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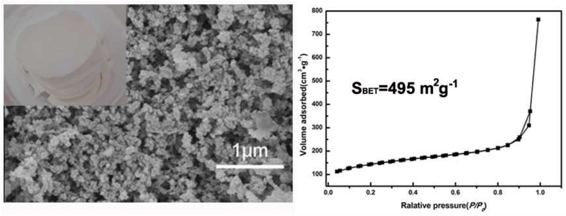
Graphical Abstract



Monolithic titania (TiO_2) aerogels with high were successfully synthesized by the sol-gel process combined surface modification, followed by ambient pressure drying.

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ARTICLE TYPE

Preparation of monolithic titania aerogels with high surface area by a sol-gel process combined surface modification

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Monolithic titania (TiO_2) aerogels with high surface area were successfully synthesized by the sol-gel process combined surface modification, followed by ambient pressure drying to remove the solvents from the gels. The effects of surface modification used polyethylene glycol (PEG) 2000 as surfactant on the gelation and microstructure of the aerogel were studied in detail. The resultant aerogel with the PEG 2000:TBOB (molar ratio) of 0.005 exhibits specific surface area as high as 495 $m^2 \cdot g^{-1}$, apparent density of 0.716 $g \cdot cm^{-3}$ and porosity of 81.6%. The crystallization of aerogels after heat-treatment does not spoil the monolithic shape and morphology of the aerogel basically, and the specific surface area still keeps a relative high value of 209 $m^2 \cdot g^{-1}$. The facile route provides a low-cost strategy for the preparation of metal oxide aerogels with high surface area.

Introduction

Aerogels are designated as dried gels with a very high relative pore volume, and are a class of mesoporous materials assembled by fine particles with network structure and gaseous dispersion mediums[1, 2]. Among aerogel materials, TiO_2 aerogel is an important aerogel material combining catalytic activity, nontoxicity, good chemical stability of TiO_2 with low density, high surface area and high porosity of aerogels[3-7]. According to the literature, the catalytic activity and application of TiO_2 aerogel strongly depends on the physical properties of aerogel, such as crystal structure, surface area, and porosity.

TiO_2 aerogel and its element doped aerogels have been widely produced by sol-gel methods followed by controlling drying process of gels[8-13]. As well known, the drying process of gels is a key factor for the preparation of aerogels, and mainly has supercritical drying and ambient pressure drying. The present monolithic or particulate TiO_2 aerogels are usually obtained by the supercritical drying. The process at such high pressures needs the use of expensive autoclaves, which restricts its industrial application due to production costs. It is of interest to decrease operating pressures and temperatures. Many works have been performed to avoid the supercritical drying step in recent years, and have developed ambient pressure drying in silica and its composite aerogels[14, 15]. However, TiO_2 gel has a weaker network skeleton than SiO_2 gel, and it is very difficult to prepare single TiO_2 aerogel (not composite aerogels, such as TiO_2-SiO_2 aerogel) with monolithic shape and no cracking by ambient pressure drying. Therefore, surface modification is being developed as supplement for ambient pressure drying to try to reduce the capillary force derived from solvent evaporation in drying process, which can prevent the shrinking and crack of TiO_2 gel network and obtain the TiO_2 aerogels. Current attention has been focused on the post-modification by siloxane-base surfactant after gelation, few attentions has been paid to the surface modification during the gelation.

In the present work, we demonstrate the preparation of monolithic TiO_2 aerogels by the sol-gel process combined surface modification, followed by ambient pressure drying. Tetrabutyl titanate (TBOT) as a precursor is adopted to synthesize the TiO_2 aerogels in the presence of polyethylene glycol as a surfactant. The monolithic TiO_2 aerogels with a high specific surface area before and after heat-treatment will produce a lot of benefits and extend its application fields.

Experimental

Synthesis of monolithic aerogels

Tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT, Sinopharm Chemical Reagent Co., Ltd (China)) was used as titanium source. Mixtures of distilled water (H_2O) and ethanol (EtOH, Sinopharm Chemical Reagent Co., Ltd (China), 99.5%) were used as the solvent. Ethylic acid (HAc, Sinopharm Chemical Reagent Co., Ltd (China)) was used as catalyst as well as chelating agent. Formamide (FA, Shanghai Lingfeng Chemical Reagent Co., Ltd) was used to initiate gelation as well as a drying control chemical additive (DCCA). Tetraethoxysilane (TEOS, Sinopharm Chemical Reagent Co., Ltd (China)), ethanol (EtOH) and n-hexane were used to solvent exchange. Polyethylene glycol (PEG, average molecular weight (M_w) of 2,000, Sinopharm Chemical Reagent Co., Ltd (China) was used as a surfactant for the surface modification of gel. All the chemical reagents were used as received.

The detail of aerogel preparation was as follows. TBOT was dissolved in the EtOH, and the mixture was named as Solution A. HAc, PEG 2000, deionized water and EtOH were mixed, and the mixture was named as Solution B. The Solution B was dropped into the Solution A by 40-50 drops per minute under a strong stirring condition. After continuously stirring for 20 min, FA was then added to the mixed solutions under ambient conditions (25 ^{o}C). The container was sealed and kept at 60 ^{o}C for gelation. After gelation, the obtained wet gel was aged at 60 °C for 48 h. The aged gels were solvent exchanged in EtOH at 60 ^{o}C for 24 h three times, in TEOS/EtOH (TEOS: EtOH =1:4, volume ratio) solution at 60 ^{o}C for 18 h twice, in n-hexane at 60 °C for 48 h. The wet gel was dried at room temperature and 60 ^{o}C for 24 h, respectively. Followed by drying at 80 and 100 ^{o}C for 6 h respectively. The dried gel has a volume contraction of about 5~10 % compared with the wet gel. Some of the dried gels were heat-treated at various temperatures between 500 and 900 ^{o}C for 2 h in air. In this study, the molar ratios of TBOT: EtOH: HAc: water: FA: PEG 2000 are designed to be 1: 24: 1.8: 6: 0.6: x (x= 0.001, 0.002, 0.003, 0.004, 0.005 and 0.006), which were named as P01, P02, P03, P04, P05 and P06. The sample without adding PEG 2000 was named as P00.

Characterization of aerogels

Apparent density was determined by measuring the volume and mass of aerogel samples. Porosity was calculated by using apparent density (ρ_a) and true density (ρ_t, 3.9 $g\cdot cm^{-3}$) as follows: porosity= $(\rho_t-\rho_a)/\rho_t\times100\%$. Differential thermal analysis (DTA) was performed using a WRT-3P analyzer. The crystalline phases of aerogels were analyzed by the X-ray diffraction (XRD) on a Rigaku.D/Max-RA X-ray diffractometer using nickel filtered Cu-Kα radiation in the range of 2θ is 10~80° with a scanning speed of 2°/min. The morphology and structure were examined by scanning electron microscope (SEM, FEI SIRION, 25 KV) and transmission electron microscopy (TEM; FEI, Tecnai G2 F30) equipped with an energy dispersive spectroscopy (EDS) detector. Contact angle measurement was performed to determine the surface character of the monolithic aerogels using a GBX Digidrop system. The nitrogen adsorption–desorption of aerogels were characterized by a nitrogen adsorption–desorption apparatus (Quantachrome Autosorb-1-C). Before each nitrogen adsorption–desorption measurement, the samples were degassed at 200 °C under vacuum for more than 6 h. Specific surface area and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) respectively.

Results and discussion

Effects of surfactant on gelation and microstructure of aerogels

In the system, the hydrolysis and polycondensation of tetrabutyl titanate will produce titanium-oxygen based (≡Ti-O-Ti≡) polymers, and form an alcogel-gel with a spatial network structure. The structure and properties of the gel are largely determined by subsequent drying and surface modification. Fig. 1 shows the gelation time of TiO_2 sols with different PEG 2000 contents. The gelation time of TiO_2 sol firstly increases, and then decreases, with the increase of PEG 2000 content. When the molar ratio of PEG 2000:TBOT increases from 0 to 0.006, the gelation time decreases from 18 to 13.5 min. It indicates that the surface modification of PEG 2000 accelerates the gelation of TiO_2 sol to some extent.

Fig. 2 shows the apparent densities and porosities of TiO_2 aerogels with different PEG 2000 contents. The apparent density of TiO_2 aerogels slightly decreases and the corresponding porosity increases, with the increase of PEG 2000 content. The apparent density and porosity of the TiO_2 aerogels without surface modification are 0.818 $g\cdot cm^{-3}$ and 79% respectively, and the apparent density becomes the minimum as low as 0.716 $g\cdot cm^{-3}$ and the corresponding porosity is about 81.6%, when the molar ratio of PEG 2000:TBOT reaches to 0.005 (P05 sample). With the further increase of PEO 2000 content, the apparent density increases and the corresponding porosity decreases.

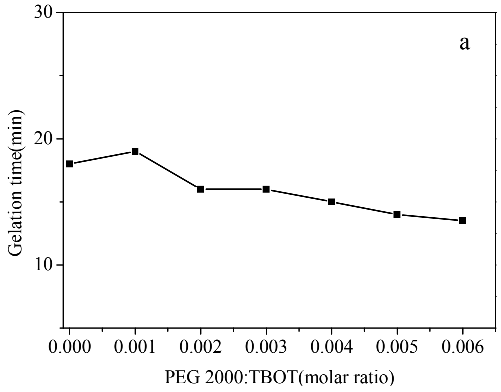


Fig. 1 The gelation time of TiO_2 sols with different PEG 2000 contents

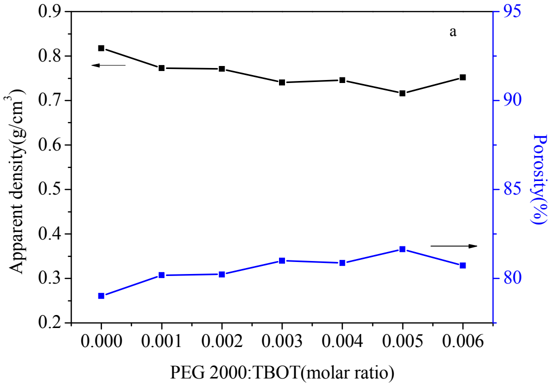


Fig. 2 Apparent densities and porosities of TiO_2 aerogels with different PEG 2000 contents

Fig. 3 shows the morphology of fracture surface of TiO_2 aerogels with different PEG 2000 contents. Compared with the aerogel without surfactant (Fig. 3g), the P05 aerogel sample (Fig. 3e) shows a pore structure with smaller pore size and uniform pore size distribution. With the further increasing amount of surfactant, the macropore size become larger and the particles aggregate to form skeleton. The dried aerogel (P05 sample) shows monolithic shape without cracks, although its outside is not smooth, as shown in Fig. 3h.

As well known, the TiO_2 compounds are hydrophilic, which restricts the drying of TiO_2 products in the aqueous system. Therefore, the modification of TEOS was adopted to improve ambient pressure drying of the wet TiO_2 aerogel. Fig. 4 shows contact angle tests for water of TiO_2 aerogels before and after modified by TEOS. The surface of the monolithic aerogels before modification was found to be super-hydrophilicity with the contact angle of almost 0°. However, the surface after modification was confirmed to be hydrophobic with the contact angle of 122°. The hydrophobic surface could be attributed to the formation of $–OSi(CH_3)_3$, which stems from the hydrolysis reaction of TEOS on the surface of the wet gel network. As a result, the super-hydrophobic character is in favor of ambient pressure drying of the aerogel. From the EDS analysis of dried TiO_2 aerogel after modification (Fig. 5), there exist Ti, Si, C and O elements in the TiO_2 aerogel, which also confirms the modification of TEOS.

Fig. 6 shows N_2 adsorption-desorption isotherms and pore size distribution of the typical TiO_2 aerogels. It shows that isotherms of three samples are type IV isotherms with H3 hysteresis loops according to the IUPAC classification, signifying the existence of slit-shaped pores. As revealed from the BJH pore size distribution[16], the plate-like particles gives rise to the slit-shaped pores, and the pores are basically distributed in mesopore region. The variation of the size and shape of the pores may be associated with the surface modification of PEG 2000. From the BET surface area and median pore size in Table 1, the dried gel without surfactant possesses a surface area of 415 $m^2 \cdot g^{-1}$ with a average pore size of about 8 nm and a whole pore volume of 0.86 $cm^3 \cdot g^{-1}$. The addition of surfactant (P05 sample) increases surface area to 495 $m^2 \cdot g^{-1}$, and increases the pore size to 10 nm and the pore volume to 1.181 $cm^3 \cdot g^{-1}$, respectively. With the further increases in surfactant (P06 sample), the surface area decreases to 411 m^2/g, and the pore size and volume rapidly decrease to 8 nm and 0.84 $cm^3 \cdot g^{-1}$, respectively. The huge changes in pore size and volume could attributed to the formation of macropores, which derived from the occurrence of the phase separation due to spinodal decomposition. The result is in agreement with the previous works reported by Kazuki Nakanishi et al. [17-19].

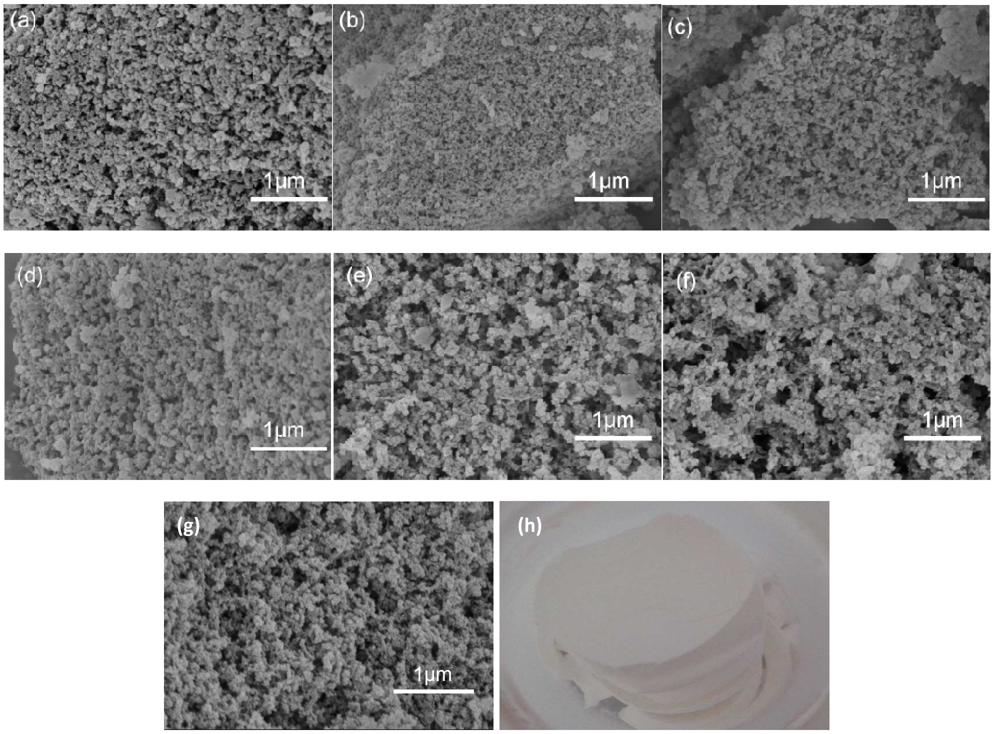


Fig. 3 Morphology of fracture surface of TiO_2 aerogels with different PEG 2000 contents

(a- PEG 2000:TBOT=0.001, b- PEG 2000:TBOT=0.002; c- PEG 2000:TBOT=0.003; d- PEG 2000:TBOT=0.004; e- PEG 2000:TBOT=0.005; f- PEG 2000:TBOT=0.006; g-without PEG; h- monolithic aerogel with PEG 2000:TBOT=0.005;

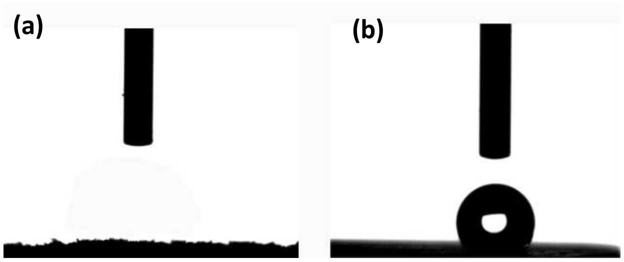
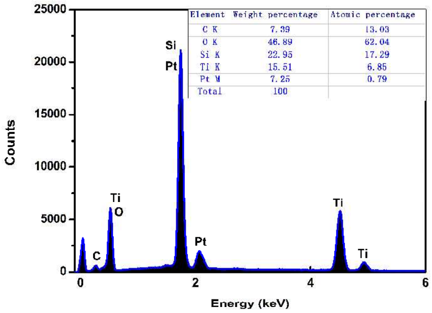


Fig. 4 Contact angle tests for water of TiO_2 aerogels before (a) and after (b) modified by TEOS



Element	Weight percentage	Atomic percentage
C K	7.39	13.03
O K	46.89	62.04
Si K	22.95	17.29
Ti K	15.51	6.85
Pt M	7.25	0.79
Total	100	

Fig. 5 EDS analysis of dried TiO_2 aerogel after modified by TEOS

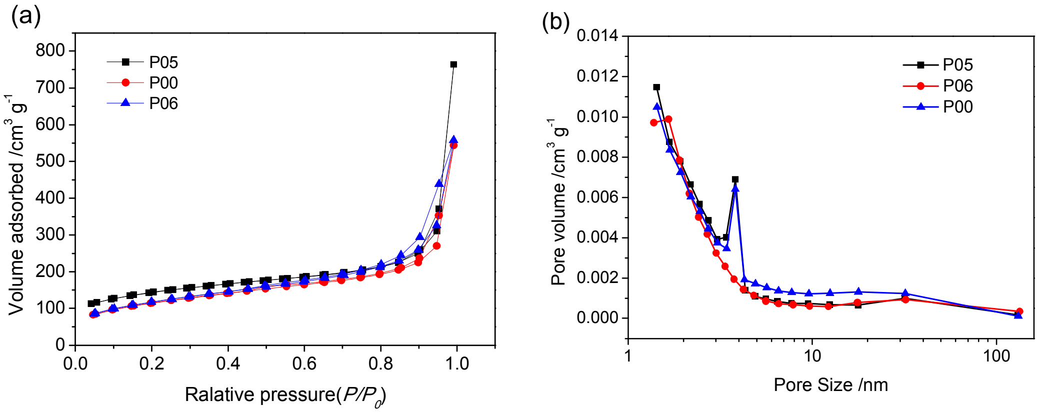


Fig. 6 N_2 adsorption-desorption isotherms and pore size distribution of the typical TiO_2 aerogels

Heat-treatment and characterization of aerogel after surface modification

Fig. 7 shows the DTA curve of monolithic TiO_2 aerogel after surface modification (P05 sample). A endothermic peaks near 104 and 225 °C are attributed to the volatilization of adsorbed water and the fracturing of -OH groups, and a small exothermic peak at 305 °C is ascribed to the pyrolysis of organic species and the evaporation of water in the pores[10]. A very small exothermic peak at 668 °C is possibly attributed to the crystallization of anatase phase. Štengl has also reported that an exotherm appears at 420 °C for anatase crystallization in titania gel by low temperature supercritical drying[6]. In contrast, high crystallization temperature in Fig. 7 indicates that the formation of macropore structure derived from surface modification can restrict the crystallization of anatase from titania gel to some extent. A relative big exothermic peak at 910 °C is possibly attributed to the transition of anatase-rutile.

The heat-treatment of the typical monolithic TiO_2 aerogel after surface modification was carried out at 500, 700 and 800 °C with a heating rate of 1-2 °C·min^{-1}. Fig. 8a shows the variation of XRD patterns of typical TiO_2 aerogels at different heat-treatment temperatures. There are no discernible peaks found from the dried gel heat-treated at 500 °C. The gel heat-treated at 700 °C still belongs to the amorphous structure, while very small peak attributed to anatase phase appears, indicating that amorphous structure begins to transform into anatase phase at this temperature. When the heat-treatment temperature increases to 800 °C, the diffraction peaks ascribed to anatase phase diminishes completely, while the width of these diffraction peaks is very broad, indicating the formation of nanoscale anatase crystallites. In general, the transition to anatase of TiO_2 aerogel is at temperature 420 °C, and transition of anatase-rutile at temperature 600-700 °C[6,12]. It also confirms that the surface modification can restrict the crystallization of anatase phase and the transition of anatase-rutile, which coincides with the results of DTA (see Fig. 7)[20].

Table 1 Properties of typical titania aerogels containing different PEG 2000 contents

Sample	Specific surface area /m^2·g^{-1}	Total pore volume /cm^3·g^{-1}	Average pore size /nm
P00	415	0.86	8
P05	495	1.181	10
P06	411	0.84	8

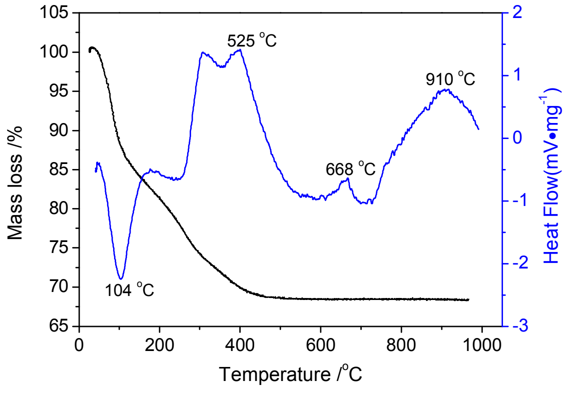


Fig. 7 DTA curve of monolithic TiO_2 aerogel after surface modification (P05 sample)

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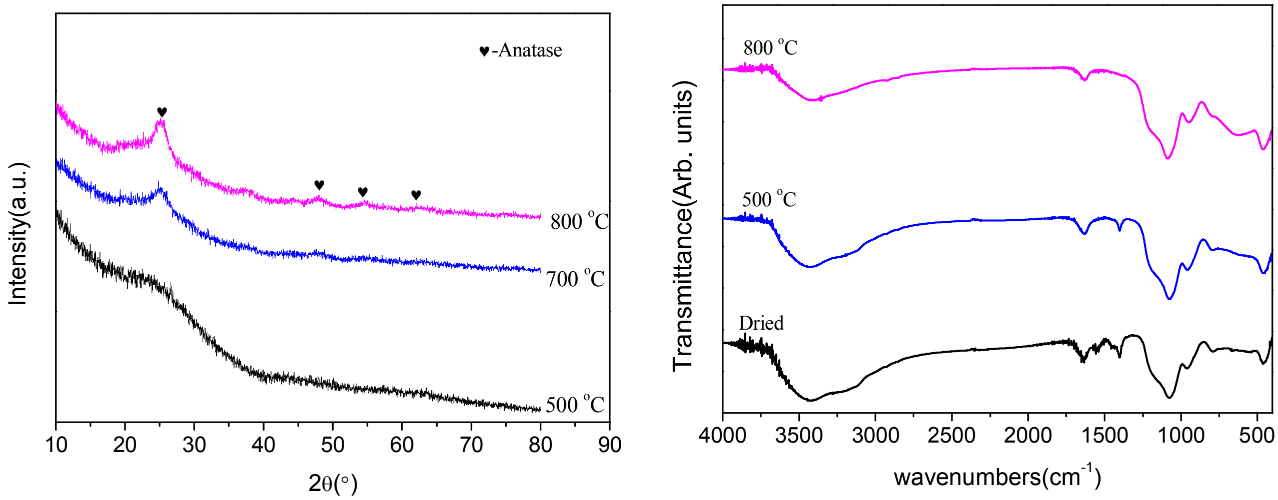

Fig. 8 XRD patterns and IR of typical TiO_2 aerogels at different heat-treatment temperatures

Fig. 8b shows the IR spectra of typical TiO_2 aerogels before and after heat-treatment. The intense broad bands at 3450 and 1630 cm^{-1} are assigned to stretching vibrations of the hydroxyl groups on the surface and bending vibrations of the adsorbed water molecules, respectively[21]. These peaks become weak after heat-treatment, indicating the removal of water. The two bands at 1070 and 800 cm^{-1} are attributed to Si-O antisymmetric and symmetric stretching vibration, and do not vary after heat-treatment[18]. The broad band attributed to Ti-O stretching vibration appears at 650 cm^{-1} after heat-treatment, indicating the crystallization and transition of anatase phase. The band at 450 cm^{-1} is corresponded to the superimposing of Ti-O bending vibration and Si-O bending vibration, and the band at 950 cm^{-1} is ascribed to the Ti-O-Si asymmetric stretching vibration[22-24]. It indicates that the gel network of titania is actually reacted with the hydrolysis production of TEOS to strengthened the gel network. The three bands at 1550, 1450 and 1400 cm^{-1} are attributed to the C–H vibrations derived from the residual organic groups[17], and eliminate after heat-treated at 800 °C, indicating that the removal of organic matters.

The variation of microstructure and properties of crystalline titania aerogel after heat-treatment was examined. It is found that compared with the aerogels without heat-treatment, the crystalline titania aerogel has a shrinkage about 10 %, while still keeps the shape and morphology before heat-treatment. Fig. 9 shows the morphology and N_2 adsorption-desorption isotherm of aerogel heat-treated at 800 °C. The morphology is basically maintained after heat-treatment, indicating that the formation of crystalline phase does not spoil the morphology of aerogel, although some agglomerations exist. In contrast to the macrostructure, the micro-mesoporous structure is slightly altered by the heat-treatment. From Fig. 9b, the aerogel heat-treated at 800 °C still exhibits the type IV isotherm with H3 hysteresis according to the IUPAC classification. A comparison with Fig. 6a and Fig. 9b reveals that the number of the pores, especially micro-mesopores decreases and the aerogel becomes much denser, after heat-treatment. After heat-treatment, the specific surface area decreases from 495 $m^2 \cdot g^{-1}$ (before heat-treatment) to 209 $m^2 \cdot g^{-1}$, which indicates that specific surface area still keeps a relative high value after heat-treatment. The variation of surface area and pore size after the heat-treatments is mainly due to the formation of anatase phase and the sintering of nanocrystalline titania particles.

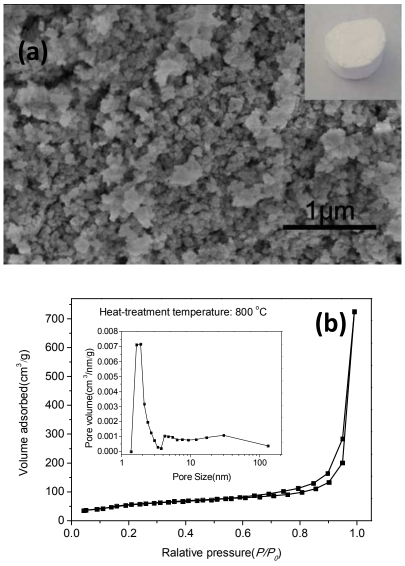

Fig. 9 Morphology (SEM image and photograph (inset)) (a) and N_2 adsorption-desorption isotherm (b) of aerogel heat-treated at 800 °C

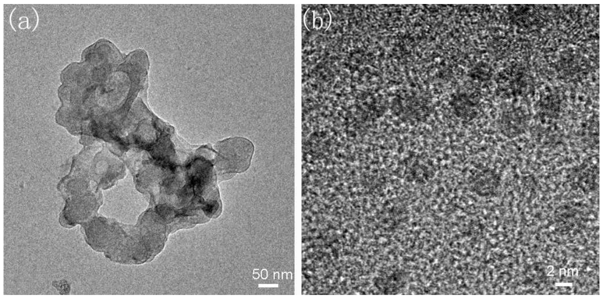

Fig. 10 Low (a) and high (b) magnification TEM image of the resulting TiO_2 aerogels

As shown in Fig. 10a, the aerogels were constructed by nanoparticles. The nanoparticles interconnect into a network porous structure. Fig. 10b indicates monolithic TiO_2 aerogels are well crystallized, which is in good accordance with the results of XRD (Fig. 8a).

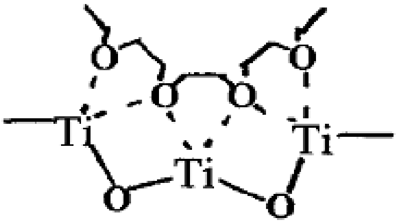

Fig. 11 Crown ether composed of PEG chain segments and Ti atoms

Surface modification mechanism of polyethylene glycol 2000

Polyethylene glycol 2000 is a polymer of ethylene oxide with a molecular weight of 2,000 $g{\cdot}mol^{-1}$. In the present system, the PEG firstly forms the micelles in the solution, and the O atoms on the micelles will combine with Ti atoms of tetrabutyl titanate through weak coordination bonds to obtain the crown ether structured organic-inorganic compounds (as shown in Fig. 11) [17, 25, 26]. After the hydrolysis of tetrabutyl titanate on the structure, the –OH groups on the sol particles can preferentially combine with the PEG chain segments mediated by HAc *via* hydrogen bonds. Then, the resulting complexes self-assemble based on the mesoscopic ordering directed principally by the microphase separation of PEG. Subsequent, titania/PEG composites with porous structure are formed through occurrence of cross-linking and polymerization of Ti atoms [26].

The modification mechanism of PEG 2000 on the titania aerogel can be built according to the combination of PEG chain segments and sol particles, as shown in Fig. 12. Due to long chain segments, PEG is prone to twisting and crosslinking, which leads to the wrapping and intertwining in the solution system. Therefore, wrapping sol particles and crosslinking sol particles possibly are two main mechanisms for the combination of PEG 2000 and sol particles. The former hinders the growth of individual sol particles, while the latter promotes the aggregation of sol particles to form clusters. The relative superiority of two mechanisms is related to the addition amount of PEG 2000.

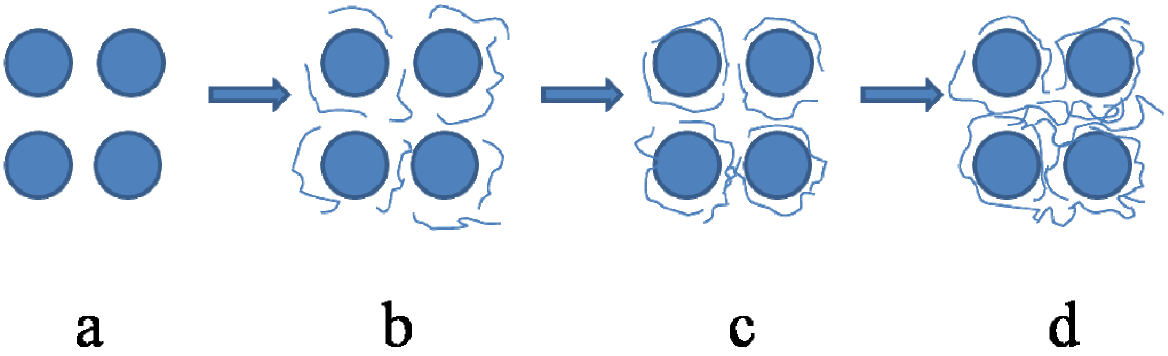

Fig. 12 Function mechanism of PEG in sol (a, sol particles; b, PEG chain segments dispersing in sol; c, PEG chain segments wrapping sol particles; d, PEG chain segments crosslinking with sol particles)

When the addition amount of PEG 2000 is small, the wrapping mechanism occupies the superiority to produce steric hindrance between the sol particles, which inhabits the polycondensation and delays the transition of sol-gel (as seen in Fig. 1). With the increase of PEG 2000 content, the crosslinking mechanism will gradually become strong and occupy the superiority, and makes the number and size of clusters increase, which leads to the formation of three-dimensional network structure and induce occurrence of phase separation owing to the spinodal decomposition[18]. It is why the gelation time decreases with the further increase of PEG 2000 content (Fig. 1). When the PEG 2000 is added much, one part of PEG 2000 participates the formation of gel skeletons through the wrapping and crosslinking mechanisms, the other part will stay in the solvents in the form of aggregates. These aggregate will be replaced and removed during solvents changing, which results in the formation of the macropores in the gels (as shown in Fig. 3f).

Conclusions

Monolithic titania (TiO_2) aerogels were successfully synthesized by the sol-gel process combined surface modification, followed by ambient pressure drying. The addition of polyethylene glycol (PEG 2000) as surfactant basically reduced the gelation time of TiO_2 sol, slightly decreased the apparent density of the prepared TiO_2 aerogels, and obviously increased specific surface area (up to 495 $m^2{\cdot}g^{-1}$). The modification mechanisms of PEG 2000 on the TiO_2 sol particles were wrapping and crosslinking due to its long chain segments, whose relative superiority was related to the addition amount of PEG 2000. The crystalline anatase phase was obtained after heat-treated at 800 ^{o}C. Heat-treatment did not spoil the monolithic shape and macrostructure of titania aerogels, and still kept a surface area as high as 209 $m^2\cdot g^{-1}$. The monolithic TiO_2 aerogels will produce a lot of benefits and extend its application fields such as catalysis, separation and absorption.

Acknowledgements

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Notes and references

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1 C. P. Alain, and M. P. Ge´rard, s, ©., 2002, **102**, 4243.
2 C. Daniel1, D. Alfano1, and V. Venditto, *Adv. Maters.*, 2005, **17** 1515.
3 B. Malinowska, J. Walendziewski, and D. Robert, *Int. J. Photoenergy*, 2003, **5**, 147.
4 G. Dagan, and M. Tomkiewicz, *J. Phys. Chem.*, 1993, **97**, 12651.
5 W.I. Kim, D. J. Suh, and T.J. Park, *Top. Catal.*, 2007, **44**, 499.
6 V. Štengl, S. Bakardjieva, and J. Subrt et al, *Micropor. Mesopor. Mater.*, 2006, **91**, 1.
7 L. Zhang, Z. Liang, and K. Yang, *Anal. Chim. Acta.*, 2012, **729**, 26.
8 Y.C. Chiang, W.Y. Cheng, and S.Y. Lu, *Int. J. Electrochem. Sci.*, 2012, **7**, 6910.
9 W.J. Sung, S.H. Hyun, D.H. Kim, *J. Mater. Sci.*, 2009, **44**, 3997.
10 Z. Zhao, X. Jiao, and D. Chen, *J. Mater. Chem.*, 2009, **19**, 3078.
11 L. Abramian, and H. El-Rassy, *Chem. Eng. J.*, 2009, **150**, 403.
12 M. Popa, L. Diamandescu, F. Vasiliu, and C. M. Teodorescu, *J. Mater. Sci.*, 2009, **44**, 358.
13 M. Popa, D. Macovei, E. Indrea, and I. Mercioniu, *Micropor.Mesopor. Mater.*, 2010, **132**, 80.
14 Z. Xu, L. Gan, Y. Jia, Z. Hao, M. Liu, and L. Chen, *J. Sol-Gel Sci. Technol.*, 2007, **41**, 203.
15 X.J. Liu, L. Bai, F. Shi, and Z. Hu,, Adv. Mater. Res., 2012, **534**, 101.
16 K. S. W. Sing, *Pure & Appl. Chem.*, 1985, **57**, 603.
17. A. Du, B. Zhou, J. Shen, S. F. Xiao, Z. H. Zhang, C. Z. Liu and M. X. Zhang, *J. Non-Cryst. Solids*, 2009, **355**, 175.
18. K. Kanamori, M. Aizawa, K. Nakanishi and T. Hanada, *J. Sol-Gel Sci. Techn.*, 2008, **48**, 172.
19. K. Kanamori, M. Aizawa, K. Nakanishi and T. Hanada, *Adv. Mater.*, 2007, **19**, 1589.
20. Y. Wang, Y. C. Zou, J. Chen, G. D. Li and Y. Xu, *Rsc. Adv.*, 2013, **3**, 24163..
21. C. C. Huang, Z. J. Wei, L. Zhang, X. Luo, H. B. Ren and M. M. Luo, *J. Porous Mat.*, 2013, **20**, 1017.
22. S. J. Bu, Z. G. Jin, X. X. Liu, H. Y. Du and Z. J. Cheng, *J. Sol-Gel. Sci. Techn.*, 2004, **30**, 239.
23. F. J. Heiligtag, N. Kranzlin, M. J. Suess and M. Niederberger, *J. Sol-Gel. Sci. Techn.*, 2014, **70**, 300.
24. Y. N. Kim, G. N. Shao, S. J. Jeon, S. M. Imran, P. B. Sarawade and H. T. Kim, *Chem. Eng. J.*, 2013, **231**, 502.
25. J. H. Sun, B. Zhang, W. H. Fan, D. Wu, and Y. H. Sun, *Chin. J. Maters. Res.*, 1999, **13**, 301.
26 P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, 396: 152-155.