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新型铀酰 **MOF** 高效光催化 **CO2** 还原

摘要

在过去的几十年里，随着化石燃料的大量消耗，空气中的二氧化碳含量逐渐增加，全球变暖和能源危机等环境问题日益严重。利用太阳光将 CO2 光催化还原为 CO、CH4 等高附加值产物是保护环境、解决能源危机的重要手段之一。金属-有机框架（MOFs）是由有机配体和无机金属离子/团簇组成的一种晶态多孔结构，具有高结晶性、高的比表面积、灵活可调的多孔结构以及易修饰等特点，在光催化领域具有广阔应用前景。此外，独特的光化学性质和多样的配位模式使得铀酰离子既可以作为 MOFs 材料的金属节点，又可以作为光催化反应的活性中心。因此，铀酰 MOFs 有望成为新型异相光催化剂。在此，我们设计并制备了一种新型铀基 MOF 材料 IHEP-101[(CH3)2NH2][UO2][UO2(L)(DMF)][UO2(L)(H2O)]0.5·(DMF)1.5。其中，Salen 配体的 N2O2 空腔被铀酰离子占据，形成线性的 [UO2L] 金属化二羧酸配体，该金属化配体继续与铀酰离子配位，形成一个扭曲的二维蜂窝网状结构。相邻层通过 π - π 相互作用堆叠成三维框架结构。IHEP-101 表现出良好的光催化 CO2 还原活性，在不添加任何牺牲剂的条件下，CO 的产率可达 458 μmol·g-1·h-1，CO 的选择性可达 98.6%。通过原位红外光谱、DFT 计算进一步揭示 IHEP-101 活化 CO2 的反应机理，IHEP-101 活化 CO2 在热力学和动力学上是可行的，并伴有 U 原子氧化态在 +VI 和 +V 之间的转变。根据已有的实验数据和文献报道，提出了 IHEP-101 光催化还原 CO2 的可能反应路径。本研究揭示了 UO22+ 阳离子作为光催化 CO2 还原反应活性位点的潜力，为设计和合成新型铀酰 MOFs 光催化材料提供了参考。

关键词

铀酰离子、金属-有机框架材料、光催化、二氧化碳还原、配位化学

Abstract

In the past few decades, with the massive consumption of fossil fuels, the carbon dioxide content in the air has gradually increased, and environmental problems such as global warming and energy crisis have become increasingly serious. Using sunlight to photocatalytically reduce CO2 to high value-added products such as CO and CH4 is one of the important means to protect the environment and solve the energy crisis. Metal-organic frameworks (MOFs) are a kind of crystalline porous structure composed of organic ligands and inorganic metal ions/clusters. They have the characteristics of high crystallinity, high specific surface area, flexible and adjustable porous structure, and easy modification, and have broad application prospects in the field of photocatalysis. In addition, the unique photochemical properties and diverse coordination modes make uranyl ions can be used as both the metal nodes of MOFs materials and the active centers of photocatalytic reactions. Therefore, uranyl MOFs are expected to become a new type of heterogeneous photocatalyst. Here, we designed and prepared a new type of uranium-based MOF material IHEP-101 [(CH3)2NH2][UO2][UO2(L)(DMF)][UO2(L)(H2O)]0.5·(DMF)1.5. Among them, the N2O2 cavity of the Salen ligand is occupied by uranyl ions to form a linear [UO2L] metallized dicarboxylic acid ligand, and this metallized ligand continues to coordinate with uranyl ions to form a distorted two-dimensional honeycomb network structure. Adjacent layers are stacked into a three-dimensional framework structure through π - π interactions. IHEP-101 shows good photocatalytic CO2 reduction activity. Without adding any sacrificial agent, the yield of CO can reach 458 μmol·g-1·h-1, and the selectivity of CO can reach 98.6%. The reaction mechanism of IHEP-101 activating CO2 is further revealed by in situ infrared spectroscopy and DFT calculations. It is feasible for IHEP-101 to activate CO2 thermodynamically and kinetically, accompanied by the transformation of the oxidation state of U atoms between +VI and +V. According to the existing experimental data and literature reports, a possible reaction path for the photocatalytic reduction of CO2 by IHEP-101 is proposed. This study reveals the potential of UO22+ cations as the active sites for the photocatalytic CO2 reduction reaction, providing a reference for the design and synthesis of new uranyl MOFs photocatalytic materials.

Keywords

uranyl ion, Metal-Organic Frameworks, photocatalysis, carbon dioxide reduction, coordination chemistry

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