

## Review

# Nanostructured nonprecious metal catalysts for electrochemical reduction of carbon dioxide



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## ABSTRACT

Electrochemical reduction of carbon dioxide powered by renewable electricity represents a promising solution for energy and environmental sustainability. To enable this technology, active and selective catalysts must be developed. Noble metals exhibit excellent activity but are hampered by their low abundance and high cost. Thus, searching for efficient nonprecious metal catalysts for practical applications is vital. In this review, the recent progress on nanostructured nonprecious metal catalysts for electrochemical reduction of carbon dioxide is summarized. These catalysts are classified into five categories: metals, partially oxidized metals, metal oxides and sulfides, doped carbons, and organic frameworks. The areas of focus are material synthesis, structure and components, catalytic performance, and reaction mechanisms. Several important factors that affect activity, such as particle size, interface strain, grain boundary, crystal facet, oxidation state, heteroatom configuration, and organic hybrid, are discussed. Finally, some perspectives are provided for future developments and directions of the synthesis and functionalization of nonprecious metal catalysts, with emphasis on the potential advantages of nanoporous materials for carbon dioxide reduction.

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## Introduction

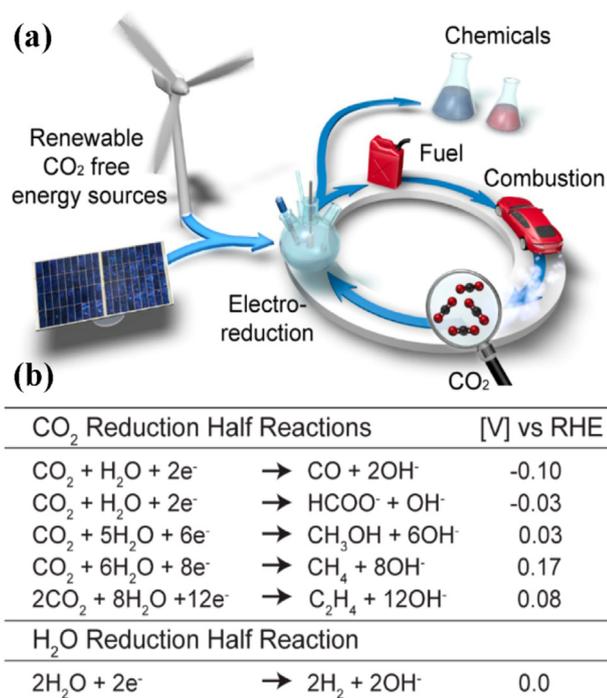
To satisfy the energy demand of an increasing world population, fossil fuels including coal, petroleum, and natural gas are being burned on an unprecedented scale. Unfortunately, this leads to the annual release of more than 30 billion tons of carbon dioxide (CO<sub>2</sub>) into the environment, with continuous accumulation over time [1]. From a pre-industrial level of about 270 ppm, the concentration of CO<sub>2</sub> in the atmosphere has now surpassed the 400 ppm mark. As is well known, CO<sub>2</sub> is a notorious greenhouse gas that traps the sun's heat and is one of the main contributors to presently observed climate change phenomena. Therefore, reducing CO<sub>2</sub> production and converting CO<sub>2</sub> into valuable materials are urgent needs for the sustainable development of human society [2–5].

In recent years, catalytic CO<sub>2</sub> reduction to fuels has been investigated actively using thermochemical, photochemical, and electrochemical approaches [6–10]. Among them, electrochemical CO<sub>2</sub> reduction has become attractive because it has several characteristic advantages over other approaches. Specifically, the reaction

can be conducted under ambient conditions, the reaction rate can be controlled easily by tuning the external bias, and the supporting electrolytes can be fully recycled so that the overall chemical consumption can be minimized to only water [11]. Moreover, an artificial photosynthesis process might be achieved if the electricity for CO<sub>2</sub> electrochemical reduction is derived from renewable energy, such as wind, solar, and tidal power [12]. With renewable electricity as an input, carbon dioxide and water could be converted into fuels and industrial chemicals (Fig. 1a). Such a process provides an efficient means to storage intermittent energy. However, CO<sub>2</sub> is very stable under environmental conditions, and a highly negative potential is needed to drive the reduction reaction. Meanwhile, there are several proton-assisted multiple-electron-transfer processes with similar potential, which makes it difficult to control the selectivity. For example, the reduction reactions can occur via 2-, 6-, 8-, and 12-electron transfer processes (Fig. 1b) and result in a variety of products, including carbon monoxide (CO), formic acid (HCOOH), methanol (CH<sub>3</sub>OH), formaldehyde (HCHO), methane (CH<sub>4</sub>), ethylene (CH<sub>2</sub>CH<sub>2</sub>), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), acetate (CH<sub>3</sub>COOH), and many others [13]. Moreover, the hydrogen evolution reaction (HER) usually prevails over CO<sub>2</sub> reduction in aqueous electrolytes. Therefore, active electrocatalysts need to be developed

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**Fig. 1.** (a) Illustration of an artificial way of carbon recycling powered by renewable electricity sources such as wind and solar. (b) Several representative half reactions and reduction potentials of CO<sub>2</sub> reduction reactions, along with that of the HER. Reproduced with permission from Ref. [12]. Copyright 2014 American Chemical Society.

that promote the CO<sub>2</sub> reduction reaction with high efficiency and selectivity while suppress the competing HER.

Nanostructured metal catalysts have attracted much attention for electrochemical CO<sub>2</sub> reduction due to their unique properties compared to their polycrystalline counterparts. They have a high catalytic surface area and contain a large portion of edge or low-coordinated sites, which have different catalytic behaviors as compared to fully coordinated sites on the flat surface of their bulk samples. The improved catalytic performances are demonstrated in nanostructured catalysts. Typically, nanostructured noble metals such as Au, Ag, and Pd have exhibited highly selective conversion of CO<sub>2</sub> to CO at relatively low overpotentials [14–26]. For example, monodisperse 8-nm Au nanoparticles showed a faradaic efficiency (FE) of up to 90% at –0.67 V vs. the reversible hydrogen electrode (RHE) in an aqueous 0.5 M KHCO<sub>3</sub> electrolyte [16]. Density functional theory (DFT) calculations suggested that edge sites on the Au nanoparticle surface favored CO evolution, while corner sites favored HER. Interestingly, based on this result, ultrathin Au nanowires with dominant edge sites on their surface were prepared and demonstrated to be significantly more active and selective than nanoparticles [18]. At –0.35 V vs. RHE, the FE reached 94% for CO production and stayed at this level for 6 h without any noticeable change. Similarly, nanostructured Ag and Pd have also shown excellent activity to selectively convert CO<sub>2</sub> to CO [27–38]. Nanoporous Ag exhibited an approximately 92% selectivity for CO at a mediocre potential of –0.6 V vs. RHE [35], while on 2.4- and 3.7-nm Pd, a maximum FE value of 91.2% was reached at –0.89 V vs. RHE [38]. However, precious metals are hampered by their low abundance and high cost, which restrict their practical and large-scale application. Thus, searching for abundant and efficient electrocatalysts with selectivity toward valuable fuels is vital for commercializing CO<sub>2</sub> electroreduction technologies.

Although several review articles related to CO<sub>2</sub> reduction have been published, nonprecious metal catalysts have not been sys-

tematically discussed [39–45]. Less expensive and environmentally friendly materials such as Cu, Zn, Sn, Bi, Co, carbons, and organic frameworks have demonstrated promise for the reduction of CO<sub>2</sub> to hydrocarbons, formic acid, and CO. In the early study, most of their bulk metals have been used as electrocatalysts for CO<sub>2</sub> reduction and shown some activities [46–51]. For example, high purity polycrystalline Cu produced CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> with FE of 33.3% and 25.5%, respectively, at –1.44 V vs. the standard hydrogen electrode (SHE) with the current density of 5 mA cm<sup>-2</sup> and *in-situ* electrodeposited Cu electrode improved the selectivity by changing the surface morphology with the overall FE of 79% [49]. Bulk Zn metal showed high selectivity for CO with FE of 79.4% at –1.54 V vs. SHE while bulk Sn metal showed excellent selectivity for HCOOH with FE of 88.4% at –1.48 V vs. SHE. Although bulk metals exhibited interesting performance, it was found they were easily poisoned by impurities due to their low surface area. Furthermore, the early results mainly reported the selectivity of metals, but the energy efficiency (*e.g.*, overpotential), activity stability, material synthesis, and structure characterization have been very little reported. By combining with the modern methods and technologies, the development of CO<sub>2</sub> electrocatalyst exhibited several new trends in the recent research. Typically, nanotechnologies are well applied in the fabrication of nonprecious metal catalysts, and nanostructured metals, partially oxidized metals, and metal compounds exhibit better activities than their bulk samples. The material structures and catalytic properties are studied in depth by newly developed analysis and characterization technologies. More importantly, the novel non-metal or little-metal doped carbons and organic frameworks have also shown outstanding performance for CO<sub>2</sub> reduction, comparable to noble metals, which may represent a future research direction. Therefore, a comprehensive review specifically focused on nonprecious metal catalysts is necessary to promote the practical applications of CO<sub>2</sub> conversion technology.

In this article, the synthesis of specific nanostructures, their unique catalytic properties, and their reaction mechanisms for nonprecious metal catalysts are systematically summarized. These catalysts are classified into five categories: metals, partially oxidized metals, metal oxides and sulfides, doped carbons, and organic frameworks. The important factors that affect activity are discussed. Future strategies are proposed for the design of highly selective and efficient CO<sub>2</sub> reduction electrocatalysts.

### Metal catalysts (Cu and Zn)

Cu has been known as an unique metal catalyst in its ability to produce a high quantity of hydrocarbon fuels from the electrochemical reduction of CO<sub>2</sub> since the first report by Hori et al. in 1985 [52–55]. A total of 16 different CO<sub>2</sub> reduction products have been observed on Cu foil using a highly sensitive electrochemical cell combined with gas chromatography and nuclear magnetic resonance spectroscopy [56]. Among them, the hydrocarbons of methane and ethylene products have the largest current efficiencies, while the remaining 14 products are oxygenates, 11 of which are C<sub>2</sub> and C<sub>3</sub> products. By comparing the activity of different transition metals, it is found that the product yield and composition of the CO<sub>2</sub> reduction depend on the transition metal's binding energy of CO, which is believed to be an important intermediate in the reduction process. Interestingly, Cu possesses an intermediate binding energy for CO, which may be the reason for its ability to catalyze the formation of more reduced products. However, Cu has three drawbacks as a CO<sub>2</sub> reduction electrocatalyst: large overpotentials, poor selectivity, and instability for a long time. In order to enhance the performance of Cu electrodes, various kinds of nanostructured Cu catalysts have been prepared, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires, two-dimensional

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