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Development of a bismuth-based metal-organic framework for photocatalytic hydrogen production

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ABSTRACT

A novel 3D bismuth-organic framework (called Bi-TBAPy) single crystal was synthesized by employing 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H₄TBAPy) as an organic linker. The study demonstrates that the Bi-TBAPy not only possesses good chemical stability and suitable band edge positions for promising photocatalytic H₂ evolution, but it also exhibits a typical ligand-to-metal charge transfer for favorable charge separation. The photocatalytic H₂ evolution rates on the as-obtained Bi-TBAPy with different cocatalysts modified were examined with triethanolamine as the sacrificial reagent. Based on this, the hydrogen evolution rate of 140 μmol h⁻¹ g⁻¹ was obtained on the optimized sample with a loading of 2 wt% Pt as a cocatalyst. To the best of our knowledge, this is the first bismuth-based metal-organic framework (MOF) that functions as an effective photocatalyst for photocatalytic water reduction. Our study not only adds a new member to the family of photocatalyst materials, but also reveals the importance of cocatalyst modification in improving photocatalytic activity of MOFs.

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Metal-organic frameworks (MOFs) composed of metal-oxo clusters and polydentate organic linkers represent an intriguing class of porous crystalline material with many attractive properties such as porosity, large surface area, and structural and functional tunability [1]. Because of these unique advantages, MOFs have been widely investigated for gas storage and separation, sensors, drug delivery, and catalysis [2]. Some photo-responsive MOFs exhibiting semiconductor behavior have been developed as photocatalysts for promising solar energy conversion. In particular, solar-driven water splitting is of great significance when considering that hydrogen evolution

from water provides an environmentally friendly and sustainable alternative to fossil fuels [3].

To date, some MOF-based photocatalysts have been explored for hydrogen production. These contain UiO-66 [4], NH₂-UiO-66 [4], NH₂-MIL-125(Ti) [5], and Al-PMOF [6]. Although major progress has been achieved, the selection of metals is often confined based on the robustness and conduction band (CB) position of the as-obtained MOF material [7,8]. Consequently, new photo-responsive MOFs composed of other metals with good robustness and a suitable band structure are desired. Bismuth, as a nontoxic and earth-abundant element, is

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a promising candidate for the construction of stable MOFs, as it has a relatively high valence state and flexible coordination geometry [9,10]. However, the synthesis of bismuth-based MOFs remains challenging because of their structural sensitivity to the reaction conditions such as solvents, temperature, and reaction time. The complicated structural behavior of Bi^{3+} ions during the solvothermal synthesis makes controlling the process of crystal growth difficult [11]. Consequently, reports on the synthesis of bismuth-based MOFs with photocatalytic activity are limited [12–14]. To the best of our knowledge, no bismuth-based MOFs have been synthesized for photocatalytic water reduction.

In this study, we report on a new stable bismuth-organic framework (Bi-TBAPy) with a 3D framework structure by employing 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H_4TBAPy) as the organic linker. The as-obtained Bi-TBAPy is demonstrated to possess good stability and suitable band edge positions for photocatalytic water reduction. Based on our optimization, Bi-TBAPy exhibits the optimal H_2 evolution rate of $140 \mu\text{mol h}^{-1} \text{g}^{-1}$ when triethanolamine (TEOA) is used as the sacrificial reagent, demonstrating its promising future in solar fuel production.

The structure of a Bi-TBAPy single crystal was investigated by single-crystal X-ray diffraction (XRD) analysis, and details of the crystal structure and refinement data are provided in Table S1. As given in Fig. S1, the Bi-TBAPy is crystallized in monoclinic space group C2/c to form a 3D rod-like structure. The typical structure is introduced in Fig. 1(a), where the Bi atom is

coordinated with eight oxygen atoms from four linkers with a bond length of $\sim 2.435 \text{ \AA}$. A dimethylamine cation serving as the counter ion is also coordinated with the Bi atom to maintain the charge balance, and the bond length of Bi–N is $\sim 2.923 \text{ \AA}$. Each TBAPy^{4-} linker coordinated to four bismuth centers shapes the backbone of Bi-TBAPy into a 3D framework (Fig. 1(b) and (c)). Two types of 1D channels with different shapes exist along the a axis (Fig. 1(c)). One channel has a rhomboid shape and is occupied by dioxane; the other has a quadrilateral shape and is occupied by dimethylamine solvent molecules. The length of the two sides of these two windows are both $7.37 \times 11.65 \text{ \AA}^2$, although their shapes are different. The total solvent-accessible volume is approximately 8.4% upon solvent removal, which is calculated with PLATON software [15]. The BET surface area of Bi-TBAPy is measured to be $594 \text{ m}^2 \text{g}^{-1}$. The coordination effect between Bi ions and H_4TBAPy linkers can be further confirmed by the results of FT-IR measurement (Fig. S2), where the hydroxyl vibration peak of $-\text{COOH}$ in the range of $3000\text{--}3400 \text{ cm}^{-1}$ disappears during the shift of the carbonyl vibration peak in the range of $1620\text{--}1750 \text{ cm}^{-1}$. The experimental XRD pattern (Fig. 1(d)) of Bi-TBAPy conforms well with the simulated pattern, which is generated based on single crystal structure analysis, thus demonstrating a good phase purity of the bulk material.

To examine the physical and/or chemical stability of Bi-TBAPy, thermogravimetric analysis (TGA) was first conducted, with results given in Fig. S3. The results reveal that the Bi-TBAPy exhibits good thermal stability with the framework

Fig. 1. Structure and analysis of Bi-TBAPy. (a) Coordination mode of the Bi atom in Bi-TBAPy; (b) coordination mode of the TBAPy moiety in Bi-TBAPy; (c) crystal structure of Bi-TBAPy viewed along the a axis; (d) XRD patterns of Bi-TBAPy and Bi-TBAPy-simulated. Color representations: red, O; yellow, N; gray, C; green, Bi. H atoms are removed for clarity.

collapsed at approximately 350 °C. Subsequently, the Bi-TBAPy sample was also demonstrated to have good solvent stability when considering the fact that no obvious change of XRD patterns could be observed in the samples before and after impregnation in water, DMF, dioxane, acetonitrile, methylene dichloride, or isopropanol for 12 h at room temperature (Fig. S4). On the whole, the as-obtained Bi-TBAPy sample has an unexpected thermal and solvent stability, demonstrating its good potential as a photocatalyst.

Fig. 2(a) shows its typical UV/vis DRS, based on which the Bi-TBAPy has a visible light response with an absorption edge of *ca.* 465 nm. The band gap of Bi-TBAPy was then estimated to be *ca.* 2.67 eV from the Kubelka-Munk function. To evaluate further the band edge positions of Bi-TBAPy, a Mott-Schottky measurement was conducted. Fig. 2(b) clearly reveals the n-type semiconductor property of Bi-TBAPy, and the flat band

potential was calculated to be *ca.* -0.15 V vs. RHE. As the bottom of the CB of an n-type semiconductor is generally more negative by *ca.* 0.1 eV than the flat band potential [16], the CB of Bi-TBAPy was estimated to be *ca.* -0.25 eV. Together with the bandgap value estimated from the UV/vis DRS (Fig. 2(a)), the valence band (VB) was thus determined to be located at 2.42 eV. The estimated band edge positions of Bi-TBAPy are shown in the insert of Fig. 2(b), in which the CB exhibits sufficient potential in the water reduction process.

Encouraged by the good stability and suitable CB position of Bi-TBAPy, we examined the performance of Bi-TBAPy for water reduction by using TEOA as the hole scavenger. The photocatalytic water reduction activity of the Bi-TBAPy sample free of a cocatalyst was very low (Fig. S5). As shown in Fig. 2(c), the loading of a suitable cocatalyst is desired to promote the H₂ evolution rate, and the platinum modified sample appeared to

Fig. 2. (a) UV/Vis diffuse reflectance spectra of Bi-TBAPy; (b) Mott-Schottky plot of the Bi-TBAPy electrode and the estimated band edge positions of Bi-TBAPy (insert). Electrolyte: 0.05 mol/L phosphate buffer solution (PH = 6.0); (c) effect of typical reduction cocatalysts (2 wt%) on the photocatalytic H₂ evolution rate of Bi-TBAPy; (d) time course of photocatalytic H₂ evolution on 2 wt% Pt/Bi-TBAPy.

promote the H_2 evolution rate most efficiently. The difference in the promotion effect originating from the cocatalyst species may derive from their distinct ability at trapping electrons from the CB of Bi-TBAPy and/or activating protons for H_2 evolution [17]. A volcanic-type curve of H_2 evolution dependence on the Pt content was observed (Fig. S5), and the optimal H_2 evolution rate of $140 \mu\text{mol h}^{-1} \text{g}^{-1}$ appeared for the sample with 2.0 wt% Pt loaded. The XPS pattern of Bi-TBAPy after hydrogen evolution verified the loading of metallic Pt based on the binding energies of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks, as shown in Fig. S6 [18]. The loading of a suitable amount of platinum could trap the photogenerated electrons and accelerate the conversion of water molecules, whereas an excess amount probably leads to the shielded light absorption of MOFs, thus resulting in decreased photocatalytic H_2 evolution performance. For comparison, the water reduction performance of 2 wt% Pt/ H_4TBAPy was also examined under the same conditions as the 2 wt% Pt/Bi-TBAPy. The negligible hydrogen evolution indicates that the formation of a framework by incorporating Bi ions is vital to the photocatalytic performance of Bi-TBAPy. The typical time course of the photocatalytic water reduction on the optimized sample is shown in Fig. 2(d), in which the linear increase of H_2 evolution as a function of the reaction time demonstrates the good photochemical stability of Bi-TBAPy. In addition, the XRD patterns of Bi-TBAPy before and after H_2 evolution were not obviously altered (Fig. S7), also indicating the good stability of Bi-TBAPy during the photocatalytic reaction. Furthermore, the transient photocurrent response on the Bi-TBAPy photoelectrode in a three-electrode setup was conducted by using a 0.5-M sodium sulfate solution as an electrolyte solution. An obvious photocathode current could be observed from the chopped photocurrent profile of Bi-TBAPy (Fig. S8), indicating the generation of electron-hole pairs in Bi-TBAPy during light irradiation and the capacity for photoelectrochemical water reduction by photoinduced electrons.

To obtain insights into the mechanism of the charge transfer during the photocatalytic process, Bi $4f$ XPS patterns of Bi-TBAPy before and after H_2 evolution were measured and compared. As shown in Fig. 3(a), in addition to the characteris-

tic peaks of Bi^{3+} ions located at 164.2 and 158.9 eV, two new peaks centered at 162.2 and 156.9 eV were deconvoluted after 3 h of irradiation and were consistent with the characteristic peaks of the lower valence state of the Bi ion [19,20]. It should be noted that although the lower valence state of Bi ions was generated, the framework of Bi-TBAPy was well maintained based on the XRD patterns shown in Fig. S7, indicating the robustness of Bi-TBAPy. Based on the XPS analysis, a ligand-to-metal charge transfer (LMCT) process was observed to occur in Bi-TBAPy, where the photogenerated electrons transferred from the excited TBAPy group to Bi^{3+} , resulting in partial reduction of bismuth ions. The LMCT mechanism is always observed for MOFs as photocatalysts because of the intrinsic charge separation process. As a result, steady-state photoluminescence (PL) measurements were conducted to evaluate the influence of this charge transfer process. The results are shown in Fig. 3(b). H_4TBAPy exhibits the strongest steady-state PL intensity, revealing that a great carrier recombination process occurs in organic linkers, and the construction of Bi-TBAPy could suppress this process, thus resulting in decreased PL intensity of pristine Bi-TBAPy. Compared to the pristine sample, the considerably diminished steady-state PL intensity of Bi-TBAPy after irradiation confirmed the separation of photoinduced carriers as a result of the LMCT process, which in turn inhibited the process of charge recombination. The proposed mechanism for photocatalytic H_2 over Bi-TBAPy is illustrated in Fig. 4. First, the TBAPy groups in Bi-TBAPy absorb light to generate electrons and holes. Then, the excited electrons can be utilized through two pathways. In one pathway, electrons first transfer to the near Bi^{3+} ions by following the LMCT mechanism and then transfer to the cocatalysts. In the other pathway, the excited electrons in TBAPy groups transfer directly to Pt particles. Subsequently, the deposited Pt act as active sites to perform the catalytic reduction of water while the photogenerated holes are simultaneously consumed by the sacrificial reagent TEOA.

In summary, we synthesized a novel 3D bismuth-organic framework (Bi-TBAPy) with good stability and suitable band edge positions for promising photocatalytic H_2 evolution. The

Fig. 3. Characterizations of typical samples. (a) Bi $4f$ XPS spectra of Bi-TBAPy and Bi-TBAPy after H_2 evolution; (b) steady-state emission spectra of Bi-TBAPy, Bi-TBAPy-irradiated, and H_4TBAPy .

Fig. 4. Proposed mechanism of photocatalytic H_2 evolution over Bi-TBAPy.

influence of cocatalysts and the amount of loading on the performance of water reduction were investigated and discussed, and the optimal H_2 evolution rate of $140 \mu\text{mol h}^{-1} \text{g}^{-1}$ was obtained. The LMCT mechanism that occurred in Bi-TBAPy during the photocatalytic process was confirmed by XPS spectra, and this intrinsic charge separation process was favorable to the photocatalytic reactions because the charge recombination was suppressed. Our study not only adds a new member to the family of MOF material, it also offers new insights into the design and manipulation of MOFs for applications in photocatalytic water splitting.

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Graphical Abstract

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A new 3D bismuth-organic framework (Bi-TBAPy) with ligand-to-metal charge transfer (LMCT) process was synthesized to exhibit for the first time robust photocatalytic water reduction, demonstrating its promising future in solar energy conversion.

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新型铋基金属有机框架的合成及其光催化产氢性能

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摘要: 金属有机框架材料(MOFs)是由金属离子或团簇与多齿有机配体配位结合形成的一种结晶性材料。因其具有三维孔道结构, 以及比表面积大、结构和功能可调变等优点, 在气体的储存与分离、传感、药物传输和催化领域等方面具有广泛的应用。近年来, MOFs材料因其独特的结构和可调变性, 在太阳能转化领域逐渐崭露头角, 其中光催化水分解制氢作为一种可行的太阳能光化学转化方法, 引起了人们的广泛关注。目前, MOFs材料用于光催化水分解制氢的研究已经取得了一定的进展, 但在合成新型具有光催化性能的MOFs材料时, 考虑到材料稳定性和能带位置的要求, 在金属离子选择上往往受到限制。铋元素无毒且储量丰富, 因其具有较高的价态和灵活的配位模式, 在构建MOFs材料时常常会表现出独特的优势。然而, 铋基MOFs对于合成条件十分敏感, Bi^{3+} 离子复杂的配位模式也使晶体结晶的过程难以调控。因此, 铋基MOFs在合成方面具有一定的挑战。目前已报道的具有光催化活性的铋基MOFs材料十分有限, 且能够实现光催化水还原的铋基MOFs材料还未有报道。本文利用1,3,6,8-四(4-羧基苯)芘(H_4TBAPy)作为有机配体, 合成了一种新型的三维铋基MOFs单晶材料(记为“Bi-TBAPy”), 并对其结构、稳定性、光催化水还原性能及电荷转移机理进行了研究。

单晶衍射结果表明, Bi-TBAPy中铋离子与来自四个不同配体的八个氧原子配位形成了立体的三维结构, 二甲胺阳离子作为抗衡离子与铋离子配位使整个骨架保持电中性。实验测得的XRD结果与模拟的一致, 表明Bi-TBAPy具有较高的相纯度。TGA以及XRD测试分析也证明了Bi-TBAPy具有良好的热稳定性和化学稳定性。结合UV/vis和莫特-肖特基的测试结果可知, Bi-TBAPy具有n型半导体性质, 带隙宽度约为2.67 eV, 导带和价带位置分别位于-0.25和2.42 eV, 表明Bi-TBAPy在热力学上能够满足光催化水还原的要求。随后, 以三乙醇胺为牺牲试剂考察了Bi-TBAPy的光催化产氢性能。研究发现助催化剂的种类对催化剂性能具有重要影响, 负载2 wt% Pt时表现出最优的产氢速率, 达 $140 \mu\text{mol h}^{-1} \text{g}^{-1}$, 其为目前报道的首个具有光催化水还原性能的铋基MOFs催化剂。长时间的光催化水还原反应测试可以持续稳定的进行, 同时反应前后Bi-TBAPy的XRD也不发生变化, 表明该材料具有很好的光化学稳定性。反应后样品的Bi 4f XPS谱图表明反应过程中有低价铋的生成, 这说明配体受激发产生的光生电荷能够转移到 Bi^{3+} 上使其部分被还原。因此, 该材料能够实现配体-金属电荷转移(LMCT)的过程, 荧光光谱测试的结果证实了该过程有利于光生载流子的分离。

关键词: 金属有机框架; 光催化; 水还原; 配体到金属电荷转移; 电荷分离

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