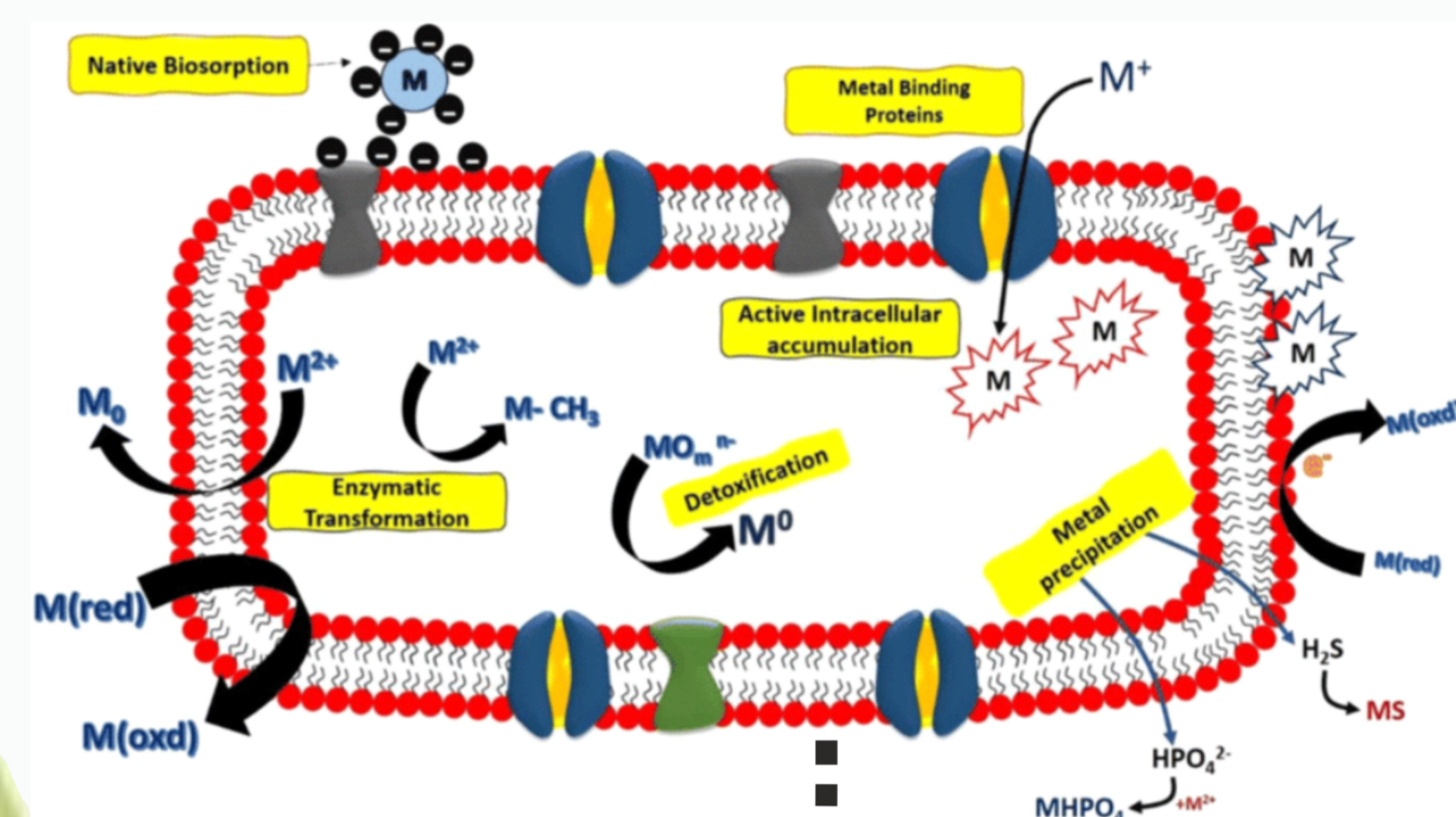


# The biosynthesis of palladium nanoparticles by microorganisms and their relationship with biomimetic structures

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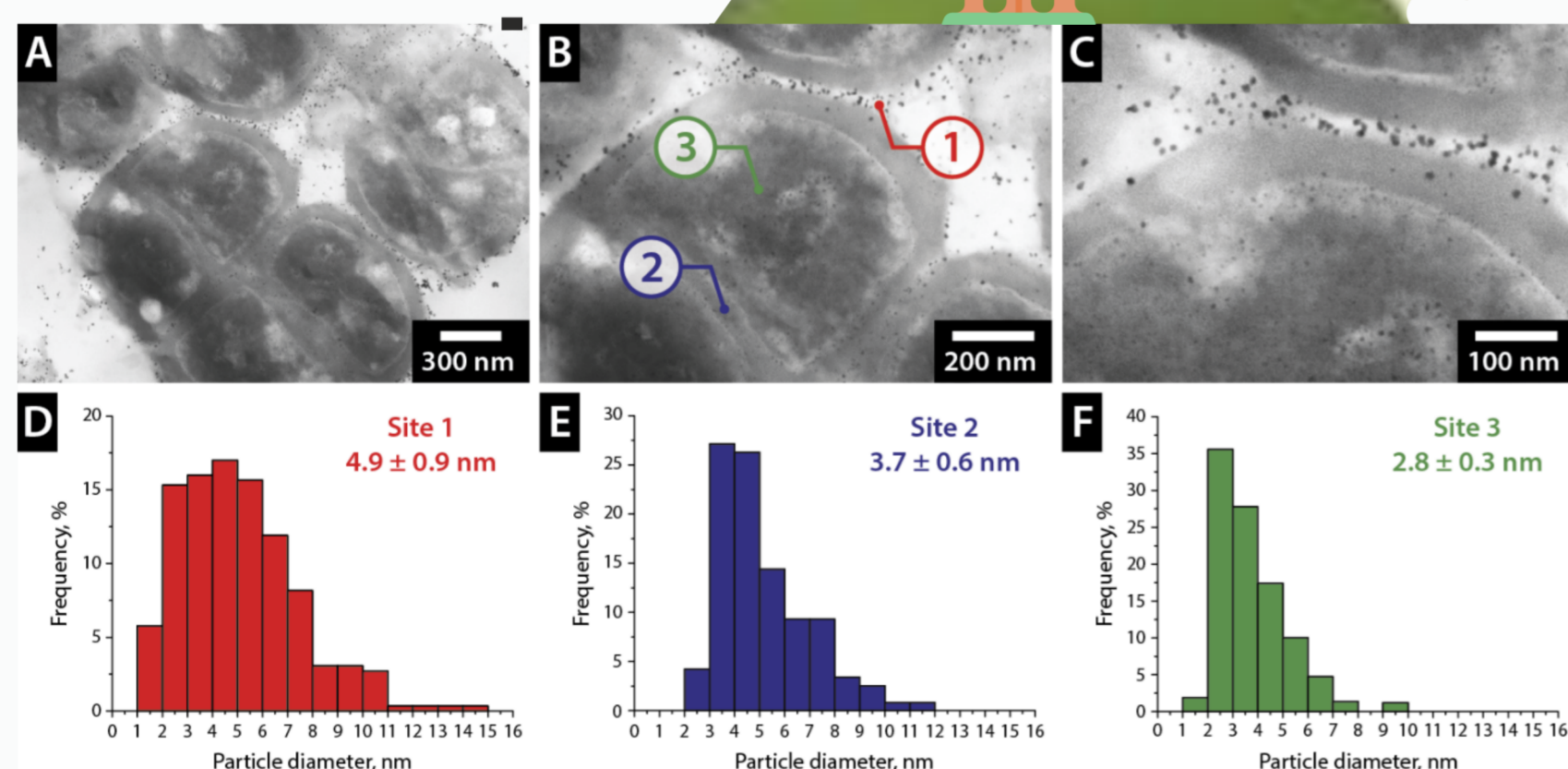
Palladium nanoparticles (Pd-NPs) are primarily employed as catalysts in numerous chemical and petrochemical processes, such as the hydrogenation and oxidation of hydrocarbons, and the synthesis of novel pharmaceutical compounds. Due to their high capacity for absorbing hydrogen, they are also promising for use as electrocatalysts, in biosensors, electronics, and for storing hydrogen.

The bioproduction of palladium nanoparticles using microorganisms is a promising area of green chemistry, combining environmental safety with high efficiency. Many bacteria can reduce palladium ions ( $\text{Pd}^{2+}$ ) to form palladium metal ( $\text{Pd}^0$ ) nanoparticles.



A key advantage of biosynthesis is the ability to produce highly homogeneous palladium nanoparticles of tightly controlled size, which is critical for catalytic and electrochemical applications. Nanoparticles formed by biogenic pathways often exhibit unique morphological characteristics, including spherical, rod-shaped or core-shell structures. The connection with biomimetic structures is evident based on the fact that biogenically synthesised nanoparticles often replicate the morphology of natural functional materials. Additionally, the principle of 'copying nature' is employed to replicate the catalytic centres of enzymes or cell wall structures. This makes biogenic palladium nanoparticles an interesting subject for developing biomimetic catalysts for organic synthesis.

In this study, palladium ( $\text{Pd}^0$ ) nanoparticles were synthesised using Gram-negative bacteria.



BF-STEM images of Pd/P. yeii biohybrid at 50k (A), 100k (B) and 200k (C) magnification. Particle size distribution for the palladium particles located on the surface of bacterial cells (D), between individual cells in the sarcina (E) or inside bacterial cells (F). The location of Sites 1-3 (D-F) is shown in panel B. See Supporting Information for the full-size BF-STEM images

Electron microscopy clearly demonstrated the presence of small palladium nanoparticles and their aggregates in Pd/P. yeii catalyst (Figures A-C). The metallic species were located at different sites of the sample: on the surface of bacterial cells (Figure B, Site 1), between individual cells in the sarcina (Figure B, Site 2) and inside bacterial cells (Figure B, Site 3). The size of the Pd NPs varied dependent on the location of the particles. Large particles and aggregates were detected exclusively outside bacterial cells, whereas small nanoparticles several nanometers in size predominated inside microorganisms. To more accurately quantify the observed patterns, comparative statistical analysis was performed (Figures D-F). Palladium nanoparticles on the surface of bacterial cells had a mean diameter of 4.9 nm (Figure D). This size was notably lower for particles located between cells in the sarcina or dispersed inside bacterial cells and amounted to 3.7 nm and 2.8 nm, respectively (Figures E-F). Thus, the BF-STEM study demonstrated the existence of small nanosized palladium particles in the biohybrid material capable of promoting the target chemical transformations. In addition, it was clearly shown that the bacterial cell environment can act as an efficient stabilizer for active metallic species, which can be considered a distinguishing feature of this bio-derived catalyst support.