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# Photocatalytic behavior and photo-corrosion of visible-light-active silver carbonate/titanium dioxide



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## ABSTRACT

Anatase TiO<sub>2</sub> containing a large amount of single-electron-trapped oxygen vacancy (denoted as TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>); V<sub>o</sub><sup>•</sup> refers to single-electron-trapped oxygen vacancies which are abridged as SETOVs) was combined with Ag<sub>2</sub>CO<sub>3</sub> to prepare Ag<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) by the precipitation method. Ag Auger MNN spectra displayed that photo-corrosion of Ag<sub>2</sub>CO<sub>3</sub> happened during photocatalytic process generating nascent metallic Ag. The photo-corrosion is originally not conducive to the photocatalysts. However, the nascent metallic Ag generated on the surface of TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) and SETOVs in TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) matrix jointly function to compensate for the gradually reduced visible light photocatalytic activity of Ag<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) owing to photo-corrosion of Ag<sub>2</sub>CO<sub>3</sub>. It is just the synergistic effect between the oxygen vacancies and nascent metallic Ag that accounts for the high and stable photocatalytic activity of Ag<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) towards the oxidation of propylene under visible light irradiation.

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## 1. Introduction

Silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>) is unsuitable for photocatalyst, because it is liable to photo-corrosion that can seriously deactivate photocatalytic performance. Surprisingly, several recent publications state that Ag<sub>2</sub>CO<sub>3</sub> possesses visible light photocatalytic behavior [1–3]. For example, Xu et al. reported in 2011 that Ag<sub>2</sub>CO<sub>3</sub> prepared by a precipitation method displays a high activity towards degradation of phenol and methylene blue under visible light irradiation [1]. Since 1 year, Dai et al. prepared Ag<sub>2</sub>CO<sub>3</sub> by a simple precipitation reaction between NaHCO<sub>3</sub> and AgNO<sub>3</sub>, aiming to reveal the photo-corrosion mechanism of Ag-based photocatalysts [2]. Based on the plane-wave-based density functional theory, Dong et al. theoretically calculated the band gap of Ag<sub>2</sub>CO<sub>3</sub> photocatalyst and proposed that Ag<sub>2</sub>CO<sub>3</sub> photocatalyst belongs to indirect band gap semiconductor [3]. Besides, other Ag-containing photocatalysts such as Ag@AgCl [4], Ag@AgBr [5], Ag<sub>2</sub>SO<sub>3</sub> [6], Ag<sub>3</sub>PO<sub>4</sub> [7,8], silver vanadates [9], and AgMO<sub>2</sub> (M=Al, Ga, and In) [10,11] might be promising high-efficient photocatalysts. These Ag-based photocatalysts, however, usually experience photo-corrosion under visible light irradiation, which causes damage to their photocatalytic activity [1,2]. Thus, it is imperative to develop novel visible-light-active

Ag<sub>2</sub>CO<sub>3</sub>-based photocatalysts with excellent stability and high visible light photocatalytic activity.

Nanotubular titanic acid (denoted as NTA) can be well adopted as the precursor to fabricate highly visible-light-active photocatalysts [12–18]. It was proposed that the generation of SETOVs accounts for the apparent visible light absorption rather than visible light photocatalytic activity of as-obtained anatase TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) matrix [12,13]. However, anatase TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) doped with N shows visible light photocatalytic activity towards air pollutant, which is ascribed to the synergistic effect between SETOVs and doped-N [15].

Bearing those perspectives in mind and viewing the important role of SETOVs in inducing visible light photocatalytic activity, in this paper Ag<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) was prepared using NTA as medium via a facile precipitation method. We aim in this paper to increase the stability of Ag<sub>2</sub>CO<sub>3</sub> as a photocatalyst and improve the visible light photocatalytic activity of TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) by making use of possible synergistic effect between Ag<sub>2</sub>CO<sub>3</sub> and anatase TiO<sub>2</sub>(V<sub>o</sub><sup>•</sup>) matrix.

## 2. Experimental section

Ag<sub>2</sub>CO<sub>3</sub> was synthesized at room temperature with the aqueous solutions of AgNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> as the starting materials. 15 mL of AgNO<sub>3</sub> (0.1 M) was added into 5 mL of Na<sub>2</sub>CO<sub>3</sub> (0.1 M) under 20 min of magnetic stirring giving yellow precipitate filtered, washed with distilled water and dried at 60 °C in an oven.

NTA was prepared according to the method reported elsewhere [12]. 1 g of as-prepared NTA was heated at 600 °C in a tubular furnace for 2 h to yield anatase TiO<sub>2</sub> (V<sub>o</sub><sup>•</sup>). Then 0.5 g of resultant

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$\text{TiO}_2(\text{V}_o^\cdot)$  was dispersed in 10 mL of distilled water and mixed with 5 mL of  $\text{Na}_2\text{CO}_3$  solution to afford a mixed suspension. Subsequently, 15 mL of  $\text{AgNO}_3$  (0.1 M) solution was dripped into the mixed suspension under magnetic stirring to yield precipitate. As-obtained precipitate was filtered, washed with distilled water, and dried at 60 °C in an oven to provide desired  $\text{Ag}_2\text{CO}_3/\text{TiO}_2(\text{V}_o^\cdot)$ . Commercial P25- $\text{TiO}_2$  was used for a comparative study.

TEM (JEM-2010) was performed to analyze the microstructures of catalysts. XRD patterns were measured with a DX-2500 diffractometer. UV-vis DRS was recorded with a Shimadzu U-4100 spectrometer. ESR spectra were obtained with a Bruker ESP 300E apparatus at a field modulation of 100 kHz, an amplitude modulation of 0.2 mT and a microwave power of 10 mW (the measurement was conducted at room temperature in ambient air, without vacuum-pumping). The  $g$ -tensors of the ESR signals were obtained by setting  $g$  of diphenyl picryl hydrazyl (DPPH; 2.0036) as the reference. XPS was performed with a Kratos Amicus apparatus (excitation source: monochromatized  $\text{Mg } K\alpha$  ( $h\nu = 1253.6$  eV) radiation). The binding energies were calibrated with reference to the adventitious C 1s line at 284.8 eV.

The photocatalytic activity of  $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_2\text{CO}_3/\text{TiO}_2(\text{V}_o^\cdot)$  samples were evaluated by monitoring the oxidation of propylene under visible light irradiation. Briefly, 25 mg aliquot of each sample was spread on one side of a roughened glass plate (ca. 8 cm<sup>2</sup>) located in a home-made glass tube reactor equipped with a 500 W xenon lamp as the visible light source. Between the

xenon lamp and reactor was inserted an ultraviolet (UV) cut 420 filter to eliminate UV light. The reactor was surrounded by a water channel so as to eliminate infrared light and keep a constant reaction temperature at room temperature. The intensity of the light with  $\geq 420$  nm irradiated on to-be-tested samples is ca. 9 mW/cm<sup>2</sup>; and the flow rate of the feed gas (pure  $\text{C}_3\text{H}_6$  and dry air stored in a high-pressure cylinder;  $\text{C}_3\text{H}_6$  concentration: about 500 ppmV) is 200 mL/h. Prior to irradiation, the feed gas was allowed to flow through the reactor continuously until the adsorption/desorption equilibrium was established. The on-line concentration of  $\text{C}_3\text{H}_6$ ,  $C$ , was determined by a chromatograph (GC7900) equipped with a flame ionization detector (FID), a GDX-502 column, and a reactor loaded with Ni catalyst for the methanization of  $\text{CO}_2$ . The removal rate of  $\text{C}_3\text{H}_6$  is calculated as  $(C_0 - C)/C_0 \times 100\%$ , where  $C_0$  refers to the initial  $\text{C}_3\text{H}_6$  concentration (500 ppmV).

### 3. Results and discussion

Fig. 1(a–c) shows the TEM morphologies of NTA,  $\text{TiO}_2(\text{V}_o^\cdot)$ , and  $\text{Ag}_2\text{CO}_3/\text{TiO}_2(\text{V}_o^\cdot)$  samples, respectively. NTA have open-ended nanotubular morphology with a length of several tens of nanometers. After NTA were thermally treated at 600 °C for 2 h, the resultant samples  $\text{TiO}_2(\text{V}_o^\cdot)$  do not remain the nanotubular morphology but were destroyed into nanorods with a diameter of

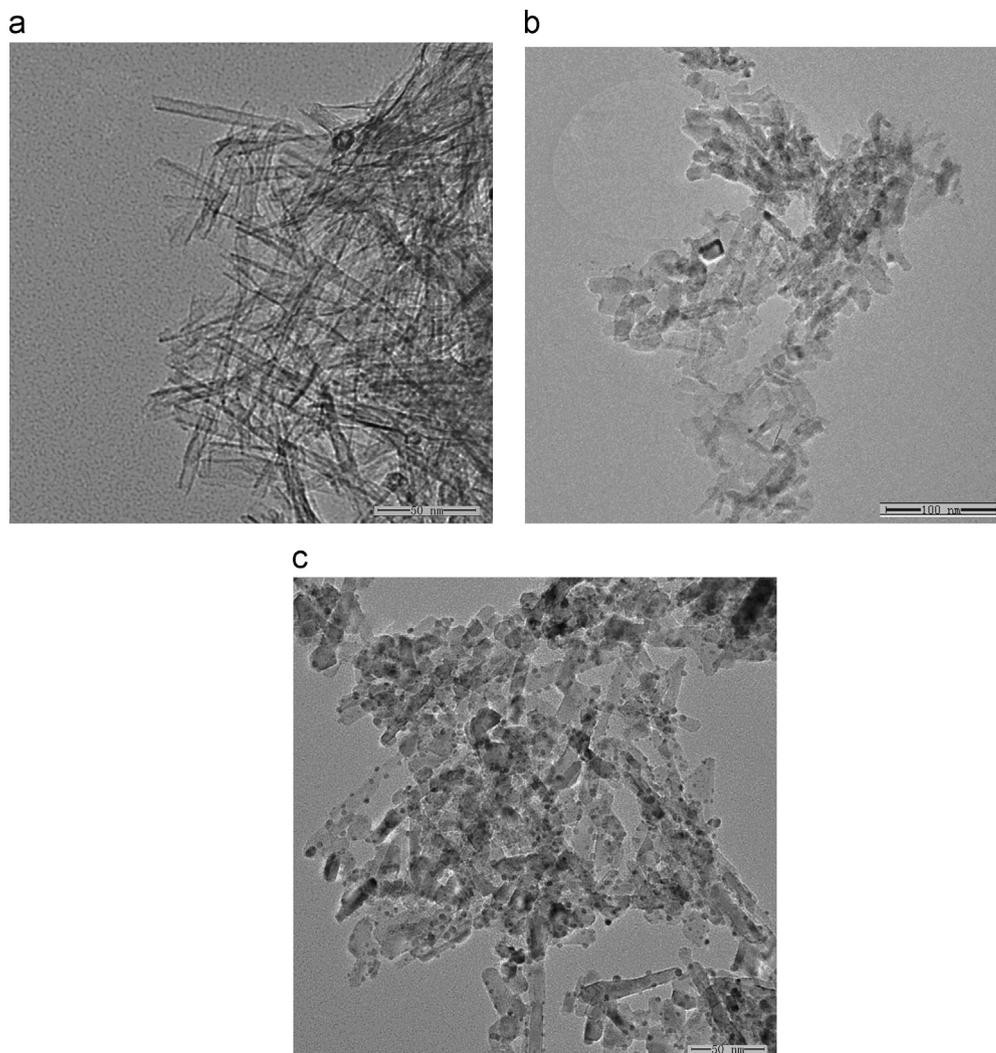


Fig. 1. TEM morphology of (a) NTA, (b)  $\text{TiO}_2(\text{V}_o^\cdot)$ , and (c)  $\text{Ag}_2\text{CO}_3/\text{TiO}_2(\text{V}_o^\cdot)$ .

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