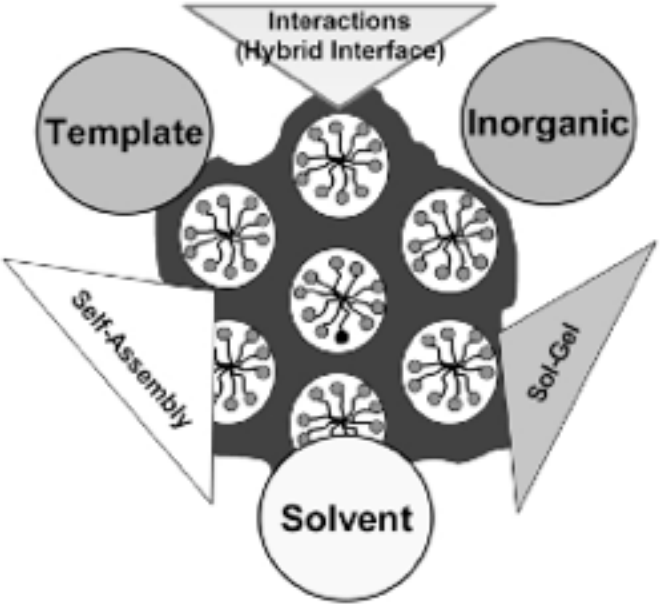

Synthesis and Characterization of Mesoporous Thin Films of Titania and Niobium Pentoxide

Master of Science Thesis in the Master Degree Programme, Materials and Nanotechnology

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Division of Applied Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2010

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This thesis work is performed in Department of Materials and Environmental Chemistry, Stockholm University under supervising of Prof. Jamses Zhijian Shen.

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Abstract

The main target of this study is to synthesize mesoporous thin films of transition metal oxide on diverse substrates, including glass slide, machined titanium substrate and porous titania substrate. The investigation was carried on two different systems: titania (TiO_2) and niobium pentoxide (Nb_2O_5). The thin films of these two transition metal oxide with mesoporous structure were achieved by surfactant templated synthesis method and dip-coating technology. The complex formation process of mesoporous thin films is studied, by tuning diverse experimental parameters, including choosing diverse species of inorganic precursors and surfactants, the ratio of reactants, pH, dip-coating method, aging conditions, etc. The resulting structure is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption.

Thin films on glass slides, machined titanium and porous titania substrates with mesoporous structure were achieved. The choosing of precursor and surfactant and the ratio of them are critical for the formation of mesophase. The morphology and mesostructure of synthesized mesoporous thin film are susceptible to evaporation rate of templating surfactant. As for the dip-coating technology, lower dipping rate leads to better morphology. Niobium Pentoxide synthesis system is very humidity sensitive, whereas the titania is not so sensitive.

Key words: mesoporous, thin film, titania, niobium pentoxide, synthesis, characterization, evaporation induced self assembly

List of abbreviations:

BC: Block Copolymer
EISA: Evaporation Induced Self Assembly
CMC: Critical Micelle Concentration
SEM: Scanning Electron Microscopy
TEM: Transmission Electron Microscopy
XRD: X-ray Diffraction
BET: Brunauer-Emmett-Teller, BET surface area analysis
P123: Pluronic P-123, a triblock copolymer ($EO_{20}PO_{70}EO_{20}$)

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1 Introduction

Since the discovery of ordered mesoporous silica materials, such as MCM-41, [1] SBA-15, [2] KIT-6, [3] and much work has been devoted to the synthesis of mesoporous transition metal oxides which are highly promising for a wide range of unique properties and potential applications. Mesoporous materials are expected to be good candidates in the applications of catalysis, separation, adsorption, and other applications, because of the superb large surface area and controllable structure and pore architecture. The aim of this chapter is to give a general introduction and a background to the project.

1.1 Mesoporous material

Mesoporous material is defined as material containing pores with diameters between 2-50 nm. A large effort is made to develop mesotextured inorganic or hybrid phases. Due to their excellent properties of highly ordered mesostructure, i.e. large surface area and tunable pore size, they are expected to be applied in the field of catalysis, photonics, magnetics, separation, adsorption, and applications in the biomedical field.

Mesoporous transition metal oxide is an important type of mesoporous materials. Synthesizing transition metal oxides without surfactant generally resulted in low surface area metal oxide samples. The metal oxides may be prepared with high surface area when a surfactant is used in the synthesis process.

Several mesoporous metal oxides have been reported, which were synthesized by neutral templated methods. Besides the first one mesoporous silica, mesoporous titanium oxide and niobium oxide attract much attention as well due to their many novel potential applications.

1.2 Surfactant templated synthesis method

Evaporation Induced Self-Assembly (EISA) is one of the most important methods applied in synthesis of mesoporous materials. A general definition of self-assembly is the spontaneous organization of materials through noncovalent interactions (hydrogen bonding, Van der Waals forces, electrostatic forces, etc.) with no external intervention. Self-assembly typically employs asymmetric molecules that have a tendency to organize into well-defined supra-molecular assemblies. Most common are amphiphilic surfactant molecules or polymers composed of hydrophobic and hydrophilic parts. [4]

Amphiphilic block copolymers (BC) belong to an important family of surfactant, widely used in detergency, emulsifying, coating, thickening, etc. [5] They are composed of hydrophobic and hydrophilic parts. In aqueous solutions above the critical micelle concentration (CMC), surfactants assemble into micelles, spherical or cylindrical structures that maintain the hydrophilic parts of the surfactant in contact with water while shielding the hydrophobic parts within the micellar interior. If the concentration keeps increasing, it will result in self-organization of micelles into periodic hexagonal, cubic, or lamellar mesophases, as shown

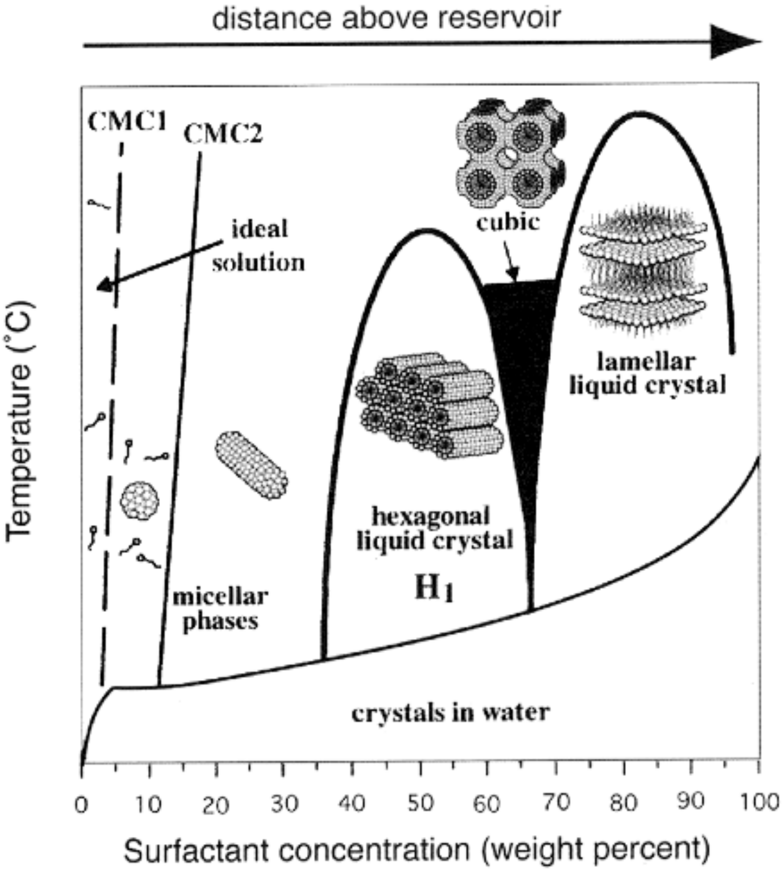


Fig. 1-1. Schematic phase diagram for CTAB in water. Arrow denotes evaporation-driven pathway during dip-coating, aerosol processing, etc. Adapted from Raman et al. [6]

in Fig. 1-1. The self-assembly characteristics of these BC permit to control the porous structure of metal oxides. The evaporation-induced self assembly (EISA) denomination was coined by Brinker et al. [4] to encompass the synthesis method leading to ordered hybrid mesophases from dilute solutions, upon solvent evaporation.

Starting from solutions below the critical micellar concentration permits one to obtain thin films or gels with excellent homogeneity (high dilution disfavors inorganic polymerization).

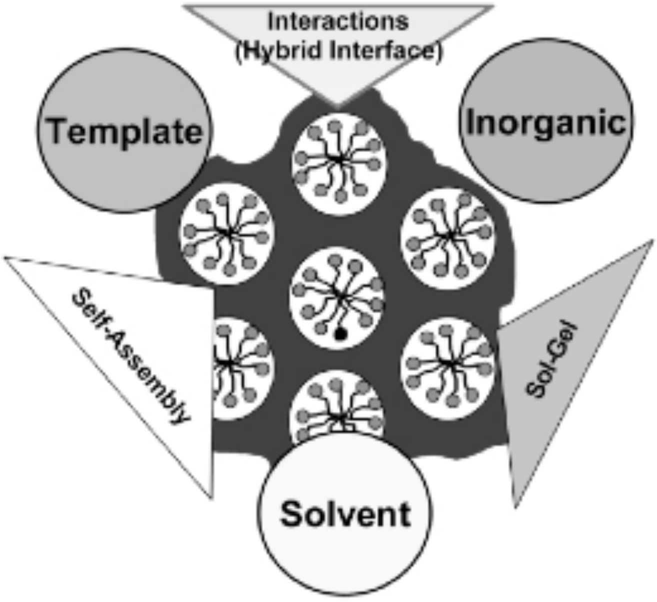


Fig. 1-2. Scheme of the main relationships between the solvent, the template and the inorganic center. [5]

The main method of synthesizing mesoporous materials in this study is the block copolymer-templated method. The choice of the organic template to spatially control the mineralization process in the mesoscale, is a key issue in the synthesis of textured or porous materials. Starting from solutions below CMC, permits one to obtain homogeneous thin films. This method is especially interesting in work with non-silica systems, where condensation has to be thoroughly controlled. Increasing the concentration of surfactant by evaporation drives self-assembly of titania-surfactant or niobium oxide - surfactant micelles and their further organization into mesostructured hybrid (Fig. 1-2). By aging or mild treatment, consolidated mesostructured hybrid is formed. After UV or heat treatment, the surfactant is extracted from the solidified mesophase, and thus the mesoporous material is achieved, as shown in Fig. 1-3. The resulting mesostructure varies by differences in the initial alcohol/water/surfactant mole ratio. In order to obtain mesophase in the form of thin film. Dip-coating is an easy and efficient way to achieve steep evaporation gradient, as depicted in Fig. 1-4, which represents a rather steep concentration gradient, due to the large surface of thin film. The control of the evaporation rate is thus critical in this system.

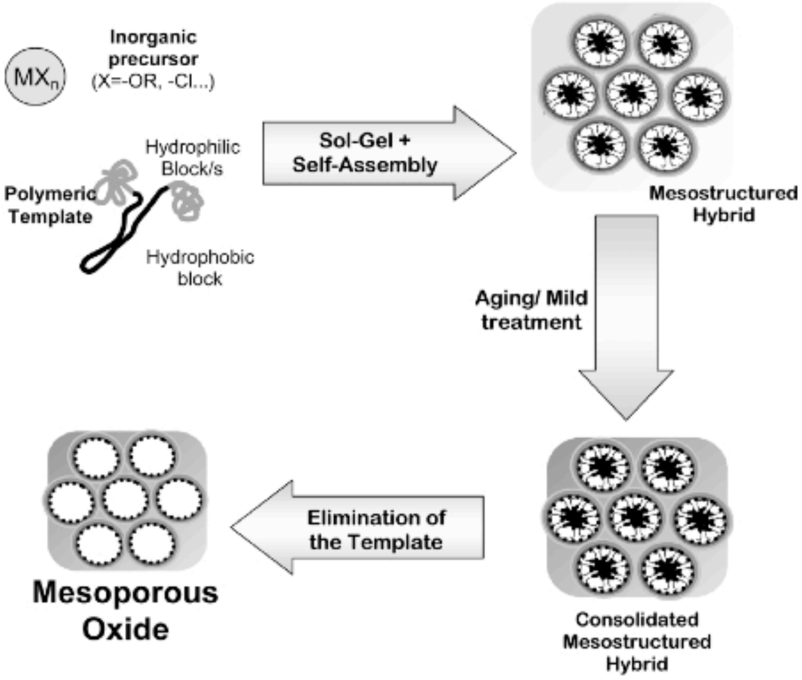


Fig. 1-3. Schematic view of the steps leading from a solution to a mesoporous oxide network. [5]

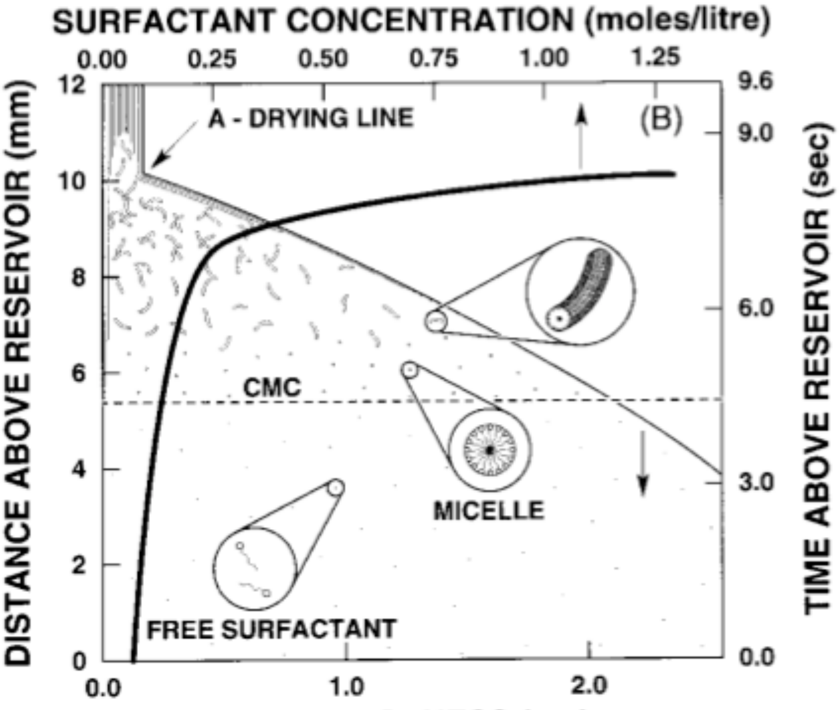


Fig. 1-4 Schematic illustration of self-assembly of organic-inorganic nanolaminates during dip-coating. Evaporation induces micelle formation and concurrent incorporation of organic precursors into micellar interiors. Further evaporation drives continuous accretion of nanolaminated form. [7]

1.3 Coating technology

Dip-coating is applied in the experiments. Dip coating techniques can be described as processes where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal rate under controlled temperature and atmospheric conditions. A uniform thin film of liquid will solidify upon solvent evaporation into a coating. The coating thickness is mainly defined by the withdrawal rate, viscosity of the liquid and gas overhead. Thickness and uniformity can be sensitive to flow conditions in the liquid bath and gas overhead. The faster the substrate is withdrawn, the thicker the film deposited. The schematics of a dip coating process are shown in Fig. 1-5.

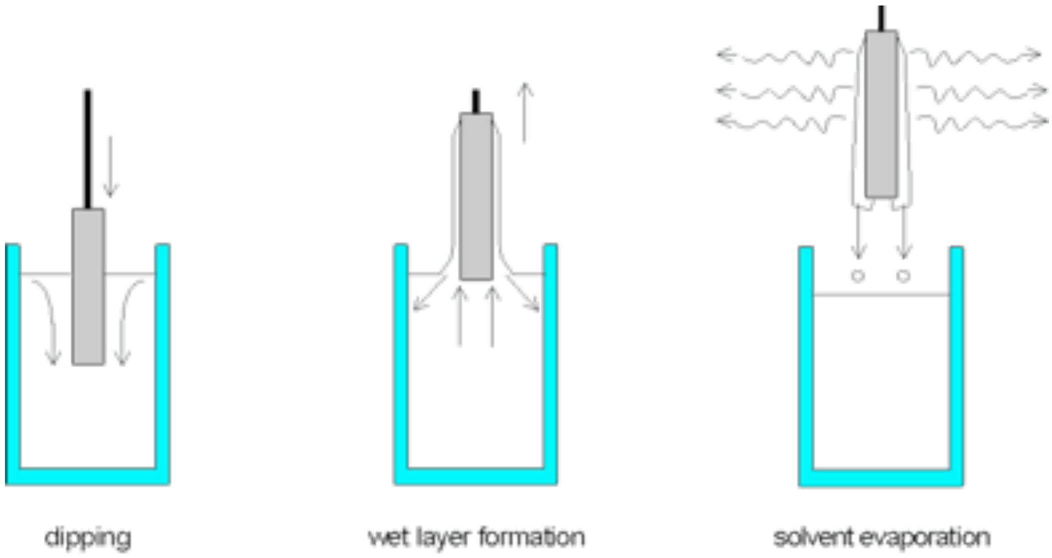


Fig. 1-5 Stages of the dip coating process: dipping of the substrate into the coating solution, wet layer formation by withdrawing the substrate and gelation of the layer by solvent evaporation

1.4 Characterization techniques

1.4.1 SEM (Scanning electron microscopy)

SEM is one of the electron microscopy methods and is used for analyzing for example nano-materials. Electrons have a shorter wave length and thus give a better resolution than the photons and that is why electron microscopes are used when the ordinary light microscopes do not give a sufficient analytical resolution.

The electron beam has high energy and is concentrated to a small spot that could have a diameter as small as 1 nm. The scanning electron microscope has a large depth of field (the size of the scene that are sharp in the image) which gives a 3D appearance of the sample's surface. The electron beam will scan over the surface in a certain pattern and in the same time the detector will measure the number of electrons that bounce back. This information goes from the detector to a picture tube that creates a second electron beam. This and the first beam go synchronous which gives a picture without any lenses. The picture that is achieved is seen from the angle of the electron beam so the surfaces that are not directed towards the detector will not give the same intensity as the ones that are directed to it (the probability that electrons that hit surfaces not facing the detector will bounce back to the detector is not so big). Fig. 1-6 illustrates what happens to the incident beam as it hits the sample in a SEM.

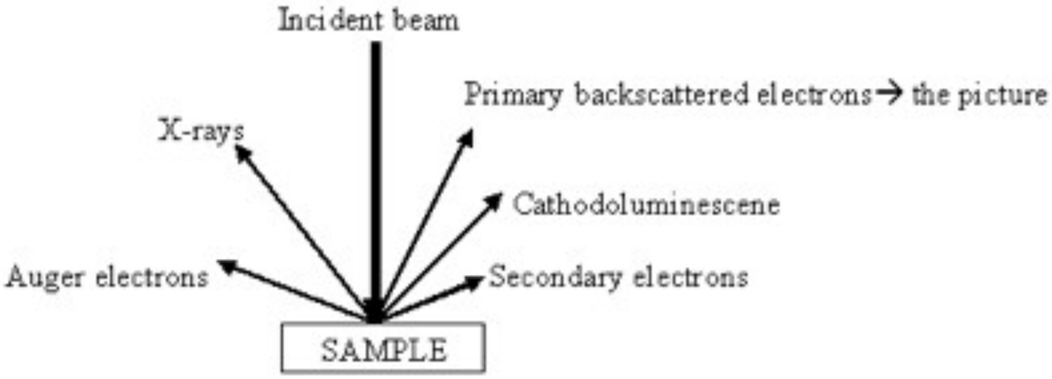


Fig. 1-6 Illustration of what happens to the indicent beam when it hits the sample.

The biggest advantage of this type of electron microscope is that it gives a picture of the surface with a large magnification. Information that this method gives are for example topography, morphology, composition and crystallographic information. In opposite to the TEM method the thickness of the sample does not matter due to that the detected electrons in this case are the ones that are bouncing back from the sample, not the ones that are passing through the material. If the sample that should be studied has electrical conductivity there is no need for further preparing and the study can be done directly. If the sample has no electrical conductivity there will be a need to coat the surface with a thin conducting layer. One drawback of this method is that it has been done in vacuum because gas molecules could interfere with the electron source which may lead to erroneous results. Due to this samples containing liquids have to be dried before analyzing them so the liquid does not evaporate. [8]

1.4.2 TEM (Transmission electron microscopy)

Transmission electron microscopy is used to analyze ultra thin materials such as nano films. Electrons are transmitted through the material that is to be analyzed and form a 2D image from a 3D sample. To avoid electron absorption within the material the sample thickness needs to be very thin (100 nm). In case of biological materials that mainly consist of light atoms they are analyzed with a typical thickness of 50 nm whereas a substrate containing heavier atoms i.e. metallic atoms a thickness around 20 nm is recommended. This is due to that heavy atoms scatter electrons more than light atoms.

An electron beam is generated by an electron emission source i.e. tungsten or lanthanum hexaboride (LaB_6). Electrons are removed from the electron source and accelerated by a high voltage in an electron gun. These electrons have a very short wavelength which results in a high resolution. The electron beam that is formed is focused by a series of electromagnetic lenses on a sample. To be able to control and manipulate the electron beam lenses and electrostatic plates are used. The electrons interact with the sample and are transmitted through the sample and thereby forming an image. The analysis method must be done under vacuum pressure otherwise the electrons would immediately have lost their energy and thereby be slowed down. Moreover the electron source needs to be under vacuum pressure to be able to form an electron beam.

Fig. 1-7 illustrate what happens to the incident beam as it hits the sample in a TEM. The electrons in the beam spread in different directions when they are passing through the sample. Different areas in the sample spread electrons differently which result in an image. Dark spots represent areas that strongly spread electrons and light spots represent areas where nearly no electrons change direction.

To get an image usually a fluorescent screen combined with a monitor is used. Alternatively a sensor, i.e. a CCD camera (charge-coupled device camera) is used as a detector or the beam is focused on a layer of a photographic film. The biggest advantage of TEM is that a very high resolution is achieved with this method. Disadvantages with this analysis method are that the sample may be damaged when electrons are passing through and that the equipment is rather expensive. [9]

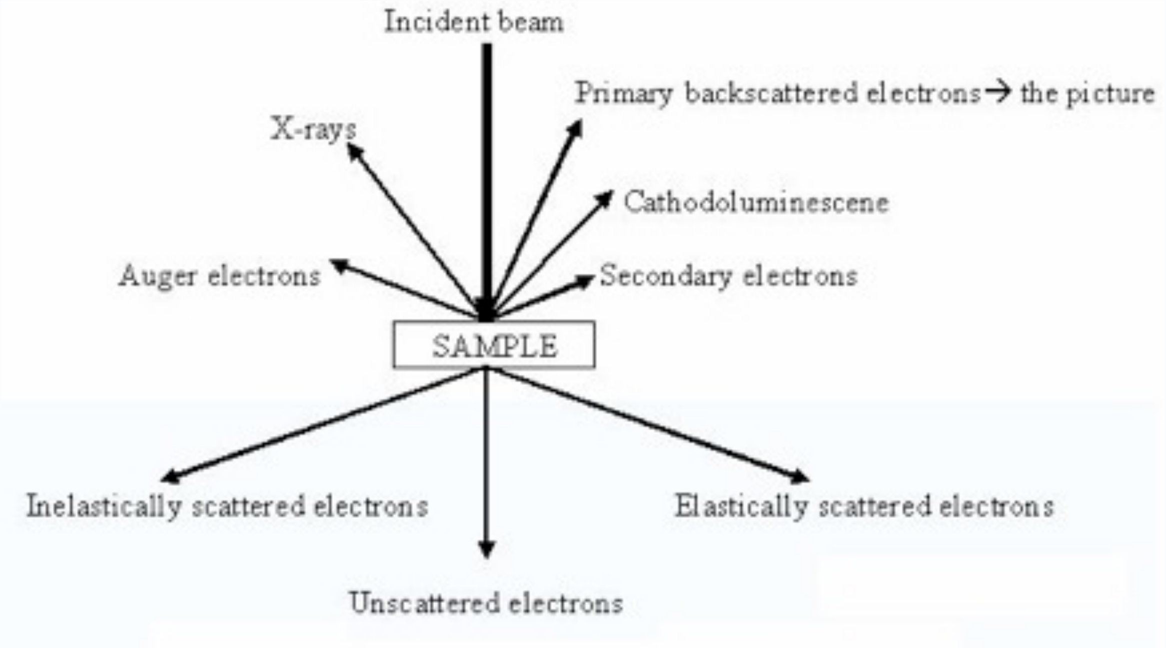


Fig.1-7 Illustration of what happens to the indicent beam when it hits the sample in a TEM.

1.4.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a common characterization method, which provides information of the crystallographic structure and chemical composition of materials using X-rays. The working mechanism is based on an interference of the elastically scattered X-rays from structures which have long range order. A regular array of atoms or cavities, produces a regular array of spherical waves. They interfere with each other, and then the interference can be destructive or constructive, determined by Bragg's law, $2\ d \sin\theta = n\lambda$, where d is the distance between two parallel arrays of scatterers, 2θ is the scattering angle between incoming and outgoing beams, and λ is the X-ray wavelength. [10] Usually powder XRD is adopted first. The unit cells of mesoporous crystal are very large, and as a result the reflection appears at low scattering angles, and hence small angle X-ray scattering (SAXS) schematically shown in Fig. 1-8 is often used.

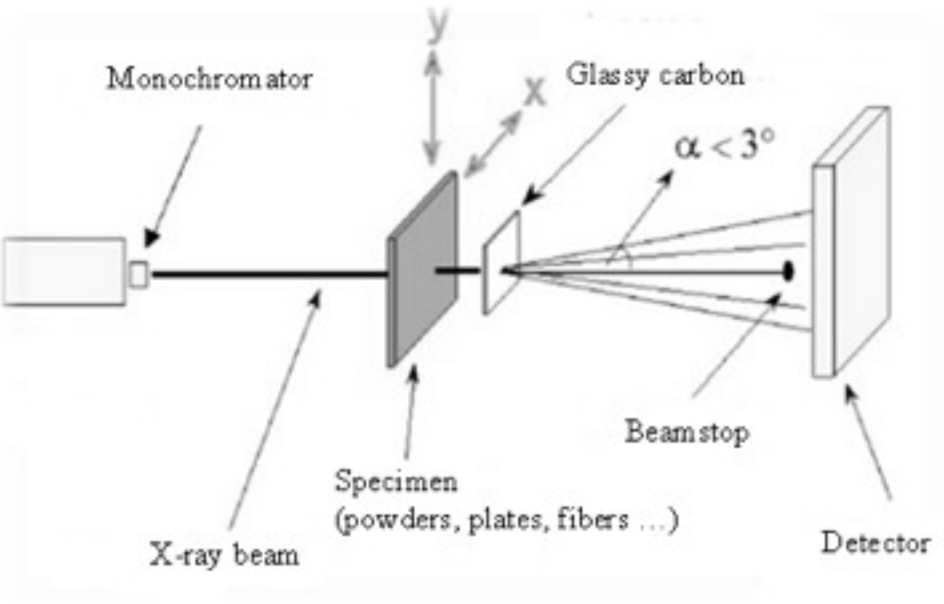


Fig.1-8 Schematic picture of the SAXS method. [11]

1.4.4 Gas adsorption

Physical adsorption is the accumulation of molecules of a gas to form a thin film on the surface of a solid. Mesoporous materials are frequently characterized by the nitrogen adsorption-desorption method. The adsorption is usually described by isotherms. The amount of adsorbate on the adsorbent is measured as a function of its pressure at constant temperature. The specific surface area is mostly derived using the BET model, the pore size distribution and pore volume of the materials are often obtained using the BJH model.

1.5 Research goal

The aims of the work is to successfully coat diverse substrates by mesoporous transition metal oxide, namely titania and niobium (V) pentoxide, with relatively good homogeneity. The research goal also includes exploring the technology of synthesis and characterization of mesoporous material and achieving deeper understanding of the formation mechanism of mesoporous materials.

2 Experimental Section

2.1 Chemicals

All chemicals were used as purchased without further purification.

The inorganic precursors and block copolymer surfactant used in the experiment are listed in Tables 1 and 2.

Table 1

Inorganic Precursor	Abbreviation	Supplier
Titanium Tetra-ethoxide	TEOT	Sigma Aldrich, USA
Titanium Butoxide	TBT	Sigma Aldrich, USA
Niobium Ethoxide	/	Multivalent Ltd. Great Brittain
Niobium Chloride	/	Sigma Aldrich, USA

Table 2

Block Copolymer Surfactant	Abbreviation	Mw(g/mol)	Supplier
$EO_{20}PO_{70}EO_{20}$	P123	~5800	Sigma Aldrich, USA
$EO_{97}PO_{69}EO_{97}$	F127	~12,500	BASF, USA

Other chemicals used in the experiment includes ethanol and concentrated hydrochloric acid.

2.2 Synthesis process

The synthesis of mesoporous coatings was carried out on two different systems namely titania and niobium pentoxide. Different substrates for coating in this study include glass slide, machined titanium disc, and porous titania substrate. To avoid unnecessary cost, the synthesis was always begun with attempts on glass slides and subsequent work was done on other substrates afterwards.

Titania

Synthesis

The method used in the synthesis followed the approach of Alberius et al. [12] Besides the glass slides used in the work of Alberius group, porous titania substrates with diverse pore size were used in this study.

A solution of P123 and ethanol was prepared by mixing with a magnetic stirrer. The inorganic precursor (TEOT or TBT) was mixed with concentrated hydrochloric acid at room temperature under vigorous stirring, using a magnetic stirrer. After 5 minutes the P123 solution was added into the mixed solution, by pouring the P123 solution into it. Aging of the solution was done with stirring at room temperature, where different amount of aging was evaluated. The glass slides were dip-coated manually or using a dip-coater, depicted in Fig. 2-1 into the solution by holding the substrate with a tweezer and manually controlling the dip-coater. The dip-coated substrate was held in the air for several minutes and then put in a petri dish, where it was aged. Calcination in furnace, was done by increasing the temperature with 1 ˚C/minute to 350 ˚C/400 ˚C with a dwell time of 4 hours. Samples were kept in petri dishes until characterization.

Fig. 2-1 Dip-coater

The specific parameters that varied among the experiments are listed below in Tables 1,2,3. The synthesis is applied on two different kinds of substrates: 1. glass slide and 2. porous titania substrate.

When the synthesis was applied on the glass slides, considering the mesoporous formation mechanism and the collapse of mesoporous structure in high temperature, the ratio of surfactant and precursor, aging time and calcination temperature were tuned. To achieve a homogeneous thin film, different dip-coating speeds were evaluated. Viscosity was also taken into account to enhance the morphology of the resulting thin film, which is tuned by different aging time before and after dip-coating.

In the syntheses on porous titania substrates, variable precursor species, dip-coating speed, aging time and temperature were chosen in order to control the thickness and the morphology of the coatings. The different samples synthesised with diverse parameters are listed below in Tables 3 and 4.

Table 3 Syntheses of mesostructured titania on glass slide

Name of sample	Molar ratio of surfactant/ precursor/HCl/ EtOH	Aging time before/after dip-coating	Aging temperature after dip-coating	Calcination conditions	Precursor used
TG1	1:107:188:1515	10 min / 1 h	< 9 ˚C	400 ˚C for 4 h	TEOT
TG2	2:107:188:1515	10 min / 1 h	< 9 ˚C	400 ˚C for 4 h	TEOT
TG3	1:107:188:1515	10 min / 1 h	< 9 ˚C	300 ˚C for 4 h	TEOT
TG4	1:59:188:1515	10 min / 2.5 h	RT	350 ˚C for 4 h	TBT
TG5	1:107:188:1515	1 h /1 h	RT	400 ˚C for 4 h	TEOT
TG6	1:107:188:1515	1 h /4.5 h	RT	400 ˚C for 4 h	TEOT

Note: The samples with names initial with letter TG refer to titania samples coated on glass slides.

Table 4 Syntheses of the mesostructured titania on porous titania matrix

Name of sample	Molar ratio of surfactant/ precursor/HCl/ EtOH	Aging temperature	Aging time before/after dip-coating	Calcination conditions	Dip-coating speed
TC1	1:107:188:1515	RT	1 h / 1 h	400 ˚C 4 h	1mm/s
TC2	1:107:188:1515	RT	1 h / 1 h	400 ˚C 4 h	1 mm/s
TC3	1:107:188:1515	RT	1 h / 1 h	400 ˚C 4 h	0.5 mm/s
TC4	1:107:188:1515	RT	1 h / 1 h	400 ˚C 4 h	0.25 mm/s
TC5	1:107:188:1515	RT	1 h / 1 h	400 ˚C 4 h	0.1 mm/s
TC6	1:107:188:1515	8˚C	1 h / 1 h	400 ˚C 4 h	0.25 mm/s

Note: The samples with names initial with letter TC refer to titania samples coated on porous titania matrix.

Niobium pentoxide

Synthesis type 1.

A solution of 1 g P123 (density 1.018 g/ml) and 15.2 ml ethanol (density 0.789 g/ml), was prepared by mixing with magnetic stirrer. 5.859 g niobium ethoxide (4.62 ml, density 1.268 g/ml) was mixed in a separate beaker with 2.712 ml HCl (3.2 g, density 1.18 g/ml) at room temperature under vigorous stirring, using a magnetic stirrer. After 5 minutes the P123 solution was added to the mixed solution, by pouring the P123 solution into it. Aging of the solution was done at room temperature for 1 h. The beaker was covered with parafilm to avoid too fast evaporation. The substrates were dip-coated using the same speed for both immersion and withdrawal (1 mm/s). Aging of the films was done at room temp for 1h in a petri dish with cover. Calcination was done in furnace, where the temperature was increased with 1 ˚C/minute to 400 ˚C where it was kept for 5 hours. The samples were put in petri dishes until characterization. The syntheses were applied on glass substrates, and named NG1 and NG2. The different samples synthesised with diverse parameters are listed below in Tables 5.

Table 5 Syntheses of niobium pentoxide of Synthesis 1

Name of sample	Molar ratio of surfactant/ precursor/HCl/ EtOH	Aging temperature	Aging time before/after dip-coating	Calcination conditions	Dip-coating speed(mm/s)	Relative Humidity (%)
NG1	1:106:188:1515	22.6 ˚C	1 h/1 h	400 ˚C for 4 h	NG1-1: 0.1 NG1-2: 0.2 NG1-3: 0.5	23
NG2	1:106:188:1515	22.7 ˚C	1 h/1 h	400 ˚C for 4 h	NG2-1: 2 NG2-2: 1 NG2-3: 0.5	24

Note: The samples with names initial letter NG refer to niobium pentoxide samples coated on glass slides.

Synthesis type 2. [13]

1 g P123 was dissolved in 20 ml EtOH and stirred until the block copolymer was fully dissolved. 1.89 g $NbCl_5$ was added to P123/EtOH solution with vigorous stirring for 30 min. About 3 ml deionised water was added into the mixed solution which was stirred for 1 h/2 h under RT (23.5 ˚C). Machined titanium discs and porous titania substrates were dip-coated with dip-coating rate of 0.5 mm/s or 1 mm/s. The resulting sol solution and the dip-coated substrates are then aged at 40 ˚C/90 ˚C for 2/4/6 days, and then calcined at 400 ˚C for 5 h. The temperature was increased with a heating rate of 1 ˚C/min. The pH of the resulting gel was kept approximately at -0.66. The relative humidity (RH) was around 24 %. This synthesis was performed on machined titanium discs and porous titania substrates.

Samples with variable aging time, aging temperature, dip-coating speed and aging time before dip-coating at RT were synthesised and compared in order to explore the inner relationship between synthesis method and resulting structure. The different samples synthesised with diverse parameters are listed below in Tables 6.

Table 6 Syntheses of niobium pentoxide of Synthesis 2

Name of sample	Amount of surfactant/ precursor/ deionized water/ EtOH	Aging temperature	Agine time before dip-coating at RT	Aging time after dip-coating	Dip-coating speed(mm/s)	Calcination conditions	Relative Humidity (%)
NT1	1:40:958:1969	40 ˚C	1 h	2 days	1	400 ˚C 5 h	24.0
NT2	1:40:958:1969	90 ˚C	1 h	2 days	1	400 ˚C 5 h	24.0
NT3	1:40:958:1969	90 ˚C	1 h	4 days	1	400 ˚C 5 h	24.0
NT4	1:40:958:1969	90 ˚C	1 h	6 days	1	400 ˚C 5 h	24.0
NT5	1:40:958:1969	90 ˚C	2 h	6 days	1	400 ˚C 5 h	24.0
NC1	1:40:958:1969	90 ˚C	1 h	6 days	1	400 ˚C 5 h	23.6
NC2	1:40:958:1969	90 ˚C	1 h	6 days	0.5	400 ˚C 5 h	23.6
NC3	1:40:958:1969	90 ˚C	1 h	4 days	1	400 ˚C 5 h	49.0
NC4	1:40:958:1969	90 ˚C	1 h	4 days	0.5	400 ˚C 5 h	49.0

Note: The samples with names with initial letter NT and NC refer to niobium pentoxide samples coated on machined titanium discs and porous titania substrates respectively.

2.3 Phase composition and microstructure characterization

2.3.1 Powder X-ray Diffraction

Powder XRD patterns were recorded on a X'Pert PRO PANalytical Diffractometer/MAX-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at a scanning rate of 2 deg. min^{-1} over the range of 10 - 60˚ (2θ).

2.3.2 Scanning Electron Microscopy (SEM)

Surface morphologies of the porous surfaces were studied by scanning electron microscopy (SEM) using a JSM-7000F microscope (JEOL, Tokyo, Japan) equipped with a Schottky type field emission gun. The accelerating voltage was varied in the range 5 kV - 15 kV. Coating of the samples with carbon or a metal layer was found to be unnecessary when conducting materials (machined titanium or porous titania) are used as a substrate for the porous material, and it was avoided in order to preserve all surface details, especially mesopores.

2.3.3 Transmission Electron Microscopy (TEM)

High resolution transmission electron microscopy (HRTEM) investigations were carried out with a JEM-3010 microscope operated at 300 kV (JEOL) equipped with a KeenView CCD camera (1.4 k x 1 k; Olympus Soft Imaging Solutions, Münster, Germany). Samples of the mesoporous materials were scratched off glass substrates and dispersed in ethanol. A droplet of the dispersion was then transferred onto a copper grid coated with holey carbon film.

2.3.4 Nitrogen Adsorption-Desorption

The nitrogen adsorption-desorption isotherms were measured with Micromeritics ASAP 2020 Surface Area & Porosity Analyzer. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

3 Results and Discussion

The formation of mesoporous material is a relatively complex process, which is susceptible to many factors, such as the molar ratio of inorganic precursor and surfactant, the pH, the rate of solvent evaporation, the ambient humidity, aging time, etc.

When the formation process is applied on diverse substrates, the system become even more complex due to some extra critical factors because the substrate as an extra phase in the system interacts with the formed material, and therefore affects the microstructure of the resulting material.

The main part of this chapter is based on the results of experiments, discussing the coating of transition metal oxide on diverse substrates, effect of dip-coating technology on homogeneity, aging effect on mesoporous structure and other experimental factors.

3.1 Titania

3.1.1 Macroscopic film homogeneity

The synthesis was carried out on different types of substrate: glass and porous titania substrate. Thin films formed on glass slide as shown in Fig. 3-1-1. It was observed that homogenerous film formed in macroscopic scale. It can also be observed from the fracture that granular polycrystal with large size (around 100 nm) grew inside the thin film. On porous titania substrate, titania coating formed, as shown in Fig. 3-1-2 (a), with a certain number of cracks and extimated high thickness. The size of each fracture is estimated to be around 1 μm. Top of each fracture are very flat and homogeneous. Ordered porous structure can be clearly observed. The result indicate that heterogeneous nuleation induced film formation happened on this kind of substrate.

Different dipping rate and aging temperature was tried to enhance homogeneity of the coating. In sample TC3, TC4, lower dip-coating speed 0.5 mm/s, 0.25 mm/s were used with resulting of thinner film and even smaller pores in the substrate are able to be observed, which shows a tendency that with relatively lower dipping rate (0.25 mm/s) and longger aging time before dip-coating (1 h) lead to homogeneous and probably thinner film with ordered mesoporous structure as shown in Fig. 3-1-2. The thickness is estimated by experience, which is better to be replaced by data from cross polishing section in future work. 0.1 mm/s as dipping rate was also performed, but no obvious enhancement comparing with 0.25 mm/s. Due to the instrument limitation, lower dipping rate cannot be achieved by precisely control so far.

The RT is normally arround 20 ˚C. 8 ˚C was chosen as ageing temperature to perform and make comparision with the sample aged under RT. The temperature difference have strong effect on the evaporation situation. The evaporation rate is decreased under lower temperature, which may affect both the homogeneity and mesostructure formation.

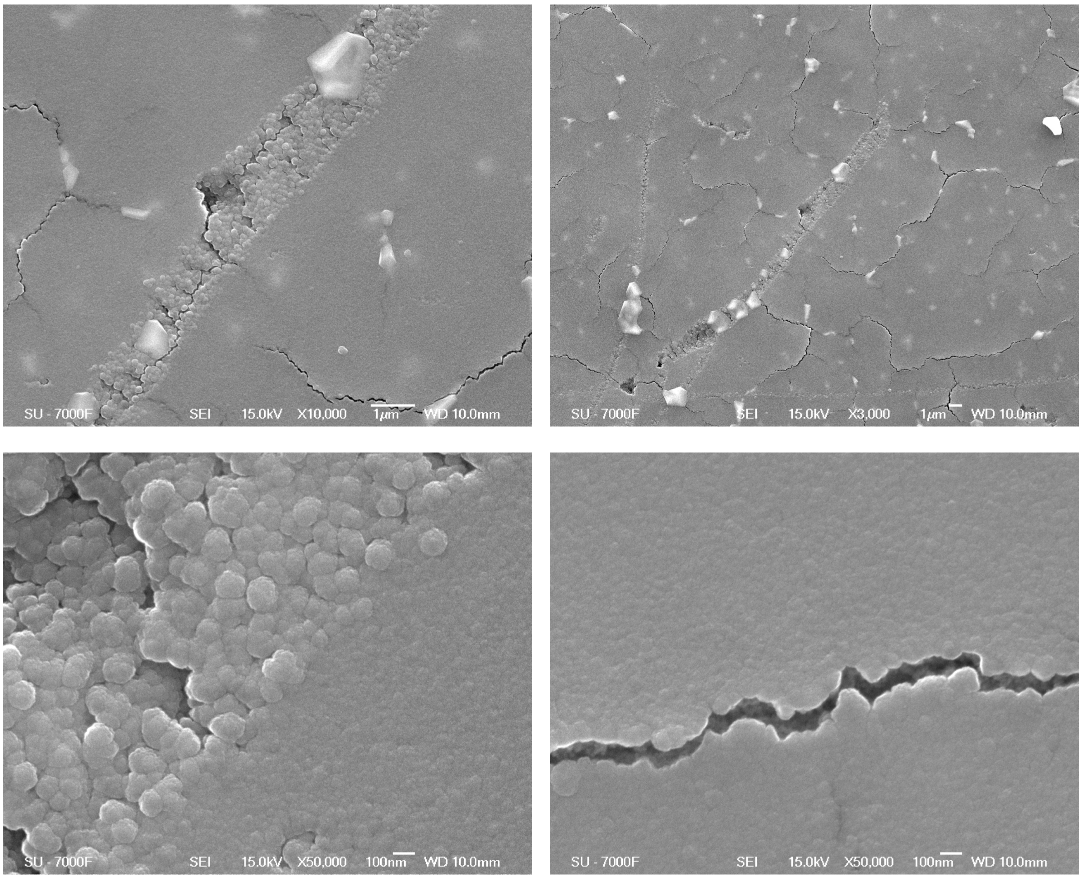
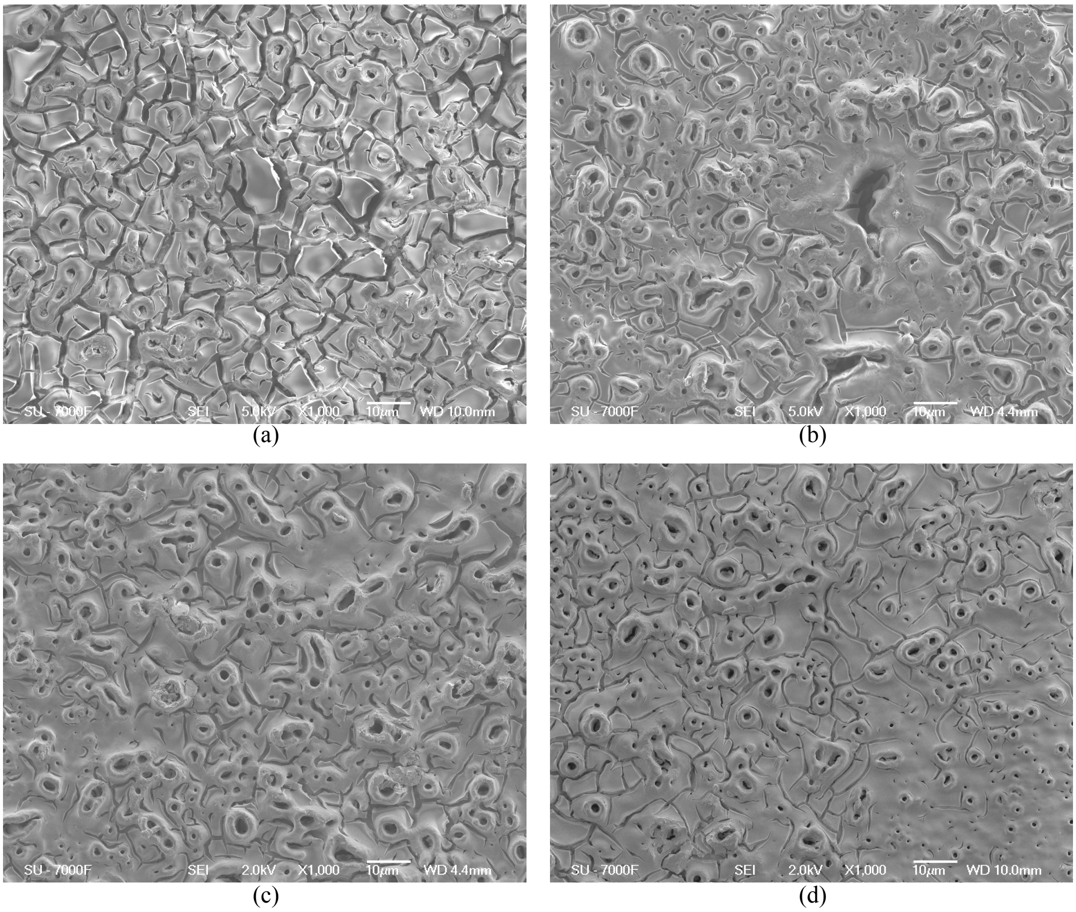


Fig. 3-1-1 SEM images of sample TG2 (titania coating on glass substrate) after calcination.



(a) (b)

(c) (d)

Fig. 3-1-2 SEM images of samples (a)TC2: aging at RT for 1h before dip-coating, dipping rate = 1 mm/s, (b) TC3: aging at RT for 1h before dip-coating, dipping rate = 0.5 mm/s, (c)TC4: aging at RT for 1h before dip-coating, dipping rate = 0.25 mm/s, (d) TC6: aging at 8 ° C for 1h before dip-coating, dipping rate = 0.25 mm/s after calcination.

3.1.2 Mesoscopic order of the pores

The coating on glass slide shows well ordered mesoporous structure which means the ratio of reactants and control of evaporation rate is relatively proper for mesostructure formation as shown in Fig. 3-1-3.

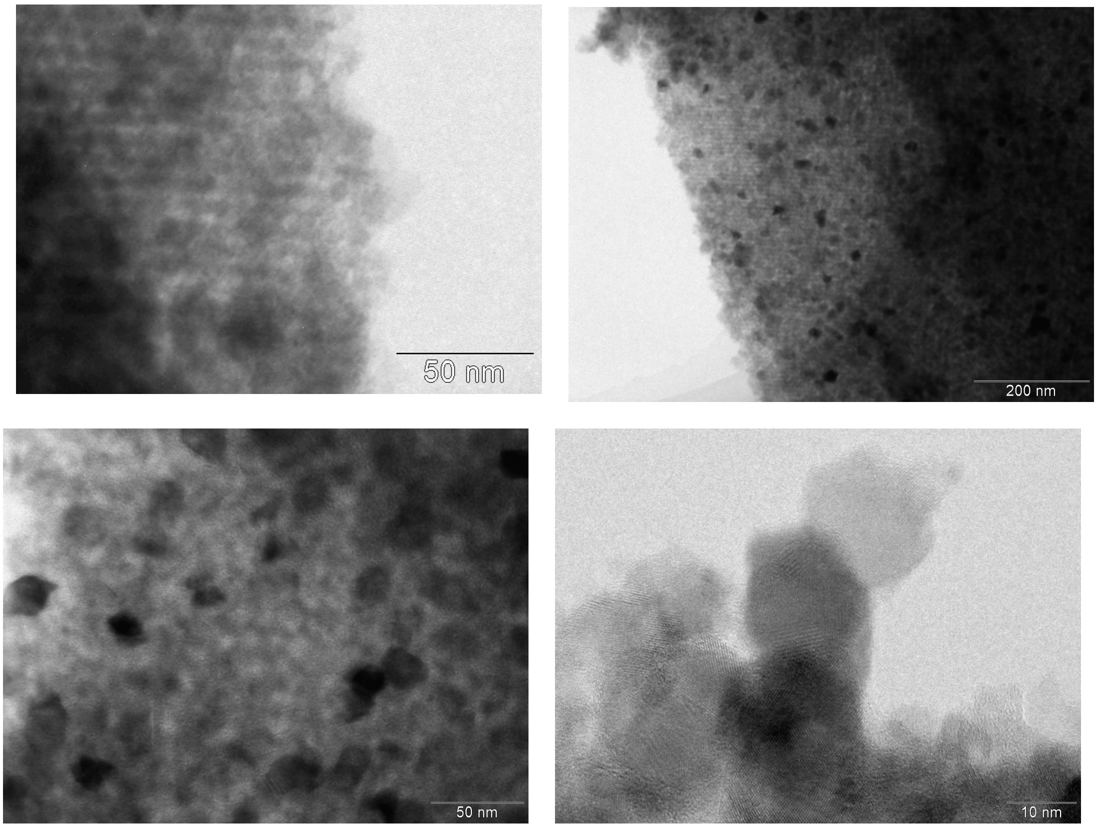


Fig. 3-1-3 TEM images of sample TG5 with ordered mesostructure on glass slide (molar ratio of surfactant/precursor/HCl/EtOH = 1:107:188:1515, aged for 1h/1h before and after dip-coating, after calcination at 400 ˚C).

On porous titania substrate, the same experimental conditions (molar ratio of surfactant/precursor/HCl/EtOH = 1:107:188:1515, aged under RT for 1h/1h before and after dip-coating, calcined at 400 ˚C for 4 h, dipping rate = 1 mm/s) resulted in well ordered mesopores as shown in Fig. 3-1-4. The pore size is around 5~10 nm.

Different dipping rate was compared among samples TC 2, 3, 4, with SEM images shown in Fig. 3-1-4, Fig. 3-1-5 and Fig. 3-1-6, respectively. It is observed that lower dipping rate results in more ordered mesostructure, but the trend is not very obvious. It is probably due to the thickness change by differing the dipping rate and the corresponding effect on evaporation rate, which is critical to mesostructure formation.

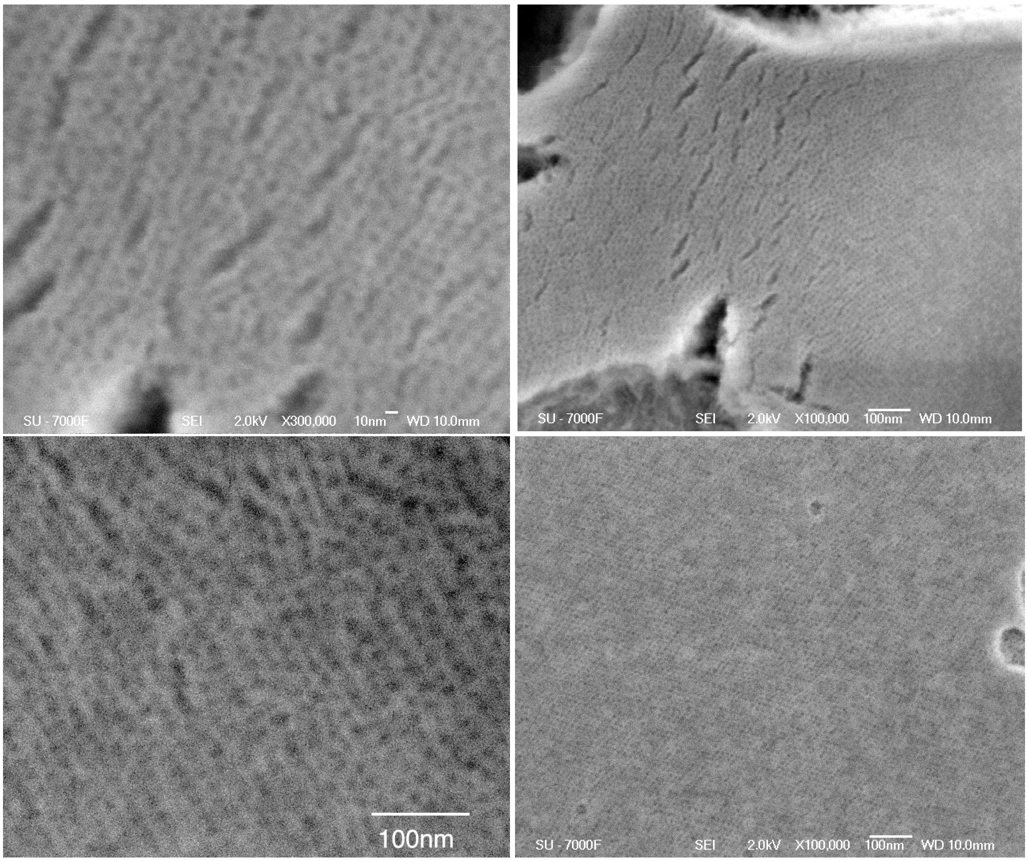


Fig. 3-1-4 SEM images of TC2 after calcination (dipping rate = 1mm/s).

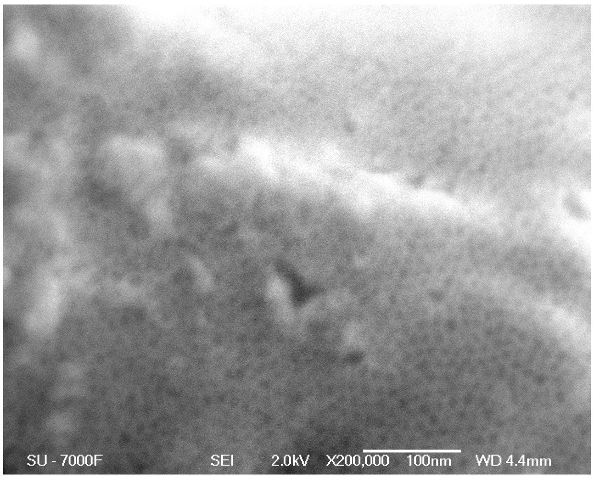


Fig. 3-1-5 SEM image of sample TC3 after calcination (dipping rate = 0.5 mm/s).

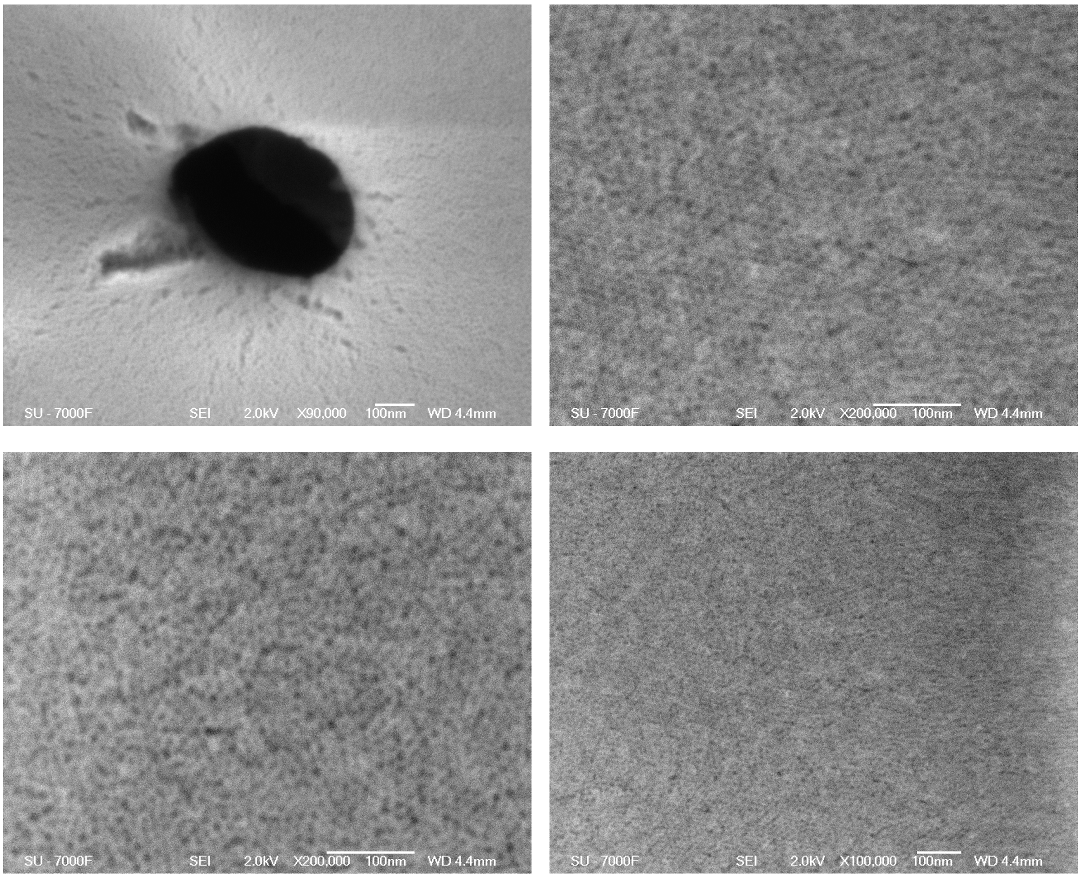
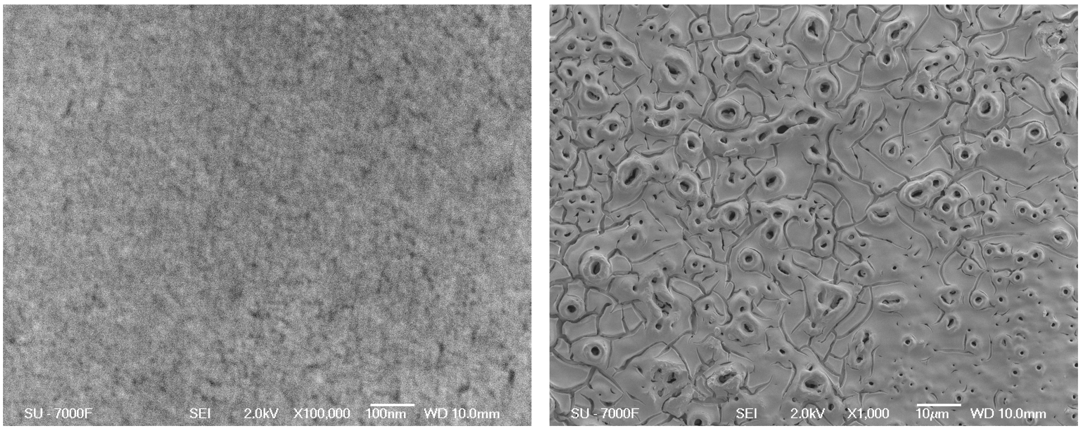


Fig. 3-1-6 SEM images of sample TC4 after calcination (dipping rate = 0.25 mm/s).

When the aging temperature was changed from RT (around 20 ˚C) to 8 ˚C, the degree of order decreased a lot which is shown in Fig. 3-1-7. Comparing sample TC6 with TC4 (Fig. 3-1-6) and Fig. 3-1-2 (c), it is observed that the coating in TC6 looses the order in TC 4 but with much better homogeneity. TC 6 and TC 4 are with the same synthesis parameter except aging temperature. It shows that aging temperature is important for formation of ordered mesostructure. And aging temperature can affect homogeneity and order degree in two different way. Therefore in order to achieving homogeneous coating with ordered structure, the synthesis parameter should be chosen carefully and as a compromise.



(a) Mesopores without order

(b) Relatively good homogeneity

Fig. 3-1-7 SEM images of TC6 with dipping rate of 0.25 mm/s and aging temperature of 8 ˚C after calcination.

3.2 Niobium pentoxide

3.2.1 Macroscopic film homogeneity

For niobium pentoxide system, the synthesis was carried out on different type of substrate: glass and porous titania substrate. The most optimized coating of meso phase on machined titanium disc and porous titania substrate is shown by SEM images of Fig. 3-2-1 and Fig. 3-2-2, respectively.

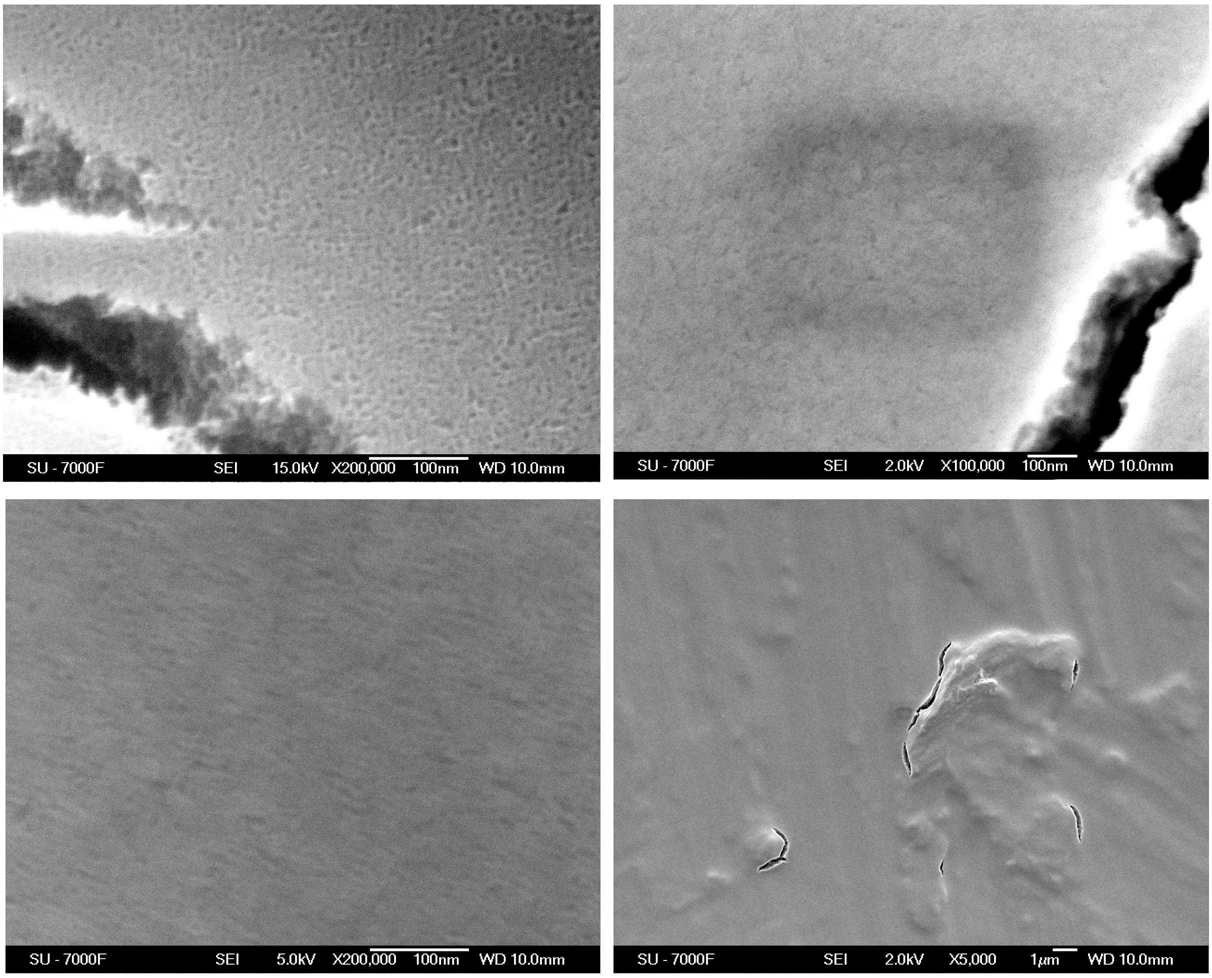


Fig. 3-2-1 SEM image of sample NT3 (Nb_2O_5 thin film on machined titanium substrate) after calcination.

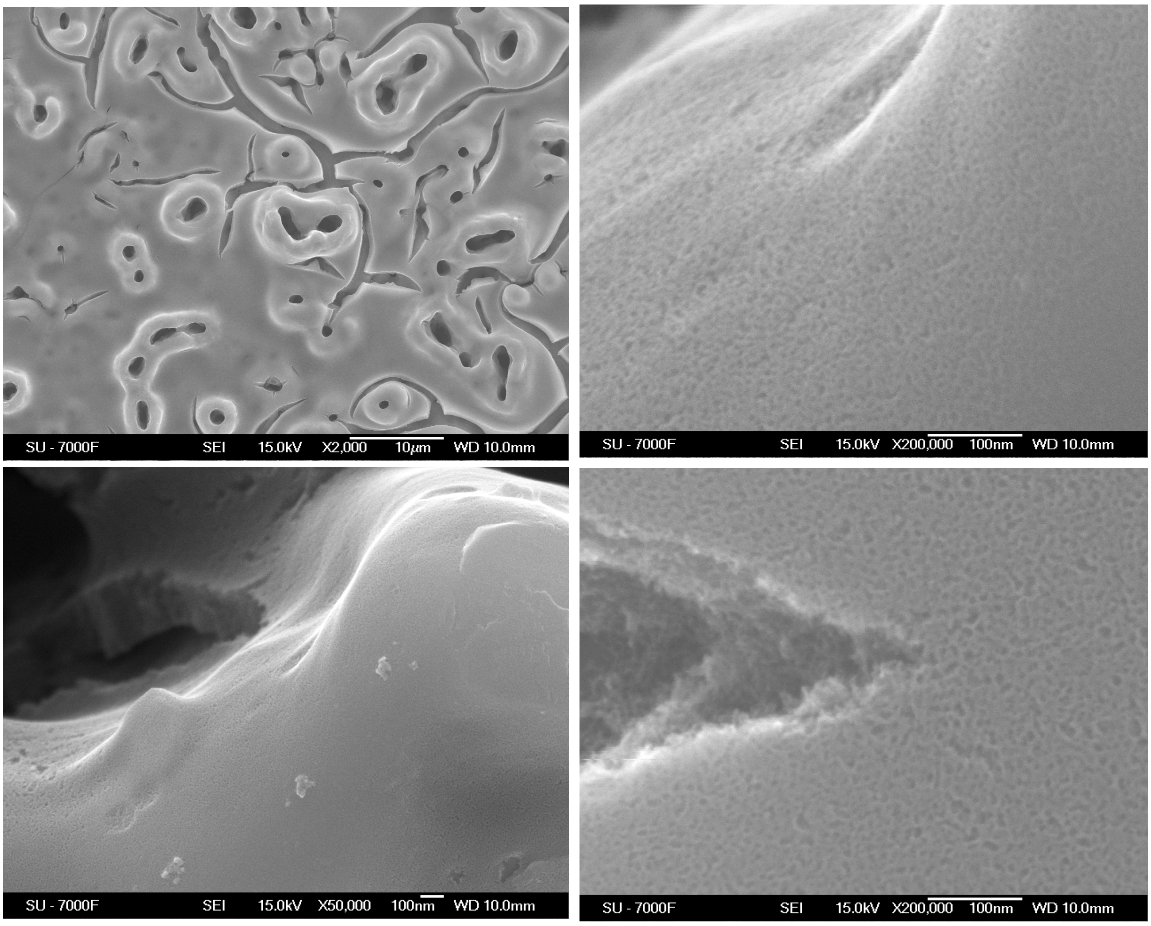
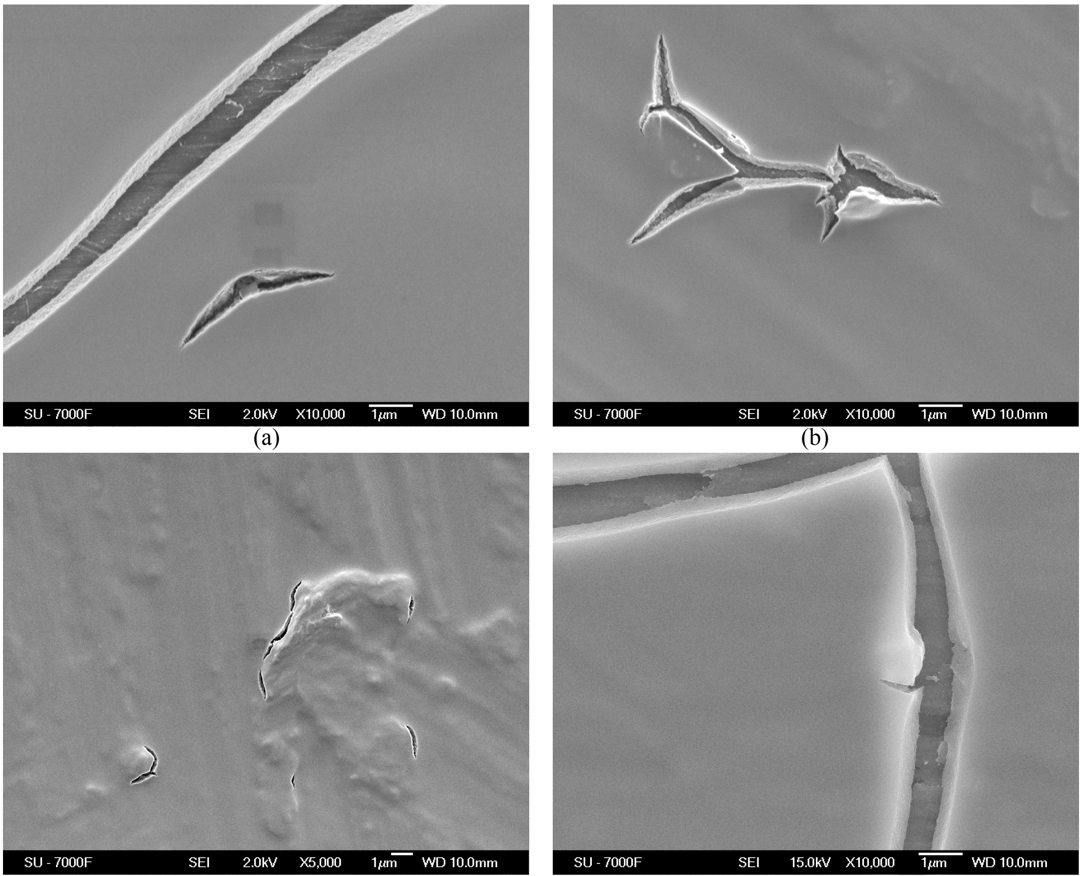


Fig. 3-2-2 SEM image of sample NC2 (Nb_2O_5 thin film on porous titania substrate with dipping rate of 0.5 mm/s) after calcination.

Like shown in Fig. 3-2-3, the film forming on the machined titanium substrate is homogeneous without big amount of cracks. No big difference can be observed from the SEM images of the samples synthesized with different aging time and temperature. The thickness is estimated to be 300 nm.

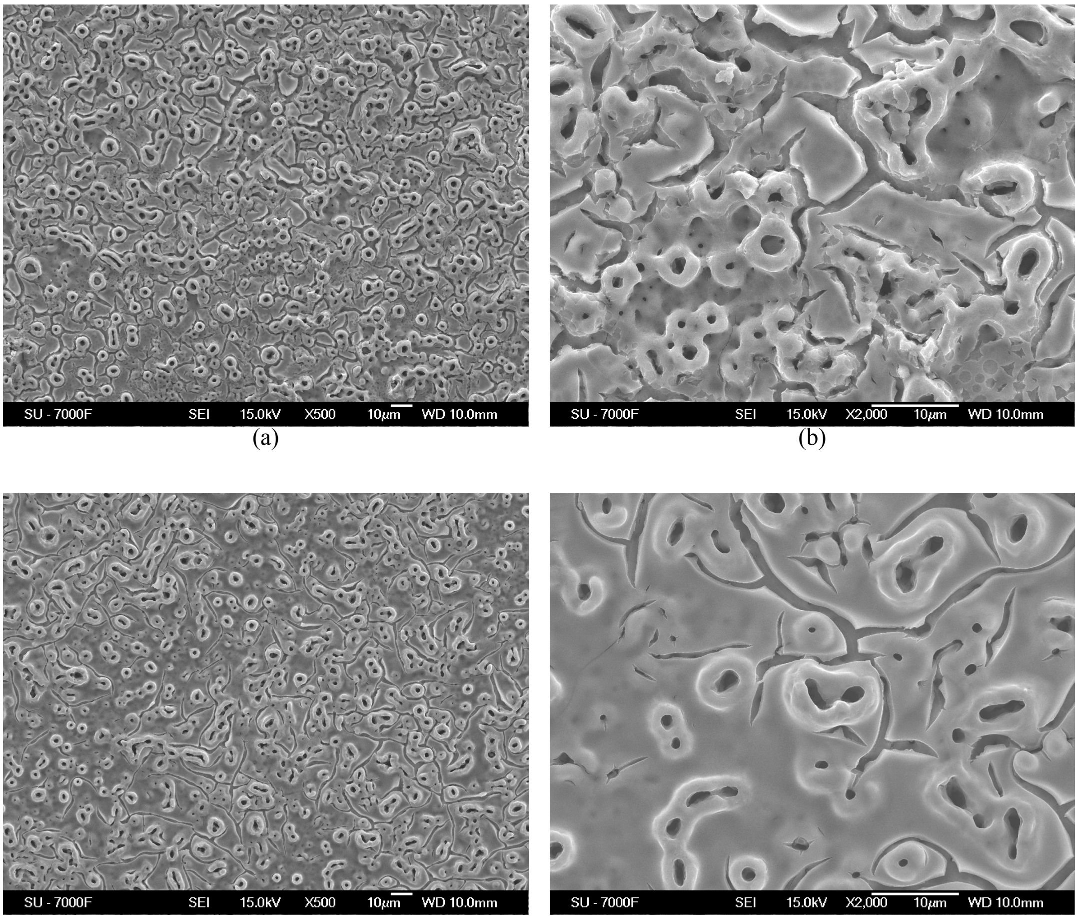
On porous titania substrate, the coating of niobium oxide is formed with bad homogeneity, as shown in Fig. 3-2-4. By comparing the SEM images of two samples with different dipping rate, it is obviously observed that the one with 0.5 mm/s dipping rate is with less cracks, i.e. better homogeniety, which indicates that better homogeneity is achieved by decreasing the dipping rate. There was a mistake during the experiment effecting the result which is worth mentioning. The samples were taken into aging chamber with 40 ˚C or 90 ˚C directly from RT environment. They could be with better homogeneity if increasing the aging temperature from RT to target aging temperature (40 ˚C or 90 ˚C) gradually, for instance, by the increasing rate of 1 ˚C/min. Therefore a repeat experiment was performed to correct the mistake. Due to the huge humidity change of the environment, an optimal result was not achieved. The result of morphology is shown in Figure 3-3-3 (c), (d), big amount of crystals formed on the coating under RH of 49%, which indicate that the niobium oxide synthesis system is very humidity-sensitive.



(a) (b)

(c) (d)

Fig. 3-2-3 SEM images of samples (a) NT1: aged at 40 ˚C for 2 days after dip-coating, (b) NT2: aged at 90 ˚C for 2 days after dip-coating, (c) NT3: aged at 90 ˚C for 4 days after dip-coating, (d) NT4: aging at 90 ˚C for 6 days after dip-coating.



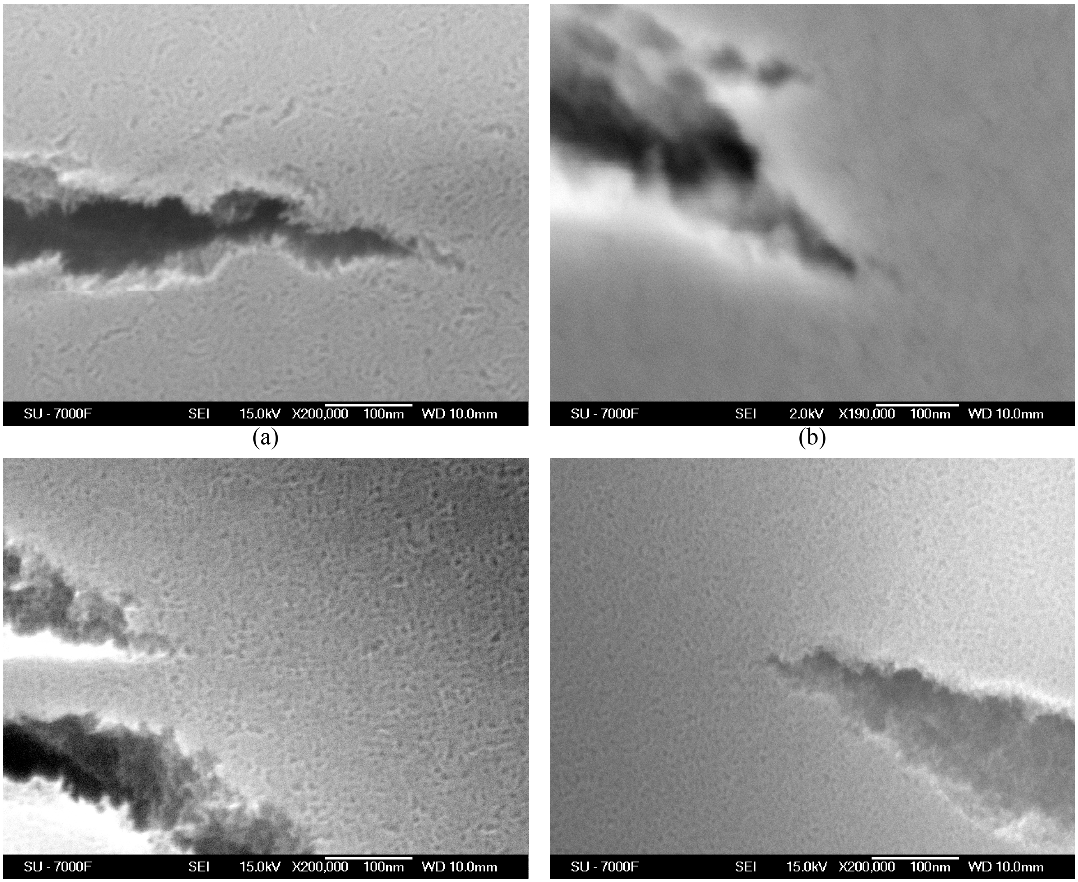
(a) (b)

(c) (d)

Fig. 3-2-4 SEM images of (a), (b) sample NC1 with dipping rate = 1 mm/s, (c), (d) sample NC2 with dipping rate = 0.5 mm/s. Both of them are with 1h aging time in RT before dip-coating. All the images are taken after calcination.

3.2.2 Mesoscopic order of the pores

In Synthesis 1, niobium (V) ethoxide was chosen as inorganic precursor initially, resulting in smooth surface without mesophase formed. But when the niobium chloride was used as inorganic precursor in Synthesis 2, mesophase coating was achieved as shown in Fig. 3-2-1. Therefore the control of hydrolysis speed by choosing different species of precursor is supposed to be critical for meso phase formation. From the experiments, the experience value of pH of the resulting gel is approximately -0.65.



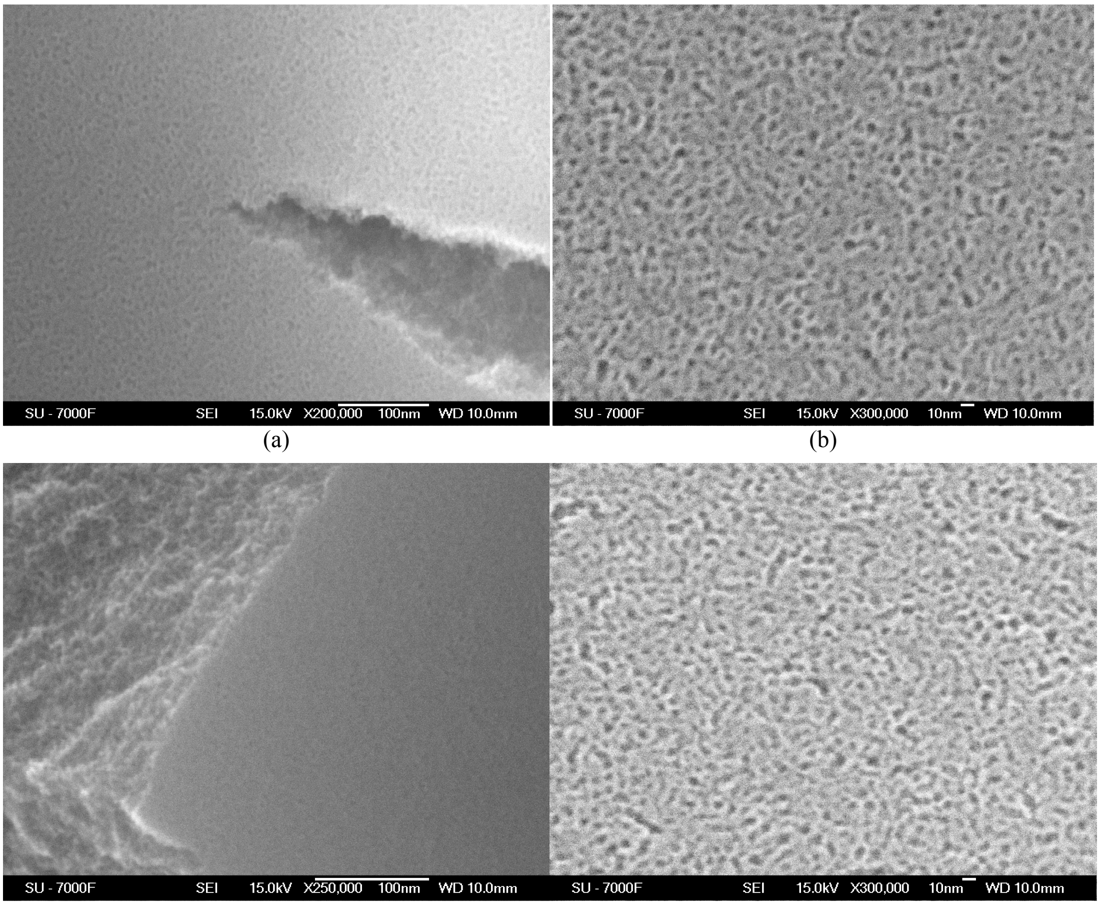
(a) (b)

(c) (d)

Fig. 3-2-5 SEM images of (a) sample NT1: aged at 40 ˚C for 2 days after dip-coating, (b) sample NT2: aged at 90 ˚C for 2 days after dip-coating, (c) sample NT3: aged at 90 ˚C for 4 days after dip-coating, (d) NT4: aging at 90 ˚C for 6 days after dip-coating. All the images are taken after calcination.

Different aging time after dip-coating and temperature was evaluated to study the aging effect on meso phase formation. The results of aging temperature of 40 ˚C or 90 ˚C and aging time of 2 days, 4 days, and 6 days are shown in Fig. 3-2-5. All the mesopores are not ordered. In Fig. 3-2-5 (b), the sample are with channel-like pores. The sample with 6-day-aging-time is with smaller pores compared with the one with 4-day-aging-time. It can be hypothesized that 4 days and 40 ˚C is separately the boundary aging time and temperature for getting nice porous structure.

The homogeneity of coating is susceptible to aging time before dip-coating due to different viscosity. Whether the aging time has effect on mesophase formation is also studied. 1 hour and 2 hours were chosen as aging time before dip-coating under RT (around 23 ˚C). The result is shown in Fig. 3-2-6, which does not show obvious difference between the samples. The effect is not clear within the range studied.



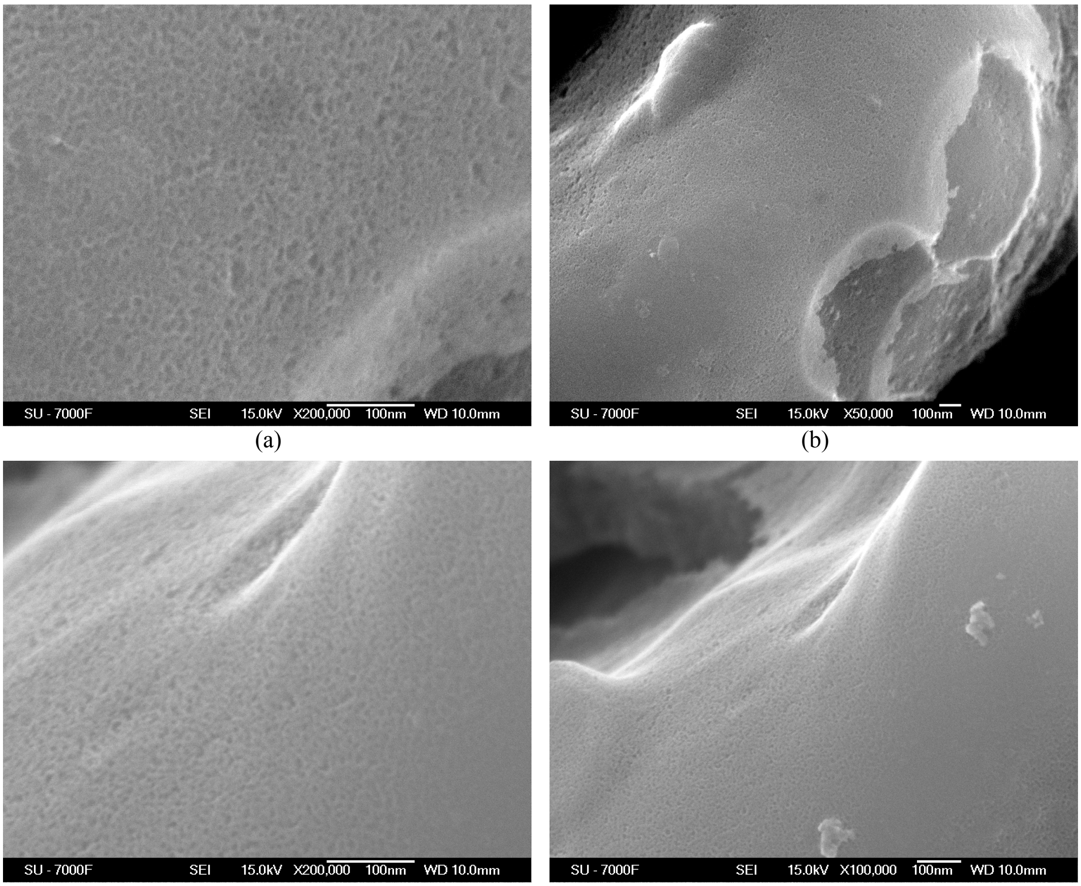
(a) (b)

(c)

Fig. 3-2-6 SEM images of sample (niobium pentoxide coating on machined titanium disc) (a), (b) NT4 with 1 h aging under RT before dip-coating, (c), (d) NT5 with 2 h aging time under RT before dip-coating, after calcination.

On the porous titania substrate, the proven (by synthesis on machined titanium disc) relatively proper synthesis conditions were used. Different dipping rate were chosen to study the effect of dipping rate on coating. On mesoscale the order degree of pores and pore size do not have significant difference between the samples with 1 mm/s and 0.5 mm/s dipping rate, shown in Fig. 3-2-7, even though the evaporation rate might be changed by different dipping rate.

By observing the resulting gel before calcination, amber like fractures were observed in the powder sample synthesized with the same experimental parameters as the coating samples. It may indicates that the inorganic precursor hydrolized and polymerized into long chains, which is a prior requirement for forming mesophase thin film. As the appearence, milky light is observed on the fractures (due to Rayleigh scattering), which sometimes indicate the cross-link of polymerized inorganic precursor based on previous experience.



(a) (b)

(c) (d)

Fig. 3-2-7 SEM images of sample (niobium pentoxide coating on porous titania substrate with different dipping rate) (a), (b) NC1: 1mm/s, (c), (d) NC2: 0.5mm/s after calcination.

3.3 Comparison of titania and niobium pentoxide system

3.3.1 Wall of the porous structure

The SEM images indicate clearly that in both systems, the coating on different substrates was successfully formed. The films are relatively homogeneous but with some cracks. From XRD measurements of titania samples, the results indicate that the mesoporous wall of titania is crystalline, as shown in Fig. 3-3-1. After comparing the pattern in database, the synthesised material is probably rutile.

The wall of mesopores in niobium oxide is amorohous, as shown in Fig. 3-3-2, in which a broad peak indicates the amorphous phase of the wall.

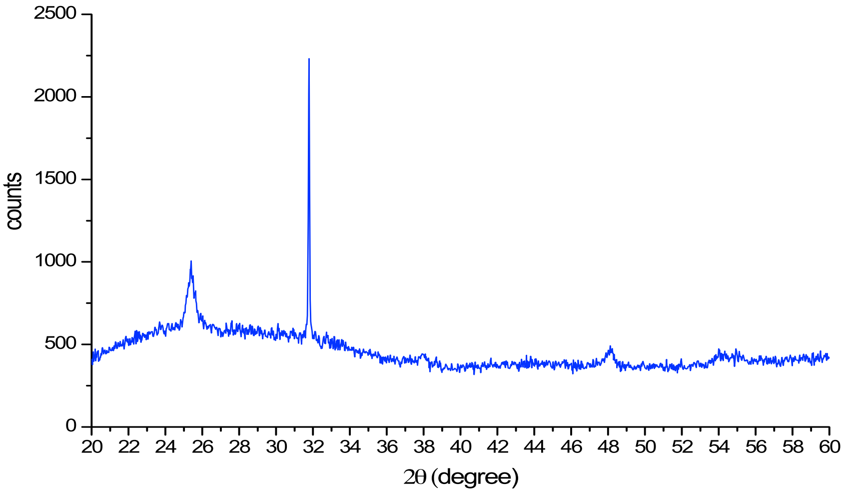


Fig. 3-3-1 Wide-angle X-ray diffraction pattern of calcined mesoporous titania at 400 ˚C (sample TG1)

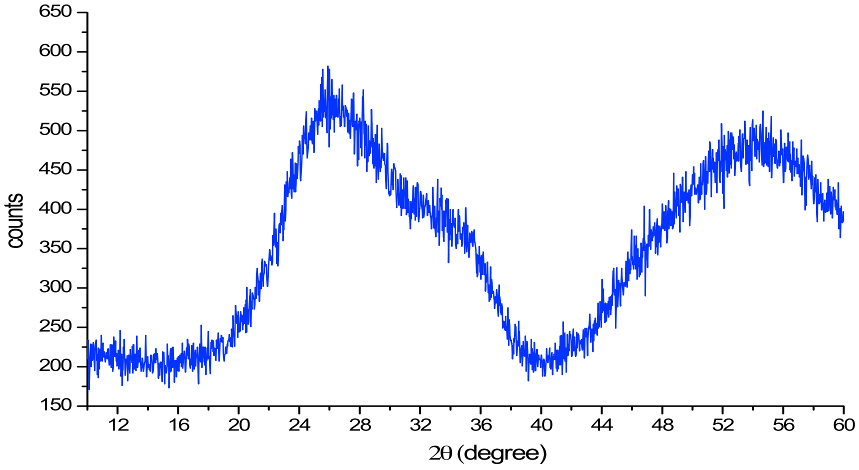


Fig. 3-3-2 Wide-angle X-ray diffraction pattern of calcined mesoporous niobium pentoxide at 400 ˚C (sample NT2)

3.3.2 Synthesis Mechanism

In order to achieve the mesophase in the form of homogeneous thin film, another critical step is assumed to be the hydrolysis and copolymerization process, which can be tuned by varying the species of inorganic precursors and reaction-trigger method.

For titania this is achieved under acidic conditions. Cooperative titania-surfactant self-assembly was allowed to proceed unimpeded, and the resulting as-deposited films exhibit semi solid behavior. And the ageing step with controlled temperature and time solidifies the titania skeleton.

In the niobium oxide system, the addition of water initiated surfactant self-assembly, alkoxide hydrolysis, and metal oxide condensation, and generated an acidic environment providing an envionment with proper pH, under which the synthesis performs well.

3.3.3 Homogeneity

Results show that the homogeneity of the samples in both systems is strongly related to the control of aging time before and after dip-coating, aging temperature, the two of the most critical parameters, which will affect the resulting coating condition indicated in this study. In other words, the proper viscosity of gel is necessary for achieving good homogeneity of the thin film, which can be controled by varying the aging time (before and after dip-coating) and aging temperature (including the increasing rate of temperature). If the ambient temperature increases too fast, the resulting coating is likely to be with lots of cracks. The results in both system show that, too long aging time before dip-coating results in thick bulk material due to too high viscosity of the gel.

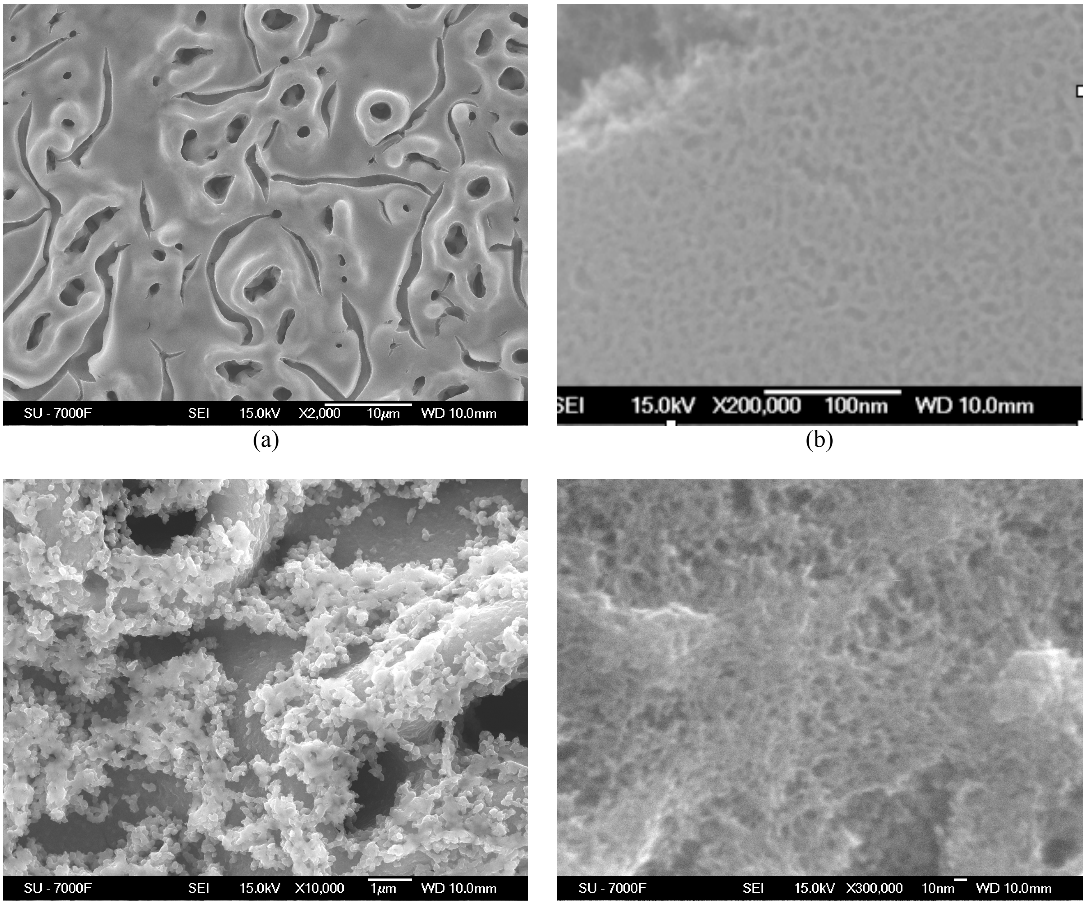
3.3.4 Mesopores

In the titania system, the mesopores are ordered with pore size of around 10 nm. And the diameter of mesopores is even. Whereas in niobium oxide system, the pores are not ordered. The pore size is not even in some samples with a range of 5 ± 2.5 nm. The chain length of template P123 is fixed which should result in even diameter of pores. Therefore the not-even diameter is probably due to collapse of part of the solid skeleton. Thus smaller pores combine as bigger pores as observed.

3.3.5 Humidity sensitivity

The experiments were carried out without humidity control due to instrument limitation. The two systems show different reaction to the ambient humidity. Niobium pentoxide synthesis is very sensitive to humidity while titania is not. The relative humidity varies from day to day. When the RH is relatively high (49.0 %), the morphology of the resulting material is different to the samples with the same experimental conditions under RH of 23.6 %, as shown in Fig. 3-3-3 (a), (b). It is observed that a coating of niobium pentoxide formed with cracks, and there are big amount of particles (with size around 100 nm) formed on the coating. Big amount of pores are observed in the material, randomly distributed with various pore size (approximately 8-18 nm). It was demonstrated that the humidity of aging atmosphere during the EISA process has a significant influence on the mesostructure of resulting material in niobium pentoxide system.

When the RH is comparably high, the high humidity gives a slower evaporation rate. The longer evaporation time leaves more possibility of crystal growing. Then probably not only heterogeneous nucleation on the substrate, but also homogeneous nuleation in the bulk material took place.



(a) (b)

(c) (d)

Fig. 3-3-3 SEM images of (a), (b) sample NC2 with dipping rate 0.5 mm/s and RH = 23.6 %. (c), (d) sample NC4 with dipping rate 0.5 mm/s and RH = 49.0 %.

It has also been reported that the formation of wormhole-like or hexagonal mesoporous niobium oxides can be observed when the RH is above 50 % or below 30 %.[14] It indicates that the pore structure of mesoporous niobium oxide could also be susceptible to RH. [15] Therefore RH is a critical factor that has strong effect on both mesophase and thin film formation.

When different aging temperature is applied, the relative humidity naturally changes with the temperature changing. It is better to choose a chamber with precisely temperature and humidity control function, which is beneficial to enhance the repeatability of the synthesis.

3.3.6 Surface property

BET measurement was performed on the samples of both syntheses in this study. Due to too low sample mass of the films, reliable data could not be obtained.

4 Conclusion

The species of inorganic precursor, surfactant and the ratio between them are critical for the formation of mesophase.

The morphology and mesostructure of synthesized mesoporous thin film are susceptible to evaporation rate which can be tuned by changing aging conditions (time, temperature and humidity) and dipping rate.

Dip-coating is a convient and efficient method of coating thin films on solid substrates. Lower dipping rate leads to better morphology.

Niobium pentoxide synthesis system is very humidity sensitive, of which the morphology is strongly dependent on the ambient humidity. Whereas the titania is not so sensitive to humidity.

5 Future work

It is necessary to perform the synthesis experiment under precise humidity control for researching the effect of RH on the material formation in the future, since the niobium oxide system is already proved to be very humidity-sensitive.

The dip-coating rate would be better to be controlled by an automatic machine rather than manually controlled to achieve better repeatability.

Cross section polishing can be performed to measure the thickness of coating precisely.

Structure study of mesopores architectures can also be involved in the future perspectives..

The pore size can be tuned by using mixed surfactant, for instance P123 / Brij 35.

Other inorganic precursors could be used as attempts to optimize the synthesis method by lower the cost and shorten the synthesis time.

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