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Review

# Rational design of Cu-based electrocatalysts for electrochemical reduction of carbon dioxide

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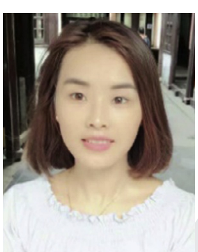
ABSTRACT

The recent development of Cu-based electrocatalysts for electrochemical reduction of carbon dioxide ($CO_2$) has attracted much attention due to their unique activity and selectivity compared to other metal catalysts. Particularly, Cu is the unique electrocatalyst for $CO_2$ electrochemical reduction with high selectivity to generate a variety of hydrocarbons. In this review, we mainly summarize the recent advances on the rational design of Cu nanostructures, the composition regulation of Cu-based alloys, and the exploitation of advanced supports for improving the catalytic activity and selectivity toward electrochemical reduction of $CO_2$. The special focus is to demonstrate how to enhance the activity and selectivity of Cu-based electrocatalyst for $CO_2$ reduction. The perspectives and challenges for the development of Cu-based electrocatalysts are also addressed. We hope this review can provide timely and valuable insights into the design of advanced electrocatalytic materials for $CO_2$ electrochemical reduction.





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## 1. Introduction

At present, fossil fuels are the main energy source (over 80%) to sustain our society and economy [1]. As a result, the excess emission of carbon dioxide ($CO_2$) leads to the climate change and serious environmental issues [2,3]. The conversion of $CO_2$ to useful chemicals or liquid fuels as the renewable energy resources is a highly promising approach to addressing the forthcoming energy crisis and environmental issues [4]. Due to the sluggish reaction kinetics of carbon dioxide reduction (CDR), various approaches (such as photochemical, thermochemical, and electrochemical method) are developing to reduce the energy barrier and improve the activity, selectivity for achieving the sustainable carbon recycling [5]. Electrochemical reduction of $CO_2$ with the help of a proper electrocatalyst is attracting increasing attention due to its unique features. Unlike the other catalysis methods in which harsh conditions (e.g., high pressure and high temperature) needed to initiate the reaction, the electrochemical reduction reaction not only can proceed in ambient temperature and pressure, but also can generate the targeted products by reasonably adjusting the electrocatalyst, operating potential, electrolyte, and others [6,7]. Therefore, it is an important technology option for the conversion of electricity to chemical energy sources, offering the potential to create organic fuels when combined with renewable energy such as solar or wind power as shown in Fig. 1(a). Considering the sluggish reaction kinetics of the liner $CO_2$ molecule with a large activation energy barrier, robust and efficient electrocatalysts are

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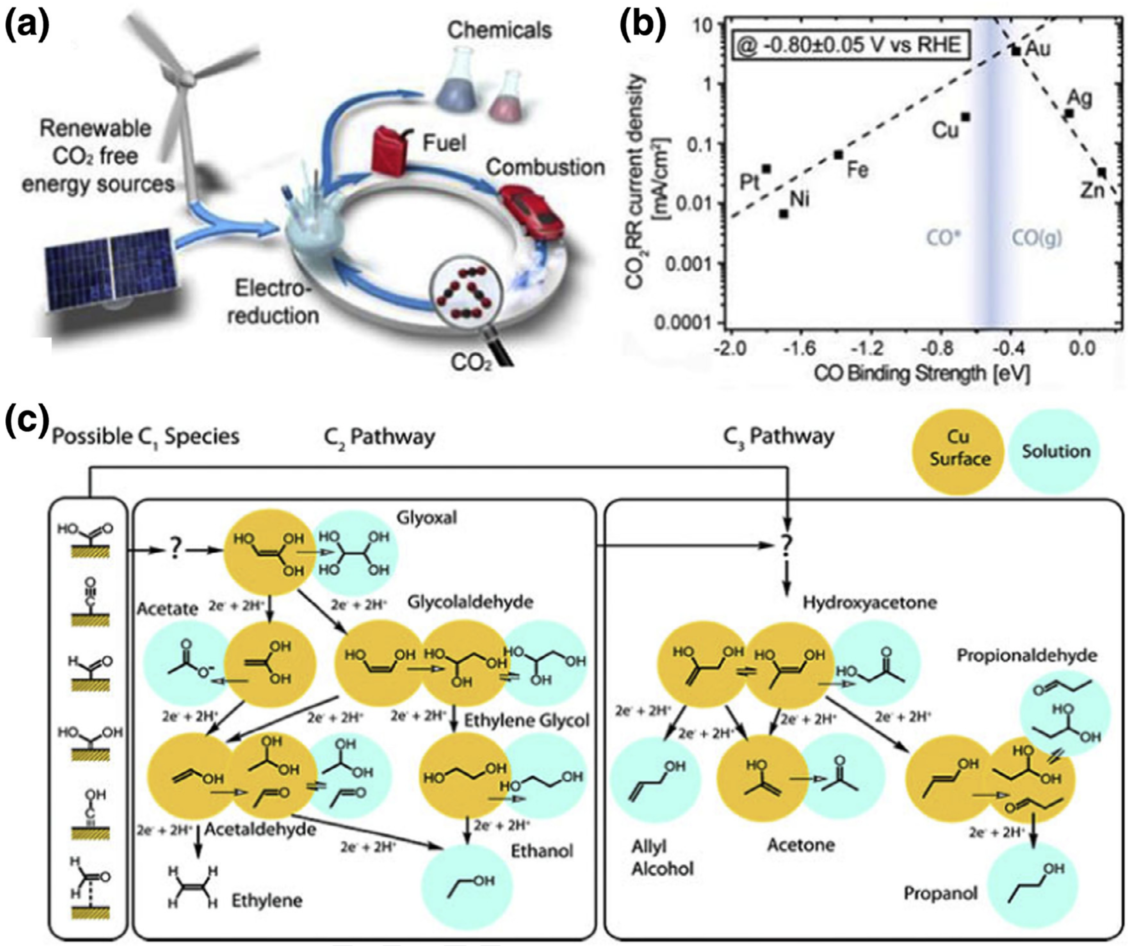


**Fig. 1.** (a) Electrochemical reduction of $CO_2$ coupled with renewable energy sources, such as solar or wind power, enables a sustainable energy cycle in which $CO_2$ is converted to industrial chemicals and fuels in a renewable and sustainable manner. (b) Volcano plot of partial current density for $CO_2$ electrochemical reduction at −0.8 V vs. CO binding strength on various metals. Reproduced with permission from Ref. [10]. (c) Proposed reaction pathways for different products on Cu electrocatalysts. Reproduced with permission from Ref. [36].

required to improve conversion efficiency of $CO_2$ reduction reaction [8]. However, the extensively development of this technology suffers from the high cost, low efficiency, and poor selectivity of the electrocatalysts [9,10]. Specifically, the high price of the noble metal materials hampers their extensive applications. Furthermore, the hydrogen evolution reaction as a competitive reaction often results in the poor selectivity for CDR. To resolve these tricky issues and improve the activity and selectivity of electrocatalysts for CDR, much efforts have been devoted to exploit non-noble metal electrocatalysts on the basis of nanostructure [11,12], alloying [13,14], surface modification [15,16] and so on.

In a $CO_2$ saturated aqueous solution, the typical $CO_2$ electrochemical reduction generally involves three elementary steps: first, the chemical adsorption of $CO_2$ molecules on an electrocatalyst surface; second, the broken of C–O bonds to form C–H bonds along with the electron transfer and/or the proton migration; finally, the rearrangement and desorption of products from the electrocatalyst surface [17,18]. As a typical example, the electrochemical reduction of $CO_2$ to CO is proposed according to the following process, given in Eqs. (1)–(4) [19,20]:

$$CO_2\ (g) + {}^* \rightarrow {}^*CO_2\ (ads) \quad (1)$$

$$CO_2\ (ads) + H^+\ (aq) + e^- \rightarrow\ {}^*COOH \quad (2)$$

$$^*COOH + H^+\ (aq) + e^- \rightarrow {}^*CO + H_2O(l) \quad (3)$$

$$^*CO \rightarrow CO\ (g) + {}^* \quad (4)$$

where asterisk (*) indicates a catalytic site for adsorbing a surface-bound species. $CO_2$ electrochemical reduction is a multistep reaction process including two-, four-, six-, or eight-electron reaction processes [21]. A series of products including CO and hydrocarbons (e.g., formic acid, methanol, ethanol, methane, aldehyde, ethylene, ethane) would be synthesized on the basis of the different reaction pathways (reactions (5)–(10)) [22,23]. The generated products such as ethanol and methanol can be directly used as fuels, usually being used to partly replacement gasoline for internal combustion engines [24]. Carbon monoxide can be converted into valuable liquid fuels or other useful chemicals through further Fischer–Tropsch process [25]. In addition, methane is main component of natural gas and ethylene can be used to produce plastics. A wide range of valuable reduced carbon compounds further concretely illustrates the significance of $CO_2$ electrochemical reduction.

$$CO_2 + 2H^+ + 2e^- \rightarrow\ CO + H_2O\ E^0 = -0.52\ V \quad (5)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH\ E^0 = -0.61\ V \quad (6)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O\ E^0 = -0.51\ V \quad (7)$$

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