JOURNAL OF
Materials
CHEMISTRY

Acid-prepared mesostructures modified with TiO_2 by a template–titanium tetrabutoxide displacement process

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Received 27th June 2001, Accepted 3rd October 2001
First published as an Advance Article on the web 26th October 2001

A simple template–metal alkyloxide displacement process has been used to modify the pore surface of acid-prepared mesostructures with titanium dioxide. Spectroscopic studies indicate that the complete removal of surfactant template and the pore surface modification could be simultaneously realised. Structural analyses show that the high surface area, large pore size, and well-ordered mesostructure could be fully retained after modification. Elemental analyses with X-ray energy-dispersive spectroscopy (EDS) and inductively coupled plasma–atomic emission spectroscopy (ICP–AES) give a Si/Ti molar ratio of around 18. It was therefore concluded that titanium dioxide has been homogeneously dispersed in the pore channels. Additionally, the simplicity of this process makes it suitable to be used for the pore surface modification of mesoporous thin films.

Introduction

The discovery of the mesoporous molecular sieve, designated as M41S,[1,2] has stimulated wide interest for its potential applications in adsorption, catalysis, and in modern nanotechnology as functional and/or host materials. Compared to conventional microporous zeolites, this novel material possesses many advantages such as high surface area ($>1000\ m^2\ g^{-1}$), large pore size (2–30 nm),[1–4] narrow pore size distribution, and ordered structure. However, unlike microporous zeolites, in which the framework is crystalline and have abundant active sites, the amorphous framework and the lack of active centers in the pure mesoporous silica materials, to a great extent, have limited their direct applications. As a result, much research work concerning mesoporous materials has been focused on enhancing their reactivity through chemical modification. In most cases, incorporation of metals, including elements,[5,6] ions,[7–9] and oxides,[10,11] is a major research interest. Up to date, three processes have been utilised: (I) one-step synthesis,[7–9,12–14] in which metal organic or inorganic precursors are directly added in the parent sol with silicon sources; (II) template–ion exchange,[15–17] in which the template ions of the as-prepared materials are exchanged with other metal ions in solution; (III) post-synthesis modification,[5,13,18,19] in which the abundant pore surface Si–OH bonds of calcined materials react with an organometallic complex or other metal compounds. In addition, the pore surface modification route utilizing a silane coupling agent followed by adsorption of the metal ions is also a development in process (III).[20] Though all these three processes are efficient for mesoporous materials modification, they are complicated and sometimes are detrimental to the pore structure and pore ordering of the materials. For example, process (I) often lowers the structural ordering of the materials and the location of the modifying element (on the pore surface or into the framework) is unpredictable while process (III) leads to a decrease of pore size, pore volume and surface area after modification. Therefore a better modification method is required.

In this paper, we describe a simple method, a template–titanium tetrabutoxide displacement process, for the pore surface modification of mesoporous materials with titanium dioxide, which is an important semiconductor and effective photocatalyst.[21,22] This method is originated from a recent report concerning surface functionalization of MCM-41 (the main member of M41S) with organic groups, in which the authors reported that, through template displacement with organosilane (TDS), the electrostatic interactions between negatively charged silica species and surfactant cations could be directly replaced by strong siloxane bonds.[23,24] Pore opening and pore surface modification could be simultaneously obtained.[23,24] Based on this idea, we inferred that it would be possible to introduce TiO_2 into the pore channels through substituting organosilane with titanium alkyloxides. Though Aronson *et al.*[25] also reported a similar process by reacting $TiCl_4$ in hexane with as-prepared MCM-41 materials, a subsequent extended calcination was necessary to remove the surfactant template. Besides, in that process, some TiO_2 anatase crystallites of *ca.* 100–250 Å in diameter were observed on the external surface, though the amount was not very high.[25] In the present report, using the template–titanium tetrabutoxide displacement method, no apparent anatase crystallites or Ti-rich clusters were found on the external surface according to high-resolution transmission electron microscopy (HRTEM) images or according to EDS spectra of the treated materials.

Another feature of this experiment is that the parent materials were prepared in acid conditions under which high quality mesoporous thin films can be prepared.[26] Mesoporous thin films are a recent research focus for convenient uses in membrane-based adsorption/desorption, catalysis, novel sensors and optical/electric fields.[27–29] However, due to the structural instability and constraints from the substrates, processing simplicity is very important for film modification. The simple method reported in this paper can be easily transferred to the modification of thin film materials.

Experimental section

Materials and sample preparation. Tetraethyl orthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) were from Shanghai Chemical Co., concentrated HCl was from Shanghai ZhenXing No. 2 Chemicals Factory, titanium

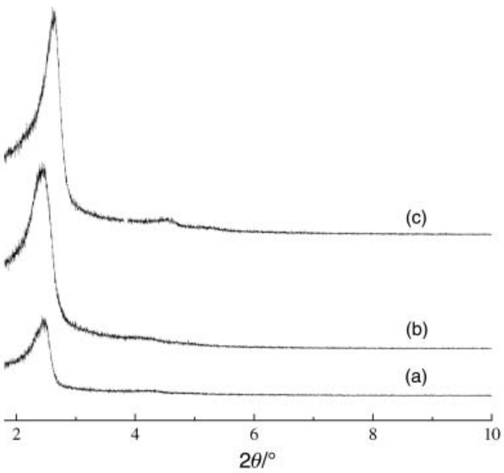

Fig. 1 SAXRD patterns of sample (a) A0 (as-prepared), (b) A2 (TiO_2-modified) and (c) A3 (calcined).

tetrabutoxide (TBOT) was from Shanghai SSS Chemical Co., toluene was from Shanghai LingFeng Chemical Co. and anatase TiO_2 powder was from Shanghai Institute of Fine Chemistry Science and Technology.

According to the procedure published previously,[26] the parent materials (sample A0) were prepared at room temperature using the following composition: 0.17 CTAB : 1 TEOS : 9 HCl : 130 H_2O. After drying at 100 °C for 12 h, the uncalcined mesoporous material was treated with TBOT without any solvent. In a typical process, 20 ml TBOT was added to about 0.5 g of as-synthesized materials, and the mixture was refluxed for 24 h under nitrogen atmosphere. The resulting slightly yellow solid was filtered off, washed with toluene and dried under vacuum at 80 °C for 10 h (sample A1). To complete the hydrolysis of TBOT, the modified material was calcined at 500 °C for 2 h (sample A2). For comparison, using a heating rate of 1 °C min^{-1}, a small amount of parent material (sample A0) was calcined at 550 °C for 10 h under flowing air (sample A3).

Characterization. Small angle X-ray diffraction (SAXRD) patterns were collected with a Rigaku D/MAX-Π diffractometer equipped with a rotating anode, and using Cu-Kα radiation ($\lambda = 1.5418$ Å, 40 kV, 60 mA) over the range of $1.8 \leqslant 2\theta \leqslant 10°$ with a step size of 0.002°. HRTEM images and electron diffraction (ED) patterns were recorded on a JEOL 200CX electron microscope operated at 160 kV. EDS spectra were obtained from an attached Oxford Link ISIS energy-dispersive spectrometer fixed on a JEM-2010 electron microscope operated at 200 kV. Chemical composition analysis was performed with Varian Vista AX ICP-AES spectrometer. Fourier Transform infrared (FTIR) spectra were obtained on Nicolet 7000-C or Bio-Rad FTS-185 spectrometers with 4 cm^{-1} resolution. Powder samples were dispersed in KBr pellets or in paraffin oil for IR analysis. Nitrogen adsorption and desorption isotherms at 77 K were measured on a Micromeritics Tristar 3000 system. Before being measured, the sample was pretreated at 150 °C overnight under flowing helium. The specific surface area and the pore size distribution were calculated using the BET and BJH methods, respectively. UV–Vis diffuse reflectance spectra were collected on a Shimadzu UV-3101PC UV–VIS–NIR scanning spectrophotometer with an integrating sphere accessory and $BaSO_4$ as the reference.

Results and discussion

Though it has been pointed out that it is possible to perform TDS with solvent,[24] our preliminary experiments indicated that even a very low content of solvent reduces the displacement efficiency. Thus, in this experiment, no solvent was employed during the modification process. Fig. 1 shows SAXRD patterns of samples A0, A2 and A3. The intense (100) diffraction peak with weaker (110) and (200) peaks proves that these materials are of hexagonal mesostructure. Furthermore, it is obvious that after the elimination of surfactant template, due to the intensification of diffraction contrast between pore channels and framework,[30] the diffraction peaks of the resulting materials become stronger compared with those of the parent materials, regardless of the treatment processes. Therefore, these two different treatment methods, template–titanium tetrabutoxide displacement and calcination, have a similar effect on the removal of surfactant template. On the other hand, the XRD spectrum of sample A3 appears superior to that of sample A2, which may result from the existence of a second phase (TiO_2) in the pore channels of samples A2 reducing the diffraction contrast.[30] In addition, it should also be noted that for differently treated materials, their d_{100} spacing values were different (see Table 1). After calcination at elevated temperatures, the d_{100} spacing decreased from 3.61 nm (sample A0) to 3.33 nm (sample A3) due to the effect of structure shrinkage. However, the d_{100} spacing showed no apparent change after template–titanium tetrabutoxide displacement, since this process was carried out under relatively "mild" conditions for the removal of the surfactant template in which some Si–OH bonds are directly replaced with Si–O–Ti bonds (detailed evidence from FTIR spectra, below). As a result, the decreased number of Si–OH bonds leads to a lower degree of condensation between Si–OH bonds and reduced framework contraction.

Fig. 2 shows the FTIR spectra of samples A0, A1 and A2. Comparing spectrum (a) with (b) in Fig. 2, the disappearance of the strong infrared absorption bands at around 2850–2930 and 1490 cm^{-1}, which are assigned to C–H stretching and C–H deformation vibrations of CTAB micelles,[31] confirms the elimination of the surfactant template from the parent materials. This is consistent with the above SAXRD results. Furthermore, some new absorption bands appear at around 1463 and 1372 cm^{-1} in spectrum (b) corresponding to the C–H bending vibrations of TBOT.[32] The absorption bands corresponding to Ti–O–C vibrations of butoxy groups directly bonded to titanium were not observed (below 1125 cm^{-1}). This phenomenon can be attributed to the overlapping of this band with the matrix Si–O–Si vibrations. It can thus be concluded that the surfactant template is successfully replaced with TBOT with the latter incorporated into the pore channels. After thermal treatment (spectrum (c)), all these newly appeared bands completely disappeared and only the matrix Si–O–Si vibrations remained. This indicates the successful transformation of TBOT to TiO_2.

Table 1 Pore structure parameters for sample A0 (as-prepared), A2 (TiO_2-modified) and A3 (calcined)

Sample	d_{100}/nm	a_0[a]/nm	BET surface area/$m^2\ g^{-1}$	[b]Pore volume/$cm^3\ g^{-1}$	[c]Pore size d_{BJH}/nm	[d]Wall thickness/nm
A0	3.61	4.17	—	—	—	—
A2	3.62	4.18	1128	0.78	2.85	1.33
A3	3.33	3.85	1270	0.83	2.73	1.07

[a] $a_0 = 2/(3)^{1/2} d_{100}$. [b] Derived from the amount of N_2 adsorbed at P/P_0 of 0.97. [c] BJH pore size calculated from the desorption branch. [d] Wall thickness $= a_0 - d_{BJH}$.

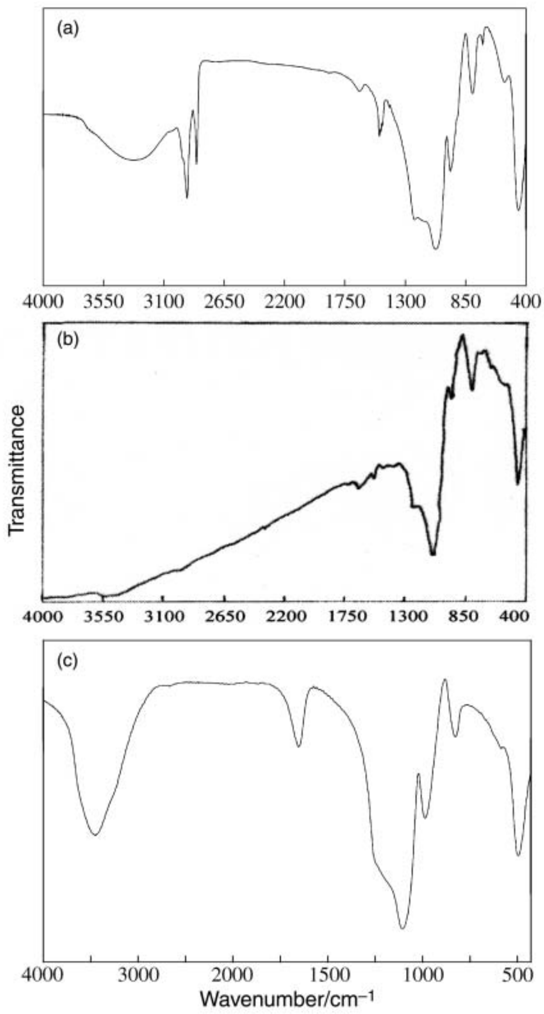

Fig. 2 FTIR spectra (KBr pellet) of sample (a) A0 (as-prepared), (b) A1 (TBOT-treated) and (c) A2 (TiO_2-modified).

On the other hand, as KBr pellet preparation in the FTIR experiment would lead to deterioration of the mesoporous structure and some characteristic bands may be lost[33] we also recorded FTIR spectra in paraffin oil. Fig. 3 shows the results for samples A2 and A3. In Fig. 3, spectrum (a), the absorption bands at around 3687 cm^{-1} can be assigned to the vibrations of pore surface Si–OH bonds, while in spectrum (b) this band intensity decreases because of the replacement of Si–OH by Si–O–Ti bonds. Although the assignment of absorption bands at around 960 cm^{-1} in terms of Si–OH groups or Si–O–Ti bonds is not very clear,[34] it was confirmed by UV resonance Raman spectroscopy that the formation of Si–O–Ti bonds would enhance the vibrational intensity at around 960 cm^{-1}.[35]

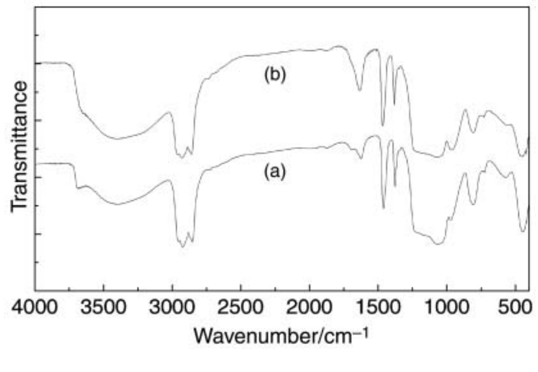

Fig. 3 FTIR spectra in paraffin oil of sample (a) A3 (calcined) and (b) A2 (TiO_2-modified).

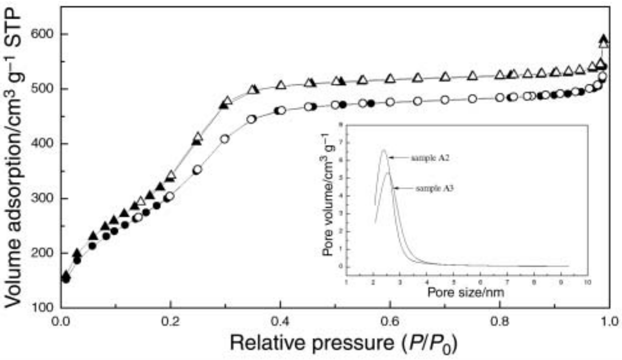

Fig. 4 Nitrogen adsorption–desorption isotherms of sample A2 (TiO_2-modified) (●, adsorption; ○, desorption) and A3 (calcined) (▲, adsorption; △, desorption) and the corresponding pore size distribution curve (inset).

Thus, the apparent higher intensity ratio between the absorption bands at around 960 and 800 cm^{-1} (SiO_4 symmetric stretching) in spectrum (b), as compared to that of spectrum (a), could also serve as a proof of the formation of Si–O–Ti bonds.[36]

Consistent with the above SAXRD and FTIR studies, the nitrogen adsorption–desorption isotherm of sample A2 is similar to that of sample A3 (Fig. 4). The typical type IV isotherm curves with a well-defined step at relative pressure P/P_0 0.2–0.3 clearly indicate that these materials possess mesoporous structures.[37] Combined with SAXRD results, all the pore structure parameters are summarized in Table 1. Little difference in surface areas and pore volumes between samples A2 and A3 was observed. It is concluded that TiO_2 had been homogeneously dispersed on the inner surface of the pore channels. To identify the homogeneous distribution of titanium in the whole sample, further evidence could also be found in the EDS spectrum shown in Fig. 5(c). More importantly, it was found (Table 1) that sample A2 possessed a larger pore size and thicker walls than sample A3. From the viewpoint of practical applications, the larger pore size aids the fast diffusion of bulk molecules in the pore channels and the thicker modified walls are likely to improve the thermal stability of the materials.

Fig. 5 shows representative HRTEM images of sample A2 in different orientations while the insets are the corresponding selected-area diffraction patterns. In agreement with above SAXRD results, the well-ordered characteristic structures imply that sample A2 is of hexagonal mesostructure. Simultaneous EDS analysis, as shown in Fig. 5(c), indicates that titanium content slightly varies with the direction of incident electron beam, but no apparent anatase crystallites or Ti-rich clusters were found on the external surface. From the results of Fig. 5(a) and (b), the Si/Ti molar ratios are *ca.* 14 and 18, respectively. This small difference could be explained by the fact that the template–titanium tetrabutoxide displacement process is diffusion-controlled and the Ti composition would be slightly enriched near the pore openings. However, considering the composition analysis results from ICP–AES, the titanium content is *ca.* 4.02 wt% and the Si/Ti molar ratio is close to 18, in agreement with the EDS results from Fig. 5(b). It is believed that the Ti composition is only enriched at pore openings with very limited depth, and more generally, Ti is homogeneously dispersed in the pore channels of the samples.

A blue shift of the band edge is observed in the UV–Vis diffuse reflectance spectra of nanosized semiconductor particles, which is a consequence of quantum size effects. Fig. 6 shows the UV–Vis diffuse reflectance spectra of samples A1, A2, and a TiO_2 anatase phase. The absence of absorption peaks at *ca.* 210 and 260 nm, corresponding to isolated tetrahedral and octahedral titanium species, respectively,[33] together with a significant blue shift of band edges from *ca.* 390 nm for the TiO_2 anatase phase to *ca.* 350 nm for the modified sample A2,

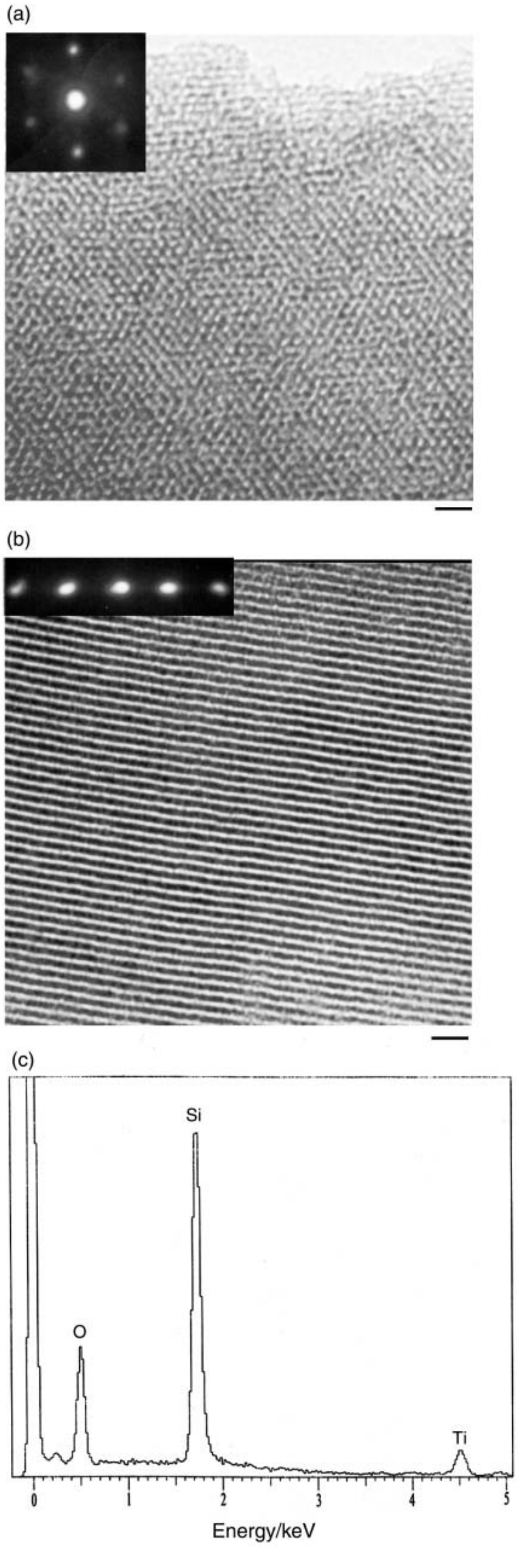

Fig. 5 HRTEM images and electron diffraction patterns (inset) of sample A2 (TiO_2-modified) with the incident beam direction (a) parallel and (b) perpendicular to the pore channels direction, (c) EDS spectrum corresponding to (a) (scale bar: 20 nm)

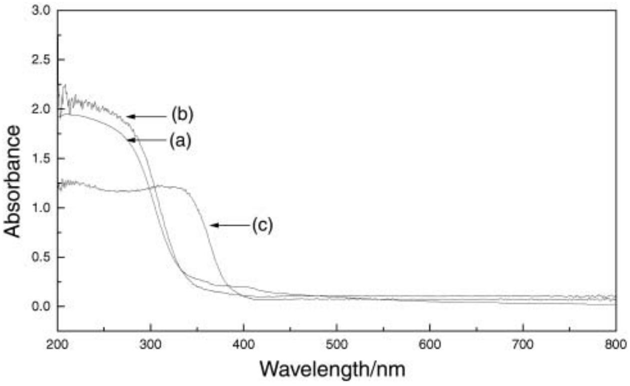

Fig. 6 Diffuse UV–Vis reflectance spectra for sample (a) A1 (TBOT-treated), (b) A2 (TiO_2-modified) and (c) TiO_2 anatase phase.

suggests the formation of nanosized TiO_2 particles in the pore channels. In addition, there was no apparent difference of the absorption band edges between spectra of samples A1 and A2, which implies that the thermal treatment is simply an *in situ* hydrolysis process. Because of the constraints imposed by the pore walls and the Si–O–Ti bond linkages within the framework, during thermal treatment nanosized TiO_2 particles in the pore channels can not move, grow or agglomerate with each other.

Conclusion

Using a template–metal alkyloxide displacement process without any solvent, pore surface modification with titanium dioxide in acid-prepared mesostructures has been achieved using titanium tetrabutoxide as a precursor. The electrostatic interaction at the organic–inorganic interface has been successfully replaced by covalent Si–O–Ti bonds and therefore mesoporous material modification and pore opening are simultaneously realised. All the characterization experiments support this conclusion. Besides, because extended calcination at elevated temperatures for the removal of the surfactant template can be avoided, the process proposed and used in this work is easy to operate and practical for mesoporous thin films modification.

Acknowledgement

This work was supported by National Natural Science Foundation of China, grant No. 59882007.

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