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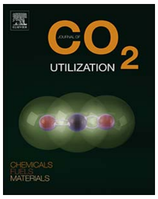

Cu/TiO_2 nanoparticles modified nitrogen-doped graphene as a highly efficient catalyst for the selective electroreduction of CO_2 to different alcohols

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ABSTRACT

The construction of an efficient and robust catalyst for the electrochemical reduction of carbon dioxide into energy-rich products has recently received considerable attention. Herein, a Cu/TiO_2 nanoparticles modified nitrogen-doped graphene ($Cu/TiO_2/NG$) carbon material is fabricated for the selective reduction of CO_2 into different alcohols. We found the $Cu/TiO_2/NG$ nanocomposite across a range of potentials for the electroreduction of CO_2 exhibits dual catalytic ability, possessing an outstanding ability to produce methanol (reaching a maximum faradaic efficiency of 19.5% at a potential of −0.20 V vs. the reversible hydrogen electrode (RHE)) and a capability to produce ethanol (with a high faradaic efficiency up to 43.6% at −0.75 V vs. RHE). In addition, the $Cu/TiO_2/NG$ composite shows remarkable stability and reusability at both reductive potentials in the electrochemical process. The designed $Cu/TiO_2/NG$ composite may offer a new simple method based on earth-abundant metals to construct robust electrocatalysts for CO_2 reduction.

1. Introduction

Over the past few decades, the excessive combustion of fossil fuels has rapidly increase the concentration of CO_2 to the atmosphere, leading to serious environmental concerns, such as global warming and sea level rise [1,2]. CO_2 capture and conversion to various liquid or gaseous products has been proposed as a potential and feasible method to maintain a carbon balance when combined with renewable energy sources, which can effectively address these issues [3,4]. To achieve this goal, the electrochemical reduction of CO_2 has been explored as a simple and efficient technical solution to mitigate atmospheric CO_2 through utilizing renewable energy sources, such as wind and solar energy [5,6]. Unfortunately, CO_2 is a stable molecule and is difficult to reduce to organic fuels [7]. This has encouraged us to design some efficient catalysts, which should ideally possess excellent faradaic efficiencies (FEs), sufficiently low overpotentials and high selectivities. In the present decades, a wide range of materials, including transition metals, [8,9] transition metal oxides, [10,11] metal complexes, [12–14] metal alloys [15,16] and heteroatomic carbon materials [17,18] have been investigated for the electroreduction of CO_2. Compared with other materials, carbon materials, due to their high surface area, excellent electrical conductivity and flexible/easily modified structure, are promising and desirable materials for CO_2 electroreduction.

Graphene-based carbon materials, especially nitrogen-doped graphene (NG), due to their low-cost, high surface areas and significant electrocatalytic activity, are worthy electrode choices, which are being rapidly researched for energy and environment applications [19,20]. Recently, Wu et al. [21] noted that an N-doped three-dimensional graphene foam requires negligible onset overpotential (−0.19 V) for CO_2 reduction to CO, and it exhibits superior activity over Au and Ag, achieving a similar maximum FE for CO production (~85%) at a lower overpotential (−0.47 V). Ensafi et al. [22] used a Pt@nitrogen-doped reduced graphene oxide for the direct electrochemical conversion of CO_2 to methanol at an applied potential of −0.30 V (vs. Ag/AgCl) and a pH equal to 2.0 with a high FE (41%) that operates in water and at ambient temperature and pressure.

This has inspired us to explore new NG-based catalysts with high catalytic activity and high selectivity for the electroreduction of CO_2. Copper, as a distinguished and low-cost metal catalyst in the field of the electrochemical reduction of CO_2, can convert CO_2 into hydrocarbons in aqueous solution [23]. Achieving high efficiency in the Cu-catalyzed CO_2 reduction process requires Cu catalysts with sufficient active sites [24]. Numerous efforts have been made to develop Cu electrodes with splendid electrocatalytic ability for CO_2 reduction. For example, copper

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electrodes, fabricated using a pulse electrodeposition method, exhibited a high FE of 85% at an applied potential of −2.8 V vs. the saturated calomel electrode (SCE) and enhanced partial current density (J, 38 mA/cm^2) for methane [25]. Jaramillo's group reported that copper as an electrocatalyst has the unique ability to produce a total of 16 different CO_2 reduction products across a range of potentials in the CO_2 electroreduction process [26]. Additionally, Yang's group conducted investigations on the electrocatalytic CO_2 reduction to methane with improved performance on ultrathin 5-fold twinned Cu nanowires [27].

Moreover, TiO_2, due to its peculiar chemical and physical behaviors, [28,29] has been widely investigated in recent years for versatile applications including photocatalysis for hydrogen production [30], solar cells [31], sensors [32], self-cleaning [33] and drug delivery [34]. Nevertheless, considerably fewer reports have been focused on the use of TiO_2 as a co-catalyst or support material in the electroreduction of CO_2 [35]. Notably, TiO_2 can act as a redox electron carrier to facilitate various reduction reactions, including CO_2 conversion [36]. Additionally, the TiO_2 surface has been reported to assist in CO_2 adsorption, where it may stabilize CO_2 reduction intermediates and also be capable to reduce the overpotential [37]. We previously reported various Cu electrocatalysts supported on titanium dioxide (Cu/TiO_2) for the electroreduction of CO_2 with reasonable FEs for ethanol [38].

In the present work, a Cu/TiO_2 nanoparticles (NPs) modified NG substrate was synthesized and used as an electrocatalyst for the reduction of CO_2 to alcohols in aqueous media. With this system, we measured different CO_2 reduction products by controlling the potential over a wide range on the same Cu/TiO_2/NG catalyst. The catalyst displayed incomparable performance with a low overpotential of 0.12 V for the production of methanol and a maximum FE of 19.5% at a potential of −0.20 V vs. the reversible hydrogen electrode (RHE). And the catalyst is capable of producing ethanol with a high FE up to 43.6% at an overpotential of 0.84 V. In addition, the Cu/TiO_2/NG composite had superior stability with a high efficiency retained for 20 h in the electrochemical process.

2. Experimental

2.1. Chemicals

$Cu(NO_3)_2{\cdot}3H_2O$, sodium citrate, hydrazine hydrate and TiO_2 (AR grade) were purchased from Sinopharm Chemical Reagent Co. (SCR) with 99% purity. NG was provided by Beijing HWRK Chem Co., Ltd (3.0–5.0 wt%). Carbon paper (CP, HCP010) was purchased from Shanghai Hesen Electrical Co. All the chemicals were used without further purification.

2.2. Materials characterization

Crystal-phase X-ray diffraction (XRD) patterns were recorded using an Ultima IV X-ray powder diffractometer equipped with Cu Kα radiation (k = 1.5406 Å).

Microstructure and energy dispersive X-ray (EDX) mapping were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK).

Transmission electron microscope (TEM) patterns were recorded by TECNAI G^2F30 Transmission Electron Microscope.

The X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing.

All the electrochemical experiments were performed using a CHI 660C electrochemical station (Shanghai Chenhua Instrument Co. Ltd).

2.3. Materials synthesis

In our work, we used a simple, inexpensive and novel procedure to synthesize a series of graphene-based materials. As an example, Cu/TiO_2/NG was synthesized by the following procedure: 10 mg of NG was first dispersed into 60 mL of deionized water by sonication to yield a homogeneous NG suspension. Then, 3.57 mg of TiO_2 was added into the turbid solution, and the solution was sonicated for 30 min. Then, 5.73 mg of $Cu(NO_3)_2{\cdot}3H_2O$ was poured in the above solution. To stabilize Cu^{2+}, sodium citrate was added. Hydrazine hydrate was also dropwise added at room temperature to reduce Cu^{2+}. After stirring the solution gently overnight, it was undergone those process: centrifuged, washed with deionized water, and dried in a vacuum oven at 80 °C for 4 h. Moreover, Cu/NG and TiO_2/NG were prepared using the same process, except for the absence of TiO_2 or $Cu(NO_3)_2{\cdot}3H_2O$ in the solution, respectively.

2.4. Electrochemical study

To prepare the Cu/TiO_2/NG/CP electrode, 2 mg of the above prepared Cu/TiO_2/NG was suspended in 40 μL of deionized water with 20 μL of a Nafion®117 dispersion (5 wt%) to form a homogeneous ink assisted by ultrasonication. Then, the ink was spread onto the CP surface by a micropipette and then dried under room temperature. The loading of the Cu/TiO_2/NG catalyst was 1.0 mg/cm^2.

Electrolysis experiments were conducted at 25 °C in a gas diffusion electrode cell, which consisted of a cathode (the Cu/TiO_2/NG/CP electrode mainly involved in CO_2 reduction and the hydrogen evolution reaction), an anode (platinum plate auxiliary electrode, inducing water oxidation), and an SCE as the reference electrode. In the experiments, the cathodic and anodic compartments were separated using a Nafion® 117 proton exchange membrane. A 0.2 M KI aqueous solution, as the electrolyte, was used in the cathode and anode compartments, respectively. Under continuous stirring, CO_2 was bubbled through the catholyte for 20 min before electrolysis. Then, potentiostatic electrochemical reduction of CO_2 was continuously carried out with CO_2 bubbling.

Linear sweep voltammetry (LSV) measurements were carried out in a single compartment cell with a three-electrode configuration, which consisted of the Cu/TiO_2/NG catalyst coated onto a glassy carbon (GC) electrode as the working electrode, a platinum gauze auxiliary electrode, and an SCE reference electrode. The electrolyte was bubbled with N_2 or CO_2 for at least 30 min to form a N_2- or CO_2- saturated solution. The LSV measurements in gas-saturated electrolyte were conducted in 0.2 M KI solution at a scan rate of 100 mV/s. J was normalized to electrochemically active surface area (EASA, see supporting information for details). The potential, measured against the SCE electrode, was converted to the potential versus RHE according to the equation:

$$E\ (RHE) = E\ (SCE) + 0.059 \times pH + 0.241.$$

2.5. Product analysis

Liquid phase products were analyzed by ^1H NMR spectroscopy recorded on an Ascend 400 (400 MHz, Bruker, Germany) spectrometer in D_2O with Me_4Si as an internal standard.

3. Results and discussion

The structural characterizations of Cu/TiO_2/NG, Cu/NG, TiO_2/NG and NG were performed by XRD, as shown in Fig. 1A. As seen in the XRD patterns of the four different composites, diffraction peaks at 43.3°, 50.4° and 74.1° are ascribed to Cu (111), (200) and (220) reflections, respectively, which are represented by dashed lines. The typical diffraction peaks of TiO_2 are expressed by solid lines. The