

An open cell environmental transmission electron microscopy technique for in situ characterization of photocorrosion of particles in aqueous solutions.

Levin, B.¹, Haiber, D.¹, Liu, Q.¹ and Crozier, P.A.¹

¹ Arizona State University, United States

Photocorrosion negatively impacts many important areas including energy conversion technologies and structural materials. The process takes place in aqueous environments and, for semiconductors, is driven by electron-hole pair generation from photon illumination¹⁻². For example, cadmium sulphide (CdS) based photocatalysts, undergo severe photocorrosion during photocatalytic water splitting³. Understanding the nano- and atomic scale changes induced by photocorrosion at the may offer new insights into fundamental questions regarding the initiation and evolution of photocorrosion and the impact of factors such as the presence of solute ions. We have developed a novel open cell method for condensing liquid water around catalytic nanoparticles and illuminate them inside an environmental transmission electron microscope (ETEM). We apply this approach to CdS nanoparticles in a variety of solutes and light illumination conditions to investigate photocorrosion.

To facilitate liquid water formation, CdS is dispersed on a TEM sample grid alongside ball milled sodium chloride (NaCl) (Figure 1a). In ETEM, NaCl will deliquesce below the saturation vapor pressure of water, forming a salt solution⁴. Samples are loaded into the ETEM in a cryogenic holder, which is held at ~5°C and are then exposed to 4-10 Torr of water vapor in the ETEM column. In our experiment, liquid water droplets that form around NaCl particles, envelope neighboring clusters of CdS particles (Figure 1b-c). CdS clusters within the bounds of the water remain relatively stationary over time, suggesting that either the clusters are held in position on the inside surface of the droplet, or by interaction with the carbon film at the base of the droplet. We are able to detect CdS and estimate the local concentration of the NaCl solution using in-situ X-ray energy dispersive spectroscopy (Figure 2).

To illuminate particles immersed in solution, we have modified an earlier *in situ* light system⁵ to use a 405 nm laser connected to the TEM with an optical fiber inserted through the objective aperture port of the microscope. Aberration corrected TEM imaging before and after exposure to light and water will allow us to characterize changes that occur in clusters of particles.

References:

1. Gerischer, H. *J. Electroanalytical Chemistry & Interfacial Electrochemistry* **82**, 133-143 (1977).
2. Chen, S.Y. & Wang, L.W. *Chem. Mater.* **24**, 3659-3666 (2012).
3. Meissner, D. et al. *Chem. Phys. Lett.* **127**, 419-423 (1986).
4. Wise, M.E. et. al. *Aerosol Science and Technology*, **42**, 281 - 294 (2008).
5. Liu, Q. et. al. *Microsc. Microanal.* **22**(S3), 730-731 (2016).

We gratefully acknowledge support from the U.S. DOE (DE-SC0004954) and ASU's John M. Cowley Center for High Resolution Electron Microscopy.

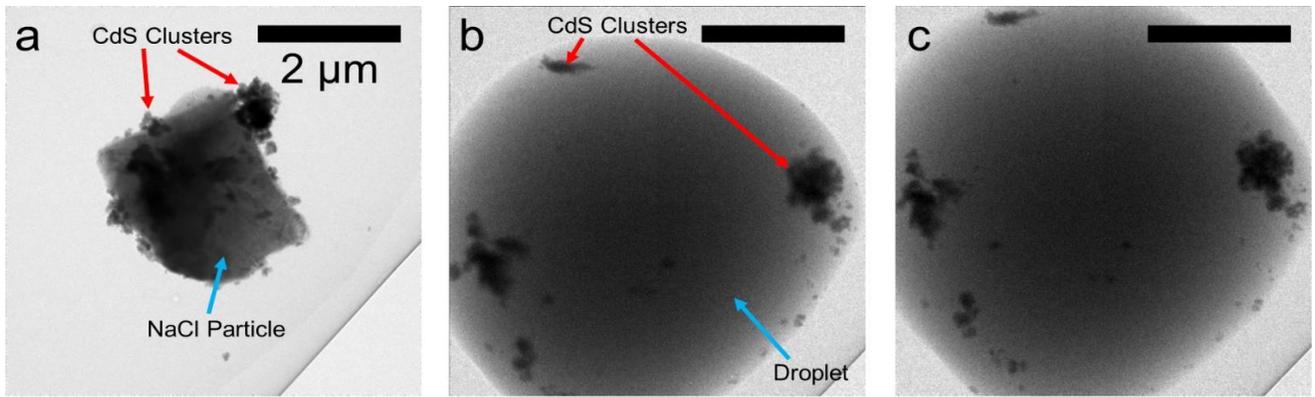


Figure 1. (a) TEM image of typical sample particles before water vapor exposure. (b) Image of same area after ~20 minutes exposure to >5 Torr water vapor (c) Image of same area after additional 10 minutes exposure to water vapor at ~8 Torr.

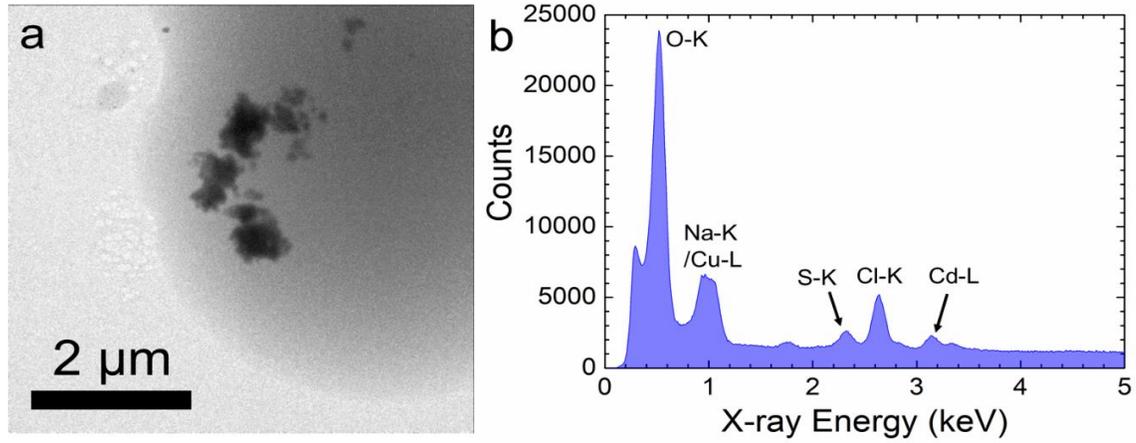


Figure 2. (a) TEM image and (b) X-ray spectrum of CdS nanoparticles in solution. Comparing Cl-K and O-K peak size with spectra simulated using NIST DTSA II suggests a ~0.03M NaCl solution in this area.