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Modifications of morphology and hydrogen evolution activity for the potassium niobate nanoscrolls by introducing reduced graphene oxide

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ABSTRACT

A new type of potassium niobate/reduced graphene oxide (RGO) composite nanoscrolls was prepared by the intercalation of RGO in the process of curling of the potassium niobate nanosheets. The as-prepared potassium niobate/RGO composite nanoscrolls were characterized with powder X-ray diffraction, transmission electron microscopy, Raman spectroscopy, solid diffuse reflectance UV–visible spectroscopy and fluorescence spectroscopy. The photocatalytic activity of the composite nanoscrolls was evaluated by hydrogen evolution from aqueous methanol under UV irradiation. It was found that the photocatalytic activity was enhanced as 3.1 times after introducing 2% RGO, compared with the pure potassium niobate nanoscrolls. It was ascribed to the enhanced separation efficiency of electron/hole pairs as testified by electrochemical impedance spectrum and fluorescence spectrum. Moreover, the composite photocatalyst was stable and easy to be recycled.

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Introduction

As the predominant substitute for fossil energy, hydrogen energy is considered as an ideal energy source due to its storability and environmental friendliness [1]. Photocatalytic water reduction to produce hydrogen is a promising technique in recent years because the solar energy is clean, safe and inexhaustible [2]. Enormous interests are focused on the preparation of novel and active photocatalysts [3–5].

Nowadays, it is found that potassium niobate based photocatalysts show many charming characteristics, such as low cost, non-toxicity, universal applicability, and chemical stability [6,7]. So this class of photocatalysts receives more attentions. Such as, a series of nickel oxide nanoclusters intercalated $K_4Nb_6O_{17}$ prepared by a two-step solid-state reaction exhibit a much higher photocatalytic activity for water splitting than unloaded $K_4Nb_6O_{17}$ catalyst and $NiO_y/K_4Nb_6O_{17}$ catalyst prepared by the conventional impregnation method. The high catalytic performance was mainly attributed to the

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well dispersed nickel oxide nanoclusters intercalated into the bulk structure of $K_4Nb_6O_{17}$ catalyst [7]. In addition, direct intercalation of a $[Pt(tpy)Cl]Cl$ complex into a layered $K_4Nb_6O_{17}$ has been successfully accomplished with the aim of developing a bifunctional and recyclable photocatalyst [8].

For tunable mesopore size, large internal surface area, convenient recycling, and fast electron transport between interfaces, $K_4Nb_6O_{17}$ nanotubes have been extensively investigated due to their potential applications in optoelectronics, biosensors, catalysis, drug delivery, and the separation of chiral compounds [9,10]. But the photo produced electrons in conduction band and the holes in valence band can recombine and dissipate easily within a few seconds, which leads to the lower photocatalytic activity like other semiconductors [3]. It greatly limits their practical application. So, to improve the separation efficiency of electron/holes is still one of the important research subjects.

And, many researchers focus attentions to solve this problem. Integrated with the co-catalyst is an efficient way to improve the charge mobility [11]. For example, Pt doped TiO_2 nanotubes shows the improved photocatalytic activity for hydrogen generation [12,13]. Although the noble metals with larger work function and lower Fermi level are expected to trap electrons more readily [14]. But high price and poisoning problems restrict its application.

Graphene, an expeditiously rising star on the horizon of materials science in electronic, optical, and catalytic fields [15], has become one of the most exciting topics of research in recent years. Like single-walled carbon nanotubes, conducting/semiconducting fullerenes, graphene is also expected to be used as an electron efficient acceptor to enhance photo induced charge transfer for improved catalytic activity [16]. Compared to graphene, the reduced graphene oxide (RGO) can be facilely prepared, and exhibit many characteristics similar to those of graphene. The effective combination of some semiconductors and RGO is expected to be very effective in increasing the charge transfer rate of electrons [17–19].

Herein, with the RGO as the controllers of morphology and photocatalytic activity of potassium niobate, potassium niobate/RGO composite nanoscrolls are prepared by a facile process. The purpose is to improve the separation efficiency of electron–hole pairs of potassium niobate based photocatalyst. The photocatalytic activity for hydrogen evolution over the potassium niobate/RGO composite nanoscrolls is evaluated. In addition, the interfacial electron transfer in the photocatalyst is also investigated.

Experimental section

Preparation of the samples

Preparation of potassium niobate nanoscrolls

All chemical reagents were of analytical grade. Potassium niobate was prepared by heating a mixture of K_2CO_3 and Nb_2O_5 powders at 1373 K for 24 h in air. An excess amount of K_2CO_3 was added to compensate for the volatilization. The as-obtained product was washed with water and ground into a powder using a mortar and pestle. Proton exchange of the potassium niobate powder was carried out in aqueous

hydrochloric acid (200 mL, 2 mol L^{-1}) at room temperature for 48 h. By the above procedure, potassium niobate nanosheets were obtained.

Potassium niobate nanoscrolls were prepared by stirring the potassium niobate nanosheets in aqueous tetra(*n*-butyl) ammonium hydroxide (TBA^+OH^- , 125 mL, 10 wt %) at room temperature for 72 h. The top 75% of the solution in the flask was removed, centrifuged, washed to neutral, and dried.

Preparation of potassium niobate/RGO composite nanoscrolls

Graphene oxide (GO) was prepared using a modified Hummers' method [20]. 100 mg of GO was dispersed into 100 mL of water under ultrasonication to obtain a yellow–brown dispersion.

For the synthesis of potassium niobate/RGO composite nanoscrolls, 0.5 g of potassium niobate nanosheets was dispersed into 50 mL of distilled water with stirring, followed by the addition of 10 mL GO suspension with continuous stirring for 60 min. Then, TBA^+OH^- aqueous solution was added until the pH of the mixed solution was 10. After stirring for 3 days, the top 75% of the mixture was removed, centrifuged, washed to neutral and dried. Potassium niobate/GO composite nanoscrolls were obtained. Finally, 0.5 g of potassium niobate/GO composite nanoscrolls was dispersed into 50 mL of distilled water, and the obtained suspension was reduced by $NaBH_4$ at 80 °C for 1 h. The target product was achieved in the end.

In addition, 0.5 g of potassium niobate nanoscrolls and 10 mL of GO suspension were dispersed into 50 mL of distilled water with stirring for 60 min. Then, the obtained suspension was reduced by $NaBH_4$ at 80 °C for 1 h. By this means, the control sample was obtained.

Preparation of working electrodes

Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in ethanol, acetone, chloroform, and deionized water for 15 min, respectively, and then dried in the air. Various working electrodes were prepared via impregnation and subsequent calcination method. In brief, 10 mg of sample (potassium niobate nanoscrolls or potassium niobate/RGO composite nanoscrolls) was added into 2 mL of alcohol, and the obtained mixture was sonicated for 30 s. After that, the FTO glass ($1 \times 3 \text{ cm}^2$) was soaked into the slurries for 5 min for 3 times and heat-treated at 100 °C for 1 h.

Photoelectrochemical behavior measurement

The photoelectrochemical measurements were carried out at room temperature using Chenhua CHI 660E computer-controlled electrochemical analyzer with a standard three-electrode system (Chenhua Instruments Co., Shanghai, China). A platinum wire electrode was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode. The electrolyte was 0.1 mol L^{-1} of Na_2SO_4 aqueous solution. The scan rate was 50 mV s^{-1} . Electrochemical impedance spectra (EIS) were tested in the potentiostatic mode with the frequency range of 1 to 1 MHz, and the bias potential was 0.5 V. The amplitude was 5 mV. The light source was a 150 W Xe lamp. The distance between light source and

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