices that existed since the invention of broad-beam electron microscopy by Ernst Ruska, who placed the selected area diffraction aperture behind the sample to obtain a large field of view at the cost of a precise control of the sample illumination. The impact of our approach is currently highlighted in a special volume of the microscopy journal “Micron”.[8] Opportunities for new research are exceptionally rich since progress can be made with the imaging of radiation-sensitive materials, such as catalysts or molecules. In addition, low-dose-rate in-line holography is exceptionally beneficial to environmental electron microscopy.[16] Certainly, its capabilities are needed to better understand artificial photosynthetic systems, as described in in ref. [17] This contribution describes underlying principles in detail and points toward first applications. It is available at the Molecular Foundry, which houses the two TEAM microscopes that allow a Nelsonian illumination scheme to be set up using Wien filter monochromators for imaging.[11]

First, benefits are described by contrasting the new approach with traditional practices using nanoparticles. Consider gold particles of various sizes that are dispersed on an amorphous carbon support, as shown in Figure 2a–c). Figure 2a–c) show three images of a time series that are of graphene is visible that is marked by the circle in Figure 1b. The usage of high dose rates is quite common to capture single high-resolution images, and they are often exceeded in the day-to-day operation of high-resolution transmission electron microscopes. In each individual frame, the atom clusters or columns appear sharp, and there is no reason to believe that they would not show the genuine structure of the gold nanoparticles. Therefore, one would conclude from any single image that the ca. 6 nm large particle is crystalline and strongly faceted, showing a characteristic surface reconstruction, that the ca. 2 nm large particles marked by boxes are amorphous or exhibit short range order, and that single gold atoms are dispersed on the substrate (arrows). Surprisingly, none of these conclusions appear to be unambiguous if time dependences are considered. Figure 2a–c) show three images of a time series that is available as a movie in the Supporting Information. It reveals that the nanoparticles and the support film are continuously altered if the material is irradiated in the described, traditional manner, and the occurring alterations are seen in Figure 2a–c): Large particles rotate (line) and their surfaces restructure continuously; smaller particles change their entire crystal structure from frame to frame and often appear amorphous (boxes); single gold atoms are removed from the particles, dispersed

![Figure 1. A schematic description of approaches aimed at resolution improvements for the imaging of radiation-sensitive matter and at capturing dynamic processes. The structure of a benzene molecule is used in the example. Adapted with permission.[13] Copyright 2013, American Physical Society. For details see text. a) “Hit and destroy”;[13] b) “Divide and conquer”[14] c) Conformational changes.](image-url)
across the substrate and agglomerate temporarily (arrows); even the amorphous carbon support is sputtered and can be transformed into local patches of graphene (circle). Strictly speaking, it is debatable whether the genuine structure of the material was imaged at any time because an undocumented exposure of the material to the electron beam commonly occurs long before an image is taken when the traditional broad-beam condenser set-up scheme is used. Unfortunately, it is common not to mention the exposure parameters at all in the literature. The impression that such images of nanoparticles would faithfully represent their genuine structure only occurs because atom diffusion is commonly rapid compared to the image exposure time, and it is difficult to detect the loss of single atoms from atom columns unless advanced microscopy equipment is used in combination with quantitative image processing.

A few similar examples are already reported in the literature using scanning and broad beam illumination modes, but only suggestions for solutions emerge.\cite{11,12} Our approach addresses this shortcoming by using a Nelsonian illumination scheme that eliminates any uncontrolled sample irradiation in broad-beam mode\cite{11} and allows dose rates as low as attoamperes per square-Ångstrom to be worked with, which were found to delay sample degradation and improve image contrast.\cite{15} Its effect on image contrast is depicted in Figure 2d–g, which show a second set of previously unexposed gold particles on the carbon support. Figure 2d shows a single image recorded with $10 \text{ e Å}^{-2} \text{s}^{-1}$ (1.6 aA Å$^{-2}$) at 80 kV. Naturally, nanoparticles can hardly be recognized in the image because only a few scattering events occurred, which necessarily yields a poor image contrast. However, the contrast can be boosted by recording large image series that are averaged in some manner. In this example, a focus series of 80 images was recorded with an exposure and readout time of 1.7 s per image yielding an accumulated electron dose of 1360 e Å$^{-2}$. Post-acquisition, the images were aligned with sub-pixel accuracy and reconstructed to obtain the complex electron exit wave function, which is a smart averaging scheme that boosts image contrast, solves the phase problem, and creates an in-line hologram.\cite{11} Atom column positions are marked by contrast maxima in the phase image of the in-line hologram. In addition, it is straightforward to probe for

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**Figure 2.** A comparison of the traditional approach to acquire high-resolution images (a–c) with the new approach (d–g). Gold particles on an amorphous carbon support are shown. Details are given in the text. a–c) Smaller and larger gold particles with fluctuating structures are highlighted in boxes. Circle: a graphene patch is formed from the amorphous carbon support. Arrows: single gold atoms or atom clusters. The line marks particle rotation. Dose rates for the acquisition of one frame are listed. The accumulated electron dose for the recording of 50 images in 1.4 min is listed in (g).
atom displacements or particle motion that may have occurred during the recording time by reconstructing in-line holograms from different image subsets of the same focus series. In the example, we first used images #1–50 to reconstruct the phase image of Figure 2e and then images #49–80 of the series to create Figure 2f. Comparing both images, it is seen that the pictures of the ca. 10 nm wide nanoparticle remain identical within noise limits and that the particle exhibits considerably smaller facets compared with the one in Figure 2a, such that its unprotected surfaces almost form a circle. These observations imply that the electron-beam-induced particle motion is reduced to distances that are smaller than the image alignment precision of <0.24 Å per pixel. In addition, it suggests that pronounced facets are generated if the particles are exposed to large electron-beam currents that strip atoms from surfaces, like peeling back the layers of an onion. Even the small particles ca. 2 nm in size (boxes) stay in place and exhibit homogeneous lattice fringes, proving that the structure of the small gold particles was initially crystalline and not amorphous as previously suggested in Figure 2a–c. Indeed, an electron-beam-induced amorphization of small particles occurs commonly, even if moderate beam currents are used, because the energy deposited by the electron beam easily exceeds the total binding energies of nanoparticles 3–4 nm in size.[11] Finally, the electron exit wave function is available, which allows single images to be recalculated at any focus value (Figure 2g) that can be directly compared with the initial recording in Figure 2a. This comparison also indicates the large contrast enhancement obtained by reconstructing the electron exit wave function from 50 images, which not only maintains the targeted resolution and single-atom sensitivity, but also helps to preserve the genuine structure of radiation-sensitive objects. In fact, it is striking that a similar image contrast is obtained in Figure 2g with a significantly lower accumulated electron dose. This beneficial aspect of the method is caused by delivering the electrons slowly, which allows reversible sample excitations to decay in time before the next scattering event occurs.[15]

The baseline performance of the method is currently explored. It is instructive to mention emerging threshold values for the onset of characteristic physical or chemical processes that are naturally material dependent. For example, oxide-based catalysts exhibit electron-beam-induced loss of atoms or molecules from their surfaces, even if irradiated with only ca. 100 e Å−2 s−1 at 80 kV.[17] It occurs because their binding energy is lowered in surface proximity, and varies greatly since it is structure specific. Thus, the damage to nanoparticles sets in “softly” and cannot be characterized by a single threshold value, in contrast to the atom displacement from bulk sites. Also, structural phase transitions can be readily observed if similar dose rates are applied. Electron-beam-induced amorphization of crystalline catalysts is reported if the dose rate exceeds 900–1000 e Å−2 s−1.[17] The inverse process of creating crystalline material from an amorphous structure occurs for the transformation of amorphous carbon into graphene[11] using dose rates that exceed 10 000 e Å−2 s−1. It is visible in Figure 2c and holds similarities to the transformation of hydrocarbons into graphene at elevated temperature.[18]

Clearly, beam-induced structure fluctuations are size dependent and can include boundary motion, crystal-structure fluctuation, or transitions into an amorphous state if the particles are small and the beam currents are high. The visibility of fringes in small particles is a matter of particle size, beam current, and microscope performance. For the particles 2–3 nm in size, in Figure 2, and a resolution of 0.6–0.7 Å at 80 kV in a broad-beam illumination mode,[11,15] fringes are visible across the whole range of tilt angles, and their absence indeed indicates the absence of long-range order, which is now detectable with single-atom sensitivity. Similar structure fluctuations have been observed before and were labeled as a “quasi solid state” if characterized at lower magnification lacking single-atom sensitivity. Typically, only bulk-threshold values have been employed to describe the onset of atom displacements and the dynamic behavior of nanocrystals.[20] Such an approach ignores the “soft” onset of damage in surface proximity or in small particles where binding energies are variable and largely reduced. In addition, our evolving view suggests that beam-current control is indeed as important as voltage control, and that ionization, displacement, and temperature effects are intimately coupled, yielding reversible and irreversible system excitations in surface proximity and small particles that can be tracked now.[15]

3. Application Examples

3.1. Catalysis

Our approach is of general validity and Figure 3 is an application example that targets investigations of oxygen-evolution
catalysts when electron-beam-induced object alterations must be absent, even in surface proximity, in order to come to relevant conclusions.\cite{16,17} The depicted phase image of the 3–6 nm large particles was reconstructed from 60 images recorded at a dose rate of 40 e Å\(^{-2}\) s\(^{-1}\) in the vacuum of the TEAM 0.5 microscope. The supporting carbon film is outside the field of view and current densities are well below the threshold values given above. A 3D network of randomly fused particles is seen, and crystallographic studies can be performed to determine their crystal structure locally, which is possible because the phase problem is solved during the reconstruction of the electron exit wave function. In this case it is determined that the Co\(_9\)O\(_4\) particles exhibit a spinel structure, and three particles are imaged along their [100], [211] and [103] zone axes. Image simulations are used to verify these assignments. The particle surfaces are generally rough and not at all atomically flat, as is often reported for catalysts or other nanoparticles. In contrast, the traditional approach to record single images with high dose rates rapidly removes isolated surface atoms or islands, thereby enhancing a regular geometrical appearance before the irradiated object is altered beyond recognition. Obviously, thereby enhancing a regular geometrical appearance before dose rates rapidly removes isolated surface atoms or islands, often reported for catalysts or other nanoparticles. In contrast, simulations are used to verify these assignments. The particle surfaces are generally rough and not at all atomically flat, as is often reported for catalysts or other nanoparticles. In contrast, the traditional approach to record single images with high dose rates rapidly removes isolated surface atoms or islands, thereby enhancing a regular geometrical appearance before the irradiated object is altered beyond recognition. Obviously, control of these processes is mandatory in E-TEM,\cite{16} where the irradiated object is altered beyond recognition. Certainly, similarities to temperature variations exist, but they are modulated by additional processes such as ionization effects that occur in electron microscopy because of the negative electron charge. A direct comparison of temperature variations and beam-current variations is possible if the energy absorbed from the electron beam by nanocrystals can be kept below the existing thermal excitation, which is

\[ k T/e = 25.6 \text{ meV} \] at room temperature. This boundary condition forces the utilization of low voltages in combination with very low beam currents in the vicinity of atomic sizes. It can be relaxed by sample heating at the cost of ignoring low-energy excitations, since atomic-resolution imaging can be performed at temperatures exceeding 1000 °C\cite{16} while maintaining all other capabilities. The similar impact of temperature- and electron-beam-induced object excitations suggests that, beyond the ability to maintain static structures, it is equally attractive to study collective system excitations on a mesoscale with single-atom sensitivity that are stimulated by either temperature- or by electron-beam-induced object excitations or by both. Concerning electron-beam-induced object excitations, pioneering experiments were recently reported.\cite{13}

### 3.2. Atom Dynamics

Turning toward the recording of dynamic processes, it is pointed out that electron-beam-induced object excitations are highly reproducible if the illumination is confined to the imaged sample area.\cite{11} This finding suggests that a well-defined amount of energy from the impinging electron beam is absorbed by the material and can be tuned by current variations to stimulate dynamic behavior that ultimately leads to functionality. Certainly, similarities to temperature variations exist, but they are modulated by additional processes such as ionization effects that occur in electron microscopy because of the negative electron charge. A direct comparison of temperature variations and beam-current variations is possible if the energy absorbed from the electron beam by nanocrystals can be kept below the existing thermal excitation, which is

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![Figure 4](https://www.materialsviews.com)  
**Figure 4.** Electron-beam-stimulated atom excitations in rhodium (a,b) and in graphene (c) captured in real time. a) Atomic-resolution image of a Rh [110] catalyst. Image #57 of a time series of images is shown. Dose rate: 6000 e Å\(^{-2}\) s\(^{-1}\). Blue circles: projected atom positions. \(I_0\) = projected octahedral interstitial positions. \(I_t\) = projected tetrahedral interstitial positions. The red arrow points to spontaneously occurring extra contrast that causes a characteristic image blur between adjacent columns and only occurs in selected images. b) The same image as in (a). The yellow circles depict a projected atom trajectory determined by first-principles calculations. It is the projected path of an atom from an ordinary lattice site (blue circles) into a (110) surface corrugation site that matches the local image blur of (a) perfectly. The excitation is reversible and occurs across energy barriers of 1 eV (forward motion) and 0.1 eV (backward motion). c) Equilibrium positions of carbon atoms in graphene are calculated for a thermal excitation at 0.75\(T_m\) (\(T_m\) = melting point temperature) using molecular dynamics. Image contrast is simulated using the calculated structural configurations. The red dots mark the local atom positions on a time scale of picoseconds. The blue dots mark regular atom positions. A and B mark repetitively occurring displacement sites where atoms succeed temporarily. The arrow points toward contrast residuals in such locations that are caused by these excitations and can be captured in experimental images. a,b) Reproduced with permission and c) adapted with permission.\cite{13} Copyright 2013, American Physical Society.
and two of these results are shown in Figure 4. In Figure 4a, a largely magnified (110) surface of a rhodium catalyst is depicted in a plane-view configuration, such that the empty space between atom columns becomes a significant distance. Image #57 is part of a time series of images where unexpected contrast occurs temporarily (red arrow) close to projected interstitial sites. In Figure 4b a calculated single-atom trajectory is superimposed on the image, describing the reversible excitation of a single rhodium atom from its regular lattice site into the Rh (110) surface corrugation. The calculated trajectory perfectly matches the shape of the contrast blur between the 2 atom columns marked by the arrow in Figure 4a. Therefore, it is attributed as originating from this elemental excitation, which is known to occur in different metals as temperature increases. For the first time, it is directly imaged in real time using the electron beam as stimulus and probe. A dose rate of 6000 e Å² s⁻¹ is used in this case to overcome a largest energy barrier of ca. 1.0 eV[15] and the reversible atom displacement is large compared to thermal excitations that are commonly described by Debye–Waller factors. Thermal displacements are typically only ca. 0.1 Å at room temperature, while the projected atom displacement detected here exceeds 1 Å. Certainly, the deep sub-Ångstrom resolution of the TEAM 0.5 microscope and its outstanding mechanical and electrical stabilities are needed[11] to observe atom motion in the empty space between atom columns. Similarly, we calculated collective excitations of carbon atoms in graphene using molecular dynamics and find uncommonly large atom displacements into specific sites that are stabilized temporarily and shown in Figure 4c. They are experimentally observed at room temperature using beam currents exceeding 14 000 e Å² s⁻¹, which are used to capture the images of Figure 2a–c. The temperature equivalent for theoretically studies of this phenomenon is (0.5–0.75) × T_m, where T_m is the melting point temperature of graphene.[13]

In contrast, low-energy processes around 0.1 meV typically shape catalytic pathways and can already be stimulated if attoamperes are delivered into a square-Ångstrom at 80 kV. In summary, atom dynamics can be captured in real time in atomically resolved images from high-performance electron microscopes, since atom motion generates extra contrast in the images of Figure 2a–c. The temperature equivalent for the described experiments is only the beginning of a new route for electron microscopy that can help in reaching the goal of imaging radiation-sensitive matter and functionality of mesoscopic systems at atomic resolution. The approach can be complemented and extended to better include time resolution and environmental capabilities. In any case, it seems that the climax of electron microscopy is yet to come.

4. Conclusions

Low-dose-rate electron microscopy allows electron-beam-induced sample excitations to be controlled and utilized, thereby offering the opportunity to extend applications of electron microscopy to include atomically resolved studies of radiation-sensitive objects and their conformational changes or atom dynamics in general.

The described experiments are only the beginning of a new route for electron microscopy that can help in reaching the goal of imaging radiation-sensitive matter and functionality of mesoscopic systems at atomic resolution. The approach can be complemented and extended to better include time resolution and environmental capabilities. In any case, it seems that the climax of electron microscopy is yet to come.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. A supplementary movie is provided where the image sequence is accelerated. The initial recording was done at 1 frame per second and 0.7 s of readout time.

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