



Effect of calcination temperature on physical parameters and photocatalytic activity of mesoporous titania spheres using chitosan/poly(vinyl alcohol) hydrogel beads as a template



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sol-gel method using chitosan/poly(vinyl alcohol) hydrogel beads as a template. Effects of calcination temperature on physical parameters were investigated by X-ray diffraction (XRD), N₂ adsorption-desorption, Fourier transform infrared (FT-IR) spectra, thermogravimetry and differential thermal analyses (TG-DTA), high-resolution transmission electron microscope (HRTEM) and scanning electron microscopy (SEM). The photocatalytic activity of mesoporous titania spheres prepared was also evaluated by photocatalytic degradation of phenol as a model molecule under UV irradiation. With increasing calcination temperature, average crystallite size and pore size increased. In contrast, Brunauer-Emmett-Teller (BET) specific surface areas, porosity and pore volumes steadily decreased. Results of characterization proved that prepared titania spheres with highly organized pores were mesoporous structure. The photocatalytic activity of mesoporous titania spheres calcined at 500 °C was more effective than those calcined at other temperatures, which were attributed to the porous structure, large BET surface area, crystalline, and smaller crystallite size. This work may provide new insights into the preparation of novel mesoporous titania spheres and further practical applications in the treatment of wastewater.

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1. Introduction

To solve increasingly serious problems of water pollution, various novel materials are being applied in the field of environmental pollution control [1–4]. Among all kinds of materials, titanium oxide (TiO₂) is an extremely interesting semi-conductor material due to its excellent properties such as high photocatalytic activity, low cost, environmental friendliness and chemical stability [2,5]. It is well known that effectiveness of titania as a photocatalyst is very sensitive to its crystal phase, particle size, surface area and crystallinity [6–8]. Recently, many research attentions have been focused on the fabrication of mesoporous TiO₂ with high BET surface area and photocatalytic activity [7–11]. Mesoporous titania materials have been reported for applications in photocatalysis,

adsorption, separation, etc. [9,11–14]. However, practical use of such mesoporous titania materials in nano grade presents some drawbacks, such as agglomeration during utility and difficulty in separating and reclaiming them from treated effluent [15].

To overcome above drawbacks, the development of mesoporous TiO₂ microspheres supported in porous frameworks such as structured silica and alumina (Al₂O₃) became a good alternative to extra beneficial properties due to synergistic effects with the porous matrix [16–19]. Additionally, those mesoporous TiO₂ materials obtained by such synthesis method have been defined particle size and suitable mean pore size [19]. However, it is difficult to remove those porous frameworks used in the preparation of mesoporous TiO₂ materials. Chitosan (CS), (1,4)-2-amino-2-deoxy-D-glucosamine, is a natural basic, hydrophilic, nontoxic and biocompatible biopolymer obtained by the alkaline deacetylation of chitin [20]. Moreover, chitosan has good chelating ability with transition metal ions, which makes it possible for its metal ion complexes to be used as precursors to synthesize nanoparticles [3,21–23]. All the above-mentioned properties also make chitosan a very good candidate to design all kinds of functional materials [21,23]. Previous study has revealed that chitosan

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exhibited a multifunctional performance with TiO₂ in heterogeneous photocatalysis technology by enhancing adsorption-photocatalysis [23]. As distinctive intermolecular interactions and formation of hydrogen bonds between poly(vinyl alcohol) (PVA) and chitosan, chitosan/PVA composite has good mechanical property, unique three-dimensional structure, favorable film- and particle-forming property and adjustable pore size, which allows considering chitosan/PVA hydrogel beads as ideal adsorbents for removal of metal ions and organic dye from aqueous solutions [24–29]. Therefore, it also becomes possible that chitosan/PVA hydrogel beads will be used as an alternative template to prepare mesoporous materials. However, to the best of our knowledge, study on the effect of calcination temperature on physical parameters and photocatalytic activity of mesoporous titania microspheres using chitosan/PVA hydrogel beads as a template has not yet been studied.

In this study, mesoporous titania spheres were prepared using chitosan/PVA hydrogel beads as a template. Effects of calcination temperature on physical parameters of mesoporous titania microspheres were studied by using X-ray diffraction (XRD), N₂ adsorption-desorption, Fourier transform infrared (FT-IR) spectra, high-resolution transmission electron microscope (HRTEM) and scanning electron microscopy (SEM). The photocatalytic activity of mesoporous titania spheres was also evaluated by photocatalytic degradation of phenol as a probe pollutant under UV irradiation. This work may provide a new insight into preparation of novel mesoporous titania spheres.

2. Experimental

2.1. Chemicals and materials

Titanium dioxide (P25) with purity of at least 99.5% was obtained from Degussa. A commercial anatase TiO₂ (a-TiO₂, purity >99.7%) was purchased from Xiamen Micaren Technology Co., Ltd. (Xiamen, China). Chitosan with 91% of deacetylation degree prepared from shrimp shell was purchased from Yuhuan Ocean Biochemical Co., Ltd. (Zhejiang, China). Titanium isopropoxide (reagent grade, 98%) was purchased from Aladdin Industrial Co., Ltd (Shanghai, China). Poly(vinyl alcohol) (98% hydrolyzed, average molecular weight 105,000) purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) was of analytical reagent grade. Other chemical agents used were all analytical grade and all solutions were prepared with double distilled water.

2.2. Preparation of mesoporous titania spheres

A formation scheme of mesoporous titania spheres using chitosan/PVA hydrogel beads as a template is presented in Fig. 1. Firstly, chitosan/PVA hydrogel beads were prepared by an instantaneous gelation method [29]. Two grams of chitosan was dissolved into 50 mL of 5% (v/v) aqueous acetic acid to obtain a chitosan solution. Two grams of PVA was dissolved in 50 mL of double distilled water to form PVA aqueous solution under mechanical stirring at 70 ± 1 °C. Then, PVA solution was mixed homogeneously with chitosan solution to form composite gel-forming mixture with vigorous stirring for 3.0 h at 30 °C. The resulting mixture was dropped into sodium hydroxide bath (500 mL, 0.5 M) through a 0.8 mm internal diameter syringe needle, forming chitosan/PVA hydrogel beads. The hydrogel beads were kept overnight in sodium hydroxide solution for complete solidifying, and then washed with double distilled water, ethanol and isopropyl alcohol to obtain swollen chitosan/PVA hydrogel beads, respectively.

Swollen chitosan/PVA hydrogel beads were soaked in the 98% titanium isopropoxide solution for 48 h at room temperature under

closed conditions. Titanium isopropoxide molecules diffused slowly into swollen chitosan/PVA hydrogel matrix. Then, hydrogel beads with titanium isopropoxide were immersed into excess water for 24 h to cause the hydrolysis and condensation of titanium isopropoxide to take place in the chitosan/PVA polymer matrix. The resultant spheres were washed with double distilled water to remove titanium hydroxide deposited on the surface of these spheres. Finally, the spheres were dried in the oven at 60 °C till constant weight. Uncalcinated titania spheres prepared in the above-described method were labeled as UTS. Following the drying process, the samples were calcined under 400, 500, 600, or 700 °C for 4 h in air at a heating rate of 1 °C/min, respectively. During calcination, the polymeric template was burnt off, and the inorganic precursor crystallized, forming inorganic spheres of mesoporous titania spheres [30]. Calcined titania spheres were labeled as CTS-400, CTS-500, CTS-600 and CTS-700 according to different calcination temperature, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using Cu K α irradiation (0.1540 nm) in a 2 θ range of 5–75°. Thermogravimetric (TG) curves were performed on Model STA 409 PC Luxx at a heating rate of 10 °C/min. Nitrogen adsorption-desorption isotherms were carried out on a Micromeritics ASAP2020 apparatus at 77 K. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) measurements were performed on a Hitachi S-4800 and JEOL JEM-2010, respectively. FT-IR spectra were measured at room temperature on a FT-IR-8400 spectrometer (Shimadzu, Japan).

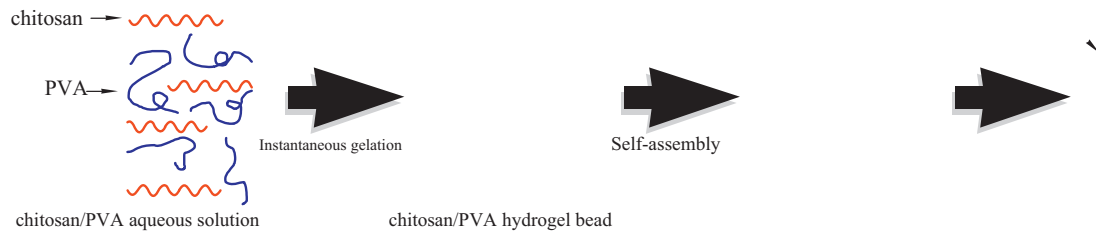
2.4. Photocatalytic activity measurements

Photocatalytic experiments were carried out in a Pyrex-glass reactor (inner diameter: 29 mm and height: 9.1 mm), thermostated at 25 °C with a water jacket. An aqueous suspension (50 mL) containing 0.43 mM phenol and 1.0 g/L photocatalyst was first stirred in dark for 1 h to attain adsorption-desorption equilibrium and then irradiated with a high pressure mercury lamp (300 W, Shanghai Mengya) with a 320 nm cutoff filter. The distance between the reactor and the lamp was fixed at 10 cm. The light intensity reaching external surface of the reactor was 1.41 mW/cm², as measured by an UV-irradiance meter (UV-A, Instruments of Beijing Normal University, China). At given intervals, 2.5 mL of suspension was withdrawn by a microsyringe and filtered through a mephenol-rane (0.22 μ m in pore size). Organic substrates were analyzed by high-performance liquid chromatography (HPLC) on a Dionex P680 (Apollo C18 reverse column, and 50% CH₃OH aqueous solution as an eluent).

3. Results and discussion

3.1. Optical photographs

Fig. 2 displays typical optical photographs of chitosan/PVA hydrogel beads, UTS and CTS-500. Transparent chitosan/PVA hydrogel beads and white UTS are spherical with a diameter of ca. 3–4 mm as shown in Fig. 2a and b. Fig. 2c indicates that calcined titania spheres (UTS-500) have a little bit poor sphericity. At the same time, average out diameter of UTS-500 was decreased from 3–4 mm to 1.5–2 mm, which resulted from a shrinking from original size during calcination [19]. The result is in a good agreement with the fact that surface area and pore volume decreased significantly after calcination.



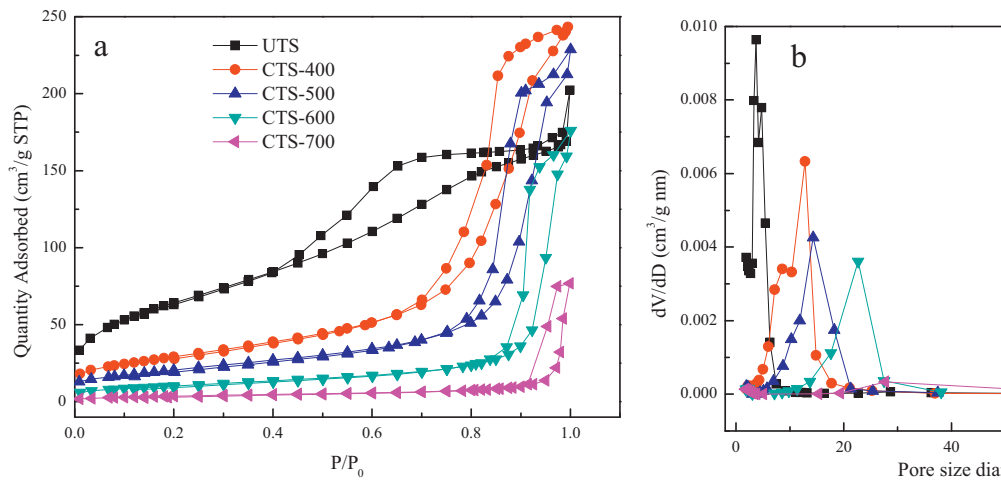


Fig. 4. N_2 adsorption–desorption isotherms (a) and pore size distribution curves (b) of (a) UTS, CTS-400, CTS-500,

a much lower surface area ($13.39\text{ m}^2/\text{g}$). As reported in literature, this is caused by a collapse of pore structure of the system of particle size [18]. It is clear that corresponding pore volumes of CTS-400 and CTS-500 are greater than UTS, indicating that chitosan/PVA template was removed gradually from those materials. However, when calcination temperature increase further from 500 to 700°C , pore volume of CTS decreased obviously from 0.354 to $0.119\text{ cm}^3/\text{g}$. On the other

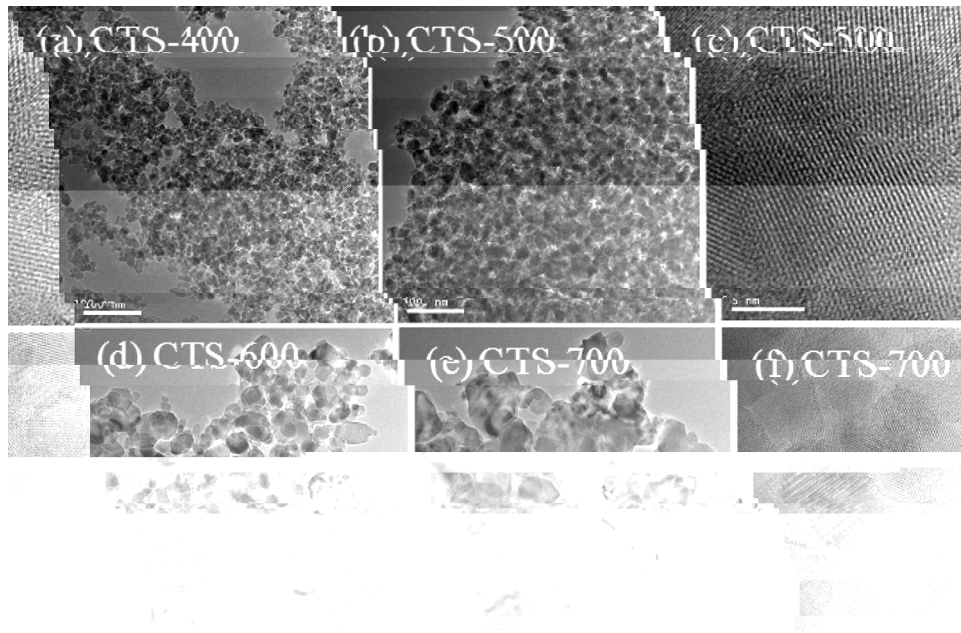


Fig. 5. The TEM patterns of samples: (a) CTS-400, (b and c), CTS-500, (d) CTS-600 and (e and f) CTS-700.

C–O vibrational stretching [26]. The absorption peak at 1629 cm^{-1} was assigned to N–H bending vibration in amine groups of chitosan [38]. In FT-IR spectrum of as-synthesized UTS, C–C stretching (1074 cm^{-1}) of PVA is also found [39]. After calcination, two absorption peaks at 1629 and 1074 cm^{-1} weakened and disappeared. Additionally, compared with FT-IR spectrum of uncalcined sample (Fig. 7a), the absorption peak at 3400 cm^{-1} disappeared in FT-IR spectra of calcined titania spheres. This phenomenon has proven that calcined titania spheres possess less surface hydroxyl content, which resulted from the fact that chitosan/PVA template

was removed gradually from those materials. However, all calcined titania spheres display a strong absorption peak around 500 cm^{-1} attributed to Ti–O–Ti lattice vibrations [39], indicating that the crystallization of mesoporous titania appeared and was enhanced.

3.6. TG-DSC investigation

To determine calcined temperature at which chitosan/PVA template was removed and inorganic phase began to crystallized, thermogravimetric and differential thermal analysis was

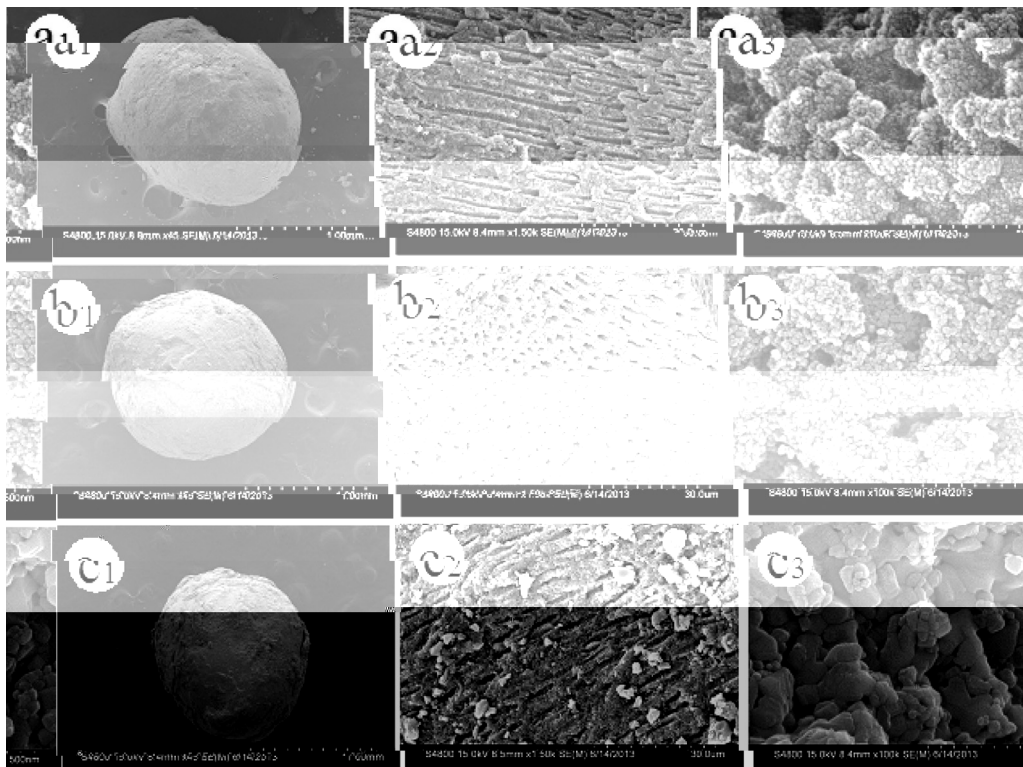
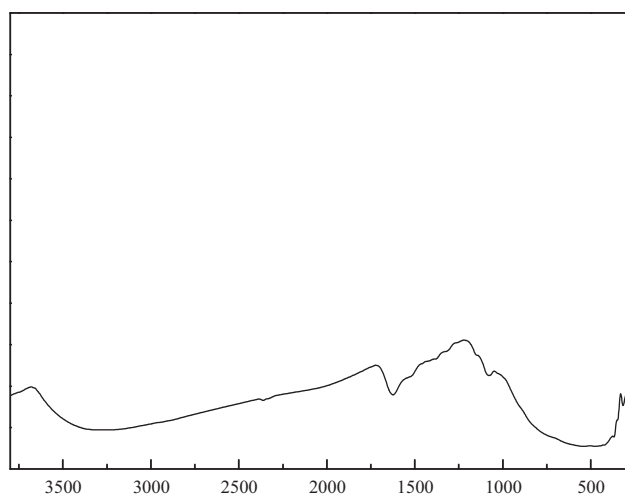


Fig. 6.



4. Conclusions

Mesoporous titania spheres using chitosan and PVA hydrogel beads as template have been successfully synthesized. Nitrogen adsorption–desorption isotherm measurement, XRD, FT-IR, SEM and TEM have been used to characterize the mesoporous titania spheres. With increasing calcination temperature, the average crystallite size and average pore size increased while the Brunauer–Emmett–Teller (BET) specific surface areas, porosity and pore volumes steadily decreased. Results of characterization proved that prepared titania spheres were mesoporous structure. The photocatalytic activity of the mesoporous titania spheres calcined at 500 °C was more effective than those calcined at other temperatures, which were attributed to the porous structure, larger BET surface area, higher crystalline, and smaller crystallite size.

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