



Visible light active Ru-doped sodium niobate perovskite decorated with platinum nanoparticles via surface capping

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ARTICLE INFO

Article history:

Received 20 June 2013

Received in revised form 1 October 2013

Accepted 1 November 2013

Available online 15 December 2013

Keywords:

Ru-doped niobate

Octahedral framework

Photocatalysis

Platinum nanoparticle

Charge separation

ABSTRACT

An efficient visible light active $\text{NaNb}_{1-x}\text{Ru}_x\text{O}_3$ perovskite was hydrothermally fabricated and characterized. Various amounts of ruthenium substitution (0–5%) for Nb^{5+} in the niobate framework caused structural evolution from nanocubes to nanowires. 1% Ru-doped niobates [NR(1)], which had a highly crystalline orthorhombic structure, adsorbed visible light most substantially with an optical band gap of ~ 2.3 eV. With the aid of ^1H MAS NMR examination, the addition of protons into the niobate by acid treatment was convinced and its projected structure of $[\text{RuO}_6]$ plus $[\text{NbO}_6]$ octahedra with some defects was proposed. NR(1) itself was not effective at carrying out photocatalytic decomposition of phenol in water. To enhance visible light driven charge separation, platinum was dispersed onto NR(1) using surface capped Pt nanoparticles (PtNP) and Pt complexes (e.g., $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$). PtNPs laden NR(1) exhibited superior photocatalytic degradation of phenol in water. This increased photocatalytic activity was attributable to synergistic effects of facilitated electron transfer by PtNPs.

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1. Introduction

Nanostructured materials and their potential applications have motivated much research to utilize solar energy to clean the environment and solve energy crisis. Significant advances have been achieved in nano-scale fabrication of UV active catalysts into visible light photocatalysts by substitutional doping with foreign metal ions or anions [1]. The majority of visible light photocatalysts were developed from titanium-based oxides, but the photocatalytic performances of nanostructured perovskite oxides have also attracted considerable interest [2,3]. Most of the perovskite oxide photocatalysts (NaNbO_3 , NaTiO_3 , $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$) are active under ultraviolet light, which constitutes only a small fraction of solar radiation [4,5]. A nanowire-shaped semiconductor photocatalyst of sodium niobate has been demonstrated to have high activity for water splitting in the presence of sacrificial reagents, but this only occurs under UV due to its large energy band gap (3.2–3.5 eV) [2]. Highly dispersed RuO_x -doped $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheets enabled UV illuminated hydrogen production [3]. Of the various niobates, the perovskite phase of $\text{RbPb}_2\text{Nb}_3\text{O}_{10}$ could exhibit absorption in the visible light region [6] and another attempt to use niobates under visible light by dye sensitization has been reported [7].

Catalysts with perovskite phases are able to accommodate large quantities of different organic and inorganic species in their interlayer regions and the resulting host-guest interactions could establish a hydrogen bonded interlayer network within regions where photo-oxidation and heterogeneous catalysis occur [8,9]. Like other ABO_3 perovskites, alkaline niobates are mainly composed of octahedral units, which facilitates the transport of charge carriers (electrons and holes) during photo-excitation [10]. The separation and migration of photo-excited carriers are influenced by phase purity, crystal size, chemical composition, crystalline structure, and surface properties [3,11].

Layered alkaline niobates are usually synthesized using solid state methods at very high temperatures and these are somewhat inefficient in terms of producing a homogenous distribution of structures [12,13]. During solid state synthesis, the production of layered phases is only possible when the interlayer cation is K^+ , Rb^+ or Cs^+ . Ion-exchange reactions provide a means of inserting cations in the interlayer space. Other synthetic methods of niobates are available in the literature, such as hydrothermal, sol-gel, and crystal growth processes [14,15]. Niobate photocatalysts are also loaded with Pt, RhO_2 , or RuO_2 by intercalation methods [16]. Most of these co-catalysts are directly involved in the separation of charges against recombination and thus, they act as active centers for oxidation and reduction of adsorbed species. In fact, these layered perovskite-type oxides have high charge densities that cause some difficulties loading foreign species. Therefore, chemical exfoliation techniques have been devised for these layered oxides to improve the intercalation of organic or inorganic species [17].

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Here, we investigated the partial substitution of niobium by ruthenium in the niobate framework using a hydrothermal method, and studied the preparation of niobates with strong visible light absorption. Replacement of niobium by ruthenium in the niobate framework was conducted to control electron densities and enable visible light activity. The structural and optical properties of the final products were controlled by adjusting the amount of ruthenium doped. To retard or minimize the recombination of electrons and holes, Pt was introduced onto the niobate framework by ion exchange using $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ and by using a colloidal solution of surface capped Pt nanoparticles (PtNPs). The photochemical activity of the designed niobate-based catalyst was examined under visible light by monitoring the photocatalytic degradation of phenol in water.

2. Materials and methods

2.1. Reagents and catalyst synthesis

Ruthenium doped sodium niobates were prepared hydrothermally using Nb_2O_5 and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ as precursors. Incorporation of ruthenium into niobates was performed by dissolving Nb_2O_5 and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ in a 10 M NaOH solution at different Nb:Ru weight ratios in the range 0–5%. For example, 0% Ru niobate was prepared by dissolving 1 g Nb_2O_5 in 60 mL 10 M NaOH, stirring vigorously for 1 h, and then injecting the solution into a 110 mL Teflon vessel. The vessel was sealed in a stainless steel chamber, placed in an autoclave, and heated at 200 °C for 140 min. After the autoclave had cooled down to room temperature, the products were washed several times by centrifugation, first with distilled water, later with ethanol, and dried at 80 °C for 24 h. Four samples with different Ru contents were prepared and designated as NR(0), NR(0.5), NR(1), NR(2) and NR(5), respectively.

2.2. Preparation of platinum nanoparticles using ascorbic acid

In a typical preparation, 6 mL of ascorbic acid (100 mM), 0.6 mL gum arabica (1%), and 0.1 mL NaOH (1 M) were added to 12.3 mL of ultrapure water and incubated to 60 °C for 60 min. To start the reduction of the platinum ion precursor, 1 mL of H_2PtCl_6 (20 mM) and 20 mL of the above mixture were maintained at 60 °C up to 48 h in an oven.

2.3. Protonation and loading of platinum

Protonation was carried out by shaking 50 mL of 1 M HCl solution with 0.6 g of the as synthesized 1% Ru doped product for 24 h at room temperature. The solid product was then centrifuged, washed with deionized water several times, and dried at 80 °C for 24 h. The framework cavities were clearing up by shaking 50 mL of 7.7 mM tetrabutylammonium hydroxide (TBA^+OH^-) solution with 0.6 g of the protonated solid product for 24 h. The mixture was centrifuged, and the product was soaked in 1 M HCl for 24 h. It was then rinsed several times with deionized water to remove excess HCl and dried in an oven at 80 °C for 24 h. The product (0.3 g) was treated with 0.5% HF at least for 2 h (to create H-terminated surfaces), washed with deionized water, mixed with 12 mL of a colloidal solution of PtNPs for 6 h, filtered, and finally dried in an oven at 80 °C for 24 h. The resulting product was calcined at 200 °C for 2 h to remove the surface capping of PtNPs and to anchor Pt to the framework cavity. In another catalyst preparation, 0.6 g of the protonated solid product was treated with 100 mL of 5 mM $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ for 24 h so as to exchange H^+ , and the resulting product was calcined at 200 °C for 2 h.

2.4. Evaluation of photocatalytic activity

Phenol was used to evaluate the photocatalytic activities of the fabricated catalysts. Catalyst (0.5 g/L) was added to 10 ppm of phenol solutions. Reactions were all performed in a completely mixed batch reactor at room temperature and pressure. Samples were illuminated with the light from a 150-W xenon arc lamp (Ushio, Model 13014) filtered using an UV filter (<425 nm). The xenon arc lamp was set 35 cm from the surfaces of target solutions in the reactor. Phenol concentrations were determined using a high performance liquid chromatograph (SPD-20A, Shimadzu Corp., Japan) equipped with a Discovery® C18 column.

2.5. Characterization of niobates and Pt nanoparticles

The microstructures of samples were observed using a scanning electron microscope (S-4300 Hitachi, Japan). XRD patterns were recorded using $\text{Cu K}\alpha$ radiation ($n = 1.5418 \text{ \AA}$) on a Rigaku D/Max-2500 X-ray diffractometer operating at 40 kV and 100 mA at a scanning speed of 6 degree/min in the scan range of 10–80 degrees. UV–vis diffuse reflectance spectra of powder samples were measured using a Shimadzu UV-2450 diffuse reflectance spectrophotometer. TEM images were taken using a Hitachi H-7600 instrument at an accelerating voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI Quantera SXM instrument with an Al $\text{K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) X-ray source and with an angle of 45° between the source and the detector. ^1H MAS NMR spectra were acquired at 14.1 T using a Unity INOVA 600 NMR spectrometer. The absorbance spectra of aqueous NPs were measured using a UV spectrophotometer (Model 8453, Agilent, USA).

3. Results and discussion

3.1. Characterization of surface morphologies and structures of Ru-doped niobates

The scanning electron microscope (SEM) images in Fig. 1 show the structural evolution of niobates from nanocubes to nanowires at different ruthenium contents. The sample NR(0) is composed of irregular nanocubes and had a thickness of several hundred nanometers. NR(0.5) and NR(1) had a similar morphology, but they were brick red rather than white. Most of the submicron particles produced appeared as well defined cubes linked in clusters. NR(2) and NR(5) were dark gray and had wire-like morphologies with diameters of a few hundred nanometers and lengths from several hundred nanometers to several micrometers. These results demonstrate the effect of the amount of ruthenium doped on size and shape of niobates at the nanoscale level.

Fig. 2(a) shows the XRD patterns of the niobates prepared at different ruthenium weight ratios. The diffraction peaks of NR(0) and NR(1) correspond to orthorhombic crystal symmetry (JCPDF 0033-1270, space group Pbma , $a = 5.569 \text{ \AA}$; $b = 15.523 \text{ \AA}$; $c = 5.505 \text{ \AA}$; $\alpha = 90.00^\circ$; $\beta = 90.00^\circ$; $\gamma = 90.00^\circ$). Its host lattice consists of distorted perovskite layers linked to each other by corner-sharing octahedral units [18]. The framework of the NaNbO_3 structure is composed of several octahedral units, where the Nb atoms in octahedral units are located off center. This means that the six neighboring O^{2-} sites are non-equivalent. As a result of the distorted octahedral arrangements, the sodium ions are positioned in different crystallographic environments [19]. The samples containing >1% Ru (e.g., NR(2) and NR(5)) possessed unidentified small peaks in their XRD patterns and gave a complete change in crystal structure. In the present study, we focused on NR(0) and NR(1) samples, which had a highly crystalline orthorhombic structure. The replacement of a host Nb^{5+} site by ruthenium created a

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