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Catalytic activity of biomass-supported Pd nanoparticles: Influence of the biological component in catalytic efficacy and potential application in 'green' synthesis of fine chemicals and pharmaceuticals☆

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ABSTRACT

Five gram negative and two gram positive bacterial strains known for their heavy metal tolerance or ability to reduce metal ions were coated with Pd(0) nanoparticles (NPs) via reduction of soluble Pd(II) ions under H_2 following an initial uptake of $PdCl_4^{2-}$ without added electron donor ('biosorption'), where the gram negative strains had a 5-fold greater capacity for Pd(II). *Cupriavidis metallidurans* accumulated Pd(II) exceptionally; the possibility of reduction to Pd(0) via an endogenous electron donor was not discounted. The initial rate of subsequent H_2-mediated Pd(II) reduction correlated with the Pd(II) removed during biosorption ($r^2 = 0.9$). TEM showed strain-specific variations of Pd-NPs. At a 1:3 loading of Pd:biomass the cell surfaces of *Escherichia coli* and *Desulfovibrio desulfuricans* showed uniform coverage with small NPs with the other strains showing larger aggregates. NPs made by the gram positive cells appeared larger than their gram negative counterparts. At a loading of 1:19 all were active catalysts in Cr(VI) reduction and in two Heck coupling reactions. $BioPd_{E.\ coli}$ and $bioPd_{D.\ desulfuricans}$ and $bioPd_{A.\ oxydans}$ were consistently the best and worst catalysts respectively. $BioPd_{E.\ coli}$ was further tested as a process catalyst according to industrial protocols in Heck and Suzuki coupling reactions. Laboratory and industrial tests (coupling of phenyl iodide and ethyl acrylate) gave 75% and 78% conversion to ethyl cinnamate, respectively. The biomaterial catalysed Heck and Suzuki reactions using bromoacetophenone and 4-bromoanisole (Heck) and 4-chloroanisole (Suzuki) but not 3-chlorotoluene. In accordance with known chemical catalysis the catalytic efficacy was related to electron-withdrawing substituents on the phenyl ring, with more than 90% conversion (Suzuki) using 4-bromobenzotrifluoride.

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1. Introduction

Due to their often unequalled catalytic properties, platinum group metals (PGMs) are widely used in many catalytic processes of the petrochemical and chemical manufacturing industries. Since the development of PGM-based catalysts as pollution control devices for the automotive industry, PGM demand and market price have increased concurrently. At the same time, the use of petrochemicals for 'platform' chemical synthesis is of concern due to the dual effects of dwindling oil supplies and the environmental impact of CO_2. Hence more efficient use of increasingly scarce and expensive materials via 'green chemistry' is pressing.

The development of efficient, cost-effective recycling and green chemistry technologies is a first step towards the conservation and sustainable use of resources. Due to limited global resources and the high market value of PGM, their recovery often takes priority over environmental concerns, for example more than 14 tonnes CO_2 is generated per kilo of Pt produced from primary sources [1]. Traditional PGM recycling methods (electrochemical recovery, solvent extraction) are energy-demanding or rely on the use of aggressive chemicals [2,3].

The reduction of transition metals by some bacteria is believed to exert a considerable impact on the ecology of the environment

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[4]. This microbial ability can be harnessed for biotechnological applications such as bioremediation of metal contaminants and metal biorecovery [5,6]. Recent work on the biorecovery of precious metals (Ag, Au, Pd, Pt) demonstrated the efficacy of this approach from solutions of metal salts as well as from secondary waste sources. In the latter such biorecovered metal can be more effective than pure metal when subsequently used as a catalyst e.g. [7,8], a 'step change' which offers potential clean alternatives to traditional metal refining, greater efficiency with respect to continued supply of rare metals and 'green' synthesis of pharmaceuticals and fine/platform chemicals via catalysts biofabricated from wastes.

Bacterially bound catalytic nanoparticles (NPs) can be comparable to or more effective catalysts than traditional homogeneous or heterogeneous catalysts in hydrogenation [9] and in a classical synthetic reaction, the Heck coupling [10] and they also show high stability for recovery and recycle, attributed to a reduced tendency for the nanoparticles to agglomerate when stabilised by the biomatrix [10].

The continuous recovery of Pd and Pt from spent automotive catalyst leachates was first shown by Yong et al. [11] using an electrobioreactor coated with a biofilm of the sulfate-reducing bacterium (SRB) *Desulfovibrio desulfuricans*. Later work used palladised biofilm of a *Serratia* sp. as a catalyst for continuous detoxification of highly toxic and environmentally problematic Cr(VI) to less toxic Cr(III) in flow-through reactors interrogated via magnetic resonance imaging [12]. Heat-treated palladised cells of *D. desulfuricans* produced an applied film (in activated carbon) electrocatalyst for a fuel cell (FC) anode that produced power comparably to a commercial fuel cell catalyst [13]; use of molecular biology tools later enhanced the corresponding activity of *Escherichia coli*-based FC catalyst [14] that was improved still further by sourcing the metallic catalyst from mixed PGMs from a commercial waste water [15].

Early attempts to elucidate the precise mechanism of Pd deposition and NP synthesis implicated a role for bacterial hydrogenases in Pd(II) reduction [16]. Later, Mikheenko et al. [17] constructed strains of *Desulfovibrio fructosovorans* deficient in its periplasmic hydrogenases, observing relocation of the Pd(0) deposits to the cytoplasmic membrane, the site of the remaining hydrogenase. Similar results were obtained with hydrogenase-deficient *E. coli* mutants [18]. Due to their role in formate and H_2 metabolism the cytoplasmic Hyd-3 is a component of the formate hydrogenlyase (FHL) complex responsible for formate oxidation under fermentative conditions while periplasmic Hyd-1 and Hyd-2 operate as 'uptake' hydrogenases for energy conservation under fermentative (Hyd-1) and anaerobic respiratory (Hyd-2) conditions), and direct evidence [17,18] hydrogenases are implicated in a primary step of Pd(II) bioreduction and to act as a focus for the initial formation of Pd(0) 'seeds', on the hydrogenase itself or on nearby biochemical entities. These 'seeds', in turn, promote further abiotic autocatalytic Pd(II) reduction to Pd(0) [19,20] or of Pt(IV) to make a metal catalyst [8]. This mechanism has been affirmed [21]. Once an initial 'seed' of Pd is formed (regardless of whether via non-enzymatic or enzymatically steered mechanisms) further abiotic autocatalytic metal deposition continues, even from concentrated acids [8,11,22], with the synthesis steered by the initial patterning and also by the nature of the surrounding biochemical ligands [23]. A high resolution TEM study [10] showed unique Pd atomic arrangements at the interface with the supporting biomatrix over and above the Pd NP itself and extending from it but the reactivity of the interface as compared to the bulk NP is not known.

The cell-bound Pd nanoparticles (bioPd) exhibit remarkable catalytic properties in a number of test reactions of environmental and 'green chemistry' significance (see for reviews [7,24,25]). Pd biocatalysts made from various strains, or mutants of a single strain, show variable activity for a given reaction [14,18,26] probably attributable to strain-specific differences in cell surface composition/patterning and/or the enzymatic apparatus responsible for Pd(II) reduction. Early studies suggested that the pattern of deposition of Pd nanoparticles on the cell surface (and the resulting catalytic activity of the bioPd) is a function of both the initial biosorption of Pd(II) (crystal nucleation) and the subsequent bioreduction to Pd(0) [19,27]. Critically, the ability to 'adjust' the sites of Pd(0) deposition via molecular engineering is a key feature which sets enzymatic nucleation apart from simple biosorption methods.

The gram negative cellular envelope contains many potential Pd(II) nucleation sites, e.g. the peptidoglycan moiety of the bacterial cell wall (located in the periplasm between the cytoplasmic and outer membranes) is rich in carboxyl and amine groups, the preferred ligands for coordination of Pd(II) complexes [28], as well as various proteins, some of which co-extract with Pd nanoparticles [10]. In *D. fructosovorans* two hydrogenases are located in the periplasm (an aqueous gel matrix) and their removal re-locates Pd(0) to the inner membrane site of the remaining hydrogenases (a lipid environment) [17] with corresponding effect on the catalytic activity of the bioPd formed [26].

In contrast to gram negative organisms, gram positive strains have been less well studied with respect to bioPd manufacture although a strain of *Bacillus sphaericus* was highlighted due to its ability to make catalytically active bioPd [9], probably via deposition of Pd(0) onto the protein array of its external S-layer [29]. In *Bacillus* more recent work Lin et al. [30] have suggested a second mechanism whereby Pd(0) locates within the wall layers beneath the S-layer with hydrolysates of polysaccharides or peptidoglycan serving as endogeneous electron donor in *B. licheniformis*, in accordance with the observation of Pd(0) layer beneath the S-layer in *B. sphaericus* [31].

Gram negative and gram positive strains present major differences in cell wall composition, the former having a more complex double-membrane structure. The outer membrane assembly (comprising membrane phospholipids with extruded lipopolysaccharide chains) and inner cytoplasmic membrane enclose peptidoglycan within a discrete aqueous gel 'compartment' (the periplasm). Gram positive bacteria have a cell membrane but lack the outer membrane (i.e. they have no periplasm) but they often have an 'S-layer' protein array located beyond a peptidoglycan layer, thicker but of similar composition to that found in the gram negative periplasm. Beveridge [32] describes two types of gram positive bacteria. The first, typified by *B. sphaericus*, have a relatively thin peptidoglycan layer which may be overlaid with S-layer, whereas the second type (e.g. *Arthrobacter*, *Micrococcus*) have thick, robust walls with a thicker peptidoglycan layer. This second type has not been examined previously in the context of deposition of Pd(0).

Spectroscopic studies on Pd(II) reduction on the surface of the S-layer of *B. sphaericus* showed preferred coordination of Pd(II) complexes to carboxyl groups of this protein [29], with non-enzymatic reduction of Pd(II) to Pd(0) to produce bioPd NPs of similar activity as hydrogenation catalyst to the enzymatically made NPs on *D. desulfuricans* [9].

Although the *B. sphaericus* and *D. desulfuricans* exemplars of protein-supported Pd-nanoparticles are now reasonably well understood, future rational catalyst design targeted to specific reactions dictates that the precise microbial mechanisms (and their interplay) that dictate catalyst activity and also specificity are known; the literature will otherwise continue to expand with a potentially infinite catalogue of untargeted, largely descriptive examples.

As a step change towards catalyst targeting for 'green chemistry' applications (i.e. greater selectivity and reaction specificity and reduced waste) in this work gram negative and gram positive strains with known high metal tolerance and/or hydrogenase activity were allowed to deposit Pd nanoparticles under a common set of conditions and the resulting bioPd catalysts were

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