

## Full Length Article

Effect of crystalline/amorphous structure on light absorption and carrier separation of CeO<sub>2</sub>-TiO<sub>2</sub> heterojunctionsNing Fang<sup>a,\*</sup>, Yongyi Ding<sup>a</sup>, Chengbao Liu<sup>b,c,d</sup>, Zhigang Chen<sup>a,b,c,d,\*</sup><sup>a</sup>School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, China<sup>b</sup>School of Chemistry, Biology and Materials Engineering, Suzhou University of Science and Technology, Suzhou 215009, China<sup>c</sup>Jiangsu Key Laboratory for Environment Functional Materials, Suzhou 215009, China<sup>d</sup>Jiangsu Collaborative Innovation Center of Technology and Material for Water Treatment, Suzhou 215009, China

## ARTICLE INFO

## Article history:

Received 8 January 2018

Revised 7 April 2018

Accepted 30 April 2018

Available online 2 May 2018

## Keywords:

Heterojunction

Amorphous

Light absorption

Carrier separation

Cerium

Titania

## ABSTRACT

Three types of heterojunctions with crystalline ceria/amorphous titania (cC/aT), amorphous ceria/amorphous titania (aC/aT) and crystalline titania/amorphous ceria (cT/aC) structures were prepared to study the effect of structure on their light absorption and carrier separation. The formation mechanism of both crystalline and amorphous phases was studied in this paper. The light absorption and carrier separation efficiency of the heterojunction are markedly enhanced relative to two pure oxides (TiO<sub>2</sub> and CeO<sub>2</sub>). Defects such as oxygen vacancy from the lattice disorder in the aC/aT sample enable the highest absorption of visible light, but also reduce its carrier separation efficiency. The highest separation efficiency of the carrier was observed in the cT/aC sample due to excellent carrier transport from the crystalline phase to the amorphous phase. The experiment confirmed that the aC/cT sample has more separated charge carriers to react with organic pollutants compare with the cC/aT and aC/aT samples. The work in this paper is useful for rational design and preparation of heterojunctions made by other oxides with high visible light absorption and carrier separation efficiency.

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## 1. Introduction

Titania (TiO<sub>2</sub>) has been extensively studied as a photocatalyst [1–3] because of its favorable band-edge positions, chemical stability and abundance. The practical applications of TiO<sub>2</sub> are substantially limited due to its large band gap and rapid recombination of photogenerated electrons and holes (e<sup>-</sup>-h<sup>+</sup>) [4,5]. Despite various methods such as metal or nonmetal doping [6,7], co-deposition of metals [8], and dye sensitization [9], there is still a long way to go to obtain an ideal titania photocatalyst.

Recently, black TiO<sub>2</sub> has attracted significant attention due to its increased charge transfer and visible light absorption [10–12]. Black TiO<sub>2</sub> is composed of two types of TiO<sub>2</sub>: the core is a crystalline phase (anatase) and the shell is a disordered layer obtained by hydrogenation treatments [10]. The disordered shell determines the band gap narrowing in TiO<sub>2</sub>, and the order/disorder interface improves the separation and transfer efficiency of e<sup>-</sup>-h<sup>+</sup> pairs as well as the photocatalytic performance. The biggest problem with

black TiO<sub>2</sub> is its harsh preparation conditions such as hydrogenation via high pressure.

Heterojunctions are another feasible way to improve photocatalytic activity [13–15]. The heterojunction provides a narrow bandgap to increase the visible light absorption [16]. More efficient charge separation can be achieved by the offset in the energies of the band edges from the heterostructure [17]. The interface of different crystals can sometimes becomes the carriers' barrier due to the lattice and electron mismatches, and thereby reduces the photocatalytic efficiency [18]. Finding a solution of the interfacial problem is essential to getting an active heterojunction. By referring to the order/disorder structure of black TiO<sub>2</sub>, the amorphous phase may be one of the solutions. Mismatches at the interface can be fault-tolerant due to the disorder of amorphous phase. In addition, the amorphous phase can provide more unsaturated active sites to improve photocatalytic activities [19].

Cerium dioxide is one of the most attractive materials and is widely used in gas sensors [20], in fuel cells [21], and as a photocatalyst in water and air pollution treatment [22]. Ceria has the unique ability to store and release oxygen due to the redox pair Ce<sup>3+</sup>/Ce<sup>4+</sup> [22]. CeO<sub>2</sub>-TiO<sub>2</sub> heterojunction got many attentions [23–25]. But most of the researches focused on the effect of low amounts of ceria on the photocatalytic activity of TiO<sub>2</sub>, the

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researches on the crystalline and amorphous structure in CeO<sub>2</sub>-TiO<sub>2</sub> heterojunction are rare [26–28]. The formation mechanism of crystalline and amorphous phases in the heterojunction is still not found a clear answer. The influence of crystalline/amorphous phases on photocatalytic activity is also lacking.

In the present paper, we report an investigation on CeO<sub>2</sub>-TiO<sub>2</sub> heterojunction with three kind's structures (cC/aT, aT/aC and cT/aC). Thermal analysis of thermogravimetry-differential scanning calorimetry (TG-DSC) test was used to study the formation mechanism of crystalline and amorphous phases. The samples were characterized by various techniques including X-ray Diffraction (XRD), N<sub>2</sub> adsorption to evaluate BET surface area, diffuse reflectance UV-Vis spectroscopy, transmission electron microscopy (TEM with EDS), X-ray photoemission spectroscopy (XPS) and photoluminescence spectroscopy (PL). Aim of this investigation was a deep insight into the effect of crystalline/amorphous structure on the light absorption and carrier separation of the heterojunction.

## 2. Experimental

### 2.1. Preparation of samples

All reactants used in the experiment were purchased from China National Medicines Corporation Ltd. The CeO<sub>2</sub>/TiO<sub>2</sub> heterojunction was synthesized via a sol-gel method. At first, solution A [a mixture of 0.06 mol of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, 0.06 mol of C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O (citric acid) and 150 mL of C<sub>2</sub>H<sub>5</sub>OH] and solution B [a mixture of Ce(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O with

a stoichiometric amount, 150 mL of C<sub>2</sub>H<sub>5</sub>OH and 150 mL distilled water] were prepared. Then solution B was added dropwise to solution A with stirring, until a stable sol was formed. The sol was then aged in air until form a gel, and then dried at 333 K for 12 hours. Finally, the powder was calcined at 873 K in air for 4 h.

Concentrations of five heterojunctions were prepared with Ce/Ti molar ratios of 1, 0.5, 0.25, 0.1, 0.05 and 0.01; these samples labeled as Ce1.0Ti-O, Ce0.5Ti-O, Ce0.25Ti-O, Ce0.1Ti-O, Ce0.05Ti-O and Ce0.01Ti-O, respectively. In order to compare properties, pure oxides were prepared with the same method for TiO<sub>2</sub> (using Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, citric acid, C<sub>2</sub>H<sub>5</sub>OH and distilled water) and CeO<sub>2</sub> (using Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, citric acid, and distilled water).

### 2.2. Characterization of samples

Thermal analysis of thermogravimetry-differential scanning calorimetry (TG-DSC) of the precursor was performed using a simultaneous thermal analyzer TA-SDTQ600, with a heating rate of 10 °C min<sup>-1</sup> in air up to 800 °C. The phases and crystallite sizes of the samples were examined over a 2θ range of 20–80° using a Bruker D8 ADVANCE diffractometer with a nickel-filtered Cu Kα (λ = 0.15418 nm) radiation source with a working voltage and current of 40 kV and 40 mA, respectively. The crystallite sizes were estimated using the Debye-Scherrer formula. The Brunauer-Emmett-Teller (BET) of the samples were determined by adsorption of nitrogen (N<sub>2</sub>) using a Micromeritics Tristar 3020. Transmission electron microscopy (TEM) and high-resolution TEM images were obtained using a JEOL 2100 with an energy dispersive spectrum (EDS) analysis module. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained with a spectrophotometer (Shimadzu, UV-2450). X-ray photoelectron spectroscopy (XPS) analysis was taken on an X-ray photoelectron spectrophotometer, ESCA (Thermo Fisher Scientific, an ESCALAB 250, Mono Al Kα source, 1486.6 eV). The room temperature photoluminescence (PL) spectroscopy measurements were performed by using an Edinburgh Instruments FLS980 fluorescence spectrophotometer with a 325 nm excitation.

### 2.3. Photocatalytic tests

The value of the photocatalytic efficiency was obtained by subtracting the degradation efficiency in the dark from that under light. A 0.1 g sample was dispersed into 500 mL of Methylene blue (MB) solutions. The initial concentration of the MB solution was 20 mg/L. The sample was stirred in dark for 30 min to achieve the adsorption-desorption equilibrium of MB. In one case, A Xenon lamp (500 W) was used as sunlight simulation and irradiated the samples. In the other one, degradation test was conducted without light. The suspension was extracted and centrifuged to separate the sample particles at different intervals. The concentration of MB solution was tested using a UV-vis spectrometer Shimadzu UV-3150.

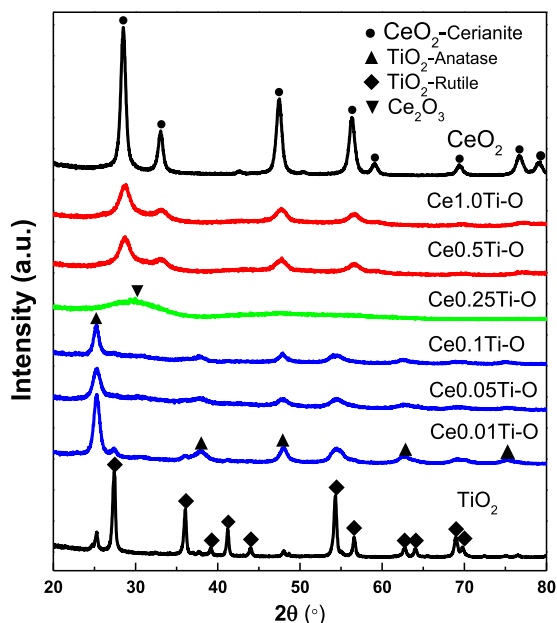


Fig. 1. XRD patterns of all samples.

**Table 1**  
Physiochemical properties of all samples.

Samples	Crystal phase	S <sub>BET</sub> (m <sup>2</sup> /g)	TiO <sub>2</sub> (Anatase)/TiO <sub>2</sub> (%)	Crystallite size		
				Anatase (nm)	Rutile (nm)	CeO <sub>2</sub> (Ce <sub>2</sub> O <sub>3</sub> )(nm)
CeO <sub>2</sub>	CeO <sub>2</sub>	69	n.d.	n.d. <sup>a</sup>	n.d.	11.4
Ce1.0Ti-O	CeO <sub>2</sub>	87	n.d.	n.d.	n.d.	6.8
Ce0.5Ti-O	CeO <sub>2</sub>	96	n.d.	n.d.	n.d.	5.6
Ce0.25Ti-O	Ce <sub>2</sub> O <sub>3</sub>	117	n.d.	n.d.	n.d.	1.7
Ce0.1Ti-O	Anatase-Rutile	96	95	10	5.5	n.d.
Ce0.05Ti-O	Anatase-Rutile	85	90	13.3	7.6	n.d.
Ce0.01Ti-O	Anatase-Rutile	71	88	17.5	11.1	n.d.
TiO <sub>2</sub>	Anatase-Rutile	64	17	20.7	26.1	n.d.

<sup>a</sup> Not detected.

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