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Biosynthesis of FeS nanoparticles from contaminant degradation in one single system

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ABSTRACT

Biogenetic nanomaterials have attracted growing interests in recent years attributed to their "green" synthesis nature, but expensive precursors are typically needed. On the other hand, release of hazardous intermediates during contaminant biodegradation/conversion is usually encountered in wastewater treatment processes. This study reports an effective coupling of both processes in one simple system to overcome the individual limitations. By using *Shewanella oneidensis* MR-1 as the inoculum, the Fe^{2+} ions released from naphthol green B (NGB) bioreduction and H_2S from thiosulfate reduction were utilized in-situ to generate ferrous sulfide (FeS) nanoparticles, with an average size of ~30 nm. In addition, we discovered for the first time that FeS nanoparticles could be synthesized both extracellarly and intracellularly by this strain, and identified the essential role of the Mtr respiratory pathway in the biosynthesis process. This study deepens our understanding of the bioconversion behaviors of metal-complex dyes, and may provide implications for development of sustainable nanomaterial fabrication processes.

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1. Introduction

The biosynthesis of nanomaterials has attracted growing interest as a clean, nontoxic and environmentally-friendly approach [1]. Especially, *Shewanella* species, attributed to their great reduction ability [2–4], have been utilized as nano-factories to produce a range of nanomaterials, from single metals such as Pd [5–7], Pt [8], Au [9] and Ag [10], to composite materials such as As-S nanotubes [11] and Ag_2S nanoparticles [12]. The synthesis of metal sulfide nanomaterials from wastewater can also bring extra benefits of recovering sulfur species, including sulfite, thiosulfate and their reduction product H_2S, which may otherwise cause severe pollution and corrosion problems [13,14].

On another frontier, biological processes have been widely adopted for dyeing wastewater treatment due to their low cost and environmental benignity [15]. However, the degradation of many metal-complex dyes, which are extensively used in textile dyeing, color photography, cosmetic, and other industries [16], frequently leads to toxic metal ions release [17,18] and cause secondary pollution. A previous study showed that naphthol green B (NGB), a typical metal-complex dye, could be biodegraded by *Shewanella oneidensis* MR-1 and release ferrous ions under anaerobic conditions [19]. Considering that *Shewanella* species can also reduce thiosulfate and in-situ assemble sulfide nanomaterials, we hypothesize that these processes might be combined in a single system to produce ferrous sulfide (FeS) nanoparticles, thereby achieving dual benefits of contaminants removal and nanomaterial synthesis. Ferrous sulfides are recognized as advanced inorganic materials for applications in the fields of environmental remediation [20], high-energy density batteries [21], and photoelectrolysis systems [22]. Thus, it is of interest to synthesize ferrous sulfide nanocrystals via such biofabrication routes.

This study aims to validate the feasibility of the above process. A model bacterium, *S. oneidensis* MR-1 [23], and NGB were selected as the degrader and metal-complex dye respectively for the proof-of-concept tests. The contaminant degradation was monitored and the formed nanoparticles were identified and characterized. The biosynthesis mechanism was elucidated by using the *S. oneidensis* MR-1 wild-type strain and its Mtr-pathway mutants. This work may facilitate a better understanding of the biodegradation behaviors of metal-complex dyes and lay a foundation for green synthesis of nanomaterials.

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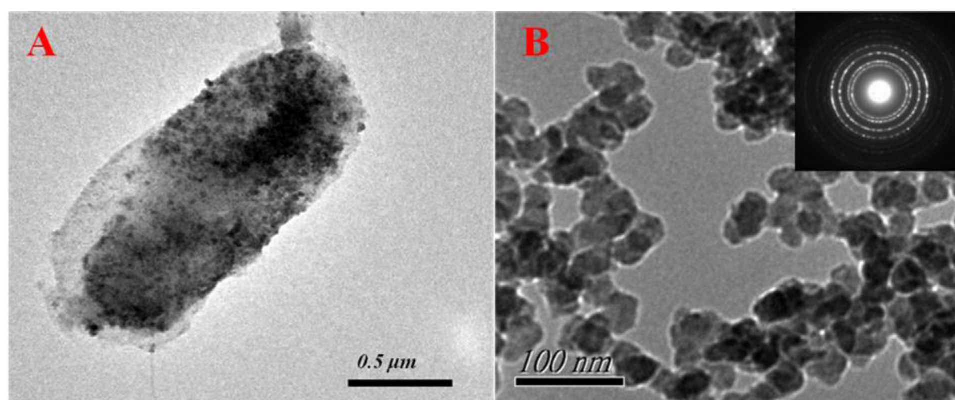

Fig. 1. TEM images of biosynthesized FeS nanoparticles by *S. oneidensis* cells after 5-d incubation with NGB and thiosulfate for 5 days. (A) Nanoparticles adhered to the cell surface; and (B) Nanoparticles suspended in the medium (the inset was the SAED pattern).

2. Materials and methods

2.1. Strains and growth conditions

The wild type *S. oneidensis* MR-1 and strains deleted of the genes *cymA* (Δ*cymA*), *mtrA* (Δ*mtrA*), *mtrB* (Δ*mtrB*), or both *mtrC* and *omcA* (Δ*mtrC/omcA*) were aerobically cultured in LB medium at 30 °C until the late stationary phase. The cell pellets were collected after centrifugation at 5000 rpm for 15 min, and then washed twice with sterile deionized water.

2.2. Biofabrication of nanomaterials

The mixture medium for the anaerobic NGB decolorization and FeS biofabrication experiments was prepared by adding 18 mM lactate as the sole electron donor and 100 mg/L NGB, 10 mM thiosulfate as the electron acceptors (unless otherwise stated) to a defined medium [24]. Thiosulfate also served as the sole sulfur source for the bacterial cells. The mixture medium was buffered with 50 mM 4-(2-hydroxyerhyl) piperazine-1-erhanesulfonic acid (HEPES) at pH 7.0. Each serum vial contained 80 ml mixture medium. To ensure an anaerobic condition, the solution was bubbled with high purity N_2 gas (>99. 999%) for 10 min and then the vials were sealed with butyl stoppers. The collected bacterial cells were inoculated into the serum vials using a syringe and the initial cell density was adjusted to 4–6 × 10^6 CFU ml^{-1}. All serum vials were cultured on a shaker of 180 rpm at 30 °C.

The NGB concentration was measured using a UV–vis spectrophotometer (UV-2501PC, Shimadzu Co., Japan) at 714 nm. The decolorization efficiency was calculated as:

$$\text{Decolorizationefficiency}(\%) = 100 \times (OD_i - OD_t)/OD_i$$

where OD_i and OD_t refer to the absorbance (at 714 nm) at the reaction beginning and at time *t*, respectively. Each experiment was conducted in quintuplicate.

2.3. Characterization of nanomaterials

The *S. oneidensis* cells after 5 days incubation were collected by centrifugation at 5000 rpm for 15 min. The biomass with synthesized nanoparticles were characterized by TEM (Model JEM-2100, JEOL Co., Japan) coupled with selected area electron diffraction (SAED).

For the component analysis, the suspension was centrifugated at 5000 rpm for 15 min and washed three times with Milli-Q water under anaerobic conditions. The precipitate was washed sequentially with 75% ethanol, 100% ethanol and acetone. After being dried

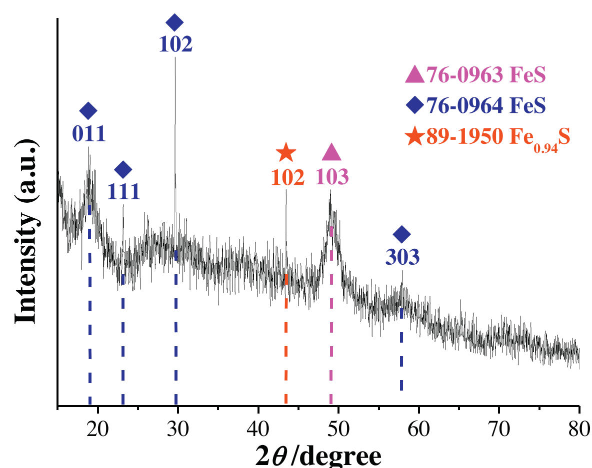

Fig. 2. Powder XRD patterns of the FeS nanoparticles biosynthesized by *S. oneidensis* MR-1.

under N_2 atmosphere, the obtained materials were analyzed using XRD with a Rigaku D/MAX Ultima III high resolution X-ray diffractometer with Cu Kα irradiation. The generator was operated at 40 kV and 40 mA. The samples were scanned between 2θ = 15–80°.

Spatial distribution of biogenic nanomaterials was analyzed by TEM with ultrathin sections of samples. The cell suspensions incubated for 5 days with NGB and thiosulfate were centrifuged, and the cell pellets were prefixed in 2.5% glutaraldehyde. The bacterial cells were then washed with 0.1 M PBS, and subsequently fixed with 1% osmium tetraoxide in distilled water at 4 °C for 1.5 h. After being washing again with 0.1 M PBS, the cells were then dehydrated at room temperature with ethanol (70–100%). Embedding was carried out using a mixture of resin (Epon 812), hardeners (dodecenyl succinic anhydride and methyl nadic anhydride), and accelerator (dimethylaminomethyl phenol). The mixture was polymerized at 60 °C for 2 days. Ultrathin sections of 70 nm were cut using an ultramicrotome (EMUC6, Leica Co., Germany), and mounted on a carbon-coated copper TEM grid. All sections were stained with 2% uranyl acetate in distilled water and removed of the staining solution prior to TEM analysis (Tecnai 12, Philips Inc., the Netherlands).

3. Results and discussion

3.1. Formation and characterization of FeS nanoparticles

The TEM analysis reveals that black nanoparticles were homogeneously deposited on the surface of *S. oneidensis* MR-1 after

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