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Synthesis of Sn catalysts by solar electro-deposition method for electrochemical CO_2 reduction reaction to HCOOH

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ABSTRACT

The electrochemical conversions of CO_2 to valuable products have gained much interest to mitigate the increasing CO_2 concentration in the atmosphere. Selective syntheses of differently shaped tin (Sn) catalysts of rod, rectangular sheet, and dendrite structures were reported here using a new solar electro-deposition method, and their catalytic performance was investigated for the electrochemical reduction of CO_2 to liquid fuel in an electrolyte solution of CO_2 dissolved pure water. The crystal orientation and structural properties of the prepared Sn catalysts were investigated by XRD and SEM analyses. The selective formation of HCOOH on the prepared Sn electrocatalyst was observed with high faradaic efficiency and HCOOH formation rate over the rod shaped Sn catalysts, resulted in a maximum faradaic efficiency of 94.5% at 1.6 V vs Ag/AgCl and a maximum formation rate of about 0.5 mol/g_{cat} h at 2 V vs Ag/AgCl. The present work may open up a new approach for a selective catalyst synthesis of known structural properties for effective CO_2 reduction reaction.

1. Introduction

Rapidly rising energy consumption due to the society advancement is expected to be doubled by 2050 [1–4]. During the combustion process in the extraction of energy from fossil fuels, a large amount of CO_2 is evolved in the atmosphere which causes a global rise in temperature [5,6]. This emission of CO_2 can be decreased by utilizing the CO_2 itself as other carbon source in various applications of fuel production [7–9]. Electrochemical reduction reaction of CO_2 has gained attraction for the last few decades since this process can simultaneously decrease the CO_2 concentration and produce fuels as well [10–13]. Various products are generated from the electrochemical process depending on catalyst material, electrolyte, pH and applied conditions in the reaction [14–17]. Therefore, the main challenge in this field of research is the development of catalyst that can selectively convert the CO_2 to fuels [18–20]. Ohya et al. studied the CO_2 reduction on copper catalysts in different electrolytes for different product formation [21]. Among the several products reported, formic acid (HCOOH) is one of the valuable products as it has wide applications in chemical industries and direct formic acid fuel cells [22–24]. Because, the catalysts for the electrochemical reduction reaction of CO_2 need to show high faradaic efficiency, some catalysts such as Pb, Sn, Zn, Hg, Cd and Pd have been reported for the HCOOH production [25–29]. By considering the cost and environmental aspects, there is a significant requirement to develop an efficient catalyst with high selectivity and faradaic efficiency [30,31]. Therefore, non-noble, eco-friendly, and low-cost Sn metal is considered in the current research for the efficient electrochemical CO_2 reduction.

In the present work, Sn catalyst is selected for the HCOOH production with high faradaic efficiency. To the best of our knowledge, no studies have been reported for the synthesis of Sn catalysts by a solar electro-deposition method. This method has wide applications compared with other processes [32,33], because this process is inexpensive with use of solar energy and time to synthesize the catalysts is very short. More importantly, very high purity of products can be obtained due to uses of merely metal-based electrolyte solution during its synthesis. Morphology of catalyst plays a vital role in the product selectivity with high faradaic efficiency [34–36]. In this end, three different morphologies of Sn catalysts were prepared by using the solar electro-deposition method. The electrocatalytic activity of the synthesized Sn catalysts was studied in a three-electrode system for the electrochemical CO_2 reduction by varying catalyst loading, applied voltage and reaction time. The present study could help in synthesizing the catalysts of different morphology using an efficient solar electro-deposition method in various electrochemical applications.

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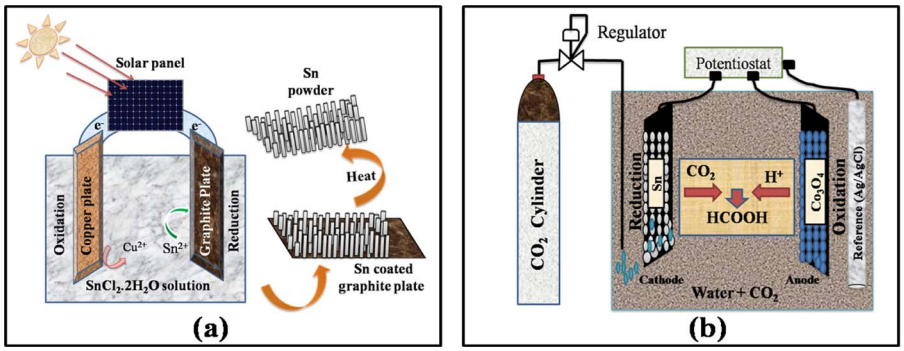

Fig. 1. Schematic illustration of the experimental setup for the (a) preparation of Sn catalysts by solar electro-deposition method, (b) electrochemical CO_2 reduction reaction.

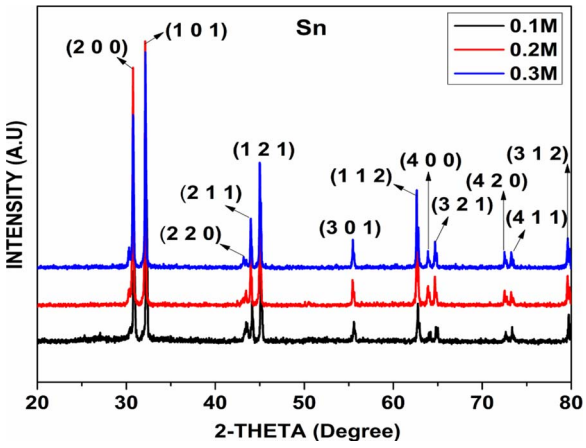

Fig. 2. XRD patterns of the Sn catalysts synthesized at different electrolyte concentrations The average particle size was calculated using the Scherer formula from the diffraction peak of Sn (101). The particle sizes were estimated to be 0.1 M (54.4 nm), 0.2 M (59.2 nm) and 0.3 M (58.1 nm), respectively.

2. Experimental

2.1. Synthesis of Sn catalysts by solar electro-deposition method

The different morphologies of Sn catalysts were synthesized by electro-deposition method assisted by photovoltaic cell. The electrochemical reduction of Sn precursor was performed in a two-electrode system that was conjugated with copper oxidation process (Fig. 1a). The experimental setup consists of copper foil acting as the anode and graphite plate as the cathode (2 × 3 cm^2, Bansuk Carbon, South Korea), whose electrodes were connected with a solar panel (9 V, 220 mA, Scipia, South Korea). The synthesis reaction was individually conducted in 0.1, 0.2 and 0.3 M $SnCl_2.2H_2O$ (Sigma Aldrich) solutions. The synthesis was finished within 3 min. The electro-deposition of Sn catalyst took place on the graphite plate surface via the reduction of Sn ions present in the electrolyte. The prepared metallic Sn catalyst was washed in millipore water and followed by heating at 80 °C for 30 min to obtain the pure Sn catalyst. The morphologies of the Sn catalysts were examined by scanning electron microscopy (SEM; Jeol; JSM-6510). The X-ray diffraction patterns were recorded using an X-ray diffractometer (XRD; Rigaku Corporation; Ultima IV) between 10° to 80° of 2θ.

2.2. Fabrication of electrodes for the electrochemical CO_2 reduction

The Sn- and Co_3O_4-coated graphite plates were fabricated for the cathode and anode electrode, respectively. For a typical preparation process, graphite plate (2 × 2 cm^2), a binder solution (200 µl) and catalysts were used. The binder solution was a blend of 1:5 ratio of Nafion (Sigma Aldrich) and iso-propyl alcohol (Fischer). The catalyst ink was made by sonication of the Sn metal catalyst with the binder solution for 30 min. Different proportions of Sn catalyst (2 and 4 mg) with the binder solution were coated over the graphite plate at 70 °C to obtain the catalyst loadings of 0.5 and 1 mg/cm^2, respectively. Similarly, the anode was made at 1.5 mg/cm^2 with Co_3O_4 (Alfa) and the binder solution, which was used for all experiments. The coated electrode was dried for 30 min at 80 °C to obtain the final form of electrode.

The electrochemical reduction of CO_2 was carried out in a three-electrode glass cell fabricated with the prepared Sn and Co_3O_4 electrodes (Fig. 1b). In all experiments, 100 ml of millipore water was bubbled by CO_2 gas stream for 1 h to prepare the fully CO_2 saturated solution. The potentiostatic electrolysis was carried out with the prepared electrodes and a reference electrode (Ag/AgCl) in the CO_2 saturated solution. The reactions were conducted for 2.5 h with 0.5 h interval at the applied voltages (1.6, 1.8, and 2.0 V) in the electrolyte solution. The analysis of products was carried out by using gas chromatography (GC; Agilent G1530A, TCD-detector). A solution of 1 µl to be analyzed was injected into the Porapaq-Q column and confirmed the formic acid as the only product formed in the applied conditions. The formation rate of formic acid was also reported at the applied voltages in the present experimental conditions.

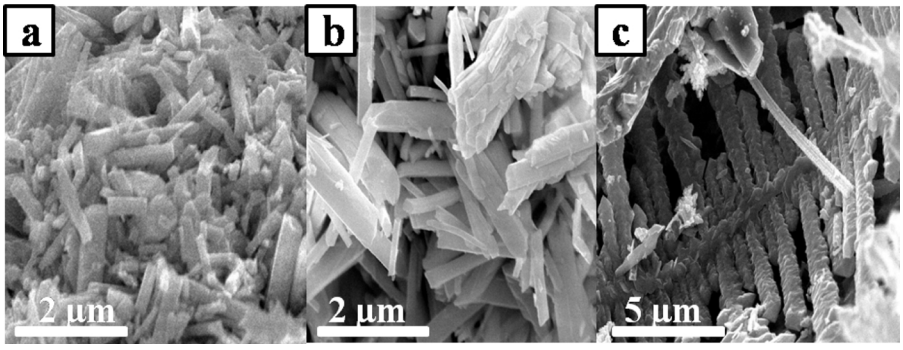

Fig. 3. SEM images of Sn catalyst samples synthesized at different electrolyte concentrations (a) 0.1 M (tiny rods), (b) 0.2 M (rectangular sheets) and (c) 0.3 M (dendrites).