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Green synthesis of two-dimensional copper nanomaterials using biomass for the reduction of carbon dioxide

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Abstract:

The problem of greenhouse gas emissions has become increasingly severe, so energy conservation and emissions reduction have become a critical challenge for our society. In response to the challenge of lowering carbon dioxide (CO_2) emissions and transforming them into valuable energy molecules, this work explores the eco-friendly preparation of two-dimensional (2D) nanocopper-based catalysts. In this study, biomass was utilized as both the reductant and the capping reagent to prepare these catalysts. The structure and morphology of the resulting products were analyzed using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Their crystal structures were characterized by X-ray diffraction (XRD). The synthesis process of this type of nanomaterials was also studied. These copper-based catalysts were then evaluated for their efficiency in reducing CO_2 into small energy molecules of HCOOH. A significant innovation of this study is using biomass as the reductant and capping agent, which guarantees the green synthesis process and exhibits great potential in converting CO_2 into valuable energy molecules. This research is significant for creating new energy sources and protecting the environment.

Keywords: Copper; Nanomaterials; Reduction of Carbon Dioxide.

1. Backgrounds

The earth's greenhouse effect is intensifying, and the glaciers at the poles are melting at an accelerated rate, bringing tremendous pressure to the survival of human beings, so if human beings want to develop in the long term, they can only start from themselves and slow down the pace of the global greenhouse effect as much as possible. Greenhouse gases, including atmospheric carbon dioxide (CO_2), methane, and nitrous oxide (NO_x), significantly cause global change. Increasing the concentration of CO_2 in the air leads to two effects. On the one hand, it promotes the accumulation of substances produced by photosynthesis in terrestrial ecosystems, which increases carbon stocks in the soil, creating a soil carbon sequestration effect (A). On the other hand, it increases the emission of other greenhouse gases, such as methane and nitrous oxide, enhancing the greenhouse effect (B). Therefore, in the context of rising atmospheric carbon dioxide concentration, two effects, A and B, respectively, will occur. The problem of greenhouse gas emissions has become a primary environmental concern due to the escalating carbon dioxide (CO_2) levels, closely connected to global warming and climate change. Therefore, measures to counter these effects have called for the development of new technologies to reduce CO_2 emissions while simultaneously utilizing them. Among the prospective solutions, applying nanomaterials as electrocatalysts was viewed as the most prospective approach. However, the conventional methods of preparing catalysts are always associated with the following disadvantages: the use of hazardous chemicals and many more steps that are always a significant risk to the environment and human well-being. Although there have been improvements in the design of the catalysts recently, there are still challenges in formulating efficient and eco-friendly catalysts. Therefore, developing other green synthesis routes for catalysts is highly desirable for further enhancing CO_2 reduction technology and energy conservation goals.

CO_2 and water are the best raw materials for organic synthesis. Still, due to the inertness of CO_2, the general chemical method of synthesizing organic matter from CO_2 has very harsh conditions, so the electrochemical reduction of CO_2 under mild conditions and ease of operation has become a cutting-edge topic of concern in recent years. The key to the electrochemical reduction of CO_2 is the preparation of catalytic electrodes with high catalytic activity, high selectivity, and high stability. Over the years, a lot of research has been carried out on the reduction of O_2 and CO_2 by conductive metal oxides such as nail oxide and titanium oxide for anodic process or cathodic process, and the results show that they are substances with good catalytic activity. In addition, they have high conductivity and electrochemical stability, especially when mixed with other oxides. Copper (Cu) is a superior metal catalyst for reducing CO_2 to hydrocarbons and alcohols, especially C2+ products. However, Cu catalysts also have specific problems (e.g., high overpotential and poor CO_2RR selectivity), which limit their applications. Copper-based catalysts are the only catalysts that can profoundly reduce CO_2 to multicarbon products among many electrocatalytic CO_2 reduction systems. Copper-based catalysts undergo surface remodelling during electrocatalysis, which can significantly impact their performance.

This work addresses these challenges by establishing a green synthesis route for nano copper-based catalysts using biomass-derived reducing agents. The goal is to develop an eco-friendly catalyst that can also improve the process of CO_2 reduction. The research entails the preparation of the copper-based catalysts by biomass-mediated reduction process and characterization through scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD). In addition, the study evaluates the efficiency of these catalysts in the application of electrochemical reduction of CO_2 with a focus on the ability to synthesize the energy-rich molecule formic acid (HCOOH). This work aims to provide a sustainable solution to the challenges of greenhouse gas emissions and energy sustainability through green synthesis methods and efficient CO_2 reduction and conversion.

2. Design strategies for Cu-based catalysts

In ECO$_2$RR, Cu-based catalysts catalyze the electro-reduction of CO_2 to various organic compounds with high carbon numbers, such as ethylene, ethanol, propylene, etc. Cu has different oxidation states and can participate in several different electrochemical reaction steps, which helps to produce diverse products. Its surface has a good adsorption capacity for CO_2 molecules, allowing CO_2 molecules to be locally enriched on the electrode surface and increasing reaction opportunities. However, the drawbacks of Cu-based catalysts must be addressed, such as poor selectivity, poor stability, and easy contamination by impurities leading to deactivation in the CO_2 reduction reaction. The researchers have improved their activity and selectivity by modulating the Cu-based catalysts' size, surface morphology, and composition to obtain a wider variety of products.

As a metal catalyst, Cu is more likely to bind to *CO intermediates than other metals, promoting C-C coupling by further forming *COH or *CHO intermediates to enable the subsequent reaction to proceed smoothly and form multi-electron transfer products more stably. Although Cu catalysts have many advantages, they also have many problems, such as poor stability, considerable opening potential, low product selectivity, etc. Therefore, modifying them to improve ECO-RR's catalytic activity and product selectivity is of excellent research significance. By changing the catalyst's size, crystal surface, and composition, the arrangement of atoms and electron distribution on its surface can be significantly affected to regulate the adsorption capacity of intermediates on the catalyst's surface and improve the target product selectivity.

2.1 Size and shape control

The size and morphology structure of nanocatalysts can directly affect the reactivity and product selectivity of ECO_2RR. By regulating the size and morphology of catalysts, the crystal surface and lattice structure of the catalyst surface can be changed, and the distribution and exposure of unsaturated ligand sites can be regulated, which in turn can regulate the reactivity and selectivity of the catalysts. For catalysts with specific morphology, the catalytic activity can be improved by increasing the number of unsaturated ligand sites, which makes it easier to adsorb activated reactant molecules.

In addition, the crystallographic effect of Cu-based catalysts may also impact their catalytic performance because different crystallographic structures may lead to different atomic arrangements and chemical properties on the catalyst surface, which may affect the reaction rate, selectivity, and catalytic activity.

2.2 Composition control

The electronic structure, surface activity, and catalytic activity of Cu-based catalysts can be optimized by precisely modulating their composition. Currently, the main modulation strategies include the synthesis of Cu oxides, the development of Cu-based alloy catalysts, and the doping of non-metallic elements.

Although Cu-based catalysts have shown remarkable potential in ECO_2RR, challenges remain, such as poor selectivity for specific products and lack of stability. Future research needs to continue exploring new modification strategies, such as developing new synthesis methods, exploring new doping elements, and optimizing the structural and surface properties of the catalysts to improve the performance of Cu-based catalysts and make them more promising for industrial applications.

3. Experiments

3.1 Material

Chemicals were utilized as received unless otherwise specified. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, AR) and Ethanol (C_2H_5OH, AR) were bought from Aladdin Company Limited in China. Pure water with a resistivity exceeding 18.2 MΩ cm was used as the solvent. Fresh bamboo leaves collected in the Hubei province of Center China were repeatedly washed with pure water and the above ethanol, followed by overnight drying at 80 °C.

3.2 Preparation

2D copper was synthesized with the following method: Initially, 300 mg $CuSO_4 \cdot 5H_2O$ was dissolved in 36 ml pure water. Then, 30 mg of dried biomass was mixed into the previous solution, moved to a 50 mL autoclave, and stored under 200 °C for 24 hours. Furthermore, the obtained products were then repeatedly rinsed with pure water and ethanol, followed by drying under 80 °C. The impact of varying the reaction time was also explored, maintaining the hydrothermal temperature at 200 °C.

3.3 Measurements

The X-ray diffraction analysis was introduced to characterize the crystallographic structure, while SEM and TEM images were recorded to obtain the detailed architecture for as-prepared 2D copper.

For the electrochemical performance test, the working electrode was first prepared. To create a uniform paste, 20 mg 2D copper powder was ground with 3 mg polyvinylidene fluoride and a specific volume of N-methyl-2-pyrrolidone. It was followed by spraying on the carbon paper and heating at 80 °C for 12h. An H-type electrolyzer was used for the electrocatalytic CO_2 reduction performance test. The test was conducted using a solution of 0.5M $KHCO_3$. The cathode and anode chamber electrolytes were 0.1 mol/L $KHCO_3$ and 0.1 mol/1L H_2SO_4, respectively. A cation exchange membrane separated the anode and cathode chambers. The reference electrode was Ag/AgCl, the counter electrode was Pt mesh, and the working electrode was carbon paper loaded with catalyst. Electrolysis was carried out at potentials controlled by ambient conditions, and CO_2 bubbles were continuously passed into the cathode chamber. All potentials were directed to the reversible hydrogen electrode (RHE). Gas analysis was performed using a gas chromatograph, while liquid products were analyzed using 1H NMR.

4. Results

4.1 Preparation

As shown in Fig. 1, the reactants used in the preparation procedure were solely H_2O, $CuSO_4$, and dried leaf, combined in a straightforward hydrothermal reaction. It highlights the simplicity and eco-friendliness of this method. The leaves were severed as the reductant and capping agent in the synthesis, providing notable advantages over other processes requiring various chemical reagents.

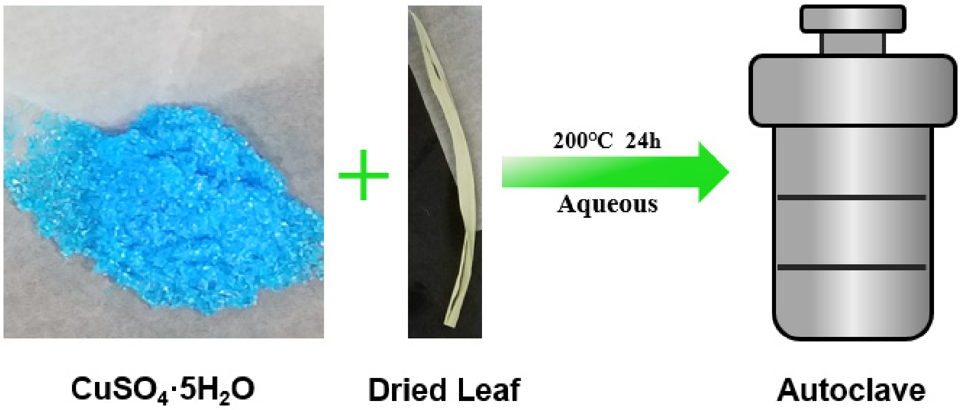

Fig. 1 Diagram of the preparation procedure.

We carried out XRD characterization of the samples to verify the crystal structure of the copper-based nanocatalyst arrays. As shown in Fig. 2a, the leaves settled at the bottom, allowing easy separation from the products. The insert image shows the product after drying, clearly visible as a brick-red material with a metallic luster. As shown in Fig. 2b, the XRD results of the products display three peaks at angles of 43.4°, 54.5°, and 74.3° by the crystal planes of (111), (200), and (220) with the standard card of PDF#04-0836. There are no apparent peaks of any oxidation state of copper, indicating the copper is pure and unoxidized. These results suggest that the copper ions were successfully reduced to elemental copper.

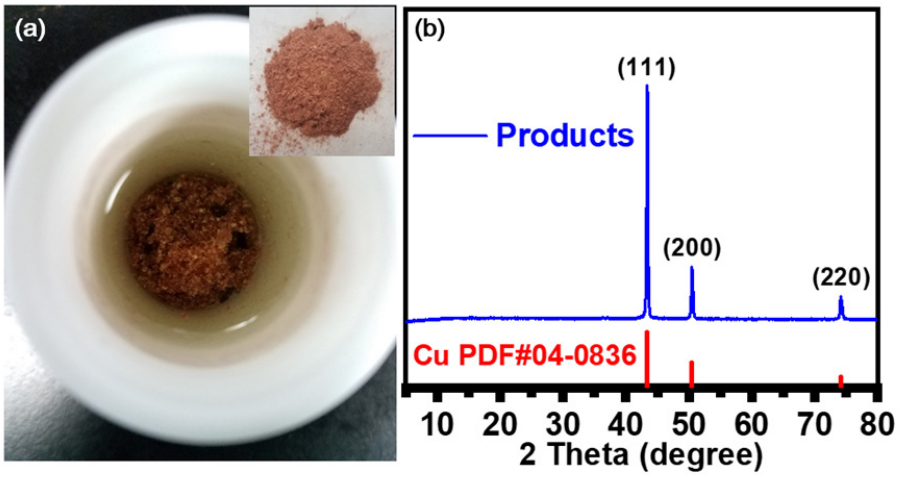

Fig. 2 (a) Optical image of the final reaction, inset (a) is the optical image of as-prepared products. (b) XRD pattern of the products.

SEM was used to characterize the morphology of the Cu-based nanocatalysts. Figures 2a and 2b show high-magnification SEM images of 2D Cu nanocatalysts obtained hydrothermal. SEM was introduced to investigate the morphology of the products, which showed a 2D structure with several wrinkles (as indicated with arrows in Fig. 2a). From the reported work, reductant with less ability or the process is not fast, the whole procedure will be controlled in a kinetic way. This condition is good for the growth of two-dimensional structures. Upon further magnification, as shown in Figure 3b, the as-prepared 2D copper exhibits a well-developed porous structure, indicating a relatively large specific surface area.

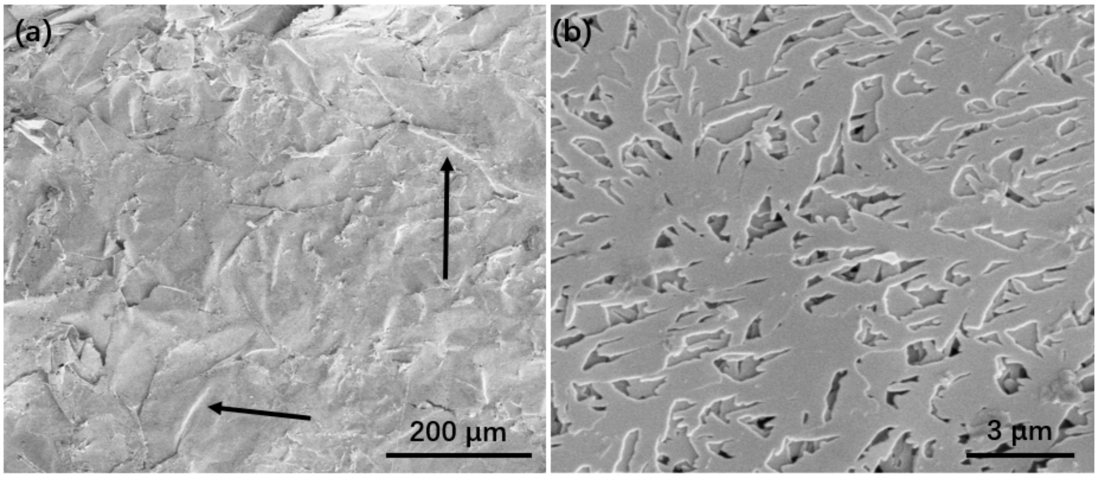

Fig. 3 (a, b) SEM images of obtained samples.

Furthermore, HRTEM was introduced to investigate the detailed morphology of the products. Fig. 4a illustrates the 2D structural characteristics consistent with the previous SEM results. In the magnified image, distinct lattice fringes are observed, with spacings that match the distance of the Cu (111) crystal plane. Distinct lattice stripes were observed, featuring a spacing of approximately 0.208 nm, in accord with the crystal plane of Cu(111), which confirms the successful synthesis of single copper nanomaterials.

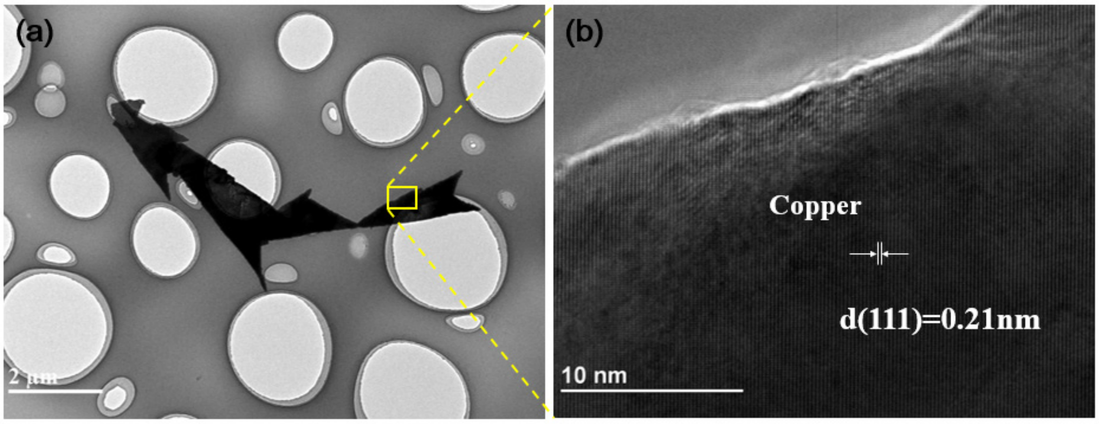

Fig. 4 (a, b) HRTEM images of obtained samples at 200 °C.

4.2 Growth mechanism

The morphology of samples was characterized after the reaction with 0.5, 1, 2, 6, 12, and 24 h. Initially, no significant products were observed, and only bamboo leaves could be seen (Fig. 5a-d). Then, the biomass was hydrolyzed into a reductant, which tuned copper ions into nanoparticles. As the process progressed, many more nanoparticles accumulated. After two hours, the nanoparticles began to arrange themselves along a one-dimensional architecture. At the reaction times of 6 h, much more specific structures developed, covering the biomass surface with close-packed copper crystals. By 12 h, a significant amount of copper nanomaterials was observed in the solution, with the materials forming a dendritic hierarchical structure composed of interwoven ribbon-like units.

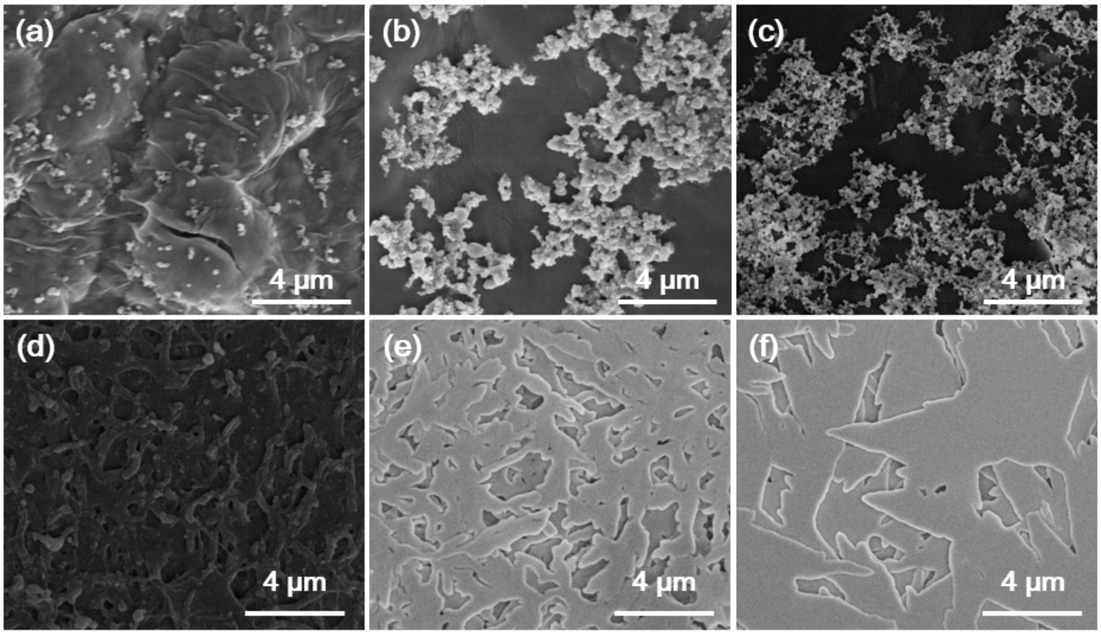

Fig. 5 SEM images of samples for various reaction completion times: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 6 h, (e) 12 h, and (f) 24 h.

4.3 Performance test

The as-prepared nanomaterials were further used as catalysts for the 3-electrodes test of the electrochemical reduction and conversion of carbon dioxide. The reaction product of HCOOH was analyzed, and the formation of Faradaic efficiencies (FE) was summarized in Fig. 6. At four different voltages, the corresponding FEs occurred the highest at -0.8 V (voltage vs RHE). Thanks to the advantages of the two-dimensional structure and abundant porous structure, the nanomaterials exhibit good electrocatalytic activity, suggesting that this material has a promising application in reducing and converting carbon dioxide.

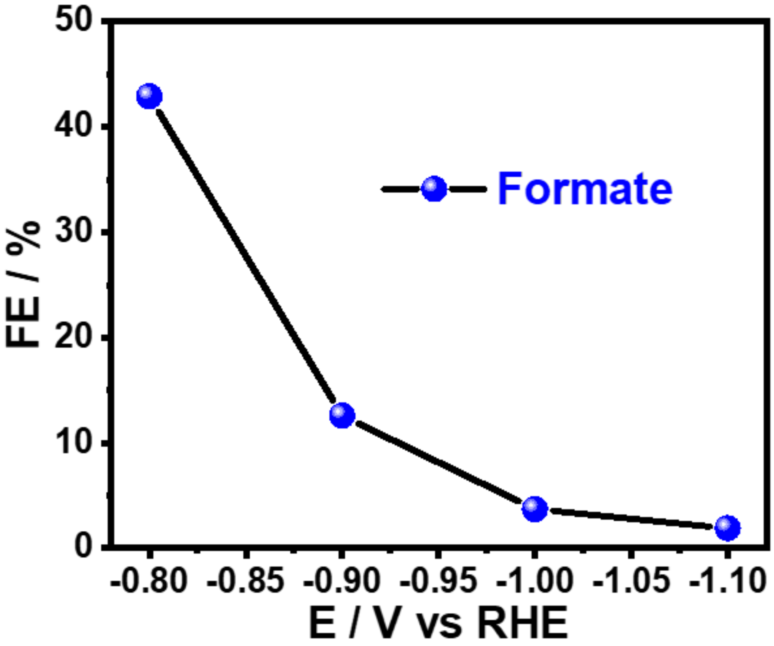

Fig. 6 FE of catalysts for the electrochemical reduction of CO_2.

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4.4 CO_2 reaction mechanism on the surface of Cu-based electrocatalysts

ECO_2RR is a reaction process in which CO_2 is used as a feedstock to generate carbon-containing products by electrochemical reduction, and understanding its reaction mechanism is crucial for designing efficient electrocatalysts, which can be analyzed from thermodynamic and kinetic aspects.

From a thermodynamic point of view, CO_2 molecules are linear and stable under normal environmental conditions, and nearly 750 kJ/mol of energy is required to break the C=O bond, so it is difficult for CO_2 molecules to be activated to participate in the reaction. CO_2 molecule contains two σ bonds, by the C atom sp hybridized orbitals respectively in the two O atom p orbital production; two off-domain π orbitals, by the C atom on the two, did not participate in the hybridization of p orbitals from the side and the O atom's p orbitals respectively shoulder to shoulder to overlap occurs. The electron cloud is mainly bound to the two O atoms, which are more electronegative. Thus, the electrons in these two pairs of highest occupied orbitals are relatively less reactive, resulting in a less chemically active CO_2 molecule. However, C in CO_2 is an electron-deficient center, which can act as one electrophile and react with nucleophilic reagents and electron-carrying groups. The lower energy antibonding orbitals allow CO_2 molecules to be reduced to form products with different valence states.

From the kinetic point of view, ECO_2RR is a slow process involving multiple electron gains and losses, and its products are diverse and complex in composition. ECO_2RR is a complex reaction process involving multiple intermediate steps and electron transfer, which can usually be summarized as CO_2 adsorption, electron transfer, formation of intermediates, further conversion of intermediates, and product release. ECO_2RR is a complex reaction process involving multiple intermediate steps and electron transfer, which can usually be summarized as CO_2 adsorption, electron transfer, formation of intermediates, further conversion of intermediates, and product release. The conversion of CO_2 to hydrocarbons can be summarized by the equation: $xCO_2+yH^++ye^-\rightarrow C_xH_{y-2n}O_{2x-n}+nH_2O$, which usually involves multiple electron transfer processes such as 2, 4, 6, 8, and 12 depending on the type of product desired and the reaction conditions. Different numbers of electron transfers yield different products, and the applied electrode potential strongly influences the final target product.

The generation of HCOOH can be detected by performing the test. For the reaction product formic acid, utilizing biomass as a reducing agent to produce a copper-based catalyst can reduce the overpotential of ECO_2RR, thus improving the selectivity of the target product and effectively inhibiting the occurrence of hydrogen precipitation side reactions. The introduction of biomass makes it easier to adsorb the activated reactant molecules, thus improving the catalytic activity.

5. Conclusion

Dealing with carbon dioxide has become a complex problem, and converting carbon dioxide into higher value-added chemicals is an up-and-coming method to effectively solve the environmental problems caused by carbon dioxide and provide solutions for the future energy crisis and resource depletion. Compared with thermal catalysis and photocatalysis, electrocatalytic carbon dioxide conversion also has a broad application prospect in the future catalytic conversion of carbon dioxide due to its good environmental compatibility and mild and controllable conditions. This study successfully demonstrates the green synthesis of nano copper-based catalysts using biomass-derived reducing agents, addressing the pressing issue of greenhouse gas emissions and energy conservation. The synthesized catalysts were thoroughly characterized using SEM and HRTEM for structural morphology and XRD for crystal phase analysis, which provided insights into the synthesis mechanism. The catalysts were then tested for their effectiveness in reducing and converting CO_2, showing encouraging results in converting CO_2 into valuable energy molecules of HCOOH. Using biomass as a reducing agent to produce copper-based catalysts not only ensures an environmentally friendly approach but also enhances the efficiency of CO_2 conversion. The high added value of the resulting small energy molecules underscores the potential of this green synthesis method in advancing sustainable energy technologies and addressing environmental challenges. This research highlights the feasibility of utilizing renewable resources for catalyst preparation and provides a viable path for effective CO_2 reduction and utilization. It is hoped to contribute to the fundamental understanding and broader application of carbon dioxide electrocatalysis.

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