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Review

Recent advances in Cu-based nanocomposite photocatalysts for CO_2 conversion to solar fuels

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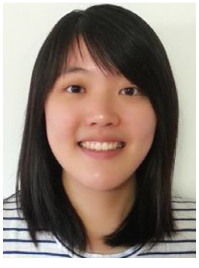
ABSTRACT

CO_2 conversion *via* photocatalysis is a potential solution to address global warming and energy shortage. Photocatalysis can directly utilize the inexhaustible sunlight as an energy source to catalyze the reduction of CO_2 to useful solar fuels such as CO, CH_4, CH_3OH, and C_2H_5OH. Among studied formulations, Cu-based photocatalysts are the most attractive for CO_2 conversion because the Cu-based photocatalysts are low-cost and abundance comparing noble metal-based catalysts. In this literature review, a comprehensive summary of recent progress on Cu-based photocatalysts for CO_2 conversion, which includes metallic copper, copper alloy nanoparticles (NPs), copper oxides, and copper sulfides photocatalysts, can be found. This review also included a detailed discussion on the correlations of morphology, structure, and performance for each type of Cu-based catalysts. The reaction mechanisms and possible pathways for productions of various solar fuels were analyzed, which provide insight into the nature of potential active sites for the catalysts. Finally, the current challenges and perspective future research directions were outlined, holding promise to advance Cu-based photocatalysts for CO_2 conversion with much-enhanced energy conversion efficiency and production rates.

Huan Xie received her bachelor degree in 2011 and attained a doctorate in 2016 in Material Science from Wuhan University of Technology. She is currently a postdoctoral fellow at Huazhong University of Science and Technology under the supervision of Professor Qing Li. Her current research interests focus on electrocatalysis and photoelectrocatalysis for CO_2 reduction and hydrogen evolution.



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1. Introduction

In our modern world, energy is one of the most crucial aspects of human begins. For the past century, the continuous consumption of traditional fossil fuels such as coal, petroleum, and natural gas as the primary source of energy is not sustainable. The utilization of fossil fuel has caused prodigious CO_2 emission into the atmosphere, which leads to the severe global environment and climate changes [1–4]. Currently, both climite changes and energy shortage are one of the most critical issues that need to be addressed [1]. Plausible approaches are to reduce CO_2 emission and recycle excessive CO_2 from the atmosphere [4]. Renewable energy technologies such as solar, water, wind, and tide energy can be used to mitigate the emission of CO_2. Meanwhile, the development of efficient technologies to recycle and utilize CO_2 is still a challenge that needed to overcome to achieve the carbon neutralized society [5,6]. Photocatalytic CO_2 conversion to solar fuels is an attracting technology to approach this challenge. The technology can directly utilize the endless solar energy to transform CO_2 into reusable C1 or C2 solar fuels at ambient conditions. The solar fuels mentioned above are CO, CH_4, CH_3OH, HCHO, HCOOH, and C_2H_5OH [7,8]. Importantly, there would be zero secondary pollution generated during the process, which indicates that photocatalytic conversion of CO_2 is a promising solution to address both global warming and energy shortage [7].

Semiconductors are attractive materials for light-harvesting because of their unique band gap structures [9]. Photocatalytic CO_2 conversion commonly performs in a gaseous environment with H_2O vapor as the source of proton on semiconductors. Electrons then are generated by the absorption of external photons, which are accompanied with the formation of holes within the semiconductors. The band gap structure of semiconductor catalysts is one of the critical factors that govern catalysts performance for CO_2 conversion. The reductive power of electrons generated from the photo-excitation process is strongly dependent on the energy levels of both valance band (VB) and conduction band (CB) of the semiconductor catalysts as shown in Fig. 1. Ideally, the photocatalyst for CO_2 conversion process must have the conduction band (CB) of the semiconductor catalysts positions at the more negative potential than the redox potential of product(s)/CO_2, and must have the valence band (VB) positions at the more positive potential than the redox potential of O_2/H_2O [1]. Furthermore, the efficiency of charge carrier separation, the morphology and composition of photocatalysts, and the intensity of applied illumination are another crucial factors in governing the performance for CO_2 photoreduction. Recently, Cu-based heterogeneous photocatalysts have received considerable attention [10–12] due to their competitive prices relative to precious metal based photocatalysts [13,14] such as Pt [15–19], Pd [20–24], Au [25–30], Ag and In [31–37]. The combination of copper, copper alloy nanoparticles (NPs), and copper oxides with other semiconductors or photosensitizers such as TiO_2 [13,38–46], Ce_2O_3 [47], Fe_2O_3 [48], $SrTiO_3/TiO_2$ and graphene oxide [49–51] are beneficial to the separation of electrons and holes through the formation of metal–semiconductor or p–n heterojunctions. Cu-based NPs or copper oxides can be adopted as the photosensitizer with large band gap semiconductors to increase light adsorption capability [13,38–46,52–57]. Because copper-based nanoparticles have the plasma resonance induced visible light absorption and copper oxides have the narrower band gaps. Despite several well-established reviews regarding the overall introductions of heterogeneous photocatalysts for CO_2 conversion [1,7,9,58,59], few review focuses on Cu-based photocatalysts.

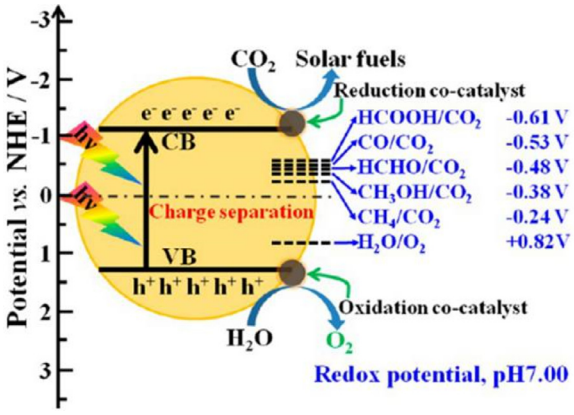

Fig. 1. Mechanism schematic of photocatalytic CO_2 conversion on a semiconductor photocatalyst for solar fuels production. The process mediated by suitable redox co-catalysts and relative energy levels of various redox couples in aqueous solution with pH at 7.0 [7]. Copyright 2016, American Chemical Society.

In this review, we have systematically summarized the representative works of literature concerning Cu-based photocatalysts for CO_2 conversion to solar fuels, including copper and copper-alloy nanoparticles (NPs) based photocatalysts, copper oxides, and copper sulfides based photocatalysts. The relationships between synthetic method, morphology, band structure and the photocatalytic performance of Cu-based photocatalysts for CO_2 conversion have been considered. Additionally, the mechanism of photocatalytic activity, stability enhancement, and possible reaction routes on different Cu-based photocatalysts for CO_2 conversion has been discussed. The current achievements on Cu-based photocatalysts were summarized. Furthermore, future research directions were outlined to inspire researchers to advance heterogeneous Cu-based photocatalysts for efficient CO_2 conversion.

2. Copper and copper–alloy nanoparticles based photocatalysts

Copper nanoparticles (NPs), with the size of 30 nm were coupled with black TiO_2 for the investigation of the role of Cu during photocatalytic CO_2 reduction [13]. Cu NPs were fabricated by co-precipitating CuO with Al_2O_3 by using a solution of $Cu(NO_3)_2$, and $Al(NO_3)_3$, containing Na_2CO_3. After calcination at 450 °C, the composite was washed with NaOH to remove Al_2O_3, followed by heat treatment in H_2 at 280 °C. The composite was then dispersed into titania sol forming a gel after hydrolyzation. As a result, Cu NPs decorated on black TiO_2 photocatalysts with different loading amounts (1, 2 and 4 wt%) were obtained after calcination in a vacuum. The visible light source of 400–800 nm with an intensity of 0.220 W cm^{-2} was applied for CO_2 photoconversion. The visible light absorption capability of Cu/TiO_2 composites was consistently enhanced with an increase of Cu loadings, which was ascribed to the presence of Cu NPs facilitating the formation of oxygen vacancy in TiO_2. Additionally, the photocurrent density of Cu/TiO_2 photocatalyst with a Cu loading of 4 wt% was improved over 12 times compared to that of undecorated black TiO_2. This phenomenon was attributed to the formation of Schottky barrier between TiO_2 and Cu, which results in the aggregation of electrons in Cu NPs, and thus promots the charge carrier separation efficiency of TiO_2. Consequently, the activity of Cu/TiO_2 composite for CO and CH_4 gener-

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