Bacterial Defenses against Quantum Dots and Released Toxic Metals

The use of manufactured nanomaterials (MNMs) is exploding. Semiconductor nano-crystals, called quantum dots (QDs), are used in bio-imaging, solar cells, drug delivery, and many other areas, increasing the possibility of their release into the environment. QDs are coated with stabilizing polymers, which enhance their biocompatibility and protects them from breaking down chemically. However, weathering may expose the core and shell components to chemical breakdown, releasing toxic heavy metals. Cadmium and selenium promote stress responses in a variety of organisms and threaten ecosystems. Bacteria provide essential ecosystem services, so understanding the effects of toxic chemicals released from MNMS on microbes is crucial. Also, research on microbial responses to QDs can help us estimate their potential effect on animals and humans. In this study, researchers working at the MR-CAT 10-ID-B beamline at the APS set out to understand the adaptations and defense mechanisms that microbes have against QD toxicity.

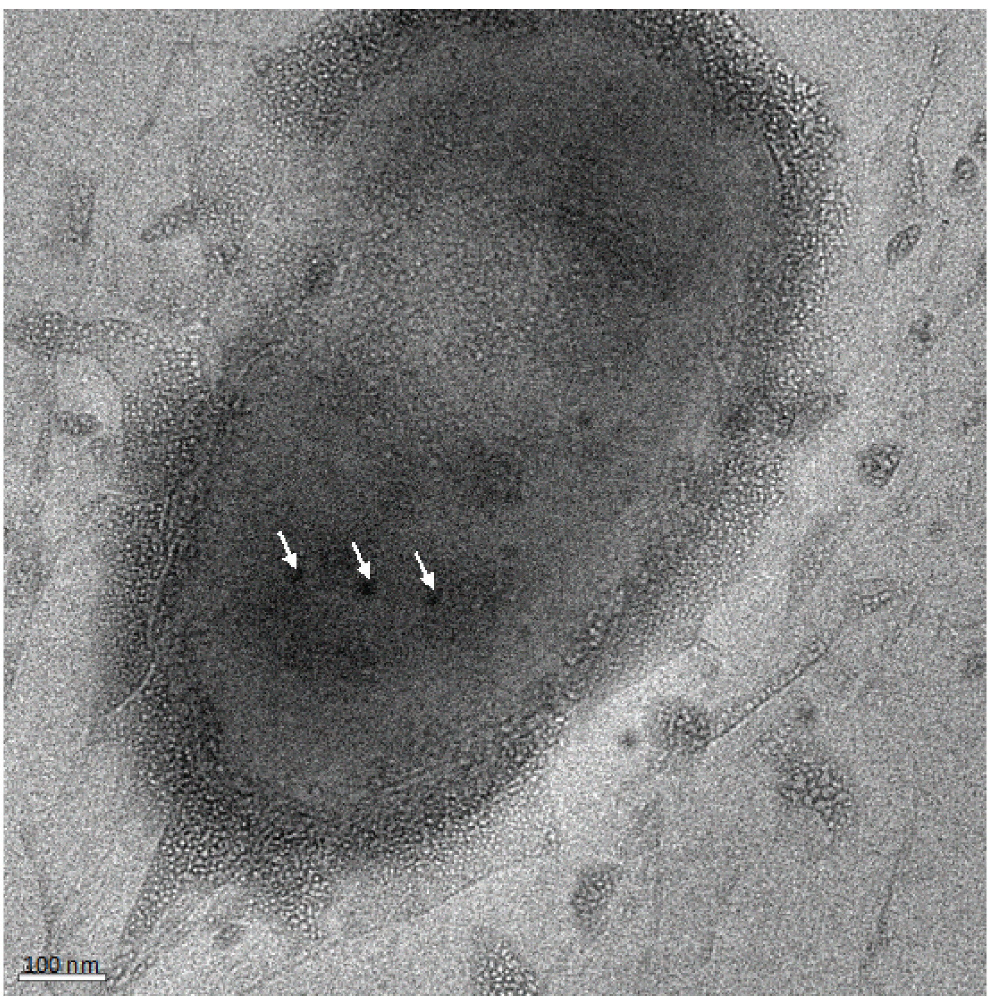

Fig. 1. Transmission electron microscopy image of a PAO1 and biogenic NPs, pointed by white arrows, synthesized during exposure to Cd-and Se-salts.

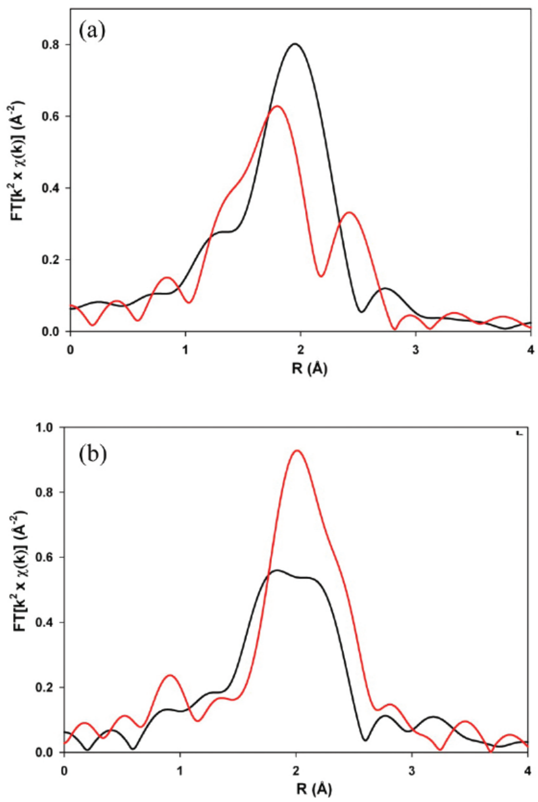

Fig. 2. The magnitude of k^2-weighted Fourier transforms (FT) of EXAFS spectra. Panel (a) shows PAO1 exposed to Cd plus Se (red) and Cd alone (black) at Cd K edge, and panel (b) shows PAO1 exposed to Cd plus Se (red) and Se alone (black) at Se K edge. From Y. Yang et al., ACS Nano **6**, 6091 (2012). ©2012 American Chemical Society

The common bacterium *Pseudomonas aeruginosa* PAO1 was chosen as a model for this study, because it has a greater capacity to resist heavy metals than other bacterial strains. The researchers exposed PAO1 to intact QDs, weathered QDs, and dissolved cadmium (Cd) and selenium (Se) salts at sub-lethal levels to mimic the low concentrations at which these compounds would enter the environment.

PAO1 is thought to defend against sub-lethal exposures to QDs in several ways. Increased expression of heavy metal efflux pumps and up-regulation of antioxidant enzymes within the cell, in addition to extracellular biosynthesis of metallic NPs, is believed to decrease metal bioavailability.

Figure 1 shows one bacterium growing with Cd and Se salts, and the formation of extra-cellular nanoparticles (arrow). With electron microscopy and energy-dispersive spectrometry, these particles were confirmed to contain Cd and Se. All three treatments up-regulated *czcABC* metal efflux transporters, although intact QDs had little to no release of metals and thus the least effect on *czcABC* expression. Surprisingly, weathered QDs had a greater transcriptional response than dissolved Cd and Se salts at similar concentrations.

Weathered QDs induced the superoxide dismutase gene *sodM*, which could be generated to repair oxidative damage. Again, there was a greater response in cells exposed to weathered QDs than to heavy metal salts. The up-regulation of DNA binding stress proteins suggests that PAO1 required DNA repair, possibly as a result of oxidative stress.

QDs also induced antibiotic resistant (ABR) genes, which increased antibiotic minimum inhibitory concentrations by between 50 and 100%. This increased tolerance to different antibiotics is similar to that observed in response to osmotic stress and pH extremes, suggesting the induction of a global defense mechanism.

Another adaptive mechanism is cell-mediated precipitation of released metals, which is likely a method of detoxification by reducing the bioavailability and toxicity of the metals. X-ray absorption fine structure (EXAFS) measurements at beamline 10-ID-B were collected by researchers from Rice University, the Illinois Institute of Technology, and Argonne to aid in understanding the structure and Cd and Se content in the biogenic NPs (Fig. 2). EXAFS showed extracellular synthesis of biogenic cadmium- and selenium-NPs after exposure to Cd-nitrate and SeO_2.

Uncovering the exact metabolic pathways and enzymes involved in NP biosynthesis requires further research. Given the tremendous variety of bacteria, the number of possible responses to NPs is great. Further research will be needed to determine whether the responses uncovered in this study are common among other microbes.

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •