**Purdue University**
## Purdue e-Pubs

Birck and NCN Publications

Birck Nanotechnology Center

3-2014

# Gas mixing system for imaging of nanomaterials under dynamic environments by environmental transmission electron microscopy

M. Cem Akatay
*Purdue University, Birck Nanotechnology Center*, mcakatay@purdue.edu

Yury Zvinevich
*Purdue University*, yuryzv@purdue.edu

Philipp Baumann
*University of Applied Sciences - Switzerland, Yeshiva University*

Fabio H. Ribeiro
*Purdue University, Birck Nanotechnology Center*, fabio@purdue.edu

Eric A. Stach
*Purdue University, Birck Nanotechnology Center*, eastach@purdue.edu

Follow this and additional works at: http://docs.lib.purdue.edu/nanopub

Part of the Nanoscience and Nanotechnology Commons

# Gas mixing system for imaging of nanomaterials under dynamic environments by environmental transmission electron microscopy

M. Cem Akatay, Yury Zvinevich, Philipp Baumann, Fabio H. Ribeiro, and Eric A. Stach

---

**Articles you may be interested in**

Defect microstructural evolution in ion irradiated metallic nanofoils: Kinetic Monte Carlo simulation versus cluster dynamics modeling and in situ transmission electron microscopy experiments
Appl. Phys. Lett. 101, 101905 (2012); 10.1063/1.4748980

Ultrananocrystalline diamond film deposition by direct-current plasma assisted chemical vapor deposition using hydrogen-rich precursor gas in the absence of the positive column
J. Appl. Phys. 109, 023303 (2011); 10.1063/1.3533764

In situ imaging of electromigration-induced nanogap formation by transmission electron microscopy
Appl. Phys. Lett. 91, 072107 (2007); 10.1063/1.2767149

In situ determination and imaging of physical properties of metastable and equilibrium precipitates using valence electron energy-loss spectroscopy and energy-filtering transmission electron microscopy
J. Appl. Phys. 101, 054308 (2007); 10.1063/1.2437576

Structural dynamics of gas-phase molybdenum nanoclusters: A transmission electron microscopy study
Appl. Phys. Lett. 86, 113113 (2005); 10.1063/1.1886261

---

# Gas mixing system for imaging of nanomaterials under dynamic environments by environmental transmission electron microscopy

M. Cem Akatay,[1] Yury Zvinevich,[2] Philipp Baumann,[3] Fabio H. Ribeiro,[2,a)] and Eric A. Stach[4,a)]

[1]*School of Materials Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA*
[2]*Forney Hall of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA*
[3]*Computer Sciences, University of Applied Sciences of Northeastern Switzerland, 4132 Muttenz, Switzerland and Department of Physics, Yeshiva University, New York, New York 10016, USA*
[4]*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA*

A gas mixing manifold system that is capable of delivering a stable pressure stream of a desired composition of gases into an environmental transmission electron microscope has been developed. The system is designed to provide a stable imaging environment upon changes of either the composition of the gas mixture or upon switching from one gas to another. The design of the system is described and the response of the pressure inside the microscope, the sample temperature, and sample drift in response to flow and composition changes of the system are reported. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867903]

## I. INTRODUCTION

Transmission electron microscopy (TEM) provides high spatial resolution morphological and chemical information about catalyst materials and thus plays an important role in understanding the nature of catalysis.[1–4] Nevertheless a conventional TEM operates under high vacuum and fails to reflect the true nature of materials under working conditions, as the state of material depends to the environment.[5] The development of differentially pumped environmental cells for transmission electron microscopes[6] and the use of heating holders[7] has allowed researchers to create a reactive environment within the microscope that broadly approaches the working conditions of catalysts, while maintaining the ability to perform high resolution imaging, diffraction, and spectroscopy.[8] However, many reactions involve the use of multiple gases where the composition of the gas mixture is dictated by the specifics of the reaction. Further, effective investigation of the dynamic behavior of materials necessitates the ability to vary the composition of individual gases in a mixture and also to switch from one specific environment to another with operational ease and imaging stability. This paper describes the gas manifold system developed in our group for environmental transmission electron microscopes (ETEMs) and delineates its performance.

Pressure variations inside the microscope affect the sample temperature strongly, leading to significant sample drift. This is particularly problematic: sample drifts can be rapid, and in excess of several $\mu$m. As a result it can be impossible to track a specific sample region following changes to the reactive gas stream. The performance of a gas manifold system thus depends on how well it can regulate the pressure inside the microscope, allowing maintenance of a constant pressure after changes are introduced to the gas composition. This

paper quantifies how the pressure inside the microscope, the sample temperature, and the sample drift respond to changes induced in the incoming gas composition.

## II. EXPERIMENTAL SETUP

The gas manifold system is designed as a cart for easy handling and transportation (Figure 1). The gas rack holds up to six cylinders (40 cubic feet each). The controller units – including the eight-channel mass flow and pressure programmer (MKS 647C) – are placed at the front of the cart. The unit is equipped with two CO sensors, one located inside the gas rack and the other one placed above the cart. The sensors actuate the alarm shut-off valve on the CO cylinder in the case of a CO leak. The schematic of the system is shown in Figure 2. There are seven mass flow controllers (MFC) connected to gas cylinders in the rack via 1/4 in. stainless steel tubes. The solenoid pressure control valve (MKS 148J) receives feedback from the Barathron transducer (MKS 626) and regulates the relief valve to release gas when it is in excess of the set point pressure which is set to a pressure slightly higher than the atmospheric pressure (currently 780 Torr) to avoid air flow into the system. A check valve is placed after the relief valve to further secure the system from the backflow of released gases or air. The servo-driven pressure control valve (MKS 245) receives feedback from the DualMag transducer (MKS 972B), and thereby regulates the gas flow into the microscope, providing a constant pressure flow. Since the volume of gas to enter the microscope is small compared to the volume of the lines, the gas is fed through a 1/16 in. diameter line directly to the entrance of the MKS 245 valve (Figure 3). This modification allows the composition of the gases to be changed in a reasonable time (about 5 min). The gas line leading to the microscope has an alarm shut-off valve which closes automatically when the pressure at the DualMag transducer exceeds the set-value. The system

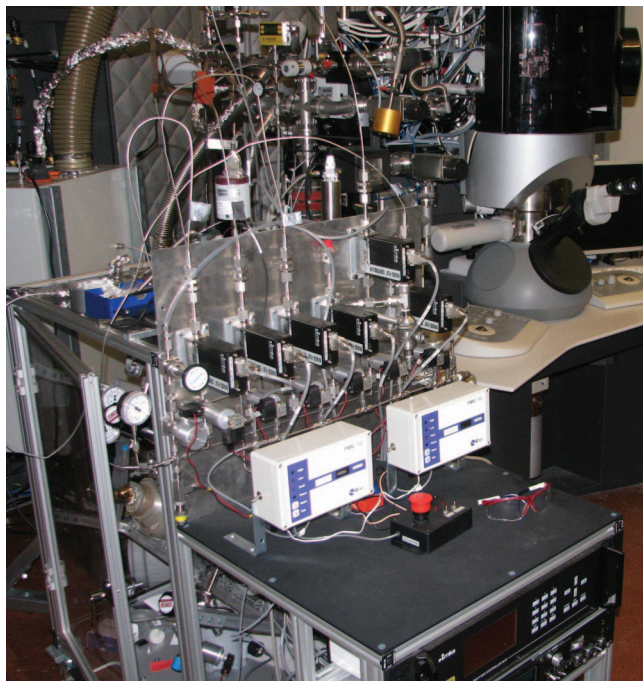a)Authors to whom correspondence should be addressed. Electronic addresses: fabio@purdue.edu and estach@bnl.gov
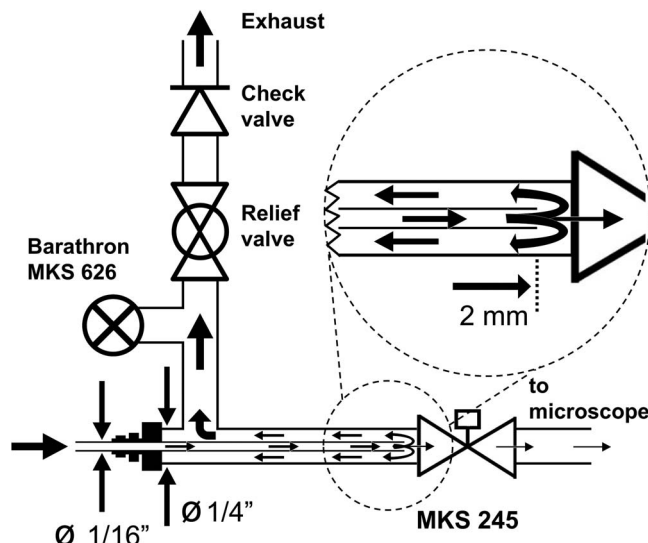
FIG. 1. Photograph of the gas manifold system.



FIG. 3. Close-up schematic diagram of the servo-driven pressure control valve (MKS 245) entrance. The 1/16 in. tube delivers excessive amount of the mixture as close as 2 mm to the orifice of the MKS 245. Only a small portion of the gas is leaked through the servo-valve. This unique design ensures fast switch of gases (5 min) and high-precision control over the gas composition entering microscope.

can be pumped by a scroll pump (XDS10, not shown) at Segment-1 and Segment-3. The operation of the system is assisted by NC/NO pneumatically assisted membrane (PAM) valves actuated by 40 psi compressed nitrogen gas. The exhaust hose connects to the gas rack volume from the top and negative pressure at this exhaust hose is monitored to ensure removal of exhaust gases.

The operation of the system is best described by considering it as three line segments, as shown in Figures 2 and 4. In the first segment, six low-flow MFCs (0–5 sccm, MKS 1479A) prepare the mixture of the desired composition. A PAM valve separates this segment from the next one, where the mixture is fed on top of the carrier flow by the seventh MFC (0–20 sccm, MKS 1479A). A 1/16 in. tube delivers

the mixture to the orifice of the servo-driven pressure control valve (MKS 245) (Figure 3). Prior to operation, the servo valve is kept closed and the mixture fills up this segment of the line (25 cm$^3$) around the 1/16 in. tube. Once this volume is filled up, the solenoid pressure control valve (MKS 148J) regulates the pressure by releasing the excess gas into exhaust. Gas is fed into the next segment through the servo-driven pressure control valve. Since the 1/16 in. tube delivers excess amount of the mixture immediately at the entrance to the orifice (Figure 3), the composition of the gas fed into this segment is dictated by the six MFCs and not the residual gas in the second segment. The last segment connects to the needle valve at the entrance of the microscope and has an automatic shut-off valve to protect the microscope from
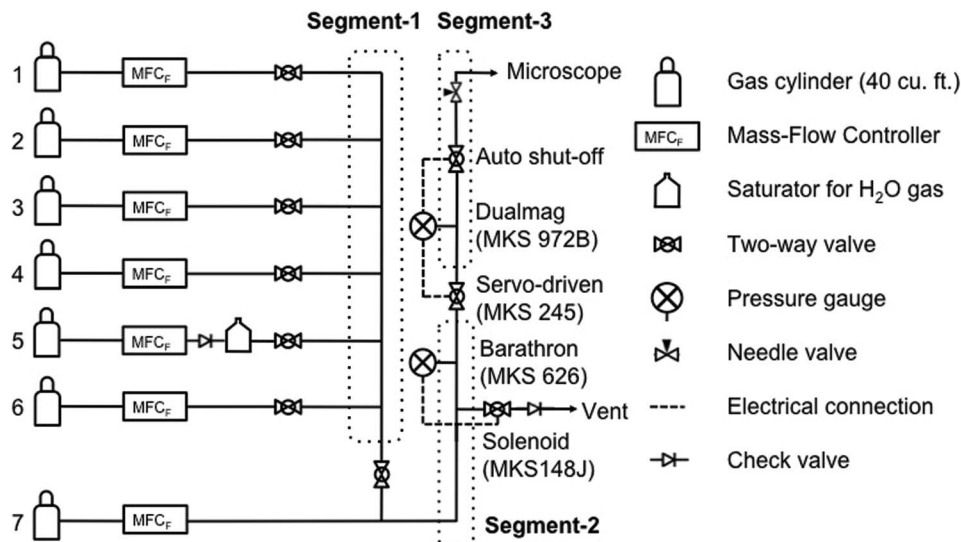


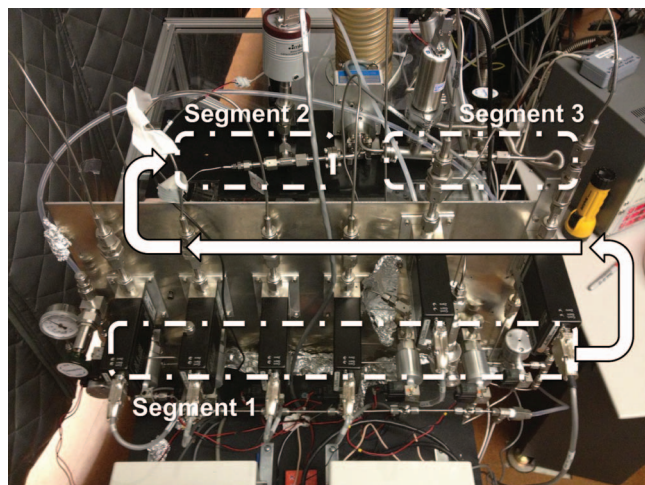FIG. 2. Schematic diagram of the gas manifold system.

FIG. 4. Close-up photograph of the gas system showing operational segments.



FIG. 6. Pressure at the gas cell as a function of the needle valve set value at two different servo controller set-point pressures.

uncontrolled pressure spikes. The entire system is controlled via a Labview interface, which allows simple input of gas mixtures and includes additional safety controls to prevent mixing of incompatible gases.

The experiments in this paper are performed on FEI dedicated environmental Titan 80–300 kV equipped with a Pfeiffer Prisma 80 quadrupole mass spectrometer QMS200 at the exhaust (Figure 5). Experiments at high temperature are performed using a Hummingbird Scientific E-TEM Heating Holder 1500F. The TEM samples were prepated on holey carbon supported on molybdenum grid (Electron Microscopy Sciences).

## III. RESULTS

There are two parameters that control the pressure inside the microscope: the pressure set-value on the servo-driven
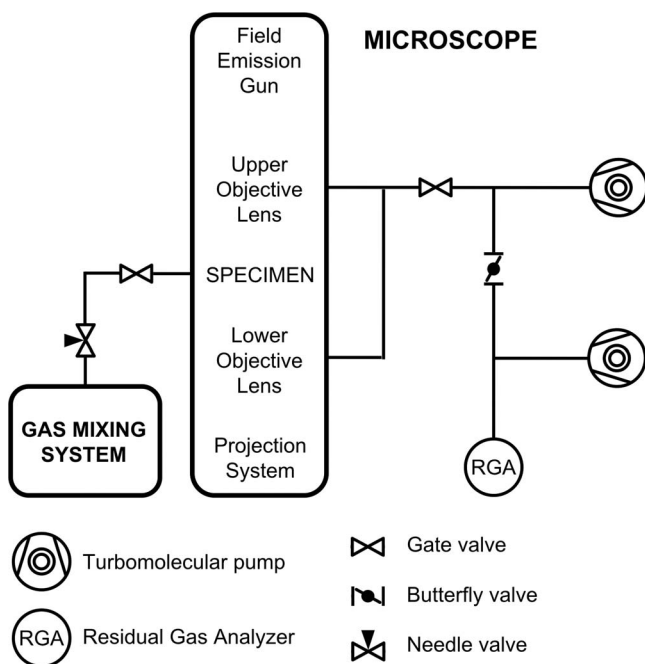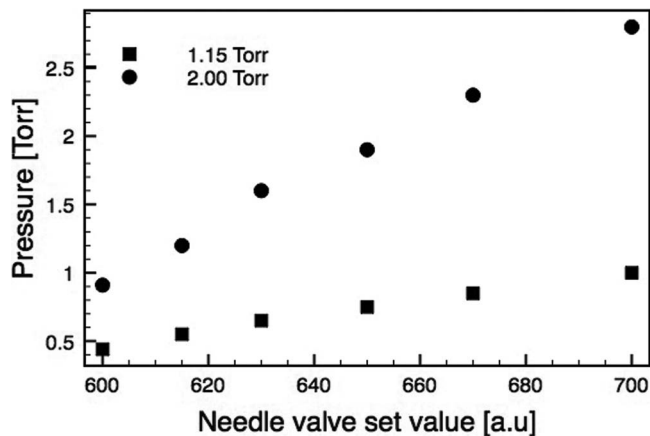
pressure control valve and the displayed value on the needle valve, which ranges from 500 to 1000. To test the synergic effect of the two, the former was fixed at different values while the latter was varied under 10 sccm helium flow. The maximum pressure inside the microscope is recorded and plotted in Figure 6. At a given set value on the servo-driven pressure control valve, the pressure inside the microscope increased almost linearly with respect to the needle valve set point. On the other hand, the maximum attainable pressure at a given needle valve set point is controlled by the set value at the servo driven pressure control valve. Thus, the final pressure inside the TEM is controlled by a synergy between the servo pressure setting and the observed pressure, and they are not the same. During the test, the feed-back control mechanism succesfully kept the pressure constant at the servo driven pressure control valve and the entirety of test ran smoothly without any pressure spike. One can therefore conclude that the pressure inside the microscope is well controlled.

In order to test how fast a new gas composition is introduced into the microscope, a mass spectrum is recorded while introducing carbon monoxide (CO) (flow of 5 sccm CO and 15 sccm He) into an existing helium flow (20 sccm He) (Figure 7). The switch for carbon monoxide gas was turned on at $t = 0$. The onset of the CO curve is delayed by less than a minute since the mass spectrometer is located at the exhaust of the microscope's gas cell. The graph is scaled linearly and the helium curve is not shown as its ion current is off scale at around $10^{-9}$ A. The introduction of CO does not cause significant variation in the read-out values of other gas species. The introduced gas equilibrates in approximately 6 min after the switch. The pressure inside the microscope remained constant during the whole process, as the servo-driven pressure control valve keeps the pressure in segment 3 constant. Thus no matter how drastically the composition of the incoming gas or the total flow is changed, there is negligible effect on the pressure inside the microscope. As a result, the gas manifold system provides a reliable imaging session that is safe for the field emission gun (FEG). Notably, we find that if the maximum pressure in the TEM increases above about 1.5–2 Torr, we begin to see a degradation in the ion pump vaccum near the FEG, leading to a automatic shut-off of the system.
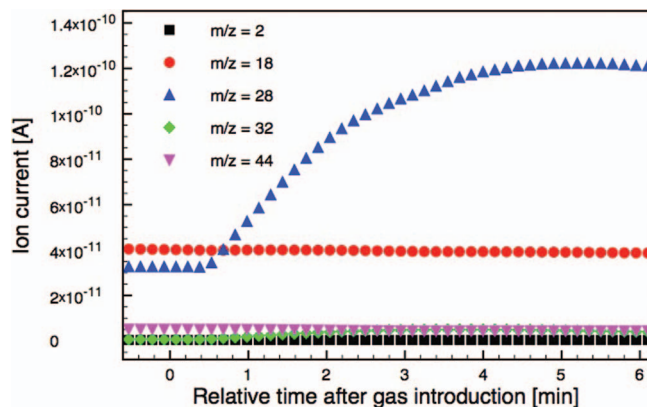


FIG. 5. Simplified schematic diagram of the whole system.

FIG. 7. Mass-spectra acquired during the introduction of CO (m/z = 28) at 0.5 Torr on top of helium flow (helium curve not shown). Gas stream switched from 20 sccm He to a mixture of 5 sccm CO and 15 sccm He.



FIG. 9. Amount of sample drift after different perturbations: CO introduction under constant pressure (square), 19% increase (circle), 82% decrease (triangle), and 562 400% increase (diamond) in pressure.

The imaging stability depends heavily on the amount of drift caused by external factors such as changes in pressure, gas composition, and temperature. Among these, temperature is the most critical external factor and other factors mainly have an effect since they cause the temperature to change. To verify the effect of pressure variation on the sample temperature, the pressure was changed while monitoring the sample temperature (Figure 8). The temperature on the sample was maintained by the feed-back control mechanism of the heating holder. Despite this, a 19% increase of the initial pressure (1.6 Torr) caused the computer controlled sample temperature to deviate 1.1 °C from the set temperature value of 100 °C. On the other hand, decreasing the pressure from 2.8 Torr to 0.5 Torr – a change of 82% – caused the sample temperature increase to 103.3 °C. To verify the stability of the gas manifold system, CO gas was subsequently added to the helium flow while monitoring the pressure and temperature of the system. The pressure was constant during the whole process and the composition change alone had neglible effect on the temperature of the sample, as shown in Figure 8. This result is exactly what the system was designed to achieve: this allows one to modify the composition of the reactive gas stream with-

out affecting the pressure around the sample or the temperature of the sample and thus maintain a stable environment for imaging.

To quantify the imaging stability, the sample drift was recorded using a Digital Micrograph script (Figure 9). As expected the amount of drift correlates well with the temperature change caused by each process. The perturbation due to the 82% pressure decrease caused the sample to drift 165 nm/s, whereas that of an 19% increase results a maximum of 55 nm/s drift. To demonstrate the effect of an enormous pressure difference on the sample drift and show how the drift settles over time, an excerpt of the drift data is shown in Figure 9, where 300 nm/s drift reduces over three minutes to 240 nm/s. Again, varying the composition only does not cause any significant drift and provides a stable imaging environment. To visualize how stable the sample is in response to compositional changes, the following experiment was performed. First, a specific region of the sample was imaged under 1 Torr He flow. Then 5% hydrogen balance helium was introduced on top of the helium flow to achieve a final composition of 1.7% hydrogen balance helium. Subsequently hydrogen was cut off and 5% carbon monoxide balance helium was introduced changing the composition of the gas to 1.7% carbon monoxide balance helium. Finally, the carbon monoxide was cut off, and hydrogen was re-introduced. During this test no external adjustments were made to the sample position, and the sample was imaged as shown in Figure 10. During the entire experiment the same area of the sample remained within the field of view. This clearly demonstrates that the reaction system described herein functions as desired: it is possible to observe the same area of the sample during changes to the reactive gas stream. Not all environmental TEM experiments are amenable to having a reduced reactive gas composition within a balance of He carrier gas, and thus these results represent a best case scenario. The presence of more dramatic changes in gas composition can be expected to lead to greater sample drift due to differences in the cooling of the sample by the gas stream. However, even in this case, the minimization of pressure changes can be expected to lead to a
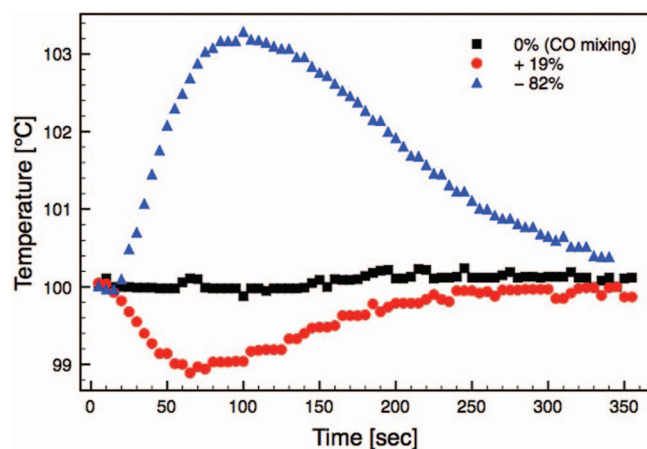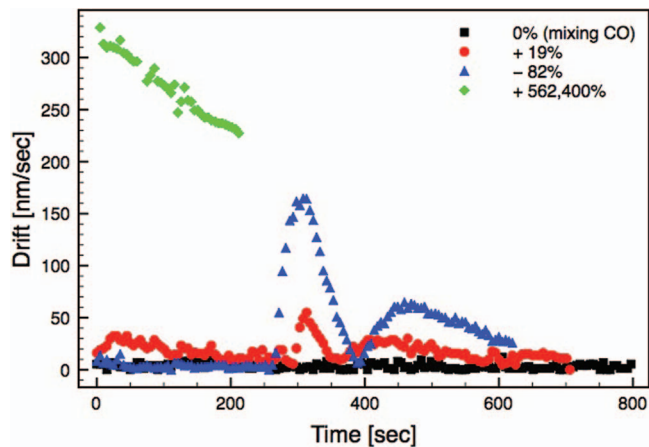


FIG. 8. Sample temperature after different perturbations: CO introduction under constant pressure (squares), 19% increase (circles), and 82% decrease (triangles) in pressure.
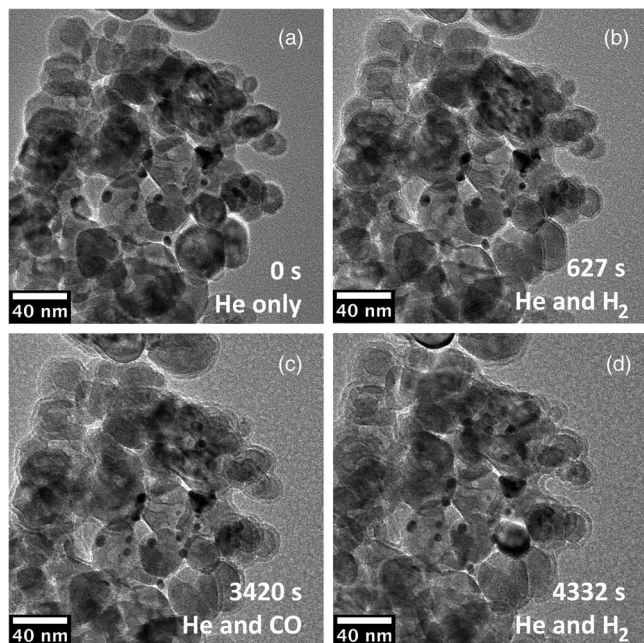
FIG. 10. TEM micrographs captured after various compositional perturbations without external manipulation to the sample position: (a) pure helium, (b) and (d) 1.7% hydrogen, and (d) 1.7% carbon monoxide balance helium.

substantial net reduction in drift when compared with more dramatic changes due to sudden pressure excursions.

## IV. CONCLUSION

A gas manifold system has been developed for ETEMs that is capable of preparing and delivering a mixture of up to six different gases. The system accommodates compositional variation in the gas stream without perturbing the pressure inside the microscope. This leads to a stable sample temperature and thus provides a drift-free environment for stable imaging. This system is expected to significantly impact our ability to investigate how changes in gas composition affect the structure, morphology, and electronic behavior of nanomaterials under different gas environments.

[1]J. M. Thomas and P. L. Gai, Adv. Catal. **48**, 171–277 (2004).
[2]M. José-Yacamán and M. Avalos-Borja, Catal. Rev. **34**(1–2), 55–127 (1992).
[3]A. K. Datye and D. J. Smith, Catal. Rev. **34**(1–2), 129–178 (1992).
[4]M. Shekhar, J. Wang, W.-S. Lee, M. Cem Akatay, E. A. Stach, W. Nicholas Delgass, and F. H. Ribeiro, J. Catal. **293**, 94–102 (2012).
[5]P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, and H. Topsøe, Science **295**(5562), 2053–2055 (2002).
[6]P. L. Gai, R. Sharma, and F. M. Ross, MRS Bull. **33**(02), 107–114 (2008).
[7]H. Nair, J. T. Miller, E. A. Stach, and C. D. Baertsch, J. Catal. **270**(1), 40–47 (2010).
[8]P. A. Crozier, R. Wang, and R. Sharma, Ultramicroscopy **108**(11), 1432–1440 (2008).