

***In Situ and Operando* Transmission Electron  
Microscopy of Catalytic Materials**

Peter A. Crozier\*

School of Engineering of Matter, Transport and Energy, Arizona State University,  
Tempe, AZ, USA 85287-6106, crozier@asu.edu

Thomas W. Hansen

Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kgs.  
Lyngby, Denmark

**Abstract**

Catalytic nanomaterials play a major role in chemical conversions and energy transformations. Understanding how the materials control and regulate surface reactions is a major objective for fundamental research on heterogeneous catalysts. *In situ* environmental transmission electron microscopy (ETEM) is a powerful technique for revealing the atomic structure of materials at elevated temperatures in the presence of reactive gases. This approach can allow the structure-reactivity relations underlying catalyst functionality to be investigated and explored. ETTEM has been limited by the absence of *in situ* measurement of gas-phase catalytic products. To overcome this deficiency, *operando* TEM techniques are being developed that combine the atomic characterization with the simultaneous measurement of the catalytic products. This article will provide a short review of the current status and major developments on the application of ETTEM to gas phase catalysis over the last 10 years.

**Keywords:** transmission electron microscopy (TEM); catalysis; nanoscale; *in situ*; *operando*

## Introduction

Heterogeneous catalysis is a key process for converting reactants into products and plays a critical role in chemical and energy transformations(1, 2). An industrial heterogeneous catalyst typically consists of nanostructured particles of variable shape and composition. The surfaces of catalytic particles interact with gas or liquid phase reactants and promote product generation. Reactions typically take place at temperatures up to 1000°C. While the catalytic materials convert gas or liquid phase reactants into products, the ambient gas or liquid environment also change the surface and even the bulk form of the nanoparticles. During catalysis, the structure of the catalyst may vary in a complex way with changes in the pressure of reactants and products as well as temperature. To build a structure-reactivity-performance correlation and achieve a fundamental understanding of catalytic mechanisms, the electronic and geometric structure of the catalyst must be determined at the atomic level. Environmental transmission electron microscopy (ETEM) is at present the only high spatial resolution technique available to perform *in situ* characterization of a high surface area catalyst. In this approach, reactants are allowed to flow over the TEM sample (often during *in situ* heating) and the changes in the nanocatalysts are recorded using TEM imaging, diffraction or spectroscopy techniques.

Catalysts are dynamic entities that change not only during each reaction cycle, but also on a longer time scale via phase transformations, surface restructuring and particle growth. This is illustrated in Figure 1 which shows a

supported Ru catalyst for ammonia synthesis. In vacuum each Ru particle is encapsulated in a shell of BN but under a reactive environment, this shell is no longer present (3).

To build a direct correlation between catalyst structure and catalytic performance, structural information at the atomic or nanoscale level obtained under reaction conditions is critical. Environmental electron microscopy in both broad beam (transmission electron microscopy (TEM)) and focused beam mode (scanning transmission electron microscopy (STEM)) has played a key role in elucidating the structures of the sub-surface and bulk of high surface-area heterogeneous catalysts(4, 5). Atomic resolution imaging, spectroscopy, and diffraction have proven to be a powerful combination for understanding the local structure of catalytic materials.

The value of the ETEM approach for characterizing high surface-area materials was recognized by early workers in the field. Baker was the first to extensively apply the technique to heterogeneous catalysts in a series of early works(6, 7). In the current article, it is not possible to provide a comprehensive review of the field so we limit ourselves to select examples drawn mostly from the last 10 years focusing on gas-phase reactions/products only. For reviews of earlier work, the readers are referred to the following sources(4, 8-10).

### **Atomic Resolution Environmental *In Situ* Microscopy**

A critical technical requirement for all gas systems compatible with TEM is that they maintain both a high gas pressure around a sample and a high vacuum throughout most of the column and the electron source. There are two common approaches that are currently employed to satisfy this requirement:

a) Window method - gas or liquid is confined around the sample region by using thin electron transparent windows, e.g. SiN or graphene films.

b) Differential pumping – a pressure difference is maintained by installing small apertures above and below the sample area and using additional pumping.

In the window method, thin electron transparent membranes are employed to separate the high pressure atmosphere around the sample from the high vacuum in the rest of the microscope. This is usually accomplished via a sample holder which incorporates windows along with a gas inlet and outlet system and atomic resolution has been demonstrated(11, 12). Recent application of MEMS (micro electro-mechanical systems) technology has resulted in the development of structures where the area of the thin window is rather small permitting higher pressure to be maintained (Figure 2). The group at the Technical University of Delft first demonstrated atomic resolution of 0.18 nm at pressures above 1 atmosphere and temperatures up to 500°C(13). Recent results show that controlled atmosphere experiments with windowed cells can be performed at pressures up to 4 atmospheres and elevated temperatures(14, 15). The issue of temperature measurement when gas of variable pressure and composition is introduced is an

ongoing challenge in the MEMS based windowed cells. Approaches are being developed which exploit changes in membrane conductivity and changes in the gas density to address this issue(16).

The second approach to creating a reactive gas atmosphere is to employ a differentially pumped system, historical reviews can be found elsewhere(10, 17). Modern differential pumping systems are designed following the basic principles outlined by Swann and Tighe(18). In this type of cell, the large pressure difference between the sample area and the microscope column is maintained by inserting a series of differential pumping apertures and adding additional pumping capacity. Atomic resolution was first achieved by the Oxford group on a modified JEOL 4000(19) and the approach was continuously developed throughout the 1990s often involving substantial modification of the objective lens polepieces as pioneered by Boyes and Gai(20-22). Differential pumping systems compatible with field emission electron sources were demonstrated(23) and modern systems are currently available with aberration correction (24, 25).

A schematic diagram of a differentially pumped system is shown in Figure 2b. The microscope column (an FEI Titan) has been modified to add three sets of differential pumping apertures for three pumping stages between the gun valve and viewing chamber. The first two sets of apertures are placed within the upper and lower objective lens pole pieces and most of the gas leaking through this first set of apertures is pumped out using a turbo-molecular pump. The second stage is between the condenser aperture and selected area aperture and is pumped using a

second turbo molecular pump. An additional ion pump is employed for the last stage before the gun valve.

## **Atomic Scale Structural Changes during Gas Exposure**

### ***Catalyst Preparation***

Catalyst preparation often involves oxidation and reduction treatments of metal precursors to generate dispersions of metallic nanoparticles on high surface area supports like Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> or TiO<sub>2</sub>. ETEM has also been employed to follow the evolution of metal supported catalysts during calcination and reduction. One advantage of the ETEM approach is that it allows the spatial distributions of the metal precursor, the intermediate oxide and the final metal to be correlated from the same region of the catalytic material. Li *et al.* followed the evolution of a variety of metallic systems (Ni, NiCu, Co, and CoRu) prepared using impregnation techniques and high surface area supports(26). The ability to perform *in situ* high spatial resolution electron energy-loss spectroscopy (EELS) in STEM mode is very beneficial in the study of bimetallic systems where compositional heterogeneity may not be apparent from the TEM or STEM images. Compositionally distinct domains in a 5 nm NiCu particle were observed in H<sub>2</sub> at 300°C demonstrating the promotional effect of Cu in reducing NiO to Ni metal in bimetallic particles(26). Banerjee also undertook an investigation of the preparation of model Ni catalysts supported on SiO<sub>2</sub> spheres during both the calcination and reduction steps(27). The simple geometry of this support made it easier to see metal diffusion during reduction and it demonstrated that, for this

system, finer metal dispersions were obtained by eliminating the calcination step and performing a direct reduction in H<sub>2</sub>.

Dehghan *et al.* investigated the reducibility of cobalt oxide on 12wt.% Co/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with and without 0.5wt% Re promoter(28). They were able to show with imaging and electron energy-loss spectroscopy (EELS) that in 2.5 Torr of H<sub>2</sub>, the initial Co<sub>3</sub>O<sub>4</sub> started to transform to CoO at 180°C and that Co metal started to appear at 260°C with complete reduction at 360°C. A similar result was also found for a CoO<sub>x</sub>/SiO<sub>2</sub> composite system and also showed nucleation and growth of metal particle during reduction(29).

Catalyst activation may be thought of as a process taking place inside a reactor which leads to the formation of the catalytically active species with the desired activity and selectivity. For example, the as-prepared anode on a solid oxide fuel cell is often composed of a composite consisting of NiO and yttria stabilized zirconia (YSZ). The fuel cell anode must be activated by reducing the NiO to Ni metal which then acts as both a current collector and a catalyst. ETEM has been employed to follow the evolution of the anode under both reducing and oxidizing conditions(30). Figure 3 shows the evolution of the anode during a reduction and oxidation cycle. The initially dense NiO grains convert to a porous Ni metal structure during reduction (due to the volume shrinkage associated with the oxide to metal phase transformation). Interestingly, during re-oxidation, NiO oxide forms void-like structures leading to an overall expansion in the NiO phase compared to the original NiO resulting in strain in the adjacent YSZ grains as seen in Figure 5 and eventually leads to anode failure.

### ***Structural Evolution Under Reaction Conditions***

This broad category focuses on performing *in situ* imaging, spectroscopy and diffraction on metal and oxide catalysts under near-reaction conditions. Some of the examples below illustrate how the catalytic structure can change upon exposure to reactive gases and how structure may be correlated with reactivity.

#### ***Gold for CO Oxidation***

Au nanoparticles have received considerable attention due to their high activity for CO oxidation(31). Giorgio and co-workers have conducted several studies on the shape of Au nanoparticles on MgO, TiO<sub>2</sub> and carbon supports in 1.5 Torr of O<sub>2</sub>, H<sub>2</sub> and CO + O<sub>2</sub> at room temperature(11, 32). Exposure to H<sub>2</sub> resulted in the particles assuming truncated octahedron shapes bounded by (111) and (100) facets whereas exposure to O<sub>2</sub> resulted in the particles assuming a more rounded shape. This was interpreted to indicate that O<sub>2</sub> chemisorbs at edges and defect sites. They repeated these experiments for CO oxidation and also found that the Au particles were predominantly round when CO<sub>2</sub> was produced.

Takeda's group has investigated the structure of Au particles on CeO<sub>2</sub> at room temperature in the presence of CO and O<sub>2</sub>(33). They also find truncated octahedrons forming when CO is present and more rounded shapes forming in the presence of only oxygen (or air). Interestingly, even very low concentrations of CO mixed with oxygen stabilize the (111) and (100) facets on Au presumably because of the much larger chemisorption energy of CO compared to O<sub>2</sub>. Under CO oxidation conditions, predominantly faceted particles with slightly rounded corners were observed. The same group recently repeated some of this work using

aberration corrected ETEM in 1% vol CO in air (0.34 Torr) at room temperature(34). They find that there is an outward relaxation of about 0.5 Å of the top (100) layer in the presence of CO (see Figure 4). By operating the ETEM at 80kV, the sensitivity to light atoms is increased. In this way, contrast on the surface of the Au nanoparticles was observed which appeared to be consistent with direct imaging of CO adsorbates. This may open up the exciting possibility of directly imaging gas adsorbates on the surfaces of nanoparticles.

### ***Structure-Reactivity Relations from ETEM***

Phase changes in the Ni catalysts have also been correlated directly with catalytic activity for hydrocarbon reforming. Chenna and co-workers(35, 36) used ETEM to determine the phase changes taking place on Ni/SiO<sub>2</sub> catalysts during temperature ramp-up and correlated these structural changes with changes in activity and selectivity determined with *ex situ* reactor studies. During ramp-up in 1 Torr of 2CH<sub>4</sub> + O<sub>2</sub>, at 400°C, the initial metallic Ni particles convert to NiO particles showing Kirkendall voids (see Figure 5). The NiO catalyzes complete oxidation of CH<sub>4</sub> resulting in the production of CO<sub>2</sub> and H<sub>2</sub>O. As the temperature continues to rise, all the oxygen in the reactor is converted and the atmosphere becomes reducing resulting in the NiO reducing back to Ni metal at about 700°C. At this point, reforming begins and the products change from CO<sub>2</sub> and H<sub>2</sub>O to CO and H<sub>2</sub>. The major changes in catalyst selectivity that appear at 400°C and 700°C correlate very precisely with structural transformations determined by ETEM. The structure-reactivity relation derived from ETEM is shown schematically Figure 5.

## Oxides

Reducible oxides undergo changes in reactive atmospheres often associated with Mars-van Krevelen type mechanisms in which oxygen for a reaction with an adsorbate comes directly from the oxide lattice. Consequently, there has been interest in exploring the changes that take place in oxides under redox conditions. While catalysis takes place on the surface, the introduction or elimination of oxygen vacancies on the surface may be influenced by processes taking place in the bulk. Ceria is an interesting oxide in which Ce can exist in the +3 or +4 oxidation state. In a reducing atmosphere, oxygen vacancies produced at the surface may diffuse to subsurface sites resulting in reversible phase transformations in the entire ceria nanoparticle. The ease with which the entire particle can reduce and re-oxidize is important in automotive catalysts and intermediate temperature fuel cells(37, 38). *In situ* electron energy-loss spectroscopy in the ETEM has been employed to determine the local oxidation state of the cerium and thus the degree to which oxygen vacancies are present in the cerium-based oxides. This approach has also been employed to investigate surface restructuring and reversible oxygen vacancy ordering under reducing conditions(39, 40). Figure 6 shows a redox cycle for a CeO<sub>2</sub> crystal where the temperature is cycled in about 1 Torr of H<sub>2</sub>. At 693°C the Ce M<sub>45</sub> white lines in the energy-loss spectrum reverse showing an abrupt change in the oxidation state of Ce. Simultaneously, superlattice fringes appear in the atomic resolution image and superlattice spots in the electron diffraction pattern caused by ordering of oxygen vacancies. The reaction is completely reversible and the structure

vanishes upon cooling to 600°C as the ceria re-oxidizes. The phase transformation is associated with a doubling of the lattice parameter and the formation of a body centered cubic structure.

The ease with which this redox process takes place can be influenced by doping and also metal nanoparticles can be employed to enhance the reduction kinetics via a hydrogen-spillover effect(41). Using ETEM Sharma *et al.* found a preferential reduction of ceria in the vicinity of Ni particles at temperatures much lower than the reduction temperature observed for the pure oxide.

### ***Photocatalysts***

Photocatalysis, where light irradiation provides most of the energy for a reaction, has great potential for solar fuels(42). In order to understand structure-reactivity relations at the atomic level it is necessary to introduce light as a stimulus in the ETEM. ETEM compatible light illumination have been developed and interested readers should see the references(43-45).

### ***Catalyst Sintering***

De-activation due to sintering is important for many supported metal catalysts that operate at high temperature and there is considerable interest in trying to understand the fundamental atomic level processes (see for example(46) and references therein). There is considerable discussion about the sintering mechanism in the catalysis community because particle sintering can occur either through Ostwald ripening or particle migration and coalescence. However, significant progress has been made with *in situ* observations of catalysts sintering.

Liu *et al.* investigated the sintering of Pd on an industrial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support in 500mTorr of H<sub>2</sub>O at 700°C over a period of 8 hours(47). The mean particles size increased from 7 nm to 10 nm and image sequences showed that small particles shrunk and larger particles grew demonstrating that Ostwald ripening was the dominant mechanism in this case. Similar experiments were carried out by Hansen *et al.* on a steam reforming catalyst consisting of Ni particles on a MgAl<sub>2</sub>O<sub>4</sub> support(48, 49). The sample was reduced *in situ* in flowing H<sub>2</sub> at 500°C and after reduction, the samples were exposed to either pure H<sub>2</sub> or a mixture of H<sub>2</sub> and H<sub>2</sub>O at higher temperatures. Samples exposed to H<sub>2</sub>O containing environments sintered considerable more than those exposed to pure H<sub>2</sub>. Challa *et al.* investigated the sintering of Ni/MgAl<sub>2</sub>O<sub>4</sub> methane steam reforming catalyst in a mixture of H<sub>2</sub> and H<sub>2</sub>O at 750°C at few Torr pressure and found that sintering proceeded mostly via Ostwald ripening(49, 50). They analyzed the evolution of the system to extract energetic parameters for a mean-field ripening model and were able to predict ripening behavior over a short time period.

Simonsen and co-workers have conducted a series of sintering experiments on Pt particles supported on amorphous Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> films(51). These systems are considerably simpler than industrial supports and can be used to determine fundamental mechanisms and parameters associated with sintering models. For Pt on Al<sub>2</sub>O<sub>3</sub>, experiments conducted in 10 mbar of air at a temperature of 650°C showed clear evidence for coarsening taking place via Ostwald ripening over a 7 hour period. Simonsen *et al.* used a mean field theory to model the rate of change

of the distribution with time and found that this gave good agreement with experiment but there were local deviations in certain regions of the support.

Benavidez *et al.* investigated the sintering of Pt particles on a SiO<sub>2</sub> amorphous film under O<sub>2</sub> at 500°C and Pd on an amorphous carbon film heating in H<sub>2</sub> at 600°C(52). In both cases, sintering proceeded via Ostwald ripening and much of the distribution could be described by a mean field theory. Ostwald ripening was the sintering mechanism for Pt on amorphous planar SiO<sub>2</sub> annealed in air at 650°C and the data were well described with a mean field theory but with local variations in behavior(53). The authors developed a kinetic model that takes the local mass distribution into account using a Voronoi weighting scheme and were able to make a reasonable prediction of the particle size evolution starting from the initial particle configuration.

### ***Operando* Transmission Electron Microscopy**

The term *operando* originates from the field of Raman spectroscopy and is used when structure and catalysis were detected simultaneously(54). In a strict sense, term is applied when structure is determined simultaneously with reaction kinetics. For the current discussion of ETEM, we use the term *operando* or *near-operando* to mean application of ETEM to determine catalyst structure and composition while simultaneously quantitatively detecting the formation of catalytic products. Such an approach should allow structure-reactivity correlations to be determined without the need for *ex situ* reactor studies. Suitable spectroscopic methods must be developed to detect the product gas molecules and most ETEMs are equipped with residual gas analyzers. Giorgio *et al.* used such a

set up to confirm CO conversion to CO<sub>2</sub> over an Au catalyst in experiments performed in a windowed cell reactor in a TEM(32). They were able to correlate the shape of the Au particles with an increase in the CO<sub>2</sub> signal although no quantitative conversion or activity data was presented. The approach was recently applied by Vendelbo *et al.* to investigate the oscillatory behavior of Pt nanoparticles catalyzing CO oxidation(55). In this work, the output from a nanoreactor was fed to a residual gas analyzer in order to identify the onset of oscillatory catalytic behavior. The authors were then able to correlate changes in CO<sub>2</sub> production with changes in particle shape. The result is shown in Figure 7 and is a remarkable demonstration of the power of ETEM to determine structure-reactivity correlations in catalysis.

In the larger cells associated with differentially pumped ETEMs, the detection of catalysis can be more challenging because the volume of the catalyst is small compared to the volume of the reactor. This problem can be addressed by fabricating pellets that can fit in the TEM hot stage and allow increases in catalysts loadings of 10-100 times over conventional TEM preparation so that catalytic products can easily be detected using residual gas analysis (RGA) (56). However, quantification of the mass spectrometry data from an RGA in the ETEM is challenging because the signal may have a non-linear dependence on gas concentration and calibrating across different pressures and compositions is challenging. To address this limitation, electron energy-loss spectroscopy (EELS) can be used to quantify the gas composition inside the reaction cell(57). This approach was employed to detect and quantify reaction products on a Ru based

catalyst performing CO oxidation inside the ETEM(58). CO<sub>2</sub> has a  $\pi^*$  peak that is 3 eV higher in energy than the  $\pi^*$  peak from CO making quantification straightforward. Figure 8a shows the change in the energy-loss spectra as a function of temperature when 1 Torr of (2CO + O<sub>2</sub>) is flowing through the ETEM reaction cell. At 150°C a second peak appears and grows as the catalyst activates and converts the CO to CO<sub>2</sub>. The spectra can be quantified to determine the CO conversion in the cell and the insert shows the CO conversion determined from ETEM EELS.

The quantitative determination of products present in the cell allows relative changes in reaction kinetics to be measured. This is illustrated in Figure 8b during a thermal cycle during CO oxidation over a Ru catalyst (59). The catalyst is initially in the form of RuO<sub>2</sub> and is heated progressively to 500°C and then cooled to room temperature in flowing CO and O<sub>2</sub>. At 300°C on ramp-up, the CO<sub>2</sub> mole fraction present is 0.04 whereas at the same temperature on ramp-down the CO<sub>2</sub> mole fraction is 0.3. Since the reactor geometry and catalyst loading remain constant, the change in CO conversion is a consequence of the catalyst activity increasing by a factor of 7.

This demonstrates that with the *operando* approach, changes in reaction kinetics can be measured. This provides a powerful technique for exploring how different *in situ* treatments such as reduction and oxidations can change the activity of a catalyst. *Operando* TEM will allow atomic level structure to be correlated with changes in relative reaction kinetics and will greatly enhance the determination of structure-reactivity relations.

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## Figure Captions

Figure 1. Boron nitride supported ruthenium particles (3). In vacuum a), the BN support creates shells encapsulating the metal particles. When exposed to a reactive environment of  $N_2$  and  $H_2$  at  $552^\circ C$  b), the shells are removed.

Figure 2. a) Schematic diagram of MEMs based windowed cell reactor (13). b) Schematic diagram of differentially pumped ETEM (24).

Figure 3. *In situ* reduction and re-oxidation of a Ni/YSZ fuel cell anode (30). a) initial structure composed of NiO/YSZ b) fully reduce anode showing porous Ni metal regions c) re-oxidized anode showing formation of porous NiO regions and bend contour in YSZ indicative of strain..

Figure 4. Gold nanoparticles supported on cerium oxide in vacuum A) and a mixture of CO and air B) (34). When exposed to the gas mixture, the top most Au layer on the  $\{100\}$  facets indicated by white rectangles, expands by 0.05nm.

Figure 5. In situ ETEM images and electron diffraction patterns of Ni/SiO<sub>2</sub> :a) In presence of 1 Torr of  $H_2$  at  $400^\circ C$ ; b) from the same region in presence of 1 Torr of mixture of  $CH_4$  and  $O_2$  in 2:1 ratio at  $400^\circ C$ . Insert shows schematic of structure-reactivity relation (35).

Figure 6. Dynamic changes in atomic level structure characterized by high resolution imaging (upper) and electron diffraction (middle) and oxidation state change determined from EELS (lower) at a) 245, b) 693 and c)  $600^\circ C$  in 0.5 Torr of  $H_2$  along the  $[21-1]$  zone axis from the same individual  $CeO_2$  nanoparticle during a redox cycle. After reduction (b), arrows in the high resolution image and extra spots along the (220) plane (40).

Figure 7. Atomic scale visualization of dynamic refacetting of a Pt nanoparticle during oscillatory CO oxidation (55). The particles show rounded (a,c,and e) or a more faceted shape (b,d) as the CO conversion oscillates.

Figure 8. a) The carbon K-edge from gas phase recorded as a function of temperature from the CO oxidation *operando* experiment with the glass fiber pellet (56).b) Plot showing results from a CO oxidation experiment in which the Ru-RuO<sub>2</sub> catalyst was heated from room temperature to  $460^\circ C$ , and then cooled back to  $100^\circ C$  in CO and  $O_2$ . Inset high resolution images were taken at different point in the heating and cooling cycle. The initially RuO<sub>2</sub> converts to hcp Ru metal at around  $500^\circ C$  giving a much more active form of the catalyst (59).

### Peter A. Crozier

Crozier obtained a BS and Ph.D. in physics from the University of Glasgow with specialization in electron microscopy. He was Director of the Industrial Associates Program at Arizona State University and worked with many petrochemical companies on characterization problems of industrial catalysts. He has 15 years of experience in developing and applying environmental transmission electron microscopy to problems in catalytic materials. In 2011 he was elected a Fellow of the Microscopy Society of America and is currently an Associate Professor in the School for Engineering of Matter, Transport and Energy at Arizona State University.



### Thomas W. Hansen

Hansen is a senior researcher at the Center for Electron Nanoscopy (Cen) at the Technical University of Denmark (DTU). He received his MSc degree from the University of Copenhagen in 2001 and his PhD degree from DTU in collaboration with Haldor Topsoe A/S in 2006. From 2005-2008 he was a post doc at the Fritz Haber Institute of the Max Planck Society and has since worked at DTU Cen. His current research interests include understanding the fundamentals of nanoparticles specifically for use in catalysis primarily using electron microscopy.

