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RuO₂/TiO₂ nanobelt heterostructures with enhanced photocatalytic activity and gas-phase selective oxidation of benzyl alcohol



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ABSTRACT

Based on energy band matching between RuO₂ and TiO₂, the RuO₂/TiO₂ nanobelt heterostructures are designed and fabricated. The formed heterostructures can efficiently enhance the separation of photo-generated electron-hole pairs and accelerate the transport of charges. Thanks to above-mentioned advantages, the RuO₂/TiO₂ nanobelt heterostructures exhibit an improved photocatalytic performance compared with P25, TiO₂, and RuO₂ under UV and visible light irradiation. Moreover, the nanopapers based on RuO₂/TiO₂ nanobelt heterostructures have been prepared via a modified paper-making process. The paper-like porous RuO₂/TiO₂ nanobelt heterostructures are applied in heterogeneous catalysis and present enhanced activity and selectivity for catalyzing aerobic oxidation of benzyl alcohol. These results may provide a paradigm to fabricate and design the one-dimensional TiO₂ nanostructured surface heterostructures with high efficiency and performance.

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1. Introduction

One-dimensional TiO₂ nanostructured surface heterostructures (1D TiO₂NSH), such as ZnO nanorods/TiO₂ nanotubes and ZnIn₂S₄ nanosheets/TiO₂ nanorods, have been widely investigated owing to their fascinating synergistic effect in a myriad of fields, e.g. photocatalysis, water splitting, photovoltaic devices, and heterogeneous catalysis [1,2]. According to the physical mechanism, including band structure matching, p-n junction, surface plasmon resonance, and Schottky junction, many different 1D TiO₂NSHs have been designed and prepared, which can achieve efficient separation of photo-induced charge carriers and broaden the light absorption band from UV to visible region. Thus, the excellent photocatalytic performance can be achieved for photocatalytic splitting of water and environmental decontamination [3,4]. On the other hand, when the second phases are assembled on the 1D TiO₂ nanostructures, some novel properties can be obtained because the second phases have various morphologies and nanostructures, thus present different properties [5,6].

Photocatalysis provides a cost effective method for both renewable energy synthesis and environmental purification [7,8].

Photocatalytic activity is dominated by the material design strategy and synthesis method [9,10]. So far, multifarious technologies have been investigated to achieve photocatalysis, among which TiO₂ is a very promising candidate [11]. Compared with TiO₂ nanoparticles, one-dimensional TiO₂ nanomaterials, such as TiO₂ nanobelts, possess a larger surface-to-volume ratio, more rapid diffusion-free electron transport along the long direction, and the lower number of grain boundaries, thus achieve better photocatalytic performance [12]. However, their poor visible light utilization, few surface active sites, as well as the high recombination of photogenerated electron-hole pairs significantly limit their practical applications [13]. Some semiconductors (Bi₂O₃, Ag₂O) and noble metals (Au, Ag) can be assembled onto the surface of TiO₂ nanobelts and form the heterostructures, which can effectively improve the separation of photoinduced carriers and broaden the absorption wavelength, which contribute to enhance the photocatalytic performance [14].

Ruthenium dioxide (RuO₂), as the family of transition-metal oxides with rutile-like structure, has been investigated intensively due to its unique properties, such as high chemical stability, electrical conductivity, and excellent diffusion barrier properties. Because of its great advantages, it has been applied for supercapacitor, photocatalytic water splitting, and heterogeneous catalysis [15]. The conduction and valence band positions of RuO₂ are both lower than that of TiO₂, so they are expected to have the band

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overlap [16]. Therefore, constructing RuO₂/TiO₂ heterostructures might enhance the photocatalytic activity by hindering the charge recombination and improving the charge transfer process. However, to the best of our knowledge, very few studies have been performed on the RuO₂/TiO₂ heterostructures for photocatalysis applications [17].

Moreover, RuO₂ is a very powerful oxidation catalyst and well-known for its application in heterogeneous catalysis [18]. Numerous molecules, such as CO, O₂, NH₃, NO, methylene, and methane, adsorb well on the RuO₂ (110) surface via the under-coordinated Ru atoms, which is a prerequisite for catalytic reactions [19]. It has reported that the smaller RuO₂ nanoparticles can lead to higher catalytic activity due to the numerous active sites with the increased specific surface area [20]. However, the RuO₂ nanoparticles with small sizes tend to cause deactivation due to the occurrence of particle sintering during the catalytic process at elevated temperature [21]. So RuO₂ nanoparticles need to be finely dispersed on the supports to achieve high mass activity and resistance to aggregation [22]. One-dimensional TiO₂ nanobelts can be used as support materials for noble metal or metal oxide catalysts because of its large surface area, distinctive formability and ability to assemble above catalysts [23,24].

Herein, we demonstrate a facile synthetic strategy for fabricating the RuO₂/TiO₂ nanobelt heterostructures by a co-precipitation method using TiO₂ nanobelts as template. RuO₂ nanoparticles with an average size of 2.4 ± 0.5 nm are well dispersed on the surface of TiO₂ nanobelt. The obtained RuO₂/TiO₂ nanobelt heterostructures exhibit higher photocatalytic activities for the degradation of methyl orange (MO) than that of P25, TiO₂ nanobelts, and RuO₂ nanoparticles under UV and visible light irradiation. Besides, the formed RuO₂/TiO₂ nanobelt heterostructures are assembled to form nanopaper catalysts using a modified paper-making process, which exhibit high activity and selectivity for the gas-phase selective oxidation of benzyl alcohol to benzaldehyde at elevated temperature.

2. Experimental section

2.1. Materials

The chemicals used in this work were of analytical reagent grade. Solutions were freshly prepared with deionized water. Titania P25 (TiO₂; ca. 80% anatase, and 20% rutile), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and ruthenium chloride trihydrate (RuCl₃ · 3H₂O) were purchased from Sinopharm and used without further treatment.

2.2. Preparation of TiO₂ nanobelts

TiO₂ nanobelts were synthesized by a hydrothermal procedure. Typically, P25 powders (0.1 g) was mixed with an aqueous solution of NaOH (20 mL, 10 mol/L), followed by a hydrothermal treatment at 180 °C in a 25 mL Teflon-lined autoclave for 48 h. The treated powders were washed thoroughly with deionized water followed by a filtration and drying process. The obtained Na₂Ti₃O₇ nanobelts were then immersed in an aqueous solution of HCl (0.1 mol/L) for 48 h and then washed thoroughly with water to produce H₂Ti₃O₇ nanobelts. The H₂Ti₃O₇ nanobelts were added into a 25 mL Teflon vessel, which was filled with an aqueous solution of H₂SO₄ (0.02 mol/L) up to 80% of the total volume and maintained at 100 °C for 12 h. Finally, the products were isolated from the solution by centrifugation and sequentially washed with deionized water for several times, and dried at 70 °C for 10 h. Thermal annealing of the H₂Ti₃O₇ nanobelts by acid corrosion at 600 °C for

2 h led to the production of TiO₂ nanobelts with roughened surfaces.

2.3. Preparation of RuO₂/TiO₂ nanobelt heterostructures

RuO₂/TiO₂ nanobelt heterostructures (2 wt %) were prepared by a deposition-precipitation method. TiO₂ nanobelts (0.2 g) were added to distilled water (50 mL) under magnetic stirring. Then RuCl₃ · 3H₂O (5 mL, 6.18 mmol/L) solution was added to the suspension, and the mixture was stirred for 30 min. Subsequently, NaOH solution (0.1 mol/L) was slowly added to the resulting mixture. In this process, the sol-like RuO₂ adsorbed onto the surface of TiO₂ nanobelts at about pH=7, thus leading to homogeneously dispersed RuO₂ nanoparticles. The product was washed with deionized water and ethanol to remove any ionic residual, and then dried in oven at 70 °C for 12 h. For comparison, pure RuO₂ nanoparticles were also synthesized in the same manner without the addition of TiO₂ nanobelts.

2.4. RuO₂/TiO₂ nanobelt heterostructure nanopapers

RuO₂/TiO₂ nanobelt heterostructure nanopapers were fabricated by a modified paper-making process. Briefly, 1 g RuO₂/TiO₂ nanobelt heterostructures without any surfactants were dispersed in 1 L distilled water under magnetic stirring, followed by filtering the resultant pulp on a sub-microporous filter paper (pore size of 0.22 μm) surface through a vacuum-filter (SHB-III Yuhua, and the vacuum is 0.1 MPa) with ceramic filter (pore size of 0.45 μm). Then the obtained wet RuO₂/TiO₂ nanobelt heterostructure nanopapers were dried at 70 °C for 24 h. The P25, TiO₂ nanobelt and RuO₂ nanoparticles nanopapers were also fabricated by the same process.

2.5. Characterizations

X-ray powder diffraction (XRD) pattern of catalysts were recorded on a Bruker D8 Advance powder X-ray diffractometer with Cu Kα (λ=0.15406 nm). HITACHI S-4800 field emission scanning electron microscope (FE-SEM) was used to characterize the morphologies and size of the synthesized samples. High resolution transmission electron microscopy (HRTEM) images were carried out with a JOEL JEM 2100 microscope. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Avatar 370 infrared spectrometer in the range 400–4000 cm⁻¹ using pressed KBr pellets. The KBr pellets technique was used where 10 mg of each sample is mixed with 1000 mg of KBr in an agate mortar. From this stock, 200 mg were then pressed into pellets of 13 mm diameter. UV–vis diffuse reflectance spectra (DRS) of the samples were recorded on a UV–vis spectrophotometer (UV-2550, Shimadzu) with an integrating sphere attachment within the range of 200 to 700 nm and with BaSO₄ as the reflectance standard.

2.6. Photocatalytic activity test

The photocatalytic activity of the RuO₂/TiO₂ nanobelt heterostructures was investigated by means of the photodegradation of methyl orange (MO, 20 mg/L, pH=6). In a typical measurement, 20 mL of an aqueous suspension of MO and 20 mg of the heterostructure powders were placed in a 50 mL beaker and were conducted in an XPA-photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). Prior to photoirradiation, the suspensions were magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium between the dye and the surface of the catalysts under ambient conditions. A 350 W mercury lamp with a maximum emission at 356 nm (Table S1)

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