



Enhanced electrochemical reduction of carbon dioxide to formate with in-situ grown indium-based catalysts in an aqueous electrolyte

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ABSTRACT

Electro-catalytic conversion of greenhouse gas CO₂ to value-added chemicals is an attractive way to alleviate the environment and energy crisis. Here we prepared in-situ grown In₂O₃ nanoparticles on carbon black (In₂O₃@C) by a two-step process of coprecipitation and pyrolysis, with high electrocatalytic activity and excellent stability for CO₂ producing formate. The In₂O₃@C catalyst exhibited highest Faradaic efficiency (FE = 87.6%) at 0.9 V vs. RHE in a 0.5 M KHCO₃ electrolyte, with 4.9-fold increase in partial current density compared to In₂O₃ nanoclusters. The reduced Tafel slop (125 mV dec⁻¹) and the increased electrochemical active surface area (EASA) of In₂O₃@C further revealed the positive influence of carbon black on the CO₂ reduction. Additionally, the current density and formate Faradaic efficiency of In₂O₃@C catalyst remained nearly unchanged after electrolyzing 12 h, revealing remarkable stability.

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1. Introduction

The excessive emissions of carbon dioxide (CO₂) is one of the key contributors to some undesirable environmental changes, such as global warming, desertification, ocean acidification, etc. [1] Many strategies have been proposed to address this issue. With the implementation of carbon capture technology, the conversion of CO₂ to value-added chemicals using renewable electricity is an attractive way to alleviate the environment and energy crisis [2]. Among the various products of electrochemical CO₂ reduction reaction (CO₂RR), formic acid (HCOOH) is one of the attractive candidates as a liquid fuel with high volumetric hydrogen density of 53 g of H₂/L, nontoxicity, safety and transportability [3–6]. Thus, it is very significant to develop an electrocatalyst that can reduce CO₂ to high value-added formic acid/formate with high electrocatalytic activity.

To date, numerous catalysts have been developed and applied in the electrochemical reduction of CO₂, such as metal (Au, Ag, Pd, Sn, Bi, In, Cu, Co, Ni, e.g.) [7–20], metal oxide (SnO₂, Cu₂O, Co₃O₄, e.g.) [21–25], and carbon based materials [26–33]. Among these catalysts, indium based catalysts have been proven to have good

electrocatalytic activity for formate, and have drawn a great number of attentions. Recently, Lai et al. synthesized In–Sn alloy catalysts on gas diffusion electrodes (GDEs) with formate Faradaic efficiency of 92% and high stability of more than 22 h [34]. Birdja et al. immobilized indium (III) protoporphyrin IX on different substrates, and they found that a pyrolytic graphite substrate outperformed glassy carbon and boron-doped diamond in terms of CO₂RR selectivity and reactivity, while boron-doped diamond shows the best stability [35]. Sun et al. used In-doped porous carbon as support materials for MoP-based catalyst (MoP@In-PC), which showed high Faradaic efficiency of 96% with current density of 43.8 mA cm⁻² at 2.2 V vs. Ag/AgCl in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate electrolyte [36]. Furthermore, there are also some studies on indium-X bimetal systems for producing CO [37]. Indium-modified copper-based materials are a promising family of multicomponent catalysts for CO₂ reduction with enhanced performance for CO production over a wide variety of architectures [24,38–44]. Although In-based electrodes exhibit high Faradaic efficiency toward CO₂ reduction, a poor current density and production rate are observed during the process of electrolysis. Early on, Kapusta explored the performance of CO₂ reduction to formate on an In electrode and obtained the highest Faradaic efficiency of 95%. However, the overall Faradaic efficiency was very low due to the high over-potential of the reaction [45]. Yoshio et al. reported that the In electrodes achieved a

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high Faradaic efficiency of 93% for producing formate with a low current density of 5.5 mA cm^{-2} [46]. Recently, White et al. investigated the electrocatalytic activity of indium nanoparticles (In NPs), indium oxide nanoparticles (In_2O_3 NPs), indium hydroxide ($\text{In}(\text{OH})_3$) and bulk indium. Although In NPs and In_2O_3 NPs possessed unusually high Faradaic efficiency for CO_2 reduction to formate in aqueous solution at a range of potentials and pH values, the current density for these catalysts were no more than 10 mA cm^{-2} at $1.6 \text{ V vs. Ag/AgCl}$ [47]. Rabiee and Nematollahi found that the nano-cubic mesoporous $\text{In}(\text{OH})_3/\text{carbon black}$ system achieved formate Faradaic efficiency in the range of 70–77% while its current density was only about 5.5 mA cm^{-2} at 1.1 V vs. RHE [48]. Bitar et al. prepared indium coated gas diffusion electrodes (GDE-In/C) with formate Faradaic efficiency of 45% and a current density of 6.5 mA cm^{-2} at $1.65 \text{ V vs. Ag/AgCl}$ [49]. Xia et al. prepared needle-like porous indium foam with formate Faradaic efficiency of 86% and a current density of 5.8 mA cm^{-2} at 0.86 V vs. RHE [50]. Since the CO_2 molecule is fully oxidized and extremely stable, the performance of CO_2 reduction is a kinetically sluggish reduction process [1,51]. Thus, it is very important to develop efficient and robust electrocatalysts that can reduce CO_2 with high electrocatalytic activity.

To identify efficient and environmentally benign catalysts for formate conversion, we focused on carbon black-supported indium oxide ($\text{In}_2\text{O}_3@\text{C}$). Herein, we synthesized $\text{In}_2\text{O}_3@\text{C}$ by a two-step process of coprecipitation and pyrolysis, which was a simple and green method. We explored the optimal content of carbon black of $\text{In}_2\text{O}_3@\text{C}$. Afterward, we compared $\text{In}_2\text{O}_3@\text{C}$ (carbon black ca. 11.6 wt%) with In_2O_3 and $\text{In}_2\text{O}_3/\text{C}$ (mechanical milling with In_2O_3 and carbon black) on electrocatalytic activity, in terms of formate Faradaic efficiency, current density, Tafel slope as well as electrochemical active surface area (EASA). The scheme of the experimental process is shown in Fig. 1.

2. Experimental

2.1. Materials

Indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, 99.5%) and ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%) were from Sinopharm Co., Ltd. Black carbon (Vulcan XC-72R) was from Cabot Corporation. Nitric acid (HNO_3 , 68%) was from Shanghai Hushi Laboratorial Equipment Co., Ltd. Ethanol was from Tianjin Chemical Factory. All the other

reagents were analytically pure and used as received. The carbon black was first acidized with 5 M nitric acid at 90°C for 8 h in a flask under reflux condition, in order to improve its hydrophilicity and remove impurities. The treated black carbon was washed and dried at 80°C before used.

2.2. Synthesis of $\text{In}_2\text{O}_3@\text{C}$ catalysts

$\text{In}_2\text{O}_3@\text{C}$ catalyst was prepared by a two-step process of coprecipitation and pyrolysis [43]. Briefly, 763.84 mg $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ was dissolved in ethanol-water solution (volume ratio ca. 3:1) under vigorously stirring. Subsequently, 100 mg carbon black was dispersed into the solution with the aid of sonication for 10 min. The suspension was stirred at room temperature for 30 min. Afterward, a certain amount of ethanol-ammonia solution (volume ratio ca. 3:1) was added dropwise into the suspension. At the same time, the resulting suspension was placed in preheated water bath, vigorously stirring at 80°C for 20 min. The precipitates were washed with ethanol-water solution (volume ratio ca. 1:1) through centrifugation, and dried in an oven at 80°C overnight. Finally, the $\text{In}_2\text{O}_3@\text{C}$ was obtained after calcination at 300°C under air atmosphere for 3 h. We prepared the three In_2O_3 based materials, labeled as $\text{In}_2\text{O}_3@\text{C}_{6.1}$, $\text{In}_2\text{O}_3@\text{C}_{11.6}$ and $\text{In}_2\text{O}_3@\text{C}_{34.4}$. The subscript 6.1, 11.6 and 34.4 corresponds to the weight percent of carbon black in the catalyst precursor.

2.3. Synthesis of In_2O_3 catalysts

The In_2O_3 catalyst was prepared as above without adding carbon black. Briefly, 763.84 mg $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ was added into ethanol-water solution (volume ratio ca. 3:1), vigorously stirred at room temperature for 30 min. Subsequently, a certain amount of ethanol-ammonia solution (volume ratio ca. 3:1) was added dropwise into the above solution. The mixture was vigorously stirred at 80°C for 20 min under water bath. After this, the precipitates were washed with ethanol-water solution (volume ratio ca. 1:1) through centrifugation, and dried in an oven at 80°C overnight. Finally, the In_2O_3 was obtained after calcination at 300°C under air atmosphere for 3 h.

2.4. Synthesis of $\text{In}_2\text{O}_3/\text{C}$ catalysts

$\text{In}_2\text{O}_3/\text{C}$ was synthesized via mechanical mixing of In_2O_3 and carbon black. Briefly, as-prepared In_2O_3 were mixed with carbon black, and then the mixture was grounded in an agate mortar for 30 min. The molar ratio of indium and carbon black in $\text{In}_2\text{O}_3/\text{C}$ is close to that of $\text{In}_2\text{O}_3@\text{C}_{11.6}$.

2.5. Preparation of electrode

A substrate electrode was fabricated by carbon cloth ($1 \times 2.2 \text{ cm}$, 0.03 cm), which was sonicated in 5 M hydrochloric acid, acetone and deionized water for 15 min, successively. Firstly, 10.0 mg sample was mixed with the 90 μL of 5 wt% Nafion and 450 μL isopropanol with the aid of sonification, and then the mixture was coated on the electrode to achieve an amount of 1 mg cm^{-2} . Subsequently, the obtained electrode were dried at room temperature overnight.

2.6. Electrochemical experiments

All the electrochemical experiments were carried out in a gas-tight H-cell, which was separated by a Nafion N117 membrane. The working electrodes were prepared by coating $\text{In}_2\text{O}_3@\text{C}$ or $\text{In}_2\text{O}_3/\text{C}$ on the surface of carbon cloth. The Ag/AgCl (saturated

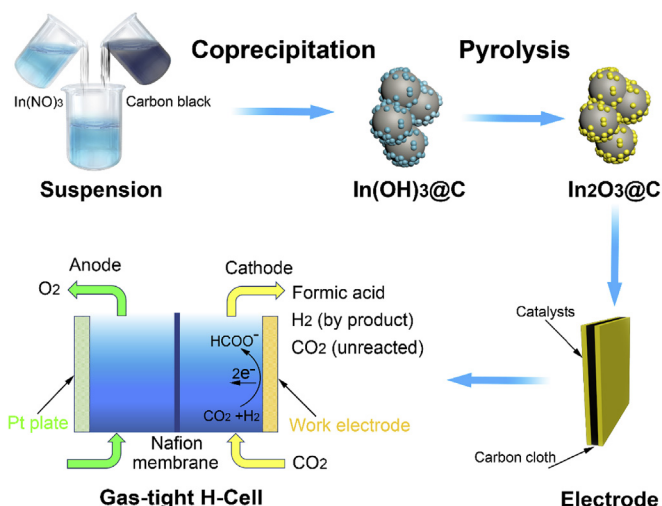


Fig. 1. Scheme of the experiments process and an electrolysis reaction unit.

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