Transition Metal Oxides-based Photocatalysts for Enhanced CO_2 Reduction

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Photocatalytic reduction of CO_2 using solar energy to energy-rich fuels (i.e., artificial photosynthesis) is an ideal solution for simultaneously reliving worldwide environmental and energy problems. Albeit great efforts have been done to explore the potential of artificial photosynthetic materials for CO_2 reduction, the conversion of CO_2 by artificial photosynthesis is still a challenge. Transition metal oxides (TMOs) such as TiO_2, Fe_2O_3, Cu_2O, ZnO, and their composites with well-controlled structural, crystalline, and surface features function as promising photocatalytic scaffolds for CO_2 reduction. This is supported by their massive abundance, non-toxicity, and high stability in the reaction systems.

Despite these merits, TMO-based semiconductors are only UV-responsive and have limited activity under sunlight irradiation. Besides, photocarriers generated over single-component TMOs suffer from detrimental recombination due to the lack of driving forces for separation. Therefore, various approaches have been proposed to improve the photocatalytic performance of TMOs-based photocatalysts towards CO_2 reduction. In this work, different modification strategies for TMOs have been presented to promote their activity towards CO_2 photoreduction, including plasmonic metal loading, hollow structure formation, co-doping, and S-scheme heterojunction construction, as follows:

(1) We employed a facile electroless reduction strategy for the in-situ growth of plasmonic Cu nanoparticles (NPs) over ordered Cu_2O octahedrons. Amorphous carbon formed at the Cu_2O surface *via* calcination provides an electroless reduction configuration for the conversion of Cu ions within Cu_2O lattice into Cu NPs. The in-situ growth guarantees rational coupling of Cu_2O with Cu NPs, enabling the extension of optical absorption range as well as achievement of plasmon-induced interfacial charge-transfer transition (PICTT) upon excitation of Cu-localized surface plasmon resonance (LSPR). The PICTT involves direct electron transfer from the plasmonic metals to the acceptor states in a semiconductor (SC). Such plasmonic decay is fostered by strong orbital coupling and mixing of electronic levels in plasmonic metals and SC. Due to the unique features of plasmonic Cu NPs, the integrated Cu/Cu_2O system attains a desirable CO_2 photoreduction activity with a rate over two times higher than Cu_2O. The fascinating PICTT mechanism induces a CO_2 reduction activity over Cu/Cu_2O even under near-

infrared irradiation.

(2) A facile one-pot approach was implemented to design triple-core-shell Mn, C-codoped ZnO hollow spheres as efficient photocatalysts for CO_2 reduction. The Mn ions with switchable valence states function as “ionized cocatalyst” to promote the CO_2 adsorption and light-harvesting efficiency of the system. Besides, they can capture photogenerated electrons from the conduction band of ZnO and provide the electrons for CO_2 reduction. This process is continuous due to the switchable valence states of Mn. The structural complexity and the co-doping of the prepared photocatalyst culminate in vast light absorption, improved charge separation, and adequate CO_2 adsorption, as prominent features for efficient CO_2 reduction catalyst. Benefited from such unique features, the prepared photocatalysts demonstrated excellent CO_2 conversion performance.

(3) A robust S-scheme heterojunction composed of 3D ZnO hollow spheres wrapped by 2D g-C_3N_4 layers was fabricated. The electrostatic attraction between both components not only facilitated the exfoliation of g-C_3N_4 layers but also strengthened the photocatalyst framework. The prepared g-C_3N_4/ZnO photocatalyst afforded an enhanced CH_4 production rate, which is *ca.* 40 and 7 times higher than those of pure ZnO and g-C_3N_4, respectively. The improved activity was attributed to extended light absorption and suppressed charge carrier recombination. Moreover, apart from other characterization techniques that are used to assess the charge transfer dynamics, electron paramagnetic resonance (EPR) was used to probe charge movement in the fabricated S-scheme heterojunction. An observable shift of the relevant EPR peak is noticed after the construction of g-C_3N_4/ZnO heterostructure, indicating the electron transfer process.