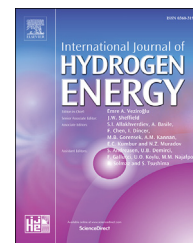




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Short Communication

Giant enhancement of photocatalytic H₂ production over KNbO₃ photocatalyst obtained via carbon doping and MoS₂ decoration



Jingxiong Yu ^a, Zhiqiang Chen ^a, Qianqian Chen ^b, Yan Wang ^d,
Hongjun Lin ^c, Xin Hu ^b, Leihong Zhao ^b, Yiming He ^{a,*}

^a Department of Materials Science and Engineering, Zhejiang Normal University, Jinhua, 321004, China

^b College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, 321004, China

^c College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua, 321004, China

^d Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, USA

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ABSTRACT

This paper was designed for the first time to improve the photocatalytic activity of KNbO₃ via carbon doping and MoS₂ decoration simultaneously. The efficient photocatalytic hydrogen production was realized on the MoS₂/C-KNbO₃ composite under simulated sunlight irradiation in the present of methanol and chloroplatinic acid. The optimal composite presents a H₂ production rate of 1300 μmol·g⁻¹·h⁻¹, which reaches 260 times that of pure KNbO₃. Characterization results of the synthesized composite indicates that the introduction of a small amount of carbon into the KNbO₃ lattice greatly hinders the recombination of electron-hole pairs. The decoration of MoS₂ further induces the separation of charge carriers via trapping the electron in the conduction band of C-KNbO₃, which is proven by the EIS and transient photocurrent response analyses. The remarkably enhanced separation efficiency of electron-hole pairs is believed to be the origin of the excellent photocatalytic performance, though other changes in surface area and optical property may also contribute the photocatalytic process. This study provides a feasible way for the design and preparation of novel photocatalysts with high efficiency.

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Introduction

Hydrogen is considered as one of the ideal alternatives to fossil fuels due to its properties of cleanness, abundance, sustainability, high combustion energy, and null CO₂

emission. Compared with the reformation of petroleum and natural gas which process is energy intensive, photocatalytic water splitting is a better and sustainable route to obtain hydrogen, and hence attracts much attention. Since the pioneer work of Fujishima and Honda in 1972 [1], significant efforts have been devoted to designing and synthesizing

* Corresponding author.

E-mail address: hym@zjnu.cn (Y. He).

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highly efficient photocatalysts for hydrogen generation from water splitting, and a great variety of photocatalysts have been reported, such as NaTaO₃ [2], CdS [3], Ga₂O₃ [4] and g-C₃N₄ [5]. The separation efficiency of electron-hole pairs is widely accepted as one of the key factors in determining the activity of a semiconductor photocatalyst. Some approaches, including noble metal loading and semiconductor coupling, have been developed to improve the property. The potential difference between the photocatalysts and the loaded noble metals (semiconductors) can induce the photogenerated electron to accumulate on the decorated species, and thus hindering the recombination of charge carriers [6–10]. However, this process can only change the distribution of electron on the surface of photocatalyst (the surface charge separation), the bulk recombination of electron-hole pairs which accounts for a large part of the disappearance of the photogenerated electron is not prevented (the bulk charges separation). Actually, inspired by the motivation of achieving highly efficient solar-energy conversion, scientists have found out some approaches to suppress the bulk recombination process. It is recognized that the bulk recombination is closely correlated with the catalyst's structure and the particle size. The photocatalyst with layer structure usually has nonuniform charge distribution, which induces an internal electric field (IEF) and subsequently boosts the bulk charge separation [11]. A small particle size is also beneficial to the process. Additionally, the incorporation of a tiny amount of external elements into the lattice can modify the bulk charge distribution, tune the IEF, and thus increasing the bulk charges separation efficiency [12]. For example, the metal ion doping ((Cr,Ta)-codoped SrTiO₃ [13], Sr-doped NaTaO₃ [14]), nonmetal ion doping (N–TiO₂ [15]; C–TiO₂ [16,17]), and constructing solid solution structures (Ga_{1-x}In_xO₃) [18], Zn_xCd_{1-x}S [19]) may effectively increase the bulk charge separation efficiency. Clearly, although the reported photocatalytic hydrogen production performance is still not satisfying, the awareness of the recombination process is gradually deepening under the effort of researchers. Meanwhile, based on the obtained achievements, different strategies should be combined to increase both the bulk and surface charge separation efficiency.

Perovskite-type mixed metal oxides are an important family of materials and exhibit numerous applications in thermal catalysis, electronic device and photonic crystal. Meanwhile, they are good candidates for photocatalytic H₂ production from water splitting due to their availability, low toxicity, and more negative conduction band edge than the H⁺/H₂ energy level. As a member of them, KNbO₃ shows great potential in photocatalytic hydrogen generation, and thus attracting scientists' interest [13]. Lots of work about the modification of KNbO₃ have been reported. A variety of semiconductors or noble metals, including g-C₃N₄ [20], CdS [21], Nb₄O₅ [22], and Au nanoparticles [23], were decorated to improve the surface charges separation of KNbO₃, while some external elements such as N [24] and Ta [25] were introduced into the KNbO₃ lattice to enhance the bulk charges separation efficiency. However, significantly improved photoactivity has not been observed in these newly-designed KNbO₃ based materials. An important reason may be that only a part of the recombination process is retarded.

Therefore, in this work, the strategies of carbon doping and MoS₂ decoration were firstly simultaneously applied to improve the photocatalytic activity of KNbO₃. Carbon doping has been reported to be highly efficient for the photoactivity improvement [16]. Meanwhile, in our knowledge, no work on carbon-doped KNbO₃ has been reported. Due to a similar reason, MoS₂ was chosen to further modify the carbon-doped KNbO₃ because the semiconductor is seen as efficient doper in retarding charge recombination [26–32]. The synthesized MoS₂/C-KNbO₃ presents significantly higher photocatalytic H₂ production performance than pure KNbO₃. Thoroughly characterizations and experimental tests are also carried out to reveal the origin of the excellent photocatalytic performance of the sample.

Experimental section

The detailed information of the preparation, characterization, and photocatalytic test of the MoS₂/C-KNbO₃ catalyst is listed in supplementary materials.

Results and discussion

SEM analysis (Figure S1) indicates that KNbO₃ and C-KNbO₃ present the morphology of microcube and microtower, respectively. The MoS₂ products are mainly composed of flower-like hierarchical assemblies. The MoS₂/C-KNbO₃ displays nearly the same morphology as C-KNbO₃. No MoS₂ is observed in the composite due to its low content. The XRD patterns of KNbO₃, C-KNbO₃, MoS₂, and MoS₂/C-KNbO₃ composite are shown in Fig. 1a. It can be seen that pure KNbO₃ is in its orthorhombic phase (PDF# 32-0822) and shows strong diffraction peaks at $2\theta = 22.0^\circ, 31.3^\circ, 45.0^\circ, 50.7^\circ, 55.9^\circ$, indicating its high crystallinity. The addition of glucose during the hydrothermal process shows negligible effects on the XRD patterns. The C-KNbO₃ sample still presents the orthorhombic phase of KNbO₃. However, the amplified XRD patterns within the range of 30–32° indicate that the peak of C-KNbO₃ shifts to low diffraction angle compared with that of KNbO₃. This phenomenon indicates that carbon atom is doped into the lattice of KNbO₃. XPS analysis (Fig. 2) proves that the doped carbon exists in the form of C⁴⁺, indicating that the doped carbon does not replace the position of lattice oxygen. The K⁺, Nb⁵⁺ and C⁴⁺ radius is about 0.152 nm, 0.064 nm and 0.029 nm, respectively. Given the similarity in radius and charges, it is mostly possible that some Nb⁵⁺ may be substituted by carbon ions. The same peak shift is also observed in the MoS₂/C-KNbO₃ composite, suggesting the decoration of MoS₂ does not further change the structure of C-KNbO₃. However, no XRD peaks corresponding to MoS₂ are detected, which may be ascribed to the low MoS₂ content and the weak signals of MoS₂. Actually, even pure MoS₂ displays very weak XRD diffraction peaks (the inset image). Fig. 1b shows the UV–vis diffuse reflection spectra of the four samples. MoS₂ shows strong absorption in the visible light region, whereas pristine KNbO₃ can only absorb UV light. The band gaps of KNbO₃ and MoS₂ are estimated to be 3.07 and 1.88 eV, respectively (Figure S2). C-KNbO₃ sample presents a similar UV–vis

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