Facet-dependent bioavailability of mercury sulfide nanoparticles for microbial methylation

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Owing to their unique nano-scale reactivity, mercuric sulfide nanoparticles are important precursors of microbial methylmercury (MeHg) production in soil and sediment porewater. However, accurate prediction of MeHg production remains elusive due in part to the lack of mechanistic understanding of microbial methylation potential of particulate-phase mercury. Here we show that the methylation potential of nanoparticulate metacinnabar, formed during the early stages of mercury mineralization is determined by the exposed facets of metacinnabar. The (111) facet of metacinnabar diminishes during nanocrystal growth and this process is inhibited by natural ligands. The adsorption experiments and theoretical calculations prove that natural ligands preferentially adsorb to the (111) facet relative to the other facets of metacinnabar which prevent it from disappearance. Moreover, methylation experiments using facet-engineered model nanomaterials exposed to *Desulfovibrio desulfuricans* ND132 reveal that metacinnabar with higher content of (111) facet of metacinnabar lead to larger methylmercury production and exhibited significantly greater binding affinity to the methylating bacterium. This ligand-modulated facet evolution and its effect on microbial methylation provide new mechanistic insights for interfacial processes in nanoparticle-microorganism interactions that have important implications for mercury methylation potential of nanoparticulate mercury during mineralization.