



Full Length Article

Photocatalytic removal of elemental mercury from flue gas using multi-walled carbon nanotubes impregnated with titanium dioxide



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ARTICLE INFO

Keywords:

MWCNTs/TiO₂
Photocatalytic
Elemental mercury removal
Mercury species

ABSTRACT

The photocatalytic Hg⁰ (gaseous elemental mercury) removal performance of the multi-walled carbon nanotubes (MWCNTs) impregnated with titanium dioxide (MWCNTs/TiO₂) was experimentally investigated in a fixed-bed reactor with the simulated flue gas. Transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–Vis diffuse reflectance spectra (DRS) were used to characterize the prepared photocatalysts. The addition of MWCNTs inhibited the grain growth of TiO₂ and improved the pore property of the photocatalyst. Besides, the presence of MWCNTs also significantly influenced the morphology of TiO₂, and enhanced its photochemical and optical properties. The effects of the MWCNTs and the individual flue gas components, including SO₂, NO, O₂ and H₂O, on Hg⁰ removal were also investigated. The results indicated that compared to the pure TiO₂, the MWCNTs/TiO₂ exhibited a higher photocatalytic removal ability for Hg⁰ that mainly due to the higher surface area, the better properties of electrons transportation, and the abundant active species such as the surface chemisorbed oxygen (O*) and C=O bond. The removal efficiency of Hg⁰ was found to be significantly affected by the flue gas components. Oxygen promoted Hg⁰ removal by replenishing surface chemisorbed oxygen (O*) and assisting in electron-hole pair separation. Water vapor inhibited photocatalytic performance due to the competitive adsorption. SO₂ and NO were found to play an inhibitory role in the photocatalytic Hg⁰ removal reaction since SO₂ and NO scavenged hydroxyl radicals (·OH), which were produced by ultraviolet (UV) irradiation. In addition, mercury species remained on the MWCNTs/TiO₂ surface were also determined by XPS analysis to understand the further reaction mechanism.

1. Introduction

Mercury is one of the most hazardous air pollution for its toxicity, bioaccumulation and mobility in the food chain [1,2]. Mercury emitted from coal-fired power plants accounts for the largest part of atmospheric mercury emission [3]. In the coal-fired flue gas, mercury exists in three forms: gaseous elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particle-bound mercury (Hg^p). The highly water-soluble Hg²⁺ can be effectively captured in the wet flue gas desulfurization (WFGD) system [4]. Hg^p can be easily removed by dust collection system [5]. However, Hg⁰ is difficult to be removed by conventional air pollution control devices (APCDs) owing to its low water solubility and poor reactivity with fly ash [6]. Unfortunately, mercury speciation studied showed Hg⁰ is the dominant species present in flue gas when burning low-rank coal [7,8]. Therefore, the process for a low cost Hg⁰ oxidation and removal to reduce the emission of mercury from the flue

gas is urgently to be proposed.

Many studies for enhancing Hg⁰ oxidation and removal from the flue gas have been carried out, such as the activated-carbon injection technique [9,10] and catalytic oxidation technique [11,12]. As an effective way to oxidize Hg⁰, the photocatalytic oxidation technology brought a new sight for Hg⁰ removal. The photocatalytic oxidation technology using TiO₂ nanoparticles as a photocatalyst showed a good Hg⁰ removal performance. Under the ultraviolet irradiation, the strong oxidative hydroxyl radicals (·OH) can be produced on the surface of TiO₂, and then the Hg⁰ will be oxidized by ·OH from Hg⁰ into Hg²⁺, which can be effectively captured by WFGD downstream [13,14]. However, due to the rapid combination of photo-generated electron-hole pairs, the smaller BET surface area and the wide energy band gap (3.2 eV) of pure TiO₂ [15], the efficiency of Hg⁰ removal was limited. Hence, it is necessary to make many efforts to improve the photocatalytic performance of TiO₂.

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Recently, a promising method using TiO_2 coupled with carbon nanotubes (CNTs/ TiO_2) has been developed to improve the photocatalytic activity of photocatalyst [15,16]. The CNTs is advantageous owing to their better porous properties and unique characteristics of electrons transportation [17]. Ji et al. found that for the photocatalyst of CNTs/ TiO_2 , the photo-generated electrons of TiO_2 can migrate into the carbon nanotubes, thereby decreasing the recombination possibility of the electron-hole pairs, enhancing the photocatalytic ability of CNTs/ TiO_2 [18]. Balazs et al. tested the photocatalytic ability of CNTs/ TiO_2 in phenol and oxalic acid degradation under UV irradiation and reported that CNTs can not only play a role of an absorbent, but also act as conductive wires that can transfer and store photo-generated electrons, which will increase the existence time of separated charge carriers [19]. In the meantime, multi-walled carbon nanotubes (MWCNTs) have also attracted many researcher focuses due to its excellent electrical, mechanical and thermal properties [20]. Wang et al. synthesized MWCNTs/ TiO_2 through an acid modified sol-gel route and evaluated its photocatalytic ability by phenol decomposition [21]. Liu et al. reported that the modification of TiO_2 by adding MWCNTs can increase yields of radical and shift the adsorption edges toward the visible light region [22]. However, in previous investigations, most studies were emphasized on utilizing CNTs/ TiO_2 or MWCNTs/ TiO_2 for the photocatalytic decomposition of dyes, phenol, oxalic acid, etc, seldom studies on the application of MWCNTs/ TiO_2 in Hg^0 removal from flue gas has been reported. Compared to the pure TiO_2 , the introduction of MWCNTs will lead to some increase in economic cost, but the presence of MWCNTs can also inhibit the grain growth of TiO_2 , provide alternative electrons transfer pathway to assist in hole-electron pairs separation, improve the pore property of the photocatalyst, and narrow band gap energy, which will contribute to a significantly improvement on Hg^0 removal performance in flue gas.

In this work, the MWCNTs impregnated with TiO_2 were synthesized by a sol-gel method. The prepared MWCNTs/ TiO_2 photocatalysts were characterized by means of TEM, BET, XRD, XPS and DRS techniques to have insight into its physicochemical properties. The influences of MWCNTs and individual flue gas components on Hg^0 removal characteristics in a fixed-bed reactor were investigated. Moreover, mercury species retained on the surface of MWCNTs/ TiO_2 were also determined by XPS to reveal the possible reaction mechanism for Hg^0 removal process.

2. Experimental section

2.1. Photocatalyst preparation

Chemicals including nitric acid, sulfuric acid, anhydrous ethanol, tetrabutyl titanate, etc. were commercial products and all of them were

analytical grade. Raw MWCNTs with a purity of more than 95%, diameter of 10–20 nm, and length of 10–30 nm was produced by Chengdu Organic Chemicals Company. The raw MWCNTs were firstly acid-treated in an acid mixture of concentrated nitric acid and sulfuric acid with a volume ratio of 1:3. After that, the solution was ultrasonically dispersed for 2 h. Then, the acid-treated MWCNTs was collected by centrifugation and rinsed with distilled water to adjust the pH of the mixture to 7. Finally, the solid sample was dried at 80 °C for 12 h in a vacuum drying oven.

MWCNTs/ TiO_2 was synthesized by a sol-gel method. 0.86 g acid-treated MWCNTs was added into a mixture solution containing 25 mL tetrabutyl titanate, 75 mL anhydrous ethanol and 4 mL HNO_3 (6 mol/L) under vigorous stirring. After stirring for 1 h, another mixture solution (pH = 2) of 25 mL anhydrous ethanol and 5 mL distilled water was added dropwise to the solution. Next, the resultant gel was dried at 80 °C in a vacuum drying oven and followed by a calcination treatment at 500 °C for 3 h in air. Then, the MWCNTs/ TiO_2 was obtained.

In order to avoid aggregation of the photocatalysts, increase the contact area and prolong the reaction time between photocatalysts and flue gas, all tested photocatalysts were loaded on the surface of matte quartz pellets with the diameter of 10 mm. The detailed loading method was described in the work of Sannino et al. [23].

2.2. Photocatalyst characterization

The morphology of the acid-treated MWCNTs and MWCNTs/ TiO_2 was examined by JEM 2100F field-emission transmission electron microscopy (Japan). The Brunauer-Emmett-Teller (BET) surface area was determined by a Quantachrome Nova 1000e surface area and pore size apparatus (USA). X-ray diffraction (XRD) analysis was performed to confirm the crystalline phase and grain size of the synthesized TiO_2 by a D/max-2500/PC X-ray diffractometer (Japan) with a $\text{Cu K}\alpha$ radiation in the 2θ range of 5–85° at a scanning speed of 0.02°s^{-1} . Optical properties of photocatalyst were recorded on a VARIAN Cary5000 spectrophotometer (USA). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer (Japan) with $\text{Al K}\alpha$ as the excitation source. The binding energies were calibrated using C 1s peak at 284.8 eV.

2.3. Photocatalyst tests

The schematic of the experimental setup is shown in Fig. 1. The experimental setup consisted of a simulated flue gas generation system, a photocatalytic reaction system and an analytical system. The flue gas simulation system included a Hg^0 vapor generator, a water vapor generator and a multi-component gas generator. In Hg^0 vapor generator, the Hg^0 permeation tube (VICI Metronics, USA) was placed in a

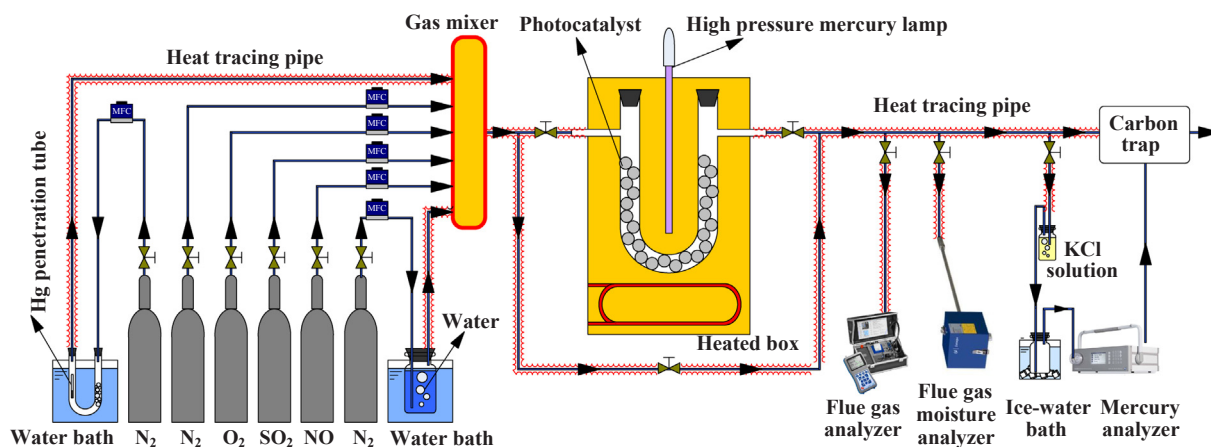


Fig. 1. Schematic diagram of experimental setup.

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