Effect of catalyst layer on electrochemical reduction of carbon dioxide using different morphologies of copper

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ABSTRACT

Electrochemical reduction of carbon dioxide (ERC) is one of the promising technologies for the renewable energy storage challenge and mitigation of the CO$_2$ levels. Till now Cu has been found the best electrocatalyst for ERC but still the potential of Cu is not fully explored. This paper illustrates the effect of electrocatalyst layer formed by four different morphologies of cupper (nanorods, octahedral, spherical, and dendrite) with similar crystallite phases. Pre and post-ERC analysis of the catalyst in different environment shows that same crystal facet is formed at the end of ERC, indicating that the crystal rearrangement occurred during ERC is independent of the environment and does not promote any particular reaction. Nanorods form intercalated layers with an extended surface giving maximum faradaic efficiency of 26% at a lower cell voltage of −2.75 V. Dendrites forms porous layers, which are filled by the gas formed during ERC and thus decreases the active surface. However, the entrapped intermediates provide sufficient residence time and conditions for C$_2$H$_4$ and C$_2$H$_6$ formation. Spherical nanoparticles and octahedral nanoparticles formed a smooth, and thin layer with minimum faradaic efficiency towards ERC.

1. Introduction

Overthe past couple of decades, the conversion of carbon dioxide (CO$_2$) to the value added products and other chemical feedstocks, has attracted a lot of interest in both fundamental science and process development [1,2]. The usage of CO$_2$ as the feedstock for fuel will not only help to mitigate the atmospheric CO$_2$ levels but will also provide an economical and environmentally viable method for renewable energy storage in the form of chemical bonds. Electrochemical reduction of CO$_2$ (ERC) to value added products could be one of the promising technologies. Electrocatalyst plays a critical role in ERC and various type of electrocatalysts such as metallic, bimetallic, metal oxides as well as nanostructured carbon are being tried for efficient ERC process [3,4]. Copper, among various electrocatalysts, has shown comparatively good results and a strong potential towards efficient ERC due to its unique property to convert CO$_2$ to hydrocarbons at ambient conditions.

Though, Cu has unique property to produce hydrocarbons but it has some challenges. Copper requires high overpotential (around 1.0 V) as well as shows poor selectivity towards ERC products [5]. Moreover, its low overpotential for hydrogen evolution reaction (HER) is another critical issue. Therefore, most of the electrical energy provided for ERC is used by the HER [6]. Initially, Hori et al. reported ERC on copper foil in aqueous media at −1.4 V vs RHE, and CH$_4$ and C$_2$H$_4$ were observed

as primary products with Faradaic Efficiency (F.E.) of ~40% and ~20%, respectively [7]. Surface morphology and crystallographic phases were found to play critical role in determining ERC product selectivity using copper electrocatalyst. In comparison to Cu foil, Cu nanoparticles showed lower onset potential and higher electrocatalytic activity towards ERC with F.E. of around 30% and 35% for CO and C$_2$H$_4$, respectively, in aqueous media [8]. This higher activity was primarily attributed the effect of the morphology, rather than the effect of increase in surface area, which was in contradiction to other literatures. Reske et al. studied the effect of variation in size of Cu spherical nanoparticle and observed that CO selectivity was enhanced with the decrease in particle size [9]. It is reported that the nanoparticles have more number of low-coordinated sites, which are more active towards CO$_2$ to CO formation as also confirmed by density functional theory (DFT) calculations [9]. Recently, Cu with nanowires and dendrite structures have also been used in ERC to improve the selectivity and to reduce the overpotential requirements [10]. Cu nanowires are found to be more selective towards CO formation, F.E. ~60% at −0.4 V vs RHE, which shows reduced overpotential requirements. Whereas, in case of Cu nanocuboids [11], CO formation was suppressed along with CH$_4$, while C$_2$H$_4$ was formed with F.E. of about 26% at −1.0 V vs RHE. Roberts et al. have also observed similar trends of suppression in CO and CH$_4$ formation on Cu nanocubes with evolution of C$_2$H$_6$ at only

−0.6 V vs RHE [12]. Similarly, copper nanofoams with dendrite structure have also shown CO suppression and HCOOH formation with F.E. of about 29% [13]. Moreover, oxide derived copper nanoparticles with pyramidal morphology have shown a shift in selectivity towards C$_2$H$_6$ from C$_2$H$_4$ with increase in oxide layer thickness [14].

Crystallographic facet dependency leading to different morphologies was also investigated. Copper (111) facets showed higher selectivity towards CH$_4$ formation, whereas copper (100) facet favours C$_2$H$_4$ formation; this could be due to different surface binding energies at different copper facets [15]. DFT studies have shown that copper (100) facet offers lowest energy barrier for C$_2$H$_4$ formation which is further decreased as the surface is covered by CO adsorption [16]. Based on the above observations, it can be said that the selectivity, so observed, would be a combined effect of morphology, crystallographic plane and the catalyst layers formed. Therefore, in the present study, the research work is focused on understanding the effect of different morphologies, crystallographic plane and the catalyst layers of copper electrocatalyst on the continuous electrochemical reduction of carbon dioxide in full cell configuration. Herein, four different morphologies of copper including spherical, octahedral, nanorods and dendrite were synthesised using facile methods by controlling the nucleation and growth rates.

2. Experimental section

2.1. Materials

Carbon paper was purchased from CeTech (Japan). Nafion membrane (117) was purchased from Fuel cell stores (USA). Copper sulphate pentahydrate (CuSO$_4$·5H$_2$O), copper nitrate trihydrate (CuNO$_3$·3H$_2$O), sodium borohydride (NaBH$_4$), potassium bicarbonate (KHCO$_3$), hydrazine solution (H$_6$N$_2$O) and isopropanol (IPA) were procured from Loba Chemie. Nafion dispersion solution (5 wt%) was purchased from DuPont (USA). All the chemicals were of analytical grade and used without any further purification.

2.2. Catalyst synthesis

Different morphologies of copper were synthesised by controlling the nucleation formation rate, growth as well as their concentration. This was done by using different precursor salt of copper along with altering the reaction condition. All the morphologies were synthesised using co-precipitation method.

2.2.1. Synthesis of copper with spherical morphology
Copper nanoparticles with spherical morphology were synthesised by wet chemical method [4]. 50 ml of 1.5 M NaBH$_4$ solution (pH adjusted to 12 with 1 M NaOH) was gradually added to 100 ml of 0.5 M CuSO$_4$ solution. The reduction was carried out in an ice bath at 10 °C. Formation of black precipitates of copper oxide indicated the completion of the reaction. After the completion of the reaction, the solution was filtered and washed with copious amount of water and then subsequently with ethanol. The residue was collected and dried at 110 °C in vacuum for overnight.

2.2.2. Synthesis of copper with nanorods morphology
Copper nanorods were also synthesised by the wet chemical method. A 100 ml of 0.5 M CuSO$_4$ solution was heated to 80 °C and in this solution, 15 g of NaOH was added and stirred for 15 min (till the colour changed to black). Then 1 ml of hydrazine solution was gradually added and stirred for 5 min. The solution colour changed to reddish brown, which indicated the completion of the reaction. Finally, the solution was filtered and washed with copious amount of water and subsequently with ethanol. The residue was collected and dried at 110 °C in vacuum oven for overnight.

2.2.3. Synthesis of copper with dendrite morphologies
Copper dendrites were directly grown on to the surface of carbon paper (electrode) by electro-deposition of copper. A 250 ml of 0.1 M CuSO$_4$ solution acidified by adding 60 μl of H$_2$SO$_4$ was used as an electrolyte for copper electro-deposition. Electro-deposition of copper over carbon paper (2 cm^2) was carried out at a constant current of −0.2 A for around 150 s using pure copper strip as an anode. After the electrodeposition, the electrode was rinsed with water and dried at 110 °C in a vacuum oven for overnight.

2.2.4. Synthesis of copper with octahedral morphologies
Copper with octahedral morphology was synthesised by a similar method as mentioned in the above sections. However, the molarity of the solution for this case was different, i.e., 100 ml of 3.75 M NaOH solution was added to 100 ml of 0.5 M CuSO$_4$ solution and then reduction was carried out in a similar fashion as described above. In the final step, the mixture was heated at 80 °C for 60 min.

2.3. Electrode preparation

A mixture solution of 10 mg of synthesised catalyst and 5 μl of Nafion dispersion was prepared in 10 ml of IPA. This mixture was further sonicated for 60 min to form homogeneous catalyst ink, which was then sprayed uniformly on to the surface of carbon paper (2 cm^2) using air spray technique with nitrogen as carrier gas.

2.4. Physical characterization of electrocatalyst

Morphological properties of as synthesised electrocatalyst were characterised by SEM (Zeiss) and HR-TEM (FEI Tecnai TF20). Crystallographic phase and structures were determined using powder XRD (MiniFlex 600 Rigaku) having Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 20 mA. Elemental composition was determined by SEM-EDX mapping (TM3000, Hitachi).

2.5. Electrochemical characterization

Linear sweep voltammetry (LSV) was conducted in N$_2$ as well as CO$_2$ saturated 0.5 M KHCO$_3$. All the half-cell electrochemical measurements were performed in a 3-electrode assembly. Here, catalyst coated on carbon paper (1 cm^2) was used as working electrode, Ag/AgCl/1 M (KCl) (CH Instruments) as reference electrode, and platinum rod as the counter electrode. All the potentials were converted to NHE by using the following relationship (Eq. (1)) unless otherwise stated.

$$E_{RHE}(V) = E_{Ag/AgCl}(V) + 0.222\,(V) + 0.059 * pH\,(V) \qquad (1)$$

Electrochemical impedance spectroscopy (EIS) was carried out at different voltages to gain insight into the reaction mechanism. It was also performed, prior to each chronoamperometry experiments, to evaluate the solution resistance between the two electrodes. These losses were compensated using the IR drop feature.

2.5.1. Experimental setup
Chronoamperometry experiments were carried out in a 2-chamber electrochemical reactor, where anodic and cathodic chambers were separated by a pre-treated Nafion-117 membrane [4]. In order to pre-treat the nafion membrane, it was put in 10% H$_2$O$_2$ solution at 80 °C for 1 h to remove organic impurities, followed by rinsing in DI water at 80 °C for 1 h. It is then treated in 0.5 M H$_2$SO$_4$ at 80 °C for 1 h again followed by rinsing in DI water at 80 °C for 1 h. Both, anodic and cathodic chambers have equal volume and were filled partially by a solution of 0.5 M KHCO$_3$ and rest was left as the head space for the gas. Prior to each experiment, solution was saturated with dissolved CO$_2$ by purging with CO$_2$ gas for 1 h. During all the experiments CO$_2$ was purged at a constant flow rate of 15 ml/min into the cathode chamber. Area of the working electrode was 2 cm^2 with a catalyst loading of