Ph.D defense Seminar on the topic of

Photocatalytic CO_2 reduction using Metal-Organic Framework (MOF) based nanocomposite

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Abstract

The design and development of sustainable and cost-effective photocatalysts necessitate significant effort for improved CO_2 reduction efficiency. Metal-organic framework (MOF) especially zeolitic imidazole framework (ZIF-67) has shown tremendous efficiency in the field of CO_2 adsorption, storage, and conversion due to its huge surface area and metal-ligand charge transfer effect (MLCT).

In the first phase of the research a metal-organic imidazole framework-based heterojunction, Zn_2GeO_4/ZIF-67 nanocomposite has been successfully synthesized where Zn_2GeO_4 nanorod deposited on the surface of high crystalline ZIF-67 to form an electronic Z scheme mechanism. The Zn_2GeO_4/ ZIF-67 nanocomposite containing 20% Zn_2GeO_4 nanorod exhibit at about 1.62 times higher methanol production (41.16 μmolg^{-1}) than pure ZIF-67 (25.39 μmolg^{-1}) and the highest ethanol production was 1.53 times higher (32.66 μmolg^{-1}) than pure ZIF-67 (21.34 μmolg^{-1}) after 8 hours of light irradiation. The electronic interaction of ZIF-67 and Zn_2GeO_4 has been studied theoretically using density functional theory calculation. Molecular orbital transition and excitation states were also calculated using time-dependent density functional theory calculation. The reaction pathway for CO_2 reduction was determined by calculating the free energy for each charge transfer intermediate.

The second phase of the research work adopts a convenient but more efficient method to prepare an S-scheme composite photocatalyst integrating narrow band gap semiconductor $ZnMn_2O_4$ (ZMO) and zeolitic imidazole framework ZIF-67 (ZIF-67) for improved photocatalytic CO_2 reduction. The designed photocatalyst ZMO(X)/ZIF-67 shows the more significant ability to capture visible light to individual ZMO and ZIF-67. The ZMO(X)/ ZIF-67 nanocomposite containing 3% ZMO nanosphere exhibits 1.91 times higher methanol generation (48.64 μmolg^{-1}) compared to pure ZIF-67 (25.36 μmolg^{-1}) and ethanol generation was 1.42 times higher (30.32 μmolg^{-1}) compared to pure ZIF-67 (21.28 μmolg^{-1}) for 8 hours visible light. The composites' increased photocatalytic performance might be attributed primarily to excellent photogenerated charge separation and transfer via the linked S-scheme heterojunction between ZMO nanospheres and ZIF-67. Various characterization methods are used to explore the structural, morphological, optical, and electrochemical features of synthesized photocatalysts, and a thorough photocatalytic mechanism is provided. After four recyclings, the composite photocatalyst demonstrated good stability and recyclability. This study attributed to a viable method for constructing a direct S-scheme heterojunction for photocatalytic CO_2 reduction.

Metal-organic frameworks (MOFs), with high surface area, are gaining popularity in photocatalysis, but their high electron-hole (e^-, h^+) recombination and low light harvesting capacity limit their utility. Graphene nanoflake (GNF) is a novel, low-cost carbon nanomaterial that has received attention owing to its non-toxicity, high aqueous solubility, unique photoluminescence properties, and excellent photostability. In the third phase of the research work, graphene nanoflake (GNF) decorated zeolitic imidazole framework ZIF-67 (GNF(X)/ZIF-67) has been synthesized for improving visible-light-driven photocatalytic CO_2 reduction performance. The composite GNF6/ZIF-67 decorated with 6% GNF nanoflake achieves the highest methanol generation of 50.93 µmolg^{-1} and the highest ethanol generation of 33.97 µmolg^{-1} after 8 hours of visible light irradiation, compared to pure ZIF-67 which is 1.93 and 1.59 times respectively. The effect of GNF on boosting the visible-light photocatalytic activity of ZIF-67 was explored based on the UV-Vis DRS spectra, electrochemical impedance spectra (EIS), transient photocurrent response, and photoluminescence (PL) experiment. This work may discover a new way to synthesize carbon-based photocatalysts for applying CO_2 photoreduction.

In the fourth phase of the research work the synergistic effect of semiconductors CdS, g-C_3N_4 (GCN), and metal-organic framework NH_2-MIL-101(Fe) (NML-101(Fe), on efficient photocatalytic CO_2 conversion to CH_3OH was investigated. The successful synthesis and design of a dual Z-scheme NML-101(Fe)/CdS/GCN (NMCG(X)) ternary hetero-nanostructured system (THS) was demonstrated, in which CdS nanoparticles and NML-101(Fe) are deposited on the surface of GCN to form a Dual Z-scheme mechanism with excellent photocatalytic performance. After 8 hours of visible light irradiation, NMCG8 nanocomposites containing 37.5% GCN, 25% CdS, and 37.5% NML-101(Fe) exhibit 1.53 times higher methanol production (53.89 µmolg^{-1}) than pure NML-101(Fe) (35.11 µmolg^{-1}). The efficient reduction of CO_2 was largely attributed to the systematic transportation of photo-exited e^- and h^+ mediated by the dual Z-scheme mechanism, as demonstrated by PL spectra, electrochemical impedance spectra (EIS) studies, and Transient photocurrent response testing.

Keywords: Photocatalysis, Photocatalytic CO_2 reduction, Metal-organic framework, Graphene nanoflake, Metal ligand charge transfer effect, Z scheme, S-scheme, Dual Z-scheme.