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TEMPLATE DIRECTED SYNTHESIS OF POROUS TIN (IV) OXIDE

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Abstract

In the past fifteen years, porous inorganic materials templated by organic molecules have exhibited superior properties over their conventional counterparts from simple sol-gel technique. However, synthesis of porous metal oxides usually suffers from two challenges: high reaction rates of oxide precursors and low thermal stability of porous structure. As a result, ill-defined porous structures are formed and the subsequent calcination can lead to destruction of porous skeletons. Therefore, developments of techniques that can overcome these problems are in high demand.

In this work, Tin (IV) oxide (SnO_2) was chosen as the study material because of its unique physical-chemical properties for applications in optoelectronics, sensors, catalysts and surface coatings. Short-chain neutral surfactant and long-chain polypeptide were selected as the templates for fabricating mesoporous and macroporous SnO_2 structures, respectively.

Templated by neutral surfactant, disordered mesoporous SnO_2 with high thermal stability (400 - 800 °C), large surface area (up to 360 m^2/g), large pore volume (0.17 – 0.33 cc/g), uniform mesopores (3 – 10 nm), and small SnO_2 crystallites (~ 3 – 8 nm) have been produced. Several techniques including aging, hydrothermal treatment, and impurity doping have been systematically investigated based on materials structural and chemical characterizations.

Using polypeptide, multilevel porous SnO_2 structures containing both meso- (4 - 6 nm) and macropores (0.1 to 0.4 μm) were also synthesized. The results revealed that surface complexation of SnO_2 nanoparticles using citric acid is a critical step. Citric acid increases the SnO_2 colloidal stability and promotes binding with polypeptides through electrostatic

forces. It was also found that materials morphology can be controlled by varying the processing condition, such as citric concentration and pH value. Due to the large specific surface area ($180 - 210 \text{ m}^2/\text{g}$) as well as ease in gas diffusion, the synthesized materials were demonstrated superior in H_2 gas sensing property.

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List of Publications

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- [1] J. Zhu, T. S. Zhang, B. Y. Tay & J. Ma, *Fabrication of porous/hollow tin (IV) oxide skeletons from polypeptide mediated self-assembly*, **Journal of Materials Research** 22 (2007), pp. 2448-2453.
- [2] J. Zhu, B.Y. Tay & J. Ma, *Hydrothermal synthesis and characterization of mesoporous $\text{SnO}_2/\text{SnO}_2\text{-SiO}_2$ on neutral template*, **Journal of Materials Processing and Technology**, 192 (2007), pp. 561-566.
- [3] J. Zhu, O. K. Tan, Y. C. Lee, T. S. Zhang, B. Y. Tay & J. Ma, *Hierarchical porous/hollow tin oxide nanostructures mediated by polypeptide: surface modification, characterization, formation mechanism and gas-sensing properties*, **Nanotechnology**, 17 (2006), pp.5960-5969.
- [4] J. Zhu, B. Y. Tay & J. Ma, *Synthesis of mesoporous tin oxide on neutral surfactant templates*, **Materials Letters**, 60 (2006), pp. 1003-1010.
- [5] J. Zhu, B. Y. Tay & J. Ma, *Synthesis and mechanism study of mesoporous $\text{SnO}_2/\text{SiO}_2$ composites*, **Journal of Nanoscience and Nanotechnology**, 6 (2006), pp. 2046-2055.

Conference papers:

- [1] International Conference on Materials for Advanced Technologies 2007 (ICMAT 2007), Singapore, 2007.
- [2] The 7th Asia Pacific Conference on Materials Processing (7th APCMP), Singapore, 2006.
- [3] The 13th International Conference on Processing and Fabrication of Advanced Materials (PFAMXIII), Singapore, 2004.

Chapter 1

Introduction

Chapter 1 Introduction

1.1 Background

According to the International Union of Pure and Applied Chemistry (IUPAC) [1], porous materials are classified into three regimes: microporous (pore diameter, $d \leq 20 \text{ \AA}$), mesoporous ($20 < d < 500 \text{ \AA}$), and macroporous ($d \geq 500 \text{ \AA}$) materials. Because of their high specific surface area (m^2/g) and pore volume (cc/g), porous materials with open pore frameworks are used in a wide range of important applications such as catalysis, sorption, filtration, sensing, drug delivery and tissue engineering [2-4]. In the past 60 years, a great number of studies have been dedicated to the development of microporous materials, such as zeolitic molecular sieves [5-8]. In general, these materials have a crystalline solid network with pore channels in sub-nano scale. However, their small pore size restricts their applications where large guest molecules may be present, e.g., oil refinement and drug delivery. As a result, there has been a demand to increase the pore size to meso- and macroscale to expand their applications [3, 9].

Conventionally, materials containing meso- and macropores can be obtained by sol-gel technique [10]. However, porous materials synthesized from this technique usually suffer from uncontrollable pore size/geometry/symmetry and exhibit a broad pore size distribution. Moreover, gelation during which a 3-D solid network enclosing a continuous solvent phase was formed and subsequent drying can be time consuming. Any lack of control at the drying stage usually induces collapse of the porous frameworks and eventually leads to a decrease in the surface area and porosity. Other techniques based on the processing of zeolite materials have also been investigated, e.g., intrazeolite fabricating technology and variation in gel composition [11, 12]. Nevertheless, the resulting materials are either thermally unstable or show weak acidity, which are not desired in applications such as catalysis.

In 1992, Mobil researchers reported a new class of mesoporous aluminosilicates/silicates, known as the M41S family, templated by self-assembled amphiphilic surfactant micelles in aqueous condition [13, 14]. These materials possess ordered mesoporous skeletons with uniform and tailorable mesopore size ranging from ~ 16 to $100 \text{ \AA}$, sharp pore size distribution, very large surface area ($\sim 1000 \text{ m}^2/\text{g}$) and pore volume ($0.7 - 1.2 \text{ cc/g}$). Their high structural uniformity and symmetry made them an ideal candidate for practical application extending their uses to other fields such as electronics, optics, and energy conversion. Since then, the discovery of M41S materials has triggered a resurrection in the research field of mesoporous materials [9, 15-17]. And, there are a continuous efforts in the study of self-assembled porous materials with controlled pore size, construction and morphology using other types of macromolecular templates, e.g., block copolymers, peptides, biomaterials (proteins, bacteria, DNA/RNA strands), organogels, organic crystals [18-21].

Compared to the conventional un-templated routes (e.g., sol-gel processing), the use of organic templates in self-assembly for creating meso- and macroporous materials has the following advantages:

- 1) Depending on the molecular weight/size of the templates used, the synthesized materials usually display tunable pore size and possess narrow pore size distribution. Such property is a critical issue for selective sorption/filtration applications.
- 2) Unique shapes (such as hollow spheres/tubes) can be obtained by transcription of template morphologies.
- 3) Generation of pores at different scales or multi-level porous structure is possible by a combinatorial use of templates of different dimensions. Recently, such multilevel porous structures have attracted much attention due to their improved transport property and selectivity for guest molecules (e.g., tissue implants materials) [18, 22].

4) Well ordered pore channels can be obtained from well controlled self-assembly with the use of pre-existing crystalline phases of organic templates, as those found in M41S materials.

5) Organic templates with modifiable surface functional groups have influences on the formation kinetics of inorganic materials and therefore may lead to novel porous structures/morphologies.

1.2 Challenges

In spite of many successes that have been made using organic templates to fabricate meso- and macroporous materials over the 20 years or so, the field is still advancing in a fast pace. One of the major interests of the community is the synthesis of non-siliceous porous metal oxides due to their diverse applications in many fields. However, the synthesis of porous metal oxides using organic template usually suffers from two main challenges. Firstly, quick hydrolysis and condensation reactions of metal salts usually cause severe particle agglomeration and therefore fail to interact with the organic species. In certain cases, fast reaction rates can lead to ill-defined particle morphology, as will be shown in Chapter 6. Secondly, rapid crystallization of metal oxides against heat treatment can destroy the obtained meso-/macroporous structures. This can happen either during the removal of organic templates through calcination (usually ≥ 400 °C) or when operating in devices at elevated temperatures. As a result, there will be substantial losses of surface area, pore volume, symmetry of the porous structure, as well as enlargement of the average pore size and broadening of pore size distribution. In addition, fast crystal growth can further deteriorate material performances when materials properties (e.g., electronic and optical) are strongly size dependent (e.g., quantum size effects). Therefore, it is very important to find general solutions to overcome the two challenges, so that highly thermal stable meso- and macroporous metal

oxides with novel desired structures and morphologies can be obtained, e.g., uniform pore size, large surface area, large pore volume and small crystallites.

1.3 Objectives

In the present work, tin (IV) oxide which is a transparent semiconductor with a wide energy band gap of 3.6 eV (at 300 K) was selected as the study material because of its diverse applications in catalysts, gas sensors, and conducting electrodes for optoelectronic devices. To synthesize meso- and macroporous SnO₂, short-chain nonionic surfactant (C₁₄H₃₁N) and long-chain (M_w > 30 kD) synthetic polypeptide were selected as the structure directing agents, respectively, based on their chemical and structural considerations (see details in Chapter 2). In general, this work was aimed to synthesize meso- and macroporous SnO₂ with large surface area and pore volume using organic templating technique. The main objectives of the present study are:

- 1) to synthesize and characterize mesoporous and macroporous SnO₂ materials using nonionic surfactant and polypeptide as templates, respectively,
- 2) to explore the techniques for controlling the reaction kinetics and enhancing the thermal stability of meso- and macroporous SnO₂ with desired porous structures and novel morphologies, and,
- 3) to investigate the influences of key processing parameters on final materials properties and to understand the possible structure formation mechanisms.

Chapter 2 of this thesis will give a historical review and state of the art advances of mesoporous siliceous and non-siliceous materials templated by surfactants as well as macroporous siliceous materials templated by polypeptides. In chapter 3, the experimental details will be described, including raw materials, synthesis procedures, characterization methods, and gas sensing property measurement. The results and discussions on mesoporous SnO₂, mesoporous SnO₂-SiO₂ composites, and

macroporous/mesoporous SnO₂ will be presented in chapter 4, 5, and 6, respectively.

Finally, a conclusion and future work will be given in Chapter 7 and 8, respectively.

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Chapter 2

Literature Review

Chapter 2 Literature Review

In this chapter, a historical review on mesoporous siliceous materials and the recent development of mesoporous metal oxides, in particular, mesoporous SnO_2 will be presented. The surfactant chemistry, sol-gel basics, synthesis of mesoporous silica, mesostructure formation mechanisms and characterization techniques related to mesoporous silicates will be discussed. The next section (2.2) will describe the synthesis of macroporous materials templated by an emerging class of biomaterials, i.e., synthetic polypeptides. The topics of basic chemistry/structure of polypeptides, polypeptide templated macroporous silica, as well as the current challenges for templating metal oxides will be detailed.

2.1 Mesoporous materials templated by surfactants

2.1.1 Silicate mesoporous materials

In 1992, Mobil researchers synthesized a new family of mesoporous silicates/aluminosilicates known as M41S using cationic surfactant template [1, 2]. The M41S family consists of three members which are MCM-41 (hexagonal space group of $p6mm$), MCM-48 (cubic, $Ia3d$), and MCM-50 (lamellar, $p2$). Each has a unique and ordered arrangement of mesopore channels. MCM-41 and MCM-50 contain straight cylindrical pore channels, while interconnected gyroidal pore channels are obtained in MCM-48 (Fig. 2.1).

Fig. 2.1 Schematic drawings of M41S materials: (a) hexagonal MCM-41, (b) cubic MCM-48, and (c) lamellar MCM-50 [2].

These materials are characterized by a high symmetry of mesostructure and uniform pore size distribution (PSD) from ~ 16 to $100 \text{ \AA}$. Very large surface area (up to $1000 \text{ m}^2/\text{g}$) and high porosity ($\sim 69\%$) can be obtained. The so called surfactant templating technique was quickly recognized due to its easy processing and ability to tailor materials properties such as mesopore size and mesostructural symmetry. For example, the mesostructure can be changed from MCM-41 to MCM-48 by increasing the molar ratio of surfactant to inorganics. Since then, many studies have been devoted to the synthesis of mesoporous materials with expanded compositions, structures and morphologies, as well as to the understanding of the formation mechanisms [3-14].

In the synthesis of the original M41S materials, mesostructured hybrids were formed in a self-assembly process in which the silicate/aluminosilicate species tend to occupy the continuous solvent regions in between the ordered liquid crystal phases. The assembly is driven by the surface interaction between the polar head groups on template molecules and the negatively charged silicate/aluminosilicate precursors. Hydrothermal treatment was then applied to the hybrids at elevated temperature ($150 \text{ }^\circ\text{C}$) for desired periods, and followed by calcination to remove the organic templates. Two possible formation mechanisms have been proposed, based on the similarity of structural symmetry between M41S and liquid crystalline phases. However, later works revealed that the structural formation and transformation are very complex and highly dependent on many variables [15-19], such as surfactant type/concentration, surfactant to inorganics molar ratio, pH value, reaction time and temperature, thermal treatment, types of co-solvent (e.g. alcohol) and auxiliary organics, etc.

Amongst these variables, a good control of surfactant and inorganic behaviors is primarily important for obtaining successful self-assembly, which involves the micellization of the surfactant, and hydrolysis and condensation kinetics of the inorganic precursors.

2.1.1.1 Surfactant chemistry

A typical amphiphilic surfactant molecule contains a non-polar hydrophobic tail and a polar hydrophilic head group. Many of the surfactant's properties such as adsorption, micelles, solubility, solubilisation, micro-/macro-emulsions, wetting, foaming/defoaming, dispersing/aggregation of solids, and detergency are determined by the geometry (size and shape) of the hydrophobic and hydrophilic parts [20]. Fig. 2.2 illustrates the various adsorption behaviors of surfactant molecules at different interfaces. Surfactant monolayer (e.g., Langmuir-Blodgett film) is usually formed when surfactant concentration is extremely low and the orientation of surfactant molecule is determined by the nature of two phases in contact.

Fig. 2.2 Schematic drawing of surfactant alignment behaviors at various interfaces [20].

In general, surfactants can be classified into four categories based on the property of the hydrophilic groups: cationic, anionic, neutral and amphoteric surfactants, as listed in

Table 2.1 Classification of surfactant and their respective examples [21]

Types of surfactants	Nature of hydrophiles	Typical examples
Anionic	Negatively charged	Carboxyl (RCOO^-M^+), Sulfonate (RSO_3^-M^+)
Cationic	Positively charged	Quaternary ammonium halides ($\text{R}_4\text{N}^+\text{Br}^-$)
Noionic	Neutral	Polyoxyethylene ($-\text{OCH}_2\text{CH}_2\text{O}-$)
Amphoteric (Zwitterionic)	Both positive and negative charges	Sulfobetaines ($\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$)

Table 2.1 which also provides some of their typical examples [21]. In the case of cationic and anionic surfactants, the hydrophilic part consists of a charged functional head group (e.g., RCOO^-) and a counter ion with opposite charge. The counter ion can be replaced by other ions present in solution, which have a stronger affinity to the head groups. During synthesis of mesoporous materials, ion exchange usually occurs between the counter ions and the small inorganic monomers or oligomers. Neutral surfactant has a hydrophilic group that ionizes only marginally and therefore its solubility strongly depends on the chemistry of the polar part. Typical examples are the ether group ($\text{R}_1\text{-O-R}_2$) and hydroxyl group (R-OH). The solubility of the neutral surfactant containing only one hydroxyl group in water is very low as compared to that of ionic surfactants. In practice, the solubility of neutral surfactants is usually improved by increasing the number of monomers on hydrophilic group, e.g., ethoxylation. Amphoteric surfactants have both a cationic and an anionic group. Therefore, they can form cations in acidic solutions but anions in alkaline solutions. However at some intermediate pH, both groups show equal ionization ability and this pH value is called the isoelectric point (IEP). Amphoteric surfactants usually have excellent solubility in aqueous solution, good compatibility with aqueous ions and other surfactants, as well as high chemical stability in both acidic and alkaline conditions.

One property that differentiates a surfactant from other chemical entities is the abnormal increase in solubility when a particular concentration is reached. At a very low concentration, almost all the surfactant molecules lie flat at the liquid/vapor interface. As the number of surfactants at the interface starts to increase with increasing concentration of surfactants, the surfactant molecules begin to orient themselves perpendicular to the interface. At a particular concentration, a monolayer of surfactant molecules is formed at the interface and any further increase in the concentration will lead to the formation of micelles and subsequent liquid crystalline phases in the solution. This particular point is named as critical micelle concentration (cmc). In water, a micelle contains an inner region consisting of compacted hydrophobic hydrocarbon tails and an outer region of hydrophilic head groups. Micelles can have different geometries such as spheres and cylinders. A liquid crystalline phase is an ordered arrangement of spherical/cylindrical micelles, e.g., hexagonal, cubic, and lamellar phases. Beyond the cmc, many physical properties (e.g., surface tension, electrical conductivity, and osmotic pressure) either change sharply or remain unchanged when the concentration of the surfactant increases. Based on this phenomenon, three techniques are commonly used to determine the cmc of surfactants: UV-absorption spectroscopy, fluorescence spectroscopy, and electrical conductivity method. Fig. 2.3 shows the behaviors of several physical properties when the surfactant concentration is near and higher than cmc.

Another important factor influencing the solubility of surfactants is temperature. Both ionic and neutral surfactants show different solubility-temperature relationships due to different solubilisation mechanisms. In the case of ionic surfactants, their solubility will normally undergo a sharp and discontinuous increase at a characteristic temperature known as Krafft temperature (T_K). Below T_K , the solubility of the surfactant is a function of crystal lattice energy and heat of hydration of the system. Above T_K , the solubility of the surfactant

Fig. 2.3 Effects of critical micellization concentration (cmc) on various physical properties of surfactant solution [20].

molecules is equal to the cmc, and the formation of micelles become thermodynamically favored. Therefore, the total solubility of surfactants above T_K is the sum of the monomers (or single molecule) and micelles [21]. However, in the case of neutral surfactants, the surfactants become less soluble in water as temperature increases. Phase separation can occur at certain temperature and therefore leading to a cloudy surfactant suspension (cloud point).

When the surfactant concentration is much higher than cmc, micelles can change in their geometry and pack into liquid crystalline phases (LCP) to further reduce interfacial energy. The formation of liquid crystalline phases usually takes place in a broad range and at a high surfactant concentration. Three common LCP have been observed: hexagonal, lamellar and cubic symmetry. Fig. 2.4 shows the typical phase diagram of a cationic surfactant (e.g., Cetyltrimethyl ammonium bromide, CTAB) in water. It is noted that cylindrical micelles are normally formed prior to hexagonal LCP. Depending on the temperature and surfactant concentration, spherical micelles can be first formed and then transit to cubic LCP which is favored instead of the hexagonal phase. Finally, when the

surfactant concentration is increased to a very high level, lamellar LCP is formed in which the surfactant molecules form bi-layer micelles and packing together in a lamellar structure.

Fig. 2.4 Schematic phase diagram of cationic surfactant (Cetyltrimethyl ammonium bromide, CTAB) in water (by permission of Prof. C. J. Brinker) [3].

Several models and theories have been developed to understand the micelles and LCPs formation behaviors: the mass-action model, phase separation model and surfactant packing parameter “ g ” approach. The first two models describe the overall process of micellization from a thermodynamic approach [22]. Qualitatively, the cmc of a given surfactant is determined by the relative strength of two forces. One of them arises from the mutual charge repulsion between the polar groups of ionic surfactants. The larger the repulsion force is, the less the tendency for micelles to be formed. The other force is the attractive force between hydrophobic groups of surfactant molecules. This attractive force is complex in nature and is mainly due to the enthalpy and entropy changes when alkyl group is transferred from a bulk to an aqueous environment. Another useful model, developed by Israelachvili et al., considers the steric effects of surfactant molecules [23]. In this model, the geometry of micelles (i.e., spherical, non-spherical, bi-layer, inverse micelles) is determined by a surfactant packing parameter “ g ”, expressed by Equation (1):

$$g = v / a_o l_c \quad \text{--- (1)}$$

where, v is the alkyl chain volume, a_o is the effective hydrophilic group area, and l_c is the maximum length of the alkyl chain. Chain length l_c can be estimated by Equation (2):

$$l_c = 1.5 + 1.265n \text{ (Å)} \quad \text{--- (2)}$$

where, n is one less than the total number of carbon atoms in the alkyl chain.

Based on this model, the “ g ” values of some common micelle structures are given in Table 2.2. This model suggests that one can manipulate the micelle geometry by changing the values of v , a_o , and l_c , and therefore the symmetry of liquid crystal phases. For example, a_o can be increased by using a co-solvent which is able to diffuse to the hydrophilic regions of micelles and therefore expand the effective area occupied by each head group. This can transform the geometry of a micelle from non-spherical to spherical shape.

Table 2.2 A list of micelle geometry and the respective “ g ” value

Micelle Geometry	Surfactant packing parameter (g)
Spherical	$< 1/3$
Non-spherical	$1/3 - 1/2$
Bilayers	$1/2 - 1$
Inverted micelles	> 1

2.1.1.2 Sol-gel behaviors

Sol-gel is a versatile technique for producing high purity ceramics of homogeneous composition at low processing temperature. However, the material properties are sensitive to the processing parameters. For example, any small changes in the pH value of the solution

can change the sample morphology and size dramatically. Therefore, the structures of surfactant templated mesoporous materials is very sensitive to the working condition and several critical factors including kinetics of hydrolysis/condensation, precursors/particles sizes, surface charges, and agglomeration should be carefully controlled. Systematic studies, both theoretical and experimental, in recent years were made to advance the understanding of the effects of processing parameters, i.e., the pH value, materials concentration, types of inorganic precursors, nature of solvent/co-solvent, temperature, aging process, and use of catalyst, etc [24, 25]. For example, it was found that the kinetics of hydrolysis and condensation can be controlled by varying the solution pH value and/or using different solvents.

Compared with metal oxides, the synthesis of ordered mesoporous silica is much easier because of the mild reactivity of the silica precursors. Its kinetics of reactions during hydrolysis and condensation can be controlled easily due to a lower partial positive charge on the silicon atom as well as the stable oxidation state and coordination structure of Si^{4+} . In contrast to the condensation of organic polymers, the gel network of silica is formed through three stages, as proposed by Iler [25]:

- a) Polymerization of monomer to form oligomers.
- b) Growth of particles, e.g., through Ostwald ripening.
- c) Chain formation through the linking of monomers/oligomers, and finally the thickening to a gel network throughout the liquid media.

So far, as many as 25 basic silicate monomer and oligomers have been identified by ^{29}Si NMR (Nuclear Magnetic Resonance) in alkaline solution [26]. In most cases, silicon alkoxides (e.g. Tetraethylorthosilicate or TEOS) was used as a source of silicate precursors

and a mineral acid (e.g., HCl) or a base (e.g., NaOH) as the catalyst. Generally, the hydrolysis and condensation of TEOS can be described by three reactions [24]:

Where, -R is ethyl group, C₂H₅. In hydrolysis reaction (1), the alkoxide group (-OR) is replaced by hydroxyl group (-OH), and subsequent condensation reaction (2) produces siloxane bonds (Si-O-Si) by the elimination of an alcohol or a water molecule.

The structure and property of silicates can be modified by varying the synthesis conditions such as, water to Si molar ratio, type of the catalyst and its concentration, property of solvent/co-solvent, temperature and pressure [27-29]. In particular, the kinetics of hydrolysis and condensation can be most effectively adjusted by using catalysts. Investigations by McNeil et al. [30] and Pohl et al. [31] showed that the rate of hydrolysis reaction can be catalyzed by either an acid or a base. This is illustrated in Fig. 2.5 which shows the variation of the rate of hydrolysis with the pH of the solution. The graph indicates that reaction rate is minimum near neutral pH and increases when pH is adjusted to either acidic or basic condition.

Aelion et al. [32] found that the rate and extent of the hydrolysis reaction was greatly influenced by the strength and concentration of the acid or base catalyst, while temperature

Fig. 2.5 Hydrolysis rate of γ -glycidoxypentyltriethoxysilane at various pH values in aqueous solution [24].

and solvent were of secondary importance. In the case of a basic catalysis, the hydrolysis of TEOS was a function of the catalyst concentration, as similar as under an acidic condition.

The kinetics of hydrolysis is also be affected by steric (spatial) and inductive effects. Any increase in chain length or branching of alkyl groups tends to retard the rate of the reactions. Induction effects to the hydrolysis rate was observed when the alkoxy groups (-OR) were substituted by alkyl and hydroxyl groups [33, 34]. In the case when the alkoxide group was replaced by alkoxy group, there is an increase of the electron density of the silicon atom. Conversely, substitution of hydroxyl group by an alkoxide group decreases the electron density on the silicon. As a result, substitution of alkyl and hydroxyl groups increases the stability of positively and negatively charged transition states, respectively [24]. In an acidic condition, the transition states are positively charged. Therefore, substitutions of alkyl groups promote the rate of hydrolysis, whereas in the basic condition the reverse trend can be observed [34].

According to reaction (1), the rate of hydrolysis is expected to increase when water to Si molar ratio increases. By primarily varying the water to Si molar ratio while maintaining the pH value and concentration of co-solvent, polysilicate products with different morphologies can be obtained. Co-solvents are usually applied in the synthesis of surfactant templated mesoporous materials as homogenizing agents. However, they may also affect the material property depending on the characteristics of the co-solvents. The effects of various co-solvents (such as ether, ethanol, and formamide) on micellization and micelle size, periodicity of pore arrangement, and morphologies of the products have been investigated by Anderson et al. [35]. Co-solvents/solvents may be classified as polar and non polar or as protic (ability to donate an H^+ ion) and aprotic. Important characteristics of the co-solvents for influencing sol-gel process include polarity, dipole moment and the availability of labile protons. The ability of a liquid to dissolve ionic solids depends strongly, although not exclusively, on its dielectric constant. The higher the co-solvent's polarity is, the higher its dielectric constant. Meanwhile, molecule with higher polarity has a stronger ability to solvate ions present in the solution. The dipole moment of a co-solvent molecule determines the length over which the charge on one species can be affected by surrounding species. The lower the dipole moment is, the larger this length will be [24]. The availability of labile protons determines whether anions or cations are solvated more strongly through hydrogen bonding. Since the hydrolysis and condensation are generally catalyzed by acid or base, the use of aprotic and protic co-solvents/solvents will be able to reduce the catalytic effect of hydronium ions and hydroxyl ions in acidic and basic conditions, respectively.

Iler [25] and Keefer [33] proposed a mechanism for base-catalyzed hydrolysis, in which the hydroxyl ions (OH^-) displace OR^- with inversion of the silicon tetrahedron, as shown in reaction (4).

Studies on the condensation of aqueous silicates at high pH values [36] showed that the following typical sequence of products is yielded during condensation: monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer, and higher-order ring. Through the kinetic analysis, the authors also showed that protic solvents retard base-catalyzed condensation but promote acid-catalyzed condensation. The reverse is expected for the aprotic solvents.

2.1.1.3 Key variables

Inspired by the synthesis of M41S materials, many efforts have been devoted to synthesize new mesoporous materials by controlling the processing conditions, such as, nature and concentration of surfactant, different inorganic sources, surfactant to inorganic(S/I) molar ratio, pH value, reaction time and temperature, organic and inorganic additives, post-synthesis treatment, and the method to remove the surfactants. The results have shown that ordered mesoporous silica with varying properties can be synthesized within a wide processing window, i.e., from acid to basic solution, minutes to several days, low to high temperatures. A list of typical mesoporous silica reported in literature is given in Table 2.3.

The first modification to M41S was to change the surfactant systems: anionic, neutral and acid-treated surfactant assemblies were explored to produce numerous mesoporous silica [37-46]. Based on the type of interaction at the organic-inorganic interfaces (electrostatic, hydrogen bonding, and etc), the synthesis routes can be classified into six approaches [7]: S^+I^- (S = Surfactant, I= Inorganic), S^+I^- , $\text{S}^+\text{X}^-\text{I}^+$ (X= Halides), $\text{S}^-\text{M}^+\text{I}^-$ (M= Alkali metal ion),

and S^0/N^0I^0 (S^0/N^0 = Neutral/non-ionic surfactant). The interaction can be altered by adjusting the nature of charge on the inorganics surfaces through pH variation.

Table 2.3 Typical mesoporous silicas with different mesophases

Sample	Mesophase symmetry	Average pore size (Å)	Ref.
MCM-41	2D Hexagonal (P6mm)	37	[1, 2]
MCM-48	Cubic (Ia3d)	35	
MCM-50	Lamellar (p2)	36.2 for (100) plane	
MSU-1	Hexagonal (disordered)	31	[37]
MSU-2	Hexagonal (disordered)	35	
MSU-3	Hexagonal (disordered)	58	
MSU-4	Hexagonal (disordered)	N/A	[38]
MSU-V	Lamellar	N/A	[39]
MSU-G	Lamellar	32	[40]
HMS	Hexagonal (disordered)	28	[41]
FSM-16	2D Hexagonal (P6mm)	28	[42]
SBA-1	Cubic (Pm3n)	20	[43, 44]
SBA-2	3D Hexagonal (P63/mmc)	22	
SBA-3	2D Hexagonal (P6mm)	27.7	
SBA-8	2D Rectangular (cmm)	18.7	[45, 46]
SBA-11	Cubic (Pm3m)	25	
SBA-12	3D Hexagonal (P63/mmc)	31	
SBA-14	Cubic (Pm3n)	24	

When neutral surfactants were used as templates, hydrogen bonding was considered to be the driving force for the formation of the disordered mesophase [37]. Use of neutral surfactants has two advantages: (1) relatively expensive neutral surfactants can be recovered by extraction technique, such as refluxing; (2) stable mesoporous structure can be formed

because thicker framework walls are generally obtained. For example, MSU-V (Michigan State University) materials with lamellar structure and vesicular particle morphology were prepared from neutral bola-amphiphiles ($\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$). These materials are thermally stable upon calcinations and the mesoporous lamellar structure has a high surface area.

Liquid crystal templating approach is not limited to the use of amphiphilic surfactants. Lamellar mesophase composite has also been synthesized by using non-amphiphilic molecules [47]. Other types of micelle-templates amphiphilic block-copolymers and glycosilicate surfactants have also been used as templates for the preparation of mesoporous silica [48-50].

Stucky et al. [43-46] reported several mesostructured silica synthesized under acidic conditions, termed as SBA-n (SBA: Santa Barbara, $n=1-3, 8, 11-12, 14$). These materials were prepared using a cationic surfactant in the presence of halogen acids through balanced Columbic hydrogen bonding, and van der Waals interactions. Impressive progress was made by the work from Zhao et al. [48], in which triblock polyoxyalkylene copolymers were used to produce large mesopore materials and the resulting materials were denoted as SBA-15. This family of materials possesses pore size between 46 and 300 Å and wall thickness of 31 to 64 Å.

Anionic and cationic block copolymers have also been used to produce even bigger pores of up to 500 Å with wall thicknesses of up to 100 Å. In a very recent study, emulsion method was applied to synthesize well-defined mesoporous materials of spherical morphology and less agglomeration compared with conventional hydrothermal method [51]. In their study, oil in water emulsion was applied and the yielded structure has a narrow pore size distribution with mesopore size varied from 30 to 100 Å.

The effects of surfactant concentration on materials structures were investigated by Coleman and Attard [52] who employed tetramethyl orthosilicate (TMOS)/Brij 56/HCl (0.5 M) system. They found that for a fixed TMOS: Brij56 weight ratio, a very low surfactant concentration gave a disordered structure. The mesostructural order was improved when the surfactant concentration was increased and finally a hexagonal mesoporous structure was produced when the surfactant concentration reached a critical value. Further increase in the concentration led to progressive deterioration of the mesopore ordering and a wormhole-like structure was obtained.

The surfactant to inorganic (S/I) molar ratio is another critical variable influencing the phase formation of mesoporous silica. The effects of S/I ratio were systematically investigated by Vartuli et al. [53, 54]. The synthesis process involved a ternary system (TMOS/CTMA/Water) with S/I ratio changing from 0.5 to 2. Their result showed that the symmetry of the structure is highly dependent on S/I ratio. Hexagonal phase was usually produced when S/I ratio < 1 . At slightly higher S/I ratio (1 - 1.5), a cubic phase was obtained. When this ratio varied from 1.2 to 2, lamellar phase was the major component. Results from this work support the liquid crystal templating mechanism proposed by Mobil researchers, since the final mesostructural orderings agreed well with the phase prediction based on pure surfactants behaviors in water.

The rate of hydrolysis and condensation were usually controlled by adjusting the pH value of the solution. To obtain a stable solution of inorganic oligomers, the pH value can initially be adjusted to a point that is relatively “neutral” to silica ($\sim 2 - 4$), as reported by Boissiere et al. [55]. In the second step, the pH value was increased to ~ 7 to promote the condensation of silica particles. Stepwise adjustment of pH values usually allows time for the silicate precursors to assemble adequately on the templates. As aforementioned, the pH value

of the solution also affects the type of surface charges on the inorganic precursors. Depending on the type of surfactants used (e.g., cationic or anionic), well ordered mesoporous silica materials have been fabricated under both highly acidic and alkaline conditions.

The morphology of the mesoporous silica particles is also affected by a change in the reaction temperature. Sakamoto et al. [56] showed that faceted single crystals of 3-D cubic SBA-1 materials could be synthesized by lowering the temperature to 0°C and increasing the reaction period to one week. According to the work by Che et al. [57], a highly isotropic crystal growth (faceted final morphology) could be achieved by slowing down the process of crystallization under a thermodynamically controlled condition. These works again reveal that the properties of mesoporous materials are both kinetically and thermodynamically related.

Additives such as co-solvent, auxiliary surfactant, inorganic electrolyte, organic molecules (benzene), and Hofmeister anions were reported to have effects on the final properties of materials. Zhao et al. [45] found that the morphology of Pluronic-templated mesoporous SBA-15 could be modified by co-solvents, auxiliary surfactants, and inorganic electrolytes. The modified particle morphologies include fiber, rope, doughnut, sphere, gyroid, and discoid. The formation of specific morphology was strongly dependent on curvature energy at the interface of inorganic silica and organic block copolymers. Ion-exchange was believed to have taken place at the interface between the head groups of the organic surfactant and the surrounding water-rich regions. Based on the detailed multinuclear NMR experiments by Firouzi et al. [19], bromide anions were found to be replaced by negatively charged silica oligomers due to a greater charge shielding effect of the latter. The

effects of Hofmeister anions (SO_4^{2-} , HPO_4^{2-} , OH^- , F^- , HCO^- , CH_3COO^- , Cl^- , Br^- , NO_3^- , I^- , SCN^- , AND ClO_4^-) on the formation of mesoporous solids were also reviewed by E. Leontidis [58]. The Hofmeister anions are able to change the hydrolysis rate of silicate precursors and hence the surface property and morphology of the final products. The affinity of Hofmeister anions towards cationic micelles is usually found to follow the order: $\text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. E. Leontidis also concluded that the presence of Hofmeister ions may promote the ordering of surfactant aggregates through charge neutralization (cationics), interfacial dehydration, and interfacial charging by adsorption (non-ionics). Faster hydrolysis in cationic systems can be achieved with the presence of more chemotropic Hofmeister ions (e.g., NO_3^-). The reason is likely due to a reduction in interfacial charge resulting from the adsorption of Hofmeister ions on micellar surfaces.

2.1.1.4 Structure formation mechanisms

Many possible mechanisms have been proposed to explain and predict the formation of surfactant templated mesoporous materials: Liquid Crystal Templating (LCT) approach [2], Layered Mesophase Puckering model [15], Folded Sheets mechanism [16], Charge Density Matching route [17, 18], and Silicatropic Liquid Crystals model [19]. Because of the complexity of the synthesis process, none of them is applicable to a universal situation.

The first attempt to explain structure formation was by Mobil researchers who proposed a 'liquid crystal templating' mechanism based on the similarity between surfactant LCP and mesophase of M41S [2]. It was found that the symmetry of mesostructure was highly dependent on surfactant concentration, hydrophobic carbon chain length and the presence of auxiliary swelling agents. As aforementioned (section 2.1.1.1), these factors also determine the type of surfactant LCP formed in aqueous condition. Hence, two possible pathways were postulated. In pathway 1, silicate/aluminosilicates precursors occupy the

regions between preformed hexagonal lyotropic LCP through interfacial interactions and subsequently deposit onto rods surfaces to form mesophase composite. In the second pathway, ordered mesophase is induced concomitantly when the inorganic precursors interact with the surfactant micellar rods. During processing, the randomly oriented micellar rods are encapsulated by two or three monolayers of silicate species through Columbic attraction. Subsequently, these rods spontaneously pack into a highly ordered hexagonal arrangement to further reduce surface energy. Investigations by XRD, ^{29}Si NMR, in situ ^{14}N NMR, and thermogravimetric analysis techniques have shown that no hexagonal LCP was detected prior to assembly, hence showing that M41S is very likely formed via pathway 2.

Based on NMR study, Steel et al. [15] proposed a ‘silicate layer puckering’ mechanism in which ordered mesophases were formed directly upon the addition of silicate precursors. Hexagonal and lamellar mesoporous structures can be synthesized as schematically illustrated in Fig. 2.6. According to this model, the silicate layers were formed in the first stage during which the surfactant rods were arranged in a hexagonal order between silicate layers. After ~ 15 min, the silicate framework transformed from lamellar to hexagonal ordering when the layers pucker and close together. As a result, hexagonal pore

Fig. 2.6 Schematic formation of (a) hexagonal, and (b) lamellar M41S materials based on “silicate layer puckering” mechanism (by permission of Royal Society of Chemistry)[15].

channels were formed, accompanied by the surfactant reverting to an isotropic solution (Fig. 2.6-a). When the concentration of silicate was increased, layer thickness increased and therefore lamellar structure was maintained as the inorganic framework condensed to final product (Fig. 2.6-b).

Folded sheets mechanism was proposed by Inagaki et al. [16] in their synthesis of FSM-16, which was very similar to MCM-41. The authors suggested that hexagonal mesophase was formed by intercalation of surfactants into layered silicates (kanemite) through ion exchange process. In the next stage, silicate sheets were believed to fold around the surfactants and condense into a hexagonal mesophase composite. However, one argument about this mechanism is that the layered structures were still observed in the kanemite-derived mesoporous materials.

Another important formation mechanism was proposed by Stucky et al. [17, 18] who suggested that the final hexagonal mesostructure was transformed from an initial lamellar phase. It was shown that structure formation was dominated by charge density matching, coordination states, and steric requirements of inorganic and organic species at the interfaces. Strong evidence revealed that lamellar structure was obtained during the first 20 min of reaction, and then transformed to hexagonal ordering. When the lamellar phase was hydrothermally treated at 100 °C at a relatively low pH, hexagonal mesostructure was obtained after 10 days. Hence, Stucky et al. proposed that in a surfactant/silicate mixture with a relatively low pH, a low degree of polymerization of inorganic precursors, and low temperature, small silica oligomers (3 - 8 silicon atoms) are important for the formation of ordered mesoporous structures. Although these small oligomers belonged to Hofmeister ion series, they may have stronger binding strength to the cationic surfactant head group because

of the higher degree of shielding effect due to multicharges. Multi-dentate binding of silicate oligomers to cationic surfactants can lead to further polymerization of very large ligands, and enhance the cooperative binding between the surfactant and silicate species [4]. As the polymerization of the silicate species continues, the average surface area of head group of surfactant increases due to the reduced charge density of larger silicate poly-anions. This finally leads to corrugation of silicate layers and the resultant formation of hexagonal mesophase.

When polymerization of silicate species were limited by lowering temperature or increasing pH to ~ 14 , a true cooperative self-assembly between silicates and surfactants was found feasible. Firouzi et al. [19] suggested that ion exchange between surfactant counter-ions (OH^- , Br^- , Cl^-) and multiply charged silica oligomers D4R (double four-ring, $[\text{Si}_8\text{O}_{20}]^{8-}$) may take place through enhanced Columbic interactions due to the high charge density of oligomers. A schematic model for transformation from lamellar to hexagonal mesophase (the final lamellar and hexagonal phases are also referred as ‘Silicatropic liquid crystal’ phase) via ion exchange is shown in Fig. 2.7. Electrostatic repulsion between surfactant head groups can be effectively reduced by multi-dentate bonding screen effect and therefore resulted in increased surfactant packing parameter (g). The D4R oligomers may not be necessarily formed in the initial aqueous mixture. Instead, they can be evolved due to strong interaction between the surfactant and the silicate precursors. It was suggested that this behavior was attributed to the close match of projected areas of D4R anion and an ammonium head group (0.098 nm^2 vs. 0.094 nm^2) as well as the correct distribution of charges on the projected surfaces.

Fig. 2.7 Diagram shows the formation of lamellar and hexagonal mesostructures from Silicatropic liquid crystal phase [19].

Phase transformation from hexagonal MCM-41 to cubic MCM-48 in an epitaxial manner without dissolution of the initially formed MCM-41 was observed by Monnier et al. [59] using in situ XRD technique. Two competing mechanisms (cylinder merging and branching approaches) were proposed based on the assumption that structural transformation from hexagonal to cubic can be achieved through either longitudinal (cylinder merging) or transverse (cylinder branching) linkage of the adjacent pore channels. Although two models were proposed, results showed that it is likely that phase transformation is controlled by both approaches. The actual energy barrier for structure change will determine which mechanism is more favored. Generally, the cylinder merging approach is a reversible process and kinetically favored while cylinder branching is thermodynamically favored but less reversible than the former. In a further study, they found that phase transformation was dominated by surfactant packing [60]. However, kinetics of change was mainly affected by charge density matching between silica inorganic framework and surfactant head groups. High activation energy value of 170 kJ/mol was calculated from kinetic data for phase transformation in

water. Important concepts from this work suggest that new mesoporous structures could be obtained through solid-solid phase transition approaches.

2.1.1.5 Structure characterization

For mesoporous materials, three techniques are most commonly used to obtain information on the type of mesostructure ordering, surface area, pore volume, pore size and pore size distribution. They are Small Angle X-ray Scattering (SAXS), Transmission Electron Microscopy (TEM) and Brunauer-Emmett-Teller gas adsorption measurement (BET method). In the following sections, typical uses of these techniques and related discussions will be provided.

Small Angle X-Ray Scattering (SAXS)

In contrast to the wide-angle X-ray reflection technique, SAXS is used to detect the periodicity/symmetry of the materials in nanoscale (a few nanometers). In the original work of MCM-41, SAXS was applied to detect the ordering of mesopore arrangement. Ordered mesophase structures can yield a group of reflection peaks (normally $2\theta < 10^\circ$) that can be used to identify the type of symmetry. A schematic representation of common mesophases and their respective SAXS patterns can be found elsewhere [8].

X-ray scattering signals of mesophase materials in this technique arise from electron density contrast between the inorganic and organic regions [61]. Upon calcination, the surfactant template was removed and the pore channels were mainly occupied by air. Therefore, intensity of the reflection peaks usually increases due to enhanced electron density contrast between the inorganic framework and air. With the use of SAXS, several information on mesoscale can be obtained: i) type of mesophase ordering, e.g., hexagonal, cubic or lamellar, ii) d-spacing value ($d = \lambda/2\sin\theta$, where λ and θ are the wavelength of X-ray source and half of the reflection peak angle, respectively) and therefore the deduction of wall

thickness if the average pore size is known, and iii) average length of mesostructure ordering from Scherrer equation (similar to calculation of crystal size). Normally, ordered mesoporous materials give more than one SAXS reflections while disordered/poorly ordered mesostructure shows only one peak.

Unlike wide-angle X-ray reflection technique, it is not practical to quantify the purity of mesoporous materials using SAXS. Study has shown that samples with one SAXS reflection have also been found to contain substantial amount of MCM-41 [4]. Other limitations of this technique to analyze mesoporous structures include: interpretation of the results is dependent on the model being adopted, and the measurements are time-consuming for those non-silica mesoporous materials which may contain a lot of defects.

TEM characterization

Transmission electron microscopy is a modern technique which can provide almost all of the structural, phase, and crystallographic data [62]. TEM technique is a useful method to directly examine the mesoporous structure under the microscope in real space. Numerous sophisticated and beautiful high resolution TEM images of M41S with well ordered pore channels have been observed and reported (Fig. 2.8) [8].

Fig. 2.8 TEM images of MCM-41 synthesized by Feng et al. (by permission of American Chemical Society) [49].

Improvement of TEM technique such as high accelerating voltage (≥ 200 keV), enhanced vacuum, reduction in coefficients of spherical aberration and development of charge-coupled devices (CCDs) have enabled more precise and unambiguous characterization on a wide range of micro and mesoporous materials. Ultra-high resolution (probe ca. 8 Å) and simultaneous collection of different signals (X-ray, Auger and electron-energy loss spectroscopy) further enable TEM to elucidate information such as: i) coherent intergrowth, ii) atomic structures of micro-porous catalysts, iii) nanoparticle composition and distribution in bifunctional catalyst, iv) mixed metal clusters in mesoporous silicas, and v) structure of mesoporous solids with hybrid organic-inorganic frameworks [63].

Due to the focus problem, exact analysis of mesopore diameter and thickness is very hard if no additional simulation is performed [7]. In addition, TEM characterization only gives localized information instead of average features of samples. There are several reports on the use of TEM to study the hexagonal, cubic and lamellar mesostructures [64-67]. Two important results based on the TEM observations from MCM-41, were given by Alfredsson et al. [64]: i) the shape of pore channel is hexagonal rather than round, and ii) equidistant parallel lines were recorded and proved the coexistence of a lamellar phase with hexagonal phase after removal of surfactant.

However, through detailed studies of tubules in MCM-41 by Chenite et al. [65], it was concluded that the fringes could also arise from a hexagonal array of very long silicate tubules rather than a lamellar phase. This may take place if the 6-fold hexagonal axes of pore channels are perpendicular to the beam direction. Two evidences have been observed to explain their proclamation: i) the observed spacing of fringes (39 Å) is well related to the distance between pore centers (~ 44.3 Å) by the $\sqrt{3}/2$ factor as expected, and ii) with a slight

tilt around the axis of the channels, the fringes disappears, while the honeycomb stacking of channels remains.

In a further study, Schacht et al. [66] constructed a computer model of amorphous silica with a one-dimensional pore system (MCM-41) and hexagonally shaped pores. They concluded that TEM images often not only show hexagonal areas but also other domains. To obtain a clearer understanding, tilt experiment and inspection of large area of sample are usually necessary. Alfredsson et al. [67] generated a computer simulated model of cubic mesoporous silicate MCM-48 based on gyroid minimal surface. They compared the simulation results with the observed TEM images of synthesized samples and showed that structure of MCM-48 indeed fit to the gyroid minimal surface as was previously conjectured by Monnier et al. [17]. All the diffraction patterns obtained from micrographs could be indexed well according to the space group 230 (Ia3d).

BET N₂ gas sorption measurement

Gas adsorption method using N₂ at 77 K is a reliable and convenient technique to measure the specific surface area, pore volume, pore size, and pore size distribution as compared to other approaches such as, Hg porosimetry [68]. Use of Hg porosimetry may lead to the collapse of mesoporous structures [8]. Gas adsorption technique is based on the phenomenon that adsorbate (normally inert gas) molecules are able to condense on the adsorbent due to various interactions (dispersion force and repulsive force, etc) to form monolayer and subsequent multilayer on the external surface. The quantity of the gas (e.g., N₂) being adsorbed at a particular temperature (usually 77 K, which is the temperature giving rise to saturation vapor pressure of liquid N₂) can be used to calculate the surface area, pore volume and pore size distribution of the sample using various models. Fundamental theories

and applications of adsorption technique can be found elsewhere [69]. One basic equation is the BET equation that has been modified by Brunauer and his coworkers [70]. This model assumes that the number of molecular layers of adsorbate is finite (5 or 6) at saturation pressure, even on an open surface. Based on this equation, one can reasonably obtain the structural information of a sample from the BET gas sorption isotherm which relates the amount of adsorbed gas (cc/g or mol/g) to the relative pressure (p/p_0 where p_0 is the saturation vapor pressure of adsorbate gas) during adsorption and desorption processes. In spite of the large variety in the shape, all the isotherms can be classified into 6 groups (Type I to VI), as shown in Fig. 2.9 [71]. The shape of isotherm is determined by many factors such as adsorption and desorption behaviors of gas in the adsorbents, as well as pore geometry. Mesoporous materials usually give Type IV isotherm [72].

MCM-41 materials usually have high porosity (0.7-1.2 cc/g) and large specific surface area (up to 1400 m²/g). Adsorption at very low relative pressure ($p/p_0 < 0.2$) is due to the formation of N₂ monolayer on the external surface of mesopores. As the relative pressure increases (0.2 - 0.5), the amount of adsorbed volume increases sharply due to capillary condensation inside the uniformly distributed mesopores.

The isotherm is usually reversible from material with pore diameter smaller than a critical value, which is theoretically predicted to be ~18 - 32 Å [73-75]. When there are pores with average size greater than 40 Å, normally a hysteresis loop can be found in the isotherm. This is because evaporation pressure of adsorbate during desorption is lower than the relative pressure at which capillary condensation takes place during adsorption. However in practice, the occurrence of the hysteresis loop also depends on the testing environment, e.g., the types of adsorbate [8].

Fig. 2.9 Six types of BET sorption isotherms [71].

Several geometrical and classical methods have been applied to determine the average pore size of M41S materials. One basic model for the transformation of gas sorption data into pore size distribution (PSD) is the Kelvin equation [76]. This approach is widely used but is only accurate when pore diameters are greater than 20 Å, since below this range of pore diameter the adsorbate liquid cannot be considered as a fluid with bulk property.

Other methods have also been developed based on Kelvin equation, including Barrett-Joyner-Halenda (BJH) model, Broekhoff and de Boer (BdB) methods, Horvath-Kawazoe (HK) and Saito-Foley (SF) methods, and density function theory (DFT) [8].

Methods for calculating pore size distribution (PSD) have been developed based on geometrical consideration [69], thermodynamic or a statistical thermodynamic approach [74]. Based on the Kelvin equation, Barrett-Joyner-Halenda (BJH) method was particularly useful for analyzing mesopore size distributions [77]. However, since BJH method is based on thermodynamic consideration, it underestimates the pore diameter by about 10 Å during desorption. In addition, it requires that large desorption of N₂ at 77 K occurs above $p/p_0 = 0.42$, because this is considered to be the stability limit of the meniscus.

The BET model is one of the most widely applied methods for estimating the pore volume. It assumes that the density of the adsorbed N₂ is equal to the density of liquid N₂ at the same temperature. Another method, t-plot (thickness plot) method is often used to obtain accurate and reliable pore volume data if information on porosity is of greater interest. This method is based on the observation that a plot of the adsorbed volume per unit surface area, i.e. the statistical thickness (t) of the adsorbed layer, versus pressure follows a single curve independent of the type of solid. The slope of the straight line is directly proportional to the total surface area. After complete filling of the mesopores, a new straight line with a slope corresponding to the external surface area is observed. Pore volume associates with meso and macropores, if any, can also be deduced by subtracting the total pore volume with that due to microporosity.

2.1.2 Non-siliceous mesoporous materials

Comparing with M41S materials, the diversity in the framework chemistry of non-siliceous mesoporous materials is expected to give more functional applications in catalysis, electronic, optical, and optoelectronic devices. Several review papers on the progress of non-siliceous mesoporous materials have been published [78, 79, 11].

A large number of non-siliceous mesoporous materials (such as oxides or sulfides of Sb, W, Zn, Al, Pb, Fe, Mg, Mn, Co, Ni, Zn, and Ga) are synthesized and their formation are based on the charge density matching mechanism [43, 80, 81]. Mesoporous lamellar structure was usually obtained. In addition, other mesophases were also found for Sb_2O_3 (hexagonal, cubic), WO_3 (hexagonal) and PbO (hexagonal) depending on the synthesis conditions such as pH and metal/surfactant molar ratio. Sayari and Liu [78] suggested that three conditions should be met for the successful synthesis of ordered mesoporous materials: i) inorganic precursors should have the ability to form polyanions or polycations, allowing multidendate binding to the surfactant; ii) polyanions or polycations should be able to condense into rigid walls; iii) a charge density matching between surfactants and inorganic species is necessary to control the formation of a particular phase. However, upon calcination, the synthesized materials lost their mesostructure ordering to different extent due to the collapse of inorganic frameworks. It was argued that for WO_3 , the repeated changes in oxidation state of metal cations led to structural collapse, even if fully condensed inorganic framework was originally formed. Other techniques to remove surfactants have also been exploited, e.g., varying the heating rate and gas flow composition, dissolution of surfactant by organic solvent using reflux method, supercritical fluid extraction, and plasma calcination. However, no obvious improvement on final mesoporous structures was found from any of the above modifications [82].

Alumina is widely used as catalyst and catalyst support in various industrial applications. However, its working performance was limited by the presence of micropores which may cause pore plugging during deactivation by coke formation. Therefore, synthesis of mesoporous alumina with larger pore size and higher porosity is of high demand. Pinnavaia et al. [83, 37] prepared mesoporous alumina with hexagonal-like symmetry using neutral templating method. However, results from SAXS indicate that the pore arrangement was actually disordered. ^{27}Al NMR study showed that the six-coordinated species were mainly inorganic component in the as-prepared materials. After dehydroxylation at 773 K, both four- and five-coordinated centers (i.e., coordination number = 4 or 5) increased at the expense of the six-coordinated species. The presence of five-coordinated aluminum species is especially important as they may prove to be of catalytic significance as Lewis acid sites [78]. Later, Pinnavaia and other co-workers [84, 85] reported a new three-step synthesis process to produce crystalline mesostructured alumina of lath-like $\gamma\text{-Al}_2\text{O}_3$ nanoparticles. In the first step, block copolymer was applied as the structure directing agent and Al_{13} oligocations and hydrated aluminum cations were used as inorganic precursors to form wormhole mesostructure with amorphous inorganic framework. Subsequently, the framework was transformed to a surfactant-boehmite mesophase with a lath-like framework at elevated temperature, and this was then converted to a crystalline $\gamma\text{-Al}_2\text{O}_3$ mesostructured framework at the final thermal reaction. The final products possess high specific surface area (300 - 350 m^2/g) as well as large pore volume (0.45 - 0.75 cc/g).

A systematic study on the preparation of mesoporous alumina was reported by Vaudry et al. [86]. The reaction system contains aluminum alkoxides, long-chain carboxylic acids with controlled amounts of water in the presence of low molecular alcoholic co-solvent. The products possess very large specific surface area (710 m^2/g) and disordered pore

arrangement with average pore size at 20 Å. Deng et al. [87] reported synthesis of alumina with multilevel nanopores using surfactant templated method. The PSD of products showed two peaks located at 40 and 3000 Å, and remained stable upon the removal of surfactant. However, the formation mechanism of macroscale pore structure was not investigated.

Synthesis of oxides of transition metals: vanadium, niobium, molybdenum and tungsten were studied independently by Stein et al. [88]. In the case of WO_3 , UV-visible, IR and chemical analysis showed that the salt contained unconnected Keggin ions $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$. The presence of isolated metal oxide units was revealed by blue shift (decrease of the wavelength) of UV bands relative to those of bulk tungsten trioxide and sodium metatungstate. Spherical cavities were created by puckered layer arrangement of Keggin ions. Dense WO_{3-x} phase was finally obtained after removal of surfactant template during calcination.

The first stable mesoporous TiO_2 was synthesized by Antonelli and Ying [89]. It involved the hydrolysis of organometallic precursors in the presence of surfactant template. Careful control of kinetics of hydrolysis and condensation of inorganic precursors (titanium iso-propoxide) is the key factor to obtain the desired hexagonal mesostructured phase. To permit the hydrolyzed species and surfactant molecules to react sufficiently before condensation, complexing agent such as acetyl acetone was used to slow down the hydrolysis reaction. Among the various surfactants used, only alkylphosphates led to a stable hexagonal phase.

Several studies have been devoted to the synthesis of metal sulfides [90-92]. The only systematic work was reported by Anderson and Newcomer [93] on the preparation of Mo, W, Co, Fe, Zn, Ga, Sn and Sb sulfides. All the final products showed lamellar mesostructure and

consisted of bilayers or interconnected layers of surfactant molecules sandwiched between metal sulfide lamellae [78]. Recently, mesoporous tin (IV) sulfide with a basal spacing of 25.5 Å was obtained using CTAB as template [91, 92]. By using a much lower CTAB concentration, larger d-spacing (39.2 Å) could be obtained. Through aqueous approach, mesoporous CdS templated by hexagonal phase of oligoethylene oxide oleyl ether was prepared by Braun et al. [90]. This approach was the closest available example dominated by Liquid Crystal Templating mechanism, as the nature of mesophase never changed throughout the synthesis [78].

Mesoporous materials can also be synthesized from non-aqueous system. Such approach is especially important for the formation of mesostructured thin films. Stucky et al. [94] prepared non-siliceous materials with large mesopores using Evaporation Induced Self-Assembly (EISA) in a non-aqueous medium. Later, Chemelka and coworkers [95] proposed a generalized synthesis strategy to produce various mesophase (hexagonal, cubic or lamellar) thin films by varying the metal/surfactant volume ratio guided by the surfactant bi-system phase diagram. The formation mechanism of EISA has been systematically studied by Sanchez et al. [96, 97] using neutral surfactant (polyethylene oxide) and transition metal precursors (Y-Zr, Ti, Zr, V, Al, Fe, etc).

Syntheses of non-siliceous mesoporous materials without using any surfactant template were also reported [98, 99]. Instead, preformed inorganic mesoporous material was used as hard template. After loading the desired inorganic species into the mesopore channels, thermal treatment is necessary to cause condensation. This method is particularly important for those materials with low combustion temperature, e.g., carbon, since the removal of hard template can only be done by using dissolution method such as dissolution in HF.

2.1.3 Mesoporous SnO₂

Various mesoporous metal oxides, sulfides and phosphates have been synthesized based on surfactant templating strategy. However, poor thermal stability against calcination limits many of their applications [79]. Amongst many semiconducting metal oxides, SnO₂ is one of the most attractive materials due to its unique optical and electrical properties [100]. Tin (IV) oxide is a wide band gap (3.6 eV), n-type transparent semiconductor with rutile structure. It has found many practical applications, such as, gas sensors [101, 102], electrodes for dye-sensitized solar cells [103, 104], catalysts [105], and electrodes for lithium batteries [106]. Despite different working mechanisms in these applications, porous and microstructural properties such as, large surface area, mesoporosity, small and uniformly distributed crystallites (< 4 nm), and high thermal stability (usually 200 ~ 600 °C) are common essential requirements.

Nanocrystalline SnO₂ can be prepared by a variety of chemical techniques [107] using starting materials such as, tin (IV) chloride (pentahydrate) [108], tin (IV) iso-propoxide [Sn(OiPr)₄•iPrOH] [109], tin (II) citrates [110], and pure metallic tin [107], etc. Among many techniques, sol-gel method is an attractive approach for the synthesis of SnO₂ films, powders and monoliths with various porous structures [111-113] due to low cost and easy processing control. Inspired by the surfactant templating strategy used for MCM-41 [2, 1], several works have been reported on surfactant templated mesoporous SnO₂ materials. Ulagappan et al. [114] prepared the first SnO₂ powders with disordered mesoporous structure using anionic surfactant (Sodium dioctylsulfosuccinate, AOT) as template and SnCl₄ as inorganic source. The as-prepared SnO₂ powders showed disordered mesostructure as revealed by a single peak (100) by SAXS. The average pore size was confirmed to be ca. 30 Å by both TEM and atomic force microscopy images. However, the mesoporous structure collapsed completely

upon calcination at 427 °C which was indicated by the disappearance of low-angle reflection. Continuous investigations applying different types of surfactants (cationic, neutral and block copolymer) and alternative processing methods have also been reported by several other groups [109, 115-120, 94], as listed in Table 2.4. Their results indicate that: i) specific surface area of mesoporous SnO₂ fabricated from cationic surfactant and block copolymer is greater than that of SnO₂ fabricated from neutral surfactant templates, and ii) additional chemical treatment is necessary to improve thermal stability of mesoporous SnO₂. Hyodo et al. [118] treated the as-prepared samples with phosphoric acid, while Wu et al. [119] used hexamethyldisilazane (HMDS) to replace the surface hydroxyl groups of as-prepared SnO₂ powders.

Using neutral dodecylamine as the surfactant, mesoporous tin oxide prepared by Li et al. [120] was stable up to 350 °C with surface area of 325 m²/g. However, the mesoporous structure destroyed completely and the surface area was reduced to 112 m²/g after 400 °C calcination. Poor thermal stability is directly related to the crystal growth during calcination, particularly from 400 - 600 °C. Large loss of surface area (> 50%) and fivefold increase in crystal size (from ~ 20 to 100 Å) have been found elsewhere after annealing of the hydrous SnO₂ gel at 400 °C for 1 hour [121]. At the same time, there was also < 80% reduction in the concentration of surface hydroxyl groups (-OH). Therefore, it is necessary to form a rigid 3-D inorganic frame work of Sn-O-Sn bonds to avoid the collapse of the mesostructure at the removal of templates [116]. This implies that surface hydroxyl groups on freshly prepared SnO₂ particles need to be removed, as they will facilitate SnO₂ crystal growth during calcination through dehydroxylation. Usually, thermal treatment such as aging at elevated temperature can further condense the sol-gel derived inorganic structures.

Besides the low thermal stability of mesoporous SnO_2 , another main problem is its lack of mesostructural ordering. Unlike ordered mesoporous silica, the reported mesoporous SnO_2 in Table 2.4 only possess disordered structure. The reason is probably related to that the rate of hydrolysis and condensation of SnO_2 precursors is too fast to form ordered assembly with surfactant micelles. To obtain thermally stable as well as ordered mesoporous SnO_2 , issues related to both inorganic and organic materials need to be considered. Neutral surfactant is chosen as the template for the present study based on the following considerations. It has been shown that neutral surfactant is able to improve the textural mesoporosity of mesoporous silica, as compared to ionic surfactants [83]. The reason is proposed to be due to the relatively weak hydrogen bonding force between inorganic species and neutral surfactant. It has also been shown that the use of neutral surfactant templates usually results in mesoporous structures with thicker framework walls, and hence improved hydrothermal stability [122]. Furthermore, the expensive neutral surfactant is expected to be recovered in an environmentally benign manner by dissolution in organic solvent under refluxing.

Table 2.4 A list of reported mesoporous tin oxides and their respective key properties.

	Surfactant	Inorganic source	BET surface area (m ² /g)	Average pore size (Å)	Average crystal size (Å)	Calcination temperature (°C)	Ref.
Anionic	Sodium Dodecyl Sulfonate (C ₁₂ S)	SnCl ₄	N/A	ca. 20	20-50	400	[115]
Cationic	CTAB	[Sn(OH) ₆] ₂ ⁻	ca. 143	N/A	N/A	500	[116]
	CTAB	SnCl ₄ (5H ₂ O)	136	39	N/A	400	[117]
	C ₁₆ PyCl	Na ₂ SnO ₃ (3H ₂ O)	305	ca. 16	20	600	[118]
			206	20	33	700	
			270	ca. 30	ca. 28	400	
	CTAB	SnCl ₄	220	ca. 45	ca. 40	500	[119]
Neutral	Tetradecylamine (TDA)	Tin isopropoxide	99	43	44	400	[109]
	TDA	Tin isopropoxide	ca. 107	N/A	N/A	500	[116]
	Dodecylamine	SnCl ₄ (5H ₂ O)	112	N/A	N/A	400	[120]
Block copolymer	Poly(alkylene oxide)	SnCl ₄	180	68	30	400	[94]

2.2 Macroporous silica templated by polypeptides

Currently, an emerging topic in the field is to synthesize silica materials through (biomimetic) templating technique using polypeptides. Polypeptides have a diverse chemistry and hierarchy organization over several length scales [123, 124]. A large number of polypeptides have been investigated as the structure directing agents, and they can be grouped into three categories: i) natural proteins, ii) genetically engineered proteins for inorganics (GEPIs), and iii) synthetic homo/block (co)polypeptides.

A typical example of the natural proteins is the silaffins which are used to nucleate and condense biosilica materials [125-127]. Silaffin-1A(1) and-1A(2) contain covalently modified lysine-lysine elements, and are a set of natural polycationic peptides separated from diatom cell walls (*Cylindrotheca fusiformis*). Under an acidic pH condition, positively charged amino acid groups on these polypeptides are able to catalyze precipitation of silica nanospheres within seconds when mixed with a silicic precursor solution. Proper functionalization of the templates is important to affect the kinetics of the inorganics through surface interactions (ionic charge and hydrogen force). Other examples of natural proteins that have been investigated include, ferritins for inorganic nanoparticles fabrication [128], S-layer protein for patterned ultrathin films [129], and collagen fibers for templating hollow silica tube [130].

Genetically engineered proteins for inorganics (GEPIs) normally refer to the relatively short polypeptides/small proteins of $M_w < 3000$ that can specifically bind to the surface of an inorganic material [131]. Each peptide segment grafted on surface can serve as a molecular erector to link nanoparticles, functional polymers, or other nanostructures on molecular templates. There are still many challenges in the use of suitable techniques for GEPIs selection (called display technology), and this can be tedious and difficult. One technique is to isolate biomineralizing proteins from hard tissues and followed by

purification and the cloning of their genes. Some examples include silicatein in sponge spicular cell formation [132], amelogenins in mammalian enamel fabrication [133], and calcite- and aragonite-forming polypeptides in mollusk shells [134, 135]. Recently, an emerging route is to use combinatorial biological techniques in which a large and random collection of peptides is screened to select those with specific binding property to an inorganic surface of interest. The three most common approaches based on this concept are phage display (PD, a screening technique used to display protein on the surface of a phage as a fusion with one of the coat proteins of the virus), cell surface display (CSD), and ribosome display (RD) [136-141]. Using these techniques, many polypeptides with different amino acid sequences and surface charges have been selected to bind to inorganic materials such as, Au, Pt, Ag, Pd, SiO₂, Cu₂O, ZnO, CaCO₃, Cr₂O₃, Fe₂O₃, GaAs, ZnS, CdSe, ZnSe, and zeolites [131, 142, 143].

Compared to GEPIs, synthetic homo/block (co)polypeptides have relatively simple amino acid sequences but much larger molecular weights between $15,000 < M_w < 70,000$. Due to the great potential applications of proteins in bio/nanomaterials, fabrication of polypeptides with well defined amino acid sequences has attracted great interest since the 1950s [144]. However the final products usually suffer from a wide molecular weight distributions arising from unwanted side reactions, hence leading to the formation of poorly defined structures [145-148]. In 1997, this problem was solved by T. J. Deming [149] who reported a facile route for the synthesis of block copolypeptides using organonickel as initiators to suppress chain-transfer and termination side reactions. The resultant products are characterized by well defined amino acids sequences and low polydispersity (M_w/M_n). Since then, synthetic polypeptides have been used as templates to direct the assembly of inorganic materials (mainly silica). In the following sections, an introduction on the chemical and structural properties of proteins/polypeptides will be briefly described. This will be followed

by a review on the recent development of biomimetic synthesis of silica using synthetic homo/block (co)polypeptides, the challenges and prospects of the field.

2.2.1 Polypeptides structure and chemistry

Synthetic homo/block (co)polypeptides are large molecules composed of one or two different types of amino acids, and they can be considered as a simple model of proteins. A brief introduction of the basic chemical and structural properties of proteins will be given in this section, as by which the assembly behaviors of these molecules are controlled.

Protein is made up of one or more polypeptide molecules which contain a chain of amino acids polymerized through peptide bond ($-C-N-$). In nature, there are 20 different types of amino acids with the general formula $NH_2C_\alpha HRCOOH$. The C_α is the center of amino acid molecule with 4 substituents connected to it, i.e., alpha proton ($-H$), amine group

Fig. 2.10 A list of side chains of 20 amino acids (by permission of Biophysical Society) [150].

(-NH₂), carboxyl group (-COOH), and side chain (-R). Therefore it is the chemical construction of side chains that distinguish the intrinsic chemical, biological and structural properties of each polypeptide molecule. The side chains possess a wide chemical variety and can be non-polar, uncharged polar, and charged polar, as displayed in Fig. 2.10 [150].

Polypeptides with polar side chains are of particular interest for assembly synthesis, since the formal charges on polar groups (e.g. amine and carboxylic groups) can be switched between positive and negative depending on pH and pK_a values. For example, the amine group on lysine side chain $-(CH_2)_4NH_2$ has a pK_a value of $\sim 10.5 - 11$ and can carry a positive charge (NH_3^+) when pH value is below its pK_a [151]. As a result, formation of hybrid materials containing polypeptides and inorganic precursors (usually with charged surface) is possible through ionic/hydrogen forces.

Proteins are characterized by a four-level structural hierarchy organization. The primary structure is known as the linear sequence of amino acids in a polypeptide chain. For homopolypeptide, the primary structure is relatively simple as there is only one type of amino acid in the chain. Secondary structure corresponds to certain conformation of the chain. When polypeptide chain forms through peptide bonds amongst adjacent amino acids, steric restrictions arising from both back bone and side chains lead to the formation of secondary structures, e.g., α -helix and β -strand structures (Fig. 2.11) [152]. Tertiary structure of a protein is intimately related to its secondary structure and results from long range contacts in the chain. A well organized tertiary structure usually has stable and close packed liquid-like oil interior composed of hydrophobic residues contributed from all or most of the secondary structure elements. Quaternary structure is the highest level of protein organization and generally results from cooperation of independent tertiary structures through surface interactions. However, more evidences have shown that there is codependence of quaternary and tertiary structures [153, 154].

Fig. 2.11 Representative diagrams of two conformations of a typical polypeptide chain, (A) α -helix structure, and (B) β -strand structure [152].

Many techniques have been developed to characterize conformations of protein chains (mainly secondary structure). These include IR spectroscopy, X-Ray diffraction, light scattering, UV absorption, optical rotatory dispersion, circular dichroism (DC), hydrogen-exchange method, Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy [155, 156].

Amongst these techniques, the IR spectroscopy plays an important role in analyzing the protein structures with its information from the characteristic bonds. When the proteins fold to form certain secondary structures (i.e., α -helix, β -strand and random coil structures, or a mixture of them), characteristic spectral features from the peptide bond (amide bond involving vibrations of C=O, C-N, and N-H groups) can be used to identify individual folding structure. Three major spectral regions are commonly selected for structural analysis, i.e., amide I, amide II and amide III regions. Usually one needs to combine the information from these three regions to eliminate problems due to peak overlapping and weak signals. Other advantages of IR spectroscopy include high sensitivity, high signal to noise ratio, easy sampling, and low concentration of sample required for analysis.

2.2.2 Polypeptides directed silica

Since the preparation of polypeptides with well-defined structures [149], Stucky et al. [157] were among the first to report ordered silica structures templated by block copolypeptides that mimic the functions of silicatein protein during the process of biological silica formation. The self-assembly behaviors of several block copolypeptides were investigated, as well as their ability to direct shape formation and reaction kinetics of silica. The results illustrated that the presence of water-insoluble (e.g., poly-cysteine and serine) and polycationic domains (e.g., poly-l-lysine) is essential for the successful biomimetic synthesis of silica microspheres. In addition, Stucky et al. have also shown that the oxidation of the poly-L-cysteine side groups influenced the structures of the self-assembled polymer aggregate significantly and hence the final shape of silica. With careful control of synthesis parameters, i.e., cysteine/lysine composition ratio, chemical states of sulphydryl groups on cysteine chain, silica in the form of either spheres or columns could be successfully obtained. Subsequently, many different types of polypeptides have been explored for templating synthesis of other inorganic structures including, silica hollow spheres with/without quantum dots of Au, Ag, AgBr, CdSe, and CdSe/CdS [158-162], novel silica morphology (spherical, hexagonal, fiber-like, petal-like) [163-165], and porous silica [166].

Adopting a similar but modified method, Stucky et al. [158] further modified the methodology and reported assembly of nanoparticles into hollow spheres of micrometer size with composite shells (Au/Ag-SiO₂) using block copolypeptides (Lys_xCys_y). It was demonstrated that the reaction sequence of the inorganic precursors with template solution was critical for the successful assembly of sphere composites. Hollow spheres formed only when Lys_xCys_y (Lysine-b-Cysteine) is pre-reacted with gold nanoparticles before reacting with SiO₂ precursors. In the first step, Au can specifically bind to the cysteine chains through interaction with sulfide and disulfide groups, and round aggregated Au nanoparticles were

obtained. Subsequently, negatively charged SiO_2 particles interacted with the lysine parts (NH_3^+) through ionic/hydrogen forces and stabilized the obtained hybrids. Several working parameters have been identified to affect the size of obtained hollow spheres, i.e., chain length of lysine domain, template concentration, and inorganic particles/template ratios.

Replacing inorganic nanoparticles with citrate stabilized CdSe/CdS quantum dots (QDs), resonators with microcavity lasing property have also been fabricated using block copolypeptides [159]. Citrate ions grafted to the inorganic QDs are important for the interaction between inorganics and organic templates. The obtained microspheres proved excellent optical confinement by coupling the electronic states of CdSe/CdS nanoparticles to the photonic states of the microcavity. Later, citrate stabilized quantum dots were further applied to assembly with homopolypeptide to form QDs vesicles [160]. These vesicles can be subsequently coated with silica to form stable microspheres with multishells. To verify the hypothesis that the citrate ions act as “linkers” to connect polypeptide templates with QDs, assembly was performed under different pH values. Results showed that only when the citrate ligand and polypeptide side chains have opposite charges, can the vesicles be formed. Therefore the assembly process is dependent on the surface charges of reactants, and particularly related to the deprotonation of C3 carboxylic acid of citric acid and protonation of side chains of poly-L-lysine.

The first synthesis of silica hollow spheres templated by homopolypeptides without the use of other inorganic species (e.g., Au, Ag) was reported by Stucky et al. [161]. In their work, the authors prepared spherical homopolypeptides aggregates co-assembled with multidendate counter ion molecules (e.g., citric acid) prior to mixing with a silica source. They concluded that the number of formal charges on counter ion molecules as well as pH value were the key factors for obtaining pre-stabilized polyelectrolyte spheres. The size of spheres was strongly dependent on polypeptide/stabilizer ratio. Coating of silica shell on

templates was then accomplished by the ionic/hydrogen forces between silica precursors and polypeptides side chains.

Besides hollow spheres, polypeptides were also able to direct the formation of silica particles with other morphologies, including hexagon, plate-, petal-, and fiber-like particles [163-165]. Furthermore, Shantz et al. [166] have demonstrated the ability of poly-L-lysine to control the micropore architectures of silica. When the α -helix structure of poly-L-lysine was used as template, highly porous silica with cylindrical pores of ~ 15 Å was fabricated. Larger pores (~ 20 Å) were obtained when the poly-L-lysine possessed β -strand conformation. In both cases, the pore sizes were dependent on the concentration of template used. As such it is possible for the secondary structures of polypeptides to direct the porosity as well as the pore sizes of silica material.

There is great potential to use synthetic polypeptides for templating novel inorganic structures at mild conditions. However, little study has yet been reported on metal oxide systems, although they are more technically important. Comparing with silicates, synthesis of stable metal oxide sols is more difficult because of the lower electronegativity of metals and variation of their coordination states (e.g., transition metals) [167]. Fast hydrolysis and condensation of oxide precursors may hinder effective and uniform self-assembly of inorganic particles. Organic substances (e.g., alcohol) derived in situ from hydrolysis of metal alkoxides may also destroy polypeptides conformations and hence limit the choice of proper oxide precursors. Therefore, it is highly appealing to investigate the systems containing metal oxide precursors and polypeptides, and to establish a facile and general self-assembly route.

2.3 Conclusion

In this chapter, the background of surfactant templated mesoporous materials and polypeptides templated macroporous materials have been provided. The discussed topics include basic chemistries of templates and inorganic materials, structural properties, structure formation mechanisms, commonly applied characterization techniques, as well as the currently facing challenges.

SnO_2 is selected as the study material for the present work. Synthesis of both mesoporous and macroporous SnO_2 through assembly pathway is limited by its poor thermal stability and fast reaction kinetics which usually result in low surface area, small pore volume, wide pore size distribution, large crystallite size, and poor porous structural ordering. To improve the thermal stability of SnO_2 , thermal treatment such as aging and hydrothermal processing are possible ways because more rigid frameworks can be expected. Moreover, it is also expected that the use of silica as impurity dopant is able to further enhance the thermal stability of SnO_2 by hindering SnO_2 crystal growth.

Synthesis of polypeptide templated macroporous SnO_2 has not been reported yet. The reason is probably due to fast reaction rate of SnO_2 which prevents uniform interaction with the template. Therefore, preparation of well-dispersed SnO_2 particles is essential in obtaining successful self-assembly. To controlling the reaction rate of SnO_2 , complexing agent such as citric acid may be used. It is expected that the citrate ligands grafted onto SnO_2 particles is able to reduce the condensation rate and prevent severe agglomerations.

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Chapter 3

Experimental

Chapter 3 Experimental

This chapter describes experimental details of the work, including raw materials, synthesis procedures, characterization methods and gas sensing property measurement. The synthesis consists of three parts: 1) surfactant templated mesoporous SnO_2 , 2) surfactant templated mesoporous $\text{SnO}_2\text{-SiO}_2$ composites, and 3) poly-l-lysine templated macroporous and mesoporous SnO_2 .

3.1 Raw materials

3.1.1 Surfactant templated mesoporous SnO_2 & $\text{SnO}_2\text{-SiO}_2$

Tin tetrachloride (SnCl_4 , 99.0%) and 28% ammonium hydroxide solution (NH_4OH , 99.99%) were purchased from Sigma-Aldrich. Neutral surfactant, tetradecylamine with 14-carbon hydrophobic chain (TDA, $\text{C}_{14}\text{H}_{31}\text{N}$, 98.5%) was selected as structure directing agent and was obtained from Sigma-Aldrich. Iso-propanol ($\text{C}_3\text{H}_7\text{OH}$, AR grade) was used as co-solvent and homogenizing agent for surfactant solution preparation. Deionized water was used to prepare aqueous solution in all instances. Silver nitrate (AgNO_3) was applied to test any residual chlorine ions left in waste solution after sample collection by centrifugation. Tetraethylorthosilicate (or TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, $\geq 99.0\%$) was obtained from Fluka and was used as silica source. All the chemicals were used as received.

3.1.2 Poly-l-lysine (PLL) templated macroporous and mesoporous SnO_2

All the chemicals employed in this experiment were purchased from Sigma-Aldrich, and were used as received without further purification. Poly-l-lysine ($M_w > 30 \text{ kD}$) was used as template and stored at -20°C . Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was selected as the complexing agent.

De-ionized water and ammonia solution (≤ 14 wt. %) were always used as solvent and pH adjusting agent, respectively. Tin (IV) tetrachloride (99%) was applied as SnO_2 source material.

3.2 Synthesis of mesoporous SnO_2

3.2.1 Preparation of SnO_2 /surfactant composites

The surfactant solution was prepared by mixing 1.28 g of Tetradecylamine (TDA) with 65 ml of iso-propanol and 160 ml of deionized water. Here, iso-propanol was primarily applied to improve surfactant solubility. The mixture was stirred at ambient temperature until a semi-transparent and homogenized solution was obtained. In order to maintain the TDA/Sn molar ratio at 0.3 in the final mixture, 200 ml of 0.1 M SnCl_4 sol solution was prepared by mixing SnCl_4 (5.21 g) with deionized water at room temperature. Diluted ammonium hydroxide solution of 14 wt.% concentration was added into SnCl_4 solution dropwise to cause precipitation, and the pH value was finally adjusted to 9.8. During pH adjustment, white precipitates occurred at pH value of ~ 1.8 suggesting the formation of agglomerated SnO_x or tin hydroxide particles. SnCl_4 sol solution became gelatinous when pH value was increased to ~ 4 due to continuous polymerization of precursors. Further addition of NH_4OH reduced the solution viscosity and solution was still turbid when the final pH value was reached. SnO_2 sol solution was subsequently added into the previously prepared surfactant solution with strong agitation, and the mixture was allowed to react at room temperature for 4 hrs.

3.2.2 Aging and hydrothermal treatments

Aging was performed in an autoclave glass bottle at 75 °C for 5 different durations, i.e., 1 d (day), 2 d, 3 d, 5 d, and 12 d. No stirring was applied during aging. After the desired periods, the white precipitates in the samples were separated and collected by centrifugation. The obtained white precipitates were washed repeatedly using deionized water and iso-propanol to remove any residual Cl^- ion and surfactant. Washing was stopped until no precipitate was observed when the waste solution was tested by AgNO_3 . The resulted wet precipitates were dried using filter paper and subsequently transferred to an oven at ~ 80 °C for overnight. The thermally aged samples were designated as T_x , where “x” refers to the aging period (in day). Table 3.1 lists the T_x samples prepared in this study.

Table 3.1 A List of T_x samples under various working conditions

Sample group	Aging duration (day)	Calcination temperature (°C)
T_1	1	no calcination
	1	400
	1	500
T_2	2	no calcination
	2	400
	2	500
T_3	3	no calcination
	3	400
	3	500
T_5	5	no calcination
	5	400
	5	500
T_{12}	12	no calcination
	12	400
	12	500

Hydrothermal treatment (HT) was conducted by loading part of the dried powders into a Teflon-lined tube containing 20 ml of deionized water inside a steel autoclave. All the T_x samples were hydrothermally treated at 120 °C for 24 hrs. To study the effects of HT temperature on materials structures, sample with aging time of 2 d was treated at three different temperatures, i.e., 120 °C (vapor pressure, $P = 1492$ mmHg), 150 °C ($P = 3594$ mmHg), and 200 °C ($P = 11855$ mmHg). After HT, all the samples were collected by centrifugation and dried in an oven at 80 °C overnight. The hydrothermally treated samples were designated as $T_{x/y}$, where “x” and “y” refer to the aging period (in day) and HT temperature (in °C), respectively. Table 3.2 shows the $T_{x/y}$ samples prepared in this study.

Table 3.2 A List of $T_{x/y}$ samples under various working conditions

Sample group	Aging duration (day)	HT temperature (°C)	Calcination temperature (°C)
$T_{1/120}$	1	120	no calcination
	1	120	400
	1	120	500
$T_{2/120}$	2	120	no calcination
	2	120	400
	2	120	500
$T_{2/150}$	2	150	no calcination
	2	150	400
$T_{2/200}$	2	200	no calcination
	2	200	400
$T_{3/120}$	3	120	no calcination
	3	120	400
	3	120	500
$T_{5/120}$	5	120	no calcination
	5	120	400
	5	120	500
$T_{12/120}$	12	120	no calcination
	12	120	400
	12	120	500

3.2.3 Removal of template

The surfactant was removed by calcinating the samples in a furnace with air flow. The calcination procedure is schematically illustrated in Fig. 3.1. To study the effects of calcination temperature on structural change, samples which were aged and hydrothermally treated were calcined at two different temperatures, i.e., 400 °C and 500 °C. During calcination, the temperature was firstly increased to 120 °C and held for 30 minutes, and then increased to 320 °C and held for another 30 minutes. Finally, samples were calcined at targeted temperatures for 3 hrs. Heating rate used in all the calcination was 2 °C/min.

Fig. 3.1 Calcination procedure for surfactant templated mesoporous SnO₂. The samples were calcined at 400 °C and 500 °C.

For the purpose of comparison, pure SnO₂ without the use of surfactant template was prepared in a similar way as described in section 3.2.2. This sample was aged at 75 °C for 3 d, but no HT was performed. Finally, the sample was calcined at 400 °C using the same procedure as described for T_x samples. This sample was designated as sample R.

3.3 Synthesis of mesoporous SnO₂-SiO₂ composites

3.3.1 Synthesis of C_x samples

The surfactant solution for synthesis of SnO₂-SiO₂ composites was prepared in a similar way as described for SnO₂ (section 3.2.1). To study the effects of surfactant concentration on materials structural properties, various TDA/Sn molar ratios from 0 to 0.7 were selected. For simplicity, the samples are designated as C_x, where *x* represents the TDA/Sn molar ratio with values of 0, 0.1, 0.3 and 0.7. Silicon to tin molar ratio for C_x samples was fixed at 0.25.

Tin oxyhydroxide precursor solution with 0.1 M concentration was prepared by mixing 3.9075 g of SnCl₄ with 150 ml deionized water at room temperature. The pH value of the solution was slowly adjusted (4 - 6 drops every minute) to ~ 6 - 7 using diluted ammonia solution (14%). White precipitates were observed during pH adjustment. 0.78 g of TEOS (Si/Sn molar ratio = 0.25) was then slowly introduced into the prepared sol solution (precursor solution) with vigorous stirring. The sol mixture was allowed to react at room temperature for ~ 30 minutes. Subsequently, the pH value of the mixture was gradually adjusted to ~ 10.8 to initiate alkaline catalyzed condensation of both SnO₂ and SiO₂.

TDA of different weights were dissolved by 120 ml of deionized water and 45 ml of iso-propanol at ambient temperature, so that the final TDA/Sn molar ratio varies from 0 to 0.7. After stabilization by magnetic agitation, a semi-transparent solution was obtained. The inorganic sol mixture was then slowly added into the surfactant solution with stirring. Within a short period upon mixing, white precipitates were formed. This was allowed to further react at room temperature for 4 hrs. The solution was aged at 75 – 80 °C for 24 hrs. After aging, the precipitates were filtered and washed repeatedly with distilled water and iso-propanol to remove any adsorbed surfactants and Cl⁻ ions. The removal of the residual Cl⁻ ions was

considered almost complete by testing the waste solution with AgNO_3 which yields no precipitate. The filtered samples were dried in an oven at $\sim 80^\circ\text{C}$.

The residual surfactants were subsequently removed by stepwise calcination under airflow, as illustrated in Fig. 3.2. The temperature was firstly increased to 120°C and held for 30 minutes, and then increased to 320°C and held for another 30 minutes. Two final temperatures were selected in order to study the effects of calcination temperature on structural change (i.e., 400°C and 600°C). The calcination period at each final temperature was 3 hrs. The heating rate used in the whole experiment was $2^\circ\text{C}/\text{min}$. To study the structural changes of samples after calcination for long period or at high temperature, as-prepared $C_{0.3}$ was calcined for a period of 55 hrs at 400°C and at a higher temperature of 800°C for 3 hrs, separately.

Fig. 3.2 Calcination procedure for surfactant templated mesoporous $\text{SnO}_2\text{-SiO}_2$ composite. The samples were calcined at 400°C and 600°C .

3.3.2 Effects of Si/Sn molar ratio

A series of S_y samples was synthesized to investigate the effects of SiO_2 concentration on SnO_2 crystal size, surface area and pore volume, where y is Si/Sn molar ratio. The synthesis procedure of the S_y samples was the same as that used for $C_{0.3}$. The Si/Sn molar ratio was selected as 0.25, 0.06 and 0 while keeping TDA/Sn ratio at 0.3.

3.4 Synthesis of macroporous and mesoporous SnO_2

3.4.1 Synthesis of chelated SnO_2 sols

In a typical procedure, 0.7851 g of SnCl_4 was added into 30 ml of deionized water at room temperature with stirring. Citric acid used as a chelator to stabilize the SnO_x precipitates, was added into the sol solution at different amount to vary the citric/Sn molar ratio (r_M) from 0 to 4.5. The pH of the mixture was adjusted from 7 to 11 by slow addition of diluted NH_4OH solution at ambient temperature. The freshly prepared SnO_2 sol solution was used immediately upon the pH adjustment.

3.4.2 Synthesis of hierarchical porous structures

Solution of the pre-stabilized poly-L-lysine (PLL) by citric acid was prepared as described elsewhere [1]. In a typical procedure, desired amounts of poly-L-lysine (6 wt.%) and citric acid (5 wt.%) were dissolved into deionized water at room temperature with stirring. Subsequently, diluted ammonium solution (14 wt. %) was used to adjust the pH of PLL/citric solution to ~ 7 . The solution turned from clear to turbid after pH adjustment. The SnCl_4 solution containing citric acid was mixed with PLL/citric solution at ambient temperature with constant agitation. The volume ratio (r_V) of sols/PLL solutions was varied from 5% to 100%. After reaction of up to 2 weeks, samples were obtained by centrifugation at a rotating speed of 3500 rpm, and subsequently dried at 40 - 60 °C in an oven. The organic

substances were removed by calcination with temperature profile shown in Fig. 3.3. The temperature was raised to 80, 120, 170, and 300 °C sequentially and held at the respective temperature for 0.5 hr with air flow and finally to 450 °C for 2 hrs. The ramp rate was 1 °C/min and the sample was furnace cooled to the room temperature.

Fig. 3.3 Calcination procedure for polypeptide templated macroporous and mesoporous SnO_2 . The samples were calcined at 450 °C.

3.5 Structure and chemical analyses

3.5.1 Thermogravimetric analysis

The weight loss of as-prepared samples upon heating, were measured in a Thermogravimetric Analyzer (2950 TGA HR, V5.4A) at 5 °C/min heating rate in an airflow rate of 50 mL/min. The final temperature was selected from 400 °C to 600 °C. All the selected samples were dried at ~ 60 °C overnight in an oven prior to TG analysis.

3.5.2 Microstructure analysis

Microstructures of all the samples were characterized by X-ray diffraction (XRD) analysis on a Shimadzu 6000 diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Mesoscale

structure was studied by Small-Angle X-ray Scattering (SAXS, Bruker Nanostar) with Cu K α radiation. The average crystal dimension (D) of SnO₂ was calculated using the Scherrer equation assuming that the line broadening is mainly due to the size effect, i.e., $D = \frac{\lambda \cdot K}{B \cdot \cos\theta}$, where λ is the wavelength of Cu K α X-ray, K is a constant (0.94), B is the Full Width at Half Maximum (FWHM) in radian, and θ corresponds to the half of the peak position. High-Resolution Transmission Electron Microscopy characterizations were performed on a JEM-2010 (JEOL) microscope, operating at 200 kV. For calcined samples, they were ultrasonically dispersed in absolute ethanol. In the case of uncalcined samples, they were directly transferred onto the sample holder. In some cases, sample morphology was investigated using a Field Emission Scanning Electron Microscopy (JEOL JSM-6340F) equipped with EDX at working voltages of 5 or 15 kV.

3.5.3 N₂ gas sorption measurement

Porous structural features (i.e., specific surface area (S_A), specific pore volume (S_V), pore size and pore size distribution) of samples were measured using N₂ gas sorption method. The Brunauer-Emmett-Teller (BET) isotherms were measured at temperature of 77 K for relative pressures from 0.05 to 0.995 using ASAP2000 adsorption apparatus from Micromeritics. BJH model was used to obtain the pore size distribution of all samples. The data for BJH analysis is taken from the desorption branch of the BET isotherm. Samples were degassed under vacuum at 110 °C overnight prior to analysis. Alpha-S (α_S) method is used to further analyze mesostructural properties of selected samples. Alpha-S is defined as $\alpha_S = a_{\text{sample}}(x) / a_{\text{std}}(x = 0.4)$, where a_{sample} is the amount of the gas adsorbed in the tested sample at relative pressure of $P/P_0 = x$, while $a_{\text{std}}(x = 0.4)$ is the amount of the gas adsorbed

in the reference sample at relative pressure of $P/P_0 = 0.4$. The value of a_{std} is obtained from BET instrument supplier.

3.5.4 FTIR analysis

Chemical information of the synthesized samples was elucidated from FTIR spectra with a Perkin Elmer GX spectrometer. The sample powders were mixed with dried KBr and pressed into pellets. For each run, 20 scans between 2000 and 400 cm^{-1} at a resolution of 1 cm^{-1} were recorded. All the samples were dried at $\sim 60^\circ\text{C}$ in an oven overnight prior to FTIR analysis

3.6 Gas sensing measurement

Gas sensing properties of selected SnO_2 samples templated by poly-l-lysine were measured with respect to H_2 , CO , and CH_4 . Fig. 3.4 shows a schematic diagram of SnO_2 gas sensor fabricated in the present study for gas sensing measurement. First, the top surface of an alumina substrate (1.5 cm x 1.5 cm) was sputter printed with Pt electrodes at room temperature and then baked at 100°C for 20 min. Next, a layer of SnO_2 paste (by mixing SnO_2 powder with 10 wt.% polyvinyl alcohol solution) of thickness $\sim 500\ \mu\text{m}$ was painted onto the Pt printed substrate surface. In order to remove the polyvinyl alcohol and stabilize the SnO_2 structure, the sensors were heat treated in air at 400°C for 5 hrs. The gas-sensing properties were examined in a chamber in which the testing gas or air was allowed to flow at a controlled rate. The optimum working temperature of the sensor for H_2 gas was first determined by varying the temperature from 150 to 400°C in 50°C step at gas concentration of 500 ppm. Next, the concentration response transients to three different reducing gases (i.e.,

H₂, CO and CH₄) were measured at concentrations from 50 ppm to 3000 ppm at the optimum working temperature for H₂ gas. The gas sensitivity k was defined as the ratio of electrical resistance in air (R_{air}) to that in testing gas (R_{gas}), i.e., $k = R_{\text{air}} / R_{\text{gas}}$.

Fig. 3.4 A schematic diagram of SnO₂ gas sensor fabricated for gas sensing measurement.

References.

- [1] B. J. McKenna, H. Birkedal, M. H. Bartl, T. J. Deming & G. D. Stucky, *Micrometer-sized spherical assemblies of polypeptides and small molecules by acid-base chemistry*, *Angewandte Chemie-International Edition*, 43 (2004), pp. 5652-5655.

Chapter 4

Surfactant Templated Mesoporous SnO₂

Chapter 4 Surfactant Templated Mesoporous SnO₂

4.1 Introduction

As discussed in the literature review (section 2.1.3), one of the main challenges facing mesoporous SnO₂ is its poor thermal stability which leads to substantial decrease of surface area and pore volume during the removal of the templates. The poor thermal stability is mainly a result of in situ crystal growth of SnO₂ during calcination process, particularly from 400 - 600 °C. It has been previously shown that annealing hydrous SnO₂ gel at 400 °C for 1 hr led to fivefold increase in crystal size (from ~ 20 Å to 100 Å) and > 50% loss of surface area. Meanwhile, there was also $\leq$ 80% reduction in surface hydroxyl group (-OH) concentration [1].

Therefore, elimination of surface hydroxyl groups and fabrication of dense SnO₂ nanoparticles are likely able to stabilize the mesoporous structure against calcination. In sol-gel process, thermal treatment (such as aging or hydrothermal treatment) is commonly applied to promote condensation reaction leading to elimination of surface hydroxyl groups. Furthermore, dissolution and reprecipitation during thermal treatment can produce sol particles with narrow size distribution. It has been suggested that less crystal growth of SnO₂ was observed when sample with narrow size distribution was calcined at elevated temperature [2, 3]. Instead of using ionic surfactant, neutral surfactant was chosen as the template to form mesoporous SnO₂. It has been reported that the use of neutral surfactant usually generates mesoporous structures with thicker framework walls, and therefore higher thermal stability can be expected [4].

This chapter examines the synthesis of mesoporous SnO₂ templated with neutral surfactant (tetradecylamine) and investigates the effects of aging and hydrothermal treatment

on microstructure, mesostructure and thermal stability of mesoporous SnO_2 . Characterization techniques including thermogravimetric analysis (TGA), wide/small-angle X-ray scattering, BET gas sorption, and Transmission Electron Microscopy (TEM) have been applied to study the structural evolution and formation mechanisms.

4.2 Thermogravimetric analysis

TGA curves of as-prepared R and T_x samples are shown in Fig. 4.1. Clearly, the weight losses of T_x samples (30 – 40 wt.%) are much larger than that of sample R (~ 12 wt.%). For all the samples, weight reductions below ~ 120 °C can be attributed to the evaporation of moisture physically adsorbed on the surface of the samples. In the case of sample R, this is primarily due to water evaporation and subsequent weight loss from 120 °C

Fig. 4.1 TG analysis of as-prepared samples without HT (hydrothermal treatment): (a) R, (b) T_1 , (c) T_2 , (d) T_3 , (e) T_5 , and (f) T_{12} .

to 600 °C could be due to the dehydroxylation and desorption of chemical species (e.g., -OH and CO₂) on sample surface [5]. In contrast, the major weight loss of T_x samples commenced after ~ 120 °C and proceeds in two major steps. Weight reduction in the first step (120 °C – 280 °C) was mainly due to the continuous decomposition of surfactant template and then followed by the removal of carbon residues in the second step (up to ~ 420 °C) [6]. Further increase in temperature leads to little weight variation, suggesting the complete removal of organic template. Therefore, it can be concluded that the surfactant templates have been successfully incorporated into the as-prepared composite materials and calcination temperature ≥ 400 °C is sufficient to remove surfactants completely. The observed difference in total weight losses between T_x samples may be due to different amount of physically adsorbed surfactant on the surface of samples.

4.3 XRD study on microstructure

The XRD patterns for all the samples are shown in Fig. 4.2 – 4.7. The patterns of the labeled peaks match well with SnO₂ cassiterite of tetragonal rutile phase [7]. A broad Full-Width at Half Maximum (FWHM) of (110) peak for all as-prepared sample suggests the presence of small tin oxide nanocrystallites (Fig. 4.2 & 4.3). Upon the removal of templates, the FWHMs reduced and a few minor peaks of SnO₂ evolved (Fig. 4.4-f) as a result of crystallization during calcination (Fig. 4.4 – 4.7). In all the cases, no obvious peak due to other phase was observed, indicating that relatively pure SnO₂ phase of good stoichiometry was obtained.

Fig. 4.2 Wide angle X-Ray diffraction plots of as-prepared samples aged at 75 °C without HT, (a) T₁, (b) T₂, (c) T₃, (d) T₅, (e) T₁₂, and (f) R.

Fig. 4.3 X-Ray diffraction plots of as-prepared samples with HT at 120 °C, (a) T_{1/120}, (b) T_{2/120}, (c) T_{3/120}, (d) T_{5/120}, and (e) T_{12/120}.

Fig. 4.4 X-Ray diffraction plots of samples without HT and calcined at 400°C, (a) T₁, (b) T₂, (c) T₃, (d) T₅, (e) T₁₂, and (f) R.

Fig. 4.5 X-Ray diffraction plots of samples with HT at 120 °C and calcined at 400°C, (a) T_{1/120}, (b) T_{2/120}, (c) T_{3/120}, (d) T_{5/120}, and (e) T_{12/120}.

Fig. 4.6 X-Ray diffraction plots of samples without HT and calcined at 500°C, (a) T_1 , (b) T_2 , (c) T_3 , (d) T_5 , and (e) T_{12} .

Fig. 4.7 X-Ray diffraction plots of samples with HT at 120 °C and calcined at 500°C, (a) $T_{1/120}$, (b) $T_{2/120}$, (c) $T_{3/120}$, (d) $T_{5/120}$, and (e) $T_{12/120}$.

To study the effects of aging and hydrothermal treatment (HT) on microstructure change, the crystallite size of the sample (along 110 and 211 directions) is calculated using Scherrer equation (section 3.5.2), assuming that line broadening was primarily due to the size of the crystal. The crystallite sizes of the as-prepared and calcined samples are compared in Fig. 4.8. The effects of aging periods and HT on crystal growth are clearly manifested by studying these plots, and four major findings can be obtained. Firstly, all the as-prepared

Fig. 4.8 Crystal size vs. aging time plots of samples T_x , $T_{x/y}$, and R.

samples without HT have crystal sizes in the range ~ 20 Å. With HT at 120 °C, the crystal size of as-prepared samples only increased slightly to ~ 21 Å to ~ 26 Å. Secondly, the degree of crystal growth upon calcination reduces as the aging period increases. For example, as the aging time was increased from 1 to 12 days, crystal sizes of samples with HT decreased from 56 Å to 33 Å and from 75 Å to 36 Å after calcination at 400 °C and 500 °C, respectively. A

similar trend was observed for those samples without HT. Although the crystal size of T_5 is slightly larger than that of T_3 (hollow squares), this was probably due to unexpected processing deviation since sol-gel produced material property is very sensitive to the synthesis condition (e.g., pH and temperature). Thirdly, the crystal sizes of samples with HT are always smaller than that of those without HT. The difference can be up to 14 Å in the case of T_2 calcined at 500 °C. Lastly, the effect of HT on the final crystal size is insignificant when the aging time is sufficiently long. Compare the crystallite sizes of sample R and T_3 , it is noted that sample T_3 has a smaller crystallite size in both as-prepared and calcined states. This could be due to the presence of surfactants in sample T_3 which helps to impede the crystal growth, although the effect is not as significant as that from aging period.

Sol-gel process is complicated and in most cases hydrolysis and condensation take place simultaneously. Freshly prepared precursors or particles with broad size distribution are usually obtained. According to the basic sol-gel theory, dissolution of small particles and subsequent reprecipitation on relatively large particles can take place during aging or hydrothermal treatment as a result of difference in particle solubility [8]. Smaller particles can dissolve much easier than bigger particles. To dissolve larger particles, higher aging temperature may be required. This so called Ostwald ripening which usually leads to the formation of powders with uniform particle size. In addition, the driving force of the crystal growth is determined by the difference between chemical potential of the largest and that of the smallest particles [3]. Therefore, crystals of the system with narrower particle size distribution can grow much slowly than that with broad distribution. As a result, it is reasonable to expect that crystal size distribution is narrower for the sample with longer aging time. Despite that there is no direct experimental result showing that sample with longer aging time produces narrower crystal size distribution, due to difficulty in

distinguishing the boundary of SnO₂ particles and surfactant molecules in TEM image. This conclusion is consistent with that reported by Fujihara et al. [2] who showed that aging (100 – 200 °C) is able to improve the SnO₂ particle size uniformity and is responsible for the observed smaller particle size upon calcination. In the reference work, the crystal size increased to 51 Å when the sample was hydrothermally treated at 100 °C from 24 hrs – 72 hrs. This value is ~ 15 Å larger than that of sample T_{12/120} calcined at the same temperature in the present work. The reason of larger crystal size is probably because of the larger contact area between SnO₂ crystallites, since no surfactant was used in the work reported by Fujihara et al.

Hydrothermal treatment at 120 °C increases the average crystal size of the as-prepared samples marginally (Fig. 4.8) by promoting condensation through the elimination of surface hydroxyl groups. This resulted in smaller crystals of calcined samples as compared to those without HT. However, further increase in HT temperature may not necessarily bring forth more reduction in crystal size against calcination. The effects of HT temperature on microstructure will be presented and discussed later in this chapter.

4.4 Mesostructure study by small-angle X-ray scattering

4.4.1 No calcination

Disordered or ordered mesostructure can be easily detected by small-angle X-Ray scattering (SAXS), since one or more reflection peaks can be observed at low angle positions [9]. Here, disordered mesostructure means that the distances (d-spacing) between adjacent organic parts/mesopores are close and comparable. As shown in Fig. 4.9 a – e, the SAXS patterns of as-prepared T_x samples give single reflections suggesting the formation of disordered mesophase containing inorganic crystals and organic templates [10, 11]. In

contrast, disordered mesostructure was not formed in sample R where the template was absent, as revealed by the disappearance of X-Ray reflection signal (Fig. 4.9-f). This result shows that the use of surfactant is essentially important in creating well defined disordered mesostructure. This is also consistent with the previous TG analysis that surfactants have been successfully incorporated into the as-prepared materials.

When HT was applied, it can be observed that peak positions of all the as-prepared T samples shifted to a lower 2θ position (Fig. 4.10), suggesting the enlargement of d-spacing. In mesoporous materials, d-spacing is the sum of the average pore diameter and inorganic wall thickness. During calcination, SnO_2 crystal growth leads to increased inorganic framework wall thickness and therefore increased d-spacing. Crystal growth in T samples upon HT has been previously demonstrated by XRD results (Fig. 4.8).

Fig. 4.9 Small-angle X-Ray scattering plots of as-prepared samples without HT, (a) T₁, (b) T₂, (c) T₃, (d) T₅, (e) T₁₂, and (f) R.

Fig. 4.10 Small-angle X-Ray scattering plots of as-prepared samples with HT at 120 °C, (a) T_{1/120}, (b) T_{2/120}, (c) T_{3/120}, (d) T_{5/120}, and (e) T_{12/120}.

4.4.2 After calcination

Upon calcination at 400 °C, disordered mesoporous structures were obtained for all T samples without and with HT as suggested by the single reflection peaks (Fig. 4.11 and 4.12, respectively). In addition, peak widths broadened and shifted to lower 2θ positions, which were again related to the crystal growth during calcination. Disordered mesoporous structure was not obtained in the calcined R sample, since no reflection peak was observed (Fig. 4.11-f).

Fig. 4.11 Small-angle X-Ray scattering plots of samples without HT and calcined at 400°C, (a) T₁, (b) T₂, (c) T₃, (d) T₅, (e) T₁₂, and (f) R (without using template).

Fig. 4.12 Small-angle X-Ray scattering plots of samples with HT 120 °C and calcined at 400°C, (a) T_{1/120}, (b) T_{2/120}, (c) T_{3/120}, (d) T_{5/120}, and (e) T_{12/120}.

When the calcination temperature was increased to 500 °C, disordered mesoporous structures in the T_x samples were destroyed since no reflection peak was observed (as shown in Fig. 4.13 for selected samples). This was mainly due to large or non-uniform grain growth during calcination which causes the formation of poorly defined porous structure.

Fig. 4.13 Small-angle X-Ray scattering plots of (a) T₁ and (b) T₁₂ without HT and calcined at 500 °C.

Although disordered mesostructure was not found in all the T samples calcined at 500 °C and R sample calcined at 400 °C, relatively small amount of mesopores were still detected in these samples by BET gas sorption results which will be discussed in section 4.5. The effects of aging time on structural stability (e.g., surface area and pore volume) will also be discussed based on the BET study.

4.5 Mesostructure study by N₂ gas sorption

4.5.1 BET isotherms and α -S study

In the present work, N₂ gas sorption technique was employed to determine the type of porous structure, specific surface area (m²/g), pore volume (cc/g) and pore size distribution

of the calcined samples. BET gas sorption isotherms of calcined T series samples after various aging periods without and with HT are shown in Fig. 4.14 and 4.15, respectively.

Fig. 4.14a BET N₂ gas sorption isotherms of T₁ calcined at 400 and 500 °C. P is the pressure of N₂ gas in the measuring cylinder and P₀ being the saturation vapor pressure of N₂ gas at its boiling point. The unit of ordinate represents gas volume at standard temperature and pressure (stp).

Fig. 4.14b BET N₂ gas sorption isotherms of T₂ calcined at 400 and 500 °C.

Fig. 4.14c BET N₂ gas sorption isotherms of T₃ calcined at 400 and 500 °C.

Fig. 4.14d BET N₂ gas sorption isotherms of T₅ calcined at 400 and 500 °C.

Fig. 4.14e BET N₂ gas sorption isotherms of T₁₂ calcined at 400 and 500 °C.

Fig. 4.15a BET N₂ gas sorption isotherms of T_{1/120} calcined at 400 and 500 °C.

Fig. 4.15b BET N₂ gas sorption isotherms of T_{2/120} calcined at 400 and 500 °C.

Fig. 4.15c BET N₂ gas sorption isotherms of T_{3/120} calcined at 400 and 500 °C.

Fig. 4.15d BET N₂ gas sorption isotherms of T_{5/120} calcined at 400 and 500 °C.

Fig. 4.15e BET N₂ gas sorption isotherms of T_{12/120} calcined at 400 and 500 °C.

Isotherm of calcined sample R at 400 °C is displayed in Fig. 4.16. All the isotherms typify type IV BET curve with hysteresis loop, indicating the formation of mesopores [12]. Considering the isotherm of T₁ calcined at 400 °C as an example (Fig. 4.14-a), the observed large adsorption volume of liquid N₂ at low relative pressure ($P/P_0 < \sim 0.1$) was mainly related to the monolayer formation of N₂ molecules on sample surface. Subsequently, there is a gradual increase in the adsorbed volume for $P/P_0 \leq 0.5$, which is due to the formation of multilayers of N₂ molecules on the sample surface. When the relative pressure was further increased, a sharp increase in adsorbed gas volume was observed which was attributed to the capillary filling of mesopores [12]. Continuous gas adsorption for $0.9 < P/P_0 < 1$ was related to the filling of the larger pores, i.e., mesopore and/or macropores (e.g., voids between agglomerated particles). During the desorption process, a hysteresis loop was formed when P/P_0 was reduced from ~ 0.9 to 0.5. At the same relative pressure, the adsorbed volume during desorption process is always greater than that in adsorption process. This is because

equilibrium pressure (P) over a convex surface of liquid is less than the saturation vapour pressure (P_o) at the same temperature.

Fig. 4.16 BET N_2 gas sorption isotherm of sample R calcined at 400 °C.

Further noted in Fig. 4.14-a is the “vertical” region of the hysteresis loop of the sample calcined at 500 °C is located at higher relative pressure than that from the sample calcined at 400 °C. This implies that the average mesopore dimension is larger in the former sample which was calcined at a higher temperature. It can also be observed that with increased aging time, the differentiation between isotherm shapes of each sample calcined at different temperatures reduces. This suggests that a longer aging time helps stabilize the mesostructural features and hence improved thermal stability. In addition, the pressure at which the hysteresis loop commences is lower for the sample with longer aging time (Fig. 4.14 and 4.15). Based on the model proposed by Zsigmondy [12], the commencement of hysteresis loop is related to capillary condensation of finest pores. Therefore, samples with longer aging time also tend to have smaller mesopores.

Two typical shapes, i.e., H1 (e.g., Fig. 4.14-a) and H2 (e.g., Fig. 4.14-e) curves have been observed in all the calcined samples [13]. The shape of the Type IV curve is closely related to the structure of the mesoporous framework, i.e., pore size, pore size distribution, pore geometry, as well as the degree of mesoporous ordering. Usually, a porous structure with irregular pore opening geometry gives H1 type isotherm, while H2 is obtained from a porous structure with pore opening that is larger than the pore size. However, the shape of isotherm is also determined by the average pore size and pore size distribution. Here, since the same concentration of surfactant is used, the geometry of the surfactant micelles, and hence the shape of the mesopores, should be similar for all the T samples. The difference in the shape of Type IV curves is therefore believed to be due to the different pore size and pore size distribution. The analysis of pore size and pore size distribution will be shown later.

As shown in Fig. 4.16, the type IV isotherm obtained for calcined sample R also indicates the presence of mesopores although no disordered mesoporous structures was detected by SAXS. However, it is noted that the total adsorbed gas volume is much less than those T samples with same calcination temperature. This result directly reveals that the presence of template is essential in creating mesopore volume.

To further analyze structural features, α -S plots of T₁₂ and R calcined at 400 °C were deduced and shown in Fig. 4.17 and 4.18, respectively [14]. α -S plot is a method that compares the amount of adsorbed gas with that of a reference material. Using α -S plot method, information on micropore volume and porous structure can be revealed by the y intercept at the ordinate and the shape of the plot. The plots can be divided into three regions, I, II, and III. In Fig. 4.17, the linear fit in region I passes through the origin exactly and therefore indicates that little micropores were formed in this sample. However, a small amount of micropores (diameter < 20 Å) were formed in calcined sample R as indicated by

the intercept of linear fit with y-axis above zero (Fig. 4.18). In both cases, an inflection point occurred as the plot transits from region I to II, which reflects the start of capillary condensation in mesopores. In region III, the gradient of linear fit is larger for T_{12} than that of R. This suggests that certain amount of large mesopores and/or macropores could be present in the surfactant templated samples while particles with larger amount of agglomerations were obtained in R sample.

Fig. 4.17 α -S plot of sample T_{12} calcined at 400 °C.

Fig. 4.18 α -S plot of sample R calcined at 400 °C.

4.5.2 BET surface area

A list of BET surface area (S_A) of calcined samples T_x , $T_{x/y}$ and R is given in Table 4.1. For all T samples, it can be found that the BET surface area generally increases with longer aging time. For example, the S_A of samples without HT and after 400 °C calcination has increased from 93 m^2/g to 190 m^2/g when the aging time was prolonged from 1 to 12 days. When HT was applied, it was observed that S_A is improved to different extents for the same calcination temperature. The degree of improvement reduces with increasing aging time. For example, the obtained S_A for $T_{1/120}$ and $T_{12/120}$ calcined at 400 °C are 101 m^2/g and 196 m^2/g , respectively. This maximum S_A value obtained here (196 m^2/g) is 75% more than

that reported in literature of $112 \text{ m}^2/\text{g}$ [15], both are calcined at 400°C and neutral surfactants were used. When the calcination temperature was raised to 500°C , the resulted S_A was reduced to different extent for each T sample. In Table 4.1, it can be found that S_A of $T_{1/120}$ and $T_{12/120}$ decreased from $101 \text{ m}^2/\text{g}$ to $49 \text{ m}^2/\text{g}$ and from $196 \text{ m}^2/\text{g}$ to $155 \text{ m}^2/\text{g}$, respectively, when calcination temperature was increased from 400°C to 500°C . Whereas the S_A of $T_{12/120}$ ($155 \text{ m}^2/\text{g}$) calcined at 500°C is still $\sim 38\%$ larger than the maximum value ($112 \text{ m}^2/\text{g}$) reported in the literature [15]. The large surface area obtained in the present study is mainly attributed to the small SnO_2 crystallites fabricated from aging and hydrothermal treatment. The BET surface area of sample R ($64 \text{ m}^2/\text{g}$) is only about half of that from sample T_3 ($132 \text{ m}^2/\text{g}$) although the two samples have the same aging period. The reason for the

Table 4.1 List of BET surface area and pore volume of calcined samples T_x , $T_{x/y}$, and R.

Samples	BET surface area (m^2/g)		BET pore volume (cc/g)	
	calcined at 400°C	calcined at 500°C	calcined at 400°C	calcined at 500°C
T_1	92.9	55.2	0.1981	0.2107
T_2	116.4	65.21	0.223	0.2286
T_3	132.9	92.4	0.2311	0.212
T_5	131.7	102.5	0.2075	0.2103
T_{12}	188.6	153.3	0.1832	0.1683
$T_{1/120}$	101.2	48.7	0.2287	0.2241
$T_{2/120}$	119.5	68.6	0.2382	0.2286
$T_{3/120}$	137.8	75.1	0.2522	0.23
$T_{5/120}$	133.4	96.1	0.1883	0.1789
$T_{12/120}$	196.1	154.8	0.2211	0.2089
R	64.5	N/A	0.068	N/A

relatively low surface area of sample R is mainly due to larger degree of agglomeration of SnO_2 particles, as suggested by the low pore volume shown in Table 4.1.

In fact, it was noted that S_A of calcined T samples is closely related to the crystal size when comparing S_A results and crystal size plots (Fig. 4.8). There is a reverse (but not linear) relation between S_A and the respective sample crystal size, i.e., sample with a smaller crystal size tends to possess a larger surface area. However, S_A is not only determined by crystal size, but also influenced by pore volume since easy gas diffusion can be promoted with large pore volume and less particle agglomeration.

4.5.3 BET pore volume

The specific pore volume (S_V) of calcined samples T_x , $T_{x/y}$ and R is also given in Table 4.1. Since the same template concentration was used for each T sample, it is reasonable to predict that the samples should possess similar pore volume after calcination at the same temperature. However, unlike the variation in surface area, there was no obvious trend between S_V and aging time or calcination temperature. Nonetheless, samples with HT tend to give slightly larger pore volume as compared to those without HT. It can be found that the pore volume varies from 0.1683 (T_{12} calcined at 500 °C) to 0.2311 cc/g (T_3 calcined at 400 °C) and from 0.1788 ($T_{5/120}$ calcined at 500 °C) to 0.2522 cc/g ($T_{3/120}$ calcined at 400 °C) for samples without and with HT, respectively. The maximum pore volume obtained in the present work is 0.2522 cc/g after calcination at 400 °C which is comparable with that (0.235 cc/g) reported in literature [11]. In the reference, authors applied the same surfactant as the mesoporous structure directing agent. However, no heat treatment was applied prior to the removal of surfactant.

It is interesting to note that S_V of sample R calcined at 400 °C is 0.068 cc/g, which is only $\sim 1/3$ of that from T_5 with same calcination temperature. This also explains the origin of large difference between their surface areas, although the two samples possess the same aging period and comparable crystal size. Furthermore, small pore volume in sample R indicates the formation of condensed particle agglomerations with limited amount of pores. This is consistent with the SAXS analysis showing that the disordered mesoporous structure was not obtained. Although the BET measurements revealed the presence of mesoporous structure, the mesopores are likely due to the voids between loosely packed SnO_2 crystals at the edges of agglomerations (as will be shown in section 4.6).

4.5.4 BET pore size distribution

BJH pore size distribution (PSD) curves of samples calcined at 400 °C without and with HT are shown in Fig. 4.19 and 4.20, respectively. As shown in Fig. 4.19, the average pore size of T samples without HT has reduced from 86 to 37 Å as aging time increased from 1 to 12 days (except T_5). Meanwhile, the PSD curve also narrows, indicating that the size distribution of mesopores is more uniform. When HT was applied (Fig. 4.20), the average pore size of each T sample was slightly reduced and varied from 64 to 36 Å with increasing

Fig. 4.19 BJH desorption pore size distribution (PSD) curves of samples without HT and calcined at 400 °C.

aging period. It is also noted that the pore size distribution of the HT samples is more uniform than that without HT. Similar trend was observed for T samples calcined at 500 °C, as shown in Fig. 4.21 and 4.22 for samples without and with HT, respectively. Therefore it can be concluded that although average pore size is mainly determined by aging period, the degree of uniformity in pore size can be improved by applying hydrothermal treatment. In addition, the broad pore size distribution and relatively large mesopores may also explain the resulted H1 type hysteresis loop observed in $T_1/T_{1/120}$ (Fig. 4.14a and Fig. 4.15a), while samples with narrow PSD and smaller mesopores ($T_{12}/T_{12/120}$) show H2 type curves (Fig. 4.14e and Fig. 4.15e).

Fig. 4.20 BJH desorption pore size distribution (PSD) curves of samples with HT at 120 °C and calcined at 400 °C.

In Fig. 4.19, it can be observed that the PSD curve of calcined sample R does not show any well-defined peak shape. Instead, most of the adsorbed gas volume was from pores with diameter $\leq \sim 35$ Å (including micropores). This result is consistent with the previous α -S plot analysis and again confirms that there are micropores present in this sample. The

micropores in sample R should be related to the voids between closely packed SnO_2 crystallites in large agglomerations

Fig. 4.21 BJH desorption pore size distribution (PSD) curves of samples without HT and calcined at 500 °C.

Fig. 4.22 BJH desorption pore size distribution (PSD) curves of samples with HT at 120 °C and calcined at 500 °C.

4.6 TEM characterization

TEM images of as-prepared T_1 and T_3 are shown in Fig. 4.23-a and -b, respectively. Due to phase contrast, it can be clearly observed that all the samples contain very small crystallites as well as amorphous and relatively light regions as indicated by arrows. Based on previous XRD analysis, the small crystals should be SnO_2 particles while the amorphous

Fig. 4.23 TEM images of as-prepared (a) T_1 , and (b) T_3 , in which the arrows indicate the possible locations of surfactants.

regions are possibly the surfactant templates. The average crystallite size of SnO_2 under TEM characterization is consistent with that calculated from XRD results. It can also be confirmed by TEM images that surfactant aggregates are randomly distributed inside the obtained mesophase composites which agrees with the SAXS analysis.

Fig. 4.24 shows the TEM images and selected area diffraction pattern of T_x samples after calcination at 400°C . Clearly, the results reveal the formation of highly porous structures consisting of randomly distributed mesopores as a result of the removal of surfactant templates. As labeled in Fig. 4.24-f, TEM diffraction pattern also proves that the mesoporous framework displayed in Fig. 4.24-c is made up of pure SnO_2 nanocrystallites. Although the geometry of mesopores is not well defined, it can be observed that the pores in each sample have been distributed in a disordered manner between the slightly agglomerated SnO_2 nanocrystals with comparable size. Therefore, the similar distances between adjacent pores in each sample lead to the observed single reflection from SAXS analysis (Fig. 4.11). Furthermore, it is also evident that crystallites and mesopores tend to be smaller in the sample with longer aging period which is consistent with the previous XRD and BET results.

High resolution TEM images of calcined T_1 and $T_{3/120}$ at 400°C are shown in Fig. 4.25-a and -b, respectively. These localized pictures were captured at the edges of samples and therefore are reasonably less porous than the bulk regions. Generally, the average crystal size in each TEM image agrees well with that obtained from XRD results (Fig. 4.8). As indicated in the figures, a calculation shows that the average lattice distance of selected crystallites in Fig. 4.25-a is 0.33 nm while a value of 0.34 nm is obtained from Fig. 4.25-b. The two values match well with the d-spacing of (110) plane from each sample as calculated from XRD analysis, which are 0.333 and 0.335 nm for sample T_1 and $T_{3/120}$ calcined at

Fig. 4.24 TEM images of T samples calcined at 400 °C, (a) T₁, (b) T₂, (c) T₃, (d) T₅, and (e) T₁₂, and (f) diffraction pattern corresponding to the sample in (c).

400 °C, respectively. Therefore the selected lattice planes under TEM images correspond to the (110) planes of SnO₂ crystals. This result also reveals that mesoporous SnO₂ particles of good stoichiometry and high purity have been obtained.

Fig. 4.25 HR-TEM images of (a) T₁, and (b) T_{3/120} after calcination at 400 °C.

TEM images of T_5 calcined at 500 °C and R calcined at 400 °C are displayed in Fig. 4.26-a and -b, respectively. In Fig. 4.26-a, relatively large particle agglomerates (e.g., circled region) made up of several SnO_2 crystals are formed in T_5 . As discussed earlier, T_5 calcined at 500 °C demonstrates large mesopore size as well as wide pore size distribution (Fig. 4.21). Here, it can be observed from TEM image that this could be directly related to the large particle agglomeration during calcination. As a result, disordered mesoporous structure was destroyed and no diffraction signal was observed from SAXS result.

Fig. 4.26 TEM images of (a) T_5 calcined at 500 °C, and (b) R calcined at 400 °C.

As shown in Fig. 4.26-b, the calcined sample R shows much less porous structure with severe particle agglomerations as compared with T_3 calcined at the same temperature (Fig. 4.24-c). This is also in consistent with the previous BET gas sorption result which shows that the specific pore volume of calcined sample R is only $\sim 1/3$ of that from calcined T_3 (Table 4.1). As a result of easy gas diffusion in T_3 , the measured surface area of T_3 is twice of that of calcined sample R (Table 4.1).

4.7 Effects of hydrothermal temperature

As previously demonstrated in Fig. 4.8, annealing of samples at 120 °C helped to suppress crystal growth against calcination, although the effect diminishes as the aging time increases. Therefore, increasing HT temperature might further enhance the stability of SnO₂ crystallites. The effects of hydrothermal treatment temperature on SnO₂ crystal growth behaviors in the absence of organic templates have been investigated elsewhere [2]. The authors found that the average crystal size of SnO₂ particles increases with increasing HT temperature in both cases of as-prepared and calcined samples. For example, the crystal size of 45 Å of freshly synthesized SnO₂ at HT 100 °C has increased to 54 Å and 60 Å when the HT temperature was raised to 150 °C and 200 °C, respectively. In fact, similar results have also been observed in the present study when surfactants were applied.

The XRD patterns of the as-prepared and calcined T₂ with different HT temperatures are displayed in Fig. 4.27 and 4.28, respectively. As labeled, all the XRD patterns match well with the cassiterite SnO₂ crystalline phase [7]. The average crystal dimension of each SnO₂ sample was calculated using Scherrer equation and the results are shown in Fig. 4.29. It is observed that the crystal size of freshly prepared samples (squares) increases with increasing HT temperature. The size grows substantially from ~20 Å to 41 Å when the HT temperature was increased from 120 °C to 200 °C. This is larger than that of T₁₂ calcined at 400 °C (33 Å). After calcination at 400 °C, it is noted that the crystal size is also larger for the sample with higher HT temperature. Therefore, it is demonstrated that increasing HT temperature does not help one to further reduce SnO₂ crystal size against calcination. Since continuous crystal growth is expected at higher calcination temperature, no further study was performed at temperature higher than 400 °C.

Fig. 4.27 XRD patterns of as-prepared T_2 with different HT temperature (a) 120 °C, (b) 150 °C, and (c) 200 °C.

Fig. 4.28 XRD patterns of calcined T_2 at 400 °C with different HT temperature (a) 120 °C, (b) 150 °C, and (c) 200 °C.

The SAXS results in Fig. 4.30 show that disordered mesoporous structure has also been obtained for $T_{2/150}$ and $T_{2/200}$ after calcination at 400 °C. This result reveals that increasing HT temperature was not able to increase the mesostructural ordering. Again,

Fig. 4.29 Average crystal sizes of as-prepared and 400 °C calcined T₂ with HT at 120, 150 and 200 °C.

Fig. 4.30 SAXS patterns of (a) T_{2/150}, and (b) T_{2/200} calcined at 400 °C.

when the calcination temperature was increased to 500 °C, disordered mesostructure was destroyed as observed in earlier samples (Fig. A-1 in Appendix). The measured BET

isotherms of both $T_{2/150}$ and $T_{2/200}$ belong to type IV curve (Fig. A-2 in Appendix). The surface area of calcined $T_{2/150}$ ($107 \text{ m}^2/\text{g}$) and $T_{2/200}$ ($100 \text{ m}^2/\text{g}$) are less as compared to that of $T_{2/120}$ ($116 \text{ m}^2/\text{g}$), implying again that increasing HT temperature does not help one to obtain high surface area.

4.8 Discussion on structural evolution

Based on the above experimental results, it was found that three synthesis steps are critical in obtaining the final disordered mesoporous SnO_2 with large surface area and pore volume. They are: i) initial formation of SnO_2 /surfactant mesophase composite, ii) aging of the composite mixture, and iii) the calcination process.

During the preparation of SnO_2 precursor solution, the following reaction takes place when SnCl_4 was added into deionized water [16]:

It was noted that white precipitates occurred as the pH value was slowly increased using ammonia solution, and the solution became turbid when pH value was raised to ~ 1.8 . The white precipitates could be polymerized ($-\text{Sn}-\text{O}-\text{Sn}-$) oligomers from $\text{Sn}(\text{OH})_4$. Further increase in pH value causes gelation due to polymerization of ($-\text{Sn}-\text{O}-\text{Sn}-$) through condensation reactions at pH 4. When the pH value was finally adjusted to 9.8, the solution was still turbid although the solution is less viscous due to the increased net negative surface charges. When the SnO_2 precursor solution was mixed with a neutral surfactant solution, the final pH value of the mixture should be less than 9.8. This implies that the primary amine head group ($-\text{NH}_2$) of surfactant molecule is protonated and carries one positive charge ($-\text{NH}_3^+$), since the dissociation constant of tetradecylamine hydrophilic group is ~ 10.62 [17]. When SnO_2 solution was mixed with surfactant solution, electrostatic attraction happen between negatively charged SnO_2 particles and positively charged surfactant micelles. The

electrostatic force destroys the equilibrium condition of SnO₂ particles and causes recombination of SnO₂ particles with surfactant micelles to form a mesophase composite. However, the resulted mesophase was disordered and this could be due to too fast a reaction as well as a relatively large SnO₂ particle size.

In section 4.3, it has been shown by XRD results (Fig. 4.8) that all the as-prepared samples have very close SnO₂ crystal size of ~ 20 to 26 Å. However, it was found that the crystal size of calcined SnO₂ at the same temperature was smaller for the sample with longer aging time and hydrothermal treatment (Fig. 4.8). In another word, aging and hydrothermal treatment are able to improve the thermal stability of SnO₂ crystals. In sol-gel process, hydrolysis and condensation processes usually take place simultaneously. As a result, as-prepared particles often demonstrate a broad size distribution [18, 2]. Based on the Kelvin equation (1), it can be predicted that particle with smaller size has larger solubility than bigger particles:

$$RT \ln(p_r/p_o) = 2\gamma M/\rho r \quad \text{--- (1)}$$

where, γ , M , ρ , and r are the surface tension, relative molar mass, density and radius of the particle, respectively; p_r and p_o are the solubilities of precipitates at curved and flat surfaces, respectively; and R , and T are gas constant and temperature (in Kelvin), respectively. The Kelvin equation implies that smaller particles with higher solubility tend to dissolve and reprecipitate on larger particles. This process is known as Ostwald ripening which has the effects of raising the average particle size and decreasing particle size distribution [19]. Here, it is believed that longer aging and hydrothermal treatment produce SnO₂ particles with narrower particle size distribution through Ostwald ripening. It is suggested elsewhere that if the SnO₂ particles have a narrow particle size distribution, there is less crystal growth comparing to a system which has a broad size distribution when calcined at the same temperature [3, 2]. This is because the rate of crystal growth is mainly

determined by the difference in chemical potentials between the smallest and the largest particles. Although in the present study, there is no direct evidence showing that sample with longer aging/hydrothermal treatment possesses narrower particle size distribution, due to the difficulty in distinguishing boundary of SnO₂ particles and surfactant molecules. The result observed here is consistent with that reported by Fujihara et al., who showed that hydrothermal treatment at 100 to 200 °C is able to improve the thermal stability of SnO₂ crystallites against calcination [2]. The authors also demonstrated that improved thermal stability is due to narrower particle size distribution after hydrothermal treatment. The unexpected larger crystal size of T₅ than T₃ after calcination at 400 °C (Fig. 4.8) was likely due to improper removal of Cl⁻ ions during washing process, since it is possible that the residual Cl⁻ ions can promote crystallite growth during thermal treatment [20].

Crystal growth behavior during calcination is not only determined by crystal size uniformity, but also largely influenced by average crystal size. Due to the high surface energy of nanocrystalline materials, activation energy (*Q*) for nanocrystallites growth is usually very low [21]. The rate of crystal growth for conventional polycrystalline materials can be generally described by the empirical equation [21]:

$$D^n - D_0^n = Kt \quad \text{--- (2)}$$

where, *D* is the average crystal size after calcination for period *t*, *D*₀ the initial crystal size, *n* the crystal growth exponent, and *K* a rate constant. The constant *K* is temperature dependent and can be expressed as $K \propto \exp(-Q/RT)$, where *R* is the gas constant, *Q* is the activation energy for crystal growth, and *T* is the isothermal calcination temperature. This implies that the kinetics of crystal growth is more rapid at higher calcination temperature. For the calcination temperature conducted, relatively large crystal growth has been found, especially for those samples with short aging periods (e.g., 1 - 2 days). As discussed earlier, large

crystal growth partially contributes to the loss of disordered mesoporous structure. Therefore, crystal growth can not be avoided at high temperature calcination for nanocrystalline materials. Alternative synthesis strategy may be desired to further improve SnO₂ crystal/mesostructure stability, e.g., modification of activation energy.

4.9 Conclusion

In summary, neutral surfactant templated disordered mesoporous SnO₂ particles with large surface areas (196 m²/g), large pore volume (0.2522 cc/g) as well as high thermal stability (after calcination at 400 °C) have been successfully fabricated through sol-gel based self-assembly. The results showed that microstructural and mesostructural properties can be improved by proper control of aging and hydrothermal conditions. Generally, it was found that as the aging time increases from 1 to 12 days, the crystal size of samples calcined at 400 °C (without HT) decreases from 63 to 33 Å. The surface area is increased from 93 to 189 m²/g, and the average mesopore dimension is reduced from ~ 86 to 32 Å. When the calcination temperature was raised to 500 °C, the disordered mesoporous structure was destroyed due to relatively large crystal growth. Although the structure property (crystal size and surface area) was mainly influenced by aging period, it was also found that HT at 120 °C can improve pore size distribution. However, continual increase of HT temperature to 150 and 200 °C has little effect in further enhancing the structural property. The result also showed that SnO₂ synthesized in the absence of surfactant possess both micro- and mesopores, although the pore volume is much smaller than those obtained with the use of surfactant.

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Chapter 5

Surfactant Templated Mesoporous SnO₂-SiO₂

Composites

Chapter 5 Surfactant Templated Mesoporous SnO₂-SiO₂ Composites

5.1 Introduction

In Chapter 4, it has been demonstrated that the thermal stability of mesoporous SnO₂ is influenced by the aging period and hydrothermal treatment. Results showed that SnO₂ crystals can grow rapidly by ~ 2 to 4 times at calcination temperature of 500 °C, unless the aging time is sufficiently prolonged (≥ 12 days). However, additional aging delays fabrication time and consumes more energy. Therefore the main objective in the present chapter is to develop a facile, effective and low-temperature synthesis pathway to suppress SnO₂ crystal growth so that a highly thermal stable mesoporous SnO₂ with large surface area, high porosity and uniform PSD can be obtained.

As a characteristic behavior of nanoscale materials, crystal growth can take place at relatively low temperature within a short period because of the low activation energy (~ 44 kJ/mole) [1]. For many ceramic systems with nano- to microscale grains, evaporation-condensation is the dominating growth mechanism at elevated temperatures [2]. Therefore, one effective strategy to enhance the stability of nanocrystals against calcination is to increase the activation energy barrier by the introduction of impurity dopant into the parent grain boundary. Recently, the improvement in thermal stability of SnO₂ was attempted by surface complexation using acetylacetonato ligands [3]. Due to the presence of surface ligands, the average SnO₂ crystallite size increases only from ~ 12 Å to 20 Å after calcination at 300 °C for 2 h. However, the crystallite size increases sharply to 110 Å when calcination temperature is changed to 450 °C which is mainly due to the removal of surface ligands at elevated temperature. Therefore, it is necessary to look for an inorganic impurity instead of organic ones.

However, it is important to select an impurity material in order to achieve homogeneous coating while at the same time retain as much of the intrinsic physical/chemical properties of the parent material as possible. The ideal dopant particles should serve three functions. Firstly, they can serve as the pinning sites to stop the advancing of grain boundary interfaces. In this way, crystal growth through structure relaxation or elimination of lattice defects (e.g. dislocations, twins, etc) can be hindered. Secondly, they should replace the surface hydroxyl groups (-OH) on SnO₂ crystallites through dehydroxylation since the surface hydroxyl groups are considered as the sites where SnO₂ crystal growth can happen [4]. Lastly, although evaporation of the outer amorphous layers can take place at a much lower temperature for nanocrystals, surface coating by a thermally stable impurity may restrict the evaporation process and therefore limit mass transport for the subsequent condensation and growth.

In the present study, SiO₂ is considered as a suitable impurity material for several reasons: i) amorphous silica is chemically inert and thermally stable up to 1000 °C, ii) surface grafting of silica species onto SnO₂ crystallites is achievable through dehydroxylation between Sn-OH and silanol sites (Si-OH), iii) physical and chemical properties of silica precursors can be carefully controlled over a broad range of working conditions and therefore uniform surface grafting is possible, and iv) low cost of silica raw material.

This chapter describes the synthesis, characterization and structure evolution study of mesoporous SnO₂-SiO₂ composites (Si/Sn molar ratio ≤ 0.25) which were prepared on neutral surfactant template (tetradecylamine, TDA) using a stepwise sol-gel based technique, as described in section 3.3.

5.2 Thermogravimetric analysis

Fig. 5.1 shows the TG analysis results of as-prepared and calcined C_x samples (x refers to TDA/Sn molar ratio, $x = 0, 0.1, 0.3$, and 0.7). The total weight losses of as-prepared samples range from ~ 17 to 45 wt.% as the TDA/Sn molar ratio increases from 0 to 0.7 . Variation in weight loss is clearly due to the different concentration of the surfactant.

Fig. 5.1 TGA curves of as-prepared (A) C_0 , (B) $C_{0.1}$, (C) $C_{0.3}$, (D) $C_{0.7}$, and (E) $C_{0.3}$ calcined at 400 °C.

As shown in Fig. 5.2, TGA curve of pure TDA surfactant indicates that the decomposition of TDA started at ~ 120 °C and was completely combusted before ~ 180 °C. Hence any weight reduction in $C_{0.1}$, $C_{0.3}$, and $C_{0.7}$ (Fig. 5.1) below 180 °C should be attributed to the removal of surfactants attached to the outer surfaces of particles, as well as physically adsorbed moisture and partial dehydroxylation. In the case of C_0 , the weight reduction below temperature of ~ 120 °C is mainly attributed to the water evaporation. The continuous weight loss (~ 2 wt.%) from 200 °C to 500 °C is resultant from further removal of surface hydroxyl groups during annealing. The major weight loss of $C_{0.1}$, $C_{0.3}$,

and $C_{0.7}$ took place from 200 °C to 470 °C, which were related to the gradual decomposition of neutral surfactant and the removal of carbon residues. Therefore, it can be concluded that surfactants have been successfully incorporated into the C_x samples ($x = 0.1, 0.3$ and 0.7) and the calcination process was able to remove the organic templates completely (Fig. 5.1-E). Similar TGA results were observed for S_y samples, as shown in Fig. A-3 (Appendix).

Fig. 5.2 TGA curve of pure tetradecylamine.

5.3 Microstructural and mesostructural evolution

5.3.1 X-Ray diffraction study

X-Ray Diffraction patterns of C_x and S_y (y refers to Si/Sn molar ratio, $y = 0, 0.06$, and 0.25) samples are shown in Fig. 5.3 and Fig. 5.4, respectively. All the XRD patterns can be indexed with tetragonal rutile phase ($P4_2mm$) of crystalline SnO_2 . In Fig. 5.3-a, it is observed that peak widths are quite broad for all as-prepared C_x samples. After calcination (Fig. 5.3-b and -c), phase change was not observed and there was little reduction in FWHM (Full Width at Half Maximum), suggesting slight change of SnO_2 crystal dimensions. However, FWHM of S_y samples sharpened with decreasing Si/Sn

Fig. 5.3 X-ray diffraction patterns of C_x samples, (a) as-prepared (aged at 75 – 80 °C), (b) calcined at 400 °C, and (c) calcined at 600 °C.

molar ratio and increasing calcination temperature (Fig. 5.4). The low diffraction intensity of $C_{0.1}$ was mainly due to a small quantity of sample used. A broad hump spreading with 2θ degree covering from 20 to 40° can be observed in the XRD pattern of individual C_x sample. This should be attributed to the presence of amorphous SiO_2 and/or coalesce of broadened (110) and (101) peaks from very small SnO_2 crystals.

Fig. 5.4 XRD patterns of S_y samples (aged at 75 -80 °C).

Assuming that peak broadening was primarily due to the size effect, the average crystal sizes of C_x and S_y , listed in Table 5.1, were calculated using Scherrer formula. Prior to calcination, all C_x samples have very close and small mean crystallite sizes of ~ 20 Å along the [211] crystallographic direction. This value is comparable with that of pure SnO_2 as reported in the previous chapter (section 4.3). After calcination, it is noted that very little crystal growth was experienced by the C_x samples. The maximum crystal growth in the C_x samples amounts to ~ 10 Å, as is found in $C_{0.7}$ after calcination at 600 °C. At TDA/Sn = 0.3 ($C_{0.3}$), the amount of crystal growth is the least. The change in crystal

Table 5.1 XRD and BET results for C_x and S_y samples.

Sample	Crystal size (Å)*		Average pore diameter (Å)	BET specific surface area (m ² /g)	BJH desorption pore volume (cc/g)
	(110)	(211)			
C_0	§	22	-	-	-
$C_0 @ 400^\circ\text{C}$	17	25	¶	148	0.0557
$C_{0.1}$	§	20	-	-	-
$C_{0.1} @ 400^\circ\text{C}$	18	25	35	195	0.1864
$C_{0.1} @ 600^\circ\text{C}$	20	26	37	173	0.1698
$C_{0.3}$	§	20	-	-	-
$C_{0.3} @ 400^\circ\text{C}$	15	22	25	362	0.3297
$C_{0.3} @ 600^\circ\text{C}$	22	26	34	214	0.2454
$C_{0.7}$	§	19	-	-	-
$C_{0.7} @ 400^\circ\text{C}$	18	23	25	335	0.1968
$C_{0.7} @ 600^\circ\text{C}$	23	29	33	172	0.1753
S_0	20	30	-	-	-
$S_0 @ 400^\circ\text{C}$	63	64	64	100	0.2381
$S_0 @ 600^\circ\text{C}$	114	126	217	39	0.2325
$S_{0.06}$	§	25	-	-	-
$S_{0.06} @ 400^\circ\text{C}$	34	36	37	168	0.2523
$S_{0.06} @ 600^\circ\text{C}$	56	60	64	93	0.2251

Notes *Average crystal size is calculated from both (110) and (211) planes for comparison.

§Accurate crystal size from (110) plane cannot be obtained due to partial coalescence of (110) and (101) peaks.

¶Micropores were obtained in sample and the equipment was not able to give complete data for pore size distribution plot, as shown in Fig. 5.11.

size after calcination is significant when Si/Sn ratio was reduced. In particular, when no SiO_2 was added, SnO_2 crystal size of freshly prepared S_0 has increased substantially by fourfold from 30 to ~ 120 Å after calcination at 600°C . It is also noted that the concentration of surfactant has little effect on crystal size changes, since the C_x samples with same calcination temperature have comparable crystal sizes. Hence, the XRD analysis shows that crystal growth of SnO_2 can be inhibited effectively using SiO_2 and the effectiveness is largely dependent on SiO_2 concentration.

5.3.2 TEM characterization of microstructure

Selected sample ($C_{0.3}$ calcined at 400 °C) was characterized by TEM to further explore its microstructural features. High-resolution TEM image in Fig. 5.5 shows that the average crystal size (~ 22 Å) is consistent with that obtained from XRD result (Table 5.1). To obtain chemical information, EDS analysis was also performed for the selected area under TEM and results are shown in Fig. 5.6. As given in Fig. 5.6-a, EDS line scan clearly shows that Si element is evenly distributed through the sample as suggested by the fact that EDS pattern of Si is similar to that of Sn. EDS quantitative analysis (Fig. 5.6-b) further confirms that molar ratio of Si/Sn in the sample is 0.28 which is very close that used in the starting materials (0.25) during synthesis. Therefore, it has been confirmed that SnO_2 - SiO_2 composites with desired Si/Sn molar ratio have been successfully obtained. Since silica particles are amorphous in nature, their possible locations are indicated by arrows in Fig. 5.5. Later in this chapter, FTIR result will further confirm that Sn-O-Si bonding is present in as-prepared samples.

Fig. 5.5 HRTEM image of sample $C_{0.3}$ calcined at 400 °C, particles with lattice images correspond to SnO_2 nanocrystals while arrows indicate the locations of amorphous particles at grain boundaries.

Fig. 5.6 (a) TEM image of $C_{0.3}$ calcined at 400 °C and EDS line scan patterns of Si and Sn elements, and (b) EDS spectrum along the line selected in Fig. 5.6-a, and quantitative analysis result.

5.3.3 Small-angle X-ray scattering study

Fig. 5.7 shows the Small Angle X-Ray Scattering (SAXS) patterns of C_x and S_y samples. As shown in Fig. 5.7-a, -d, and -e, as-prepared samples of $C_{0.3}$, $C_{0.7}$, S_0 and $S_{0.06}$ with disordered mesophase were obtained, as confirmed by the single diffraction peak at low angles [5-9]. For C_0 and $C_{0.1}$, mesophase was not observed although they have

Fig. 5.7 Small-angle X-ray scattering patterns of (a) C_x as-prepared, (b) C_x calcined at 400°C , (c) C_x calcined at 600°C , (d) S_0 samples, and (e) $S_{0.06}$ samples.

comparable crystal dimensions to that of $C_{0.3}$ and $C_{0.7}$ (Table 5.1). The lack of single diffraction peak was due to the absence or a lower content of surfactant template present in C_0 and $C_{0.1}$, respectively.

Upon the removal of templates at 400 °C, mesoporous structure was obtained for all C_x samples except C_0 (Fig. 5.7-b). The broad, single diffraction peak indicate that disordered mesoporous structures were obtained [6, 10]. As calcination temperature increased, the peak position shifted to lower 2- θ position, which should be directly related to the crystal growth. After calcination at 600 °C, the mesoporous structures still remained, displaying again the high thermal stability (Fig. 5.7-c). However this is not so for S_0 (no SiO_2) after calcination at 600 °C, no diffraction peak could be detected in the sample because of the complete destruction of mesoporous structure (Fig. 5.7-d). This result again demonstrates that by inhibiting the crystal growth of SnO_2 , the thermal stability of mesoporous structure can be greatly enhanced.

5.3.4 TEM characterization of mesostructure

The mesostructures of selected C_x and S_y samples are also characterized by TEM technique. The TEM images in Fig. 5.8 show that the mean crystal sizes of samples are well consistent with the results from XRD analysis. In Fig. 5.8-a, phase contrast due to the difference in nuclei and electron densities between surfactant and SnO_2 again confirms that the surfactants (relatively bright regions) have been successfully embedded into the SnO_2 aggregates. Organic surfactants which have lower nuclei and electron densities as compared to that of inorganic SnO_2 crystallites will therefore appear brighter (because of less scattering of electron beam) than SnO_2 under TEM bright field image mode. This result is consistent with that deduced from the previous TGA analysis. After calcination at 400 °C, it can be clearly seen that highly porous structures consisting of interconnected SnO_2 nanocrystals were obtained (Fig. 5.8-c to -f). The mesopores were obtained upon the removal of surfactants. However, no obvious pores can be observed for sample C_0 (Fig. 5.8-b) due to the absence of surfactant templates. It is shown previously (Table 5.1) that surfactant concentration has little effect on the final crystal size. However,

the gas sorption results will later show that TDA/Sn ratio has significant influence on pore volume. The investigations on the mesoporous structure will be given in the following sections.

Fig. 5.8 (HR)TEM images of (a) $C_{0.3}$ as-prepared, and the samples after calcination at 400 °C for (b) C_0 , (c) $C_{0.1}$, (d) $C_{0.3}$, (e) $C_{0.7}$, and (f) S_0 .

5.4 N₂ gas sorption measurement

5.4.1 BET surface area and pore volume

Gas (N₂) sorption results of calcined C_x and S_y samples are summarized in Table 5.1. The largest BET surface area of 362 m²/g and pore volume of 0.33 cc/g is obtained from sample $C_{0.3}$ after calcination at 400 °C. To the best of my knowledge up to this point of publication, these are the highest values reported for mesoporous SnO₂ synthesized with/without surfactant templates [6-8, 11, 9, 12-16, 3, 17]. When the calcination temperature was increased to 600 °C, both the BET surface area and pore volume were reduced, depending on the stability of inorganic frameworks. Compared with the S_y samples, the C_x samples possess higher mesostructural stability as reflected by a lower percentage reduction in surface area and smaller variation in average pore size as the calcination temperature is increased from 400 °C to 600 °C. Although the C_x samples of the same calcination temperature have comparable crystal dimensions in the range from ~ 22 to 29 Å, their surface areas vary from 148 (C_0) to 362 m²/g ($C_{0.3}$). This can be explained by the difference in their pore volumes which was related to TDA/Sn molar ratio. Larger pore volume means less degree of crystals aggregation and therefore more surfaces are exposed to the outer environment.

5.4.2 BET isotherms and pore size distribution

BET isotherms of C_x and S_y samples calcined at the two different temperatures are shown in Fig. 5.9. In Fig. 5.9-a, calcined C_0 shows “type I” curve with a hysteresis loop indicating the formation of microporous structure. It is well known that microporous structures can be prepared for many solids such as xerogels of silica, titania, alumina and tin oxide using conventional sol-gel method [18]. The pore volume of this sample is only 0.0557 cc/g, and therefore again shows that the presence of surfactant template is critical for creating mesoporosity. It can be observed that all the isotherms except that of C_0 at

Fig. 5.9 BET isotherms of C_x and S_y samples after calcination, (a) C_0 , (b) $C_{0.1}$, (c) $C_{0.3}$, (d) $C_{0.7}$, (e) S_0 , and (f) $S_{0.06}$.

400 °C and S_0 at 600 °C, display “type IV” curve with/without H2 type hysteresis loop, which is a characteristic of mesoporous materials [18]. Typically, three regions can be found in the “type IV” curve because of different sorption phenomenon at different stage. Taking the isotherm of sample $C_{0.3}$ calcined at 400 °C as an example (Fig. 5.9-c), there was an initial large increase in the adsorbed gas volume at low relative pressure (P/P_0) range from origin to ~ 0.2 . This corresponds to the formation of monolayer and multilayer of N_2 molecules on the sample surface. The large number of adsorbed gas volume may imply that this sample has large surface area. When the relative pressure was further increased from 0.2 to 0.5, the quantity of adsorbed gas also increased largely and then tapered at relative pressure of ~ 0.5 . Adsorption at this stage ($0.2 < P/P_0 < 0.5$) was mainly due to the capillary filling of the mesopores. In the next stage ($P/P_0 > \sim 0.5$), there was a plateau followed by another sharp increase of gas uptake at P/P_0 of ~ 0.9 . The volume adsorbed at $P/P_0 \geq \sim 0.9$ is attributed to the continuous N_2 filling of larger mesopores or macropores formed between the agglomerated particles. The absence of a hysteresis loop in this curve suggests that the average pore diameter of the sample is below a critical value and the pore size distribution is fairly uniform. As a comparison, the isotherm of the same sample calcined at 600 °C showed reductions in both the initial and total adsorbed gas volumes indicating the decrease in surface area and pore volume, respectively (as given in Table 5.1). The presence of the hysteresis loop indicates the enlargement of average pore size.

The BJH desorption PSD plots of C_x samples calcined at 400 and 600 °C are shown in Fig. 5.10 and Fig. 5.11, respectively. The results show that all the C_x (except C_0) samples have uniform PSD with peak centers ranging from ~ 20 Å to 40 Å. High thermal stability of these samples are reflected by small shifts of peak centers when calcination temperature was increased from 400 °C to 600 °C. The PSD center of calcined C_0 sample

should be less than 20 Å, although the BJH PSD plot is not complete because the equipment is not available for micropore measurement.

Fig. 5.10 Pore size distribution of C_x and S_y samples calcined at 400 °C.

Fig. 5.11 Pore size distribution of C_x and S_y samples calcined at 600 °C.

Both S_0 and $S_{0.06}$ calcined at 400 °C displayed the typical “type IV” isotherm (Fig. 5.9-e and -f), indicating the presence of mesoporous structure. However, an isotherm with H1 type hysteresis loop was obtained for sample S_0 after calcination at 600 °C, as shown in Fig. 5.9-e. This type of isotherm usually results from agglomerates of spherical particles of fairly uniform size. As plotted in Fig. 5.11, the PSD of S_0 shows a peak center at ~ 220 Å which is almost two times of its crystal size. Moreover, previous small-angle X-ray scattering result (Fig. 5.7-d) showed no diffraction peak from the sample. Therefore, it can be concluded that the “mesopores” obtained from this sample are mainly voids between the relatively large agglomerated SnO_2 particles. Compare with C_x samples, Fig. 5.10 and Fig. 5.11 show that the S_y samples have broader pore size distribution and larger average pore sizes after calcination at same temperature. Also, the shift in peak position is larger for the S_y samples than the C_x samples, therefore showing again that the thermal stability of the mesoporous structures are reduced when Si/Sn ratio was lowered.

5.4.3 α -S plot study

To further study the properties of the obtained mesoporous structure, BET adsorption branch of sample $C_{0.3}$ calcined at 400 °C is converted to α -S plot (Fig. 5.12). The mesoporous structure is again confirmed by the inflection point arising from the commencement of capillarity condensation in mesopores. The extrapolation of data in low α -S region gives a y intercept nearly zero, suggesting the absence of a detectable amount of micropores. In high α -S region ($> \sim 1$), adsorption continues in large mesopores or macropores between secondary particles. However, the amount of large mesopores or macropores are very small as indicated by the low magnitude of slope [17].

Fig. 5.12 Alpha-S plot for $C_{0.3}$ calcined at 400 °C, derived from adsorption branch data.

5.5 Effects of calcination period and temperature

The thermal stability of selected C_x sample was further explored by increasing calcination period and temperature. As a typical sample, $C_{0.3}$ was calcined at 400 °C for 55 hrs and at 800 °C for 3 hrs.

5.5.1 Effect on SnO_2 crystal growth

As shown in Fig. 5.13, the XRD patterns of the two samples match with that of SnO_2 rutile phase and the peak widths are still quite broadened. For the purpose of comparison, their crystal sizes were calculated using Scherrer equation and listed in Table 5.2 together with that of $C_{0.3}$ and S_0 (no silica doping) calcined at 400 °C for 3 hrs. The results showed that there was little change in crystal size when calcination period was prolonged from 3 hrs to 55 hrs. This result is consistent with the conclusion reported by Lai et. al. [1], who investigated the grain growth behaviors of nanocrystalline SnO_2 under long-term isothermal annealing conditions (up to 1000 hrs). They showed that the crystal

Fig. 5.13 XRD patterns of (a) $C_{0.3}$ calcined at 400 °C for 55 h, and (b) $C_{0.3}$ calcined at 800 °C for 3 h.

size increased rapidly during the first 3 hrs to 4 hrs, but reached a limiting value for each annealing temperature. According to the present study, it is reasonable to conclude that SnO_2 crystal growth has reached a metastable state after calcination time of 3 hrs. When calcination temperature was further raised to 800 °C, crystal dimension was increased slightly to ~ 33 Å which was only about half of that from S_0 calcined with the same period but at 400 °C.

Table 5.2 List of XRD and N_2 gas sorption results

Sample	Crystallite size* (Å) (110) / (211)	BJH desorption average pore diameter (Å)	BET specific surface area (m^2/g)	BJH desorption pore volume (cc/g)
S_0 @ 400°C for 3 h	63 / 64	64	100	0.2381
$C_{0.3}$ @ 400°C for 3 h	15 / 22	25	362	0.3297
$C_{0.3}$ @ 400°C for 55 h	19 / 21	34	283	0.2842
$C_{0.3}$ @ 800°C for 3 h	31 / 33	44	150	0.2189

5.5.2 Effect on mesoporous structure

Small-angle X-ray scattering plots of two samples are shown in Fig. 5.14. A single diffraction peak can still be clearly observed when calcination period was prolonged to 55 hrs (Fig. 5.14-a), indicating the presence of disordered mesoporous structure. However when the calcination temperature was raised to 800 °C, the peak signal is diminishing, suggesting the deterioration of the mesoporous framework.

Fig. 5.14 Small-Angle X-Ray Scattering patterns of (a) $C_{0.3}$ calcined at 400 °C for 55 h, and (b) $C_{0.3}$ calcined at 800 °C for 3 h.

The presence of mesoporous structures in both samples were again confirmed by the “type IV” isotherms from BET gas sorption measurement, as plotted in Fig. 5.15. BET results listed in Table 5.2 show that when the calcination period was increased from 3 hrs to 55 hrs, the surface area and pore volume were reduced by ~ 22% and 14%, respectively. However, the surface area is still relatively high, and is about three times that of sample without SiO_2 doping (S_0). Relatively narrow mesopore size distributions are obtained for the two samples, as revealed by the BJH desorption PSD curves in Fig. 5.16-b and -c.

Fig. 5.15 BET N₂ gas sorption isotherms of (a) C_{0.3} calcined at 400 °C for 55 h, and (b) C_{0.3} calcined at 800 °C for 3 h.

Fig. 5.16 BET N₂ gas sorption isotherms of (a) C_{0.3} calcined at 400 °C for 3 h, (b) C_{0.3} calcined at 400 °C for 55 h, and (c) C_{0.3} calcined at 800 °C for 3 h.

Therefore, the results show that samples with proper SiO₂ doping have high thermal stability even at extreme conditions, i.e., longer calcination period and high calcination temperature. With their high surface area, high thermal stability and larger

pore volume, these materials are promising candidates for many practical applications such as gas sensors, whose working temperatures are in the range of 400 – 600 °C.

5.6 Discussion on structure formation mechanism

The IR spectra of C_x and S_y samples are given in Fig. 5.17. Both the as-prepared (Fig. 5.17-a) and calcined (Fig. 5.17-b and -c) samples exhibit a very broad and intense peak ranging from ~ 3700 to 2000 cm^{-1} . This peak centers at $\sim 3420\text{ cm}^{-1}$ which can be attributed to the stretching vibrations of H-bonded hydroxyls (ν_{OH}) of $\text{SnO}_2/\text{SiO}_2$ [19]. The absorption bands centered at 1630 cm^{-1} are ascribed to physically adsorbed water (δOH with deformation mode) [20]. In all the as-prepared samples, there is a broad maximum located at $\sim 3155\text{ cm}^{-1}$ (Fig. 5.17-a), but this disappears after calcination (Fig. 5.17-b and -c). This absorption band was probably from traces of NH_3 which were not removed completely after washing [21]. It could also be related to amine (R-NH_2) groups from neutral surfactant. In addition, absorption bands of the as-prepared samples (except C_0) at 2958, 2923, 2853, ~ 1540 , 1465 1390, and 721 cm^{-1} (Fig. 5.17-a)

Fig. 5.17 FT-IR spectra (a) as-prepared, (b) calcined at 400 °C, and (c) calcined at 600 °C for C_x and S_y samples.

are collectively due the presence of TDA molecules [22]. However, these bands were not detected on the calcined samples as shown in Fig. 5.17-b and -c. At low wavenumber region, the peaks at $\sim 660 \text{ cm}^{-1}$ and 550 cm^{-1} were observed for all samples, and can be assigned to Sn-O-Sn antisymmetric vibrations [23]. Upon calcination at 400 and 600 °C,

additional bands were observed at $\sim 600\text{ cm}^{-1}$ and 470 cm^{-1} , which are typical Sn-O-Sn symmetric vibrations from crystal growth and coalesce [17].

In Fig. 5.17-a, the formation of Sn-O-Si bonding in as-prepared C_x and $S_{0.06}$ can be strongly evidenced by two absorption bands at $\sim 620\text{ cm}^{-1}$ and $920 - 930\text{ cm}^{-1}$ [24, 25]. These two bands were not found in the as-prepared S_0 (no silica doped) powder. Although there is a broad maxima at $\sim 925\text{ cm}^{-1}$ from the as-prepared S_0 , this is likely due to the bending mode of surface hydroxyl group on SnO_2 surface [17]. After calcination at 400 and 600 °C, the band at 620 cm^{-1} could not be observed for C_x and $S_{0.06}$, indicating the reduction in concentration of Sn-O-Si bonding. Meanwhile, the band at $\sim 920\text{ cm}^{-1}$ shifts to higher frequency position ($\sim 955\text{ cm}^{-1}$ to 965 cm^{-1}), which is related to the breaking of Sn-O-Si bonding at SnO_2 and SiO_2 interface [20]. It was also noted that a new broad maxima appears at around 1050 cm^{-1} (Fig. 5.17-b and -c). This can be attributed unambiguously to the Si-O-Si vibration [25] due to the growth of SiO_2 particles. The intensity of this new peak increases as the calcination temperature increases from 400 °C to 600 °C.

Therefore, it is demonstrated that Sn-O-Si bond was formed in the as-prepared C_x and $S_{0.06}$ samples, most probably on the surfaces of SnO_2 crystals. After calcination, the number of Sn-O-Si bond decreased with a concomitant appearance of Si-O-Si bond. Hence, it can be concluded that during the initial preparation of SnO_2 - SiO_2 sol solution, SnO_2 crystals were grafted by SiO_2 monomers or oligomers through dehydroxylation (Sn-O-Si). As the samples were calcined, nucleation and growth of amorphous SiO_2 particles took place at the grain boundaries of SnO_2 .

Several works have been reported on crystal growth kinetics of nanocrystalline SnO_2 prepared by sol-gel method [1, 26, 27]. Their results show that the SnO_2 crystal growth is controlled by surface diffusion through structural relaxation at low temperature ($300\text{ °C} < T < 1000\text{ °C}$) [1, 26, 27]. The structural relaxation model applied in their study

fits well with the evolutions of crystal growth, and produced a low activation energy ($Q = 31 - 44 \text{ kJ/mol.}$) which can be attributed to the short-range disordering-ordering rearrangement of atoms in the interface region [1, 26]. The study also shows that crystal growth of nanocrystalline SnO_2 is controlled by evaporation-condensation mechanism at high temperature ($T > 1300 \text{ }^\circ\text{C}$) [27]. In the present study, since both the starting SnO_2 average crystal size and calcination condition are comparable with that reported in the literature [1, 26], it is believed that SnO_2 crystal growth is also controlled by structural relaxation of interface atoms. Therefore, two main reasons are proposed to explain why SiO_2 effectively inhibits crystal growth of nanocrystalline SnO_2 : 1) the bonding between Si-O-Sn-O- atoms at the SiO_2 - SnO_2 interfaces restricts the relaxation rearrangement of disordered Sn and O atoms to form ordered crystalline phase, 2) the presence of SiO_2 particles reduces direct interface contact between adjacent SnO_2 particles, and therefore reduced mass transport for crystal growth. The latter reason could be more dominant when calcination temperature is high (e.g., $T = 800 \text{ }^\circ\text{C}$) or when calcination time is prolonged (e.g., $T = 400 \text{ }^\circ\text{C}$, $t = 55 \text{ hr}$). This is because that FTIR analysis has shown that Si-O-Sn bonding broke after the sample was calcined at 400 and 600 $^\circ\text{C}$. However, SnO_2 crystal size is still as small as 21 Å and 33 Å after calcination for prolonged period (400 $^\circ\text{C}$) and increased temperature (3 h), respectively. Here, there is no evidence to show that inhibition of SnO_2 crystal growth is related to the defect sites and/or vacancies due to SiO_2 , although the defects could also play important roles in crystal growth kinetics [27].

Based on the previous results and FTIR study, formation mechanism of thermally stable mesoporous SnO_2 - SiO_2 composites is postulated as follows. Initially, hydrolysis of SnCl_4 was rapid as indicated by the rapid reduction of the pH value less than 1. As the pH value was gradually adjusted to 6 - 7, white precipitates were formed from its precursor sol solution [5]. However, in this pH range, the hydrolysis rate of silica precursor is at its minimum [28]. As a result, the hydrolyzed silicate species such as monomers (Q^0) and

cyclic tetramers (Q_4^2) evolved slowly without rapid condensation because of their low concentration. The silicate species formed are grafted onto the surfaces of SnO_2 precipitates via hydrogen bonding and replaced the hydroxyl groups through dehydroxylation (Sn-O-Si). The pH value of solution was further increased to 10.8 gradually. This catalyzed the hydrolysis of TEOS and the dehydroxylation at $\text{SnO}_2\text{-SiO}_2$ interface. Hydrolysis of TEOS was nearly complete and most of the silicate species formed were grafted on the outer surface of SnO_2 particles till this stage. This also prevents the formation of separate mesoporous silica particles in the following mixing process with surfactant solution. Since the particle surfaces were negatively charged at high pH environment (Isoelectric point of SnO_2 is ~ 4), severe particles agglomeration could be minimized [29]. This was also reflected by the low viscosity and semi-transparency of the solution.

After mixing $\text{SnO}_2\text{-SiO}_2$ sol with TDA solution, white precipitates occurred within a short period, indicating the formation of large mesophase composite particles. The behavior of TDA molecules in water/iso-propanol solution was characterized by SAXS. No ordered liquid crystal phase (e.g., hexagonal, lamellar, or cubic) was detected. Since TDA concentration was much higher than its cmc (critical micellization concentration), spherical micelles should have been formed. The size of the spherical micelles is estimated to be $\sim 20 \text{ \AA}$ to $25 \text{ \AA}$, assuming they were not fully extended in the longitudinal direction [30]. This is comparable with the size of a single SnO_2 crystal or less than the dimension of lightly agglomerated particles. Furthermore, due to the improved solubility by iso-propanol, a large amount of single TDA molecules was also available in the admixed solution. Weak and nonionic interaction (e.g. hydrogen bonding) between hydrophilic groups ($-\text{NH}_2$) on TDA micelles/molecules and inorganic particles led to the formation of mesophase through self-assembly. Inorganic particles were dispersed inside organic template matrix, as observed in Fig. 5.8-a. With the removal of surfactants,

further dehydroxylation and slight SnO_2 crystal growth occurred. This resulted in the coalescence of adjacent SnO_2 particles (Fig. 5.-17) and increased d -spacing as indicated by the shift of SAXS reflection to lower angle (Fig. 5.7). Meanwhile, very small amorphous SiO_2 particles were condensed at the SnO_2 grain boundaries. Mesopores were left by the spaces between inorganic particles, and the inorganic mesoporous framework is continuous up to several hundred nanometers (Fig. 5.8-e).

Fig. 5.18 Selected TEM image of $\text{C}_{0.7}$ calcined at $400\text{ }^{\circ}\text{C}$. The picture shows the coalescence of local SnO_2 crystals after removal of surfactant.

5.7 Conclusion

In summary, mesoporous SnO_2 - SiO_2 composites with very high thermal stability are fabricated on neutral surfactant template through a one-pot synthesis route. The effects of synthesis parameters such as TDA/Si/Sn molar ratio and calcination temperature were investigated. Study on structure formation mechanism showed that amorphous silicate species were incorporated at the grain boundaries of SnO_2 crystals during the initial preparation. SnO_2 crystal growth can be hindered effectively during the subsequent calcination due to the reduction of surface hydroxyl groups and SiO_2 pinning

sites. The obtained mesostructural properties such as large specific surface area, pore volume and average pore size are mainly attributed to the disordered mesoporous SnO_2 . Mesoporous silica skeleton such as MCM-41 was not formed. As a result, specific surface area and pore volume as high as $362 \text{ m}^2/\text{g}$ and 0.33 cc/g were obtained after calcination at 400°C for the sample ($C_{0.3}$) prepared at TDA/Si/Sn molar ratio = $0.3/0.25/1$. Furthermore, average pore size ranging from $30 \text{ \AA}$ to $\sim 70 \text{ \AA}$ can be controlled by adjusting Si/Sn ratio ($0 - 0.25$).

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Chapter 6

Poly-l-lysine Templated Multilevel Porous SnO₂

Chapter 6 Poly-l-lysine Templated Multilevel Porous SnO₂

6.1 Introduction

In the previous chapters (4 & 5), mesoporous SnO₂ and SnO₂-SiO₂ powders with large surface area and high mesoporosity have been synthesized using neutral surfactant. The fabricated materials have average mesopore size ranging from ~ 30 to 100 Å. In recent years, one major interest in the field of porous materials is to synthesize multilevel porous materials, i.e., materials with pore size at different levels from micro- to macroscale [1]. Such multilevel porosity endows the materials with better size and shape selectivity for guest molecules through improved host-guest interaction in applications such as catalysis, separation, and gas sensing. Previously, it has been shown by other group that gas sensing performance of mesoporous SnO₂ is improved when larger mesopores are present [2-4]. Although the reason for the enhancement of gas sensing property is not fully understood, the authors suggest that it is probably due to easier gas diffusion. The presence of macropores can permit more effective access of gas/other reagents to smaller mesopores by reducing the pore blockage. One can expect that the use of multilevel porous SnO₂ with macro- and mesopores should enhance its gas sensing performance.

In this chapter, the key objective is to synthesize multilevel porous SnO₂ frameworks with both mesopores and macropores. Inspired by the successful fabrication of hollow SiO₂ microspheres templated by synthetic polypeptide [5], poly-l-lysine ($M_w > 30$ kD) is selected as the macropore directing agent due to its self-assembly behavior in the presence of small polyanions, e.g., citric ligand and silicate species. In this work, citric acid is used as a chelating agent to stabilize SnO₂ sol-solution as well as to provide binding with organic

template. Results show that macropores are obtained after the removal of poly-L-lysine by calcination. It is also found that the removal of citric acid during calcination can generate mesopores on macroporous SnO₂ framework. Depending on the working condition, two types of unique coral- and sea worm-like multilevel porous SnO₂ consisting of SnO₂ nanocrystallites (4 to 5 nm) are synthesized. The gas sensor fabricated using multilevel porous SnO₂ demonstrates improved H₂ gas sensing property due to its large specific surface area (180 – 210 m²/g) and easy gas diffusion.

6.2 Samples from unmodified SnO₂ sols

According to the synthesis condition, different form of SnO₂ materials such as fragments, coral- and worm-like porous structures were obtained as listed in Table 6.1. The final structure was found to be insensitive to reaction time and the results presented below are obtained for durations from 4 to 80 h. Parameters such as citric/Sn molar ratio (r_M) of SnO₂ sols, sols/PLL solution volume ratio (r_V) and mixture pH were found to have significant effects on the self-assembly process and therefore the product morphology. These will be discussed in the following sections.

Fig. 6.1 shows the SEM images of the as-prepared samples from unmodified SnO₂ precursors ($r_M = 0$). When r_V was as low as 0.05 (PLL-1), near spherical particles of 3 - 5 μm in size were obtained and assembled into nail-like secondary structures, as illustrated in Fig. 6.1 (a). When bombarded by a converged electron beam under EDX examination, the initial smooth surface disappeared and a porous core-shell structure (Fig. 6.1-b) was observed. No tin element could be detected in the spherical particles by EDX, implying that the spheres are organics which probably consist of stabilized PLL supramolecules encapsulated by a layer of

Table 6.1 Synthesis parameters and morphologies of typical samples.

Sample	Citric/Sn molar ratio (r_M)	Sols/PLL volume ratio (r_V)	Mixture pH [¶]	Product morphology after calcination at 450 °C
PLL [§] -1	0.0	0.05	7.00	Fragment
PLL-2		0.15		Fragment
PLL-3		0.3		Fragment
PLL-4	0.5	0.1	8.19	Coral-like
PLL-5	1.0	0.1	8.21	Fragment
PLL-6	1.5	0.1	8.28	Fragment
PLL-7	2.0	0.1	7.00	Sea worm-like
PLL-8		0.1	8.34	Sea worm-like
PLL-9		0.3	8.44	Fragment*
PLL-10		0.7	8.60	Fragment*
PLL-11		1.0	8.66	Fragment*
PLL-12	2.5	0.1	8.43	Sea worm-like
PLL-13	3.5	0.1	8.65	Sea worm-like
PLL-14	4.5	0.1	8.70	Sea worm-like

[§] Poly-L-lysine, [¶] pH measured at 23 ± 0.3 °C

* Selected SEM images of PLL-9, -10, and -11 are given in Appendix A-5.

citric acid. A similar result was observed by other researchers through optical microscopy [5]. Besides the spherical particles, particles with irregular shape (see SEM image in Appendix, Fig. A-4) similar to conventional sol-gel derived SnO_2 [6] were also observed in PLL-1. EDX analysis confirmed these particles to be rich in tin, with atomic ratio of oxygen to tin equal to ~ 2 . The results of PLL-1 suggest that at very low r_V there is no interaction between SnO_2 precursors and citric-stabilized PLL template. However, when r_V is increased to 0.15 (PLL-2) and 0.3 (PLL-3), crown-like as-prepared particles were observed, as shown in Fig. 6.1-c and -d. Elemental analysis using EDX indicated that the surface material has a chemical

composition that is close to stoichiometric stannic oxide (SnO_2), as shown in Fig. 6.2. During the synthesis of PLL-2 and -3, PLL solution and SnO_2 sols appeared turbid at neutral

Fig. 6.1 FESEM images of as-prepared samples, (a) PLL-1 (b) magnified region as circled in image (a), (c) PLL-2, and (d) PLL-3.

condition ($\text{pH} = 7$). Upon mixing, large precipitates were observed, indicating the formation of new hybrid materials. TG analysis of the precipitates (Fig. 6.3-a) exhibited a major weight loss during $\sim 250\text{ }^{\circ}\text{C}$ to $420\text{ }^{\circ}\text{C}$ as a result of the decomposition of organics. After calcination, the crown-like particles disappeared and only fragments of SnO_2 were left. These results reflect the fact that a higher r_v is needed to promote interfacial interaction. However, the degree of improvement is limited as revealed by the ill-defined final product morphology (Fig. 6.1-c and -d).

Fig. 6.2 EDS analysis of as-prepared PLL-2 shown in Fig. 1 c). The Sn/O atomic ratio was close stoichiometric stannic oxide. Pt and Na were from conductive coating and substrate respectively. Cl was from SnCl_4 .

Fig. 6.3 TG analysis results of as-made (a) PLL-3, (b) PLL-4, and (c) derivative weight loss of PLL-4.

It is evident that stable and monodispersed inorganic nanoparticles with chemically active surface group are critical in obtaining well controlled self-assembly. When SnCl_4 was

used to prepare the oxide precursors, hydrolysis can be completed even in an acidic condition; because of the high charge density of Sn^{4+} (Sn^{4+} ion has small ionic radius and large oxidation number). Subsequent condensation through ololation and oxolation reactions further caused severe agglomeration of SnO_2 sols. As a result, effective and uniform assembly might be hindered, and led to the irregular morphology as observed in PLL-2 and -3 (Fig. 6.1-c and -d). To prevent rapid hydrolysis and/or condensation, a reduction in reactivity of Sn^{4+} in water is a useful strategy [7, 8]. Citric acid has been widely used as a chelating agent for such purpose due to its low cost [9-12]. By adding a suitable amount of citric acid, completely colorless and transparent SnO_2 sols have been prepared in this work. They remain stable for several hours at room temperature, depending on the pH value and the concentration of chelator used. Tyndall effect was clearly observed for all the modified sols, suggesting the formation of very small and stable particles [13]. Previous studies [5, 14] revealed that the concentration of citric acid has a great influence on the shape and size of polypeptide template, as compared with other parameters, such as pH, ionic strength and temperature. Therefore it is interesting to investigate the influence of r_M ratios on the properties of final products, since the r_M ratios are related to the concentration of citric ligands in the present preparation system. As listed in Table 6.1, r_M ranging from 0.5 to 4.5 was studied in this work.

6.3 Samples from ligand-assisted SnO_2 sols

The morphology of the as-made PLL-4 with $r_M = 0.5$ and $r_V = 0.1$ is shown in Fig. 6.4-a and -b. As illustrated, side-by-side assembly of columns (Fig. 6.4-a and -b) with average length of 1.3 μm and width of $\sim 0.4 \mu\text{m}$ were synthesized. These columns appeared

to be slightly bent along the longitudinal direction, probably as a result of the formation of hybrids composed of flexible core templates and outer SnO_2 shell. After calcination, coral-like structure with cone-shape pore channels was obtained, as shown in Fig. 6.4-c to -f. The pore channels have comparable dimension with that of as-made columns. The wall thickness is ~ 100 nm (Fig. 6.4-d) and mainly composed of SnO_2 material as confirmed by EDX analysis. The pores are non-uniform with respect to morphology and this could result from

Fig. 6.4 FESEM images of as-prepared PLL-4 (a, b), and PLL-4 calcined at 450 °C (c - f).

uncontrolled rupture of the columns at their ends and partial deformation of the side walls at the decomposition of organics during calcination.

TG analysis of as-made PLL-4 (Fig. 6.3-b and -c) shows two major weight losses (35% in total) at $\sim 300\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$ due to the removal of the citric acid and PLL, respectively. Their decomposition temperatures were both retarded for about $80\text{ }^{\circ}\text{C}$ as compared to their own pure substances [15]. This observation may suggest that the tin ions are incorporated into the networks formed by PLL templates and citric ligands. The weight loss below $250\text{ }^{\circ}\text{C}$ can be attributed to evaporation of physically adsorbed moisture and dehydroxylation of surface hydroxyl groups. Above $400\text{ }^{\circ}\text{C}$, there was almost no weight variation, indicating the complete removal of organics and carbon residuals.

When r_M was raised to 1 (PLL-5) and 1.5 (PLL-6), final products were agglomerates of SnO_2 nanoparticles without distinct texture. It is interesting to note that when r_M reached 2 and beyond, sea worm like structures were obtained for both as-prepared and calcined PLL-8 (Fig. 6.5). The image in Fig. 6.5-a shows that as-prepared PLL-8 have distorted fiber/particle morphology. FESEM image with a higher magnification in Fig 6.5-b further reveals that as-prepared PLL-8 contains the highly distorted particles with hundreds of nanometers in length. Upon removal of organics, the morphology of distorted or sea worm like SnO_2 particles were clearly revealed (Fig. 6.5-c to -f). A close examination of the particles (Fig. 6.5-e and -f) showed that the particle is hollow at its core. On the other hand, it was found that r_V also has an effect on the morphologies of the final particles. Neither “sea worm” like structure nor coral like structure was obtained when r_V was ≥ 0.3 (PLL-9, -10, and -11), even though r_M was fixed at 2 (Table 6.1).

Fig. 6.5 FESEM images of as-prepared PLL-8 (a, b), and calcined PLL-8 (c-f).

X-ray diffraction patterns of PLL-3, -4 and -8 are shown in Fig. 6.6 and all match SnO_2 tetragonal rutile phase. The mean crystal size in [110] crystallographic direction was calculated using Scherrer formula, assuming that line broadening was primarily due to the size effect. As shown in Fig. 6.6, PLL-4 and PLL-8 have a smaller crystal size (~ 4 nm) than that of PLL-3 (~ 7 nm). This was mainly attributed to the effects of chelating agent (citric acid) used. It is well known that citric acid is a weak complexing agent for a range of metal

ions (such as Sn^{4+}) [7]. In the pH value range (7 – 9) used in the present study, Sn^{4+} mainly exists in the form of hydrates, which tends to form large agglomerates [16]. This was observed in the sample PLL-1 to PLL-3. With the addition of citric acid, i.e., $r_M > 0$, citric ligands can be easily trapped onto the surface of the agglomerates in SnO_2 sols through chelating bonds between the group RCOO^- and Sn^{4+} [17]. In fact, trapped citric ligands act as a dispersant for tin oxide sols through electrostatic repulsion or steric hindrance. In such a

Fig. 6.6 X-ray diffraction patterns of calcined (a) PLL-3, (b) PLL-4, and (c) PLL-8.

way, finely dispersed sols containing very small and stable particles could be synthesized for the solutions with $r_M \geq 0.5$, as confirmed by the observed Tyndall effect (Fig. 6.7) [18]. On the other hand, trapped citric ligands could also provide surface active sites for controlled self-assembly through RCOO^- with NH_3^+ group on the side chain ($\text{C}_4\text{H}_8\text{NH}_2$) of PLL template. It is evident that the presence of surface ligands and organic templates will reduce the contact area between SnO_2 nanoparticles. Both of the above reasons result in fine crystal size, as observed for PLL-4 and PLL-8.

Fig. 6.7 Simple experiment showed Tyndall effect when red laser beam passing through clear chelated SnO_2 sols with r_M of 2 (right), suggesting the presence of SnO_2 nanoparticles. No scattering was observed from de-ionized water (left).

TEM characterization in Fig. 6.8-a clearly discloses the textural features of PLL-8 worm-like particles with wall thickness of ~ 25 nm. Selected area electron diffraction (SAED) rings in Fig. 6.8-c again confirmed the cassiterite phase of nanoparticles. The outer most ring may come from either (112) or (301) plane or both, since the positions of two diffraction

Fig. 6.8 TEM characterization of calcined PLL-8, (a) image of wormlike particles, (b) HRTEM image of nanoparticles on the wall, and (c) diffraction pattern of selected area in (b).

rings are very close. The average crystal size of SnO_2 nanocrystals was estimated at ~ 4 to 5 nm through TEM images, which agrees well with XRD analysis. It is also noted that randomly distributed mesopores formed from the decomposition of citric ligands were interspersed on the macropore framework [7].

6.4 N_2 Gas sorption measurement

To identify the mesoporosity, samples with coral- and worm-like structures were characterized by N_2 gas-sorption experiments. As shown in Fig. 6.9, both samples gave the type-IV Brunnauer-Emmett-Teller (BET) isotherm with an H2-type hysteresis loop indicating the presence of mesopores [19]. The large increment of adsorbed volume at the relative pressure range of ~ 0.6 to 0.7 was due to the capillary filling of mesopores. It is well known that microporous metal oxides (e.g., TiO_2 , Al_2O_3 , and SnO_2 , etc) of large surface area can be prepared in the form of xerogels [20, 19]. However, the pore volume is usually very low (< 0.1 cc/g). Using PB-PEO block copolymers, Antonietti et al. [21] obtained well-ordered mesoporous SnO_2 with pore volume of 0.28 cc/g, while the surface area was only 66 m^2/g due to the relatively large crystal size ($6 - 8$ nm). The BET results here showed that the samples with coral- and worm-like structures have large surface area ($190 - 210$ m^2/g) as well as high porosity ($63 - 64\%$). The large surface area could be mainly attributed to the small SnO_2 nanocrystals. Multilevel porous structures further facilitate the gas sorption. The formation of mesopores are confirmed by BET gas sorption analysis as well as TEM image (Fig. 6.8). Mesopores are formed on the walls of coral- and sea-worm like particles upon the removal of citric ligands. Macropores are the hollow channels formed upon the removal of

PLL molecules, as shown in Fig. 6.4 and 6.5. For gas sensing application, large surface area usually gives high sensitivity while porous structure may reduce the response time.

Fig. 6.9 BET nitrogen gas isotherms of calcined (a) PLL-4 and (b) PLL-8, and their respective BET surface area and pore volume.

6.5 Gas sensing property measurement

Fig. 6.10-a shows a representative gas sensing response transient of SnO₂ thick film (fabricated using PLL-8 powder) subjected to 500 ppm H₂ at 200 °C – 400 °C. This sample showed a maximum sensitivity $k_{M, H_2} = 47$ at 300 °C. Sensitivity is defined as the ratio of electrical resistance (R_{air}) of sensor in air over that (R_{gas}) in the tested gas environment. This is double as compared to the reported value of $k_{M, H_2} \approx 23$ at 350 °C of phosphoric acid treated mesoporous SnO₂ (PA/m-SnO₂) fabricated by other group [4]. It is interesting to note that compared to the surface area of PA/m-SnO₂ (305 m²/g), our sample has a smaller specific surface area (210 m²/g) and slightly larger crystal size. Generally, SnO₂ powder with

Fig. 6.10 (a) Temperature-sensitivity dependence of PLL-8 sensor to 500 ppm H₂, and (b) Gas concentration-sensitivity dependences of PLL-8 sensor to H₂, CO and CH₄ at 300 °C.

smaller crystal size and larger surface area has higher gas sensitivity. However, many other factors such as contact resistance and surface defect concentration can also influence the gas sensitivity. Because of different preparation methods, same material may have different electrical resistance due to different surface defect concentration. Here, the reason for the improved gas sensitivity of PLL-8 is not clearly understood. But, it is likely due to different electrical properties of the samples. This is reflected by the fact that the maximum H₂ gas sensitivity (at 500 ppm concentration) appeared at 300 °C in the present study, while it is 350 °C in the Ref. 6.4.

In order to demonstrate the selectivity behavior, the response transients of PLL-8 were measured at 300 °C for three different common reducing gases, i.e., H₂, CO, and CH₄ with concentration ranging from 50 ppm to 3000 ppm. As illustrated in Fig. 6.10-b, the sensitivity of PLL-8 to H₂ is much higher than CO and CH₄ for the all measured concentrations. It was also noted that within the concentration level employed in the study, the saturation sensitivity to H₂ gas was not yet reached even at 3000 ppm concentration. As shown in Fig. 6.11, the adsorption response to H₂ is faster than CO at low gas concentration. The reason may be due to higher diffusivity of H₂ than CO. Compare with the response time ($t = 20$ min) of PA/m-SnO₂ synthesized elsewhere [4], the response time of PLL-8 to H₂ gas at 500 ppm concentration is only 4.6 minute. The quick response time obtained from PLL8 is likely due to the multilevel porous structure which permits faster gas diffusion.

Fig. 6.11 Response transients of PLL-8 gas sensor to H_2 and CO at (a) 50 ppm, (b) 100 ppm, (c) 200 ppm, and (d) 500 ppm concentration, measured at 300 °C .

6.6 Infrared absorption analysis

Infrared (IR) spectrum of the as-prepared PLL-8 (Fig. 6.12-a) shows two absorption bands centered at 1650 cm^{-1} (amide I) and 1551 cm^{-1} (amide II), corresponding to the CONH group on the PLL backbone in trans conformation [22]. IR is a common technique used to distinguish the secondary structures of polyamino acids [15], e.g., α -helix, β -strand or random coil. Only the IR absorption curves from PLL-8 samples are shown, since very

Fig. 6.12 IR absorption analysis of (a) as-made PLL-8 and (b) PLL-8 calcined at 450 °C.

similar results were obtained for PLL-4 samples. Another absorption band at 627 cm^{-1} in as-prepared PLL-8 indicated that the PLL template was mainly α -helix conformation. The band at 1470 cm^{-1} was probably resulted from N-H bending of NH_4^+ residues [23]. Two other peaks between 1400 and 900 cm^{-1} can be attributed to the vibrations from citrate complex and Sn-OH bonds [7, 24]. No significant band shift of amide side groups (at 1650 cm^{-1} and 1551 cm^{-1}) were detected, implying that there is no direct amide-metal coordination [15].

This suggests that self-assembly was mainly achieved through electrostatic force between the deprotonated citric ligands trapped onto tin oxide hydrate and the positively charged ε -amino groups (NH_3^+) below its intrinsic $\text{p}K_a$ value (which is equal to the minus of the logarithm of acid dissociation constant, $\text{p}K_a = \sim 10.5$) [25]. After calcination, two peaks at $\sim 614 \text{ cm}^{-1}$ and 470 cm^{-1} are observed, both are related to the vibration of Sn-O-Sn bridge [20] due to the formation of SnO_2 .

6.7 Structure formation mechanism

Based on the structural characterization and chemical analysis observed above, a possible formation mechanism is proposed. As reviewed in chapter 2, homo/hetero polypeptides have been successfully used to template vesicles or core-shell microspheres of quantum dots/silica. Here, it was found that distinct morphology other than spheres could be obtained by self-assembly of pre-stabilized PLL template with ligand-assisted SnO_2 precursors. The morphology of product was mainly determined by the concentration of the chelating agent (citric acid). Fig. 6.13-a illustrates the molecular entities involved in the reaction system, i.e., PLL helix chains, deprotonated citric ligands (L^{3-}) and L^{3-} -chelated SnO_2 precursors ($[\text{Sn}(\text{OH})_x\text{L}_y]_n$). As discussed previously, citric ligands which are trapped on the SnO_2 surface can effectively stabilize SnO_2 sols by mutual repulsion and/or steric hindrance. They also act as chemically active sites that interact with the PLL side groups ($-\text{C}_4\text{H}_8\text{NH}_2$) through columbic attraction ($\text{COO}^-/\text{NH}_3^+$). In the case of silicate, the majority of the precursor species are very small condensed oligomers ($< 1 \text{ nm}$) due to the maximized solubility and dissolution rate of silica at neutral pH [26]. Hence, amorphous silica shell can be nucleated and grown onto the spherical template with little effect on the template morphology. However for non-siliceous oxides, the precursors usually grow rapidly and form crystals of a few nanometers even in the presence of organic stabilizers [27]. The use of citric

Fig. 6.13 (a) Molecular entities involved in self-assembly, and (b) A schematic diagram of assembly process showing the formation of column ($r_M = 0.5$) and wormlike ($2.0 \leq r_M \leq 4.5$) hybrid materials.

ligands in the sols brought about an decrease in precursor size and increase in surface charge density of SnO₂ particles. These induced the formation of new template morphologies in the present study of SnO₂. It is reasonable to expect that the number of chelated ligands and surface charge density of individual SnO₂ nanoparticle increase with r_M , which is the citric acid/Sn molar ratio. When r_M is low (≤ 0.5), the negatively charged inorganic nanoparticles can disturb the equilibrium of the pre-formed sphere template through $\text{COO}^-/\text{NH}_3^+$ electrostatic interaction. This may re-distribute and re-assemble the PLL supramolecules to form new column morphology, as schematically shown in Fig.6.13-b. When citric ligand concentration increases beyond a critical level (i.e., $r_M \geq 2$), the templates seek a different morphology (e.g., distorted sea-worm like morphology) to counter balance the increase in local interface charge density. Hence the template is distorted in the manner shown in Fig. 6.13-b. It is not clearly understood why PLL-8 has a smaller size (~ 200 nm wide) than PLL4 (~ 400 nm wide). However r_M is not the sole factor determining the product morphology, as the stability of the template is also influenced by the ionic strength as well as the pH of the solution when r_M is fixed (PLL-7 to PLL-11). Table 6.1 shows that when r_V is ≥ 0.3 , worm-like particles were not observed in PLL-9, -10, and -11, presumably because of the increased ionic strength (Cl^-) which destabilized the organic template [5]. It was also noticed that the proportion of worm-like particles in PLL-12, -13 and -14 reduced as the pH value increased from 8.4 to 8.7. In fact, the mixture became transparent immediately upon the addition of clear inorganic sols into the turbid PLL solution when the mixture pH was higher than ~ 9.1 . The resultant samples showed no evidence of self-assembly due to the deterioration of interfacial forces. This result is consistent with the findings elsewhere [5] that the stability of template diminishes as pH is close to the $\text{p}K_a$ value of ϵ -amino groups. Nevertheless, the reason for the lack of self-assembly of PLL-5 and -6 is still not clearly understood in the

present study. Systematic investigation on acid-base interaction and coordination behavior by varying complexing agent and polyamino acids will need to be undertaken.

6.8 Conclusion

In summary, unique multilevel porous SnO_2 architectures consisting of SnO_2 nanocrystallites (4- 5 nm) were synthesized through aqueous self-assembly in which citric acid and pre-stabilized poly-L-lysine (PLL, $M_w > 30$ kD) perform as chelating agent and template, respectively. Samples were systematically characterized by TG analysis, FESEM, X-Ray powder Diffraction, (HR)TEM, N_2 gas sorption measurements, and IR absorption technique. The results showed that with proper control of processing parameters (i.e., citric/Sn molar ratio (r_M), inorganic/PLL solution volume ratio (r_V), and pH value), distinct template morphologies, such as, coral/sea worm-like porous structures with macropore channels (width from ~ 0.1 to $0.4 \mu\text{m}$) and mesopores (4 - 6 nm) could be obtained after the removal of the organics at 450°C . Furthermore, the presence of chelator not only stabilized the SnO_2 sols, but also functioned as surface active sites for binding with PLL side chains through electrostatic interaction ($\text{COO}^-/\text{NH}_3^+$). It has been demonstrated that citrate ligands also affected SnO_2 crystal growth during heat treatment and was responsible for the formation of mesopores. BET results showed that the samples have outstanding combination of large specific surface area ($190 - 210 \text{ m}^2/\text{g}$) and high porosity (63 – 64%) arising from multilevel porous structures. Thick film sensors fabricated using PLL-8 SnO_2 exhibited improved gas sensing performance to H_2 . The formation mechanism was discussed by considering the interfacial charge density matching and the acid-base behavior at the precursor/template interfaces.

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Chapter 7

Conclusion

Chapter 7 Conclusion

7.1 Surfactant templated mesoporous SnO₂ & SnO₂-SiO₂

Disordered mesoporous SnO₂ and SnO₂-SiO₂ (Si/Sn molar ratio ≤ 0.25) particles with high thermal stability have been fabricated in an aqueous route using neutral surfactant (tetradecylamine) as template. In the case of pure mesoporous SnO₂, it is shown that thermal treatment at low temperature (i.e., aging at 75 °C) has great influences on both micro- and mesostructural properties. In general, longer aging time can enhance the thermal stability of SnO₂ crystals and porous frameworks against calcination. When the sample was aged for 12 days, SnO₂ with very small crystallites (33 Å), large surface area (189 m²/g) and uniform mesopores (~ 32 Å) is successfully synthesized after the removal of template at 400 °C. The surface area obtained here is the highest value ever reported for pure mesoporous SnO₂ templated by surfactants. The important role of surfactant in creating mesoporous structure has been confirmed. It has also been found that hydrothermal treatment at 120 °C can further improve the structural stability of samples. However, continuous increase of HT temperature beyond 120 °C has the contrary effects. Because of the relatively large crystal growth and agglomeration, disordered mesoporous structure was lost for all the samples after calcination at 500 °C, although larger mesopores are still present in the structures.

In a subsequent study, silica doping technique was applied to further improve the mesostructural stability in a facile pathway. The effects of various working parameters including surfactant/Si/Sn molar ratio, calcination temperature and period are investigated. Results show that with proper control of doping process and dopant concentration, disordered mesoporous SnO₂ frameworks with very high thermal stability and large surface area can be fabricated without applying prolonged time aging and hydrothermal treatment. Due to the

effective inhibition of SnO₂ crystal growth by amorphous SiO₂ located at grain boundary interfaces, the final disordered mesoporous SnO₂ structure is sustainable to prolonged calcination period (e.g., 400 °C for 55 h) as well as elevated calcination temperature (even up to 800 °C). The maximum surface area and pore volume obtained are 362 m²/g and 0.33 cc/g, respectively, after calcination at 400 °C when surfactant/Si/Sn ratio is 0.3: 0.25: 1.

Although the mesopores obtained are disordered in both cases, it is shown that micro- and mesostructural properties, such as crystallites size, surface area, pore volume, as well as mesopore pore size distribution can be well manipulated by careful control of key processing parameters. In addition, the facile and low temperature doping method developed in the present work is also expected to be useful for other metal oxide systems. Mesoporous SnO₂ and SnO₂-SiO₂ with high thermal stability, large surface area, small crystallites and controlled porosity are promising candidates for gas sensors, catalysts, and electrode used in organic solar cells.

7.2 Poly-l-lysine templated macroporous/mesoporous SnO₂

Multilevel porous SnO₂ architectures are fabricated through self-assembly pathway in which poly-l-lysine and citric ligands are responsible for the formation of macro- and mesopores, respectively. Surface modification and stabilization of SnO₂ precursors using complexing agent (citric acid) is critical to the formation of well defined assemblies driven by electrostatic interaction (COO⁻/NH₃⁺). Systematic investigation has identified the influences of several processing parameters, i.e., citric/Sn ratio, pH, and SnO₂/template solution ratio. Results show that successful self-assembly can be obtained only in a confined pH range while the texture of the final structure (either coral- or worm-like texture) can be manipulated by controlling the citric/Sn and/or SnO₂/template solution ratios. Upon the

removal of template and chelator at 450 °C, both types of structures demonstrate the hierarchical porous and/or hollow textures consisting of macropore channels (width from ~ 0.1 to 0.4 μm) as well as mesopores (4 - 6 nm). Improved H₂ gas sensing performance is measured due to facilitated gas diffusion within the multi level porous structures. In fact, fast hydrolysis and particle agglomeration are the main drawbacks for many metal oxide systems in self-assembly synthesis. Therefore, the surface modification method/concept developed in this work has a wide application, and more attractive porous nanostructures of other oxides can be expected.

Chapter 8

Future Work

Chapter 8 Future Work

In this work, much attention has been focused on the synthesis, characterization, structure/morphology control, and structure formation mechanisms study of mesoporous and macroporous $\text{SnO}_2/\text{SnO}_2$ -based materials. Although there are still many works to do, unfortunately there are not enough time to pursue each of them. Some “worth to do” ideas are presented as follows.

8.1 Mesoporous SnO_2

Continuous works can be conducted for: 1) mesostructural ordering improvement, 2) metal doping, and 3) gas sensing study.

1) Two pathways should be studied to improve the mesostructural ordering: synthesis modification and change of short neutral surfactant to supramolecular block copolymers. Evaporation induced self-assembly (EISA) in non-aqueous solvent has been demonstrated to synthesize highly ordered mesoporous materials. Long range and ordered surfactant liquid crystals might be formed in situ the evaporation process, and therefore can facilitate the formation of ordered mesostructure. Instead of short surfactant template used in the present study (micelle size of ~ 2 nm), one alternative is the use of block copolymer with large molecular weight and amphiphilic property, e.g., F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, $M_w = 13388$) and P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_w = 5820$). Theoretically, these templates will form micelles with diameter of ~ 10 to 15 nm which are larger than that of freshly prepared SnO_2 crystals (~ 2 nm). Therefore, it can be expected that small inorganic precursors are easier to assemble surrounding the large surfactant micelles without changing the preformed liquid crystal phase significantly.

2) Impurity doping of metal dopants (Sb, Zn, Pd, Ag, and In, etc) can largely modify the electrical and optical properties of SnO_2 material. Although many studies have been reported for conventional micro- and nanocrystalline SnO_2 , little work has been conducted for metal-doped mesoporous SnO_2 material. Related study will help to explore the improved or new properties of metal-doped mesoporous SnO_2 .

3) The obtained mesoporous $\text{SnO}_2/\text{SnO}_2\text{-SiO}_2$ demonstrate very high thermal stability and large surface area; therefore it will be of great interest to study the gas (e.g., H_2 , CO , CO_2 , and $\text{C}_2\text{H}_5\text{OH}$) sensing behaviors of these materials. Large enhancement in sensor sensitivity and response time can be expected.

8.2 Polypeptide templated materials

Successful self-assembly of surface modified SnO_2 precursors onto polypeptide template reveals the great possibility to synthesize hollow structures of many other metal oxides (e.g., ZnO , TiO_2 , Nb_2O_5 , and Fe_2O_3) and biominerals (e.g., hydroxyl apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). Based on the present work, some ideas are proposed for future study: 1) synthesis of other oxides, 2) synthesis of hydroxyl apatite, and 3) variation of the template size/composition.

1) During the self-assembly, most of metal oxides precursors suffer from fast hydrolysis and severe agglomeration which can prevent the formation of well defined structure and morphology. Citric acid is known as a common complexing agent for a wide range of oxides. Therefore, the surface modification and stabilization concept developed here should also be applicable to other metal oxides materials.

2) Hollow and porous hydroxyl apatite (e.g., HA microsphere) will be promising candidates for many bio-related applications such as medicine and bone/dental repair. The

active surface of poly-L-lysine containing -NH_3^+ groups on the side chain should be able to serve as the nucleation sites for HA formation. Therefore, it will be of great interest to explore the use of polypeptide for templating hollow HA structure and such work will definitely enhance our understanding on biomineral formation under mild and biomimetic condition.

3) Dimension of the final hollow structure should be controllable by varying the template size. Two possible ways can be applied: variation of polypeptide molecular weight and changing the polyanions/template molar ratio.

Appendix

Appendix

A-1 Small-angle X-ray scattering pattern of T_{2/150} calcined at 400 °C

SAXS pattern of T_{2/150} after calcination at 400 °C shows that no mesoporous structure was obtained, as reflected by the absence of any reflection peak.

Fig. A-1 SAXS pattern of T_{2/150} after calcination at 400 °C.

A-2 BET results of $T_{2/150}$ and $T_{2/200}$

As shown in Fig. A-2, type IV isotherms indicate that mesoporous structure was obtained for $T_{2/150}$ and $T_{2/200}$ after calcination at 400 °C.

Fig. A-2 BET N₂ gas sorption isotherms of (a) $T_{2/150}$, and (b) $T_{2/200}$ calcined at 400 °C.

A-3 TGA results of S_0 and $S_{0.06}$

Thermogravimetric analysis curves of as-prepared S_0 and $S_{0.06}$ show that surfactant have been successfully incorporated into the materials, as reflected by the large weight loss (~ 35 wt.%) up to 400°C .

Fig. A-3 TG analysis curves of as-prepared S_0 and $S_{0.06}$.

A-4 FESEM image of PLL-1

The FESEM image of PLL-1 shows that irregular SnO_2 particles were obtained.

Fig. A-4 FESEM image of PLL-1, $r_M=0$, and $r_V=0.05$.

A-5 FESEM images of PLL-9, -10, and -11

Fig. A-5 Selected FESEM images of (a) PLL-9, (b) PLL-10, and (c) PLL-11 after calcination at 450 °C. These samples show fragments of SnO₂ particles suggesting absence of self-assembly with polypeptides.