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Review Article

Synthesis and properties of ordered mesoporous TiO_2 and their composites

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ABSTRACT

Ordered mesoporous TiO_2 and their composites have many potential applications in the fields of photocatalysis, solar-cells, and so on, due to their special microstructures. The synthesized methods of ordered mesoporous TiO_2 were classified systematically in this paper. The synthesized approaches, development history, classification and application of mesoporous TiO_2 and their composites are reviewed. Some important progress and research results are also summarized. Based on the present existing problems, the development trend is discussed.

Keywords: Mesoporous TiO_2; Composite; Photocatalysis

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1. Introduction

Since highly ordered mesoporous SiO_2 MCM-41 was synthesized for the first time by scientists of Mobil company in 1992, ordered mesoporous TiO_2 has been widely used in photocatalysis, solar cells and other fields because of its well-developed and ordered pore structure, large specific surface area, high porosity and narrow pore size distribution. It has become one of the research hotspots at home and abroad[1–4]. Mesoporous TiO_2 has experienced the process from disorder to order, from small pore sizes to large pore sizes, and from low thermal stability to high thermal stability, achieving great progress and showing high photocatalytic activity[4–6]. However, the separation efficiency of photogenerated carriers of pure mesoporous TiO_2 is still low and can only absorb ultraviolet light and has low utilization of light. Thus, further application is greatly limited[5–8]. Constructing mesoporous composites has become an effective way to solve these problems, which can not only improve the separation efficiency of photogenerated carriers, but also can expand the light response range to the visible light region and improve the utilization of sunlight[9–11]. Because this new type of composite materials has the interaction at the pore heterogeneous material interface, it has the characteristics that nanoparticles and bulk materials do not have. It greatly expands the application of mesoporous TiO_2 in optical and electrical fields[10–12]. This paper reviews the new progress in the synthesis and classification of ordered mesoporous TiO_2 and its composites in recent years.

2. Synthesis of ordered mesopore TiO_2

2.1 Ordered mesopore TiO_2 being synthesized by the soft-template method

Ordered mesoporous TiO_2 is usually synthesized by template methods. This method can design the template according to the size and structure of the synthetic material in advance. The size, morphology and structure of synthetic materials can also be regulated based on the spatial confinement of template and the regulation of template. Template methods can be divided into the soft-template method and the hard-template method according to the characteristics of templates and the difference of the domain limiting ability. The soft-template method usually takes surfactants as structural molding agents (templates). They are organic molecules or super molecules with "soft" structure including ionic surfactants (quaternary ammonium salts, alkyl phosphates, etc.) and non-ionic surfactants (amine molecules with different chain lengths, block copolymers, etc.). Using sol-gel, emulsification and other chemical processes, interaction between surfactant and inorganic precursor, the mesoscopic structure is assembled through the interaction of organic-inorganic interface. After removing the template, mesoporous materials with different structures are obtained[13–15]. Among various surfactant templates, block copolymers have attracted much attention because they can form a variety of morphologies by themselves. Ordered mesoporous materials with various morphologies can be obtained by using block copolymer as templates. This is also one of the advantages of using the soft-template method[16]. Therefore, the self-assembly of soft matter is an important means of forming a highly ordered mesoscopic structure. Self-assembly allows the material to be designed and controllable during synthesis and it has become the cornerstone of synthetic ordered mesoscopic structures[14–16].

At present, orderly mesoscopic TiO_2 materials of different structures have been prepared by using the soft-template method. Wu *et al.* used amphiphilic triblock polymer $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H(EO_{20}\text{-}PO_{70}\text{-}EO_{20}$, P^{123}) as soft templates to prepare highly ordered three-dimensional hexagonal mesoporous TiO_2 films[17]. Crepaldi *et al.* used block copolymer as soft templates to prepare two-dimensional hexagonal and three-dimensional cubic highly ordered mesoporous TiO_2 films and discussed the formation mechanism in detail[18]. Shibata *et al.* used the cationic surfactant cetyltrimethylammonium bromide (C^{16}TAB) as the soft template and $TiOSO_4$ as an inorganic precursor to prepare hexagonal ordered mesoporous TiO_2 particles with crystalline pore walls successfully, and the ordered mesoporous structure can be stabilized to 450 °C[19]. Professor Zhao Dongyuan and professor Huang Chunhui took P^{123} as the soft template and ethanol as the solvent to successfully prepare ordered mesoporous TiO_2 films with the pore size of 7.4 nm[20]. Stucky *et al.* used block polymer as the soft template to obtain mesoporous TiO_2 materials with large pore sizes[21]. Professor Fu Xianzhi prepared ordered mesoporous TiO_2 films with the pore size of 3.5 nm by using P^{123} as the soft template[22]. However, ordered mesoporous TiO_2 with small pore sizes has large gas resistance and pore confinement effect, so it is unfavorable to the entry of functional heterogeneous components. Therefore ordered mesoporous TiO_2 with a large pore size has attracted much attention. Smarsly *et al.* prepared large pore ordered mesoporous TiO_2 films with a pore size of 10 nm by using a new PHB-PEO block polymer as a template[23]. By using tetrabutyl titanate as the inorganic precursor, block polymer P^{123} as a structural guide, using the swelling effect of n-butanol release in situ (**Figure 1**), the research group successfully prepared anatase-type mesoporous TiO_2 film material with an aperture of 14 nm, which showing excellent photocatalytic performance. Thus, it lays a foundation for the further application of mesoporous $TiO_{2.}$

However, it was found in the exploration of photocatalytic process using mesoporous TiO_2, improving the crystallinity and stability of mesoporous TiO_2 are two key factors. If these two problems are not solved, they will essentially limit their application. The crystallinity of TiO_2 will directly affect its properties. Usually high crystallization facilitates

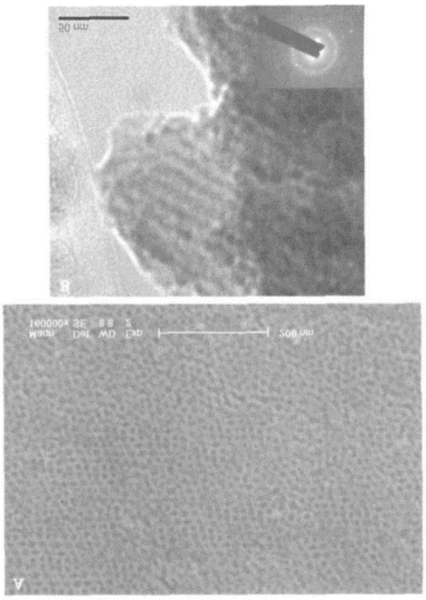

Figure 1. Typical SEM and TEM images of ordered large-pore size mesoporous TiO_2.

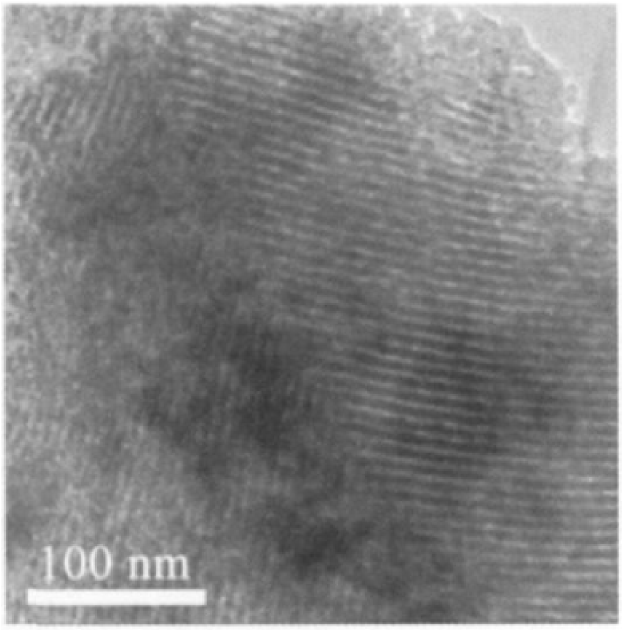

Figure 2. TEM image of the ordered mesoporous TiO_2 after being calcined at700 °C.

the separation of photocarriers and then can improve their photocatalytic properties[25]. It is widely known that mesoporous TiO_2 has poor stability. Raising the calcination temperature is necessary to improve the crystallinity. This will be accompanied by the growth and aggregation of TiO_2 grains and the transformation of crystalline phase, leading to the collapse of the mesoporous structure. Therefore, how to improve the crystallinity of mesoporous TiO_2 and maintain its perfect mesoporous structure has become an urgent problem to be solved. People have adopted a variety of means and methods to try to solve these two bottleneck factors. Professor Peng Tianyou used the composite cooperation between SO_4^{2-} and titanium precursors (such as $[TiO(H_2O)_5]^{2+}$ to protect the mesoporous structure under strong acidic conditions. The mesoporous TiO_2 with a pore diameter of about 6 nm can be stabilized to 600 °C[26]. Professor Zhao Dongyuan obtained ordered mesoporous TiO_2 with a pore size of about 5 nm by sulfuric acid carbonization of surfactant. It can be stabilized to 650 °C[27]. Based on large pore ordered mesoporous TiO_2, we took organic amine protective molecules to protect the liquid crystal mesophase structure of the primary particles of mesoporous TiO_2, thus effectively inhibiting the aggregation and growth of grains, the collapse of mesoporous network and the transformation from anatase to rutile, and successfully preparing highly stable ordered mesoporous TiO_2 with high crystallinity and large pore diameter of 10 nm (**Figure 2**). The photocatalytic activity of mesoporous TiO_2 was significantly improved. The ordered mesoporous structure of anatase phase can be stabilized to 700 °C (**Figure 2**)[28]. This large pore ordered mesoporous TiO_2 with high thermal stability can withstand high temperature heat treatment and keep the mesoporous framework unchanged. Therefore, it provides an excellent host for the construction of host guest composites.

2.2 Ordered mesopore TiO_2 being synthesized by the hard-template method

The hard-template method refers to the relatively "hard" structure of the template used, generally referring to solid materials, such as high molecular polymers with different spatial structures, anodic alumina films, mesoporous SiO_2, mesoporous carbon, etc. The interaction between them and inorganic species constituting mesoporous skeleton is weak. The template is mainly used as the filler of mesoscopic space. After removing the hard template, the corresponding occupied mesoporous structure is generated[29–31]. Compared with soft templates, hard templates have high stability and good spatial confinement, which can strictly control the size and structure of nano materials. But the hard formwork structure is relatively simple. Therefore, the structure of mesoporous materials prepared with hard templates usually changes less[32]. Ordered mesoporous TiO_2 materials with different morphologies were prepared by using various hard template materials with different mesoporous structures. Zhou *et al.* used SBA-15 as the hard template, titanium nitrate and titanium chloride as inorganic precursors to successfully prepare highly ordered mesoporous rutile and anatase TiO_2 materials. The lithium ion insertion performance of rutile mesoporous TiO_2 is higher than that of anatase[33]. Professor Zhao Dongyuan took SBA-15 and KIT-6 as hard templates to prepare rutile single crystal mesoporous TiO_2[34]. Zhang *et al.* prepared highly ordered mesoporous TiO_2 materials with KIT-6 as the hard template. It shows high hydrogen production efficiency by photolysis of water[35]. Bruce *et al.* prepared 3D ordered mesoporous TiO_2 with KIT-6 as the hard template and studied the insertion properties of lithium[36]. Wang *et al.* used anodic aluminum oxide (AAO) as the hard template and the triblock polymer P^{123} as the soft template, tetraisopropyl titanate as the titanium precursor to form the liquid crystal dielectric phase, removal of organic template by roasting and removal of AAO template by NaOH dissolution method in the pores of AAO. Thus, TiO_2 nanotubes with an ordered mesoporous structure on the side wall were obtained[37]. This unique structure of TiO_2 nanotubes has a high specific surface area (400 m^2/g). It is found that its efficiency is significantly improved when it is applied to lithium ion batteries.

3. Synthesis of the ordered mesoscopic TiO_2 composites

Although the photocatalytic activity of mesoporous TiO_2 is significantly improved, conventional TiO_2 nanoparticles still separate less efficiently and only absorbing UV light, which greatly reduces the utilization of sunlight. Therefore, how to further improve the separation efficiency of interpore TiO_2 photocarriers and expand the light response range has become an urgent problem.

3.1 Synthesis of the semiconductor oxide/mesoporous TiO_2 composites

Various semiconductor oxides are compounded with mesoporous TiO_2 to improve their thermal stability. It can also further improve the separation efficiency of photogenerated carriers so as to improve its photocatalytic activity. Gnatyuk *et al.* took P^{123} as the soft-template to prepare ordered mesoporous TiO_2/ZrO_2 composites by the sol-gel method. The stability of mesoporous TiO_2 was significantly improved[38]. Mesoporous TiO_2/ZrO_2 composites with double pore diameter distribution were prepared by in-situ synthesis (**Figure 3**). It shows good thermal stability and excellent photocatalytic activity[39]. In addition, bifunctional mesoporous TiO_2/TiO_2 was successfully prepared by nano casting α-Fe_2O_3 composite material. The composite fully reflects the high adsorption performance of α-Fe_2O_3 and high photocatalytic efficiency of mesoporous TiO_2. Effective adsorption of highly toxic As (III) and simultaneous photocatalytic oxidation convert it into low toxic As (V)[40]. Professor Fu Xianzhi prepared macroporous mesoporous TiO_2/ZrO_2 nanocomposites with hierarchical structure and showed excellent photocatalytic activity[41]. Professor Yu Jimei takes F^{127} as the soft-template to prepare ordered mesoporous CeO_2/TiO_2 composites with high thermal stability by evaporation induced self-assembly technique. Photocatalytic degradation of methylene blue proves that it has excellent visible light photocatalytic activity[42]. Jung *et al.* prepared mesoporous V_2O_5/TiO_2 composite materials by spray pyrolysis method (spray pyrolysis). Photocatalytic degradation 1,2-dichlorophenol was found to have excellent photocatalytic properties[43]. Liu *et al.* prepared mesoporous VO_x/TiO_2 composite materials. It can efficiently and selectively oxidize methanol to dimethoxymethane[44]. Stodolny *et al.* prepared mesoporous Ta_2O_5/TiO_2 composites. It shows high photolysis efficiency[45]. Mesoporous Fe_2O_3/TiO_2 fibers were prepared by Zhan *et al.* It shows high photocatalytic activity[46]. Cao *et al.* prepared macroporous mesoporous hierarchical TiO_2 supported CuO nano catalyst by template free method. Its catalytic performance for low temperature CO oxidation was systematically studied. It is found that CuO has the best catalytic performance when the loading amount is 8 wt%[47]. It is worth mentioning that SiO_2 has received special attention because of its high stability. It was compounded with mesoporous TiO_2 to construct various composite structures. Thus, the thermal stability and photocatalytic activity of mesoporous TiO_2 were significantly improved. Cojocariu *et al.* prepared ordered mesoporous TiO_2/SiO_2 xerogels by non hydrolytic sol-gel method. The mild oxidation of hydroxyl containing organic compounds was studied[48]. Yao *et al.* prepared ordered mesoporous TiO_2/SiO_2 xerogels with hierarchical pore structure[49]. Sahu *et al.* prepared ordered mesoporous TiO_2/SBA-15 composites. The effect of calcination temperature on the mesoporous structure was systematically studied[50]. He *et al.* prepared mesoporous TiO_2/SiO_2 composites with large specific surface area. It shows excellent photocatalytic activity[51].

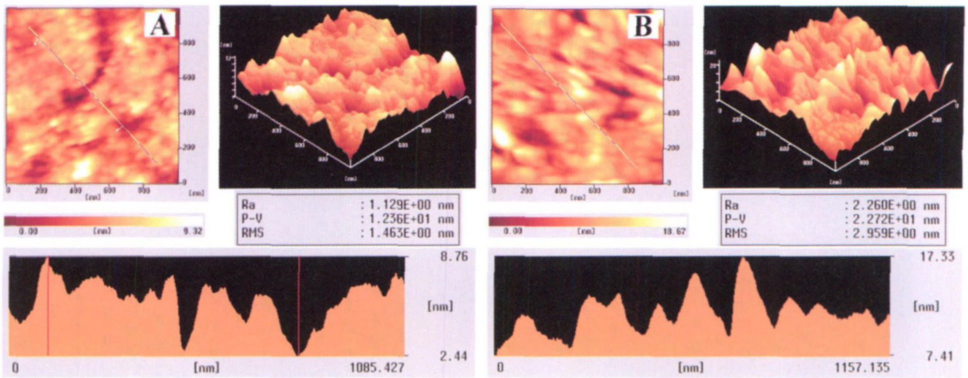

Figure 3. AFM images of bi-modal mesoporous TiO_2/ZrO_2 composite.

3.2 Synthesis of metal nanoparticles/mesopore TiO_2 composites

There are many synthetic methods of metal nanoparticles/mesoporous TiO_2 composites. But to sum up, it can be roughly divided into two types of methods. That is, one-step and two-step methods. The so-called one-step method refers to the addition of precious metal precursors while forming ordered mesoporous TiO_2; the precious metal is reduced while the organic template is removed by heat treatment. Thus, noble metal/mesoporous TiO_2 composites were synthesized in situ. Cha *et al.* used amphoteric block copolymer PS-b-PEO (poly (styrene-block-ethylene oxide)) as a template, ordered mesoporous Ag/TiO_2 composite films were prepared by spin coating method. It shows excellent photocatalytic performance[52]. Professor Li Hexing and professor Lu Yunfeng effectively coated Au nanoparticles in core-shell mesoporous TiO_2 microspheres by in-situ synthesis. It shows excellent photocatalytic activity and stability[53]. Zhao *et al.* synthesized Au clusters doped mesoporous TiO_2 films in one step. Its performance has been significantly improved[54]. Professor Yu Jiaguo prepared mesoporous Au/TiO_2 composite microspheres by hydrothermal method. Its photocatalytic activity was significantly enhanced[55]. Ismail *et al.* synthesized Pt/TiO_2 mesoporous composites by the one-step method. The photocatalytic oxidation of methanol showed excellent photocatalytic activity[56]. The so-called two-step method refers to the first synthesis of ordered mesoporous TiO_2, then take it as the host material, noble metals were compounded into mesoporous TiO_2 channels by deposition and wet impregnation. Thus, noble metal/mesoporous TiO_2 composite materials are formed. Wu *et al.* used $TiCl_4$ as inorganic precursor, F^{127} as a soft-template to prepare ordered mesoporous TiO_2 films with striped pores by evaporation induced self-assembly method, then Pt nanoparticles were loaded with the synthesized ordered mesoporous TiO_2 film as the host material. Application to direct methanol fuel cells (DMFCs) was found to have good catalytic properties[57]. Shi *et al.* used urea as precipitant to prepare highly dispersed ordered Au/mesoporous TiO_2 composites with ultra-high gold content by the deposition-precipitation method[58]. May *et al.* prepared nanocomposites of precious metals Au and Pt evenly distributed in ordered mesoporous TiO_2 channels by the phase-transfer method. The change of porosity was systematically studied by ellipsometric porosimetry[59]. Various metal nanoparticles/mesoporous TiO_2 composites were prepared by different methods and the performance has also been significantly improved. However, the nature of the interaction between metal nanoparticles and mesoporous TiO_2 pore wall needs to be further studied and discussed.

3.3 Synthesis of mesoporous TiO_2 multivariate composites

Mesoporous TiO_2 multicomponent composites have also attracted people's attention in recent years. It can give full play to the characteristics of each component and also use the interface coupling between them to produce new excellent properties. Thus, the properties of mesoporous TiO_2 can be greatly improved. Professor Zhao Dongyuan used soluble phenolic resin as polymer precursor, F^{127} as a soft-template, to prepare ordered bifunctional mesoporous TiO_2/SiO_2/polymer nanocomposite[60]. Professor Li Yadong prepared CdSe quantum dot sensitized Au/TiO_2 mesoporous composite films and its photoelectrochemical properties have been significantly enhanced[61]. Idakiev *et al.* prepared $Au/CeO_2/TiO_2$ macroporous mesoporous multicomponent composite materials and shows high catalytic activity in low-temperature water-gas shift reaction[62]. Yu *et al.* prepared MnO_x CeO_2/TiO_2 mesoporous composites by the sol-gel method. It was found that the catalytic oxidation of toluene at low temperature had a significant effect[63]. Narkhede *et al.* prepared Pt/TiO_2/MCM-48 multi-component mesoporous composites and it has high catalytic activity for CO oxidation[64]. Although various mesoporous TiO_2 multicomponent composite materials with improved performance have been obtained, there are few studies on the mechanism of performance improvement. In addition, the interaction between components in mesoporous TiO_2 multicomponent composites still need to be further studied in order to provide a theoretical basis for the construction of high-performance mesoporous TiO_2 multicomponent composite materials.

4. Prospect

Ordered nanocrystalline mesoporous TiO_2 and its composites have become one of the research hotspots at home and abroad because of their unique optical and electrical properties. Great progress has been made and shows great development potential and unique application prospects. For all that , due to the short research time in this direction, many problems still need to be deeply studied and discussed. For example, the preparation process of ordered mesoporous TiO_2 needs to be further expanded and simplified. The structural evaluation and heterostructure construction of mesoporous TiO_2 composites, the kinetics of photogenerated carrier separation, and the nature of the interaction between the inhibitory components in the mesoporous TiO_2 channels and the pore wall need to be further studied. In addition, the application of ordered mesoporous TiO_2 and its composites should also be paid attention to. Photocatalysis, as a deep oxidation method, can achieve fully mineralization of organic pollutants in wastewater, but the current photocatalytic process is not mature to meet the practical requirements. So the practical research of ordered mesoporous TiO_2 and its composites should attract more attention.

Conflict of interest

The authors declare that they have no conflict of interest.

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