



# Carbon nanotube embedded mesoporous titania pore-hole inorganic hybrid materials with high thermal stability, improved crystallinity and visible-light driven photocatalytic performance



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## ABSTRACT

Pore-hole inorganic hybrid materials: carbon nanotube (CNT)-embedded mesoporous titania (MT) (CNMT) were controlled fabricated in supercritical conditions by deposition of titanium sol containing a liquid crystal template. The as-prepared hybrid materials were characterized by using modern analytical tools. Experimental results indicate that the MT in hybrid materials maintained mesoporous structure up to 600 °C. This result may be attributed to the structure of CNTs embedded in the anatase matrix. Embedding of CNTs in the nanophase titania matrix helped protect the mesoporous framework against collapsing, inhibited undesirable grain growth, suppressed transformation of anatase into rutile, and increased the thermal stability of MT during calcination. A possible mechanism for the formation of highly thermostable MT in the hybrid materials is also proposed. Such formation could be further confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy. Calcination temperature greatly influenced embedding effect of CNTs on the microstructure of MT in hybrid materials. The maximum phenol degradation (99% after 140 min) is observed for CNMT-500 samples. It is attributed to the well mesostructure, which facilitates mass transport, the large surface area that offers more active sites and hydroxyl radicals, and perfect crystallinity that favors the separation of photogenerated electron-hole pairs, confirmed by photoluminescence emission spectrum.

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## 1. Introduction

Mesoporous titania (MT) has been demonstrated to be a more effective photocatalyst because of its environmental friendliness, large surface area, porous structure, and large pore volume, which results in increasing surface reactive sites and improving mass transport [1–3]. Since the first discovery of MT by Antonelli and Ying using a modified sol–gel method, much effort has been focused on developing diverse techniques to synthesize MT [4]. Ozin and coworkers reported a two-dimensional hexagonal MT prepared by hard template synthesis [5]. Stucky and coworkers prepared MT sub-microspheres by using an acetic acid mediated sol–gel system with aerosol-assisted self-assembly approach. In this sol–gel system, metal alkoxides are dissolved in solutions of acetic acid, hydrochloric acid, and ethanol [6]. Zhou and coworkers prepared MT with rutile and anatase phases by using mesoporous silica SBA-15 as hard template [7]. Liu and coworkers

synthesized MT through evaporation-induced self-assembly (EISA) approach, which releases butanol (a swelling agent) in situ [8]. However, there are many challenges that are yet to be met before these photocatalysts become economically feasible. Difficulties in the enhancement of thermal stability and increase in solar energy conversion. It is well-known that the high crystallinity of anatase, which possesses fewer surface defects, is one of the critical factors in improving photocatalysis [9]. Generally, high crystallinity requires high calcination temperature. However, thermal treatment of typical MT employed to transform pore walls from amorphous to crystalline usually leads to undesirable grain growth and total collapse of the mesoporous network during processing at high calcination temperature [10]. Thus, effects on the formation and thermal stability need further investigation, and preparation of MT with high thermal stability is still a great challenge.

In an attempt to improve the thermal stability of the MT framework, an alternative method is to add amorphous carbon by introducing organic precursors [11–13] into the mesostructured TiO<sub>2</sub> framework to form a glasslike phase that stabilizes

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mesostructures. Meanwhile, MT/carbon composites may have the advantages of coupling the photoactivity of anatase-type  $\text{TiO}_2$  with the adsorptive capacity of carbon [14]. Liu and coworkers synthesized MT/carbon composites that are stable above 500 °C [11]. The group of Huang prepared mesoporous crystalline titanium oxides and carbide/carbon composites that were stable up to 600 °C [12]. Recently, Zhang and coworkers prepared carbon– $\text{TiO}_2$  inorganic materials that were stable up to 650 °C [13]. These efforts were meaningful works and improved the thermal stability of MT. However, the carbon components in the aforementioned composites have high band gap energy and lower microporosity of carbon, which lead to low UV light activity and no visible-light photocatalytic activity. Furthermore, postsynthetic strategies of using organic precursors introduce impurities besides carbon into the mesoporous walls, which might affect the unique properties of single-component metal oxides and thereby limit their applications [7]. Therefore, direct introduction of inorganic carbon may be an effective way to overcome the above drawbacks.

Carbon nanotubes (CNTs), a unique carbon candidate, not only have one-dimensional carbon-based ideal molecule with excellent conductive properties and visible-light absorption due to its band gap energy (<1.1 eV) [15], but also effectively inhibit undesirable grain growth and phase transformation of  $\text{TiO}_2$  [16,17]. Therefore, CNT-based  $\text{TiO}_2$  inorganic hybrid materials have attracted much attention from researchers. Akhavan and coworkers reported that titania with highly visible-light inactivation activity could be supported by CNTs [18]. Titania/CNT composites can enhance solar energy conversion and maintain the porous feature of CNT resulting from hydrolysis of titanium isopropoxide in supercritical ethanol [19]. Through a simple hydration/dehydration procedure, Sandra and coworkers fabricated a wide variety of  $\text{TiO}_2$ /CNT composites with visible-light photocatalytic performance [20]. However, researchers have seldom analyzed the mechanism of visible-light catalytic performance of CNT-based MT (CNMT) hybrid materials. Furthermore, the effect of CNTs on the thermal stability of titanium mesostructures in hybrid materials remains unclear. It is therefore highly important to design and construct inorganic CNMT hybrid materials. Additionally, in order to avoid these limitations, such as serious particle agglomeration, small surface area and large crystal grain of titania with low photocatalytic activity, supercritical fluid was applied to synthesize nanoparticles or nanocomposites. Among supercritical fluids, supercritical  $\text{CO}_2$  is considered as alternative solvents for the synthesis and processing of porous materials. First,  $\text{CO}_2$  is inexpensive, environmentally benign and nonflammable. And its mild critical conditions ( $P_c = 73.8$  bar;  $T_c = 31.1$  °C) allow  $\text{CO}_2$  to be safely used in a laboratory. Another advantage is that  $\text{CO}_2$  can be easily and completely removed from reaction system and porous structure can be obtained without collapse structure [21].

On the basis of the above considerations and previous reports, we conducted a primary study on the synthesis of CNMT hybrid materials by using a liquid crystal template (LCT) in a supercritical  $\text{CO}_2$  system. It is well known that the characteristics of such materials are governed by their mesostructure, particle size, and crystallinity. In this paper, the effect of calcination temperature on the structural and textural parameters of the obtained CNMT was studied. The resultant CNMT were characterized by using transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), wide-angle X-ray diffraction (WAXRD), small-angle X-ray scattering (SAXS) measurements, X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (DRS), and thermogravimetric/differential thermal analysis (TG–DTA). Its photocatalytic activity in phenol degradation under visible-light illumination was also investigated.

## 2. Experimental

### 2.1. Synthesis of CNMT hybrid materials

CNMT was prepared by deposition in supercritical  $\text{CO}_2$  using tetra-*n*-butyl titanate and liquid crystal as the precursor and soft template, respectively. CNTs (purity, >95%; diameter, 40–60 nm; length, specific surface area, 40–300  $\text{m}^2/\text{g}$ ) were prepared by catalytic decomposition of  $\text{CH}_4$  using the catalyst precursor  $\text{La}_2\text{NiO}_4$  (Shenzhen Nanoport Co. Ltd.). Tetrabutyl titanate was purchased from Acros Organics. AR grade ethanol was obtained from Beijing Chemical Reagent Plant. In a typical experiment, 5 g (accurately weighed) of hexadecyltrimethylammonium bromide (CTAB) was first completely dissolved in distilled water and the mixture was stirred for a certain period of time to form a hexagonal LCT. Next, 25 mL of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  was dissolved in 50 mL of ethanol, and the mixture was stirred for 2 h (100 rpm) with a magnetic stirrer at ambient temperature. While stirring, a solution of 3.33 mL of 35% HCl and the liquid crystal was added dropwise over 1 h. After a suitable amount of precursor containing the liquid crystal, synthesized by an evaporation-induced self-assembly method, was aged for 12 h at room temperature, it was dissolved and ultrasonically dispersed in 8 mL of ethanol along with CNTs treated with strong acid. The resulting suspension was then transferred to the equipment with supercritical  $\text{CO}_2$  (7.6 MPa pressure and 80 °C temperature) for moderate time and then allowed to cool to room temperature. Subsequently, the dark precipitate was separated from the solution by extraction in a Soxhlet apparatus for 48 h. The obtained product was dried for 30 min at 100 °C in an oven, calcined at 250 °C for 30 min in air, and then further calcined at 300–700 °C for 1 h in a nitrogen atmosphere to synthesize the CNMT composite. For comparison, the aged gel was simultaneously calcined according to the same process by composite heat treatment to synthesize pure MT powders. By changing the calcination temperature, different samples were obtained. Samples prepared at calcination temperatures of 300, 400, 500, and 600 °C were labeled as CNMT-300, CNMT-400, CNMT-500, and CNMT-600, respectively.

### 2.2. Characterization techniques

TEM, HRTEM, and SAED were done on a Jeol (JEM 2100F) microscope at an accelerating voltage of 200 kV. The samples were suspended in ethanol and then embedded in epoxy resin, which was subsequently sliced by an ultramicrotome for TEM observations. SAXS measurements were taken on a Nanostar U SAXS system (Bruker, Germany) using Cu KR radiation (40 kV, 35 mA). WAXRD patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu KR radiation (40 kV, 40 mA). 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. The specific surface area was calculated from the BET isotherms, and the pore size distribution was determined by the density functional theory method. To assess the UV–visible absorption intensity, DRS at 298 K was performed by using a UV–visible diffuse reflectance spectrophotometer (Shimadzu UV-2100). Photoluminescence (PL) emission spectra were obtained by using a Spex 500 fluorescence spectrophotometer at 325 nm excitation wavelength. TG–DTA was performed on a WCT–2C analyzer (Optical Instrument Factory, Beijing) at a heating rate of 10 °C/min in air at a flow rate of 100 mL/min.

### 2.3. Photocatalytic reaction

The photocatalytic activity of CNMT composites was determined by using them in phenol degradation in aqueous solution

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