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Carbon sphere templates for TiO_2 hollow structures: Preparation, characterization and photocatalytic activity

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TiO_2 hollow structures (HS) were synthesized by carbon sphere template removal method. Nanometer sized carbon spheres (CS) were prepared by mild hydrothermal treatment of ordinary table sugar (sucrose). The size of these spheres can be controlled by the parameters of the hydrothermal treatment (e.g. time and pH). The obtained CSs were characterized by scanning electron microscopy (SEM), Raman spectroscopy, infrared spectroscopy (IR), X-ray diffraction (XRD) and thermogravimetry (TG). CSs were successfully coated with TiO_2 via sol–gel method. The phase composition of the TiO_2 hollow spheres were controlled by the annealing temperature during crystallization and CSs template removal. TiO_2 hollow structures (HSs) were characterized by SEM, XRD, Raman spectroscopy, TG and energy-dispersive X-ray spectroscopy (EDX). Photocatalytic performance of the TiO_2 HSs was evaluated by phenol degradation in a batch-type foam reactor under low powered UV-A irradiation. The degradation reaction was followed by high-performance liquid chromatography (HPLC) and total organic carbon (TOC) measurement techniques. Photocatalytic activity test results pointed out that increased rutile content up to a certain extent (resulting mixed phase anatase-rutile TiO_2) effects advantageously the photocatalytic performance of TiO_2 HSs and the unique morphology proved to enhance the photocatalytic activity (six times) as well as TOC removal efficiency (twelve times) compared to the sample which was prepared by the same method without the CSs.

1. Introduction

Since the industrial revolution the water pollution gradually became more and more significant, and nowadays it is a burning environmental issue [1,2]. Among the many hazardous water pollutants [3,4], phenol is one of the most studied because it can be originated from both anthropogenic and natural sources [5–7]. The purification of this essential media is imperative. Fortunately, there are already many effective technological and technical solutions to achieve the elimination of various water contaminants. However, there are chemicals which are not removable from water by conventional methods due to their stability and/or toxicity towards microorganisms (e.g. pesticides, antibiotics, pharmaceutical metabolites, etc.). Advanced oxidation processes (AOPs) are effective methods for the neutralization of these persistent contaminants [8]. Heterogeneous photocatalysis is a promising branch of AOP technologies.

Titanium dioxide (TiO_2) is an n-type semiconductor transition metal oxide possessing many advantageous properties to be considered one of the most promising photocatalyst materials [9,10]. It is cheap, photostable, non-toxic and biocompatible. Heterogeneous photocatalysis is a very complex photoinduced process on the surface of semiconductor particles [11–14]. During the photoexcitation of a semiconductor particle with energy equal or greater than its band gap (E_g) an electron is excited to the conduction band (CB) from the valence band (VB) leaving a vacancy (hole; h^+) behind. TiO_2 polymorphs possess inherently different band gap energies ($E_g \sim 3.2$ eV = 388 nm; $E_g \sim 3.0$ eV = 413 nm for anatase and rutile, respectively) [15]. The photogenerated charge carriers (e^- and h^+)

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are capable to migrate to the surface of the particle or being trapped at various sites [13]. If the charge carriers are able to reach the surface they may take part in redox reactions with appropriate donor and acceptor species. In aqueous media, important donor and acceptor molecules are OH^- (H_2O) and dissolved O_2, respectively, and they form highly reactive and oxidative $OH^\bullet$ and $O_2^{\bullet -}$ radicals [16]. The overall photocatalytic activity of a material is dependent of many factors [17]. In most cases, crystal phase composition is determinative regarding the photocatalytic performance. However, mixed phase (particularly anatase-rutile) TiO_2 photocatalysts may possess elevated activities most presumably due to their interfacial interactions [18–24].

There is a tremendous effort in the investigation of carbon (nano)materials since the discovery of fullerenes [25]. Researchers prepared carbon materials with various sizes and shapes (e.g. fibers, onions, horns, (nano)tubes, etc.) [26]. Carbon spheres (CS) are recently regained scientific interest due to their promising application in battery cathodes [27], fuel cells [28] and catalyst supports [29,30]. CSs can be prepared by numerous synthesis techniques: arc-discharge, CVD, hydrothermal method etc. [31]. A convenient route to produce micro- or nanosized CSs is the hydrothermal dehydration and carbonization of different carbohydrates (most commonly glucose) [32,33].

Titanium dioxide hollow spheres can be prepared by using the abovementioned CSs as removable templates. Thus, the diameter of the TiO_2 hollow structures is finely tunable. These objects are interesting not just because there low apparent density [34] but their unique optical properties [35–37]. These attributes can be exploited in either photocatalytic applications or in DSSCs [38]. As mentioned, the most commonly used route to prepare TiO_2 (and other metal oxide) hollow spheres is template removal method [39]. Lv et al. studied the efficiency of surface fluorinated TiO_2 HS prepared via hydrolysis–precipitate method (using sulfonated polystyrene beads as templates) in brilliant red X3B photocatalytic degradation reaction [40]. Ao et al. prepared TiO_2 HSs by precipataion of TiO_2 onto the surface of hydrothermally prepared CSs and demonstrated enhanced photocatalytic activity in photocatalytic decomposition of methylene blue [41].

Herein, we describe the preparation of carbon sphere templates from ordinary table sugar via facile hydrothermal method and their use as templates for TiO_2 hollow structure synthesis. We intended to investigate the effect of various synthesis parameters (time, pH) on the yield and size of the CSs. The CS sample with appropriate size distribution was selected as removable template for the preparation of TiO_2 hollow structures. We have studied the crystal phase composition of the hollow spheres formed during heat treatment at different temperatures and the effect of this parameter on their photocatalytic activity in phenol decomposition reaction.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. During the experiments, Milli-Q water (Millipore, 18.2 MΩ cm) and absolute ethanol was used (VWR Prolabo). *Carbon sphere synthesis*: Ordinary table sugar (sucrose, Magyar Cukor Zrt., Koronás^{TM}) was used as carbon source. The desired pH was adjusted with hydrochloric acid (37 wt%, a.r., Molar) or with sodium hydroxide (50 wt%, a.r., Molar). *TiO_2 hollow structure synthesis*: The titanium precursor was titanium(VI) butoxide (Fluka, ≥97% purum, [Ti(O-$CH_2CH_2CH_2CH_3$)$_4$]). *Photocatalytic test reactions*: The model pollutant was phenol (VWR, extra pure) and during the experiments oxygen gas (Messer, 2.5) was used. Methanol (VWR HiperSolv Chromanorm) was used during the eluent preparation for the HPLC analysis.

2.2. Sample preparation

First, CSs were synthesized via hydrothermal treatment. All hydrothermal experiments were carried out in a preheated drying oven at 180 °C using a Teflon-lined stainless steel autoclave with total volume of 275 cm^3. During each CS preparations, 80 cm^3 of 50 g/dm^3 sucrose solution was treated (V_{fill}/V_{tot} = 29%). The effect of hydrothermal treatment time (3, 6, 12, 18 h) was studied on the resulted product. To investigate the effect of pH, the sucrose solution was adjusted by HCl or NaOH solutions to achieve the desired values (3, 7, 12; for the sake of notation, the unmodified sucrose solution will be considered as pH 7 since sucrose does not inherently change the pH when dissolved in water, thus the pH of this solution is ~7). After the hydrothermal treatment, the autoclave was left to cool to room temperature naturally, then the brownish-black product was collected. The samples were centrifuged (4000 rpm, 20 min) and redispersed in water three times. Then, they were filtered with a membrane filter apparatus (Millipore, Durapore PVDF membrane, 47 mm, 0.1 μm) and washed with hot water, than with three aliquot 5, 15, 45 V/V% ethanol/water mixtures to remove residual organic contaminants. The solid product was dried in air at 70 °C for 18 h. Sample labeling for the CSs will be the following: CS-t-pH, where 't' is the time of hydrothermal treatment, 'pH' is the pH of the starting sucrose solution.

The CS sample with the preferred properties was used as a template for the synthesis of TiO_2 hollow structures. 2 g of the CSs was suspended in 130 cm^3 ethanol via ultrasonication and 0.64 cm^3 water was added to the suspension (named as mixture "A"). 4 cm^3 titanium(IV) butoxide was added to 70 cm^3 absolute ethanol under vigorous stirring (named as mixture "B"). Mixture "B" was added drop by drop (~2 cm^3/min) to mixture "A" under vigorous stirring. The molar ratio was n(Ti):n(H_2O) = 1:3. After the full addition of the two mixtures, it was left to be stirred for 1 h and then it was filtered and washed with 10 cm^3 ethanol three times. The product was dried in air at 70 °C for 18 h. The above described process was repeated three times and the portions were united. The whole coating process was repeated under the same conditions expect that for starting material was the previously coated carbon spheres (instead of pristine CSs) and all precursor, ethanol and water quantities were tripled. Aliquot amount of samples were annealed in a static furnace in air with a heating rate of 5 °C/min for 4 h at 400, 500, 600, 700 °C to remove the CS core and simultaneously convert the amorphous titania phase to crystalline TiO_2. TiO_2 reference sample was prepared via exactly the same method as TiO_2 HSs were, except that during the synthesis procedure CSs were not added. Reference sample was calcinated with heating rate of 5 °C/min for 4 h at 500 °C in air. (Characterization of the reference TiO_2 can be found in Supplementary material.)

2.3. Characterization techniques

The structure and morphology of the prepared samples was investigated with scanning electron microscopy (Hitachi S-4700 Type II FE-SEM). Crystal structure and phase composition was measured with X-ray diffractometry (Rigaku MiniFlex II Diffractometer) using Cu Kα radiation. Thermogravimetric analysis (Netzsch STA 409 PC connected to a Pfeiffer QMS 200 mass spectrometer system) was performed in oxygen flow (40 cm^3/min) with 5 °C/min heating rate using ~100 mg sample. Raman spectrum was taken (Thermo Scientific DXR Raman Microscope) utilizing 532 nm laser irradiation. FT-IR spectrum was taken using a Biorad FTS-60A FT-IR device using an ATR module on an air-dry sample. The concentration of phenol was measured with a HPLC technique (Merch Hitachi sys-