

Cell-nanoparticle assembly fabricated for CO₂ capture and *in situ* carbon conversion



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ARTICLE INFO

Article history:

Received 17 September 2015

Received in revised form 5 November 2015

Accepted 19 November 2015

Available online 28 November 2015

Keywords:

Actinobacillus succinogenes

Hydrophilicoleate-modified Fe₃O₄ nanoparticles

Assembly

CO₂ fixation

ABSTRACT

Some microorganisms can selectively capture carbon dioxide without light irradiation, which proposes a wide application prospect. The purpose of this study was to create a microorganism-nanoparticle assembly, which will be used for carbon dioxide fixation and *in situ* conversion into a platform chemical, succinic acid. Firstly, uniform size-controlled magnetic nanomaterial were synthesized and well assembled with non-photosynthetic carbon-fixation microorganism *Actinobacillus succinogenes* 130Z. CO₂ capture efficiency can be improved dramatically by enhancing the transfer of carbon dioxide between gas phase and cytoplasm by the hydrophilic oleate-modified Fe₃O₄ nanoparticles. The assembly will integrate the advantages of two processes, carbon dioxide sequestration by cells and carbon dioxide adsorption by chemical reagents, which resulted in 71 mmol CO₂ fixation/g dry cell in 24 h. This article provides a basic study for CO₂ sequestration and carbon resource utilization.

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1. Introduction

In recent times, the concentration of CO₂ in the atmosphere has reached a worrying level, which is mainly due to anthropogenic activities such as excessive use of fossil fuel, deforestation, intensive industrialization and urbanization. As constant rise of greenhouse gas emissions may cause global warming and climate change, demand for effective CO₂ mitigation technologies is an immense issue at present [1].

Carbon capture and sequestration (CCS) technologies as well as CO₂ utilization have attracted much attention [2]. CO₂ capture technologies usually include geological and oceanic storage, chemical and physical absorbents loading, and biological fixation. The main CO₂ absorption technologies include aqueous alkanolamine solutions and porous solids. Several different classes of solid CO₂ adsorbents have been reported, including zeolites, activated carbons, calcium oxides, hydrotalcites, organic-inorganic hybrids, and metal-organic frameworks [3]. Metal-organic frameworks are new classes of porous solids [4]. The M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn) series of metal-organic frameworks have recently been intensively studied. Some metals (like zero valent iron) had been

reported for the reduction of CO₂. As important heterogeneous catalysts, the interaction of CO₂ with oxide surfaces of metal oxides attracts many attentions [5]. Baltrusaitis et al. studied spectroscopy of CO₂ adsorption on hydroxylated metal oxide surfaces, including iron oxide and oxide-supported metal catalysts [6]. The formation of adsorbed carbonates, bicarbonates and carboxylates, has been observed in metal oxides (Fe₂O₃, Al₂O₃). Thus, the interaction of CO₂ with metal oxide surfaces is of great interest which results in high adsorption capacity. A large enhancement in the CO₂ adsorption capacity was achieved by decorating magnetite nanoparticles over the multi walled nanotube (MWNT) surface in Mishra and Ramaprabhu's study [7]. In their further research, magnetic Fe₃O₄ decorated graphite nanoplatelets can be regarded as cost effective CO₂ adsorbent, which facilitates a good adsorption capacity [8]. In the report of Tamilarasan and Ramaprabhu [9], polyaniline/magnetite nanocapsules (PANI/MNCs) adsorbed 42 mmol/g of CO₂ in the initial 90 min at room temperature. Therefore, the modification via magnetite nanoparticles can enhance the CO₂ adsorption capacity of many chemical adsorbents. To the best of our knowledge, seldom literature reported magnetite nanoparticle decorated microorganism cell that increased the biological CO₂ fixation ability.

According to Mikkelsen et al. [10], the technological options that are commonly considered for transforming CO₂ include: (a)

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chemical transformation of CO₂ to hydrogenated materials (hydrocarbons, methanol, ethanol, etc.), (b) photochemical transformation to CO, HCO₂H, CH₄, (c) electrochemical/photo-electrochemical transformation to CO, HCO₂H, methanol, (d) biological transformation to ethanol, sugar, organic acids, and (e) reforming CO₂ to generate CO and H₂. For example, Annie Modestra et al. [11] enhanced the carboxylic acids synthesis through the microbial catalyzed electrochemical reduction of CO₂.

Photosynthesis of plants is the main pathway to utilize the captured CO₂ in nature. Photosynthesis microalgae are usually regarded as prime candidates for biological fixation of CO₂ with several advantages such as faster growth rates and higher CO₂ fixation rates. CO₂ capture from *in situ* generated flue gas was reported using *Chlorella* sp. in bubble column photobioreactors to develop a cost effective process for concomitant carbon sequestration and biomass production [12]. With the addition of monoethanolamine (MEA) and CO₂ in the cultivation process of *Spirulina* sp. LEB 18, algae can be produced using medium recycle and the addition of MEA, thereby promoting the reduction of CO₂ emissions [13]. Beside photosynthesis microalgae, some non-photosynthetic carbon-fixation microorganism can selectively capture CO₂ without light irradiation, and convert CO₂ to some useful platform chemicals such as ethanol and organic acids [14], among which, succinic acid is a four-carbon diacid (C₄H₆O₄), and is a precursor in the chemical synthesis of various commodities in food, chemical, agricultural, and pharmaceutical industries [15].

A number of bacterial strains are able to produce succinic acid through fermentation, including *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*, *Corynebacterium glutamicum*, and recombinant *Escherichia coli* [16]. Bio-production of succinic acid through fermentation has the advantage of consuming 1 molecule CO₂ per 1 molecule succinic acid produced, and it is evident that bio-succinic acid production could contribute to the abatement of CO₂ emissions [17]. *A. succinogenes* is recognized as one of the most promising bacterium utilized for bio-succinic acid production, as it is a facultative anaerobe with high tolerance to sugar concentrations and succinic acid concentrations [18]. The fermentation end products of *A. succinogenes* are succinic acid as the main metabolite, in addition to formate, acetate, and ethanol. As a CO₂ fixation bacterium, the CO₂ supply is a key factor in the production of succinic acid by *A. succinogenes* 130Z [19]. A higher concentration of dissolved CO₂ in the fermentation broth could result in increasing the ratio of succinic acid to the other metabolites, the ratio of carbon recovery, and the succinic acid yield. One way to make CO₂ more available to the bacterium in the culture broth is to increase its solubility by means of increasing its partial pressure [20].

The coupled processes of chemical adsorption and biological fixation have previously been investigated. Choi et al. [21] believed that the CO₂ biofixation by microalgae could be improved if the amount of dissolved gas in the liquid was increased beyond the natural balance of the algal culture. The use of MEA in microalgae

cultures can increase the CO₂ fixation activity [13,22]. However, one of the major limitations to the implementation of the CO₂ capture technology by amine is the high-energy consumption and cytotoxicity [23].

Previous uncharted, the purpose of this study was to explore strategies to directly use microorganism-nanoparticle assembly for CO₂ fixation and *in situ* conversion into CO₂-derived succinate.

2. Experimental

As shown in Fig. 1, firstly, magnetic nanoparticles were synthesized and modified with hydrophilic external layer. Subsequently, modified magnetite nanoparticles were used to decorate *A. succinogenes* cell wall. The assembly process was characterized by atomic force microscope (AFM). Further, single cell-nanoparticle assembly were fabricated and regulated for the CO₂ capture and bioconversion to CO₂-derived succinate.

2.1. Microorganism and culture medium

A. succinogenes 130Z^T (ATCC 55618) was used as CO₂ capture cell, which was obtained from the American Type Culture Collection. As a facultatively anaerobic strain, its aerobic seed cultivation was conducted at 37 °C, 200 r/min in a 250 mL Erlenmeyer flask containing 100 mL 3% (wt/vol) growth medium (pancreatic digest of casein 17 g/L, soy peptone 3 g/L, glucose 2 g/L, NaCl 5 g/L, KH₂PO₄ 2.5 g/L). The 150 mL fermentation medium in a 250 mL flask contained per liter: 60 g glucose, 30 g yeast extract, 2 g urea, 2 g MgCl₂·6H₂O, 1.5 g CaCl₂, 0.07 g MnCl₂, 4.4 g Na₂HPO₄, 3.3 g NaH₂PO₄ and 0.5 g anti-foam reagent. Inoculation volume was 5% (vol/vol). Glucose was separately sterilized at 115 °C for 30 min and added to the medium. Solid MgCO₃ were chosen to control the fermentation pH at 7.0. The flask shaker was sparged with 1 vvm oxygen-free CO₂. Chemicals used in this study were of analytical level from Sigma-Aldrich (USA), and used as received unless otherwise described.

2.2. Synthesis and modification of magnetic nanoparticles

The magnetic nanoparticles were synthesized and modified as follow. 23.5 g FeCl₃·6H₂O and 8.6 g FeCl₂·4H₂O were dissolved in 600 mL deionized water under N₂ with mechanical stirring at 1000 rpm and 85 °C. Then we quickly added 80 mL of 7.1 M NH₄OH (25 wt.%). The color of the solution changed gradually from light brown to black. Afterwards, we added dropwisely 16 mL of oleic acid to the resulting suspension over a period of 30 min. After 10 min, we separated the magnetic precipitate by magnetic decantation and washed it with deionized water four times. We modified the magnetic precipitate with about 4 mL of 7.1 M NH₄OH to form the hydrophilic magnetic Fe₃O₄ precipitates nanoparticles, which in an aqueous solution were monodisperse. The magnetic nanoparticle concentration was expressed in terms of dry weight per unit volume of suspension medium.

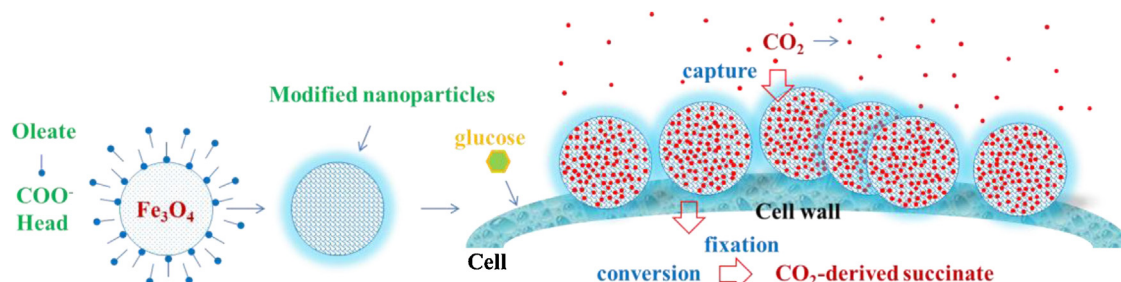


Fig. 1. Scheme of Fe₃O₄ nanoparticles preparations, microorganism-nanoparticle assembling, and CO₂-derived succinate production.

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