Synthesis of carbon-doped KNbO₃ photocatalyst with excellent performance for photocatalytic hydrogen production

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ABSTRACT

Carbon-doped KNbO₃ photocatalyst was synthesized for the first time via a simple combination of hydrothermal and post-calcination processes with glucose as the carbon source. The synthesized sample had excellent performance in photocatalytic hydrogen production under simulated sunlight. Various techniques were applied to investigate the origin of the extraordinary photocatalytic activity. X-ray diffraction and Ar^+ sputtering X-ray photoelectron spectroscopy analyses proved that carbon atom was successfully doped into the lattice of KNbO₃. Scanning electron microscopy and N_2 adsorption analysis indicated that the particle size of KNbO₃ was decreased due to the doping of carbon, which resulted in the increase of the BET surface area. UV–vis diffuse reflectance spectroscopy experiment verified that the carbon doping extended the light absorption region to visible light. Both the changes in surface area and optical property are beneficial to the photocatalytic reaction. However, the stronger H_2 generation rate of carbon-doped KNbO₃ was mostly attributed to the enhanced separation efficiency of electron-hole pairs due to the presence of carbon dopant. The promotion effect is closely correlated with the content of carbon dopant. C-KNbO₃ sample calcined at 350 °C displayed the highest hydrogen generation rate of 211 $\mu mol\, g^{-1}\, h^{-1}$, which is 42 times higher than that of pure KNbO₃. Additionally, the synthesized carbon-doped KNbO₃ also presented good photoactivity under visible-light illumination. This study provides a feasible way for the synthesis of other similar photocatalysts with high efficiency.

1. Introduction

Two urgent challenges, energy shortage and environmental pollution, currently confront humanity. The use of hydrogen as energy carriers is considered as one of the ideal approaches to address the two issues. Hence, as an effective and clean route to obtain hydrogen, photocatalytic water splitting has been extensively studied. Since 1972, great efforts have been devoted to develop high efficient photocatalysts to realize hydrogen production from water splitting. Many effective photocatalyst have been reported [1–5], such as TiO₂ [1], NaTaO₃ [2], Ga₂O₃ [3] etc. However, due to the wide-band gap, these photocatalysts can only absorb ultraviolet (UV) light, which occupies no more than 4% of the solar spectrum. For application in practical, the development of an efficient photocatalyst with high activity under sunlight is still desired.

Potassium niobate (KNbO₃) is a ternary transition metal oxide with perovskite structure and exhibits the unique physicochemical properties in acoustic-optic, electro-optic, nonlinear optic, and piezoelectric [6–8]. Meanwhile, it is also a promising material for photocatalytic hydrogen generation from water splitting, and thus attracts scientists' interest [9]. Many works on the preparation of nanosized KNbO₃ have been reported [10–12]. However, the change in morphology cannot endow KNbO₃ the capability in absorbing visible light. Hence, several approaches are applied to extend the light absorption range of KNbO₃. Lan et al. synthesized Au/KNbO₃ via deposition-precipitation method. [13]. The localized surface plasmon resonance (LSPR) effect of Au nanoparticles makes the synthesized composite can degrade RhB under visible-light illumination. Shi et al. reported that the coupling g-C₃N₄ onto the KNbO₃ surface can enhance its photocatalytic activity in CO₂ reduction under visible light [14]. G-C₃N₄ plays the role of sensitizer in the composite. Some similar works are also reported, such as CdS/KNbO₃ and Nb₄O₅/KNbO₃ [15,16]. Wang et al. synthesized N-doped KNbO₃ via heating of the mixture of KNbO₃ and urea [17]. The doped N atom narrowed the band gap of KNbO₃ and

increased its photoactivity in RhB degradation under visible light. However, significantly improved photoactivity has not been observed in these newly-designed $KNbO_3$ based materials. Systematic study on photocatalysis by modified $KNbO_3$ is still lacking, especially nonmetal doped $KNbO_3$. Since Asahi and co-workers first reported that the bandgap of TiO_2 can be narrowed by doping with nonmetallic ions (such as nitrogen, carbon, sulfur and fluorine) [18], nonmetal doping is validated as an efficient way to extend the optical absorption of photocatalysts to the visible range. Unfortunately, until now, only N-doped $KNbO_3$ has been reported [17]. No research focused on carbon-doped $KNbO_3$ photocatalyst has been reported although the carbon element is seen as effective as nitrogen in enhancing separation of charge carriers and absorption for visible light [19–21].

Therefore, in this work, a carbon-doped $KNbO_3$ photocatalyst was, firstly, synthesized through a simple combination of hydrothermal and post-calcination processes. It is found that the presence of a suitable amount of carbon dopant could significantly promote the performance of $KNbO_3$ in photocatalytic hydrogen production under simulated sunlight. A thoroughly characterization is also performed to investigate the origin of the excellent photocatalytic performance of the carbon-doped $KNbO_3$ sample.

2. Experimental section

2.1. Preparation of photocatalyst

All these reagents are analytical pure grade and used without further purification. Nb_2O_5 (99.5%), KOH (85%), and glucose (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). $H_2PtCl_6 \cdot 6H_2O$ (Pt > 37.5%) was purchased from Aldrich.

Carbon-doped $KNbO_3$ was prepared via a hydrothermal method. In a typical example, Nb_2O_5 (0.02 mol) and glucose (0.02 mol) were mixed and ground in a mortar for 30 min. The obtained mixture was then added into 70 mL KOH solution (14 M) and stirred for an hour. After that, the suspension was transferred into a 100 mL Teflon-lined steel autoclave and heated at 160 °C for 12 h. When the autoclave was cooled to room temperature, the resulting powders were separated by centrifugation, washed with water and absolute ethanol for three times, and dried at 60 °C to obtain C-$KNbO_3$ sample. In order to optimize the photoactivity, the synthesized C-$KNbO_3$ was further heated at different temperatures for two hours. The samples heated at 300 °C, 350 °C, and 400 °C were denoted as C-$KNbO_3$-300, C-$KNbO_3$-350, C-$KNbO_3$-400, respectively.

For a comparative study, pristine $KNbO_3$ and carbon dots decorated $KNbO_3$ samples were also prepared. Pristine $KNbO_3$ was prepared as C-$KNbO_3$ sample without the use of glucose during the hydrothermal process. Carbon dots loaded $KNbO_3$ photocatalysts were prepared as follows. For the first step, carbon dots containing solution were synthesized via hydrothermal method at 160 °C with glucose (0.02 mol) as precursors. Then, $KNbO_3$ powder (0.04 mol) was added to the solution with strong stirring followed by 30 min ultrasonication. After that, the powders were separated by centrifugation, washed with water and ethanol, and dried at 60 °C to obtain CD/$KNbO_3$ sample. The CD/$KNbO_3$ sample calcined at 350 °C for two hours was denoted as CD/$KNbO_3$-350.

2.2. Photocatalytic test

The photocatalytic H_2-production under simulated sunlight irradiation was performed to investigate the catalytic performance of the synthesized carbon-doped $KNbO_3$ sample. The test was performed in a closed gas circulation system (Labsolar-IIIAI photocatalytic system, Beijing Perfectlight Co., Ltd., China) with a 300 W Xe-lamp (PLS-SXE300C, Beijing ProfectLight Co. Ltd., China) as light sources. The light intensity at the center of reactor is determined to be 199 mW cm^{-2}. When the Xe lamp is equipped with a UV cutoff filter (420 nm), the light intensity decreases to 170 mW cm^{-2}. In a typical photocatalytic reaction process, 100 mg of photocatalyst was firstly suspended in a mixed solution (80 mL H_2O and 20 mL CH_3OH) under constant magnetic stirring. Then, 1 mL H_2PtCl_6 solution (0.002 M) was added for the in-situ deposition of metallic Pt (0.37 wt%) on the photocatalyst during the photocatalytic reaction. Air in the reaction system was completely evacuated via a vacuum pump before the Xe lamp is on. The released H_2 was monitored every 30 min using an online gas chromatography (GC 7900, Shanghai Techcomp Instrument Ltd.) equipped with a molecular sieve column and a thermal conductivity detector.

2.3. Characterizations

The powder X-ray diffraction (XRD) analysis was performed on a Philips PW3040/60 ×-ray diffractometer with Cu Kα radiation (40 kV/40 mA). Fourier transform-infrared (FT-IR) analysis was carried out on a Nicolet Nexus670 FT-IR spectrometer using KBr as the reference sample. Brunauer–Emmett–Teller (BET) surface area analysis was performed by N_2 adsorption at 77 K on an Autosorb-1 apparatus (Quantachrome Instruments). Scanning electron microscopy (SEM) images were collected on a Field emission scanning electron microscope (Hitachi S-4800). UV–visible diffuse reflection spectroscopy (DRS) was carried out on a UV–visible spectrophotometer (PerkinElmer Lambda900). X-ray photoelectron spectroscopy (XPS) analysis was carried out in a Quantum 2000 Scanning ESCA Microprobe instrument using AlKα. The binding energy of C1s peak (284.6 eV) originated from the adventitious carbon was used as a reference. Atomic contents of the detected elements were calculated by normalizing peak areas to the elemental sensitivity factor. The photoluminescence (PL) analysis was performed on FLS-920 spectrometer (Edinburgh Instrument) at room temperature, using a Xe lamp (excitation at 365 nm) as the light source. The electrochemical impedance spectroscopy (EIS) and transient photocurrent analyses were carried out by using an Autolab electrochemical workstation with a standard three-electrode cell. The photocatalyst coated ITO glass, Ag/AgCl, and Pt electrodes were acted as the working, the reference and the counter electrodes, respectively.

3. Result and discussion

3.1. Characterizations of C-doped $KNbO_3$ photocatalysts

3.1.1. SEM and BET analysis

The morphology of the carbon-doped $KNbO_3$ photocatalysts was investigated via SEM. From Fig. 1, it can be seen that pure $KNbO_3$ shows the morphology of microcube with a size of about 4 μm, which is consistent with the previous result [17]. It is reported that the $KNbO_3$ microcube can be prepared with a KOH content of 13–16 M [17]. The C-$KNbO_3$ sample is the aggregates of many small microtowers, indicating the added glucose changes the self-assembly process of the $KNbO_3$ nanocrystalline. Compared with $KNbO_3$, the C-$KNbO_3$ sample has smaller particle size and rough surface, suggesting the sample may have higher surface area than $KNbO_3$. This inference is confirmed by N_2 adsorption experiment. The BET surface area of C-$KNbO_3$ sample is 1.3 m^2/g, slightly larger than that of $KNbO_3$ (1.0 m^2/g). The thermal treatment of C-$KNbO_3$ sample does not change the morphology. It can be seen that the C-$KNbO_3$ samples calcined at 350 and 400 °C still present the characteristic morphology of microtowers. Correspondingly, the BET surface area of these samples changes a little. For the samples of C-$KNbO_3$-300, C-$KNbO_3$-350, and C-$KNbO_3$-400, the BET surface is equaled to 1.3, 1.6 and 1.5 m^2/g, respectively. Additionally, TEM analysis (not shown here) is also performed to investigate the microstructure of carbon-doped $KNbO_3$. However, due to the big particle size of the sample, no useful information is obtained.