



Full Length Article

Morphology controlled synthesis of CeTiO₄ using molten salts and enhanced photocatalytic activity for CO₂ reductionReshalaiti Hailili^{a,b}, Daniel L. Jacobs^c, Ling Zang^{c,*}, Chuanyi Wang^{a,b,*}^a Laboratory of Environmental Sciences and Technology, Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, China^b School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China^c Nano Institute of Utah and Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, USA

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ABSTRACT

Incorporation of visible light active semiconductors without doping noble (transition) metals results in remarkably different construction principle of visible light driven photocatalysts in which light absorptions and charge transfer become more flexible and efficiencies are no longer limited in ultraviolet (UV) region. Herein, we provide a strategy to design efficient photocatalysts by introducing visible light sensitive Ce₂O₃ into UV active TiO₂ via molten salt synthesis (MSS) of CeTiO₄ for visible light CO₂ reduction. By changing salt composition in the MSS process, the nanostructured CeTiO₄ was prepared and exhibited distinct morphologies e.g., nanorods (NaCl–NaH₂PO₄), polyhedrons (KCl–NaCl) and cubic (KCl–Na₂SO₄), respectively. Of the different morphologies, the nanorods of CeTiO₄ showed best photoactivity with quantum efficiencies of 0.36% and 0.065% for CO and CH₄ formation, respectively. The unique morphologies well positioned band edges cause such obvious differences and co-contribute to the high performance effectiveness. This study demonstrates a strategy for the rational design and fabrication of visible light driven photocatalysts with controlled morphology, which in turn, can enhance the control and production of value-added products of CO₂ reduction. This is an important step towards realizing the utilization of renewable energy sources, such as solar power, to reduce the concentration of atmospheric CO₂ and form green energy sources.

1. Introduction

The increase of industrialization driven by fossil fuel energies is causing increasing amounts of atmospheric CO₂. This increase in CO₂, an important greenhouse gas, is a leading source of the increase in global temperatures, which contributes toward to growing societal problems throughout the world [1]. One important strategy to mitigate future risk of rising CO₂ concentrations is CO₂ capture and conversion to value-added compounds such as CO, CH₄ and CH₃OH [2,3]. Semiconductor based photocatalytic technique to convert CO₂ is a very promising approach pioneered with the first milestone work of photoelectrochemical reduction reported by Halmann in 1978 and photocatalytic CO₂ reduction by Inoue in 1979 [4,5]. Photocatalysis, moreover, has the advantage that the driving force is the inexhaustible and endless supply of sun light. Numerous semiconductors have been explored for photocatalytic approach, for instance TiO₂, Zn₂GeO₄, CdS, ZnGa₂O₄, MOF (metal-organic framework) and so on [6–13]. TiO₂ in particular, has exhibited exceptional photocatalytic performance,

leading to the TiO₂-based catalysts with further improved properties [14–20]. However, widely studied semiconductors are only active under ultraviolet (UV) light and the majority of them suffer from low quantum yields and instability because of relatively large electronic band gap and quick recombination of photoinduced electron-hole pairs [1–3]. Therefore, the main challenge is searching for potential photocatalysts, which are stable, environmental friendly, have a suitable band gap and can effectively separate charge carriers, subsequently accelerate visible light conversion of CO₂ to useful fuels at a reasonable rate.

One method to improve the light absorption of high efficiency photocatalysts, such as TiO₂, is to incorporate visible light active materials, e.g., noble metals [14]. However, noble metals can be rare and expensive and therefore would be hard to scale. Incorporation of transition metals is another approach to improving the visible light efficiency. In particular, cerium has been shown to display promising co-catalytic properties in CO₂ reduction systems, is nontoxic, and is very abundant in the earth's crust (66.5 ppm), greater even than copper

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(60 ppm) [21]. More significantly, Ce_2O_3 is a visible light sensitive semiconductor with a band gap of 2.40 eV [22]. In the view of efficient utilization of solar energy, Ce–Ti–O system are widely studied, among which CeTiO_4 is considered as a promising alternative visible light active photocatalyst compared to noble metal catalyst systems [23–26].

Beyond improving the light absorption, one of the most important factors of photocatalytic reduction of CO_2 is efficient adsorption of CO_2 on the surface of catalysts [27,28]. The redox potential of the photo-induced electron–hole pairs and the surface charge distribution is dependent on the catalyst's surface, where occurs the chemical redox reaction, adsorption of the reactant to reduce the detrimental problem of fast charge carrier recombination and enhance photoreduction [29]. Moreover, the activity of photocatalysts not only depends on the intrinsic physical properties but it relates to the material's crystalline size, morphology, defects as well as other surface properties [30,31]. These extrinsic properties can be tuned by changing preparation methods and reaction conditions. Molten salt synthesis (MSS) is an effective approach to control morphology due to its advantages in facilitating crystal growth with improved phase-purity based on varying the salt compositions, molar ratio and reaction temperature [29–31]. However, compared to simple metal oxides, control of crystalline growth of complex oxide photocatalysts is proven more difficult due to the complex bonding relations and atomic charge balance interactions in the crystal lattice. Therefore, morphology tailoring of complex oxides is greatly needed to further improve their photocatalytic performance in practical applications.

Motivated by the above discussions, we present one-step, facile synthesis of a visible light active catalyst CeTiO_4 as an efficient photocatalyst for CO_2 reduction. Morphology tailoring was achieved with a MSS by changing the salt compositions, which gave short nanorods, polyhedron and cube shapes. As-obtained samples exhibited both a reduction in the band gap, compared to TiO_2 , as well as shifting of the conduction and valence band energy levels to enhance CO_2 reduction under visible light irradiation. The products of CO_2 reduction in the presence of CeTiO_4 samples showed more favourable for CO formation over CH_4 . Among obtained samples, the short nanorods of CeTiO_4 exhibited the highest efficiency with nearly 0.355% and 0.065% quantum efficiencies for CO and CH_4 formation, respectively. This is about 12 and 32 times higher than that of reported TiO_2 anatase-rutile (0.029%) and Fe, S doped $\text{Sr}_3\text{Ti}_2\text{O}_7$ (0.011%) for preferred CO formation under visible light irradiation [32,33]. The diverse morphologies, well crystallinity and suitable thermodynamics were co-contributing for the improved photocatalytic activity. To the best of our knowledge, this is the first example of controlled synthesis of CeTiO_4 with distinct morphology and visible light driven photocatalytic property towards CO_2 reduction.

2. Experimental section

2.1. Preparation of samples

All chemical reagents used in this experiment were of analytic grade and used without further purification. CeTiO_4 catalyst was prepared by molten salt method in various salt systems. The typical synthetic procedures of sample 1–sample 3 are identical, except for the salt composition, which are listed in Table 1. The stoichiometric mixture of the analytic reagent grade raw materials $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (as a Ce_2O_3

source) and TiO_2 were added to the different salts system with a mole ratio of $\text{CeTiO}_4:\text{M}_{\text{S}1}:\text{M}_{\text{S}2} = 1:8:8$ ($\text{M}_{\text{S}1}$, $\text{M}_{\text{S}2}$ is mole ratio of employed salts). The mixtures were ball-milled in a small amount of ethanol for 3 h. Then, the dried mixture was heated in the corundum crucible at 200 °C for 2 h, subsequently increased to 600 °C and dweller for 10 h, cooled to 300 °C for 2 h, further slowly cooled to 200 °C at a rate of 1 °C/min and kept for 2 h, and finally cooled to room temperature at a rate of 1 °C/min. As-obtained samples were washed with water for two days to remove the salts, dried at 60 °C for 12 h for characterization or photocatalytic testing.

2.2. General remarks

The crystal structure of the CeTiO_4 samples was studied using a Bruker AXS D8 diffractometer operating at 40 kV with a scan step width of 0.02° and a fixed counting time of 1 s/step using an graphite monochromator set for Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation in the angular of 2θ from 10° to 70°. The relative metal amounts were determined by inductively coupled plasma optical emission spectrometry (ICP, VISTA-PRO). Before the ICP measurements, the samples were hydrothermally treated with HNO_3 at 180 °C for 3 h. The morphology of samples was analyzed with field-emission scanning electron microscopy (FESEM, ZEISS SUPRA55VP). Transmission electron microscopy (TEM) characterizations of as-obtained samples were performed on a JEOL-JEM 2100 electron microscope. Optical absorption was analyzed based on diffuse reflectance spectra on 40.0 mg of as-obtained products at room temperature using in ultraviolet-visible region taken on a spectrometer (Solid Spec-3700DUV Shimadzu) equipped with an integrating sphere. The BaSO_4 was used as a reference material to base line correction within the wavelength range 200 nm–800 nm. The electron paramagnetic resonance (EPR) spectrum of per 20.0 mg samples was characterized with Bruker E500 Spectrophotometer. The specific BET surface area of per 30.0 mg samples was determined with Brunauer–Emmett–Teller (BET) method from nitrogen adsorption–desorption isotherms recorded at 77 K on a Quantachrome instrument (QUADRASORB IQ). The samples were outgassed at 180 °C for 3 h before the measurements.

2.3. Photocurrent response measurements

Photocurrent measurements were conducted on an electrochemical workstation with a standard three-electrode system in 0.1 mol·L⁻¹ of Na_2SO_4 electrolyte solution. The prepared sample electrode (per 5.0 mg of samples were dispersed in an ITO glass substrate with an area ~1.0 cm²), saturated calomel electrode and platinum electrode were used as the working electrode, reference electrode and counter electrode, respectively. The intensity of photocurrent were measured by an electrochemical workstation (CHI660, Chenhua Instrument, Shanghai, China) and the 300 W Xe lamp was used as light source.

2.4. Photoreduction experiments

The photocatalytic reduction of CO_2 with H_2O vapor was carried out in a reactor connected with mechanical vacuum pump with a gas-closed circulating system. Gaseous CO_2 was produced on site in a reactor by the reaction of NaHCO_3 (analytical grade) with 0.5 mol·L⁻¹ H_2SO_4 solution, providing a mixture of CO_2 and H_2O vapor. The photocatalyst

Table 1

The reaction conditions, ICP analyses and morphologies of sample 1–sample 3.

Sample no.	Salt composition	Ce:Ti	Morphology	Length (nm)	Diameter (nm)
Sample 1	NaCl– NaH_2PO_4	0.93:0.92	Short nanorod	200–400	30–80
Sample 2	KCl–NaCl	0.89:0.95	Polyhedron	50–100	40–60
Sample 3	KCl– Na_2SO_4	0.94:0.88	Nanocube	50–100	5–10

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