

PREPARATION OF MACROPOROUS TiO₂ BY STARCH MICROSPHERES TEMPLATE WITH ASSISTANCE OF SUPERCRITICAL CO₂

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In this work a green route is reported to prepare a TiO₂ macroporous network using corn starch microspheres flake as a bio-template. The starch microspheres prepared by emulsion technology were used as a template into which precursor tetrabutyl titanate (TBOT) was permeated using supercritical carbon dioxide (scCO₂) as a forceful carrier or infiltration media, resulting in the formation of an organic/inorganic hybrid material; then the coated template was gelled and dried during the scCO₂-coating and the depressurization processes, followed by removal of the template by calcination at 700°C; finally, TiO₂ inverse-opals-like material reversely replicating the starch microspheres template was obtained. Scanning electron microscopy (SEM), nitrogen sorption measurements, and X-ray diffraction (XRD) indicated that the products were the inverse replicas from their templates. The obtained TiO₂ inverse opals-like material showed a wide dispersion of pore sizes from mesopores to macropores – a few nanometers to several micrometers – with the BET surface area up to 103 m²/g, and a predominantly anatase crystalline phase. In addition, the wall thickness of the macropores varied with tunable pressure for closed cells or open-cell foams. So this facile and environmentally friendly process for the preparation of high-surface area, thermally-stable, metal-oxide catalysts and supports by a starch microsphere templating approach may have widespread potential applications in catalysis, absorbents, photoelectric materials, and so on.

Keywords: Supercritical carbon dioxide; Porous; Titania; Starch microsphere

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INTRODUCTION

Because of their large surface area, controllable pore structure, as well as high stability and operational convenience, porous materials have found a number of applications, including HPLC separation, catalysis, fuel cell electrode materials, biomaterials engineering, controlled drug delivery devices, and membrane reactors, etc. Incorporation of macropores in mesoporous materials combines benefits from both the mesoporous and macroporous structures. Hierarchical materials containing both interconnected macroporous and mesoporous structures have enhanced properties compared

with single-sized pore materials due to increased mass transport through the material and maintainance of a specific surface area on the level of fine pore systems. Bimodal mesoporous–macroporous inorganic materials can be prepared by using a self-assembling surfactant or amphiphilic block copolymer species in conjunction with macrotemplates such as colloidal crystals, polymer foams, bio-celluloses, emulsions, inorganic salts and ice crystals, or by macroscopic phase separations (Yuan and Su 2006). In addition, bimodal porous materials having controllability of the thickness or interior surface characteristics of pore walls may have more extensive potential in the improvement of functional and mechanical properties for further industrial application.

Typical silica and polystyrene nano- or micron-particles ordered gel templates are attaining wider application for ordered porous materials, e.g. derivative three-dimensional ordered microscopic pores (Velev et al. 2000; Xia et al. 2000) or balls (Jiang et al. 2001) from the first- or second-generation of template. However, the templating method is now also facing problems of the economic cost and environmental protection for preparing such templates as well as a challenge to achieve the needed structural variety or complexity of substrates that can be used as the guiding templates. Starch, a natural biomaterial, is easily available and environmentally friendly, but it has not gained enough applications in the synthesis of advanced materials, probably owing to the relatively difficult control of its structure and morphology. Therefore, it is of great importance to develop novel techniques that shape starch into ordered morphologies for further utilization, e.g. ordered templates for a second generation of ordered materials.

As we know, the potential of aerogels for catalysis resides in their unique morphological and chemical properties. But the conventional preparation methods require expensive organic solvents, resulting in serious environmental problems. Conventional methods also can be very energy intensive, particularly in the drying steps (Cabanas 2005a,b). Also, better properties originating from their wet-chemical preparation via the sol-gel method and the subsequent removal of solvent by supercritical drying have been demonstrated (Schneider and Baiker 1997).

Supercritical fluids (SCFs) are attracting more and more attention in the synthesis of advanced organic or inorganic materials. Supercritical carbon dioxide (scCO₂) is by far the most frequently used SCF because it is cheap, nontoxic, nonflammable, and has relatively low critical temperature and pressure ($T_c=31^\circ\text{C}$, $P_c=73.8$ bar), making it an ideal choice for the replacement of organic solvents. The scCO₂, acting as a forceful and excellent infiltration media and mass carrier for nano-sized interspace, combined with the templating method, has been fast-developed as a novel green media for the preparation of ordered materials, e.g. linear, porous, 3D-networks, and positive or negative ones, and one typical route is that for faithfully and precisely replicating the structures of natural or man-made templates such as cotton, pollen, fiber (Miao et al. 2007; Wang et al. 2005), bamboo membrane (Li et al. 2007), wood cell (Ni et al. 2008a,b), starch (Miao 2008), and swim bladder membrane (Miao et al. 2007) as bio-templates, and polymer or surfactant, e.g. PS microspheres (Cabanas 2005a,b), PEG (Jiao et al. 2007), for aerogel inverse-opals or ordered macroporous materials, which excelled over the traditional methods in some respects.

Titanium dioxide is one of the most investigated oxide materials, owing to its technological importance. Originally, TiO₂ became widely used as a white pigment for

paints, drugs, and cosmetics. Since the 1970s it has many important applications in diverse areas, such as water purification, photocatalysis, and gas sensing. Mesoporous TiO₂ gels are attractive for their potential application to photocatalysts and electrodes for wet solar cells (Doong et al. 2007), and light-harvesting macroporous channels have been successfully incorporated into a mesoporous TiO₂ framework to increase its photocatalytic activity (Wang et al. 2005).

Porous titania can be obtained by various wet chemical methods, e.g., the sol–gel method and direct deposition from aqueous solutions (Doong et al. 2007); and porous TiO₂ assemblages of various shapes were prepared using different materials as templates, such as fibrils, tubules, or microcoils obtained using porous alumina membranes (Lakshmi et al. 1997; Sun et al. 2003), carbon nanotubes (Sun et al. 2003), or carbon microcoil templates (Motojima et al. 2003), “coral-like” TiO₂ network produced using polymer gel templating procedure (Caruso et al. 1998), honeycomb structure prepared using latex spheres as templates (Holland et al. 1998), the synthesis of TiO₂ porous films by polyethylene glycol templating (Bu et al. 2005), cellulose acetate filter membranes (Caruso and Schattka 2000), or natural cellulosic substances (Shigapov et al. 2001) used to produce porous TiO₂ replicas, nanoporous TiO₂ using activated carbon fibers as template with supercritical fluids solvents by using a nanoscaled casting process (Wakayama et al. 2001), and recently the synthesis of TiO₂ using exfoliated graphite as a template and the synthesis of titanium dioxide particles anchored on carbon fibers by chemical vapor deposition (Rodriguez et al. 2007). Amongst such products, the aerogels, i.e., supercritically dried gels, are well known as highly porous materials (Doong et al. 2007).

In this work, corn starch microspheres as-prepared by emulsion technology were used as template into which the precursor tetrabutyl titanate (TBOT) was dissolved and permeated through a supercritical media, followed by the gelation and removal of the template by calcination, and TiO₂ porous material reversely replicating the template was achieved.

EXPERIMENTAL

Materials and Equipment

Corn starch powder was bought from Shandong Linghua Co., Ltd. Tetrabutyl titanate (TBOT, C₁₆H₃₆O₄Ti), sodium dodecyl-benzene-sulfonate (SDBS) and n-butanol were supplied by Tianjin Chemical Co., Ltd. CO₂ with purity of 99.9% was provided by Zhengzhou Shuangyang gas company. All chemicals were of A.R. degree and used as received.

The SCF system with the main components of single-cylinder injection pump (DB-80), high-pressure reactor (50 ml, stainless steel), flow controller and thermostat, was provided by Beijing Satellite factory and Jiangsu Hai'an petrolic scientific instruments factory. Muffle furnace with the temperature range up to 1200°C was from Shenyang energy-saving electric furnace factory.

TiO₂ Prepared from Carbohydrate Biomaterial: The Templating Process

In general, the template method is technically simple and consists of two principal steps: (i) deposition of a precursor by liquid (including SCF) or gaseous process on a templating material; (ii) elimination of the substrate, e.g. by calcination, plasma, or ionic etching. The obtained replica keeps the initial template morphology. The heating rate during calcination affects the surface area; a rapid temperature ramp is favorable to obtain a high-surface area and thermally stable material. (Wakayama et al. 2001).

Preparation of starch microspheres template

The typical process to prepare a starch microsphere template was as follows: 1.5 wt.% SDBS solution (4.5 g SDBS in 300 ml pure water) was first prepared. Subsequently, 15 g corn starch was slowly added to the solution with the fast stirring for ca. 1 h to get a homogeneous dispersion, after which 12 ml n-BuOH was added in order to increase the stability of the starch dispersion, followed by slowly stirring for ca. 0.5 h. Afterwards, the dispersion was filtered under vacuum and the obtained damp cake-like sample was cut into square pieces (e.g. 8×8×2 mm³), and then sealed under cold storage, waiting for further use.

Synthesis of TiO₂ reverse-opals-like material via starch microspheres template

The as-prepared starch piece was used as a sample for the nano-coating in scCO₂. Nano-coating was performed in a 50 ml stainless-steel high-pressure reactor, at the bottom of which 5 ml TBOT precursor and a small magnetic stirrer were placed. The starch piece loaded on a perforated stainless-steel cage was placed at the top of the reactor to prevent it from contacting the liquid precursor. Then the sealed autoclave was charged with CO₂ to a pre-determined condition (e.g. 40°C, 20 MPa), and stirring was started at the same time. The reaction process was kept for some period (e.g. 8 h), during which TBOT molecules were carried into the template and reacted with the water or/and hydrophilic groups on the surface or near-surface of the spherical templates. Subsequently, slow depressurization of CO₂ was carried out, and TiO₂/starch hybrid was obtained. Then the hybrid was taken out and transferred into the muffle furnace at 700°C for 4 h to remove the starch template, and the porous, but with the reversed micro-spherical morphology, structural material was thus achieved.

Characterization

The morphology of the products was observed by scanning electron microscopy (SEM) using a FEI Quanta-200 electron microscope. The crystalline structure of the product was characterized by a RIGAKUD MAX-III wide angle X-ray diffraction (WAXD) apparatus, scanned with a CuK α -ray and with the wavelength of 1.54 Å, at a rate of 6°/min in the range of 10°–70°. The N₂ adsorption and desorption isotherms at 77 K were collected on a Quantachrome NOVA 1000e surface energy and pore size analysis instrument to determine the surface and cavity characteristics, the diameter of the mesopores, and its distribution. BET surface areas were determined from measurements at six relative pressures of nitrogen in the range of 0.05–0.35. Pore-size distributions were determined from isotherms according to the BJH method. Prior to the measurements, the samples were outgassed at 100°C for 1 h under vacuum.

RESULTS AND DISCUSSION

Microstructure of the Product

The starch colloidal microspheres template obtained by dispersion technology and its derived material – porous titanium dioxide – are exhibited in Fig. 1. Part (a) of the figure shows a representative image of the starch microspheres. All the as-obtained gels presented a near-spherical structure with the diameter ranging from 5 to 15 μm . The anionic surfactant SDBS was used in the dispersion for smoothing the starch granules and preventing the agglomeration among them in the final solid state.

Figure 1(b) shows a typical SEM image of porous TiO_2 . It can be observed that the derived product appeared as enlarged reverse-opal-like structures that faithfully maintained the porous structures contrary to those of starch microspheres. This is attributed to the unique properties, e.g. powerful infiltration and low surface tension of the supercritical solution. In the CO_2 -assisted sol-gel process, the precursor diffused onto the fine surfaces or near-surface cavities of starch microspheres and the interspaces between starch microspheres, with the aid of scCO_2 , and then reacted with the adsorbed water and/or hydroxyl groups on the starch microspheres to form a dense coating, resulting in the starch/ TiO_2 hybrids. After calcination at 700°C for 4 h, the starch gel template was removed and simultaneously the crystallization of amorphous titania to anatase crystallites occurred. As in the case of similar mechanism we have investigated, the concept of ‘reverse replication’ (see earlier article Ni et al. 2008b), TiO_2 porous materials inversely replicated the microspheres template with a smoother inner-surface, and relatively narrow distribution of the micron-sized pores 2–5 μm . But, clearly, the pore size of the TiO_2 product shrank a lot (~ 0.8) compared to that of starch microspheres, which resulted in a larger hole density. Moreover, the derived inorganic samples showed a bimodal distribution of pore sizes, which was inherited from the characteristics of the starch granules template by our preparation route.

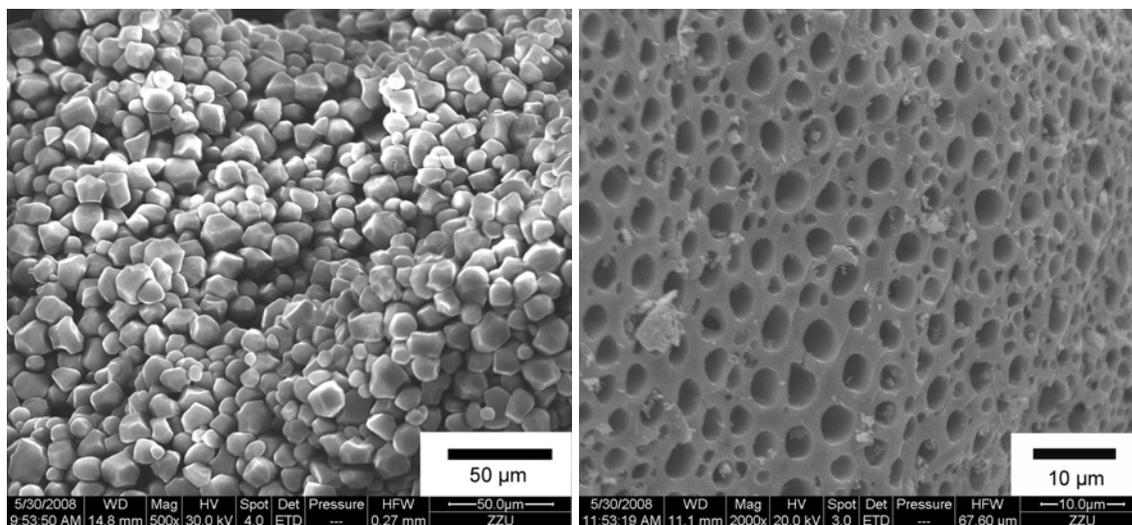


Fig. 1. SEM photos of (a, left) starch colloidal microspheres template prepared by emulsification and (b, right) the derivative TiO_2 porous material coated in scCO_2 at 24 MPa, 40°C for 8 h

Though it has been found that the morphology of as-prepared porous products could be manipulated by varying the conditions of sol-gel process, in the SCF case the effect of pressure was mainly investigated. Figure 2 shows SEM photos of TiO₂ porous materials from coating in scCO₂ at different pressures. From these images it can be concluded that the pressure may have a significant impact on the pore morphology of the products at a suitable temperature. As the pressure increased from 20 MPa to 28 MPa, the products showed properties of thinner pore walls, increased hole density, better connectivity, and higher surface area (also revealed in the N₂ sorption analysis below).

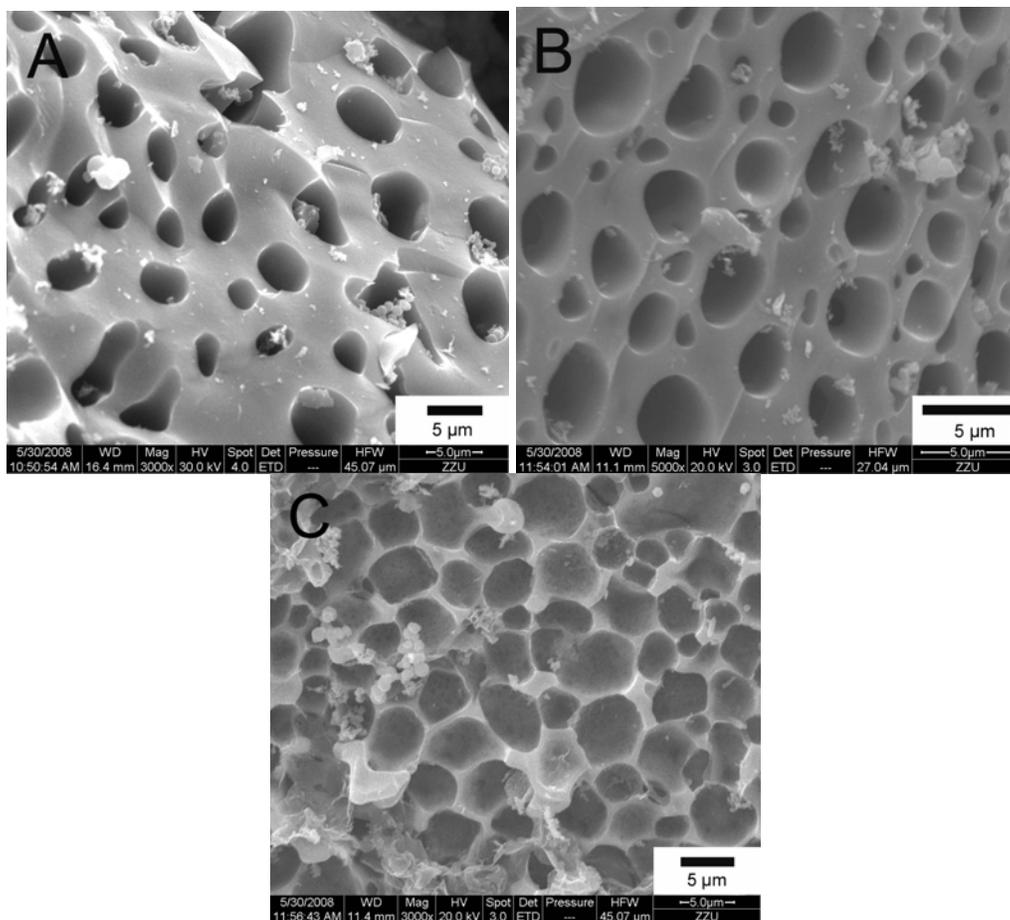


Fig. 2. SEM photos of TiO₂ porous materials coated in scCO₂ at 40°C, and pressures of (a) 20 MPa, (b) 24 MPa, and (c) 28 MPa, respectively

Such phenomenon might partly be intuitively illustrated with the following mechanistic diagram (Fig. 3). The scCO₂ has a plasticization/swelling, and even foaming effects on the polymeric matrices (Cooper 2000; Nalawade et al. 2006; Singh et al. 1996; Alavi et al. 2003); with the higher pressure and density, the scCO₂ plasticized the polymer more deeply and swelled it, the starch microspheres in this case, for a greater dilatation in volume. Thus a larger pore-size was obtained. Meanwhile, the subsequent process to remove starch template further condensed the sol/gel or some metal precursor, and crystallization and agglomeration of nanostructures occurred at the same time, which resulted in the volumetric shrinkage and so forming a higher density of pores.

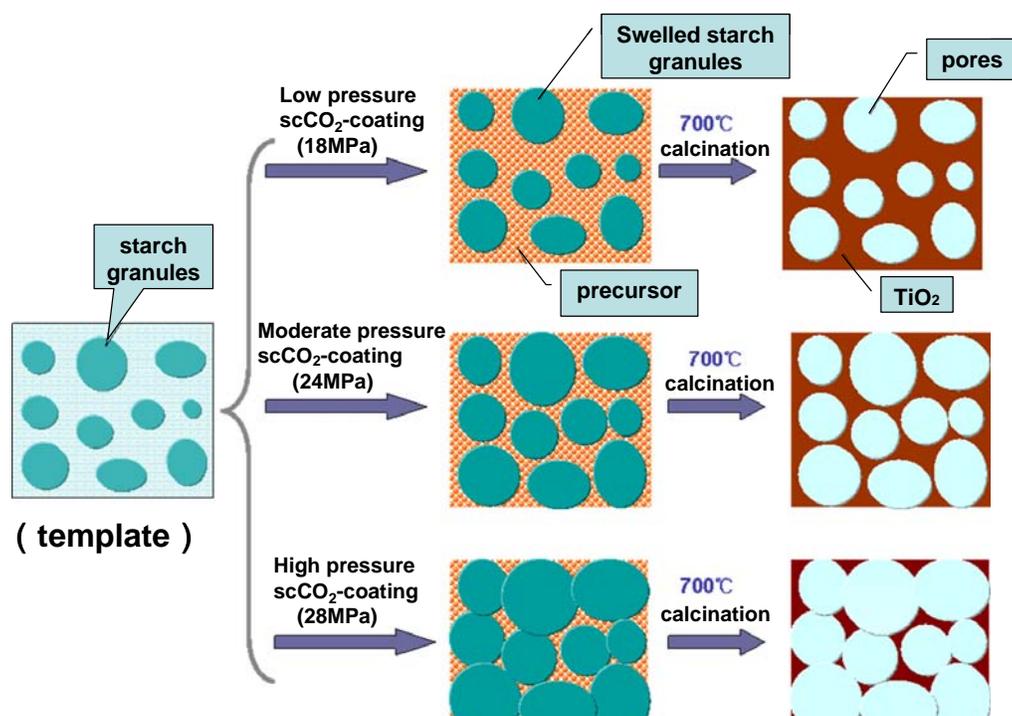


Fig. 3. Partial illustration of principle for effects of the CO₂ pressure on the morphology of pores in TiO₂ products

N₂ adsorption-desorption analysis

The typical N₂ adsorption-desorption isotherms of the as-prepared porous TiO₂ sample by scCO₂-coating route exhibited a hysteresis loop, indicating the mesoporous structure of the TiO₂ samples. Analysis of the ad- and de-sorption branches of the isotherm using BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods for a cylindrical pore model gave the pore structure data listed in Table 1. It could be revealed that the surface area, 59–103 m²/g, and total pore volume, 1.8–2.5 × 10⁻² ml/g, of porous TiO₂ samples increased with the increase of the scCO₂-coating pressure, 18–28 MPa, at a fixed temperature, which may be attributed to the increasing of swelling effect on starch template and the stronger permeation power of precursor into the template. The corresponding pore size distribution calculated from the as-prepared porous TiO₂ sample by scCO₂-coating route at 24 MPa, 40°C showed that it had a mean mesoporous diameter of 8.5 nm.

Table 1. Porous Structure Data of TiO₂ Samples

Sample	Coating Pressure (MPa)	BET Surface Area (m ² ·g ⁻¹)	Total Pore Volume (10 ⁻² ml·g ⁻¹)
1	18	59.4	1.8
2	20	78.7	2.0
3	24	91.4	2.3
4	28	103.0	2.5

Note: all samples were obtained by scCO₂-coating at 40°C for 8h at a series of pressures, and calcination in air at 700°C for 4 h.

The following reasons might be responsible for the above-mentioned phenomena. Starch microspheres may have a microscopically coarse surface morphology, and a rough and porous surface has been stated to be a property of “high quality” starch microspheres (Elfstrand et al. 2006). With the help of scCO_2 , the precursor diffused not only onto the surface, but also into the near-surface of the starch microspheres, thus, the sol-gel reactions took place simultaneously on the surface and in the near-surface layer of the microspheres. As a consequence, often higher solvent or permeation power at higher pressures gave a larger surface area in the porous products.

XRD Analysis

Using the X-ray structural analysis method, the crystal structure of pure TiO_2 powders has been investigated. The typical X-ray diffraction pattern of these samples is presented in Fig. 4, which was prepared through scCO_2 -coating route at 24 MPa, 40°C for 8 h, followed by calcination at 700°C for 4 h in dry air. The diffraction of porous TiO_2 obtained at 700°C is characteristic of a well crystallized material. These results confirmed that after complete elimination of the starch substrate by calcination under air at 700°C for 4 h, the recovered white powder was well crystallized. The resulting material was composed of a mixture of mainly the anatase form of TiO_2 (JCPDS No. 21-1272; Miao et al. 2008; Kim et al. 2007) and also some rutile as hybrid-phase (Rodriguez et al. 2007). The two observed peaks were attributed to the main peaks of anatase ($2\theta=25.3^\circ$) and rutile ($2\theta=27.7^\circ$). It can be interpreted that crystallization of the amorphous titania in the hybrids to anatase crystallites occurred, but with the removal of the starch gels template during the calcination process. A trace of rutile TiO_2 served as a hybrid-phase also coexisted in the product.

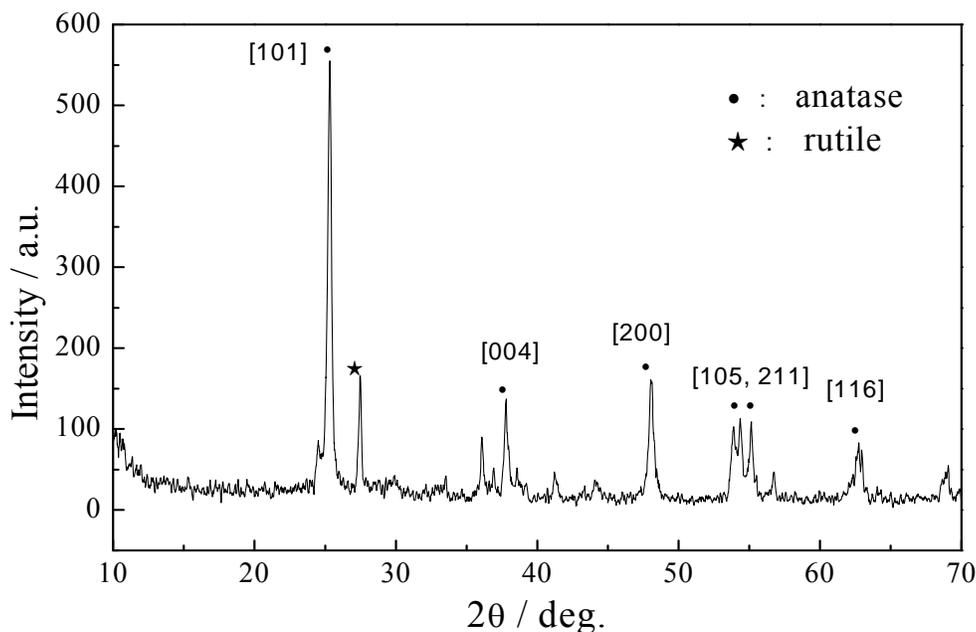


Fig. 4. Powder XRD pattern of TiO_2 porous material obtained by calcination at 700°C for 4 h.

CONCLUSIONS

A novel green and practical route for the fabrication of three-dimensional interconnected macroporous inorganic material, TiO₂, using solvent-free supercritical carbon dioxide (scCO₂) technology combined with colloidal starch microspheres templating approach was presented. The results showed that the as-prepared products were mesoporous-macroporous materials, having an extraordinarily broad pore size distribution range from 2 nm to 5 μm, and anatase crystals were revealed to be the predominant solid phase.

Due to the utilization of scCO₂ acting as a forceful and excellent carrier or infiltration media for micro- or nano-sized interspace, the products have inversely replicated the structure and morphology of templates faithfully and precisely. These as-prepared porous the porous TiO₂ materials, which may be of shapes of membrane, massive block, microsphere, or power, with the extraordinarily broad pore size distribution may find promising applications in highly effective and selective catalysis (including photocatalysis, photolysis), absorbent or separation, gas sensors, optoelectronic devices, and more extensive potential applications in the improvement of functional and mechanical properties and further industrial applications. These developed processes can be easily adapted to the synthesis of others oxides, e.g. Al₂O₃, ZrO₂, CeO₂, etc.

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