



A new type of cobalt-deposited titanate nanotubes for enhanced photocatalytic degradation of phenanthrene



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ABSTRACT

We prepared and characterized a new type of photocatalyst, referred to as cobalt-deposited titanate nanotubes, using TiO₂ (P25) as the precursor through a two-step process (hydrothermal reaction at 150 °C followed by calcination at 600 °C). The optimal catalyst (Co-TNTs-600) was obtained at a Co loading of 2.26 wt.% and calcination temperature of 600 °C. The catalyst can effectively catalyze photodegradation of phenanthrene (a model polycyclic aromatic hydrocarbon) under simulated solar light. The pseudo first-order rate constant was determined to be 0.39 h⁻¹, which is about 10 times that of the conventional photocatalyst TiO₂. TEM, XRD and XPS analyses indicate that Co-TNTs-600 is a composite nanomaterial containing titanate, anatase and CoO crystals. The hydrothermal treatment converts TiO₂ into tubular, multilayered titanate nanotubes, allowing for incorporation Co(II) ions on the matrices. The subsequent calcination partially transforms titanate into anatase and the adsorbed Co²⁺ ions into CoO. UV–vis DRS spectra suggest that the absorption edge of Co-TNTs-600 shifts to the visible light region compared to P25 and un-calcined TNTs, and the new catalyst displays a narrower optical energy band of 2.8 eV compared to 3.2 eV for P25 and 3.4 eV for TNTs. The incorporated CoO acts as an electron transfer mediator, which prevents the recombination of hole–electron pairs created mainly by anatase under solar irradiation. In addition, Co-TNTs-600 exhibits good reusability and can be gravity-separated and reused in multiple cycles of operations for phenanthrene photodegradation. This new catalyst appears promising for catalyzing photodegradation of persistent polycyclic aromatic hydrocarbons.

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1. Introduction

With increasing water pollution and growing energy demand, low-energy water treatment technologies become more and more appealing [1]. As such, catalytic photodegradation of various pollutants using solar irradiation has elicited great interest in recent years [2]. Traditionally, TiO₂-based materials have been the most widely used photocatalysts, and have been found effective in a variety of environmentally related uses, such as solar-driven hydrogen production, and photocatalytic decomposition and adsorption of organic contaminants [3–7].

TiO₂ is a typical *n*-type semiconductor with relatively large band gaps. The band gaps for the three main crystal phases, i.e., anatase,

rutile and brookite, are 3.2, 3.0 and 3.2 eV, respectively [6]. Although TiO₂ can effectively utilize UV light, its large band gaps limit its optical absorption in the solar spectrum, which consists of UV, visible and infrared (IR) radiations with a relative energy distribution of ~5%, 43% and 55%, respectively [8,9]. As a result, a great deal of effort has been devoted to improving the visible light absorption of TiO₂. While nanoscale TiO₂ has shown to offer improved catalytic activity, the sedimentation characteristics limit the separation from water and reuse of the spent catalyst [10].

Of various modifications, one-dimensional titanate nanotubes (TNTs) synthesized by hydrothermal treatment of TiO₂ have gained significant attention in recent years [5,10–12]. TNTs can serve as excellent adsorbents for heavy metals owing to their high specific area, great ion-exchange properties, easy solid-liquid separation and abundant functional groups. However, TNTs have been found to be poor photocatalysts despite their high surface area and crystalline structure due to the rapid electron-hole recombination rate upon excitation under illumination [13–15]. Therefore,

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researchers have studied various approaches to inhibit the electron-hole recombination, including calcination [16,17], H₂O₂ treatment [18], acid treatment [19], and surface modification using non-metals such as C, F and P [13,20] or metals such as Fe, Cu, Pd, and W [21–23]. Of these approaches, metal doping/deposition appears very promising. An appropriate metal dopant can not only inhibit the recombination of electron-hole pairs, but also facilitate absorption of visible light by narrowing the absorption band gaps. Cobalt is one of the commonly used dopant for modifying TiO₂, and cobalt oxides have narrower band gaps (e.g., ~2.4 eV for CoO and 2.19 eV for Co₃O₄) [24,25]. For instance, cobalt oxide/TiO₂ composite showed much improved photo-activity for organic compounds and H₂ production rate than plain TiO₂ [26–28]. However, cobalt as a potential dopant for TNTs has not been studied.

Polycyclic aromatic hydrocarbons (PAHs) are produced during incomplete combustion of fossil fuels, and important components of crude oil [29,30]. Due to their toxic, mutagenic and carcinogenic properties, PAHs represent a major environmental concern associated with oil spill, discharge and seepage, and thus, have been classified as the priority pollutants by US EPA [31]. In addition, PAHs (e.g., phenanthrene, anthracene, and pyrene) are rather persistent to photodegradation under solar light [32]. PAHs can absorb light in the UV regions, and then be transformed into excited PAH molecules and photo-oxidized [33]. Phenanthrene is one of the most commonly detected PAHs, consisting of three fused benzene rings, it is fairly resistant to natural photodegradation, and thus, has been often used as a prototype PAH for photolysis study [34–36].

The overall goal of this work was to develop and test a new type of cobalt-deposited TNTs (Co-TNTs) for efficient photodegradation of PAHs under solar light. The specific objectives were to: (1) develop an optimized hydrothermal-calcination method for preparing the desired catalyst, (2) test the effectiveness of the catalyst for phenanthrene photodegradation, and (3) elucidate the mechanisms for enhanced photocatalytic activity by characterizing the morphology, crystal phases and compositions of Co-TNTs.

2. Experimental

2.1. Chemicals

All chemicals used in this study were of analytical grade or higher. TiO₂ nanoparticles (P25, 80% anatase and 20% rutile) were purchased from Degussa Corporation (Germany) and were used as the precursor for TNTs. CoCl₂·6H₂O, NaOH, methanol (HPLC grade), dichloromethane (GC grade) and absolute ethanol were obtained from Acros Organics (Fair Lawn, NJ, USA). Terephthalic acid was purchased from Alfa Aesar (Ward Hill, MA, USA) for hydroxyl radical detection. Deionized (DI) water (Millipore Co., 18.2 MΩ cm) was used to prepare all solutions. Phenanthrene (the model PAH) was purchased from Alfa Aesar (Ward Hill, MA, USA), and was dissolved in methanol to form a stock solution of 2 g L⁻¹.

2.2. Synthesis of Co-deposited TNTs

First, Co-TNTs were synthesized through a one-step hydrothermal method. In brief, 0.1, 0.2, 0.4 or 0.6 g CoCl₂·6H₂O was mixed with 1.2 g of the TiO₂ nanoparticles in a beaker with 20 mL DI water. The mixtures were magnetically stirred for 30 min and sonicated for another 30 min. Then, a NaOH solution (prepared with 29 g NaOH in 47 mL DI water) was added dropwise into each mixture in ca. 5 min, and then sonicated for another 60 min. Afterwards, each mixture was transferred into a Teflon reactor with stainless steel coating, and then purged with pure N₂ for 10 min to remove dissolved oxygen. Then, the reactors were heated at 150 °C for 48 h to complete the hydrothermal reaction. The resulting blue

precipitates were separated and washed with DI water to neutral and then oven-dried at 80 °C for 4 h. The as-prepared materials are denoted as Co-TNTs for typographical convenience.

The Co loadings on Co-TNTs were determined according to EPA Method 3050B [37]. Briefly, 0.2 g each of the materials was dispersed into 20 mL of concentrated nitric acid (65%) and shaken for 24 h, and the resulting solution was diluted 10 times and then analyzed for Co on an inductively coupled plasma-optical emission spectroscopy (ICP-OES, 710-ES, Varian, USA). Subsequently, the Co-TNTs were calcined at 400, 600 or 800 °C in a muffle furnace for 3 h, and the resultant catalysts are denoted as Co-TNTs-xxx (xxx indicates the calcination temperature). The photocatalytic activities of the materials prepared with different Co loadings and calcination temperatures were then tested to optimize the recipe. For comparison, neat TNTs were also synthesized following the traditional hydrothermal method without Co loading [38,39], where 1.2 g TiO₂ (P25) and 10 M NaOH were mixed and heated at 130 °C for 72 h. In selected cases, the TNTs were calcined at 600 °C for 3 h, and the calcined TNTs are designated as TNTs-600.

2.3. Material characterizations

The morphology of material was analyzed using Tecnai30 FEG transmission electron microscopy (TEM, FEI, USA) operated at 300 kV, and energy dispersive spectra (EDS) of the materials were obtained at the same time. The crystal phase of the sample was obtained by means of a Bruker D2 phaser X-ray diffractometer (XRD, Bruker AXS, Germany) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate (2θ) of 4°/min. AXIS-Ultra X-ray photoelectron spectroscopy (XPS, Kratos, England) analysis was performed to determine the elemental composition and oxidation state of materials using Al K α X-ray at 15 kV and 15 mA. The standard C 1s peak (Binding energy, $E_b = 284.80 \text{ eV}$) was used to eliminate the static charge effects. The Brunauer-Emmett-Teller (BET) surface area was measured on an ASAP 2010 BET surface area analyzer (Micromeritics, USA) in the relative pressure range of 0.06–0.20. Pore size distribution was obtained following the Barret-Joyner-Halender method. Nitrogen adsorption volumes at the relative pressure of 0.99 were used to determine the pore volumes and the average pore diameters. Diffuse reflectance UV-vis absorption spectra (UV-DRS) of the materials were obtained using a UV-2400 spectrophotometer (Shimadzu, Japan). BaSO₄ powder was used as the reference at all energies (100% reflectance) and the reflectance measurements were converted to absorption spectra using the Kubelka-Munk function. The sedimentation rate tests of the materials were evaluated following the UV absorbance of the particle suspensions using a UV-vis spectrophotometer (UV1800, Shimadzu, Japan) (the particles were first dispersed in DI water with sonication) [10].

2.4. Photocatalytic degradation

Fig. S1 in Supplementary data (SD) shows the experimental setup for the photodegradation of phenanthrene, which includes a sealed glass photo-reactor (volume = 250 mL) with a quartz cover, an Oriel Sol 1A solar simulator (Newport, USA) with a 450 W xenon lamp, a water circulating system and a magnetic stirrer. The solar irradiation was set at of $85 \pm 0.5 \text{ mW/cm}^2$ (AM 1.5G). The reactor temperature was maintained at $25 \pm 0.2 \text{ }^\circ\text{C}$ through the circulating water.

Photocatalytic degradation kinetic tests were carried out with various materials under the simulated solar light. Specifically, 200 $\mu\text{g/L}$ of phenanthrene and 1.0g /L of a given material were loaded in the photo-reactor. The mixture was stirred for 2 h in dark to reach the phenanthrene adsorption equilibrium. Afterwards, the reactor was subjected to the solar irradiation. Water samples (1 mL each) were taken at predetermined times and imme-

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