

# Photocatalytic reduction of CO<sub>2</sub> on MgO/TiO<sub>2</sub> nanotube films



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## ABSTRACT

A facile development of highly efficient MgO/TiO<sub>2</sub> nanotubes network (MgO/TNTs) films is described. These MgO/TNTs films have a unique one-dimensional (1D) network nanotubular structure, and the different contents of MgO existed as amorphous thin layers located on the surfaces of TiO<sub>2</sub> nanotubes. They exhibited excellent photoreduction efficiency of CO<sub>2</sub> to methane compared with the bare TiO<sub>2</sub> film. MgO plays a critical role in CO<sub>2</sub> methanation, because it has the strong adsorption ability of CO<sub>2</sub> and initiates the reaction by binding a CO<sub>2</sub> molecule, forming a magnesium carbonate species on the surface. For further improve the photocatalytic activity, Pt nanoparticles were loaded on MgO/TNTs films by the photo-reduction method. It was found that the loading of Pt notably improved the transformation efficiency of CO<sub>2</sub> to methane, and the highest evolution rate of methane reached 100.22 ppm/h cm<sup>2</sup>. The fast electron-transfer rate in MgO/TNTs film and the efficient electron-hole separation by the Pt nanoparticles were the main reasons for the enhancement of the photoreduction activity. The synergy effect of Pt nanoparticles and MgO in the nanocomposites played an important role in CO<sub>2</sub> photoreduction.

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## 1. Introduction

The increasing of CO<sub>2</sub> emission and shortage of the fossil resource has already simultaneously stimulated scientists to research the utilization of CO<sub>2</sub> [1]. Currently, conversion of CO<sub>2</sub> into useful materials, mainly CH<sub>4</sub> or other inorganic and organic substances such as CO, HCOOH, HCHO, CH<sub>3</sub>OH, is of importance for the development of alternative fuel sources or various industry raw materials. On the other hand, this conversion also assists in preventing global warming resulting from the green house effect [2]. Therefore, the potential utilization of CO<sub>2</sub> as an abundant and inexpensive chemical feedstock has been attracted widespread attention [3]. However, it is well known that CO<sub>2</sub> is a very stable and inert compound, which cannot be easily reduced under mild conditions. Typically, a large energy input or co-feeding of a high-energy reactant such as H<sub>2</sub> is required for the activation and conversion of CO<sub>2</sub>.

Recently, photocatalysis is well-considered to be a potential solution to the worldwide energy shortage and environmental pollution, such as CO<sub>2</sub> photoreduction into hydrocarbon fuels, photocatalytic water splitting into H<sub>2</sub>, and photodegradation of organic

pollutants [4–7]. In particular, from the viewpoint of natural green plant photosynthesis, there are many reports about the photocatalytic reduction of CO<sub>2</sub> in the presence of H<sub>2</sub>O as a reductant over various semiconductors. Inoue et al. reported a pioneering study on the reduction of CO<sub>2</sub> in aqueous suspensions containing semiconductor powders [8]. Since then semiconductor-based photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O has made great progress in recent years [9–14]. Moreover, TiO<sub>2</sub>-based nanomaterials are one of the most intensively studied and widely used [15–17]. Especially the titanate network films, obtained by the hydrothermal method often have large BET surface area, and strong adsorption ability [18]. It is noticeable that the surface porous network structure of the film can enhance the adsorption of the reactive species and utilization of the incident light, and thereby increasing the photocatalytic activity [19–22].

One of the most important topics for CO<sub>2</sub> photoreduction is to improve the conversion efficiency to hydrocarbon fuels. Recently, Kohno et al. reported that MgO was prone to adsorbing CO<sub>2</sub> and enhanced the conversion efficiency of CO<sub>2</sub> [23,24]. Generally speaking, enhanced adsorption of CO<sub>2</sub> on the basic sites may promote its subsequent photocatalytic reduction. Moreover, the chemisorbed CO<sub>2</sub> molecules on MgO layer become destabilized and its reactivity is believed to be higher than that of the linear CO<sub>2</sub> molecules [25]. Liu et al. prepared mesoporous carbon stabilized MgO nanoparticles, and they also demonstrated MgO has better strong ability to capture CO<sub>2</sub> [26].

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Based on the advantage of the titanate nanotubes films and the strong adsorption of  $\text{CO}_2$  on MgO, a series of MgO/TiO<sub>2</sub> network nanocomposite films were prepared by dip-calcination method for photo-reduction  $\text{CO}_2$ . This work provides a novel strategy for the design of efficient porous film for the reduction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$ . In order to improve the reduction efficiency of  $\text{CO}_2$  further, Pt nanoparticles were deposited on MgO/TiO<sub>2</sub> porous network film, and as a result, the photoreduction yield of  $\text{CO}_2$  to  $\text{CH}_4$  improved a lot. The relationship between the morphology, structure, and their photocatalytic activity was investigated in detail.

## 2. Experimental

### 2.1. The preparation of MgO/TiO<sub>2</sub> network nanotube film

Ti foil with a size of 2 cm × 4 cm was put into an autoclave containing a concentrated 10 M NaOH aqueous solution, and then reacted at 120 °C for 24 h. After cooling down, the obtained sodium titanate nanotube films were washed with distilled water several times, and then immersed in a 0.1 M HCl aqueous solution for 12 h to obtain the titanate acid nanotubes film (TAN). After that, the TAN film was immersed in 30 mL of 0.001 M, 0.005 M, 0.01 M, 0.05 M, or 0.1 M  $\text{Mg}(\text{NO}_3)_2$  aqueous solution for 6 h, respectively. Finally, the immersed TAN film was calcined at 500 °C in air for 4 h to get MgO/TiO<sub>2</sub> porous network nanotube films, and the sample was denoted as 0.001-MgO/TNTs, 0.005-MgO/TNTs, 0.01-MgO/TNTs, 0.05-MgO/TNTs, and 0.1-MgO/TNTs, correspondingly. As a reference, the bare TiO<sub>2</sub> nanotube film was prepared by calcining the as-prepared TAN at 500 °C in air for 4 h directly. Pt was loaded on MgO/TiO<sub>2</sub> films by the in situ photo-deposition method. Briefly, the film was immersed in an aqueous solution of hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) ethanol solution, and irradiated with a mercury lamp for 1 h.

### 2.2. Characterization of samples

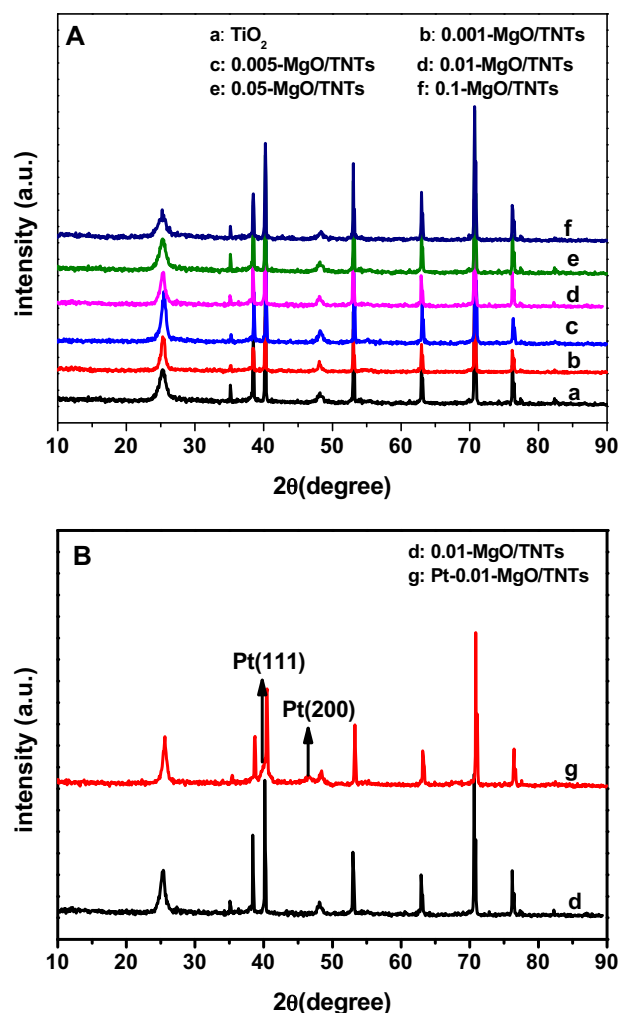
X-ray diffraction (XRD) patterns were measured on an X'Pert Philips diffractometer (Cu K $\alpha$  radiation;  $2\theta$  range 5–90°, step size 0.08°, accelerating voltage 40 kV, applied current 40 mA). Transmission electron microscopic (TEM) images were taken on a JEM-2010 electron microscope. X-ray photoelectron spectra (XPS) were recorded with a Kratos AXIS ultraspectrometer using monochromatized Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation as the excitation source (power 150 W, 15 kV and 10 mA). The C1s of hydrocarbon at 284.8 eV was used as the standard for the correction of charging shift. The atomic percentage of Mg, Ti, and O of different MgO/TNTs films was measured by energy dispersive spectrometer (EDS) technique.

### 2.3. Photocatalytic activity evaluation

The photocatalytic reduction of  $\text{CO}_2$  was conducted in a flat closed reactor with the inner capacity of 358 mL containing 20 mL 0.1 mol/L  $\text{KHCO}_3$  solution. The prepared MgO/TiO<sub>2</sub> porous network film was located in the center of the reactor, and then the ultra-pure gaseous  $\text{CO}_2$  and water vapor was flowed through the reactor for 2 h to achieve the adsorption–desorption equilibrium. The light source was the high pressure Hg lamp with 300 W. The photocatalytic reaction was typically performed at room temperature for 6 h. The products were analyzed by a gas-chromatography (GC).

## 3. Results and discussion

The phase structure of the nanotube films was analyzed by the XRD technique. As shown in Fig. 1a, the TiO<sub>2</sub> nanotubes film belongs



**Fig. 1.** XRD patterns of the photocatalysts, (a) TiO<sub>2</sub>, (b) 0.001-MgO/TNTs, (c) 0.005-MgO/TNTs, (d) 0.01-MgO/TNTs, (e) 0.05-MgO/TNTs, (f) 0.1-MgO/TNTs and (g) Pt-0.01-MgO/TNTs.

to a characteristic anatase phase, indicating that the orthorhombic titanate acid nanotubes have transformed to TiO<sub>2</sub> nanotubes completely, which is consistent with our previous work [27]. There still exist some characteristic peaks of metallic Ti at 38.5°, 40.2°, 63.1°, 70.7°, indicating that only the surface of the metallic Ti foil reacted with NaOH, and the interior still remained as Ti metal. After calcination of TAN immersed in a series of  $\text{Mg}(\text{NO}_3)_2$  aqueous solution and calcined at 500 °C for 4 h,  $\text{Mg}(\text{NO}_3)_2$  and TAN transformed to amorphous MgO and anatase TiO<sub>2</sub> respectively. Although all samples did not appear new peaks, it is obvious that the width of the (101) plane diffraction peak of anatase ( $2\theta = 25.5^\circ$ ) became narrower firstly, and then gradually broader with the increase of concentration of  $\text{Mg}(\text{NO}_3)_2$ . These facts suggested that the crystalline size of the TiO<sub>2</sub> nanotubes increased when being covered with the little content of MgO. Namely, the MgO/TNTs nanotubular structure was more perfect than pure TiO<sub>2</sub> owing to the presence of the covered MgO thin layer. When the concentration of  $\text{Mg}(\text{NO}_3)_2$  is relatively high, broader phenomenon could be ascribed to the high content of MgO formed a large number of particles on the surface of the TiO<sub>2</sub> nanotubes. The characteristic peak of 39.8°, and 46.2° in Fig. 1b is ascribed to the (111) and (200) plane of the metallic Pt, respectively [28]. That confirms the successful formation of metallic Pt nanoparticles on the surface of MgO/TNTs film, which are consistent with the results from TEM analysis (see Fig. 2e).

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