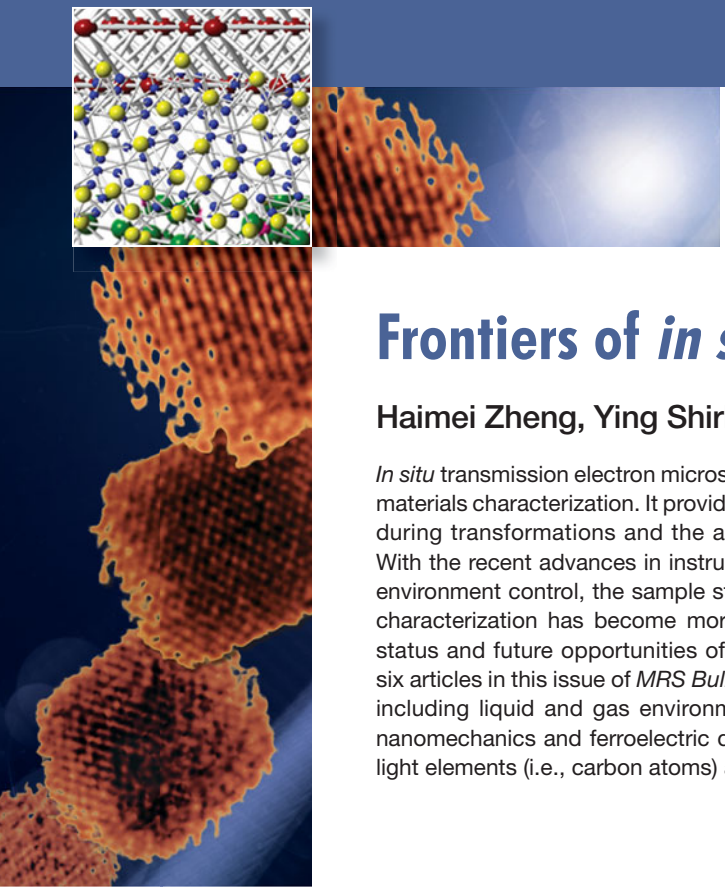

Frontiers of *in situ* electron microscopy

Haimei Zheng, Ying Shirley Meng, and Yimei Zhu, Guest Editors

In situ transmission electron microscopy (TEM) has become an increasingly important tool for materials characterization. It provides key information on the structural dynamics of a material during transformations and the ability to correlate a material's structure and properties. With the recent advances in instrumentation, including aberration-corrected optics, sample environment control, the sample stage, and fast and sensitive data acquisition, *in situ* TEM characterization has become more powerful. In this article, a brief review of the current status and future opportunities of *in situ* TEM is provided. The article also introduces the six articles in this issue of *MRS Bulletin* exploring the frontiers of *in situ* electron microscopy, including liquid and gas environmental TEM, dynamic four-dimensional TEM, studies on nanomechanics and ferroelectric domain switching, and state-of-the-art atomic imaging of light elements (i.e., carbon atoms) and individual defects.

Introduction

In situ transmission electron microscopy (TEM) is a fast-growing and fascinating area of research that has drawn tremendous attention from various fields ranging from materials science to chemistry and biology. As a powerful and indispensable tool for nanomaterials characterization, *in situ* TEM provides great opportunities to characterize dynamic changes in size, shape, interface structure, electronic state, and chemical composition in materials at and below the nanoscale.

In situ TEM has benefited from advances in electron microscopy instrumentation that have achieved spatial resolutions in the subnanometer range, energy resolution in the sub-electron-volt range, and sensitivity to individual atoms. It is now possible to image the atomic structure of materials in real time under various external stimuli while simultaneously measuring relevant properties. A variety of *in situ* TEM holders have been developed to enable imaging and measurements under applied heat, stress, optical excitation, and magnetic or electric fields, and the development of environmental cells allows experiments to be performed in different gaseous and liquid environments. Developments in *in situ* TEM combined with aberration-corrected high-resolution imaging, electron energy-loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy have enabled many discoveries in dynamic materials processes at the atomic level that were not previously possible.[1–6]

With the development of controlled-environment TEM, environmental TEM (ETEM), direct observations of the structural evolution of catalytic nanoparticles under dynamic reaction conditions has been realized. The further requirements of achieving better spatial and energy resolution of dynamic measurements under relatively high gas pressures while minimizing electron-beam effects provide a framework for the advancement of ETEM.

In recent years, a number of breakthroughs have occurred in the development of ETEM for imaging liquid samples.[2,7,8] To introduce liquids into the high vacuum of a TEM instrument, either a microfabricated liquid-cell enclosure or an open-cell configuration using low-vapor-pressure ionic liquids has been utilized. These technical breakthroughs have yielded a plethora of achievements in imaging dynamic growth of colloidal nanoparticles,[2,7,9] electrochemical processes relevant to batteries,[10,11] and biological materials in liquid environments.[8,12]

These studies have paved the way to characterize chemical reactions and dynamic processes of materials under working conditions in real time. With the continuing development of instrumental capabilities, *in situ* TEM experiments can be performed to study material behavior under various external stimuli such as electrical and magnetic fields[13,14] and mechanical stress.[15] *In situ* TEM has been applied to visualize domain dynamics during ferroelectric and magnetic switching,[14,16]

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shedding light on the switching mechanism of these fundamental processes in ferroelectric and magnetic materials. Mechanical TEM holders enabling quantitative measurements of structural evolution under an applied compressive or tensile strain have unfolded the relationship between material microstructure such as defects and mechanical properties. The recent development of ultrafast imaging and diffraction has made time-resolved four-dimensional (4D) measurement of materials a reality. In their article in this issue of *MRS Bulletin*, LaGrange et al. offer an overview of state-of-the-art dynamic transmission electron microscopy, in particular the principle and instrumentation of the single-short movie mode that has set a benchmark for practical ultrafast electron microscopy for ultrafast science and applications.

The imaging of changes in the atomic or electronic structure of materials, including size and shape evolution during chemical reactions, requires that perturbations from the electron beam be limited. Low-dose and sometimes low-kilovolt imaging are preferred, and highly efficient data acquisition is necessary.

Here, we provide an overview of recent advances in the *in situ* TEM study of dynamic processes in materials. We discuss opportunities for the future development of *in situ* TEM. This article also highlights the topics of the six articles featured in this issue of *MRS Bulletin*, where liquid and gas environmental TEM, dynamic 4D TEM, nanomechanics, and ferroelectric domain switching studied by *in situ* TEM are reported. Also in this issue, Sun et al. discuss state-of-the-art atomic imaging of light elements (i.e., carbon atoms) and single defects. *In situ* electron microscopy was featured in a recent workshop.[17] The intent of this issue is to boost *in situ* TEM research globally and advance the forefront of *in situ* characterization of materials.

Advances in the imaging of dynamic materials processes

Gas-ETEM study of catalysis

Heterogeneous nanoparticle catalysts that catalyze reduction or oxidation reactions at the solid–gas interface are of paramount importance in a wide range of chemical and energy applications. Heterogeneous catalysis is a complex process that involves a number of critical steps, including diffusion, reactant adsorption, surface reaction, and product desorption. The interaction of the active catalyst with reactant gases varies with temperature, gas pressure, and surface structure of the catalyst. Transformation and restructuring of a catalytic particle often occur under reaction conditions.[18,19] Understanding and elucidating the mechanism of catalysis requires knowledge of the structural and chemical evolution of the nanoparticle catalysts during the reaction. Because such information is difficult to access through *ex situ* characterization in a vacuum, *in situ* characterization that enables the probing of dynamic catalytic processes under real reaction conditions is necessary.

In situ ETEM studies of gas–solid reactions under controlled reaction conditions can provide great opportunities for the characterization of heterogeneous catalysts. A local gaseous environment can be created by a number of approaches, including the use of a closed-gas TEM cell and gas injection into an open sample area with differential pumping in the TEM column.[20–22] There have been many studies on the use of ETEM to visualize nanoparticle catalysts with atomic resolution during gas reactions. Local structural and chemical information about a catalyst particle can also be obtained through a combination of imaging, diffraction, and spectroscopy.[23,24] Key insights have been acquired on catalytic active sites, defect structural evolution, the nature of bonding in redox reactions, and the correlation between microstructure and catalytic performance.[6,25–28]

Some examples of the ETEM study of nanoparticle catalysts are as follows: Formation of a subsurface oxide on a metal catalyst was identified during the catalytic oxidation of carbon monoxide due to the incorporation of oxygen into the metal at elevated temperatures.[29] Copper nanoparticle catalysts were found to exhibit remarkable restructuring in various gaseous environments, including reversible surface faceting, which was a result of preferential adsorption of reactant molecules on different crystalline facets.[25] Another recent study of an Au/CeO_2 catalyst by aberration-corrected ETEM visualized the restructuring of {100} facets of gold nanoparticles during CO oxidation at room temperature.[6] The CO molecules adsorbed onto the on-top sites of gold atoms in the undulating hexagonal lattice, and the restructured {100} facets could sustain CO adsorption at higher surface coverages (**Figure 1**).

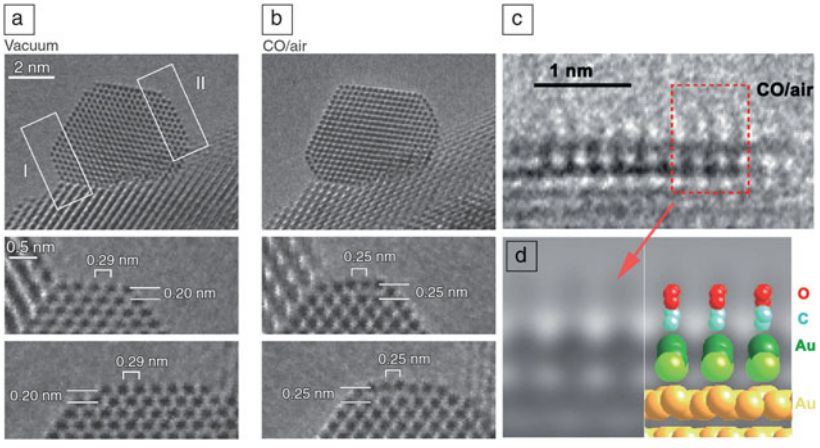

Figure 1. *In situ* environmental transmission electron microscope study of catalytic Au nanoparticles (NPs) supported on CeO_2. Au NP on CeO_2 (a) in ultrahigh vacuum (UHV) and (b) in a gas environment that contained 1 vol% CO in air at 45 Pa at room temperature. Higher magnification images of these regions are shown at the bottom of the corresponding panels. The difference between (a) and (b) shows that the interlayer distance of Au NPs in 1 Torr (~133 Pa ~1.3 mbar) CO increases in contrast to that in UHV. (c) High-magnification image of Au NPs with adsorbed CO. (d) Simulated image based on an energetically favorable model, which corresponds to the selected region in (c).[6] Adapted from Reference 6. © 2012 American Association for the Advancement of Science.

More recently, ETEM studies of nanoporous catalysts were performed to understand the dependence of catalytic activity on pore size and residual elements.[26,30] *In situ* ETEM observations of dealloyed nanoporous gold provided compelling evidence that surface defects are active sites for the catalytic oxidation of CO, and residual silver stabilizes the atomic steps by suppressing {111} faceting kinetics.[26] Another study on a nanoporous cobalt catalyst was performed in the presence of hydrogen at various temperatures using atomic imaging and EELS. The results revealed that during H_2 reduction, the valence state of CoO_x nanoporous particles changed from cobalt oxide to metallic cobalt.[30] In their article in this issue, Crozier and Hansen provide additional examples on *in situ* and *operando* TEM of catalytic materials.

Dynamic processes in liquids

Wang et al. describe liquid-cell TEM, a new experimental platform that allows imaging through liquids with subnanometer resolution. The development of liquid-cell TEM is largely due to technical advances in nanofabrication and membrane technology. Recently, graphene liquid cells have opened new opportunities to study liquid reactions *in situ* in the transmission electron microscope with improved resolution (**Figure 2**).[7]

Liquid-cell TEM has been applied to the study of nanoparticle growth mechanisms, and important insights have been achieved by direct observations of nanoparticle growth trajectories.[1,9,31–38] These studies illustrate that the growth of a nanowire involves attachment of nanoparticles grown from the solution, and recrystallization and rearrangement of nanoparticles are essential for nanoparticle coalescence.[1,36] The direct observation of Pt nanocube facet development revealed that growth by following the conventional surface-energy-minimization law breaks down at the nanoscale.[2] The application of liquid-cell TEM has become increasingly important for studying a wide range of other materials transformations in materials science, as well as in chemistry and biology.

The dynamics of nanobubbles[39] and water nanodroplets[40] were revealed using liquid-cell TEM. The properties of water at interfaces (see the December 2014 issue of *MRS Bulletin* on "Water at Functional Interfaces") play a crucial role in functional biological membranes, flow of liquids through pores and over surfaces, hydration of biomolecules, and chemical reactions in aqueous solutions. The ability to directly study water in contact with the substrate interface could provide insights into the dynamic properties of water. Liquid-cell TEM has also made it possible to directly image biomaterials in their native environment at ambient temperature.[12,40] Whole cells in liquids have also been captured at nanometer resolution with the assistance of Au nanoparticle labels.[8,41] These studies provide the basis for future nanometer-scale dynamic imaging of biological materials in liquids using TEM with proper management of the electron dosage.

The study of liquid-cell TEM is rapidly expanding. The development of electrochemical liquid cells allows monitoring of electrochemical processes in liquid electrolytes in real time.[10] There have been many recent studies in this area, and this work is of great interest to electron microscopists as well as battery researchers.

Solid-state batteries

A solid electrolyte might be the ultimate solution for safe batteries. Brazier et al. reported the first cross-sectional *ex situ* TEM observations of an all solid-state lithium ion "nanobattery,"[42] where they used a focused ion beam to make

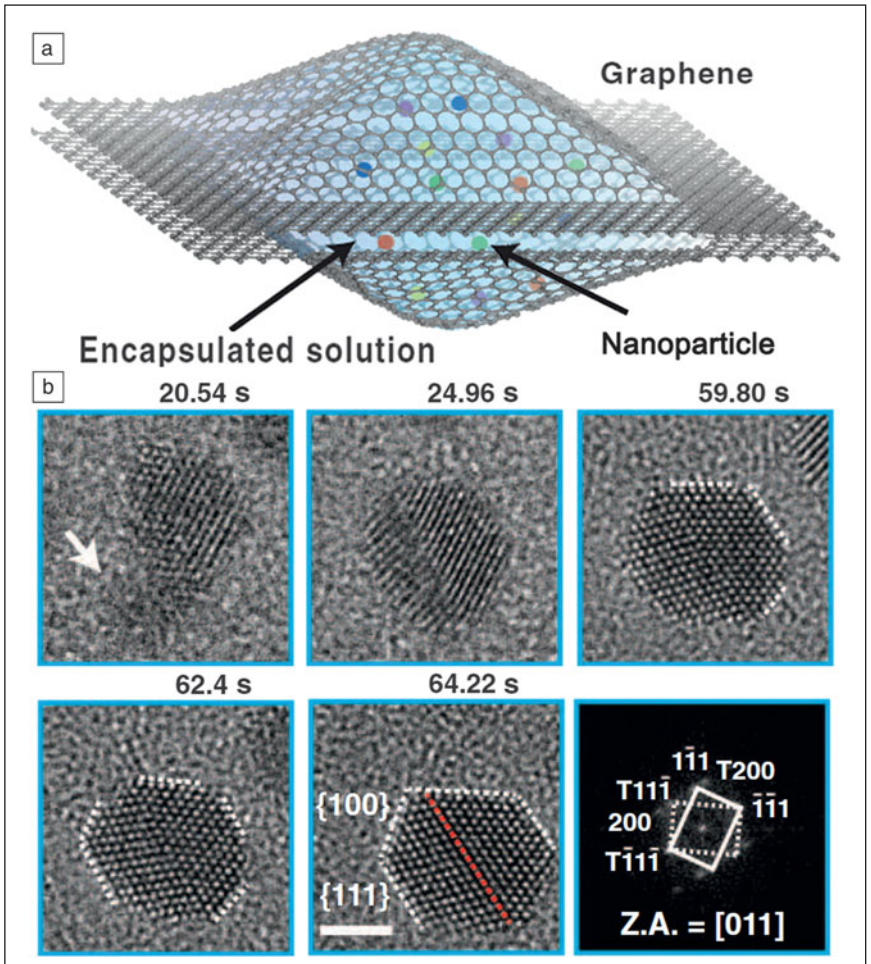

Figure 2. (a) Graphene liquid cell and *in situ* high-resolution transmission electron microscope imaging of Pt nanoparticle growth.[7] (b) The arrow indicates a small cluster attaching to the existing nanoparticle. A twinned Pt nanoparticle is achieved with a (111) mirror plane, as shown in the fast Fourier transform pattern at the bottom right. Scale bar in the image sequence is 2 nm. Note: Z.A., zone axis. Adapted from Reference 7. © 2012 American Association for the Advancement of Science.

a nanobattery from a pulsed-laser-deposited solid-state battery. For probing electrodes and electrolyte materials and their interfaces, *ex situ* experiments often provide only limited insights because of the sample preparation and transfer needed, which prevents the determination of the time constants of electrochemically induced phase transformations. More importantly, electrochemical systems often operate at states far from equilibrium, where a system tends to relax to its equilibrium state with time.

To probe the kinetics in an electrochemical system, progress has been made with *in situ* techniques that are able to probe the structural, morphological, and chemical changes that take place during electrochemical processes at the nanoscale, particularly at the interfaces between an electrode and electrolyte. Yamamoto et al. reported on the *in situ* dynamic visualization of the electric potential in an all solid-state battery with electron holography and EELS.[43] Interestingly, Ruzmetov et al. found that a substantial reduction in the electrolyte thickness, into the nanometer regime, can lead to rapid self-discharge of the battery even when the electrolyte layer is conformal and pinhole-free.[44] A procedure for fabricating electrochemically active, electron-transparent solid-state batteries using a focused ion beam were developed, and compositional and structural changes have been observed at the interfaces between the $LiCoO_2$ cathode and LiPON electrolyte as well as at the interfaces between the Si anode and Cu current collector, as shown in **Figure 3**.[45] *In situ* TEM with EELS is becoming one of the most important tools for studying solid–solid interfaces in a variety of solid-state devices, including batteries, solar cells, and solid-oxide fuel cells.

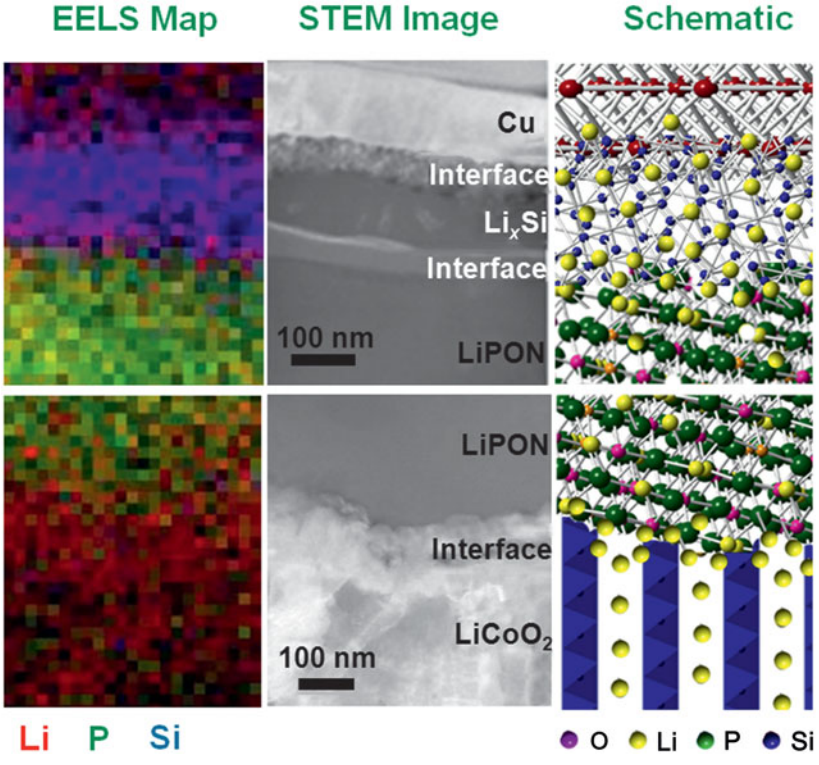

Figure 3. Electron energy-loss spectroscopy (EELS) mapping and scanning transmission electron microscopy (STEM) images of a solid-state Si/LiPON/$LiCoO_2$ rechargeable battery. Reprinted with permission from Reference 45. © 2013 American Chemical Society.

Ferroelectric and ferromagnetic switching and behavior

The need to continuously decrease the size of magnetic-bit elements in magnetic-storage media, such as magnetoresistive random access memory, is perhaps the strongest driving force underlying studies of magnetic nanostructures. A similar trend occurred for ferroelectric nanostructures. Intriguing structures and properties emerge as the size of the structure contracts. Switchable spontaneous polarization, domain engineering, and strain control of ferroelectrics were recently targeted for energy-efficient nonvolatile memories and ferroelectric field-effect transistors. Nevertheless, these efforts were hindered by a lack of experimental methods, especially ones to characterize domain-defect interactions and their dynamics, as well as to directly link local atomic displacement to polarization.[5,13,46–49]

Lorentz microscopy has been widely used to study skyrmions (a hypothetical particle related originally to baryons; skyrmions as topological objects are important in solid-state physics), including magnetic switching and domain configuration evolution. The dynamic process of generation and annihilation of magnetic biskyrmions was observed by *in situ* TEM.[48] As an alternative approach, a dedicated magnetizing stage can be used to generate a magnetic field at the specimen area. For example, a magnetizing stage can be built by adding Helmholtz coils on each side of the specimen,[50,51] which can be used to study the field-induced motion of magnetic domain walls. Another possible design is to bring a piezo-driven sharp needle made of a permanent magnet close to the specimen.[52,53] Furthermore, to obtain the relationship between magnetic structure and temperature, a thermal element also needs to integrate with the holder.

A new design capable of applying gigahertz resonance electric current and pulsed excitations *in situ* was developed, as shown in **Figure 4**, to measure the nonadiabatic spin torque effect[16] and to map strongly coupled coaxial vortex motion in the dipolar- and indirect exchange-coupled regimes.[54] In this issue, Li et al. present details on *in situ* measurements of ferroelectric domain switching using *in situ* biasing, atomic imaging, and displacement mapping. Other methods for probing ferroelectric switching, including off-axis electron holography, are described in References 3 and 14.

Mechanical properties

Many fundamental assumptions of classical mechanics and continuum mechanics fail as the

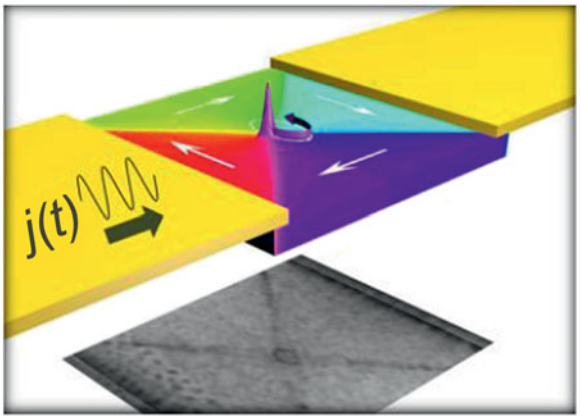

Figure 4. Visualizing vortex dynamics in a nanomagnet. Top: The spin precession measurement scheme. Yellow indicates two electrodes allowing GHz electric current ($j(t)$, where t is time) to sweep across the Landau domain structure with a clockwise chirality (in-plane magnetization) and a counter-clockwise vortex-core polarity (out-of-plane magnetization). Bottom: Lorentz micrograph of the permalloy square with the Landau state showing the vortex core orbit under resonance excitation in a transmission electron microscope. The vortex core size is approximately 20 nm.[16]

system size is reduced to the nanoscale. Thus, mechanical testing in the transmission electron microscope has emerged. The development of a dedicated mechanical TEM holder enables the *in situ* investigation of mechanical behaviors and properties at the nanoscale and even the atomic scale. Throughout recent decades, the mechanical behavior of sub-10-nm structures has been studied inside the transmission electron microscope. Several novel mechanical phenomena have been reported, such as irradiation-induced high pressure and phase transformation,[55] nanoextruder effects,[56] geometry interlocking effects,[57] cold welding,[58] partial dislocation-induced discrete plastic deformation,[59] local kinks in two-dimensional nanomaterials,[60] mechanical annealing,[61,62] stress saturation and deformation mechanism transition,[63] and liquid-like pseudoelasticity.[64] In this issue, Minor et al. highlight recent advances in *in situ* TEM probing mechanical properties at the nanoscale (see **Figure 5**).

Opportunities and challenges

Despite the many achievements in understanding structure and properties from monitoring dynamic materials processes *in situ*, challenges remain in the real-time characterization of structure, chemistry, bonding, photonic response, and electric and magnetic properties, even in a partially simultaneous manner, at the atomic level. Future revolutionary advances in electron microscopy are needed.[17] Cutting-edge technical development of *in situ* TEM involves improving time resolution, achieving liquid or gas environments, and measuring properties with multiple probes. The stringent processing requirements necessitated by nanotechnology have stimulated advances in all aspects of TEM instrumentation, including application of external stimuli, high-resolution spatial and temporal imaging, and rapid data acquisition.

The discovery of new materials, novel functionality, and chemical processes depends critically on routine access to all phases of matter and the ability to capture the dynamic processes that occur at interfaces with high spatial resolution and high temporal resolution. Ultrafast electron diffraction, imaging, and spectroscopy offer unique opportunities for understanding structural dynamics and the behavior of matter under conditions far from equilibrium. The current status and future opportunities of ultrafast electron microscopy are available in a recent report.[17]

The evolution of interfaces in chemical environments, transient nucleation events, and atomic growth during chemical reactions remain great challenges for *in situ* characterization. Significant advances have been made in the imaging of individual impurity atoms inside crystalline materials using atomic-number-(Z-) sensitive high-angle annular dark-field imaging and EELS in scanning TEM, including in three dimensions.[4,65] However, these studies are typically carried out on relatively simple structures. In the real world, defects form complex and nonuniform three-dimensional structures. Atomic-scale defects determine the optical and electronic properties of semiconducting and photonic materials, as well as

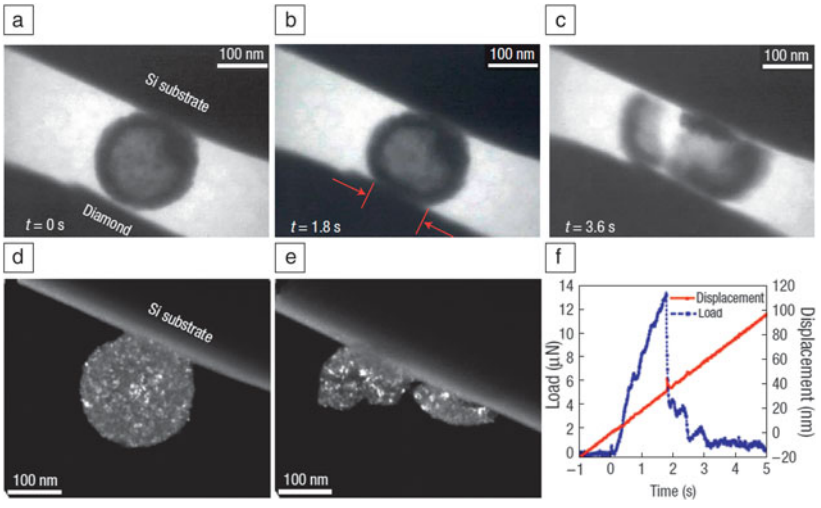

Figure 5. Example of a typical compression-to-failure *in situ* compression test on an individual nanocrystalline hollow CdS sphere. (a–c) Extracted video frames of the *in situ* compression test, corresponding to time t = (a) 0 s, (b) 1.8 s, and (c) 3.6 s. The estimated contact diameter is shown in red in (b). (d–e) Dark-field transmission electron microscope images of the hollow nanocrystalline CdS ball resting on the Si substrate (d) before and (e) after the compression test. (f) Load and displacement data from the loading portion of the *in situ* test versus time. The experiment was run under displacement control. Reproduced with permission from Reference 15. © 2008 Nature Publishing Group.

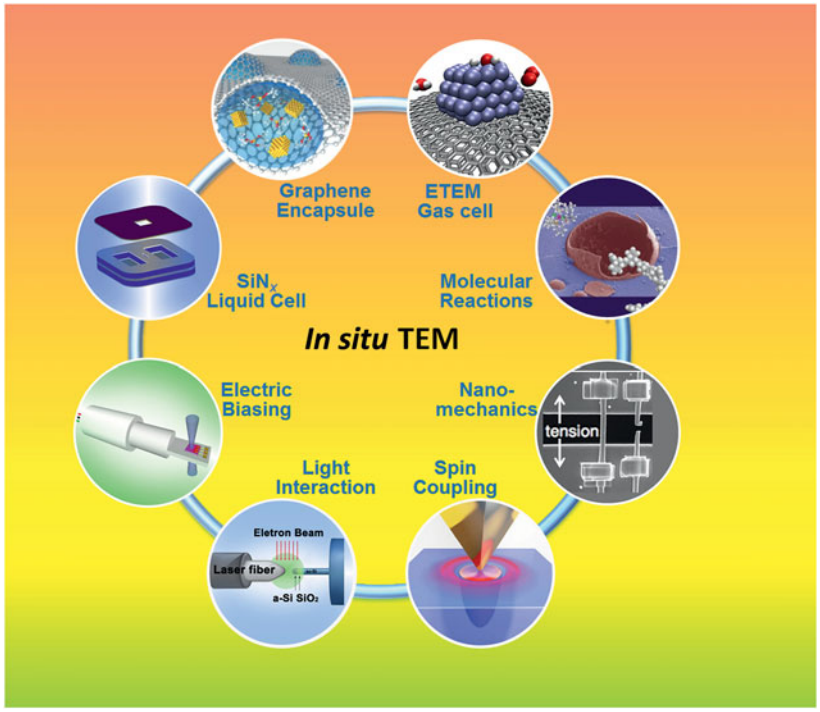

Figure 6. Future *in situ* electron microscopy allowing multimodal probing of material functionalities. (Figure created by Hong-Gang Liao and Haimei Zheng.) Note: TEM, transmission electron microscopy; ETEM, environmental transmission electron microscopy; a-Si, amorphous Si.

mass transport in materials, such as lithium-ion batteries and fuel cells. For example, the location of individual dopant atoms controls the performance of current generations of silicon transistors and spintronic devices.[66,67] Determining the local structure, displacements, or atomic reconstructions around defects often involves a measurement accuracy of better than 1 pm, which is beyond current capabilities.[17]

Future developments in *in situ* and *operando* electron microscopy require the capability for quantitative measurements of materials structure, composition, and bonding evolution in technologically relevant environments, including liquids, gases, and plasmas, thereby assuring the understanding of the structure–function relationship at the atomic scale with high temporal resolution (i.e., in the nanosecond range). As shown in **Figure 6**, the ultimate *in situ* transmission electron microscope would allow multimodal (i.e., optical, thermal, mechanical, electrical, and electrochemical) probing of material functionality with versatile, modular sample stage and holder geometries.

In situ imaging with fast recording speeds generates large and rich data sets, which impose demands for data mining and machine learning approaches to develop new, adaptive signals from the data instead of from *a priori* physical models and intuition. New hardware and software development is also needed to allow real-time processing for rapid feedback during experiments, and new tools are necessary to synthesize various image signals post-acquisition.

Concluding remarks

In situ probing of matter with electron beams will experience revolutionary growth in the near future with the ability to precisely control the temperature, environment (solid, liquid, or gas), and stimuli (e.g., electromagnetic field, tunable light, and mechanical stress) of materials under realistic conditions. Fast imaging and spectroscopy with highly sensitive detection could become routine. *In situ* electron microscopy is anticipated to continue to impact a broad range of sciences, allowing for a greater understanding of materials function and dynamics and a deeper examination of how real-world conditions and stimuli interact with and affect structures, properties, and processes at subnanometer scales.

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