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Controlled Biocatalytic Synthesis of Metal Nanoparticle-Enzyme Hybrids: Demonstration for Catalytic Hydrogen-Driven NADH or Flavin Recycling

AUTHORS

Lucy BROWNE / UNIVERSITY OF OXFORD, INORGANIC CHEMISTRY LABORATORY, SOUTH PARKS ROAD, OXFORD
Kylie VINCENT / UNIVERSITY OF OXFORD, INORGANIC CHEMISTRY LABORATORY, SOUTH PARKS ROAD, OXFORD

PURPOSE OF THE ABSTRACT

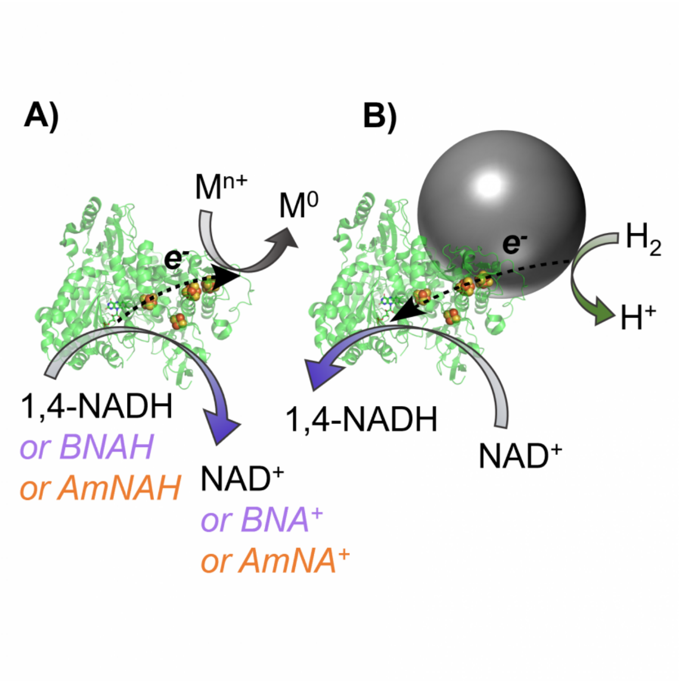
Having control over the shape and size of metal nanoparticles (NPs) is key for making them suitable for specific applications: ranging from drug delivery, biosensing to catalysis. This has given rise to substantial effort into exploring different synthesis routes for improving the control over the NPs polydispersity as well as the sustainability of the process.[1]

Here, we demonstrate the controlled synthesis of metal NPs under mild conditions. An isolated enzyme, an NAD+ reductase, oxidizes a nicotinamide cofactor (either the native NADH or the cheaper, synthetic cofactors: BNAH or AmNAH)[2] which provides electrons for metal reduction (Fig. 1A). These metal NPs can subsequently be used as H2 oxidation catalysts, supplying electrons back to the enzyme, which can then selectively reduce NAD+ to the bioactive cofactor 1,4-NADH (Fig. 1B). This biohybrid was then utilized as a H2-driven NADH recycling catalyst for an alcohol dehydrogenase to carry out an enantioselective ketone reduction.

We have also explored the synthesis of another metal NP-enzyme hybrid, which uses H2 as the reductant and therefore leads to no carbon-containing by-products. Here, the hydrogenase enzyme reduces metal salts while oxidising H2 (Fig. 2A). Initial studies have shown these metal NP-enzyme hybrids can give increased activities in comparison to the enzyme alone, likely due to the metal NP increasing the electronic surface area between the hybrid catalyst and the substrate (Fig. 2B).

In both systems we have observed the enzymes' compatibility with the metal NPs; we hope this is an area which can help bring about new reactivities for more sustainable processes by using both the enzyme and metal NP properties either in a cascade reaction or synergistically.

FIGURES



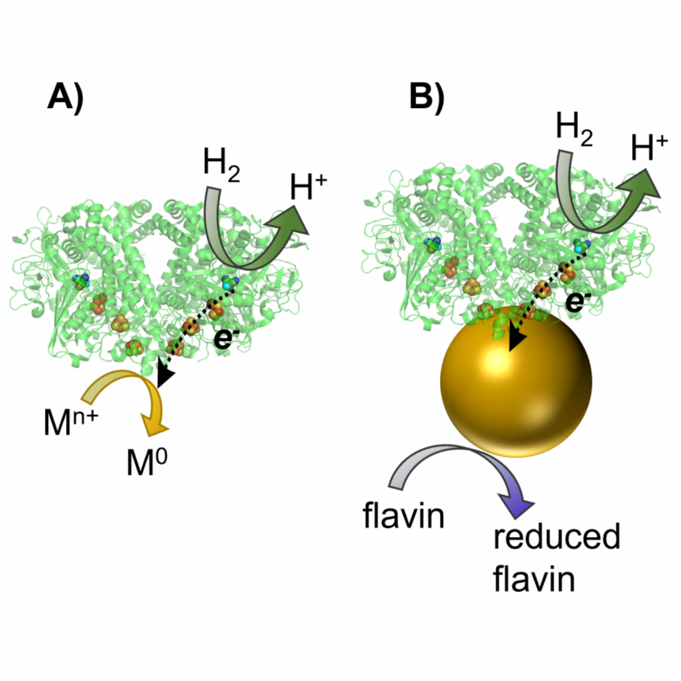


FIGURE 1

NAD+ reductase used to make metal NPs, subsequently creating a metal biohybrid catalyst.

Using NAD+ reductase enzyme to reduce metal salts, leading to the controlled synthesis of metal NPs and utilising the resulting metal NP-enzyme hybrids as catalysts for selective NAD+ reduction.

FIGURE 2

Using hydrogenase for H2-driven metal NP synthesis and flavin recycling.

Hydrogenase oxidises H2, releasing electrons for metal reduction. The resulting metal NP-enzyme hybrid can then be used for catalytic applications such as flavin recycling.

KEYWORDS

biocatalysis | biohybrid metal nanoparticles | chemoenzymatic | cofactor regeneration

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