Biomimetic photoelectrocatalytic conversion of greenhouse gas carbon dioxide: Two-electron reduction for efficient formate production

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ABSTRACT

Resource utilization of carbon dioxide (CO_2) as alternative carbon feedstock is a promising solution to problems of both the energy supply and global warming. Herein, a biomimetic photoelectrocatalytic interface was covalently constructed utilizing cobalt-containing zeolite imidazolate framework (ZIF9) as CO_2 fixation and activation substrate, and Co_3O_4 nanowires (NWs) as the photoelectrocatalyst. Adsorption experiments demonstrated that CO_2 could be concentrated on ZIF9 modified Co_3O_4 NWs. The CO_2 surface concentration exhibited a 3.44 fold increment on this hybrid interface than that on Co_3O_4 NWs. Theoretical calculation elucidated ZIF9 has the capacity for activating CO_2 molecule via binding Co atom to the O atom of CO_2, resulting in the onset potential of CO_2 reduction 284 mV positively shift on ZIF9-Co_3O_4 NWs than that on Co_3O_4 NWs. At a low overpotential of 290 mV, CO_2 has been photoelectrocatalytically conversion to formate with high conversion rate of 72.3 μmol L^{-1} cm^{-2} h^{-1} and high selectivity of nearly 100% in liquid products. And the heterogeneous electron transfer constant was 2.096×10^{-3} cm s^{-1}. This CO_2 conversion process was confirmed to be an instantaneous proton-coupled 2-electron transfer process. This work opens the opportunity for constructing biomimetic photoelectrocatalytic interface with CO_2 adsorption, activation and conversion to efficient CO_2 resource utilization.

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1. Introduction

Since the industrial revolution, fossil fuel combustion has rapidly increased the atmospheric greenhouse gases levels, leading to the most drastic environmental concern associated with global warming, climate change and seawater acidification [1,2]. In addition, depletion of fossil fuel resources along with unsustainable carbon emission threatens to create an energy crisis. Carbon dioxide (CO_2) as one of the most main greenhouse gases and a kind of potential carbon resource, the conversion of CO_2 into high value-added industrial chemicals and hydrocarbon fuels has been referred to as "reverse combustion" and persistently drawing attention [3].

In nature, the photosynthesis of green leaves can utilize solar energy to convert water and carbon dioxide into carbohydrates and oxygen [4]. This conversion process is an integrated system in which light harvesting, photoinduced charge separation, CO_2 fixation and catalysis are combined. Inspired by natural leaves, many efforts have been devoted to developing artificial photocatalysts or photoelectrocatalysts for achieving direct conversion of sunlight and CO_2 into chemical fuels [5–7]. Up to date, a large number of metal oxide semiconductors, such as TiO_2-based materials [8,9], $ZnCo_2O_4$ [10], $SrTiO_3$ [11] and so forth, have been reported that they have the ability to reduce CO_2 [12]. However, the catalytic efficiency is still not satisfactory due to the CO_2 limited adsorption and activation ability of semiconductor. The relative stability ($\Delta G_f^\theta = -394.4$ kJ mol^{-1}) and high single electron reduction energy (-1.9 eV vs normal hydrogen electrode, NHE) of CO_2 lead to a high reorganization energy of the CO_2 reduction reaction [3]. Activation of CO_2, as the first step in CO_2 reduction, is manifested mostly in the bending of the CO_2 molecule, which could considerably lower the activate energy of CO_2 reduction [1]. As is known, a net transfer of electron density from metal to CO_2 will happen when CO_2 is coordinated to transition metals, which results in an activation state of CO_2. For instance, five possible structures for adsorbed CO_2 on Cu metal was explored [13]. For each kind of structure, CO_2 molecular is activated by structure bent. And molecular catalyst, such as Ru and Re complexes, also tends to activate CO_2 by coordinating CO_2 with the central metal atoms [14].

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Encouragingly, metal–organic frameworks (MOFs) are a class of materials with central metal atoms and have impacts on CO_2 transition from linear state to bent one. A Cu porphyrin based MOF has been proved to deform CO_2 molecule, and the CO_2 photoreduction barrier was lowered [15]. Notably MOFs are a class of three-dimensional (3D) porous hybrid materials, possessing high specific surface area, acceptable CO_2 selective adsorption and separation ability [16–18]. Heterogeneous MOFs catalysts have been applied for CO_2 photocatalysis and electrocatalysis, like CR-MOF [19], NH_2-MIL-125(Ti) [20], NH_2-Uio-66(Zr) [21], cobalt-containing Zeolite Imidazolate Framework (ZIF9) [22,23]. Nevertheless, the catalytic performance of MOFs is far from satisfaction compared to metal oxides due to the low efficiency in electron excitation and charge separation.

Herein, we aim to design a biomimetic photoelectrocatalytic (PEC) platform by introducing MOFs materials to the semiconductor-based PEC system. On one hand, appropriate MOFs will facilitate selective adsorption and fixation of CO_2, enhance surface CO_2 concentrations and lower the activation energy of the reaction while achieving efficient CO_2 reduction reaction on the dynamics. On the other hand, PEC process combines the merits of both electrocatalysis and photocatalysis, proposing a more promising approach to the separate photo-induced charge carriers, reduce the CO_2 activation barrier and promote CO_2 conversion. Recently, efforts have been made to integrate MOFs with inorganic semiconductor to improve the CO_2 fixation and activation of inorganic materials. For instance, Zn_2GeO_4/ZIF-8 hybrid nanorods [24] and $Cu_3(BTC)_2$@TiO_2 core-shell structures [25] have been fabricated and applied to CO_2 photocatalytic reduction with dramatically improved performance in terms of both activity and selectivity. To further enhance PEC activity of CO_2 reduction, we wondered if tight integration between semiconductor and MOFs could effectively promote the PEC performance of materials. It is notable that ZIF9 is a microporous crystalline material composed of Co (II) ions linked to benzimidazolate, with a high specific surface area of $1607\ m^2\ g^{-1}$ and considerable adsorption capacity to gaseous CO_2 of $2.7\ mmol\ g^{-1}$ [26]. It has been used as a co-catalyst for photocatalytic reduction of CO_2 to CO [22,26]. It is interesting that similar to ZIF9, Co_3O_4 as a cobalt-based spinel is not only cheap, abundant and excellent environmental stability, but also has been proved to be effective in selective catalytic reduction of CO_2 to formic acid [27–30]. Therefore, an outstanding biomimetic PEC platform was constructed by a self-template for CO_2 resource utilization, subtly utilizing Co^{2+} in-situ dissolved from Co_3O_4 NWs coordinate with ligand to covalent growth of ZIF9 layer on Co_3O_4 NWs, see Fig. 1A. In which, ZIF9 is in the upper layer as a "stoma" for CO_2 fixation and activation, and Co_3O_4 nanowires (NWs) is in the lower layer as the photoelectrocatalyst. Driven by external electric field and the p-p heterojunction between ZIF9 and Co_3O_4 NWs, photo-induced electrons rapidly transfer to the electrode surface to react with CO_2. And formate was produced in an 8 h photoelectrochemical process with comparatively high conversion rate and its selectivity was up to 99% in liquid products.

2. Experimental section

2.1. Chemicals and materials

Fluorine-doped tin oxide transparent conductive film glass (FTO) was purchased from Nippon Sheet Glass Co. Ltd., and $Co(NO_3)_2$·$6H_2O$, urea, ammonium fluoride (NH_4F), Na_2SO_4, benzimidazole and DMF were all analytical reagent and purchased from Sinopharm Chemical Reagent Co., Ltd., SCRC, China.

2.2. Construction of biomimetic photoelectrocatalytic interface

All the biomimetic PEC interfaces were prepared on FTO. Before experiment, FTO was cleaned via ultrasonication in deionized water, mixed organic solvents (isopropanol: acetone: H_2O = 1:1:1) and ethanol successively.

In a typical solvothermal synthesis of Co_3O_4 NWs electrode, 2.93 g of $Co(NO_3)_2$·$6H_2O$, 0.74 g of NH_4F, and 3.00 g of urea were orderly dissolved in a 70 mL deionized water under magnetic stirring for half an hour. After a homogeneous solution was formed, the solution was transformed to a Teflon-lined stainless steel autoclave in which a FTO glass with $1.5 \times 4.0\ cm^2$ in size was added. The autoclave was heated at 120 °C for 9 h, and then cooled down to room temperature naturally. The as-prepared electrode was rinsed with deionized water three times and then dried in N_2 atmosphere, followed by a calcination process in a N_2 atmosphere at 450 °C for 2 h under a ramping rate of 5 °C.

ZIF9 was prepared as following procedure [22]: firstly, $Co(NO_3)_2$·$6H_2O$ (0.210 g, 7.21×10^{-4} mol) and benzimidazole (0.060 g, 5.08×10^{-4} mol) were orderly dissolved in 18 mL DMF under magnetic stirring. After stirring for 1 h, the resulting solution was transformed to a 25 mL Teflon-lined stainless steel autoclave. The autoclave was then heated to 130 °C from the room temperature with a ramp of 5 °C·min^{-1} in a programmed oven. After a 48 h reaction, the autoclave cooled down to room temperature naturally. Finally, the obtained purple crystal were washed thrice with DMF and dichloromethane respectively, and dried in a vacuum drying box.

The growth of ZIF9 on the Co_3O_4 NWs electrode proceeded via a simple chemical bath route. Typically, 0.18 g benzimidazole was dissolved with a 48 mL mixed solvent of DMF/H_2O at different ratios (4:1, 3:1, 2:1 and 1:1), and then was transformed to a Teflon-lined stainless steel autoclave. The autoclave was maintained at 70 °C for 24 h after a piece of Co_3O_4 NWs electrode was immersed. The atropurpureus ZIF9-Co_3O_4 NWs electrode was obtained and washed thrice with DMF and dichloromethane respectively in order to remove the residual benzimidazole. For comparison ZIF9 electrode was prepared on FTO glass. ZIF9 (3 mg) and Nafion solution (40 μL) were mixed with 1 mL ethanol. After a sonication for 30 min, obtained slurry was spread onto the FTO glass, and the electrode was then dried under vacuum.

2.3. Characterization

The morphology of the as-prepared electrodes were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). X-ray diffractometer (XRD, D/max2550VB3+/PC, Rigaku International Corporation, Japan) was carried out to determine the crystalline structures of Co_3O_4 NWs, ZIF9 and ZIF9-Co_3O_4. Surface elemental analysis of Co_3O_4 and ZIF9-Co_3O_4 were performed on an X-ray photoelectron spectroscopy (XPS, AXIS Ultra HSA, Kratos Analytical Ltd., UK). The binding energies obtained in the XPS were all corrected by referencing the carbon 1 s peak to 284.7 eV. The optical absorption properties were investigated by AvalightDHS UV–vis absorbance measurements (UV-DRS, Avantes, Netherlands).

In situ Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Nicolet 8700, Thermo Fisher Scientific Inc. USA). Before spectra detection, the mercury-cadmium-telluride detector was cooled down to 77 K by liquid nitrogen. All of the samples were treated at 70 °C in a vacuum drying chamber overnight to remove the adsorbed gas molecules. Then the spectra were collected using a sample cell equipped with CaF_2 window at normal temperature and atmospheric pressure (25 °C and 1 atm). CO_2 was inlet into the sample cell slowly and continuously and one hundred