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Insights into the role of Cu in promoting photocatalytic hydrogen production over ultrathin HNb_3O_8 nanosheets

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ABSTRACT

Cu was loaded on ultrathin HNb_3O_8 nanosheets via a facile photodeposition method. The oxidation state of the Cu was further verified by XPS. TEM and STEM-EDX mapping demonstrated that the Cu cluster was highly dispersed on the nanosheets. The photocatalytic H_2 evolution activity of (0.5%) Cu/HNb_3O_8 was about 23.6 times higher than that of the bare HNb_3O_8 nanosheets under simulated solar light irradiation. The role of Cu in promoting photocatalytic hydrogen evolution activity over HNb_3O_8 nanosheets was attributed to the reduction of hydrogen evolution potential and the improvement of separation of photogenerated carriers. These results were confirmed by a series of electrochemical characterizations, such as CV, LSV, I-t, and EIS. Finally, photocatalytic hydrogen evolution processes over HNb_3O_8 nanosheets with and without Cu modification were proposed, which might provide insights into the photocatalytic hydrogen evolution mechanism over niobate-based metal oxides.

1. Introduction

With the growth of population and increase of energy demand, obtaining renewable and clean energy is a desirable way to realize the sustainable development of human beings. The green energy source, hydrogen, produced by photocatalysis offers a promising prospect for solving environmental and energy issues. Since 1972 [1], many semiconductor photocatalysts have been used for photocatalytic hydrogen production, such as TiO_2 [2], C_3N_4 [3], and CdS [4]. However, large-scale utilization of these traditional bulk materials for photocatalytic H_2 production is limited to the easy recombination of photon-generated carriers because of a long distance to migrate before participating in the reaction, which is fatal for photocatalysis [5]. To shorten the path for carrier migration, lowering the dimensions in the direction of photon-generated carrier migration can suppress the quenching of carriers inside the bulk, thus facilitating the efficient separation of photogenerated carriers [6].

Recently, ultrathin two-dimensional (2D) semiconductor materials have aroused enormous scientific interest because of their extraordinary structure and optical and electronic properties [7]. Inspired by this, we can envisage that when semiconductor photocatalysts have only molecular thickness, the concept of "bulk" is gone. This means that all of the charge carriers are generated at the surface of the semiconductor and can react with the adsorption substrate directly, avoiding the quenching of the carriers inside the material, which will promote the photocatalytic reaction dramatically. Additionally, the ultrathin nanosheet generally has a defined atomic arrangement. Thus, heterogeneous photocatalysis over ultrathin nanosheets can be recognized as a reaction between quasi-molecules and molecules, providing a platform for revealing the essence of the photocatalytic reaction process. In view of these facts, developing ultrathin nanosheet photocatalysts has been considered an efficient approach to promoting the development of photocatalysis.

It was found that ultrathin niobate-based metal oxidation nanosheets such as $HCaNb_3O_{10}$ [8], $HTiNbO_5$ [9], $H_4Nb_6O_{17}$ [10], $HPb_2Nb_3O_{10}$ [11], and HNb_3O_8 [12] demonstrate enhanced photocatalytic hydrogen evolution activity due to unique 2D structural features that shorten the migration path of the carriers and improve the photogenerated net charge. Nevertheless, without co-catalysts such as Pt, Pd, and RuO_x, these ultrathin metal oxide nanosheets still suffer from low photocatalytic hydrogen evolution activity because of restrictions on the hydrogen evolution reaction in kinetics. Moreover, the large-scale use of these noble metals is limited by high cost and low global availability [13]. Recently, Cu-based species as co-catalysts for photocatalytic hydrogen evolution have aroused researchers' interest due to their abundance and excellent performance. Yu et al. [14] and Bandara et al. [15] reported that the $Cu(OH)_2$ cluster and CuO-modified TiO_2 respec-

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tively had enhanced photocatalytic H_2-production activity; Xi et al. reported that Cu_2O/TiO_2 heterostructure nanoparticles showed high photocatalytic H_2 evolution activity [16]; Wu and Lee demonstrated that Cu loaded on TiO_2 also promoted photocatalytic H_2 production [17]. However, there are few reports of the effect of Cu on photocatalytic hydrogen evolution activity over niobate-based metal oxidation nanosheet photocatalysts, and the role of Cu species in promoting photocatalytic hydrogen evolution over semiconductors is still lacking in detailed discussions.

Here, we show that Cu can be loaded onto HNb_3O_8 nanosheets via a facile photodeposition method. Compared with bare HNb_3O_8 nanosheets, the Cu-modified counterpart showed a remarkable improvement of photocatalytic hydrogen production activity, arising from the lower hydrogen evolution overpotential facilitating the hydrogen evolution reaction in dynamics, which was confirmed by a series of electrochemical analyses. This work aims to shed light on the role of Cu in the promotion of photocatalytic hydrogen evolution activity over niobate-based photocatalysts.

2. Experimental

2.1. Preparation of photocatalyst

Ultrathin HNb_3O_8 nanosheets were prepared by a top-down process followed as we have reported before [12,18]. Cu was loaded onto an HNb_3O_8 nanosheet via a photodeposition method. Briefly, 100 mg of HNb_3O_8 nanosheet photocatalysts was well dispersed into 72 ml of solutions containing different amounts of $CuCl_2{\cdot}2H_2O$ (0.86 mg/ml) aqueous solution (6, 3, 1.5, and 0.75 ml, with corresponding loadings of 2, 1, 0.5, and 0.25% of Cu); then 8 ml of triethanolamine (TEOA) was added into the mixture; last, the solution was degassed and irradiated with simulated sunlight. $Cu(OH)_2$ was loaded onto nanosheets by an impregnation–precipitation method. Briefly, 200 mg of HNb_3O_8 nanosheet photocatalysts was well dispersed into 20 ml of an aqueous solution containing 6 ml of $CuCl_2{\cdot}2H_2O$ (0.86 mg/ml) and stirred for 2 h. Then 1 ml of NaOH (1 M) aqueous solution was added into the mixture solution, stirred for another 2 h, centrifuged, and vacuum dried at 40 °C.

2.2. Characterization

X-ray diffraction (XRD) patterns with Cu Kα radiation were recorded on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA. The powdered samples were filled into the cell in the glass holder and flattened. The data were recorded in a 2θ range of 3.5–65.0° with a step width of 0.01°. To obtain the transmission electron microscopy (TEM) images, high-resolution (HR) TEM images, and scanning transmission electron microscopy energy dispersive X-ray (STEM-EDX) mapping, the sample was dropped onto a Mo grid and operated on a FEI Tecnai 20 transmission electron microscope at an accelerating voltage of 200 kV. Raman spectra were collected via a multichannel modular triple Raman system (Renishaw Co.) with a confocal microscope at room temperature using a 532 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system with a monochromatic Al Kα source and a charge neutralizer. The powdered samples were pressed into flakes and then pasted by conductive tape on a sample holder. All of the binding energies were calibrated by the C1*s* peak at 284.6 eV. The standard references were purchased directly from the National Standard Material Center of China ($CuCl_2$, 99.0%; $Cu(OH)_2$, 96%; CuO, 99.9%; Cu_2O, 99.9%; Cu(0), 99.9%). The content of Cu in the as-prepared sample was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Ultima2, Jobin Yvon Co., France). The sample was dissolved in a mixture of concentrated HNO_3 and HF (volume ratio 2:3) by a hydrothermal reaction at 180° for 12 h.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system with a homemade working electrode, a platinum foil counter electrode, and a saturated calomel electrode (SCE) as a reference at an electrochemical station (CHI660E), V_{SHE} = -V_{SCE} + 0.22 V. The working electrodes for the Mott–Schottky plots, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and photocurrent tests were prepared by dropping the samples onto conductive fluorine-doped tin oxide glass (FTO) [19]. The ones for the cyclic voltammetry (CV) test were prepared by dropping the samples onto a glassy carbon electrode (GC) [13]. Linear sweep voltammetry (LSV) was carried out in 0.2 M Na_2SO_4 aqueous solution (purged with high-purity Ar) with a scan rate of 25 mV s^{-1}. Mott–Schottky plots was recorded from 0 to 1.6 V (vs. SCE) with frequency 1.5 kHz. The typical Nyquist plots were recorded with frequencies ranging from 100 kHz to 0.1 Hz at an amplitude of 5 mV, and the photocurrent response test was performed using a 300 W Xenon lamp without an optical filter as a light source in the 0.2 M Na_2SO_4 aqueous solution. CV was carried out in 0.1 M tetrabutylammonium tetrafluoroborate CH_3OH solvent (purged with high-purity Ar) with scan rates 50 and 100 mV s^{-1}.

2.4. Photocatalytic test

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Portions of 100 mg photocatalyst and stoichiometric $CuCl_2$ aqueous solution (0.86 mg/ml) were added into 80 ml of 10 vol.% of triethanolamine (TEOA) aqueous solution (unless otherwise specified). The suspension was then thoroughly degassed and irradiated under the simulated solar light using a 300 W Xenon lamp (PLS-SXE300C, Perfectlight Co., Beijing). H_2 was detected by an online gas chromatograph.

3. Results and discussion

As shown in Fig. 1, the bare HNb_3O_8 nanosheets demonstrated a trace of H_2 evolution activity (2.5 μmol h^{-1}), similar to the case in most metal oxidation photocatalysts without the co-catalyst for photocatalytic hydrogen evolution [20]. Significantly, it was found that the photocatalytic hydrogen evolution activity increased dramatically after addition of Cu^{2+} into the reaction solution. As shown in Fig. 1A, when the content of Cu^{2+} was 0.25% or 0.5%, steady hydrogen production activity was observed and the average rates of H_2 evolution were 49.7 and 59.1 μmol h^{-1}, corresponding to 19.9 and 23.6 times the bare HNb_3O_8, respectively. However, with the content of Cu^{2+} up to 1% and 2%, photocatalytic hydrogen evolution activity decreased to 54.3 and 29.1 μmol h^{-1}, because of the shielding effect arising from excessive adding of Cu^{2+} [21]. Moreover, the photocatalytic activity of the HNb_3O_8 nanosheet modification with 1% Cu^{2+} can be improved using suitable sacrificial regents. As shown in Fig. 2A, when methanol was used as the sacrificial agent, the photocatalytic hydrogen production activity (98.2 μmol h^{-1}) was about 1.8 and 5.2 times that in the cases of TEOA and lactic acid (LAC), respectively. Furthermore, it is reported that $Cu(OH)_2$ was also efficient an co-catalyst for semiconductor photocatalytic hydrogen production [14]. It is interesting to find that the photocatalytic activity of Cu/HNb_3O_8 (1.00%, in situ photodeposition) was about twice that of $Cu(OH)_2/HNb_3O_8$ (0.92%, pre-