Selective and Efficient Electrochemical Conversion of Carbon Dioxide into Formic Acid Using Metal-Based Alloy Nanocatalyst

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Abstract - The electrochemical reduction of CO_2 has recently emerged as one of the most promising techniques to produce valuable liquid fuel, thus providing new avenues for energy storage, as well as reducing the impact of global warming caused by CO_2 emissions. In this work, a drop-casting technique was used to deposit a metal-based alloy on acid-treated Sn foil, which was then evaluated as an electrocatalyst for the electrochemical conversion of carbon dioxide into formic acid. The metal-based alloy was characterized via SEM, TEM, XRD, and XPS techniques. The metal-based nanocatalyst demonstrated exceptional catalytic activity, achieving a noteworthy 90% Faradaic efficiency and -50 mA cm^{-2} current density at -1.8 V versus Ag/AgCl. Moreover, it demonstrated a remarkable capacity for generating formic acid at a rate of 1271 ppm cm^{-2} h^{-1}, surpassing the majority of the electrocatalysts reported in the literature. The circular-shaped NPs with a particle size of 10-20 nm have a large number of active sites and a notably large surface area. The effective electrochemical conversion of carbon dioxide into formic acid was greatly aided by rapid electron transport. Furthermore, the response surface approach was employed to optimize the electrochemical conversion process. Overall, the results obtained from this work demonstrate that the metal-based alloy catalysts can be a promising candidate for efficient carbon dioxide conversion into formic acid.

Keywords: CO_2 reduction; Electrochemical conversion; Metal-based alloy; Formic acid

1. Introduction

The carbon dioxide as a greenhouse gas in the atmosphere has increased significantly in recent years, making it more difficult to maintain the carbon balance in nature [1]. The world is currently experiencing an energy crisis as a result of the worldwide shortage of energy supplies brought on by the over-exploitation of resources and fast economic development [2]. It's interesting to note that recycling carbon dioxide by converting it into high-value items can do more than just slow down global warming; it can also recycle waste into wealth by producing clean energy [3]. Currently, thermal catalytic reduction, photocatalytic reduction, electrocatalytic reduction, and biological reduction are the primary conversion techniques for carbon dioxide resource utilization. Among these methods, carbon dioxide electrocatalytic reduction can convert harmful carbon dioxide into value-added chemical compounds in mild conditions by directly utilizing electrical energy [4]. Moreover, the response device's functioning is straightforward to manage, and it doesn't require high pressure and temperature. Carbon dioxide electrochemical reduction is believed to be the most promising technology with advantages for the economy and environment [5]. Despite extensive research, the electrochemical reduction of carbon dioxide in aqueous medium at room temperature still confronts numerous challenges and has not yet reached the industrial level [6]. Because carbon dioxide is a thermodynamically stable compound, its reduction requires a high activation overpotential and produces very slow reaction kinetics. Furthermore, the carbon dioxide conversion process might involve a competitive HER, which is detrimental to the creation of reduced carbon compounds. Furthermore, poor catalyst performance results in poor product selectivity. Finding the catalysts with high selectivity and chemical activity is so crucial. The electrochemical reduction of carbon dioxide in aqueous solutions can yield a variety of compounds, including formate, CO, methanol, methane, ethanol, ethylene, and acetic acid [7]. There are benefits to using liquid materials for handling, storing, and transporting [8]. Among these, formate is a highly energy-dense liquid fuel that finds extensive use in the chemical and pharmaceutical industries. It is also regarded as a valuable hydrogen carrier for fuel cell applications. However, the process of producing formate pollutes the environment and comes at a rather significant cost both domestically and internationally. Additionally, some researchers determined that formate has a high commercial value after evaluating the viability of using several chemicals in the electrocatalytic reduction of carbon dioxide [9]. These days, there are many different catalysts, including metals and metal oxides, for the conversion of carbon dioxide to formate. Although catalysts, such as electrodes based on simple metals like Pt, In, or Pb have

demonstrated comparatively good selectivity for carbon dioxide reduction to produce formic acid, the toxicity, high cost, and limited availability of certain of these metals would unavoidably impede industrial-scale usage [1, 10]. However, because of their low cost, non-toxicity, environmental friendliness, and high formic acid production rate, Sn-based catalysts are seen as promising candidates [11]. Bismuth-based catalysts have recently attracted more interest in carbon dioxide reduction due to their strong catalytic activity and excellent formic acid production rate. Bismuth is a reasonably non-toxic and affordable metal. As a result, alloys containing Sn, Bi, and other elements make excellent formate-producing catalysts [12]. According to reports, the Faraday efficiency of formate generation on different bismuth or Pb-based catalysts varies widely, ranging from 67% to 99%. Regretfully, to attain a large current density and a relatively high Faraday efficiency, these catalysts typically need a significant overpotential. Furthermore, even at high potentials, the current density is often less than 14 mA cm^{-2}. For this reason, the development of highly active catalysts is urgently needed. Recently, alloying has been employed as a new tactic to maximize electrocatalytic reaction activity [13]. A promising option for converting carbon dioxide to formate is an alloy catalyst based on metals. For instance, tin-copper alloys with theoretical guidance suppressed CO generation and hydrogen evolution to obtain excellent formic acid selectivity. However, the complexity of the experimental process causes a challenge. To direct the continued development of carbon dioxide electroreduction, it is thus desirable to identify a straightforward method for creating metal-based alloy electrodes. Metal-based alloy nanocatalysts have been synthesized to produce formic acid efficiently and deposited on the Sn electrode using a simple and efficient drop-casting technique. The metal-based alloy exhibited outstanding performance by producing a high concentration of formic acid (1200 ppm h^{-1} cm^{-2}) and excellent selectivity and activity. The FE% of the experiment reached up to 90% during some experiments. The circular shape structure has a more active surface area which enhanced the activity. The catalyst is attached with a binder on the electrode surface to enhance the stability for long-term experiments

2. Experimental
2.1 Material
A variety of reagents, such as NaHCO$_3$ (98.6%), KOH (99.7%), ethanol (99%), H$_2$O$_2$, methanol (99%), and NaOH (99.9%), were employed with all analytical grade chemicals of metal-based alloys being purchased in high purity. Sigma-Aldrich supplied the PTFE (poly-tetrafluoroethylene) and the 99 percent pure Sn foil. For making solutions and experiments, deionized water (Millipore system 18.2 M/cm) was used.

2.2 Synthesis of metal-based alloy
The metal alloy catalyst was synthesized using a 1M solution of metal salts. The required amount of metal salts was taken and heated for 3 hours at a high temperature of 150 °C. After heating the material was cooled down to room temperature. The white paste of metal-based alloy was further dried in a furnace at a high temperature of 300 °C for 3 hours. The metal-based alloy nanomaterial was ready for experiments.

2.3 Fabrication of electrode
Using a straightforward drop-casting technique, the freshly made catalysts were applied to a Sn electrode that had been treated with acid. Before the catalyst deposition, the Sn foil (99.95%) with a thickness of 0.5 mm that was bought from Sigma was cut into small electrodes with a 1 cm square geometric area and washed with DI water. First, 1M H$_2$SO$_4$ was used to treat the Sn foil, and a potentiostat was used to apply 4V for 40 seconds. The process made the Sn foil's surface rougher. To further eliminate any leftover residues, the Sn electrode was sonicated using a solution of water, acetone, and ethanol. To create a uniform emulsion of ink, the catalyst was dissolved in a mixture of PTFE and ethanol and later sonicated for some time. The material was drop-casted on the electrode surface and heated for some time after it cooled down. The electrodes were now ready to be used for an electrochemical study.

2.4 Characterization

In order to analyze the surface structure and composition of the prepared material different characterization instruments instruments were used. The scanning electron microscopy (SEM) examination was performed on a Nova Nano SEM 450 450 (Thermo-Fisher, US) at 10 mA and 10 kV accelerating voltages. The Bruker-D8 Advance Cu ka 40mA, 40 kV, is used used in the XRD characterization. Utilizing the Kratos AXIS Ultra-DLD (Manchester, UK) X-ray photoelectron spectroscopy (XPS), the electrocatalysts were investigated. Additionally, a TEM study was performed to identify the alloy alloy particle size.

2.5 Electrochemical study

The electrochemical study was conducted in a simple H-type cell which is divided into two compartments. The anodic compartment has Pt as a counter electrode while the cathodic compartment has a working and reference electrode. The two compartments are separated by a Nafion membrane. The production identification was done by using HPLC with an RID detector.

3 Results and discussion

3.1 Structural characterization

The SEM analysis was performed to investigate the structure of the prepared metal-based alloy electrodes. Figure 1a shows the SEM images of the catalyst. The catalyst is deposited uniformly on the electrode surface and TEM analysis shows that the catalyst has a small particle size of less than 20nm (Figure 1b). The XRD patterns of the metal-based alloy electrode are shown in Figure 2a. The XRD patterns confirm the formation of the crystal structure of metal-based alloy with clear peaks of all the elements. The XPS analysis was performed to investigate the chemical and surface composition of the metal-based alloy electrodes. The complete XPS spectra of the metal-based alloy electrode are shown in Figure 2b. The complete XPS was conducted to show all the elements peaks of metal-based alloy. The metal-based electrode shows high surface area which is suitable for excellent activity of catalyst. The prepared material showed superior catalytic activity as compared to other materials in the literature.
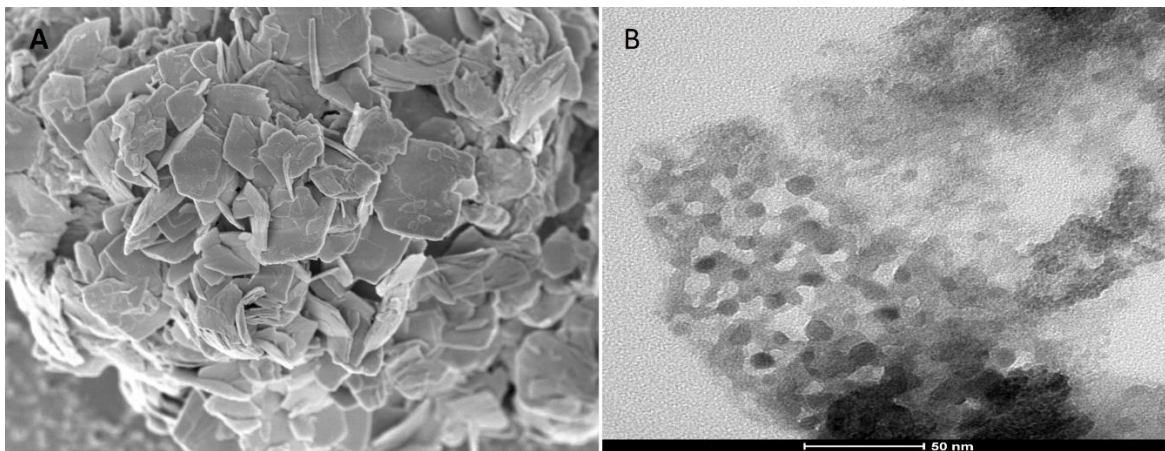

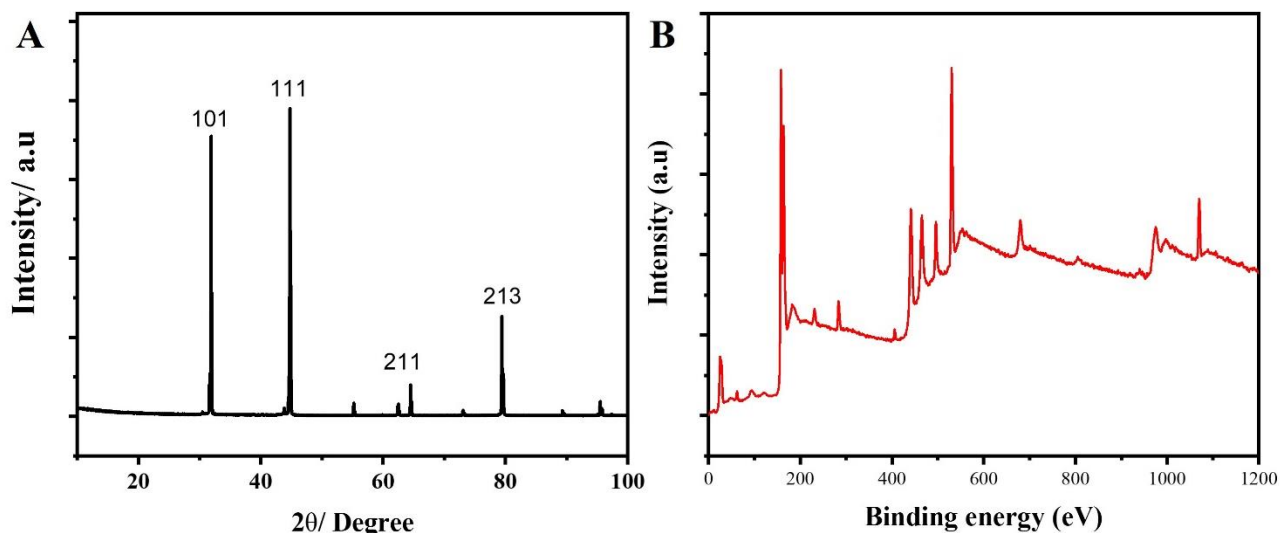**Fig. 1:** The SEM and TEM images of metal-based alloy was shown.

Fig. 2: (A)The XRD spectra and (B) complete XPS spectra of the metal-based alloy were shown.
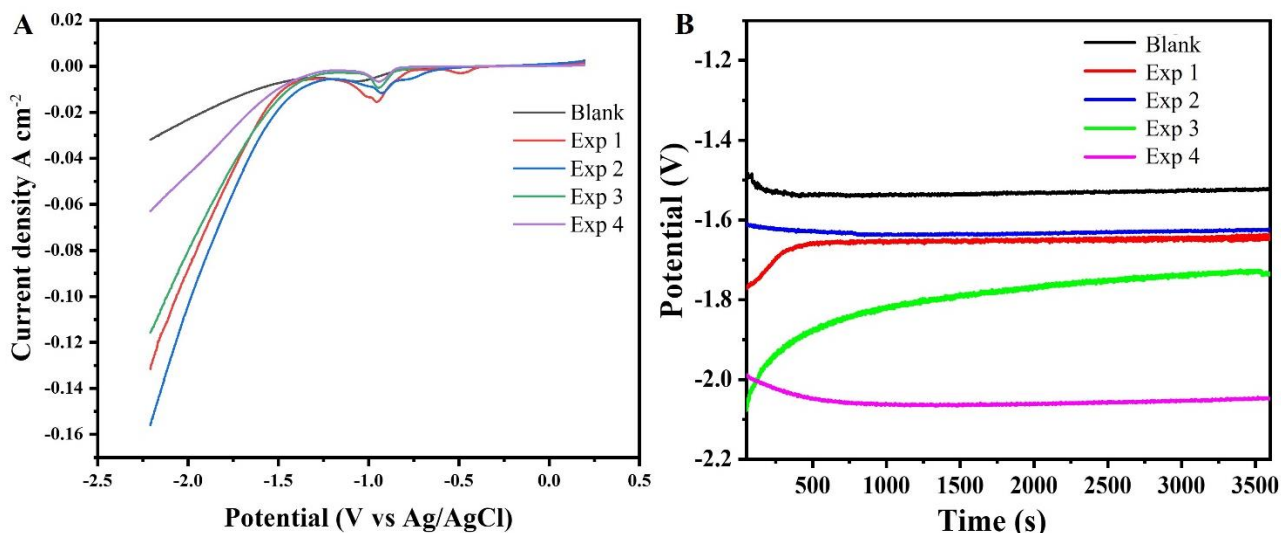

Fig. 3: (A) The LSV spectra of metal-based alloy electrodes in different $NaHCO_3$ catholyte and 0.1M KOH anolyte solution was shown. (B) The chronopotentiometry spectra of metal-based alloy electrodes in different $NaHCO_3$ catholyte and 0.1M KOH anolyte solutions for a fixed time of 1 hour.

3.2 Electrocatalytic performance

The carbon dioxide electrochemical reduction activity of the electrode was first assessed using cyclic voltammetry and linear sweep voltammetry measurements in a 0.1 M $NaHCO_3$ electrolyte that was saturated with carbon dioxide. In a N_2-saturated electrolyte, only HER typically occurs, whereas in a CO_2-saturated electrolyte, both CO_2ER and HER typically occur. As demonstrated in Figure 3a, the current density achieved in the electrolyte saturated with carbon dioxide at the same potential was significantly higher than that of the blank electrode. This suggested that the electrodes under investigation exhibited clear electrocatalytic activity for reducing carbon dioxide. The electrochemical performance of a metal-based alloy electrode for CO_2 ECR to make formic acid was revealed by several electrochemical reduction investigations carried out in H-type cells. In every study, the chromatopotentiometry technique was employed. In chronopotentiometry, the potential is varied

while the current remains constant as shown in Figure 3b. To ensure uniformity and comparability, each experiment was run at a set time of one hour. A High-performance Liquid Chromatography (HPLC) apparatus was used to analyze the concentration of formic acid. Different electrolyte concentrations and a different current were used in all the experiments. The chronopotentiometry studies conducted under various settings, with a metal-based electrode at constant current and electrolyte concentration, are shown in Table 1. The experiments were done multiple times, and the average value was determined. The concentration of formic acid as determined by several experiments is displayed in Table 1.

Table 1: The comparative chronopotentiometry results of meta-based alloy electrodes at different conditions.

Sr No.	Current (mA)	Catholyte Concentration (M)	Dosage (mg)	Formic acid concentration (ppm)	FE%
1	-50	0.1	-	325	29
2	-45	0.1	4	765	83
3	-70	0.2	3	870	76
4	-50	0.1	6	1200	90
5	-70	0.15	5	923	72

4 Conclusions

In conclusion, we were able to create a metal-based alloy under regulated conditions using an easy and straightforward procedure. The FE of 90% was achieved at a current density of -50 mA cm^{-2} demonstrated by the as-prepared metal-based alloy electrode. The high performance demonstrates enhanced activity and catalytic selectivity for electrochemical reduction of carbon dioxide to formic acid. Furthermore, the formic acid production rate reached 1200 ppm h^{-1}, which was superior to the majority of other electrocatalysts in literature. The fast charge transfer, high surface area, and number of active sites made the catalyst an efficient candidate for excellent electrochemical performance. Through electrochemical conversion into a valuable product, this discovery may provide metal-based alloys with an effective new method of reducing carbon dioxide emissions.

Acknowledgment

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