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Morphology Modulation of Cu-Based Catalysts in Electrocatalytic CO2RR

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Abstract

Electrochemical carbon dioxide reduction reaction (CO2RR) is an important means of achieving carbon neutrality. Copper-based catalysts are the only catalysts capable of producing multicarbon (C2+) products in CO2RR. Cu-based catalysts have received much attention from researchers because of the higher value of the C2+ products. However, the catalytic activity and selectivity of Cu-based catalysts have yet to be optimised due to the high bonding energy of C=O and the many pathways to produce C2+ products. This article describes interesting methods for morphology modulation of Cu-based catalysts, including facet and surface modulation of nanoparticles as well as modulation of Cu-based catalysts of other shapes.

Keywords: CO2 reduction; Cu-based catalysts; morphology modulation

Introduction

With industrialisation, carbon dioxide (CO2) emissions are increasing, leading to many environmental problems such as global warming [1]. In order to protect the Earth's ecological environment, more and more countries are recognising the importance of carbon neutrality. Many strategies have been proposed to achieve carbon neutrality, mainly four types of carbon replacement, carbon emission reduction, carbon sequestration and carbon cycle [2]. Carbon replacement means replacing fossil energy with clean energy. Carbon emission reduction involves both energy conservation and efficiency improvements. Carbon sequestration is the isolation of CO2 emissions from factories from the atmosphere. Carbon cycle is the conversion of CO2 into valuable chemical feedstocks or fuels. And CO2 reduction reaction (CO2RR) is an important part of the carbon cycle.

CO2RR can produce a variety of products including CO, HCOOH, C2H4 and C2H5OH.

It is therefore particularly important to choose the right catalyst to control the species and proportions of the products [3]. Specifically, if we use Au as the catalyst, 87.1% of the product is CO, whereas if we use Hg as the catalyst, 99.5% of the product is HCOOH. Of the many metal catalysts available, Cu-based catalysts are very special. This is because the main products of CO2RR using Cu-based catalysts are not single-carbon (C1) products such as CO and HCOOH, but multicarbon (C2+) products such as C2H4, C2H5OH and n-C3H7OH, which certainly increases the value of CO2RR.

However, due to the high energy required to break the C=O bond and the variety of C2+ products that can be formed, the activity and selectivity of Cu-based catalysts need to be further improved [4]. A number of researches have been carried out to modulate the morphology of Cu-based catalysts to improve their performance. Morphology modulation can create specific sites to reduce the activation energy and stabilise specific intermediates, thereby improving the activity and selectivity of Cu-based catalysts.

Among the many excellent researches, some of them can give a refreshing feeling and provide many ideas for research. In this article, some interesting studies will be presented in terms of facet modulation and surface modulation of nanoparticles. Other shapes of Cu-based catalysts will also be introduced. Hopefully, this article can bring more insights to researchers.

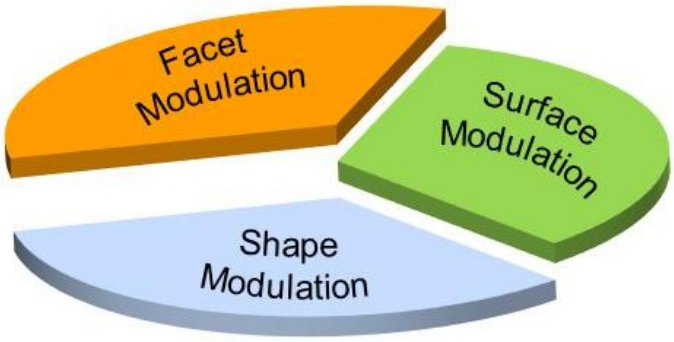

Figure 1: An overview of morphology modulation methods for Cu-based catalysts

Facet Modulation

The different crystal facets of Cu-based catalysts exhibit different activities and selectivities due to their different surface energies and different atomic arrangements. The (100) facet of Cu tends to produce C2H4 while the (111) facet tends to produce CH_4 [5]. This is because the (100) facet of Cu stabilises the CHO^* intermediate, which forms C2H4 when two CHO* intermediates are coupled. Whereas the (111) facet of Cu tends to stabilise the COH* intermediate, thus producing CH4. This example shows that one can modulate the performance of a catalyst by modulating the exposed crystal facets as required.

Capping agents are an important method of facet modulation. Capping agents can reduce the deposition rate of atoms on a specific crystal facet, thus preserving that facet. This is well illustrated by the work of Zhang et al.[6]. As shown in Figure 2a, they obtained a range of shapes of Cu2O nanoparticles including cubic, truncated cubic, cuboctahedral, truncated octahedral and octahedral by adjusting the amount of capping agent, polyvinylpyrrolidone (PVP). The larger the amount of PVP they used, the higher the ratio of the area of the (111) to (100) facets in the Cu2O nanoparticles. This is due to the higher energy and faster growth rate of the Cu2O (111) facet. So when the capping agent PVP is not present, the surface of the nanoparticles will consist entirely of the slower growing (100) facets and the nanoparticles will take on a cubic shape. When PVP is added, it will preferentially adsorb on the higher energy (111) facets, reducing the growth rate of the (111) facets and thus allowing the (111) facets to be eventually retained. Thus by regulating the amount of capping agent PVP, we can regulate the growth rate of the (111) facet of the CuO and thus the shape of the nanoparticles.

The function of continuously regulating the ratio of (111) to (100) facets can also be achieved by reductants. By increasing the amount of reductant NH2OH·HCl, Luo et al. were able to reduce the growth rate of the higher index facets, thus allowing more (111) facets to be retained, yielding a range of shapes from cubic to octahedral [7] (Figure 2b). It is worth mentioning that with further increase in the amount of $NH_2OH{\cdot}HCl$, the higher index (322) facets were retained during the growth process, and even star-shaped Cu_2O particles consisting entirely of (322) facets were obtained. Luo et al. found that the star-shaped Cu_2O particles were highly selective for C_2H_4, greatly exceeding the octahedral Cu_2O particles consisting entirely of (111) facets. This high selectivity was attributed to the high adsorption of the (322) facets and the unique shape of the star-shaped particles.

Regulating the facets of Cu_2O can be achieved not only by chemical reagents, but temperature can also play a regulatory function. In the work of Han et al.[8], they were able to obtain nanoparticles of different shapes by simply changing the temperature at which the Cu_2O particles were synthesised (Figure 2c). This further demonstrates that there are various methods to modulate the facets of Cu_2O.

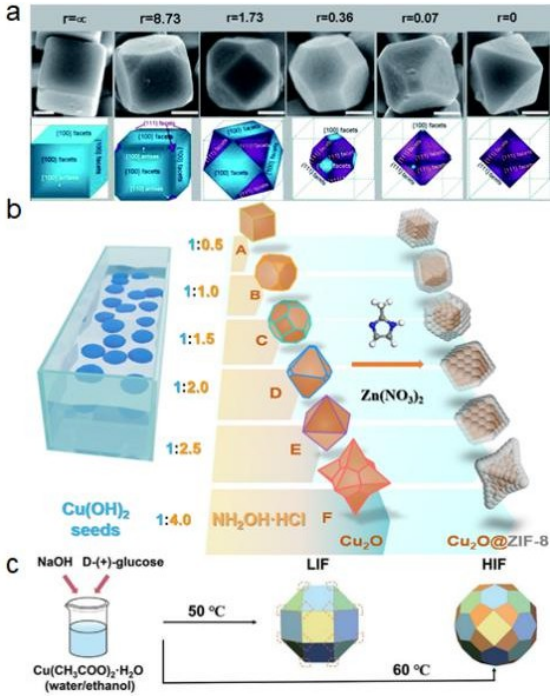

Figure 2. Facet modulation of the Cu-based catalysts. (a) FESEM images and the corresponding 3-D geometry models of the Cu2O polyhedrons with different volume ratios of {100} to {111} [6]. (b) Synthesis of Cu_2O nanoparticles by the reductant-controlling method and Cu_2O@ZIF-8 composites[7]. (c) The diagram of shape-controlled synthesis to prepare the 26-facet polyhedron and the 50-facet polyhedron [8].

Surface Modulation

Nanoparticle catalysts typically cause molecules adsorbed on its surface to form specific intermediates to achieve catalysis. The surface is therefore important for modulating the activity and selectivity of Cu-based catalysts. Modulation of surface roughness is one of the methods of surface modulation. Jiang et al. plasma-treated Cu catalyst surfaces of different durations to obtain surfaces with different roughness [9]. They tested the catalytic performance of the Cu catalysts with different surface roughness in the CO2RR and compared it with the performance of Cu catalysts with electrochemically polished surfaces. The results in Figure 3a show that the ratio of C2+ to C1 product yields increases and then decreases with increasing roughness, suggesting that surface roughness can indeed have an effect on the selectivity of the Cu catalysts. They also found that the surface current density of the plasma-treated Cu catalysts also increased compared to pre-treatment, suggesting an increase in catalyst activity as well.

Surface doping can also have an effect on the performance of the catalyst. This is because the doping atoms can have an effect on the arrangement of the atoms on the catalyst surface, thus altering the type of reaction intermediates and ultimately the product. A systematic study on the doping of elemental sulphur on the surface of Cu2O catalysts has been carried out by Ma et al.[10]. They prepared a series of Cu2O particles containing different levels of S at 0at%, 3.42at%, 6.76at%, 10.07at%, 15.87at% and 17.1 at% respectively. They found that the S-doped catalysts showed better catalytic activity and selectivity for the formate products. Moreover the catalysts containing 10.07at% S exhibited the most excellent performance. It showed a substantial increase in Faraday efficiency for formate compared to the catalyst without S and it made HCOO- the major product (Figure 3b), which is a good proof of its excellent selectivity for HCOO-. As shown in Figure 3c, the current density of the 10.07at% S--doped catalyst was the highest of the series, indicating that its catalytic activity was also quite good.

Etching is also prominent for surface modulation, as it exposes different facets of the crystal from the outer facets, and can also increase the specific surface area of the catalyst and increase the number of active sites. After synthesising truncated octahedral Cu2O particles using a wet chemical method, Li et al. etched the nanoparticles to obtain a unique hollow structure [11] (Figure 3e-g). They found that this hollow structured Cu2O catalyst exhibited a higher Faraday efficiency of HCOOH than the unetched nanoparticles at a low potential of -1.0 V (Figure 3d). This improved selectivity may be due to the presence of more oxygen vacancies in the hollow structure, allowing for enhanced adsorption of CO2 by the catalyst.

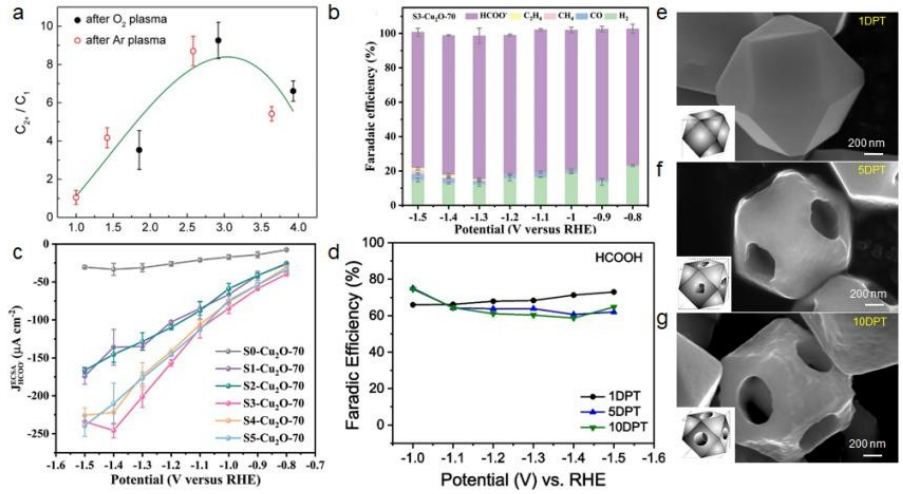

Figure 3. Surface modulation of Cu-based catalysts. (a) C2+/C1 ratio as a function of Cu surface roughness [9]. (b) FE of S3-Cu2O-70 at different potentials [10]. (c) ECSA normalized partial current density of HCOO−10. (d) HCOOH FE of 1DPT, 5DPT and 10DPT NCs at diferent applied potentials.Field-emission scanning electron microscopy (FESEM) images of (e) 1DPT; (f) 5DPT; (g) 10DPT NCs. Inset shows the corresponding crystal structures [11].

Shape Modulation

Cu-based catalysts are available in a variety of morphologies. In addition to nanoparticles, there are nanowires, nanodendrites and nanoporous structures. These very different morphologies are indicative of the different catalytic properties of each. Nanowires are another structure that has been extensively studied in addition to nanoparticles. The effect of nanowire length on the catalytic performance of Cu nanowire arrays was discovered in a study by Ma et al.[12]. Their method of regulating the length of copper nanowires is very simple, as the nanowire length can be easily regulated simply by extending the time of nanowire synthesis. As the length of the Cu nanowires increased, not only did the Faraday efficiency of the C2+ products increase, but so did the variety. As shown in Figure 4a, Ma et al. believe that when the length of Cu nanowires increases, it prevents the nanowire arrays from locally exchanging substances with the outside world, thus allowing the OH^- produced by the reaction to accumulate. Therefore the longer the nanowire length, the higher the pH, which in turn affects the Faraday efficiency and species of the products.

Nanodendrites have a large active specific surface area due to their large number of protrusions on the surface and are generally prone to high catalytic activity. Gu et al. synthesised a CuOx nanodendrite catalyst by electrochemical deposition [13]. In testing the catalyst, they found that this nanodendrite catalyst aided the production of C2H4 and also inhibited the precipitation of H2. They found that the Faraday efficiency of C2H4 was as high as 63% at a suitable overpotential. They attributed this selectivity to oxygen vacancies on the CuOx surface. As shown in Figure 4b, these oxygen vacancies contribute to the adsorption of *CO, *COH intermediates and the release of *CH2, which are further hydrogenated to C2 hydrocarbons.

Nanoporous structures are also a shape worth investigating. We can tune the performance of catalysts by adjusting several parameters such as the number, diameter and depth of nanopores. Using porous Al2O3 as a template, Yang et al. have controllably synthesised Cu meshes with different pore sizes and depths [14] (Figure 4c, d). Compared to polycrystalline Cu, the porous structure of the Cu catalysts not only had improved catalytic activity but also improved selectivity towards polycarbon products. They found that by adjusting the pore size and depth, they were also able to further tune the Faraday efficiency of the catalyst for specific C2+ products. They attributed the high selectivity of the Cu mesh for C2+ products to the porous structure favouring accelerated C-C coupling and longer retention of intermediates.

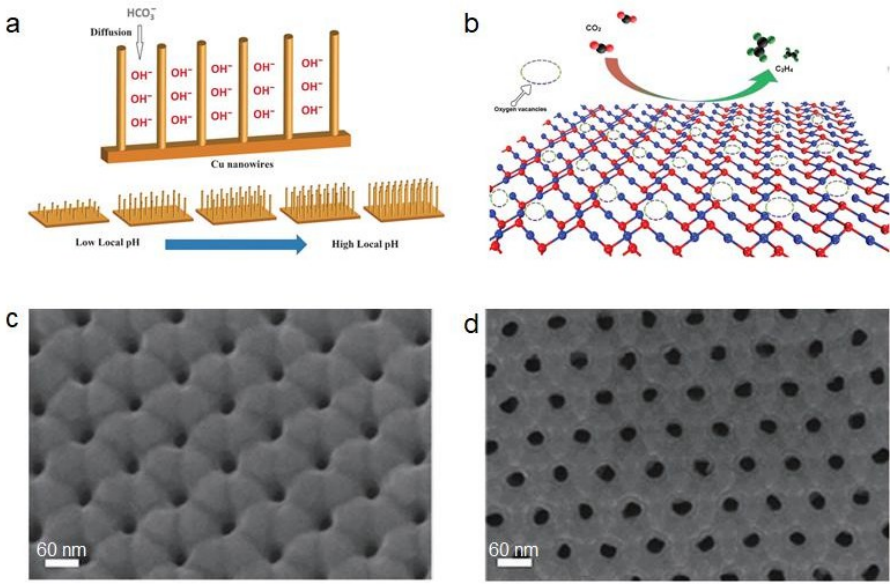

Figure 4: Cu-based catalysts of other shapes. (a) Schematic illustration of the diffusion of electrolytes into Cu nanowire arrays [12]. (b) Schematic of electrocatalytic reduction of CO_2 on Vo-rich CuO_x–Vo surface to C H 13. SEM images of mesopores with (c) 30 nm width/40 nm depth and (d) 30 nm width/70 nm depth14.

Conclusion

This article first describes the unique advantage of Cu-based catalysts in being able to produce C2+ products in CO2RR, and briefly analyses the difficulties faced by Cu-based catalysts in terms of catalytic activity and selectivity. This is followed by a description of the various methods of crystal surface modulation and surface modulation of the most common shapes of nanoparticles for Cu-based catalysts. Finally, the methods of shape modulation of Cu-based catalysts with nanowires, nanodendrites and nanoporous structures are presented. These abundant studies show that the modulation of Cu-based catalysts is a very promising research topic. We believe more and more effective modulation methods will be discovered.

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