

Electrochemical perspective on protein-aided deposition
of inorganic nanomaterials

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Proteins play a central role in the orchestration of inorganic nucleation, growth, and hierarchical structuring that leads to the outstanding properties of natural hard tissues. For materials without known proteins to direct deposition, fairly routine protocols have been developed to identify candidate polypeptides using commercially available cell surface and phage display libraries. These screening protocols have dramatically increased the availability of material-binding polypeptide sequences; the list grows daily. Moreover, there is a wide array of existing data on 2D and 3D crystalline proteins that are excellent candidate templates for growth of hierarchically structured nanomaterials from aqueous electrolytes. Despite the rapid increase in materials-relevant polypeptide/protein sequences, little attention has been paid to engineering inorganic synthesizing electrolytes that operate in the pH, ionic strength, and redox potential range where proteins retain their function. We describe overarching lessons learned working on several different systems involving both protein-aided and protein-templated deposition of metal oxides (Cu₂O, ZnO) and noble metals (Ag) on surfaces and in solutions. For example, our earliest work used a TraI mutant engineered to bind cuprous oxide with high affinity (equilibrium dissociation constant of $K_d=12$ nM) to drive selective growth of cuprous oxide from precursor reagents that were subsaturated in solution. Similarly, a silver binding mutant of MalE ($K_d = 180$ nM) and a ZnO binding variant of TrxA are used to control morphogenesis during electrodeposition. Taken together, these systems provide a solid foundation for assessing the intersection between protein science and electrochemistry of aqueous deposition systems.