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博士の専攻分野の名称

博士 (理学)

氏名 史 力

学 位 論 文 題 名

Construction of Metal-organic Frameworks Based Materials for Visible Light Photocatalysis

(可視光応答型金属有機構造体の創成と光触媒特性に関する研究)

Metal-organic frameworks (MOFs) have received much research interest in the field of photocatalysis because of their advantages, such as high surface area, visible light absorption, tunable electronic structure, etc. However, due to the fast electron-hole recombination rate and the low light absorption capability, the photocatalytic performances of the MOFs based photocatalysts are still moderate. In this thesis, the research object is to construct efficient MOFs based photocatalysts to explore their potential applications as well as understand the corresponding mechanism of photocatalysis. Three strategies, including amine functionalization, heterojunction fabrication and metal ions implantation, were proposed to enhance the photocatalytic performances of the MOFs based photocatalysts.

In chapter 1, a general background of photocatalysis and photocatalytic materials is introduced. Then the recent development of the MOFs based photocatalysts is also introduced.

In chapter 2, an iron(III) MOF based photocatalyst, named as MIL-88B (Fe), was constructed and explored for photocatalytic Cr(VI) reduction under visible light. An organic ligand modification strategy, namely amine functionalization, was demonstrated to be effective for enlarging the light absorption and improving the carrier separation and transfer efficiency of MIL-88B (Fe). It was found that in addition to the direct excitation of $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters in MIL-88B (Fe), the amine functionalized organic linker could also be excited and then transferred an electron to $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters to reduce Cr(VI). As a result, the amine functionalized MIL-88B (Fe) showed much enhanced photocatalytic activity for Cr(VI) reduction than bare MIL-88B (Fe).

In chapter 3, a MOF based heterostructure photocatalyst that composed of a zirconium MOF (UiO-66) and $\text{g-C}_3\text{N}_4$ nanosheet (CNNS) was constructed for photocatalytic CO_2 reduction under visible light. Due to the well match of the energy level between UiO-66 and CNNS, a heterojunction structure in UiO-66/CNNS hybrid photocatalyst could be formed. As evidenced by the quenching of the photoluminescence intensity and increase of fluorescence lifetime in UiO-66/CNNS compared with bare CNNS, the electrons from photoexcited CNNS could transfer to UiO-66. Such electron transfer could substantially suppress the

electron-hole pairs recombination in the CNNS, and also supply long-lived electrons for the reduction of CO₂ molecules adsorbed in UiO-66. As a result, the UiO-66/CNNS heterostructure photocatalyst exhibited a CO yield of 59.4 $\mu\text{mol g}_{\text{CN}}^{-1}$ after visible light illumination for 6 hours, which was 3.4-fold higher than that of CNNS.

In chapter 4, a porphyrinic MOF, named as PCN-224, was employed as a visible-light-active photocatalyst for isopropanol (IPA) oxidation. Coordinatively unsaturated Fe(III) ions were implanted into porphyrin units and a new hybrid structure Fe@PCN-224 was constructed. The implantation of coordinatively unsaturated Fe(III) sites into the porphyrin units of PCN-224 could not only greatly boost the electron-hole separation efficiency, but also construct a Fenton reaction to convert the *in situ* photogenerated H₂O₂ into active oxygen-related radicals ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$) during the photocatalytic IPA oxidation reaction. As a result, the newly developed Fe@PCN-224 exhibited significantly enhanced photocatalytic activity, which was equivalent to an 8.9-fold improvement in acetone evolution rate and 9.3-fold enhancement in CO₂ generation rate compared with the PCN-224.

In chapter 5, a porphyrinic MOF, named as MOF-525, was constructed for photocatalytic CO₂ reduction under visible light. The modular optimization of MOF-525 was realized by incorporation of coordinatively unsaturated single cobalt atom into its matrix. The presence of single cobalt atom in the MOF-525 could greatly boost the electron-hole separation efficiency in porphyrin units. Directional migration of photogenerated exciton from porphyrin to catalytic cobalt centers was witnessed, and thus achieved the long-lived electrons for the reduction of CO₂ molecules that were adsorbed on cobalt centers. As a result, MOF-525 comprising atomically dispersed catalytic centers exhibited significantly enhanced photocatalytic conversion of CO₂, which was equivalent to a 3.1-fold improvement in CO evolution rate (200.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$) and 5.9-fold enhancement in CH₄ generation rate (36.7 $\mu\text{mol g}^{-1}\text{h}^{-1}$) compared with bare MOF-525.

In chapter 6, an overall summary of this dissertation work was provided. This thesis carried out a systematic study on the construction of efficient MOFs based photocatalysts for visible light photocatalytic reactions, including Cr(VI) reduction, CO₂ reduction and IPA oxidation. Organic ligand modification, heterojunction fabrication and metal ion implantation were proved to be effective strategies to improve the photocatalytic efficiencies of the constructed MOFs based photocatalysts. The findings in this study present some potential applications of MOFs based materials, aid to understand the mechanism of photocatalysis, and more importantly, highlight some universal design principles to the efficient MOFs based photocatalysis.