Journal of CO_2 Utilization 13 (2016) 17–23

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Cell-nanoparticle assembly fabricated for CO_2 capture and *in situ* carbon conversion

Qiang Li[a,*], Rongyue Zhang[b], Dexi Wu[c], Yongdong Huang[a], Lan Zhao[a], Dan Wang[d], Fangling Gong[a], Liang Li[b], Han Qiu[b], Guanghui Ma[a,*]

[a] National Key Lab of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Department of Chemical Engineering, Beijing Institute of Petro-chemical Technology, Beijing 102617, PR China
[c] Department of Cardiology, The First Affiliated Hospital of Sun Yat-sen University, Guangzhou 510080, PR China
[d] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

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 Fe_3O_4 nanoparticles
Assembly
CO_2 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. CO_2 capture efficiency can be improved dramatically by enhancing the transfer of carbon dioxide between gas phase and cytoplasm by the hydrophilic oleate-modified Fe_3O_4 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 CO_2 fixation/g dry cell in 24 h. This article provides a basic study for CO_2 sequestration and carbon resource utilization.

1. Introduction

In recent times, the concentration of CO_2 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 CO_2 mitigation technologies is an immense issue at present [1].

Carbon capture and sequestration (CCS) technologies as well as CO_2 utilization have attracted much attention [2]. CO_2 capture technologies usually include geological and oceanic storage, chemical and physical absorbents loading, and biological fixation. The main CO_2 absorption technologies include aqueous alkanolamine solutions and porous solids. Several different classes of solid CO_2 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 M_2 (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 CO_2. As important heterogeneous catalysts, the interaction of CO_2 with oxide surfaces of metal oxides attracts many attentions [5]. Baltrusaitis et al. studied spectroscopy of CO_2 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 (Fe_2O_3, Al_2O_3). Thus, the interaction of CO_2 with metal oxide surfaces is of great interest which results in high adsorption capacity. A large enhancement in the CO_2 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 Fe_3O_4 decorated graphite nanoplatelets can be regarded as cost effective CO_2 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 CO_2 in the initial 90 min at room temperature. Therefore, the modification via magnetite nanoparticles can enhance the CO_2 adsorption capacity of many chemical adsorbents. To the best of our knowledge, seldom literature reported magnetite nanoparticle decorated microorganism cell that increased the biological CO_2 fixation ability.

According to Mikkelsen et al. [10], the technological options that are commonly considered for transforming CO_2 include: (a)

* Corresponding authors. Fax: +86 10 82627072.
E-mail addresses: qiangli@ipe.ac.cn (Q. Li), ghma@ipe.ac.cn (G. Ma).

http://dx.doi.org/10.1016/j.jcou.2015.11.004
2212-9820/

chemical transformation of CO_2 to hydrogenated materials (hydrocarbons, methanol, ethanol, etc.), (b) photochemical transformation to CO, HCO_2H, CH_4, (c) electrochemical/photo-electrochemical transformation to CO, HCO_2H, methanol, (d) biological transformation to ethanol, sugar, organic acids, and (e) reforming CO_2 to generate CO and H_2. For example, Annie Modestra et al. [11] enhanced the carboxylic acids synthesis through the microbial catalyzed electrochemical reduction of CO_2.

Photosynthesis of plants is the main pathway to utilize the captured CO_2 in nature. Photosynthesis microalgae are usually regarded as prime candidates for biological fixation of CO_2 with several advantages such as faster growth rates and higher CO_2 fixation rates. CO_2 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 CO_2 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 CO_2 emissions [13]. Beside photosynthesis microalgae, some non-photosynthetic carbon-fixation microorganism can selectively capture CO_2 without light irradiation, and convert CO_2 to some useful platform chemicals such as ethanol and organic acids [14], among which, succinic acid is a four-carbon diacid ($C_4H_6O_4$), 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 CO_2 per 1 molecule succinic acid produced, and it is evident that bio-succinic acid production could contribute to the abatement of CO_2 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 CO_2 fixation bacterium, the CO_2 supply is a key factor in the production of succinic acid by *A. succinogenes* 130Z [19]. A higher concentration of dissolved CO_2 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 CO_2 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 CO_2 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 CO_2 fixation activity [13,22]. However, one of the major limitations to the implementation of the CO_2 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 CO_2 fixation and *in situ* conversion into CO_2-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 CO_2 capture and bioconversion to CO_2-derived succninate.

2.1. Microorganism and culture medium

A. succinogenes $130Z^T$ (ATCC 55618) was used as CO_2 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, KH_2PO_4 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 $MgCl_2{\cdot}6H_2O$, 1.5 g $CaCl_2$, 0.07 g $MnCl_2$, 4.4 g Na_2HPO_4, 3.3 g NaH_2PO_4 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 $MgCO_3$ were chosen to control the fermentation pH at 7.0. The flask shaker was sparged with 1 vvm oxygen-free CO_2. 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 $FeCl_3{\cdot}6H_2O$ and 8.6 g $FeCl_2{\cdot}4H_2O$ were dissolved in 600 mL deionized water under N_2 with mechanical stirring at 1000 rpm and 85 °C. Then we quickly added 80 mL of 7.1 M NH_4OH (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 NH_4OH to form the hydrophilic magnetic Fe_3O_4 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.

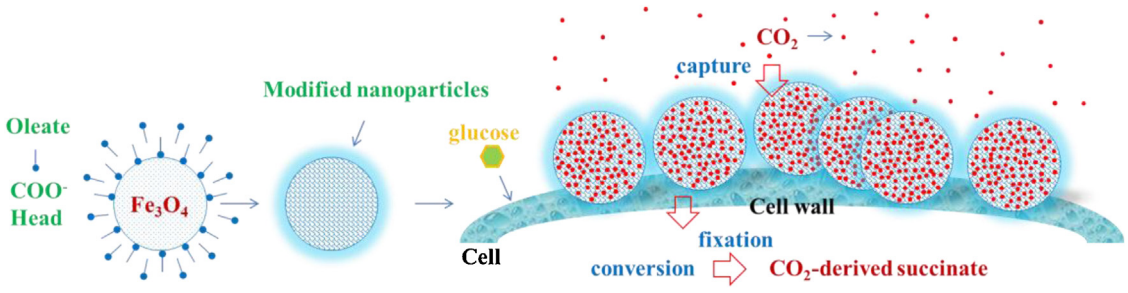

Fig. 1. Scheme of Fe_3O_4 nanoparticles preparations, microorganism-nanoparticle assembling, and CO_2-derived succinate production.