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Photocatalytic hydrogen production over various sodium tantalates

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ABSTRACT

The present study reports the preparation of a series of $NaTaO_3$, $Na_2Ta_2O_6$, composite sodium tantalates and their photocatalytic activities for hydrogen production. We demonstrate that the crystal structure, band gap, morphology and textural parameters of sodium tantalates can be controlled via a feasible hydrothermal route by changing the pH and reaction time. The prepared materials are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), N_2-sorption and UV–Vis spectroscopy. $Na_2Ta_2O_6$ with pyrochlore-type structure, that has an average particle size of around 27 nm, is synthesized at low alkali concentration. By slightly increasing the alkali concentration, another $Na_2Ta_2O_6$ sample with an average particle size of 15 nm and higher surface area is obtained. Further increasing the alkali concentration results in a series of composite materials based on a mixture of $Na_2Ta_2O_6$ and $NaTaO_3$. In addition, large $NaTaO_3$ cubes are prepared at very high alkali conditions. The catalytic activities of the prepared samples are investigated for photocatalytic hydrogen production and their efficiencies are correlated to the composition, surface area and junction between the two crystal structures of the materials. The highest photocatalytic activity is achieved with $Na_2Ta_2O_6$ nanoparticles with the highest surface area. It is noticed that the hydrogen production rate is not only correlated to the high surface areas of the materials, an enhanced H_2 production is obtained for composite materials that is attributed to junctions between the pyrochlore and perovskite phases of sodium tantalate.

1. Introduction

The world-wide concerns about non-renewable fossil fuel shortage and increasing carbon dioxide emission that causes the global warming force society to find alternative renewable and clean energy sources [1,2]. Among the alternative energies, solar energy has attracted considerable attention because of its potential to provide a huge amount of the required energy [3,4]. Solar energy can be converted to electrical or chemical energy by using a photovoltaic or photochemical cell, respectively [5,6]. The storable fuels are of great interest in various aspects and applications. The photoelectrolysis of water with light that produces clean hydrogen is an effective method to achieve this goal [7–9]. This method does not cause greenhouse gas emission and the chemical energy can be stored and utilized when it is needed [10].

There are several parameters that affect the catalytic efficiency of materials such as the crystal and electronic structure, crystallinity, morphology, porosity, shape and size, and the textural properties of materials [11]. There are also some basic specifications for water splitting, for instance the semiconductor needs a minimum band gap of 1.23 eV and the valence band position has to be more positive than the redox potential of OH^-/O_2 and the conduction band has to have a more negative level than the redox potential of H^+/H_2 [12]. Optimization of the band positions and enhancement of materials efficiency can be achieved by doping, junctions between semiconductors, solid solution compounds or dye sensitization [7,13,14]. When a semiconductor material is photo-excited, electron–hole pairs are generated and need to be separated to avoid recombination. For an efficient separation mostly a co-catalyst is used [15–17]. In addition, the junctions between semiconductors can affect electron–hole separation and overall material efficiency as well without using any co-catalyst. Enhanced photocatalytic activities due to the junctions of semiconductors have been noticed in several systems [18–21].

A broad diversity of catalyst materials is nowadays investigated to meet specific requirements that are needed for overall water splitting like a suitable band gap, photoinduced charge separation, stability against photo-corrosion, and fast water splitting reaction rate [7,22–24]. Up to now, the highest activity for photocatalytic water splitting under UV irradiation was shown for tantalates, such as porous sodium tantalates ($NaTaO_x$, $NaTaO_3$, $Na_2Ta_2O_6$) [25], $ATaO_3$ (A = Li, Na, and K) [26,27], $Ba_5Ta_4O_{15}/Ba_3Ta_5O_{15}$ [19], $A_2Ta_2O_6$ (A = Na and K), $Ca_2Ta_2O_7$ [27,28], and $Cd_2Ta_2O_7$ [29]. In particular, $NaTaO_3$ with a perovskite-type structure has shown a quantum yield of 56% at 270 nm irradiation after lanthanum-doping and application of NiO co-catalyst [30]. The doped $NaTaO_3$

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establishes a nanostructured step-like surface, generating closely neighboring active sites, which are identified to be responsible for the high activity. Later studies indicated that the nanostructured sodium tantalates with high surface areas show enhanced photo-catalytic activity without any lanthanum doping [25,31]. Furthermore, Kudo et al. report that the type of alkali ion doping affects the position of the electronic bands and energy gap [26] whereas the choice of the synthetic route influences the Ta–O–Ta angle [31], crystallinity [31,32], particle size and surface area of the materials [30,33]. These characteristics of tantalate based photocatalysts are nowadays varied by synthetic methods such as solid-state [15,30], templating [34], sol–gel [23] and hydrothermal synthesis [33,35] to achieve a better catalytic performance. Xiong et al. reported the synthesis of $NaTaO_3$ under hydrothermal conditions at 140 °C and obtained crystalline particles of about 0.2–0.7 μm [36]. Lanthanum doped $NaTaO_3$ has been prepared via hydrothermal route by Li et al. mixing $La(NO_3)_3$, Ta_2O_5 and NaOH together in solution and treat the mixture at 160 °C for 24 h, producing cubic crystalline particles [37]. Domen et al. proposed a hydrothermal-electrochemical method to yield crystalline sodium tantalate thin film materials in a temperature range of 100–200 °C [38]. Although this class of sodium and tantalum based oxides have large bandgap of around/above 4.0 eV, they show very high H_2 production rate and excellent structural stability. Therefore, it is worth to study this kind of materials even though it might be more feasible to investigate visible light absorber semiconductors from practical point of view.

In principle the crystallinity is an essential point for the efficiency of a photocatalyst, because it has been commonly accepted that the formation and separation of photoexcited electron–hole pairs benefit from high crystallinity [7]. The charge carriers can migrate freely in an ordered crystal structure with less chances of recombination if the number of defect centers is low. Therefore, photocatalytic performance of amorphous materials mostly suffers from relatively higher number of defects incorporated in the structure when comparing with the crystalline counterparts. In addition to the crystallinity, heterojunctions result in efficient charge carrier separation, thus boosting the photocatalytic activity of a material. Further, the activity of the photocatalyst is strongly affected by the size of the particles and thus correlates with the surface area and number of active sites on the surface. The two directions (crystallinity and small particle size) are inherently difficult to combine with conventional solid–solid state reaction since the procedures to obtain highly crystalline materials mostly involve high temperature treatment leading to bulk materials with larger particle size. On the other hand, the synthetic approach via hydrothermal synthesis can be applied to produce nanosized crystalline materials with a high surface area at low temperatures. Herein, we report a series of nanostructured sodium tantalates with various crystal structures, morphologies and surface areas via a straightforward hydrothermal route and investigated the photocatalytic activities of the materials for hydrogen production.

2. Experimental

2.1. Photocatalyst preparation

Sodium tantalate catalysts were prepared by hydrothermal synthesis using tantalum(V) ethoxide ($Ta(OEt)_5$, Sigma–Aldrich, 99.98%) as tantalum source mixed with an aqueous solution of sodium hydroxide (J.T. Baker, pellets). In a typical reaction, 416 μL $Ta(OEt)_5$ was added to vigorously stirred 25 mL aqueous NaOH solution (3.2, 6.4, 12.8, 17.1, 25.6, 51.2 mmol). The suspension was continuously stirred for 10 min before it was transferred into an autoclave with 45 mL volume teflon lining. The autoclave was kept in a preheated oven at 200 °C for 16 h. After that the autoclave was cooled down to room temperature. The sample was centrifuged and washed three times with deionized water and finally with ethanol. Subsequently, the white product was dried at 90 °C. The samples were named according to the phases observed from XRD patterns: $Na_2Ta_2O_6$-1 (3.2 mmol NaOH), $Na_2Ta_2O_6$-2 (6.4 mmol NaOH), Composite-1 (12.8 mmol NaOH, mixture of $Na_2Ta_2O_6$ and low amount of $NaTaO_3$), Composite-2 (17.1 mmol NaOH, mixture of $Na_2Ta_2O_6$ and $NaTaO_3$), Composite-3 (25.6 mmol NaOH, mixture of $NaTaO_3$ and low amount of $Na_2Ta_2O_6$), and $NaTaO_3$-HT (HT indicating hydrothermal, 51.2 mmol NaOH).

A second series of sodium tantalates was prepared by varying reaction times. In a typical experiment, 17.1 mmol of NaOH was dissolved in 25 mL of water and 416 μL $Ta(OEt)_5$ were added under strong stirring for 10 min. Afterwards the solution was transferred into an autoclave (45 mL teflon lining volume) and placed in a preheated oven at 200 °C for 1 h, 4 h, 8 h, 16 h, 24 h, 48 h, 96 h and 168 h (1 week). The autoclaves were cooled down to room temperature and the products were washed as described before. The samples were denoted as 1 h, 4 h, 8 h, 16 h, 24 h, 96 h, and 1 week.

As reference material perovskite-type sodium tantalate was prepared via solid–solid state synthesis, which is from now on referred as $NaTaO_3$-SS [30]. The synthesis was a conventional solid–solid state procedure with a mixture of Ta_2O_5 (Sigma–Aldrich, 99.99%) and Na_2CO_3 (Acros Organics, 99.8%). Briefly, 0.442 g of Ta_2O_5 and 0.113 g of Na_2CO_3 (5% excess) were ground in an agate mortar. The powder was calcined at 900 °C for 1 h (with a ramping rate of 5 °C/min), cooled down to room temperature and mortared again. Subsequently, the material was calcined at 1150 °C for 10 h with a ramping of 5 °C/min. Excess sodium was washed out with water after the calcination.

2.2. Characterization and photocatalytic reactions

Wide angle XRD patterns collected at room temperature were recorded on a Stoe theta/theta diffractometer in Bragg-Brentano geometry (Cu Kα1/2 radiation). The measured patterns were evaluated qualitatively by comparison with entries from the ICDD-PDF-2 powder pattern database or with calculated patterns using literature structure data. TEM images of samples were obtained with an H-7100 electron microscope (100 kV) from Hitachi. SEM micrographs were taken with a Hitachi S-3500N. HR-SEM images of the samples were taken using a Hitachi S-5500 ultra-high resolution cold field emission scanning electron microscope operated at 2, 10 and 30 kV. All samples were prepared on lacey carbon films supported by a copper grid. The obtained images were analyzed using the Scandium 5.0 software package from Soft Imaging System GmbH. BET surface areas were determined by N_2-sorption with a NOVA 3200e from the relative pressure range between 0.125 and 0.3 at liquid nitrogen temperature. UV–vis diffuse reflectance spectra were measured with a Varian Cary 4000 spectrometer equipped with an integration sphere using MgO as white standard.

Photocatalytic hydrogen production was determined in an air free closed gas system using a typical double walled inner irradiation-type quartz reactor and a 700 W Hg mid-pressure immersion lamp (Peschl UV-Consulting, set to 50% power = 350 W). For cooling the lamp is sitting in a double walled quartz mantle. The cooling water for the reactor and lamp is held at a temperature of 10 °C using a thermostat (LAUDA). Gas evolution was detected by online analysis with a multi-channel analyzer (Emerson X-Stream) equipped with a detector for the determination of the concentration of hydrogen (thermal conductivity detector), oxygen (paramagnetism) and carbon dioxide (IR). Argon was used as a carrier gas with a continuous gas flow set to 50 mL/min (Bronkhorst mass flow controller). In a typical catalytic reaction, 100 mg of photocatalyst was suspended in 550 mL water and 50 mL methanol. Before any photocatalytic reaction was initiated, the whole system