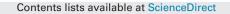
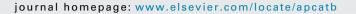
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Synergy effect in photodegradation of contaminants from water using ordered mesoporous carbon-based titania catalyst



Wei Wei, Chao Yu, Qingfei Zhao, Xufang Qian, Guisheng Li*, Ying Wan*

Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, and Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China

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ABSTRACT

A synergy effect by carbon and anatase in the mesoporous C–TiO₂ nanocomposites is reported here on the degradation of dye in contaminated water. The as-formed mesoporous C–TiO₂ composites have ordered 2D hexagonal mesostructure, high surface area $(384 \text{ m}^2/\text{g})$, uniform and large mesopores (4.5 nm), large pore volume $(0.31 \text{ cm}^3/\text{g})$, titania nanoparticles confined inside carbon frameworks, tunable TiO₂ contents (40-87 wt%), and dopant of element carbon into anatase lattice. The large mesopore space of carbon offers high capacity for the adsorption of dyes from water. Well-dispersed and carbon-doped anatase TiO₂ nanoparticles are active for photocatalysis especially in visible light region. Once the dyes are involved inside mesopores by adsorption, they are easily accessible to anatase particles through the common interface between the two, and immediately fully oxidized. The immobilization of anatase particles in the carbon framework greatly improves the stability during its usage. The mesoporous C–TiO₂ nanocomposite catalysts can be reused more than 20 times without obvious loss both in anatase content and processing ability of contaminated water.

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1. Introduction

The use of nanosized powders of TiO_2 in order to obtain a large surface-area-to-volume ratio, and therefore copious provision of active sites is well established practice, for example, the most frequently used commercial powders of P25 [1]. However, problems with the use of powders are also well recognized, specifically; (1) the loss of catalysts in the solution; (2) aggregation of particles in suspension, especially at high loadings; (3) difficulty in application to continuous flow systems [1,2]. Various supports have been adopted to fix nanosized TiO₂, including activated carbon [3–5], SiO₂ [6], ZrO₂ [7], zeolites, glass beads, stainless steels [8–10]. In particular, activated carbon (AC) has been extensively investigated as a support for heterogeneous catalyst.

Activated carbon with a porous amorphous structure can provide a high-surface area structure over which TiO_2 nanoparticles may be distributed and immobilized (typically 900–1200 m²/g). Distribution techniques include mechanical mixing, aqueous suspensions [11], sol–gel [12], hydrothermal techniques [13,14], chemical vapor deposition [5,15,16], etc. The resulting AC–TiO₂ mixtures/composites are widely reported to yield improvements in photocatalytic activity over TiO_2 alone, attributed to the porosity of the support providing high adsorption capacity and

ready passage of reacting species to the TiO₂ particles [15,17–19]. Secondly, the carbon support can improve the thermal stability of the composite, and therefore, resist the phase transformation from anatase to rutile or aggregation of anatase nanoparticles [20,21]. Thirdly, it has also been reported that the synergistic effect between the support and TiO₂ nanoparticles may also enhance the photocatalytic performance [17–19,22–25]. The synergistic effect is suggested to be possible because of weak interactions between the TiO₂ and AC support; detected by a slight change in pH_{PZC} in the composite. The synergistically improved photocatalytic activity may be explained by the adsorption of reactants on AC followed by mass transfer to the photoactive TiO₂ through the common interface between the two [17,18,23,25]. Because the adsorption rate is apparently slower by several order than recombination of photogenerated electron-hole pairs [26,27], the large surface area of activated carbon which can facilitate the adsorption of organic substances is responsible for the enhanced photocatalytic activity. As a consequence, these enhancements are obviously related to the porosities. Lastly but not least, the AC support itself is capable of a significant level of self-photocatalytic activity, actually out-performing the AC-TiO₂ composite under UV light irradiation [28]. The lower photocatalytic activity in the AC–TiO₂ is due to the drop in porosity of the composite, and blockage of the photoactive centers in the AC support after immobilization of TiO₂.

Activated carbons usually possess the porosity spanning the macro- (>50 nm), meso- (2-50 nm) and micro- (<2 nm) pore ranges [28]. The smaller pores are rarely infiltrated when dispersing TiO₂

^{*} Corresponding authors. Tel.: +86 21 6432 2516; fax: +86 21 6432 2511. *E-mail address:* ywan@shnu.edu.cn (Y. Wan).

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nanoparticles, with the TiO_2 remaining on the outer macropores [28]. On one hand, porosity cannot be fully occupied to disperse nanoparticles, especially for microporous activated carbon. On the other hand, the random dispersion and size distribution of nanoparticles potentially leaves much of the nanoscale effect related to TiO_2 under exploited. Furthermore, the need for band-gap tuning of the TiO_2 which is fundamental issue in improving photocatalytic activity by carbon doping [29], remains un-tackled by use of activated carbon as a support that does not chemically interact with the TiO_2 .

Ordered mesoporous carbons, which possess tunable and large pore sizes, high surface areas, periodically arranged monodispersed mesopore space, and alternative pore shapes, therefore provide a good opportunity to support the TiO_2 nanoparticles [30–32]. Recently, several groups including ours separately reported the formation of TiO₂-C nanocomposites. This kind of catalysts show ordered mesostructure, large pore sizes, high surface areas and large pore volumes. Anatase nanoparticles are well dispersed and immobilized inside the ordered mesoporous carbon frameworks without blockage of mesopores. However, the catalytic activity is lower by 1-2 order of magnitude in reaction rate than commercial P25 in dye degradation in solution under UV light [33]. The prominent "negative" effect by carbon support attracts our interest. Very recently, we found that a TiO₂–C composite with an anatase content of 60 wt% can behave an enhanced photocatalytic performance in degrading dye solution [32]. But the effect of titania content is not discussed.

In this manuscript, we present an adsorption-photocatalysis cycle to separate the adsorption and photocatalysis over mesoporous C-TiO₂ nanocomposites with TiO₂ contents ranging from 40 wt% to 87 wt%, and therefore highlight the role of carbon mesostructure and TiO₂ individually, and their synergy effect. The first role of carbon is dispersion and immobilization of anatase nanoparticles inside mesoporous framework, even with a high TiO₂ content of 87 wt%. High adsorption abilities are observed for all mesoporous C-TiO₂ nanocomposites, which are much related to the high BET surface area of carbonaceous materials. In the subsequent irradiation, a high efficiency in eliminating adsorbed dyes inside mesopores is obtained, due to the fact that the easy mass transfer of the dye to the photoactive TiO₂ through the common interface between the two. The separation of the adsorption and photocatalysis processes greatly improves the reaction rate. More importantly, the carbon element can be doped with anatase, playing a band-gap tuning role. The proposed route produced an excellent photocatalytic performance for degrading phenol under visible light irradiation, much higher than that of commercial P25.

2. Experimental

2.1. Synthesis of mesoporous C-TiO₂ nanocomposites (MCTs)

MCTs were synthesized by using TiCl₄ and/or Ti(OC₄H₉)₄ as titanium sources, water- and ethanol-soluble phenolic resin as the carbon source, and triblock poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide) copolymer F127 (EO₁₀₆PO₇₀EO₁₀₆, Mw = 12,600), or P123 (EO₂₀PO₇₀EO₂₀, Mw = 5800) as the structure-direct agent via the evaporation induced self-assembly (EISA) strategy [33,34]. The phenolic resin precursor was synthesized by a base-catalyzed polymerization of phenol and formaldehyde, as reported by the literatures [35]. Before use, MgSO₄ was used to remove the residual water in phenolic resin.

MCT-87: 1.4g (7.4 mmol) of TiCl₄, 4.2g (12.6 mmol) of Ti(OC₄H₉)₄, 0.68 g of resol solution which contains 0.24 g of phenol, 0.44 g of formaldehyde, and 1.4 g of ethanol were added into a clear solution with 2.0 g of P123 and 30 g of ethanol in sequence

with stirring. An orange red solution was obtained. After 10 min, the mixture was poured into Petri dishes. Then, the dishes were placed in a hood to evaporate ethanol at ambient temperature in air and in an oven to thermopolymerize at 100 °C. Both the treatments took about 24 h. The as-made orange samples were collected and heated at 350 °C for 10 h to remove the triblock copolymer template. Further crystallization for titania was adopted at 550 °C for 30 min in nitrogen atmosphere. The heating rate was 1 °C/min below 350 °C and 5 °C/min above 350 °C. The sample was named as MCT-87 (the number denotes the wt% of titania).

MCT-60, and 40: solution A contains 1.5 g of F127, 1.0 g of deionized water and 8.0 g of ethanol which were stirred at 40 °C for 2 h. Stöber solution B contains 1.92 g(10.1 mmol) of TiCl₄, 0.5 g of deionized water and 7.5 g of ethanol which were stirred at 0 °C for 30 min. Solution A and B were mixed together, and the color turned into orange rapidly. After 30 min, the solution was mixed with 5.0 g of phenolic resol. The mixture was then poured into Petri dishes. The subsequent treatments were exactly the same as those for MCT-87. The calcined product was denoted as MCT-60. Tuning the TiCl₄ mass to 0.83 g (4.4 mmol), and F127 mass to 1.13 g, the final material was denoted as MCT-40.

To remove the free carbon component, the MCT-*n* sample was treated in a muffle oven at $350 \degree$ C for 9 h in air. The resultant white solid TiO₂-*n* was collected.

For comparison, pristine mesoporous carbon (MC) [36] and mesoporous titania (MT) [37] were also synthesized according to literatures (the detailed preparation procedures were described in Supporting Information, SI).

2.2. Characterization

The small-angle X-ray diffraction (XRD) measurements were taken on a Rigaku D/max B diffractometor using Cu Kα radiation (40 kV, 20 mA). The d-spacing values were calculated by the formula of $d = 0.15408/2\sin\theta$, and the unit cell parameters were calculated from the formula of $a_0 = 2d_{100}/\sqrt{3}$. N₂ adsorption–desorption isotherms were measured at 77K with a Quantachrome NOVA 4000e analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BFT}). By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. The micropore volumes (V_m) were calculated from the V-t plot method. The t values were calculated as a function of the relative pressure using the de Boer equation, t $(nm) = [0.1399/(log(p_0/p) + 0.0340)]^{1/2}$. V_m was obtained using the equation of $V_{\rm m}$ (cm³/g) = 0.001547I, where *I* represents the *Y* intercept in the V-t plot. Transmission electron microscopy (TEM) experiments were conduced on a JEOL 2011 microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Energy dispersive X-ray spectroscopy (EDX) was performed on a Philips EDAX instrument. Thermal gravity analysis (TG) curves were monitored on a Mettler Toledo 851e apparatus. The C, H and O contents were measured on a Vario EL III elemental analyze (Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000CESCA system with a base pressure of 10^{-9} Torr. The energy positions of the peaks were calibrated by fixing the position of the C1s peak at 284.6 eV. The diffuse reflectance spectra of the samples over a range of 200-800 nm were recorded by a Varian Cary 300 Scan UV-vis system equipped with a Labsphere diffuse reflectance accessory.

2.3. Catalytic tests

The photocatalytic activity of the mesoporous carbon–titania composites (MCT-n) was characterized by measuring the titania

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