doi:10.1017/S1431927622005426
Microsc. Microanal. 28 (Suppl 1), 2022

Multimodal and Correlative Characterization of Hybrid Structures: Application to Materials for Environmental Remediation

Stephanie M. Ribet[1,2], Benjamin Shindel[1], Caroline Harms[1], Vikas Nandwana[1], Roberto dos Reis[1,2,3], and Vinayak P. Dravid[1,2,3*]

[1.] Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA.
[2.] International Institute of Nanotechnology, Northwestern University, Evanston, IL, USA.
[3.] The NU*ANCE* Center, Northwestern University, Evanston, IL, USA.
* Correspond Author: v-dravid@northwestern.edu

Scanning transmission electron microscopy (STEM) provides numerous advantages for high-resolution characterization of materials due to its versatile and multimodal nature. However, for soft and hard/soft (hybrid) materials, there are intrinsic contrast and dose challenges that can limit the analysis of these structures with STEM. Composite materials are ubiquitous in natural and synthetic systems. By leveraging the advantages of dissimilar components, hybrid structures have unique properties, which gives them promising applications in energy storage, optoelectronics, and medicine to name a few fields. Moreover, unraveling the nanoscale features and interfaces of these structures is often especially important for establishing structure-property relationships. Therefore, the development of a STEM framework to characterize these structures at high resolution is critical to tackle a variety of materials challenges [1].

We have developed a platform environmental remediation approach, where a hierarchical base material, such as a sponge or membrane, is coated with nanostructures targeted to remove a specific pollutant. First the OHM sponge, for oil adsorption was reported [2], followed by the PEARL membrane for aqueous phosphate sequestration [3]. More recently, this approach has been extended to the remediation of heavy metal pollutants from water.

These membrane architectures are examples of the aforementioned hybrid materials: the soft sponge anchor is sensitive to radiolysis, and it is difficult to get signal from the fine features in the heavier nanoparticles with STEM due to the intrinsic contrast difference between heavy and light elements. Moreover, as this material is hierarchical, we need to characterize these composites with techniques at multiple length scales. Despite the challenges, the insights gleaned from these studies inform ongoing materials development.

Here, using the example of heavy metal adsorption, we study both the material itself and its interaction with lead. The coating of this architecture has been optimized to be Fe/Mn-OOH, which has enhanced affinity for lead. Using an ultramicrotome cross section approach, we can expose key interfaces between the nanoparticles and the sponge in this system for study with SEM and S/TEM.

Figure 1 reports some results from this study. Fig. 1A shows a low mag annular dark field (ADF) STEM image of this system. The z-contrast nature of an ADF approach highlights the nanoparticles, so we can more easily visualize hard/soft interfaces. To investigate at higher resolution the nanoparticles and places with an ultra-thin coating, we move to transmission electron microscopy (TEM), which allows for an overall dose reduction. In Fig. 1B we observe the shapes of the two phases more clearly and the coherent nature of particles.

We use energy dispersive x-ray spectroscopy (EDS) to study the composition of the nanoparticles and the localization of the lead (Fig. 1C-E). Due to the overlap between the iron and manganese signals, we use only the Mn Kα and Fe Kβ peaks for mapping. We observe that both phases of nanoparticles have mixed iron and manganese composition. Moreover, in keeping with expectations based on bulk studies, the lead preferentially binds to the nanoparticles.

Ongoing work is focused on using a correlative EELS and 4D-STEM approach [1] to disentangle the contributions from the chemical and physical features of the nanoparticles to their ability to remediate lead. Thanks to the sensitivity and large dynamic range of direct electron detectors, we can use a low dose approach to probe fine features within the nanoparticles and subtle changes in electronic state. In this presentation we will share these results and discuss the broader impacts of this approach to other hybrid and hierarchical systems [4].

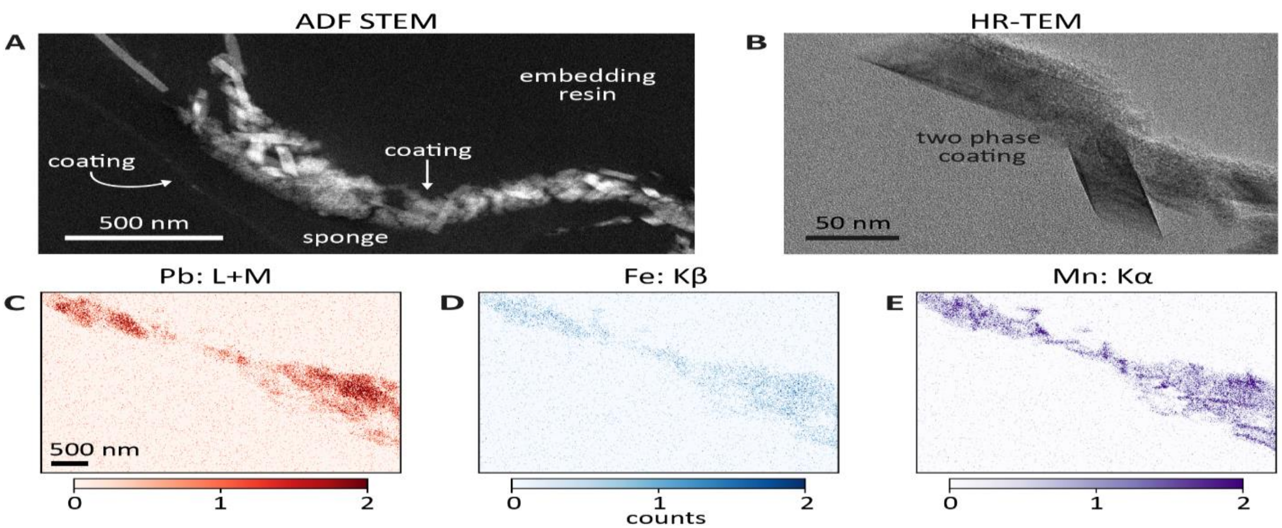

Figure 1. (A) low mag ADF STEM highlights sponge/coating interface. (B) high resolution TEM shows coating features. (C-E) STEM EDS illustrates localization of pollutants on nanoparticles and chemical composition of two phases in coating.

References:

[1] SM Ribet et al., Mater. Today **50** (2021), p. 100.
[2] V Nandwana et al., Ind. Eng. Chem. Res. **59** (2020), p. 23.
[3] SM Ribet et al., PNAS **18** (2021), p. 23.
[4] This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the SHyNE Resource (NSF ECCS-2025633), the IIN, and Northwestern's MRSEC program (NSF DMR-1720139*).* Research reported in this publication was supported in part by instrumentation provided by the Office of The Director, National Institutes of Health of the National Institutes of Health under Award *Number* S10OD026871. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. SMR acknowledges support from the International Institute of Technology, 3M, the American Membrane Technology Association, and the National Water Research Institute.

https://doi.org/10.1017/S1431927622005426 Published online by Cambridge University Press