Applied Surface Science 257 (2011) 10725–10728

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Fabrication of three-dimensionally ordered macroporous $Ta_2O_5$ films through aqueous organic gel process

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ARTICLE INFO

*Article history:*
Received 17 May 2011
Received in revised form 18 July 2011
Accepted 19 July 2011
Available online 23 July 2011

*Keywords:*
Three-dimensionally ordered macroporous (3-DOM)
Colloidal crystals
Aqueous organic gel process
Porous materials
X-ray diffraction

ABSTRACT

$Ta_2O_5$ thin films have been prepared in the forms of three-dimensionally ordered macroporous (3-DOM) materials through aqueous organic gel process guided by polystyrene (PS) colloidal templates. The structure of the films was strongly affected by the infiltration process. This suggests that the infiltration process which aims at introducing desired materials into the interstitial spaces between the PS templates is of critical importance. Dip-drawing method was adopted for infiltration in this article. However, excess precursor worked as a capping agent for films prepared from the precursor of high concentration. Spin-coating method can efficiently remove the excess precursor by high speed rotating, which makes it a promising process for the infiltration of Ta-citric precursor with concentration higher than 0.5 mol/L. X-ray diffraction (XRD) pattern showed that the products can crystallize at 600 °C and had a pure orthorhombic phase. The chemical composition of the product was also studied by X-ray photoelectron spectroscopy (XPS).



## 1. Introduction

Three-dimensionally ordered macroporous (3-DOM) materials with uniform, ordered macroporous structure have attracted extensive attention in physics, chemistry and material science communities [1,2]. Well organized 3-DOM metals, metal oxides or semiconductors are increasingly finding applications in the fields of separation, catalyst supports, chemical sensors and optical devices. Materials with ordered structure also open up opportunities to search new properties. Thus many researchers have made great efforts to design materials into ordered arrays.

$Ta_2O_5$ is of high refractive index and low absorption. This material has chemical and thermal stability in the spectra region ranging from near-UV to IR, which makes it useful as coatings. $Ta_2O_5$ can also be used to make capacitors in cell phones, pagers and high-speed tools [3]. Schmuki et al. have fabricated the highly aligned uniform $Ta_2O_5$ pores of several tens of micrometers in length by anodization of Ta [4,5]. The composition of the electrolyte and the anodization parameters was optimized to obtain high quality products. This method provides a convenient way to prepare nanotubular $Ta_2O_5$ directly on Ta substrates. Arnould et al. have successfully fabricated $Ta_2O_5$ in two-dimensionally (2-D) ordered architectures in ionic liquids [6]. However, the material can only be deposited on conductive plates. Moreover, the obtained 2-D $Ta_2O_5$ is not very desirable due to short-range ordering and non-uniform pore size. Wang et al. have reported the synthesis of 3-DOM $Ti_{1-x}Ta_xO_{2+x/2}$ by using sol–gel method, whereas the researchers paid more attention on $Ti_{1-x}Ta_xO_{2+x/2}$ rather than $Ta_2O_5$ [7]. To the best of our knowledge, research focuses on the fabrication and characterization of 3-DOM $Ta_2O_5$ through aqueous organic gel process has not been reported.

Nowadays, 3-DOM materials are synthesized basically through template-assisted route including self-assembly of the colloidal crystal templates, infiltration of the desired materials and removal of the templates. The infiltration process plays a key role in the fabrication of the architectures. Many infiltration routes such as chemical vapor deposition (CVD), atomic layer deposition (ALD), electrochemical deposition and electrophoresis have been employed. In this work, we proposed an aqueous organic gel process for the preparation of the precursor. The method has the advantages of homogeneous mixing at molecule-level, low processing temperature, use of an aqueous based processing system and no need for a special atmosphere. Dip-drawing method was adopted for introducing the precursor into the interstitial spaces between the polystyrene (PS) colloidal crystal templates. There are many difficulties when introducing the precursors into the interstices of templates. During Wang's fabrication of $Ti_{1-x}Ta_xO_{2+x/2}$ using sol–gel chemistry, it is mentioned that an excess of precursor worked as a capping agent and resulted in the formation of a thick crust on the template surface [7]. They controlled the weight

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doi:10.1016/j.apsusc.2011.07.087

ratio of template to precursor at 1:2 to ensure a good infiltration. However, the precise control of the ratio is difficult in practical applications and the weight of the template is hard to be estimated especially when the template is assembled on a substrate. In this paper, the precursor concentration was varied to investigate the relationship between the concentration and the formation of a crust. And a convenient spin-coating method was employed to avoid the aggregation of the organic precursor and hence the formation of a crust.

## 2. Experimental

### 2.1. Materials and preparation

Reagents used were monodisperse PS spheres (diameter 370 nm), $Ta_2O_5$, hydrofluoric acid, ammonium oxalate, ammonia, citric acid and isopropanol. Water used in all experiments was purified with a resistivity greater than 18 ΩM/cm. A clear transparent Ta-citric precursor, which has high stability and no precipitation for several months after preparation, was prepared according to a previous report by Zhao and co-workers [8,9]. ICP analysis was carried on to estimate the Ta content. The concentration of the precursor can be varied by dilution with water. Monodisperse PS colloidal spheres were grown on microslides by using a controlled vertical drying method to form well ordered PS thin films which display a typical iridescent behavior [10]. The coloration of the thin films is strongly dependent on the angle of viewing due to the single preferential orientation of the ordered arrays [11].

Dip-drawing method was used for the infiltration of the desired materials. The self-assembled templates were immersed into the precursor at a rate of 1–5 cm/s, and kept there for ~30 s. Then the templates were pulled out of the precursor at the rate of 1–5 cm/s to ensure a precisely controlled infiltration. The prepared precursor was infiltrated into the interstices by capillary force. The PS/Ta-citric composites were hung vertically for 24–48 h to remove the excess precursor because of gravity and solidify the infiltrated material. For the heat-treatment procedure, the samples were placed into a furnace and the temperature was raised slowly (1 °C/min) to 600 °C and kept there for 2 h to remove the PS templates and obtain 3-DOM $Ta_2O_5$ thin films.

### 2.2. Characterization

The morphologies of the products were characterized using a high-resolution scanning electron microscope (HR-SEM, Hitachi S-4800) operated at 20 kV. The phase composition of the 3-DOM $Ta_2O_5$ thin film was analyzed by using X-ray diffraction (XRD) on a Phillips X Pert diffractometer equipped with Cu Kα radiation in the range of $2\theta$ = 10–70°. The X-ray photoelectron spectroscopic (XPS) analysis of the samples was carried out on a PHI 5700 XPS system. All the binding energies were referenced to the C1s peak at 284.6 eV of surface contamination carbon.

## 3. Results and discussion

Typical morphology of the assembled PS thin film is presented in Fig. 1. In this image, the top surface of the film is in a close-packed hexagonal array and the diameter of the spheres is confirmed to be 370 nm. The ordered colloidal crystal is composed of a face-centered cubic lattice of spheres, the top (1 1 1) surface of which is parallel to the substrate, giving rise to an ideal duplicated architecture as template.

Various methods for templating oxides into 3-DOM structure have been tried. Dip-drawing method described in Section 2 is the most widely used one for the convenient operation. 3-DOM $Ta_2O_5$ thin film synthesized from 0.2 mol/L Ta-citric precursor through dip-drawing is shown in Fig. 2(a). A bigger air sphere which originates from a larger PS sphere in the original template is observed as indicated in Fig. 2(a) (marked by a circle). The bigger air sphere and some other defects in the packing of the pores can be attributed to the imperfections of the template. The architecture is of low strength as indicated by the thin pore wall which resulted from the low solid content of the precursor. Hence precursor being prepared at higher concentration is of great importance in order to maximize the density of the material in the final array. We can modify the precursor concentration and gain a range of inverse replicas through dip-drawing method. However, this is the case of precursors with moderate viscosity, but not for precursors with high viscosity. Ta-citric precursor of high concentration is very viscous which makes it solidify immediately after the substrates have been pulled out and thus can not be removed by hanging the substrates up. The excess Ta-citric precursor which is not filled into the void spaces works as a capping agent and results in a crust. Fig. 2(b) gives an illustration on the morphology of the crust. The product shown in Fig. 2(b) was synthesized from 0.5 mol/L Ta-citric precursor, and the ordered inverse array beneath the crust can also be observed.

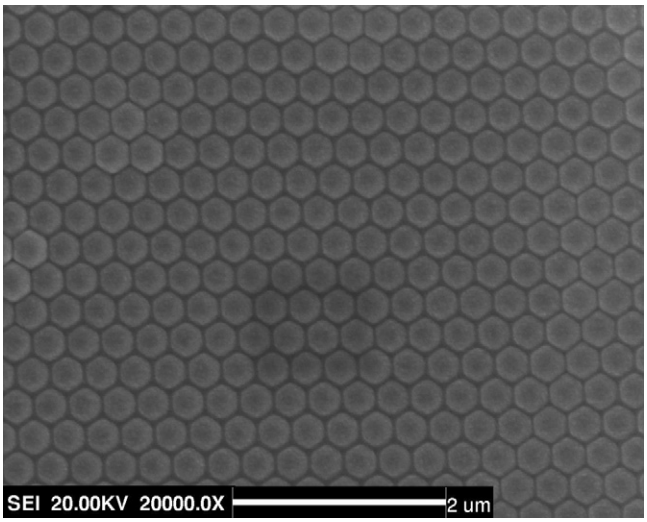


**Fig. 1.** SEM morphology of PS colloidal template prepared by a controlled vertical deposition.

The unstructured bulk crust greatly influences the observation of the ordered array and has a negative effect on the physical properties. Thus the removal of excess precursor has become a crucial factor in realizing the integrity of the inorganic inverse structures. In view of this fact, spin-coating method was employed for infiltration. The spin-coating method, interesting in that it provides force which is parallel to the substrate and removes the excess precursor instead of leaving it to evaporate in air, is a desirable infiltration-removal conjunction method to give good macroporous arrays. A standard spin coater was used to infill Ta-citric precursor into the templates. Drops of the precursor were uniformly spread on the PS template before the spin-coating was carried on. The template was spin-coated at 500 revolutions per minute (rpm) and the spinning time was 10–30 s. Then the final rotation speed (3000 rpm) was reached in a fraction of a second and kept for specific time to achieve a desired infiltration. The impregnated template was left in air for 24 h to allow the infiltrated precursor to solidify. Then the same post-treatment as we proposed in dip-drawing method (refer to Section 2.1) was applied to remove the template. The duplicated architecture obtained from 1.0 mol/L Ta-citric precursor is illustrated by Fig. 3. The SEM image shows the long-range ordering of the 3-DOM $Ta_2O_5$ product, demonstrating that the spin-coating

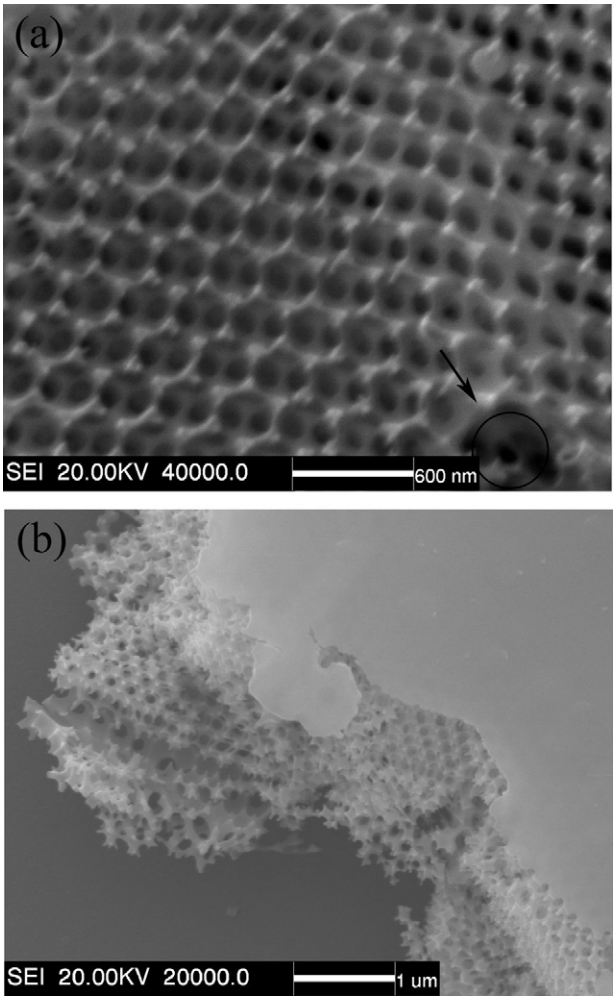


**Fig. 2.** SEM morphologies of 3-DOM architectures synthesized through dip-drawing method. The products were synthesized from Ta-citric precursor of different concentrations (0.2 mol/L (a) and 0.5 mol/L (b)). A bigger air sphere, which originates from a larger PS sphere in the original template, is indicated by a circle in (a). (b) An illustration on the morphology of the crust.

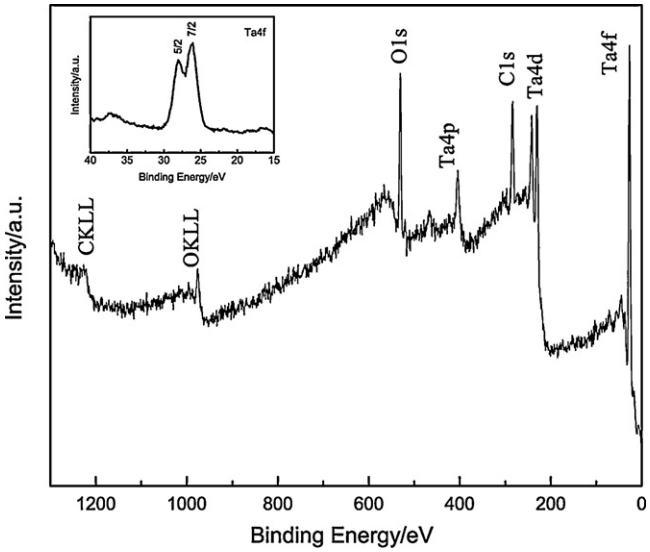


**Fig. 4.** Survey X-ray photoelectron spectrum of 3-DOM $Ta_2O_5$ film. The insert is the high resolution spectrum of Ta4f.

operation succeeded in removing the excess precursor while preserving the porous structure of $Ta_2O_5$.

The XPS survey spectrum of the sample calcined at 600 °C is shown in Fig. 4. According to the result, the as-synthesized sample contains C, O and Ta, no other element is detected. However, the result does not reflect the C content in the sample. The existence of C1s peak might be caused by organic residue, $CO_2$ adsorption or carbon compound from environment (contamination carbon). Since the PS template can be completely removed by calcination at or above 450 °C in air, the effect of residual carbon from organic raw materials can be ignored. Take $CO_2$ adsorption and carbon compound from the environment into account, the C content on the surface of the 3-DOM architecture is higher than that of the inner layers. High resolution spectrum of Ta region is shown in the insert of Fig. 4. The Ta region exhibits the 4f 7/2 peak at 26.2 eV. The spectrum is characteristic of $Ta_2O_5$, demonstrating that the replica is composed of $Ta_2O_5$.

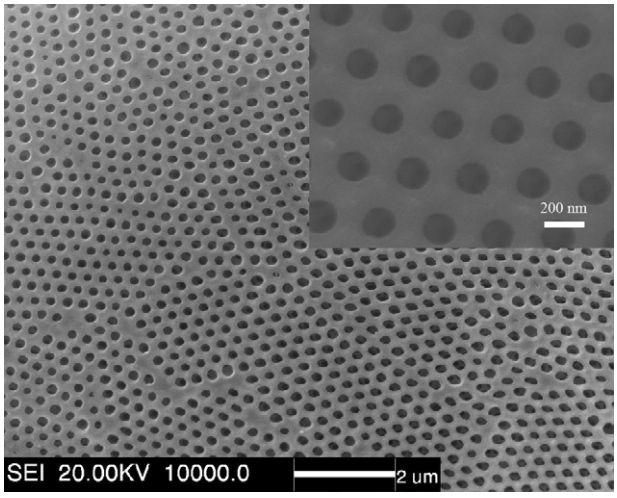


**Fig. 3.** SEM morphology of duplicated architecture obtained from 1.0 mol/L Ta-citric precursor through spin-coating.

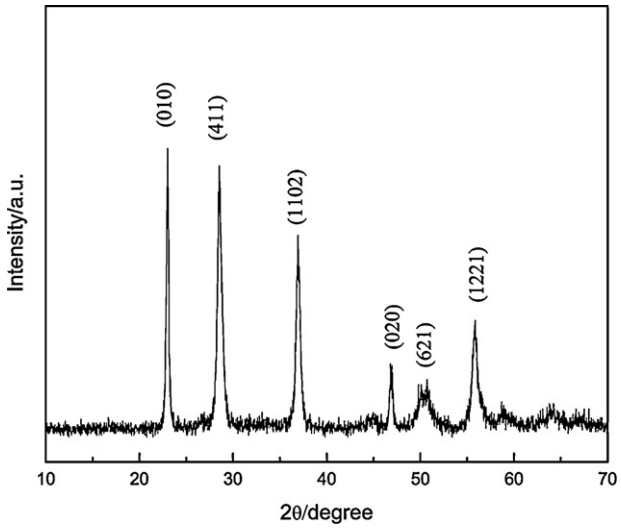


**Fig. 5.** X-ray diffraction pattern of $Ta_2O_5$ powder.

Crystallinity and crystal structure of the product is very important. However, it is difficult to obtain good-quality analytical data directly on these films, as they are of low solid content and most methods observe the substrates as well as the films. We removed the thin films from the substrates, but the sample was not enough to be characterized. Hence a bulk xerogel was produced by evaporating Ta-citric precursor at 40 °C, and then the xerogel was heat-treated under the same condition as the films. The powder sample obtained was then studied by XRD. As shown in Fig. 5, the diffraction pattern displays typical peaks at $2\theta \cong 23^\circ$, 28° and 37°, which can be indexed as (0 1 0), (4 1 1) and (1 1 0 2) reflections of orthorhombic $Ta_2O_5$ (JCPDF#79-1375). The sample is a pure phase, indicating that the product can crystallize at 600 °C. The pattern shows no preferred orientation. And the crystalline grain sizes calculated from the widths of the (0 1 0) and (4 1 1) peaks at half maxima are both ~20 nm by the Debye–Scherrer formula.

## 4. Conclusions

In summary, the results of the work represent that 3-DOM $Ta_2O_5$ can be prepared through aqueous organic gel process. The fidelity of the obtained architecture is mainly a function of the precursor properties. Excess precursor works as a capping agent and leaves unstructured bulk crust which greatly affects the structure of the product. We have shown the effectiveness of spin-coating method for the synthesis of 3-DOM $Ta_2O_5$, especially for backfilling precursor of high concentration. The merit of the method is that the capping precursor can be minimized while the structure is well retained during the replication process. The XPS survey spectrum has been carried out to ensure the binding energy is in agreement with $Ta_2O_5$. And the prepared $Ta_2O_5$ is confirmed to be a pure orthorhombic phase according to XRD analysis.

## Acknowledgements

We thank the National Natural Science Foundation of China (No. 51010005, 90916020), the Program for New Century Excellent Talents in University (NCET-08-0168) and Fundamental Research Funds for the Central Universities (HIT.ICRST.2010001) for financial support.

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