

Characterization of CoTiO₃ Nanocrystallites Prepared by Homogeneous Precipitation MethodMing-Wei Li^{1,*}, Xiao-Mei Gao¹, Yin-Ling Hou¹, Cheng-Yang Wang²¹ School of Science, Tianjin University, Tianjin 300072, China² School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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Nanocrystalline cobalt titanate (CoTiO₃) has been synthesized from a well-mixed precursor. The precursor was prepared by a homogeneous precipitation method, in which urea was used as the precipitator. The as-synthesized sample is a mixture of CoTiO₃ and rutile nanocrystallites with mean sizes of around 50 nm. It strongly absorbs visible light in the wavelength range of 500-690 nm besides ultraviolet light (wavelength < 370 nm). We found the synthetic CoTiO₃ is a semiconducting material with a direct band gap of 2.53 eV. The green CoTiO₃ has two absorbance peaks at the wavelengths of 537 and 606 nm, which correspond to the photon energies of 2.31 and 2.05 eV, respectively.

Keywords: Cobalt titanate, Nanocrystalline materials, Microstructure, Optical property.

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1. INTRODUCTION

Titania (TiO₂) and metal titanates MTiO₃ (M = Fe, Co, Ni, Mn, Zn, et al) are semiconducting materials with unique properties. They have potential applications as photocatalysts [1-4], gas sensors [5-7], electronic components [8-10], and pigments [11, 12]. CoTiO₃ exhibits some excellent properties among them. CoTiO₃ is stable and can be applied in high-temperature environments [9, 13]. Moreover, the band gap of CoTiO₃ (~ 2.25 eV [14]) is narrower than that of TiO₂ (~ 3.3 eV for anatase-phase TiO₂). Therefore, CoTiO₃ possibly utilizes visible light with less photon energy. CoTiO₃ differs from the white TiO₂, it is green and has strong optical absorption in visible light region [3, 12, 15]. The colored semiconducting materials often indicate that they selectively absorb visible light. The absorbed photon energy can promote the electron transition and the formation of electron-hole pairs. This phenomenon has recently been reported when a red metallic oxide was used as a photocatalyst [16].

In this work, we synthesized CoTiO₃ with green color and studied its band gap, optical property, and photocatalytic activity. Actually, CoTiO₃ could be easily synthesized by solid-state reaction between Co₃O₄ and TiO₂ powders at high temperatures [10], but it is difficult to control its microstructure because the raw materials are in different phases. This process often leads to heterogeneous powders, and has worse reproducibility. To synthesize well-crystallized CoTiO₃ powders, most researchers firstly prepared precursors, and then heated them at high temperatures (> 500 °C). If Co²⁺ and Ti⁴⁺ ions in the precursors were well mixed, generally CoTiO₃ crystals are easily formed. Up to now, the precursors had been prepared by varied methods, which include chemical co-precipitation [3, 5, 11, 17], aerogel method [4], polyol method [6, 7], chemical vapor deposition [8], sol-gel method [18, 19], and Pechini method [15].

Herein, we used a homogeneous precipitation method to prepare the precursor, and heated it to synthesize

well-ordered CoTiO₃ nanocrystallites. The homogeneous precipitation method had ever been successfully used to prepare uniform nanoparticles [20]. The results reveal CoTiO₃ is a direct band gap semiconductor, which can strongly absorb visible light.

2. EXPERIMENTAL

7.5 mL hydrochloric acid solution of TiCl₄ (containing 0.02 mol of TiCl₄), 0.02 mol Co(NO₃)₂·6H₂O, and 18.18 g urea were dissolved in 600 mL deionized water under vigorous stirring. Urea was used as the precipitator to control the gradual formation of precipitate. The forming suspension was stirred for 6 h at refluxing temperature, and then was filtered. After the grey filter cake being washed with deionized water and anhydrous ethanol, it was dried in air overnight at 130 °C. After being grounded, the precursor was heated at 800 °C for 6 h and formed dark green product. A commercial P-25 sample purchased from Degussa Corporation was used as the reference sample, which consists of anatase (~ 80 %) and rutile (~ 20 %) nanoparticles.

Thermal behavior of the precursor was analyzed by thermogravimetric and differential scanning calorimetry (TG-DSC) using a NETZSCH STA 409 PC/PG simultaneous thermal analyzer from room temperature to 1100 °C in air.

The as-synthesized product was characterized by a Rigaku D/max 2500 V/PC powder X-ray diffractometer (XRD) using CuKα radiation (λ = 0.15406 nm). The mean sizes of the crystallites were calculated by Scherrer formula using 0.90 as the shape factor. We found the sample consists of CoTiO₃ and rutile. The weight fraction of CoTiO₃ (x_i) was estimated by the equation [21]: x_i = [1 + (I_r/I_i)(K_i/K_r)]⁻¹, where I_i and I_r are the intensities of main diffraction peaks of CoTiO₃ and rutile, respectively. K_i (= 2.81) and K_r (= 3.68) are their reference intensity ratios values, which are selected from JCPDS 77-1373 and 84-1284, respectively. The sample's microstructures were studied using an FEI Tecnai G² F20 field emission high resolution transmission

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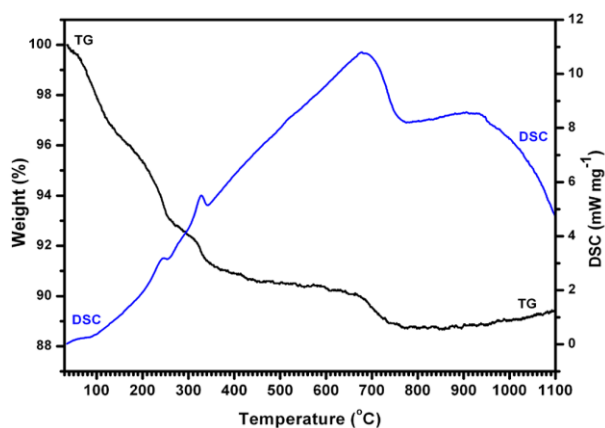


Fig. 1 – TG-DSC curves of the precursor

electron microscope (HRTEM). The ultraviolet-visible light diffuse reflectance spectra (UV-Vis DRS) were measured at room temperature with a JASCO V-570 UV-Vis spectrophotometer.

The photocatalytic activity of the samples was evaluated by using them degrading methylene blue in aqueous solution (100 mg L^{-1}) under the irradiation of a 300 W high pressure Hg lamp.

3. RESULTS AND DISCUSSION

Fig. 1 exhibits TG-DSC curves of the precursor. The sample totally lost about 11.1 % weight below 770 °C. The most weight loss, ~ 9.3 %, occurred below 430 °C, and probably resulted from the escape of surface water and crystal water. The exothermic process below 680 °C was mainly caused by the formation of anatase and CoO crystallites. Additionally, the growth of crystallites also is an exothermic process. About 1.3 % weight loss occurred between 680 and 770 °C with an endothermic process. It probably resulted from the escape of the residual crystal water, the transformation of anatase to rutile, and the formation of CoTiO_3 crystals.

Fig. 2 shows the XRD pattern of the as-synthesized sample. It is a mixture of CoTiO_3 and rutile with a weight ratio of 53 / 47 or a molar ratio of 37 / 63. No other phase, such as anatase, CoO or Co_3O_4 , was detected.

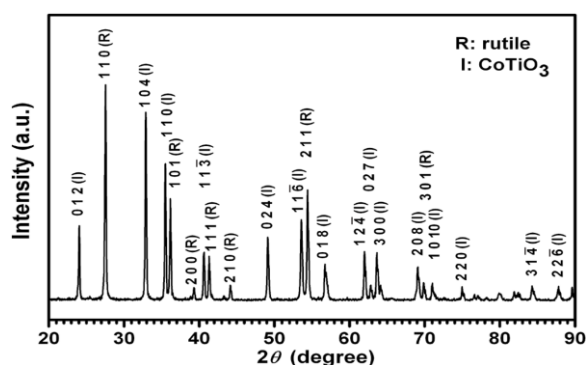


Fig. 2 – XRD pattern of the as-synthesized CoTiO_3 / rutile sample

The lattice parameters of CoTiO_3 are: R^- , 3 (148) $a = 5.0649$ (1) Å, $c = 13.9226$ (9) Å, $V = 309.31$ Å³, $Z = 6$, and $D_x = 4.9872$ g cm⁻³. The data are in good agreement with literature [19, 22].

The mean sizes of the CoTiO_3 and rutile crystallites are 49 and 51 nm, respectively. We think almost all Co^{2+} ions had been utilized to build the CoTiO_3 crystals, and the residual TiO_2 exists in rutile phase. Although the raw materials contain equimolar Ti^{4+} and Co^{2+} ions, the precursor could not keep it due to the different solubilities of Ti^{4+} - and Co^{2+} -containing precipitates and the loss of soluble $[\text{Co}(\text{NH}_3)_6]^{2+}$ during the washing process.

HRTEM images of the synthetic sample are shown in Fig. 3. Although the powders easily agglomerated as it is shown in Fig. 3a, an enlarged image (Fig. 3b) exhibits the microstructure of crystalline CoTiO_3 . The spacing 0.27 nm corresponds to the main lattice planes (104) of CoTiO_3 . The crystallite has a layered microstructure, which is clearer than a sample synthesized via sol-gel process [18].

Fig. 4 shows the samples' UV-Vis DRS. Commercial P-25 strongly absorbs ultraviolet light (wavelength < 320 nm), but hardly absorbs any visible light. It has an absorption threshold at 410 nm. However, the CoTiO_3 / rutile sample strongly absorbs visible light in

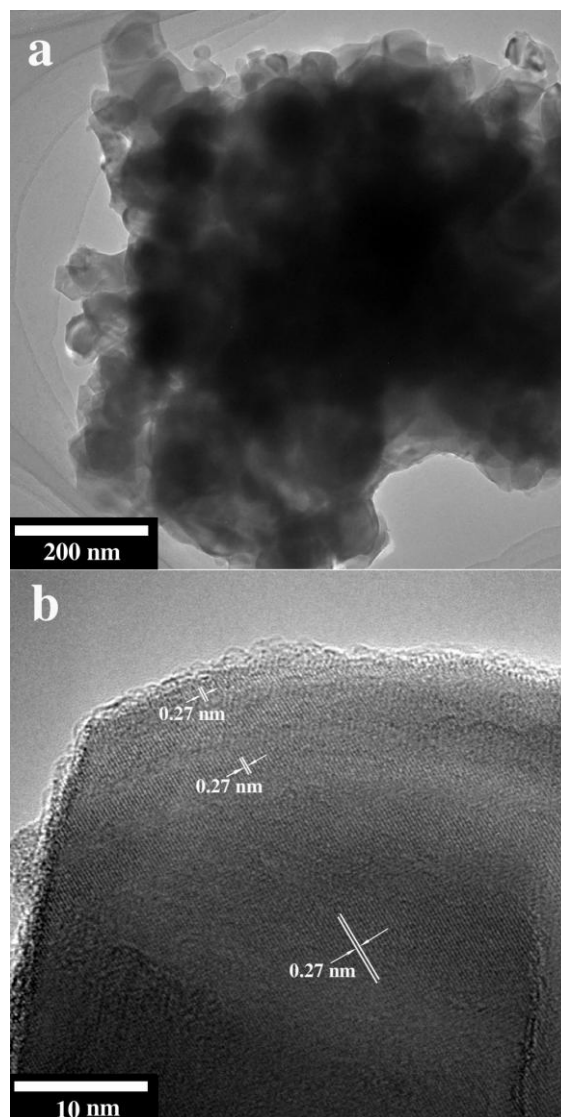


Fig. 3 – HRTEM images of the CoTiO_3 / rutile sample

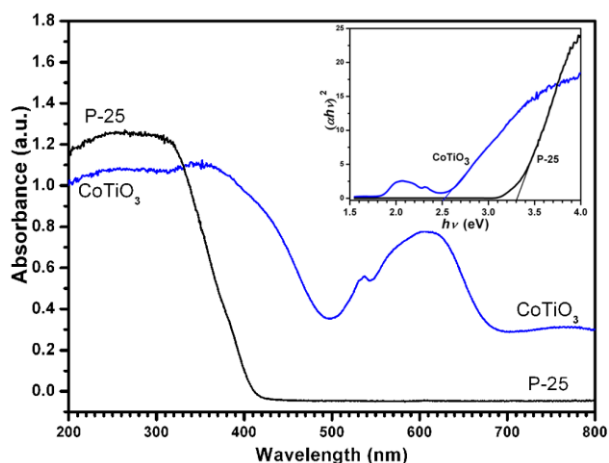


Fig. 4 – UV-Vis DRS of the as-synthesized CoTiO₃/utile sample and the P-25 sample. Tauc plots are shown in the inset

the wavelength range of 500-690 nm besides ultraviolet light (wavelength < 370 nm). Its optical absorption edge also shifts to 500 nm in visible light region. We propose the absorbance in visible light region is mainly caused by CoTiO₃ because TiO₂ hardly absorb visible light. The samples' band gaps can be estimated by Tauc plots, i.e., the curves of $(\alpha h\nu)^{2/n}$ vs $h\nu$, where α and $h\nu$ are the absorbance and photon energy, respectively [2, 23, 24]. The n value indicates the optical transition is direct ($n = 1$) or indirect ($n = 4$). The $h\nu$ value at the intersection point of the tangent and the horizontal axis is the band gap. As shown in the inset, the band gap of P-25 is about 3.32 eV, which coincides with the band gap of anatase and reflects the O²⁻ → Ti⁴⁺ charge-transfer transition. The synthetic CoTiO₃ has a band gap of 2.53 eV, which originates from the Co²⁺ → Ti⁴⁺ charge-transfer transition. Both the samples are direct band gap semiconductors because $n = 1$.

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We found the UV-Vis DRS of CoTiO₃ well coincides with literature [3, 4, 11]: There exist a small absorbance peak at 537 nm and a big one at 606 nm, which correspond to the photon energies of 2.31 and 2.05 eV, respectively. The selective optical absorbance in visible light region makes CoTiO₃ being green color. The two absorbance peaks should be defined by the crystal structure of CoTiO₃, which is an ilmenite structure being constructed by octahedral CoO₆ and TiO₆. The detailed mechanism needs further investigation.

The samples' photocatalytic activities were evaluated. Experimentally, almost all methylene blue degraded in 20 min when P-25 was used as a photocatalyst. However, the CoTiO₃/rutile sample does not show obvious photocatalytic activity. Only less than 2 % methylene blue degraded. This result is agreement with previous reports [4, 25]. Possibly, the low quantum efficiency and the poor oscillator strength for the Co²⁺ → Ti⁴⁺ charge-transfer transition weakened the performance of CoTiO₃ as a photocatalyst.

4. CONCLUSIONS

The homogeneous precipitation method can be used to synthesize CoTiO₃ nanocrystallites. The synthetic CoTiO₃ is a semiconducting material with a narrower direct band gap of 2.53 eV. The sample is dark green and strongly absorbs visible light in the wavelength range of 500-690 nm. It also has two optical absorbance peaks at 537 and 606 nm. However, the sample does not exhibit obvious photocatalytic activity.

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