Materials Science and Engineering C 30 (2010) 839–846

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Synthesis, characterizations and photocatalytic studies of mesoporous titania prepared by using four plant skins as templates

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ARTICLE INFO

Article history:
Received 12 June 2009
Received in revised form 11 February 2010
Accepted 23 March 2010
Available online 8 April 2010

Keywords:
Mesoporous titania
Photocatalysis
Degradation of dyes
Biotemplate
Plant skins

ABSTRACT

Anatase mesoporous titania with novel morphologies were synthesized by using the skins of tomatoes, bulb onions, grapes, and garlic bulbs, respectively, as templates and used for the photodegradation of Gentian violet, methyl violet, xylenol orange, and Rhodamine B under UV light. The samples were characterized by a combination of various physicochemical techniques, such as X-ray diffraction, SEM, HRTEM, N_2 adsorption/desorption, diffuse reflectance UV–Vis, and FT-IR. It was found that all of the synthesized mesoporous titania samples exhibited similar morphologies to those of the original templates. The photoactivity of P25 TiO_2 for the four dyes is nearly the same while the mesoporous titania samples synthesized by using the four skins as templates exhibited varied photoactivities for the four dyes.

1. Introduction

Mesoporous titania have attracted considerable attention in recent years because they usually show higher surface areas and much more uniform and controllable pore size and pore morphologies compared with randomly organized forms of nanocrystalline titania [1,2]. The general synthetic strategies for porous titania have been developed by using a variety of templates [3–6]. In the recent several years, biological templates have become a major area of research, because they are generally performed under mild conditions, it is energy-conserving, green, and has little requirement for equipments [7–20]. Moreover, most natural templates and building blocks can be harvested in large amounts at low costs, thus biomorphic assembly is cheap compared with conventional assembly methods to form nanostructures [20]. Up to now, diatoms [7], shell membrane [7], dog and human hair [8], mushroom gills [8], silk fiber [8], spider silk [8], insect wings [9], bacterial cellulose membranes [10], cotton/cloth textile [11], wool [11], living cells [12], paper [13–15], pollen grains [16], skeletal plates [17], and wood [18] were used as biological templates for the syntheses of porous inorganic structures (silicon dioxide, titanium dioxide, copper oxide, aluminum oxide, and iron oxide etc.). In addition, mesoporous titania prepared by using bacterial cellulose membranes as biological template exhibited good photocatalytic activity for photodegrading Rhodamine B under UV light irradiation [10]. Recently, green leaves were applied as biotemplates to synthesize *morph*-TiO_2 which exhibited activities for the degradation of Rhodamine dye under UV and visible-light irradiation [19]. However, synthesis of titania using biological templates methods was still very limited because of high reactivity of titania precursors toward hydrolysis and condensation. Furthermore, the information about the photocatalytic activity of the ordered mesostructured titania was also limited and sometimes contradictive. For example, the amorphous mesoporous titania exhibited a very low photocatalytic activity for the liquid-phase oxidative dehydrogenation of 2-propanol to acetone [21] and a poor photocatalytic performance for sulforhodamine-B dye [22]. By contrast, the photocatalytic activity of the mesoporous anatase titania for the photodecomposition of acetone and ethylene [23,24] under UV light and the visible-light photocatalytic efficiency of the pure and doped anatase mesoporous titania thin films for basic blue have been reported [25]. Therefore, it will be interesting to find out whether the plant skins (membrane of popular vegetables and fruits) can be used as templates to synthesize mesoporous titania. The plant skin, dermal tissue system of plant, consists of epidermis and periderm. It covers the surface of various organs in plants as a protective layer. In addition to a layer of compacted cells, corneous layer and ceraceous layer are usually contained [26]. Furthermore, although the effects of long-chain alkylphosphate and alkylamine surfactant templates on the structure, stability and photocatalytic activity of mesostructured TiO_2 were investigated [27], the effect of other templates, in particular biotemplates, on the photocatalytic activity have not been reported so far.

On the other hand, the effectiveness of titania as a photocatalyst depends on its crystal phase, particle size, crystallinity, and morphology,

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doi:10.1016/j.msec.2010.03.020

and so on. Among the common factors, morphology was regarded as one of the important factors in determining photocatalysis [28–31]. For example, it has been reported that the photocatalytic activity was enhanced by hollow titania spheres with tunable interior structure and urchin-like morphology because of multiple reflections of UV light within the sphere interior voids [31]. Besides, an advantage for chemists is to elaborate possible new constructions from all chemical components without any time-restricted conditions [32]. As a new attempt, we used plant skins templates for preparing titania, with expectations of achieving novel architecture or enhanced properties. Since many natural materials are composed only with ordinary composition but exhibit fascinating property owing to their unique structures [31]. Furthermore, the ability to finely tune the size and architecture of the pores is a key issue in achieving an effective control of the functional properties exhibited by materials [33].

Herein, we report that mesoporous TiO_2 with novel morphologies were synthesized by using the skins of tomato (TT), bulb onion (ON), grape (GP), and garlic bulb (GL), respectively, as templates. More importantly, we also report that the obtained mesoporous TiO_2 samples with different morphologies caused by the different biotemplates exhibited significantly different photocatalytic activities for the photodegradation of dyes under UV light.

2. Experimental section

2.1. Materials

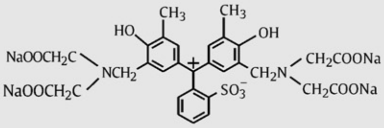
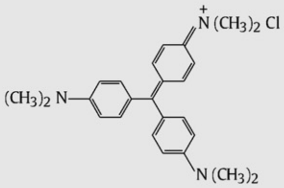
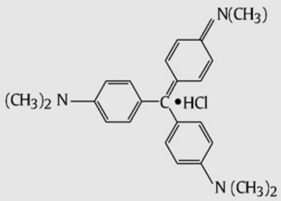
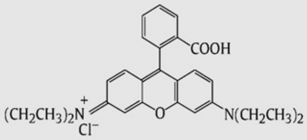
Tomatoes (*Lycopersicum esculentum* Mill.), bulb onion (*Allium fistulosum* L. var.), grapes (*Vitis* spp.), and German red garlic bulbs (*A. saticum* L.) were randomly obtained from a local farmers' market on different dates and the four dyes, gentian violet (GV), methyl violet (MV), xylenol orange (XO), and Rhodamine B (RB) were used without further purification and all of them were of analytical grade. Table 1 shows the structure of these dyes. Other chemical reagents, such as, titanium tertraisopropoxide (TTIP), 2-propanol, HCl were also of analytical grade and used as received.

2.2. Synthesis

Mesoporous titania samples were synthesized by a modified process as described in the literatures [9,10,14] as follows: tomatoes, bulb onion, grapes, and garlic bulbs were gently broken. The outer skins were manually removed. After the skins were rinsed in 1 mol/L HCl to dissolve the inorganic elements for 24 h, the skins were filtered out and washed with distilled water several times until no precipitation occurred when the filtrate met with silver nitrate aqueous solution. Then the skins were rinsed in 2-propanol repeatedly until the skins were completely dehydrated. The dehydrated skins were simply dipped into a closed vessel containing a 5vol.% solution of TTIP in 2-propanol. The samples were shaken in an ultrasonic bath (60 kHz, 320 W) for 30 min to release the air bubbles emanating from the skins and allow the solution containing TTIP to enter the skins more easily, and then placed quietly for 12 h. The above solution was added with 20 mL water. After 2 h the skins were filtered out and washed with distilled water several times. The treated skins were dried in air at room temperature. The materials were then heated to 450 °C in an oven in air to burn off the organics and crystallize titania. After naturally cooling to room temperature, pale yellow products were obtained.

The preparing process we developed combined the advantages of those methods for using biotemplates in the literatures. For example, sonochemical processing has proven to be a useful technique for the duplication of intricate hierarchical structures of biological forms in MnO_2 [9]. Therefore, similar to ref. [9] but different from refs. [10,13–15] in which ultrasonic bath was not used, in this investigation ultrasonic bath was also used. Furthermore, we also modified the sonochemical processing developed in ref. [9] by changing the

Table 1
Description of dyes.

Name of dye	Molecular formulas	Molecular structure	λ_{max} (nm)
Xylenol Orange	$C_{31}H_{28}N_2Na_4O_{13}S$		430
Gentian violet	$C_{25}H_{30}ClN_3$		576
Methyl violet	$C_{24}H_{28}N_3Cl$		578
Rhodamine B	$C_{28}H_{31}ClN_2O_3$		552