ABSTRACT

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Mechanisms of Metal Mineralization on Virus Templates for Nanorod Synthesis.
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Solution synthesis of nanorods is currently an important area of study due to the precision required to engender advantages in a wide range of fields. Viruses provide a template for synthesis in order to form uniform metal nanorods at mild operating conditions, without the use of expensive technology. In recent years, many materials involving the Tobacco mosaic virus (TMV) and its variants have been synthesized in attempts to produce high quality nanomaterials. However, the underlying processes involved in virion mineralization have not been sufficiently studied to allow for directed synthesis. The fundamental study of the hydrothermal synthesis of palladium on biotemplates, which produces uniform, controllable, monodisperse palladium nanorods, is of interest in this thesis. Three different experimental studies are outlined in this thesis.

In situ X-ray absorption spectroscopy (XAS) was employed in order to characterize the reduction and growth mechanisms of palladium (Pd) on the surface of genetically engineered TMV. XAS, via XANES and EXAFS analysis was combined with TEM to confirm an autocatalytic reduction, mediated by the TMV1Cys surface. This reduction interestingly proceeds via two first order regimes, which result in two linear growth regimes as spherical palladium nanoparticles are formed. Results in this project served as an entryway into

fundamentally understanding virus-mediated reduction and the relationship between the underlying reduction and growth processes governing mineralization.

Pd biomineralization was further elucidated by reframing it within commonly known molecular processes. These included the individual adsorption, reduction, and nanocrystal growth processes, which simultaneously occur during the hydrothermal synthesis on TMV. The adsorption of precursor and reduction of palladium were decoupled through UV-Vis Spectroscopy and *in situ* XAS studies. The role of additional cysteine (Cys) residues, ionic strength, and coating density on the fundamental parameters describing these processes were quantitatively evaluated. Primary nanocrystal growth and structural orientation of Pd nanoparticles was also probed using *in situ* small angle X-ray scattering (SAXS). The adsorption, reduction of Pd species, and nanocrystal sizes were significantly changed on addition of Cys residues to the amino terminus of the TMV coat protein (CP). Reduction of Pd on an already coated virion was dependent on the Pd surface area, and was hindered by the presence of residual salt. Furthermore, trends in Pd adsorption intensity and capacity suggested that chloride ions affected the adsorption equilibrium.

Finally, in an attempt to expand the biotemplating palette and increase mechanistic understanding of biomineralization processes, a new virus was applied to the hydrothermal synthesis. The Barley stripes mosaic virus (BSMV) was successfully used to produce metal nanorods of similar quality to those on TMV. Biomineralization was characterized in terms of the adsorption, reduction (after decoupling), and nanocrystal formation. The BSMV surface-mediated reduction of $Pd^{(2+)}$ proceeded via 1st order kinetics in both $Pd^{(2+)}$ and BSMV. The adsorption equilibrium relationship of Pd on the BSMV surface was described by a multi-step Langmuir isotherm suggesting an alternative mineralization (when compared to TMV), which is induced by both electrostatic and covalently driven affinity. Finally, all length scales of the as-synthesized materials could be characterized using ultra small angle X-ray scattering (USAXS) experiments and particle scattering models. The materials synthesized were confirmed to be of comparable quality to those on TMV. Overall, BSMV has been confirmed as a viable and promising alternate biotemplate for biomineralization of inorganic materials.

Taken together, this thesis has characterized biomineralization and then reframed it within commonly understood molecular mechanisms. This framework has allowed the possibility of understanding the salient features involved in mineralization. The parameter space for controlling the process can now be explored and the viability of other biotemplate-metal systems can be assessed. Therefore, application of this fundamental approach would facilitate directed synthesis and scale up of bioinorganic systems.