Direct experimental evidence and low reduction potentials for the electrochemical reduction of CO_2 on fluorine doped tin oxide semiconductor

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ABSTRACT

This paper reported the electrochemical reduction of CO_2 on fluorine doped tin oxide (FTO) semiconductor, which was performed in CO_2-saturated 0.1 M $NaHCO_3$ solution using cyclic voltammetry. It was found that a well-defined reduction peak at -0.39 V (vs.SCE) occurs on the cyclic voltammogram (CV), which is direct evidence for the electrochemical reduction of CO_2. This result demonstrates that the bare FTO glass electrode possesses good electrocatalytic ability towards CO_2 reduction under lower applied potentials. The result from the reduction peak current as a function of scan rate provided strong evidence for the reaction mechanism, i.e., the reduction of CO_2 is performed via adsorption of CO_2 on the FTO electrode surface and then CO_2 is reduced. The main products obtained under a constant potential electrolysis of -0.55 V are methanol and formate, the mass ratio of formate to methanol is approximately 0.54 to 1 based on the result of ^1H NMR.

1. Introduction

The combustion of fossil fuels has resulted in an increase in the evolution of CO_2 to atmosphere, which is related to the climate change. Thus, reducing CO_2 production and converting CO_2 to useful materials like formic acid and methanol are very important. Generally, CO_2 conversion can be performed by using chemical methods [1,2], photocatalytic [3,4] and electrocatalytic reductions [5–8]. Among them, electrocatalytic reduction has attracted great attention for its advantages such as the reaction rate can be controlled by applied potentials and product selectivity can be achieved via choosing the kind of electrode materials [9–11] and applied potentials. Many authors demonstrated that the reaction kinetics, reaction mechanism, product selectivity and energy efficiency for CO_2 reduction are related to electrode materials [12–25], which were reviewed extensively and deeply by Qiao et al. [26]. Authors in this review pointed out great challenges and research directions in CO_2 electrocatalytic reduction in the future, which inspired us to study the electrochemical reduction of CO_2.

Even though the successful preparation of the various electrode materials for the electrochemical reduction of CO_2 has been made, and the electrochemical reduction of CO_2 has got great achievements, challenges still remain in low reduction potential, product selectivity, avoiding hydrogen evolution, and direct electrochemical evidence for CO_2 electrochemical reduction.

To our knowledge, little is known about feature cyclic voltammogram (CV) for CO_2 reduction on metal electrodes, i.e., no reduction

peak of CO_2 was detected on the CV, only the reduction current increased quickly with increasing negative potential value, accompanied with hydrogen evolution [26]. In this work, we first reported the electrochemical reduction behavior of CO_2 on the bare fluorine doped tin oxide (FTO) glass in the aqueous solution and provided observable experimental evidence for the electrochemical reduction of CO_2 using cyclic voltammetry method.

2. Experimental

Sodium hydrogen carbonate was received from Sinopharm Chemical Reagent Company and was analytical reagent grade. FTO glasses were purchased from Huanan Xiangchen Science and Technology Company. The pH values of 0.1 M $NaHCO_3$ solution were determined with a PXD-12 pH meter.

A conventional three-electrode cell, containing a bare FTO glass working electrode, platinum foil counter electrode and saturated calomel reference electrode (SCE), was used for the electrochemical experiments that were performed on a CHI 407 workstation. High purity CO_2 was used for its electrochemical reduction. The flow rate of CO_2 was controlled at $1.0\, L\, min^{-1}$. The solution was deaerated by bubbling CO_2 for 20 min prior to measurements and then a continuous flow of CO_2 was maintained over the tested solution during the experiment process. The analysis of product solution for the electrochemical reduction of CO_2 was carried out using a Shimadzu 2550 double-beam spectrophotometer and ^1H NMR spectrum of the product solution was
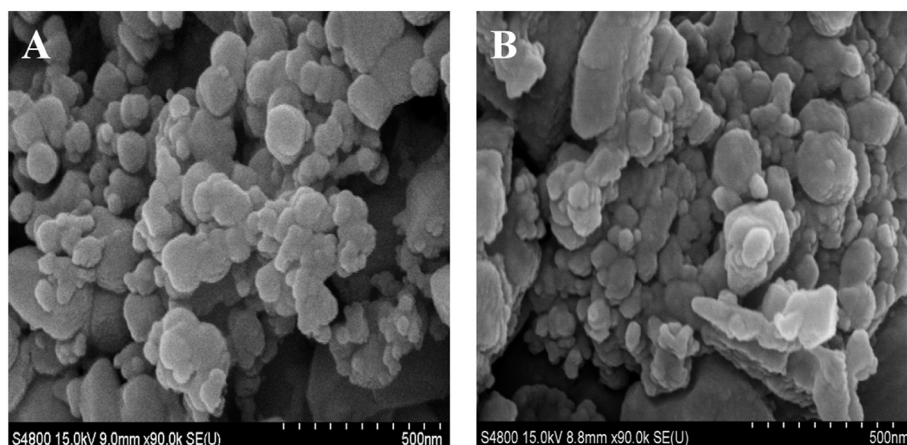
Fig. 1. SEM images of FTO glass, (A) before use in CO_2 electrochemical reduction, (B) after consecutive 50 cycles use in CO_2 electrochemical reduction.

recorded on a 600 MHz Bruker spectrometer. The images of the bare FTO glasses were observed by a field emission scanning electron microscopy (SEM) S4800 II FE-SEM. X-ray photoelectron spectroscopy (XPS) spectrum of the bare FTO glass was collected on a Thermo ESCALAB 250 spectrometer with an Al $K\alpha$ X-ray source (1486.6 eV). The crystal structure of the bare FTO glass was measured with an X-ray diffraction (XRD) using a D8 Advance (Bruker) instrument with Cu $K\alpha$ radiation (λ = 0.1541 nm).

3. Results and discussion

3.1. Characterization of the bare FTO glass

Fig. 1A and B display images of FTO glass before use in the electrochemical experiments and after consecutive 50 cycles of the bare FTO glass in the CO_2-saturated 0.1 M $NaHCO_3$ solution with pH 6.95, in a scan potential region of −0.80 and 0.60 V, respectively, clearly the images of FTO glass surface were changed hardly after use in the electrochemical reduction of CO_2. Fig. 2A and B are the XPS spectra of a bare FTO glass before use in the electrochemical reduction of CO_2 and after consecutive 50 cycles in the CO_2-saturated 0.1 M $NaHCO_3$ solution, which show a very weak XPS signal of fluorine, indicating that only a little amount of F was doped into SnO_2. In addition, the strong XPS signals of Sn3d and O1s were detected. It is clearly that the XPS spectrum of bare FTO glass after use in the electrochemical reduction of carbon dioxide was also charged hardly compared to that before use in the electroreduction of CO_2. Fig. 2C shows the XPS signal of fluorine in the FTO glass, its peak occurs at approximately 686 eV. The results of following experiments demonstrated that the bare FTO glass can be repeatedly used for the electrochemical reduction of CO_2.

The XRD result of the bare FTO glass is shown in Fig. 3. The main peaks in Fig. 3 occur at 26.585, 37.950 and 51.768 degree, which are assigned to the (110), (200), and (211) planes of SnO_2, respectively. These peaks completely correspond to SnO_2 (JCPDS no.70–4175) standard diffraction peaks, indicating that fluorine doped into SnO_2 hardly affects on the crystal structure of SnO_2 because of a little amount of fluorine in SnO_2 based on the XPS result.

3.2. Experimental evidence for the electrochemical reduction of CO_2

Cyclic voltammetry was used to study the electrochemical reduction of CO_2. Before measurements, the bare FTO glass electrode in the solutions was hold at −0.80 V for 10 s, and then the potential was scanned from −0.80 V to 0.60 V. Fig. 4A shows the CV of the bare FTO electrode in 0.1 M $NaHCO_3$ solution with pH 8.79 in nitrogen atmosphere, in which, an oxidation peak and a reduction peak occur at −0.41 and −0.61 V, respectively. Fig. 4B was obtained under the same

experimental conditions as those in Fig. 4A, but the potential was scanned from 0.60 to −0.80 V. It is clear that the anodic peak potential and cathodic peak potential in Fig. 4B are hardly changed compared to those in Fig. 4A, indicating that the potential scanning direction does not affect the redox properties of the bare FTO electrode in the nitrogen atmosphere. The reduction peak at −0.61 V is attributed to the reduction of SnO_2 in the FTO glass electrode, which results in doping of cations into FTO glass since no any redox couple in the solution. And the oxidation peak at −0.41 V would be caused by Sn oxidation, which results in dedoping of cations of the bare FTO electrode. The results in Fig. 4 are similar to that of the FTO electrode in 0.30 M Na_2SO_4 solution [27]; it seems that HCO_3^- in the solution cannot be reduced on the FTO glass electrode in this potential region. However, the recent reports demonstrate that HCO_3^- ions can be transformed into aqueous CO_2 near the bismuth-based electrode surface [28] and the oxide-derived Pb electrodes can convert CO_2 derived from HCO_3^- decomposition to HCO_2^- [29]. The result from Fig. 4 indicates that the bare FTO would be turned to n-type semiconductor at such high negative potential.

Fig. 5A presents the CVs of the FTO glass electrode in CO_2-saturated 0.1 M $NaHCO_3$ solution with pH 6.95, which were recorded in the positive-going scan from −0.80 to 0.6 V. Clearly, an anodic peak and a cathodic peak are observed at −0.26 and −0.39 V, respectively; so the difference between E_{pa} and E_{pc} (ΔE_p) is 0.13 V. Fig. 5A demonstrates that both anodic and cathodic peak currents decrease first from the first cycle (curve 1) to tenth cycle (curve 3), and then hardly changes in the subsequent cycling. The result in Fig. 5A indicates that the electrochemical behavior of the FTO electrode in the solution of CO_2 is quite different from that in the solution free of CO_2 in Fig. 4. The main difference between them is that a reduction peak at −0.61 V in Fig. 4 shifts to −0.39 V in Fig. 5A, accompanied with the marked decrease in the reduction peak current of the FTO electrode in the presence of CO_2; in addition, the CV in N_2-saturated solution occurs an anodic peak at −0.41 V, however this peak shifts to −0.26 V in CO_2-saturated solution. This discrepancy is caused by CO_2 in the solution. The reduction peak at −0.39 V may be caused either by the direct reduction of CO_2 on the bare FTO electrode and maybe also caused by doping of cations or by the reduction of the products formed during the beginning reduction process of CO_2 since the starting scan potential was set at −0.80 V for 10 s before scanning and then scanned from −0.80 V towards the positive potential direction.

To confirm the attribution of the reduction peak in Fig. 5A, the onset potential was set at 0.60 V, and then the potential was scanned from 0.60 V towards the negative potential direction, which is shown in Fig. 5B. Comparison of Fig. 5B and A shows that a current plateau around 0 V occurs in curve 1 of Fig. 5B instead of the oxidation peak in Fig. 5A; in addition, a reduction peak occurs at −0.41 V in curve 1 of Fig. 5B for the first cycle, however, the reduction peak for the first cycle