Biomineralization of copper nanoparticles: Mechanistic insights and application in Cu-Catalyzed Azide-Alkyne Cycloaddition

KIMBER, R.L[1]*., LEWIS, E[2]., PARMEGGIANI, F[3]., FIGUEROA-GARCIA, A[4]., PATTRICK, R.A.D[1]., TURNER, N[3]., LLOYD, J.R[1].

[1]School of Earth and Enviornmental Sciences, University of Manchester, UK
(*correspondence: richard.kimber@manchester.ac.uk)
[2]School of Materials, University of Manchester, UK
[3]School of Chemistry, University of Manchester, UK
[4]Diamond Light Source, Harwell, UK

Microorganisms play a key role in the cycling and mineralization of metals in environmental systems. In addition, biomineralization can be used to precipitate metals from aqueous solution allowing easy recovery of valuable and useful metals from sources such as wastewater. Metal-reducing bacteria precipitate these metals as either intracellular or extracellular nanoparticles. These nanoparticles have unique properties making them useful in a wide range of applications including as biosensors, remediation agents, and catalysts. Copper is increasingly being used as an alternative to more traditional precious metals catalysts due to its lower cost and higher abundance.

We investigate the biomineralization of copper using the metal-reducing bacterium *Shewanella oneidensis*. Using a series of knockout mutants we show that the Mtr pathway, a common pathway for metal reduction in *S. oneidensis*, does not play a key role in the bioreduction of Cu. Transmission electron microscopy images reveal the formation of intracellular copper nanoparticles (Cu-NPs). Serial block-face scanning electron microscopy was used to reveal a '3 dimensional' representation of the dispersion and localization of Cu-NPs associated with the cells. X-ray absorption spectroscopy revealed the Cu-NPs to be Cu(0). However, atomic resolution imaging and electron energy loss spectroscopy suggest that partial oxidation of the surface layer may occur upon exposure to air, forming Cu_2O. The catalytic activity of the as-prepared Cu-NPs was tested in the azide-alkyne cycloaddition reaction. Triazole derivatives were produced in good yields with complete regioselectivity from a range of alkynes with benzyl azide under mild conditions.

This study demonstrates a green synthesis method for producing highly functional Cu-NPs using *S. oneidensis*. We provide mechanistic information and detailed characterisation which may also have implications for potential pathways of Cu biomineralization in the environment.