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Research Paper

Oxygen vacancies induced visible-light photocatalytic activities of $CaCu_3Ti_4O_{12}$ with controllable morphologies for antibiotic degradation

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ABSTRACT

Searching photocatalysts with sufficient utilization of sunlight and elucidating relevant reaction mechanism are still grand challenges in the field of semiconductor photocatalysis. Herein, we developed a strategy towards morphology tailoring in conjunction with oxygen vacancy in the structure of double perovskite $CaCu_3Ti_4O_{12}$. Cube, polyhedron, nanorod and octahedron shaped $CaCu_3Ti_4O_{12}$ morphologies were obtained by varying the salt composition during molten salt synthesis, and their visible-light photocatalytic capacities were tested for degrading an antibiotic, tetracycline. The degradation process follows a first-order kinetics, and excellent photo-oxidation performance was observed for octahedron and nanorod shaped $CaCu_3Ti_4O_{12}$ giving degradation rate constants of $1.14 \times 10^{-1}\ min^{-1}$ and $8.40 \times 10^{-2}\ min^{-1}$, respectively, much higher than those of polyhedron and cube shapes (their rate constants were $5.10 \times 10^{-2}\ min^{-1}$ and $2.80 \times 10^{-2}\ min^{-1}$, respectively). The improved photoefficiency could be attributed to high abundant oxygen vacancies, surface properties, charge transfer and enhanced carrier separation due to the synergetic roles of active species, as is supported by active species trapping experiments and theoretical simulations. The detailed mechanism was proposed on the basis of crystal structure, unique morphology and spin trapping experiment, which reveals the roles of various active species for efficiency enhancement. The enhanced efficiency was further elucidated by theoretical investigations of density functional theory (DFT) calculations on the adsorption between tetracycline and $CaCu_3Ti_4O_{12}$. The findings reported here not only provide a green and rational design of high-performance photocatalysts but also show the applications ranged from catalysis to mitigation of polluted environment.

1. Introduction

A rapid development of industrialization in the past decades resulted in water pollution worldwide that has affected human health and ecology of the environment. Green and sustainable solution to global pollution is of utmost importance. Using solar light in conjunction with a catalyst is an attractive approach to treat polluted water [1–3]. Since early development of photoactive catalyst in 1960s, numerous studies have been performed in searching effective photocatalysts to treat a wide range of pollutants in water [4]. During photocatalytic treatment, remaining challenges are still insufficient sunlight utilization and ambiguous reaction mechanism. Early advancement in the field was focused on the ultraviolet (UV) light photocatalysts, which suffered from low yields of reactions and limited utilization of solar light (i.e., the UV accounts for only ~4% of solar irradiation) [5,6]. Therefore, in view of efficient utilization of solar light, the search of visible-light active photocatalysts became a main topic of intensive studies. Thus far, widely studied photocatalytic materials mainly include metal oxides (TiO_2, ZnO, WO_3) [7–10], sulfides (CdS) [11], oxynitrides [$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$] [12], oxysulfide ($Sm_2Ti_2O_5S_2$) [13], heterojunctions [14–16], perovskite [17], and layered structured materials [18,19].

As photocatalysts, oxide semiconductors attract more attention because of their high stability, decent efficiency and relative low cost [20]. However, the large electronic band gap of the oxides becomes one

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of main obstacles in efficiently utilizing solar light. It has been demonstrated that inserting transition metals into the structure of oxide semiconductors resulted in visible-light driven photocatalysts [21,22]. However, doping color metal into photocatalysts is not intrinsic and often reduces the catalytic efficiency because the dopant element may play as the recombination centers for the photoinduced electrons and holes. A promising way to address this challenging problem is to prepare complex oxide to tune the band gap and to achieve high efficiency under visible light irradiation without doping. Among various oxides, perovskite having diverse structures could overcome the drawbacks such as low efficiency, instability, and high electron – holes recombination rates [23,24]. Additionally, it is realized that modification with oxygen vacancies in their structures via different synthetic methods could also be an effective approach towards enhanced photoefficiency because these defects could trap the photoinduced chargers to accelerate electron – hole pairs separation [25,26]. Hence, design and synthesis of visible light active semiconductors with highly abundant oxygen defects to inhibit charge recombination and enhance its photocatalytic property is inspiring yet challenging task for the complex oxides.

$CaCu_3Ti_4O_{12}$ is a Ti-based perovskite, and mostly studied for dielectric property, though investigation of photocatalytic activity is still in its infancy [27,28]. Property of this newly exploited photocatalyst is related to synthetic methods and defect sites. The abundant oxygen vacancies and surface defects (e.g., Ti^{3+} and Cu^{+}) in the $CaCu_3Ti_4O_{12}$ not only make contributions to improve visible light absorption, but are deemed to be electron capture centers, which will reduce the carrier recombination, and thus leading to enhanced activity during photocatalytic process. Furthermore, in $CaCu_3Ti_4O_{12}$, the Cu 3d and O 2p levels can form a largely dispersed hybridized valence band, which also favors the separations of photogenerated electron – hole pairs and is beneficial to the oxidation reaction [27]. Therefore, in the view of unique structure property and visible light response, it is of great interest and obligatory to disclose the visible light driven photocatalytic activity of $CaCu_3Ti_4O_{12}$.

Choosing $CaCu_3Ti_4O_{12}$ as a promising photocatalyst and tetracycline as a probe molecule (as an emerging contaminant, releasing of tetracycline-like pharmaceutical residues poses threats to human health and ecobalance), the present work aims to: (i) synthesize of oxygen deficiency-containing $CaCu_3Ti_4O_{12}$ with controllable morphology using diverse salts in molten salt process, (ii) investigate morphology–-property correlation and the enhanced visible light photocatalytical activity towards antibiotic decomposition and, (iii) clarify the origins of high performance effectiveness based on crystal structure, morphology, enhanced charge separation and theoretical investigations disclosing the adsorption and binding effects of tetracycline on $CaCu_3Ti_4O_{12}$. By far, the photocatalytic decomposition of pharmaceutical pollutants over distinct morphological $CaCu_3Ti_4O_{12}$ has not yet studied. The present study suggests that $CaCu_3Ti_4O_{12}$ *is* a promising visible-light active photocatalyst with high efficiency and good stability, and could offer new inspirations on other perovskite photocatalysts for environmental implementation.

2. Experimental section

2.1. Sample preparation

Flux treatment using various kinds of molten salts was performed to synthesize $CaCu_3Ti_4O_{12}$ in different salt systems. In a typical synthesis, metal oxides were used as raw materials, in which CaO (0.0049 mol), CuO (0.0146 mol), and TiO_2 (0.019 mol, 99.9%) were grinded in different salt systems (NaF, NaCl, NaBr, LiCl and KCl) with a given molar ratio for 60 min. Then, well-grounded mixtures were heated in the corundum crucible at 800 °C by increasing at a rate of 2 °C/min, and dwell them for 6 h. After the reaction, it was cooled slowly to room temperature at the rate of 1 °C/min, and the as-obtained samples were washed thoroughly with deionized water in order to remove the utilized molten salts, which were further examined by $AgNO_3$ solution. The final obtained products were dried at 80 °C in an oven for other general characterizations. The physical properties of the selected molten salts were listed in Table 1.

Table 1
Physical properties of the molten salts used, morphology and optical property of *Sample 1*–*Sample 5*.

Sample no.	Salt composition	Melting point (°C)	Boiling point (°C)	Morphology	Band gap (eV)
Sample 1	NaF	993	1695	Cube	1.6272
Sample 2	NaCl	801	1413	Polyhedron	2.0175
Sample 3	NaBr	747	1390	Cube	1.8970
Sample 4	LiCl	650	1350	Nanorods	2.4883
Sample 5	KCl	776	1420	Octahedron	2.0432

2.2. General remarks

The Scanning Electron Microscope (SEM) characterizations were performed on a Hitachi S-3500N scanning electron microscope. The Energy-disperse X-ray Analysis (EDXA) was performed on EDX G2T20136-5 energy-disperse X-ray instrument. Powder X – ray Diffraction (XRD) measurement of the studied samples was carried out using a Bruker AXS D8 Advance Diffractometer operating at 40 kV and 30 mA with a scan step width of 0.02° and a fixed counting time of 1 s/step using an graphite monochromator set for Cu Kα (λ = 1.5418 Å) radiation in the angular of 2 θ from 5° to 80°. Optical diffuse reflectance spectra of per 40.0 mg samples were recorded on a UV–vis spectrophotometer (Shimadzu SolidSpec – 3700 DUV) in the wavelength range from 200 nm to 800 nm. The $BaSO_4$ was used as a reference for baseline correction. Electron Paramagnetic Resonance (EPR) spectra were measured at 4–298 K on a Bruker ElexsysE500 spectrometer working under the X-band and equipped with an Oxford cryostat with 20.0 mg of per samples. All the spectra were recorded at 100 K and the *g* values were determined by calibration with DPPH (Bruker spectrometer) standard. The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption – desorption isotherms recorded at 77 K on a Quantachrome Instrument (QUADRASORB IQ) after the samples were degassed at 180 °C for 3 h. Infrared Spectra (IR) were recorded on Bruker Optics TENSOR 27 Fourier transform infrared spectrometer in the range from 400 cm^{-1} to 4000 cm^{-1}.

2.3. Photocatalytic activity evaluations

2.3.1. Photocatalytic activity test

The photocatalytic activity of the obtained samples was evaluated by the decomposition of a model pollutant, antibiotic tetracycline. For a typical experiment, 40.0 mg of a prepared $CaCu_3Ti_4O_{12}$ sample catalyst was dispersed in a tubular quartz reactor containing 100 mL of 1.0×10^{-5} mol L^{-1} tetracycline aqueous solution. The mixture was put in a beaker, and stirred for 30 min in the absence of light to attain adsorption equilibrium on the catalyst surface. The reactor was irradiated with a 300 W Xe lamp (PLS – SXE300, Perfect Light Company, Beijing, China), which was equipped with a cutoff filter (420 nm) to obtain visible light source. The photon flux of the incident light was determined using a Ray virtual irradiatometer (1916-C, light intensity is about 500 mW cm^{-2} with an error value < 5%). During photocatalytic reaction, samples were taken at specific times and centrifuged for 30 min to discard any sediment. Then the degradation product at a given internal time was monitored through optical absorption, i.e., the concentration changes of tetracycline was preliminarily determined by UV–vis spectrophotometer (UV-1800, Shimadzu, Japan). For the accurate analysis, high performance liquid chromatography (HPLC, UltiMate3000, USA) measurements were carried out. The 1.0 mL of