Effect of Ti doping on microstructure of SiO$_2$-CTAB mesoporous films

YUE Chunxiao$^{1,2}$, YAO Lanfang$^2$, TIAN Linlin$^2$ and FANG Xueling$^2$, 
$^1$ Shanghai Jianqiao College, shanghai 201319, 
$^2$ University of Shanghai for Science and Technology, Shanghai 200093, China

E-mail: chunxiao.yue@gmail.com

Abstract. $n$SiO$_2$-TiO$_2$-CTAB ($n$ is the molar ratio of Si to Ti, $n=2, 10, 20, 40, 60, 80$) composite films were synthesized by sol-gel process of titanium isopropoxide (TPOP) and tetraethyl orthosilicate (TEOS) hydrolyzation using surfactant cetyltrimethyl ammonium bromide (CTAB) as the template. The microstructure of the films was investigated by Transmission electron microscopy (TEM), atomic force microscope (AFM), X-ray diffractometer (XRD) and UV- infrared spectrophotometer. The results show that Ti ions homogeneously disperse in the mesoporous SiO$_2$ matrix forming Si-O-Ti bonding when $n$ is greater than 20, and Ti ions disrupt the uniformity of the pores in the composite mesoporous films and reduce the structural order when $n$ is lesser than 10. SiO$_2$ and TiO$_2$ of SiO$_2$-TiO$_2$-CTAB mesoporous films is amorphous calcined at 450$^\circ$C, 600$^\circ$C, 700$^\circ$C, 800$^\circ$C.

1 Introduction

Mesoporous silica films have many unusual properties such as an adjustable refractive index, high porosity and low thermal conductivity and dielectric constants. Therefore, it has become increasingly attractive to use the films in optical and microelectronic applications, thermal insulation, catalyzed sorption and so on$^{[1,2]}$. Currently significant progress has been made in the fabrication and characterization of ordered mesoporous SiO$_2$ films with rigidly uniform pores$^{[3]}$. For pure SiO$_2$ material, its skeleton is absence of acid sites, and catalytic activity is low. One way to do this problem is dopant of activated element to prepare composite mesoporous material. TiO$_2$ is a wide bandgap ($E_g \approx 3.2$eV) material exhibiting excellent photoelectric efficiency and photocatalysis properties$^{[4]}$. The addition of TiO$_2$ to SiO$_2$ induces higher acidic properties to a great extent, and enhances the photocatalytic performance and mechanical property as well$^{[5]}$. Ti-doped SiO$_2$ mesoporous material can also be considered as attractive materials for high thermal stability, superior adsorption capability with active components and good redox properties$^{[6-8]}$. In syntheses through conventional sol–gel processes, however, the preparation of mesoporous TiO$_2$–SiO$_2$ mixed oxides due to the differences in hydrolysis and condensation rates of Ti- and Si-alkoxides was identified as a major problem.

In the present paper, the fabrication of SiO$_2$–TiO$_2$–CTAB mesoporous films via sol-gel processing using CTAB as template and acetylacetone as hydrolysis inhibitor of TPOP was described, and the effect of Ti doping on microstructure of SiO$_2$–CTAB mesoporous films were investigated. Such composite mesoporous materials would not only take advantage of both TiO$_2$ and SiO$_2$, but would also extend their applications through the generation of new catalytic active sites due to the interaction of TiO$_2$ with SiO$_2$. 
2 Experimental

2.1 Sol preparation

In the preparation of the sols for dip coating, TEOS and TPOT were used as silica and titanium sources, respectively. For the SiO$_2$ precursor solution, TEOS, ethanol, hydrochloric acid and deionized water were mixed at room temperature under magnetic stirring. Dilute hydrochloric acid was then added dropwise to the above sol to adjust the pH-value about 2. After aged at 50°C for several hours, the sol was added to CTAB(2.5 wt. %) and then stirred for 2h. For TiO$_2$ precursor solution, TPOT was mixed with acetylacetone (AcAc, as chelating agent of the titanium alkoxide) at a molar ratio of 1:1. Ethanol, deionized water and HAc were then added dropwise. According to the desired titanium contents in the final sol-gel films, $n$SiO$_2$-TiO$_2$-CTAB composite sols were formed. $n$ is the molar ratios of Si to Ti, $n$=2, 10, 20, 40, 60 and 80. The final composite sols were aged for about 5~7 days before coating the films.

2.2 Samples preparation

Both silicon wafers and microscope slide glass were used as substrates. The films were performed by the dip-coating method in a clean room with a relative humidity <60% at 20°C~25°C. The dip-speed was optimized at 8inch/min. The samples were baked in a SiO$_2$ tube with an inner diameter of 10 mm.

2.3 Characterization

X-ray diffraction analysis was done on the films by using RigakuD/max 2550 Series XRD operated with CuKa radiation, at 40 KV, 100 mA. A FTIR (FTS-40 Bio-Rad) spectrometer was employed to distinguish properties of the films with different TiO$_2$ content. The resolution is 2 cm$^{-1}$, and an uncoated silicon wafer was used as a reference. The UV-visible absorbance spectra (measured by a JASCO V-570 UV/vis spectrophotometer) of the films deposited on microscope glass slides were examined in the wavelength range of 200~800 nm. TEM image was recorded on a JEM-2100F HR-TEM operated at 200kV. Surface image was observed by AFM (PSIA Corporation XE-100 advanced Scanning Probe Microscope).

3 Results and discussion

![Figure 1. SXRD patterns of SiO$_2$-CTAB mesoporous films](image1.png)

![Figure 2. SXRD patterns of SiO$_2$-TiO$_2$-CTAB mesoporous films](image2.png)
As seen in figure 1, a sharp diffraction peak indexed as (100) reflection of a hexagonal structure presents in small angle region, which illuminates that the structure of SiO$_2$-CTAB films is long-term ordered mesostructure because of the orientation of the surfactant template. The diffraction peak of SiO$_2$-CTAB film precalcined locates at about 2.5°, and interplanar crystal spacing d$_{(100)}$ is 3.54 nm. After calcined at 450℃, the diffraction peak shifts to 3.3° and d$_{(100)}$ is 2.68 nm because the framework of SiO$_2$-CTAB film shrinks. Full width at half maximum has few changes and ordered mesostructure not spoiled which hole spacing is about 3.12 nm as supported by TEM image.

Figure 2 and figure 3 display SXRD patterns of nSiO$_2$-TiO$_2$-CTAB (n=2, 10, 20, 40, 60 and 80) composite films calcined at 450℃. The diffraction peak (100) can be observed distinctly as shown in figure 2, which indicates that the films are long-term ordered mesostructure. Additionally, it can be noted that the diffraction peak (100) shifts slightly towards the higher value and d$_{(100)}$ decreases with the increase content of titanium. These results suggest that Ti ions incorporate into the silicon-oxide skeleton and compose the mesoporous structures with SiO$_2$ uniformly. With the increase of titanium content, the intensity of the diffraction peak (100) decreases gradually. Especially, it becomes quite weak when n ≤ 10 (shown in figure 3). It indicates that Ti ions disrupt the uniformity of the pores in the hybrid mesoporous materials and reduce the structural order. More Ti ions could change the silica charge density and interfere with the formation of the mesoporous structures.

As regards the microstructural evolution of the films, XRD patterns of all samples calcined at 450℃ show a diffraction peak pronounced at about 24° respectively, which is characteristic of no crystalline phase. XRD patterns of SiO$_2$-TiO$_2$-CTAB mesoporous film (Si/Ti=40) calcined at 600℃, 700℃, 800℃ are shown in figure 4. It indicates the channels’ walls of the SiO$_2$-TiO$_2$-CTAB mesoporous films are essentially amorphous structures, and TiO$_2$ particles homogeneously disperse in the amorphous SiO$_2$ matrix.

As shown in Figure 5, the most intense absorption peak located at 1075 cm$^{-1}$ corresponds to a large amount of Si-O-Si stretching vibrational bonding, which constitutes the skeleton structure of films. The wide band at around 3430 cm$^{-1}$ corresponds to Si-OH stretching. An shoulder peak at around 953 cm$^{-1}$ is due to Si-O stretching vibration in Si-O-Ti$^{+4}$ sequences involving tetrahedrally coordinated Ti$^{+4}$ cations, together with Si-O vibration in Si-OH groups. And the intensity of the absorption band for Si-O-Ti bonding can be seen as an indication of degree of inclusion of titanium ions in the silica structure.
Figure 6 shows the optical absorption spectra of SiO$_2$-TiO$_2$-CTAB mesoporous films coated on microscope slide glass after subtracted the effect of substrates. A relatively strong absorption at about 220 nm can be clearly seen and it becomes stronger with the increase of Ti content. It suggests that Si-O-Ti tetrahedral structure has formed via distribution of Ti ions in SiO$_2$ framework of mesoporous films. In addition, it must be noted that the adsorption edges of SiO$_2$-TiO$_2$-CTAB mesoporous films shift to red with the increase of Ti content. Owing to agglomeration, band-gap energy decreases.

![Figure 5. FTIR absorption spectrum of mesoporous films](image1)

![Figure 6. UV-Vis absorption spectrum of mesoporous films.](image2)

![Figure 7. TEM image of SiO$_2$-CTAB mesoporous film.](image3)

![Figure 8. AFM image of SiO$_2$-TiO$_2$-CTAB mesoporous film.](image4)

Figure 7 is TEM image of SiO$_2$-CTAB mesoporous film. It clearly shows the well-ordered periodic hexagonal mesostructure, and the hole spacing being about 3.2 nm. AFM image of SiO$_2$-TiO$_2$-CTAB mesoporous film (Si/Ti=80, calcined at 450℃) is shown in figure 8. its pore channels parallel to the substrate surface which is character of hexagonal mesostructure.
4 conclusion

SiO$_2$-TiO$_2$-CTAB mesoporous hybrid thin films were successfully synthesized by a modified sol-gel process. The results show that Ti ions homogeneously disperse in the mesoporous SiO$_2$ matrix forming Si-O-Ti bonding when the molar ratio of Si to Ti is greater than 20, and Ti ions disrupt the uniformity of the pores in the hybrid mesoporous materials and reduce the structural order when the molar ratio of Si to is lesser than 10. The adsorption edges of SiO$_2$-TiO$_2$-CTAB mesoporous films shift to red with the increase of Ti content. In addition, XRD analysis suggest that SiO$_2$ and TiO$_2$ of the framework is amorphous calcined at 450$^\circ$C $\sim$ 800$^\circ$C.

5 References

[1] Yamane T, Nagai N, Katayama S and Todoki M 2002 J. Appl. Phys. 91 9772
[2] Mark E and Davis 2002 J. Nature. 417 813
[3] Zhang J L, Li W, Meng X K, Wang L and Zhu L 2003 J. Memb. Sci. 222 219
[4] Sabataitytė J, Oja I, Lenzmann F, Volobujeva O and Krunks M 2006 J. C.R. Chimie. 9 708
[5] Kwon C H, Kim J H, Jung I S, Shin H and Yoon K H 2003 J. Ceramics International. 29 851
[6] Belhekar A A, Awate S V and Anand R 2002 J. Catalysis Communications. 3 453
[7] Li Z J, Hou B, Xu Y, Wu D, Sun Y H, Hu W and Deng F 2005 J. Solid State Chemistry 178 1395
[8] Lafond V, Mutin and Vioux A 2004 J.Chem. Mate. 16 5380