



# Synergistic photocatalytic oxidation and adsorption of elemental mercury by carbon modified titanium dioxide nanotubes under visible light LED irradiation

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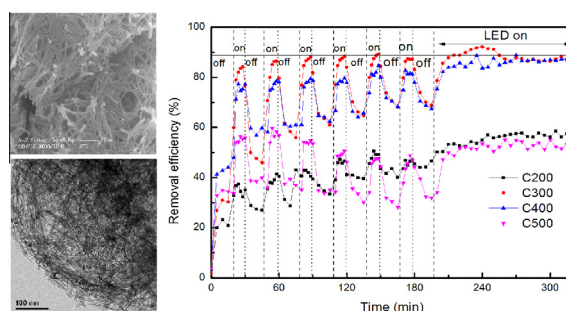
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## HIGHLIGHTS

- Carbon modified titanium dioxide nanotubes were synthesized via a hydrothermal method.
- The prepared catalysts showed a good removal efficiency of elemental mercury under the irradiation of visible-light LED.
- The activity promotion was attributed to the improved nano-structure and the expanded light adsorption.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, carbon modified titanium dioxide nanotubes (hereafter denoted as CTNTs) were synthesized via a hydrothermal method, followed by ethanol washing and then heat-treatment steps. The physicochemical properties of CTNTs were investigated by XRD, BET, HR-TEM, TG-FTIR and UV-Vis spectra. The resultant CTNTs were then utilized for the removal of elemental mercury ( $\text{Hg}^0$ ) under the irradiation of visible light LED. Experimental results revealed that the CTNTs had a good adsorption capability and photocatalytic oxidation ability for the removal of  $\text{Hg}^0$ , particularly for the catalyst that was calcinated at 300 °C. We proposed that the activity promotion for the CTNTs was mainly attributed to three aspects: the abundant adsorption sites for  $\text{Hg}^0$ , the well sustained nanotubes structure and the expanded light adsorption spectrum of CTNTs. Furthermore, the roles of influence factors such as empty bed retention time,  $\text{O}_2$  concentration,  $\text{SO}_2$  concentration and NO concentration, were investigated. The experimental results verified that white light LED lamp was a suitable light source for the application of photocatalytic oxidation process.

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## 1. Introduction

Mercury is one of the most hazardous air pollutants and has been listed on Title III of the 1990 Clean Air Act Amendments (CAAA) in the United States [1]. It poses a great threat to human

health and organism safety because of its volatility, persistence, neurological toxicity, and bioaccumulation [2–5]. Due to three gas-phase forms of mercury, i.e. elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ) and particle-bound mercury ( $\text{Hg}^p$ ), the  $\text{Hg}^0$  is most difficult to removal because it is neither soluble in water nor easily adsorbed and has a lifetime of 1–2 years in the atmosphere [6,7].

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Nowadays, the rapid growth of fluorescent lamps (FLs) and compact fluorescent lamps (CFLs) industry generated a new kind of anthropogenic  $\text{Hg}^0$  emission resource in China [8]. As a global manufacturing base, China is the largest CFL manufacturer in the world and the production of CFLs increased by 30-fold from 1996 to 2007 [8]. Actually, China produced a total of 3.65 billion CFLs (80% of the world's CFL production in 2009) [8,9]. There was over 300 manufacturers in China, mainly concentrated in Zhejiang, Fujian, Guangdong, Jiangsu and Shanghai [9]. For the FLs, one lamp contained 0.7–115 mg of Hg, whilst for the CFLs, one lamp contained 3–5 mg of mercury [10]. In FLs or CFLs plants, mercury emissions may happen in many situations, such as purification and transfer of mercury, injection operation and the broken lamps. The released  $\text{Hg}^0$  contaminated the working areas, and posed health risk to the workers.

In the past decade, various methods were developed for the removal of mercury in gas-phase, such as oxidant injection, catalytic oxidation, and photocatalytic oxidation [11–13]. Due to the usage of in-door circumstances, photocatalytic oxidation method may be the suitable  $\text{Hg}^0$  removal method in the production department of FLs or CFLs plants.

Wu et al. [14] and Lee et al. [15] had firstly utilized the photocatalytic oxidation method for  $\text{Hg}^0$  removal based on  $\text{TiO}_2$  nanoaerosols and reached extremely high efficiency of  $\text{Hg}^0$ . With the aim to decline the operation cost, they designed a UV light-on and light-off cycle mode based on the synergistic effect of photocatalytic oxidation & adsorption. In the literatures, a lot of photocatalysts, such as  $\text{TiO}_2$  doped on silica gel,  $\text{SiO}_2$ - $\text{TiO}_2$  nano-composites and  $\text{SiO}_2/\text{V}_2\text{O}_5/\text{TiO}_2$ , have been synthesized and demonstrated greater than 90%  $\text{Hg}^0$  removal efficiency under the intermittent UV irradiation in room conditions [16–19]. We also synthesized  $\text{TiO}_2$  nanotubes (TNTs) photocatalyst, which revealed excellent removal efficiency for  $\text{Hg}^0$  and showed the synergistic photocatalytic oxidation and adsorption capability [20]. However, a big drawback still remains for these synthesized photocatalysts, due to the usage of UV light. Use of UV light may led many problems in the operation of system: (1) need high voltage at initial stage; (2) power instability during long time operation; (3) low photonic efficiency; (4) less life time; and so on [21].

Recently, many studies were focused on the photocatalytic degradation of contaminants using UV-LED or Visible-light LED [22–24]. Compared with traditional light sources, LED light offers numerous advantages: (1) high energy conversion and robustness; (2) long life time; (3) low heat production; (4) suitability for operation in a pulsed regime at high frequencies [22–24]. Furthermore, non-metal doping of  $\text{TiO}_2$ , such as C and N, has displayed promising results in shifting the light absorption of  $\text{TiO}_2$  into visible light region [25–27]. To the visible light photocatalytic activity, C-doped  $\text{TiO}_2$  was proved to be more active than N-doped  $\text{TiO}_2$  [25].

With this in mind, in this paper, we synthesized carbon modified titanium dioxide nanotubes (denoted as CTNTs) via a hydrothermal method, followed by ethanol washing and then heat-treatment steps. The prepared carbon doped titanium dioxide nanotubes were tested in simulated gas flow under the irradiation of visible light LED to evaluate their photocatalytic performances in  $\text{Hg}^0$  oxidation and adsorption. The relationship between their physicochemical properties and activity performances were also studied.

## 2. Experimental section

### 2.1. Preparation of samples

The hydrogenated titanates (H-TNTs) were synthesized by a hydrothermal method that was developed by Kasuga et al. [28].

In a typical synthesis, 2.0 g  $\text{TiO}_2$  powder (P25, Evonik-Degussa Co. Ltd, Germany) was mixed with 70 ml of 10 M NaOH aqueous solution by magnetic force. Then the solution was moved into a 100 ml polyflon (PTFE) autoclave at 150 °C for 24 h. After that, the slurry was filtered and washed with 0.1 M HCl solution until the pH value of the rinsing solution reached 2.0. Thereafter, the precipitates were washed with distilled water until the pH value of the rinsing solution reached 6.5. Finally, the precipitates were mixed with ethanol for 2 h to make the ethanol adsorb in the H-TNTs and then washed with ethanol for three times. The ethanol-washed samples were dried at 80 °C for 12 h (designated as C0), and further calcined at five different temperatures (i.e. 200, 300, 400, 500 °C) for 1 h in air to get four types of TNTs (designated as CX, X represents the calcination temperature).

### 2.2. Characterization of catalysts

The crystal phases of the sample were analyzed by a Rigaku X-ray diffractometer (D/Max RA) at 40 kV and 150 mA (Cu  $K\alpha = 1.542 \text{ \AA}$ ), at an angle of  $2\theta$  from 10° to 80°. The scan speed was 1°/min. The morphology, structure and crystal size of the samples were examined by scanning electron microscopic analysis (Sirion200, USA) and transmission electron microscopy (JEM-2010, Japan). Carbon and hydrogen elemental analysis was performed in a CE instrument Model Flash EA 1112 (ThermoFingnigan Italia). The specific surface area of the samples was determined by Brunauer-Emmett-Teller (BET) method (ASAP 2020, USA). TG-FTIR was performed on a thermogravimetric analyzer (TGA) coupled with a FTIR spectrometer and used to determine the carbon species and contents in the samples. The pyrolysis of samples was carried out in a TGA (SDTA851e, Mettler-Toledo International Inc., Switzerland). Sample weight was maintained at about 15 mg to mitigate differences in heat and mass transfer. The sample was heated from 30 to 800 °C at a rate of 50 °C/min. Purified nitrogen at a flow rate of 60 ml/min was used as the carrier gas to provide an inert atmosphere for pyrolysis, and to remove the gaseous and condensable products. The gases released in the TGA were swept immediately to a gas cell, followed by FTIR (Nicolet Nexus 670 FTIR) analysis. The spectrum was located in the range of 400–4000  $\text{cm}^{-1}$  and a resolution factor of 4  $\text{cm}^{-1}$  was selected. The diffuse reflection spectra were measured with an integrating sphere equipped UV-visible recording spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., China) using  $\text{BaSO}_4$  as a reference, and the optical absorptions were converted from the reflection spectra according to the Kubelka-Munk equation.

### 2.3. Experimental studies

The photocatalytic oxidation and adsorption of  $\text{Hg}^0$  was carried out in a fixed-bed photocatalytic reactor [20]. Simulated gas flow consisted of three gas streams, whereas pure  $\text{N}_2$  was divided into two streams as the carrier gas and dilution gas, with the third gas stream being  $\text{O}_2$ . The carrier gas stream passed through the surface of a liquid  $\text{Hg}^0$  reservoir and introduced  $\text{Hg}^0$ -vapor-laden air into the system. The  $\text{Hg}^0$  reservoir was placed in an oil bath (70 °C) to maintain a constant  $\text{Hg}^0$  vapor pressure. The reactor was a flat-plate photocatalytic reactor, including a rectangle quartz cell (320 × 70 × 10 mm). Visible-light LED lamp (14.4 W, 0.24 W per lamp, White light LED) set on the top of reactor (5 cm), as shown in Fig. 1. The catalysts were loaded on the rectangle glass plates (7 × 2 cm) by using a dip-coating method. In all experiments, the weight of catalyst coated was kept to be 0.5 g ± 10%. In a typical condition, the simulated gas flow passed through the reactor at a flow rate of 1.0 L/min with an empty bed retention

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