



Supercritical-assistant liquid crystal template approach to synthesize mesoporous titania/multiwalled carbon nanotube composites with high visible-light driven photocatalytic performance



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ABSTRACT

Mesoporous titania (MPT) was deposited onto multiwalled carbon nanotubes (MWCNTs) by deposition of titanium sol containing liquid-crystal template with assistant of supercritical CO₂. The products were characterized with various analytical techniques to determine their structural, morphological, optical absorption and photocatalytic properties. The results indicate that in photocatalytic degradation of phenol under visible light, the mixtures or composites of MPT and MWCNT show the high efficiency because of synergies between absorbing visible light, releasing electrons and facilitating transfer of charge carriers of MWCNTs and providing activated centers of MPT. Because of the mutual constraint between MPT and MWCNTs on the photocatalytic efficiency, the optimal loading of MPT in MPT/MWCNT-3 for phenol degradation is 48%. Because the intimate contact between MWCNTs and MPT is more beneficial to electron transformation, photoactivity of mixture is lower than that of composites with high reusable performance. The optimum conditions of phenol degradation were obtained.

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1. Introduction

As a chemically stable, highly efficient, non-toxic, and relatively inexpensive photocatalyst, titanium dioxide has been widely used for water and air purification [1–3]. However, there are many challenges that are yet to be met before the photocatalyst becomes economically feasible. These challenges mainly included low surface and no absorbing visible light of TiO₂. It is well known that the high surface area of catalyst is beneficial for catalytic activity, as it provides for a high concentration of target organic substances around sites activated by ultraviolet (UV) radiation [4]. So, since mesoporous TiO₂ (MPT) was first prepared by Antonelli and Jackie in 1995, it has received increased attention in the degradation of contaminants due to its high surface area [5–9]. However, MPT catalyst cannot still absorb visible light and only make use of 3–5% of the solar spectrum due to a large band gap (3.2 and 3.0 eV in the anatase and rutile crystalline phases, respectively). Therefore, some efforts have been directed toward shifting the optical sensitivity of TiO₂ from the UV to the visible-light region for the efficient use of solar energy [10–12]. As an excellent conductive property, low band-gap energy with

smaller than 1.1 eV [13–16], carbon nanotubes (CNTs) may be a suitable support material for TiO₂ photocatalysts used under visible light [10,12,17–20]. It is worth noting that although there are lots of reports about composite preparation and performance of CNTs and TiO₂, the synthesis and visible-light driven photoactivity of CNT-based MPT composites have been seldom reported as far. Additionally, CNTs-supported TiO₂ composites have been fabricated by various methods, including mechanical mixing of TiO₂ and CNTs [4], sol-gel synthesis of TiO₂ in the presence of CNTs [12,17], solvothermal method [17,20], electrophoretic deposition and electrospinning [18], and chemical vapor deposition [19]. However, these conventional preparation techniques usually suffer from an inherent disadvantage, which the pretreat strategy of CNTs with strong acids would introduce impurities into the TiO₂, affecting the unique properties of single-component metal oxide and decreasing its catalytic activity [7]. Furthermore, TiO₂ layer with serious particle agglomeration and large crystal grain is easily dropped from CNT substrate. Therefore, it is necessary to explore simple and effective ways to synthesize CNT-based composites with high surface area and excellent physicochemical properties of MPT for photocatalysis. The supercritical carbon dioxide was applied to synthesize nanoparticles or nanocomposites due to its “tunable” solvent strength, “zero” surface tension, high diffusivity, and excellent wetting of complex surfaces of the nanostructures. Another advantage is that it can be easily and completely removed

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from reaction system and porous structure can be obtained without collapse structure [3]. Herein, we report a simple and effective route to deposit MPT on MWCNTs under supercritical conditions. In this method, MPT/MWCNT composites were fabricated by hydrolyzing tetra-*n*-butyl titanate (TBT), the precursor, to deposit MPT on MWCNTs. This was done under supercritical conditions with the aid of a liquid-crystal template (LCT). The MWCNTs did not require tedious surface modification, and controlling the reaction parameters facilitated deposition of the MPT layers.

Phenol is widely used as an importantly organic raw material for the manufacture of phenolic resins, producing herbicides, wood preservatives, fertilizers, explosives and rubber. However, phenol is highly toxic substances through the skin, gastrointestinal tract and respiratory tract absorption. Hence, the photodegradation of phenol is important with regard to the purification of organic effluents [15]. Thus, phenol was selected as the probe molecule in this study, and its degradation was monitored to evaluate MPT/MWCNT photocatalytic activity under visible light.

2. Experimental

2.1. Synthesis of MPT/MWCNT composites

MPT/MWCNTs were fabricated by deposition in supercritical CO₂, using tetrabutyl titanate (TBT, Ti(OC₄H₉)₄) and liquid crystal as the precursor and soft template, respectively. MWCNTs (purity, >95%; diameter, 40–60 nm; length, 5–20 μm; specific surface area, 40–300 m² g⁻¹) were provided by Shenzhen Nanoport Co., Ltd. In a typical preparation of the composites, 5 g of cetyltrimethylammonium bromide was first completely dissolved in the distilled water to form hexagonal LCT by stirring for a certain period. Ti(OC₄H₉)₄ (25 mL) was dissolved in ethanol, and the resulting solution was stirred for 2 h (100 rpm) with a magnetic stirrer. While still stirring at room temperature, a solution containing 3.33 mL of HCl (35%) and the obtained liquid crystal was added dropwise over 1 h until a liquid crystal sol was obtained. After the sol was aged for 12 h, it was dissolved and ultrasonically dispersed along with MWCNTs in 10 mL of ethanol. The resulting suspension was then transferred to an equipment of supercritical CO₂ (7.6 MPa pressure and 80 °C temperature), and then allowed to cooled to room temperature. Subsequently, the dark precipitate was separated from the solution by extraction in a Soxhlet apparatus. The obtained product were dried for 30 min at 100 °C in an oven, and then calcined at 400 °C for 1 h in a nitrogen atmosphere to synthesize MPT/MWCNT composites. For comparison, the aged sol was also calcined at 400 °C for 2 h to synthesize pure MPT powders. By changing the number of precipitation–drying cycles prior to the last cycle of drying to calcination, different samples were obtained. Samples prepared with one, three, and five cycles were labeled as MPT/MWCNT-1, MPT/MWCNT-3, and MPT/MWCNT-5, respectively.

2.2. Characterization of composite photocatalyst

The features of the MPT/MWCNT photocatalyst were observed by SEM (Hitachi S3400N, Japan) at an accelerating voltage of 20 kV. TEM, HRTEM and SAED analyses were done on a Jeol (JEM 2100F) microscope at an accelerating voltage of 200 kV. Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U SAXS system (Bruker, Germany) using Cu K_α radiation (40 kV, 35 mA). Wide-angle XRD (WAXRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu K_α radiation (40 kV, 40 mA). To assess the nitrogen adsorption–desorption isotherms were used to determine the Brunauer–Emmett–Teller (BET) surface area and pore size distribution (ASAP2010, Micromeritics Company, USA) at 77 K. UV–vis absorption spectroscopy

measurements at 298 K were performed by using a UV–vis diffuse reflectance spectrophotometer (Shimadzu UV-2100) to assess the UV–vis absorption intensity. XPS analysis of the photocatalyst was carried out by using an ESCALAB MarkII spectrophotometer equipped with two ultrahigh-vacuum chambers in which the pressure during the measurements was about 10⁻⁷ Torr. An Al K_α X-ray source ($h\nu = 1486.6$ eV) was used for the excitation of electrons. The MWCNT-supported sample was calcined up to 800 °C, and the TiO₂ loading content was determined by TGA–DSC, using calculations based on the ash weight (Mettler Toledo, Swiss).

2.3. Photocatalytic degradation of phenol

Phenol was chosen as a model organic compound to evaluate the photoactivity of the prepared samples under visible light. Experiments were carried out in an open, wide, glass photochemical reactor (8 cm in diameter and 12 cm in height), which used an air-sparging motor for internal stirring. The reactor, which was fitted with a 6 cm diameter water-cooled quartz jacket, maintained the system temperature by water cycling. A 500 W high-pressure Hg lamp with a UV filter that could eliminate the effect of UV light to produce visible light (irradiance: 100 mW/cm²) was placed about 20 cm away from the reactor. It emitted light in the range of 450–900 nm. In a typical experiment, 50 mg L⁻¹ aqueous phenol solution was mixed with MPT/MWCNT composites (1 g L⁻¹). Air was bubbled through the reaction solution at a flow rate of 560 mL min⁻¹ to ensure a constant concentration of dissolved oxygen. The mixture was continuously stirred in the dark for 30 min to establish adsorption–desorption equilibrium. The phenol concentration, initial pH, catalyst amount were selected as experimental parameters to evaluate effects of photocatalytic conditions on phenol degradation. Prior to switching on the lamp, the initial phenol concentration (A_0) of the solution was determined. Sample solutions were analyzed regularly by UV–vis spectroscopy (Tu-1800, North Division, Beijing) at scheduled irradiation times, and the phenol concentration was directly expressed as the absorbance. The total organic content (TOC) was measured using a TOC analyzer (model 820, Sievers, USA). Photocatalysis was observed in triplicate. The results, which have an error of ≤5%, were reported as mean values.

3. Results and discussion

3.1. Morphological and textural properties of MPT/MWCNTs

Representative SEM images of the MWCNT-based composites are shown in Fig. 1. In contrast to the starting MWCNTs (Fig. 1a), the SEM images MPT/MWCNT-1 show that MWCNT was enclosed by an MPT layer, as illustrated in Fig. 1b. MPT/MWCNT-3 (Fig. 1c) exhibited similar morphology besides small aggregates. The repeating time was an important factor that influenced the final morphology of the composites. At above three precipitation–drying cycles, MPT aggregates released from MWCNTs, in addition to MPT/MWCNTs, could be observed in the SEM images (Fig. 1d). Composites, prepared at a deposition repeating time of five, suggest that MPT aggregates appeared in the product (as shown by the arrow), and that the MWCNTs were embedded in these aggregates. The above results indicate that changing the deposition repeating time could be done to tune morphology of the resulting composites. The effect of deposition repeating time on the amount of MPT in the composites was confirmed by measuring the weight loss (TGA) and heat flow (DSC) of samples in air up to 800 °C (see Fig. S1, Supporting Information). The amount of deposited MPT increased with increased repeating time. MPT/MWCNTs-1, -3, and -5 contained 45, 48, and 53% MPT, respectively, as listed in Table 1. Although the MPT layers had

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