Ordered mesoporous non-oxide materials

Yifeng Shi,* Ying Wan* and Dongyuan Zhao*†

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Ordered mesoporous inorganic non-oxide materials attract increasing interest due to their plenty of unique properties and functionalities and potential applications. Lots of achievements have been made on their synthesis and structural characterization, especially in the last five years. In this critical review, the ordered mesoporous non-oxide materials are categorized by compositions, including non-oxide ceramics, metal chalcogenides, metal nitrides, carbides and fluorides, and systematically summarized on the basis of their synthesis approaches and mechanisms, as well as properties. Two synthesis routes such as hard-templating (nanocasting) and soft-templating (surfactant assembly) routes are demonstrated. The principal issues in the nanocasting synthesis including the template composition and mesostructure, pore surface chemistry, precursor selection, processing and template removal are emphatically described. A great number of successful cases from the soft-templating method are focused on the surfactant liquid-crystal mesophases to synthesize mesostructured metal chalcogenide composites and the inorganic-block-organic copolymer self-assembly to obtain non-oxide ceramics (296 references).

1. Introduction

The invention of ordered mesoporous materials in the early 1990s, separately by Japanese scientists and Mobil's scientists, has inspired prominent research interests in this area.1–3 With attractive properties, including high surface areas, periodically arranged monodispersed mesopore space, tunable pore sizes, alternative pore shapes, uniform nanosized frameworks, large...
particle sizes, and abundant compositions, ordered mesoporous materials have shown great potentials in various fields.\textsuperscript{4,8} A large number of reaction/interaction sites are related with the high surface area, which benefit for the interface related processes such as sorption, catalysis and electrochemistry application.\textsuperscript{4,5,9} The uniform and tunable large pores afford enough monodispersed void spaces for large molecules and hence break through the size restriction of conventional microporous materials, showing advantages in large molecule involved catalysis, adsorption, separation, drug and DNA delivery, etc.\textsuperscript{10–12} The uniform nano-sized framework structures bring nano-effects (surface and quantum effects), which endow the materials good performance in sensors, Li-ion batteries and nanodevices.\textsuperscript{13–16} In general, the entire particle sizes of mesoporous materials are in the micrometre range, favouring industrial processes, for example adsorption and filtration separation, but without losing their nano advantages. The diversified pore wall compositions lead to wide applications in luminescence, photovoltaic, and electronic devices.

The fabrication of mesoporous materials is mainly concerned with building monodispersed mesosized (2–50 nm) pore space and arranging them in a long-range ordered array.\textsuperscript{8} Two kinds of templates are generally used: supramolecular aggregates such as surfactant micelle arrays, and preformed mesoporous solids such as silicates and carbons.\textsuperscript{17} The corresponding synthesis routes are commonly described in literatures as soft- and hard-templating (nanocasting) methods (Fig. 1), respectively. Two classes of ordered mesostructures are thus obtained and integrated as components in mesoporous materials family: continuous framework structures with cylindrical or spherical mesopores and their counter- replica structures, which can also be regarded as nanowire/nanosphere arrays.\textsuperscript{17}

In the soft-templating method, the ordered mesopore arrangement is achieved by the cooperative assembly of amphiphilic surfactant molecules and guest species that is driven by the spontaneous trend of reducing interface energy.\textsuperscript{18,19} The constituents and properties of the organic molecule templates are critical for mesostructures. Therefore, these molecules are also called structure-directing agents (SDAs). Aqueous solution synthesis and evaporation induced self-assembly (EISA) routes are normally adopted.\textsuperscript{20} In a solution synthesis route, the key issue is that the guest species ought to have a controllable aqueous sol–gel process. While, in an EISA synthesis, the use of non-aqueous solvent media greatly slows down the hydrolyzation and condensation rate of metals species, which greatly benefits for the formation of their ordered mesostructures.\textsuperscript{21,22} In both cases, a strong interaction between SDAs and precursors is necessary to assemble ordered target materials and avoid the macroscale phase separation. The hard-templating method is also known as nanocasting because the entire manufacturing procedure is similar with the traditional casting method but in nanoscale.\textsuperscript{23} In this approach, the regular arrangement comes from the preformed ordered mesoporous template.\textsuperscript{17,24,25} It should be mentioned that the small mesotunnels inside the template’s pore wall are necessary for nanocasting. They can be replicated to small nanorods and thus support the nanowire/nanospheres which are replicated from the primary mesopores, to form stable mesostructured replica arrays (Fig. 1).\textsuperscript{24,25} Otherwise, the obtained replicas can not maintain their mesostructures once the templates are removed, resulting in isolated nanowires/nanospheres or low-symmetry mesostructured products. This synthesis strategy avoids the control of the cooperative assembly of SDAs and guest species and the sol–gel process of guest species, making it quite successful in plenty of materials. Siliceous, metal oxides and carbon based materials dominated the research society of mesoporous materials due to their plenty of practicable precursors and controllable sol–gel processes for these materials.

The huge family of inorganic non-oxide compound materials, including carbides, nitrides, sulfides, selenides, fluorides, etc. are of great interests because of their broad functional properties. Carbides and nitrides, such as SiC, TiC, WC, Si₃N₄, are well-known high temperature ceramics.\textsuperscript{26–31} ZnS, CdSe, GaN, InP, GaAs, Bi₂Te₃, and CuInGaSe₂ are the most popular semiconductors that are widely used in luminescence devices, bio-labelling, photovoltaic and thermoelectric devices, photocatalytic water splitting, and contamination remediation.\textsuperscript{32–38} Besides the wide applications, the fundamental science interests in producing ordered mesoporous non-oxide materials involves the modulation of band gap, emission properties, thermal and electrical conducting behaviours by constructing ordered mesostructures. Given that the walls of mesoporous non-oxide materials are generally less than 10 nm and patterned as a long-range ordered array, special quantum confinement effects may arise from this kind of nanostructure. The ordered mesoporous semiconductors with open continuous framework structures have been named as “exo-semiconductors” or “quantum antidots”, which have attracted considerable interests, both in theoretical and experimental.\textsuperscript{39–42}

Mesoporous inorganic non-oxide materials have been rarely studied until recently. The major reason lies in the facts of the lack of appropriate controllable sol–gel process for non-oxide materials and their air- or water-sensitive feature. Very recently, several improvements have been achieved in the synthesis of non-oxide mesoporous materials, including utilization of inorganic polymers as a ceramic precursor,\textsuperscript{43} nanocasting strategy,\textsuperscript{44} in situ post transformation from solid–gas reaction,\textsuperscript{45} and organic–organic cooperative assembly,\textsuperscript{46}
which lead to a rapid growth of publications. Here, we review the substantial progresses in the synthesis, characterization and applications of mesoporous inorganic non-oxide materials, including non-oxide ceramics (SiC, SiCN and BN etc.), metal chalcogenides, carbides, nitrides and fluorides. Although several other special classes of materials can also be technically qualified as non-oxides, they are set apart in this review, for example, metal–organic framework (MOF)\textsuperscript{47} and covalent organic framework (COF)\textsuperscript{48} materials with pore sizes larger than 2 nm, ordered mesoporous polymers and their derived carbons,\textsuperscript{49} metals and alloys.\textsuperscript{50} We are going to focus this review only on simple inorganic non-oxide compound materials due to their generalities in synthesis and characterization.

2. Ordered mesoporous non-oxide ceramic materials

2.1 Mesoporous SiC materials

Silicon carbide is a kind of well-known wide bandgap semiconductors and high temperature ceramics. The strong covalent Si–C bonds in the crystal lattice produce a very hard, strong and stable material. Well crystallized silicon carbides can be exposed in air above 1000 °C and strongly basic or acidic solution such as concentric NaOH and HNO\textsubscript{3} aqueous solution, without serious damage on its structure. The high thermal and chemical stability makes SiC a good catalyst carrier in rigorous conditions.\textsuperscript{51}–\textsuperscript{54} The reaction heat can be fleetly transmitted away in strongly exothermic reactions owing to the large thermal conductivity, and therefore the side reactions and catalyst sintering can be avoided. However, SiC materials with high specific surface areas, which are desirable for catalyst carriers, are seldom reported. Most of the reported SiC materials have a low surface area less than 20 m\textsuperscript{2} g\textsuperscript{-1}.\textsuperscript{55,56} Mesoporous SiC is expected to improve the surface area.

Carbothermal reduction is the most common way to fabricate SiC materials, in which the silica precursor is reduced by carbon.\textsuperscript{57,58} Guo and co-workers reported a carbothermal reduction method for the synthesis of disordered mesoporous SiC with specific surface area of 112 m\textsuperscript{2} g\textsuperscript{-1} by using carbon-silica nanocomposite aerogel as a precursor.\textsuperscript{59} The surface area can be increased to 204 m\textsuperscript{2} g\textsuperscript{-1} by adding 1.23 mol% nickel as a catalyst.\textsuperscript{60} The pore size distributions are broad, ranging from 4 to 50 nm, due to the absence of SDA in the synthesis. Parmentier \textit{et al.} prepared an ordered mesostructured SiO\textsubscript{2}/C nanocomposite by depositing carbon (propylene as a precursor) into the pore channels of mesoporous silica MCM-48. The nanocomposite was then treated in an inert atmosphere at high temperatures (1200–1450 °C) to produce SiC.\textsuperscript{61} Yang and Lu \textit{et al.} also fabricated mesoporous SiCs using the similar synthesis strategy but with different carbon sources \textit{i.e.} sucrose and furfuryl alcohol.\textsuperscript{52,63} The obtained SiC materials have low surface areas around 120–190 m\textsuperscript{2} g\textsuperscript{-1} with less mesoporosity, and are irregular particles, whiskers or even nanotubes rather than ordered mesoporous SiC, suggesting that the final products did not replicate the ordered mesostructure of the SiO\textsubscript{2}/C precursors. Periodic mesoporous organosilica (PMO) materials with a large number of preformed Si–C bonds inside the frameworks were also utilized as precursors to prepare SiC material via carbothermal reduction at 1350 °C.\textsuperscript{64} The ordered mesostructure collapse after reaction. These phenomena can be explained by the reaction mechanism of carbothermal reduction.\textsuperscript{57,58,65,66}

The total reaction can be described as carbon reduces silica to silicon carbide and carbon itself is oxidized to CO or CO\textsubscript{2} (eqn (i)).

\[
\begin{align*}
C + \text{SiO}_2 & \rightarrow \text{SiC} + \text{CO} + \text{CO}_2 \\
C + \text{SiO}_2 & \rightarrow \text{SiO} + \text{CO} \\
\text{SiO} + 2\text{C} & \rightarrow \text{SiC} + \text{CO} \\
\text{SiO} + 2\text{CO} & \rightarrow \text{SiC} + \text{CO}_2
\end{align*}
\]

Actually, the reaction is a multi-step process. Lots of reactions can be conducted in the systems. Some of them are listed above. The key process produces gas phase intermediate SiO as shown in eqn (ii). Gaseous SiO can transport in the reaction chamber, resulting in a non-\textit{in situ} transformation process in carbothermal reduction and mesostructure destruction. Subsequently, if SiO is consumed by carbon (eqn (iii)), the final products partially duplicate microstructure of carbon precursors.\textsuperscript{65} Otherwise, the reaction (eqn (iv)) is dominated and the morphology of the final products is totally different with their precursors. For example, Yang \textit{et al.} found that whiskers and nanotubes could be formed.\textsuperscript{62}

Very recently, Shi \textit{et al.} reported a magnesiothermic reduction synthesis method for nanostructured SiC materials by using silica/carbon nanocomposite as precursor and Mg as reducing agent at 600–900 °C.\textsuperscript{67} The magnesiothermic reduction is demonstrated to be a pseudomorphic transformation process, in which the ordered hierarchical macro-/mesoporous SiO\textsubscript{2}/C nanocomposite precursor is converted to the corresponding nanostructured crystalline SiC.\textsuperscript{67} The ordered macroporous structure is maintained fairly well after the conversion, while the ordered mesostructure was partially collapsed, as in the case of magnesiothermic reduction synthesis of mesoporous silicon.\textsuperscript{68} This synthesis method can be extend to other carbides like TiC and WC, and is expected to be a general approach for various nanostructures.\textsuperscript{67}

Silicon carbide can be directly synthesized by reacting silicon with carbon in an inert atmosphere at high temperatures (> 1200 °C, Si + C → SiC). Liu \textit{et al.} adopted this way to synthesize crystalline mesoporous SiC materials from ordered mesoporous carbon.\textsuperscript{69} The mesostructural regularity is totally...
lost after reaction, which maybe related to the huge volume expansion (more than 200% estimated from molecular weight and density) upon insertion of silicon into the carbon framework. The product is well crystallized, and possess a surface area about 147 m² g⁻¹ and a wide pore-size distribution between 5 and 20 nm.

Chemical vapour deposition (CVD) is another common route for the synthesis of SiC materials, in which gas phase silicon and carbon precursors decompose at high temperatures and react with each other to form SiC on the substrate. Kaskel and co-workers deposited SiC into mesoporous silica MCM-48 and SBA-15 channels via chemical vapour infiltration (CVI) process by using dimethylchlorosilane as a precursor. ⁷⁰ The mesopores are blocked upon deposition, which inhibited a truthful replication. The SiC product after removal of the silica template show no long-range mesostructure ordering. Notably, a BET surface area of 508 m² g⁻¹ and a pore volume of 0.96 m³ g⁻¹ are obtained, which are much higher than those of previously reported SiC materials.

An alternative method for the synthesis of SiC materials is pyrolysis of silicon-containing inorganic polymers that are also called as pre-ceramic polymers, such as polycarbosilane (PCS) and polysilanes (Fig. 3). ⁷¹⁻⁷⁵ The polymers can be easily liquefied by dissolving in an organic solvent or just by melting. Complex structures can thus be shaped, especially with the assistance of various templates, solidified and in situ converted to SiC after low-temperature pyrolysis (700–1200 °C). Kim and co-workers firstly synthesized disordered mesoporous SiC materials by using PCS as a precursor and silica spheres as a template. ⁷⁶

In 2005, Shi and Zhao reported the first synthesis of ordered mesoporous SiC materials by using silica SBA-15 or KIT-6 as a hard template and PCS as a precursor via nanocasting. ⁷⁷ PCS precursor is filled into the pore channels of the ordered mesoporous silica template and in situ converted to SiC by 1400 °C pyrolysis under nitrogen. Highly ordered mesoporous silicon carbide replicas with the two-dimensional (2D) hexagonal or 3D bicontinuous mesostructure are prepared after etching template (Fig. 2). The ordered mesoporous SiC products have high specific surface areas (up to 720 m² g⁻¹), large pore volumes (~0.8 cm³ g⁻¹), narrow pore size distributions (at the mean value of ~3.5 nm) and are composed of amorphous SiC and β-SiC nanocrystals. As expected, the open mesopore structures have high thermal stability up to 1400 °C in inert atmosphere. ⁷⁷ By comparison, the thermal stability of disordered mesoporous SiCs synthesized by CVI method using SBA-15 as a hard template is much lower. ⁷⁰,⁷⁸ The surface area decreases to below 50 m² g⁻¹ at 1300 °C, which is possibly due to the much lower loading efficiency in the CVI process than that in Shi’s synthesis. ⁷⁸

Later on, the replications of ordered mesoporous SiC materials were separately reported by several groups via a similar nanocasting process. ⁷⁹⁻⁸¹ The specific surface area values of the ordered mesoporous SiC are in the range of 260 to 800 m² g⁻¹. Although the synthesis parameters can affect the microstructure of PCS-derived SiC, ⁸²⁻⁸⁵ we contribute the large difference in surface areas to the free carbon content that are originated from the PCS precursor. If the PCS precursor contained alkyl side groups, a large number of free carbons are determined in the final SiC products due to the high carbon/silicon ratios of the precursor, for example, more than 18 wt% in Shi’s case (a PCS from National University of Defense Technology, China), 12 wt% in Kaskel’s (a PCS with low melting point, Sigma-Aldrich), and 20 wt% in Shiraiishi’s (type L PCS, Nippon Carbon Chemical Inc.) samples. ⁷⁷⁻⁷⁸,⁸¹ The free carbons can form abundant microporosity, and thus attribute a lot to the high surface areas. Accordingly, the obtained mesoporous SiCs have the surface areas higher than 500 m² g⁻¹. By comparison, AHPCS (SMP-10 from Starfire Systems, Inc.) contains almost no alkyl side groups and thus leads to the formation of stoichiometric SiC with undetectable free carbon residual. ⁷⁹ As a result, the mesoporous SiC material prepared from AHPCS by Kim and co-workers has a low surface area (260 m² g⁻¹). ⁷⁶

Kaskel and co-workers further studied the effect of synthesis conditions on the surface area, pore size distribution and structural regularity of mesoporous SiC materials. ⁸⁶ The high molecule-weight PCS precursors (> 3500 g mol⁻¹) yield a low structural regularity, possibly due to the insufficient filling of the precursors inside micropore voids of the mesoporous silica template. Interestingly, a tubular SiC array with a high surface area of 926 m² g⁻¹ can be obtained by pyrolysis of AHPCS SMP-10 in vacuum. In this case, the SiC replicas are prominently coated on the silica surface of the mesopores rather than homogeneously filled in the pores. ⁸⁶ The mesostructure can be regarded as an analog of CMK-5, a tubular carbon nanopipe array. ⁸⁷⁻⁹⁰

One important issue in the above mentioned syntheses is the high oxygen content of these ordered mesoporous SiC replicas. Almost all samples contain more than 10 wt% oxygen in frameworks. ⁷⁷⁻⁷⁹,⁸¹⁻⁸⁶ The products are actually a mixture of SiC and silicon oxycarbide (SiOC), which can be confirmed by ²⁸Si NMR and FTIR spectra. ⁷⁷,⁷⁹ The oxygen is originated from the silica template, the impurity species in the argon or nitrogen gas flow and PCS itself which may be partially oxidized during storage and nanocasting manipulation process. Small amount of oxygen can increase the oxidation resistivity of SiCs and partially contribute the high surface areas. However, it may decrease chemical stability, thermal and electric conductivity simultaneously.

Kaskel and co-workers reported that silicon could be selectively removed from the ordered mesoporous SiC materials by the treatment of chlorine gas at 700–1000 °C, leaving a specially residual mesoporous carbon as a product. ⁹¹ The mesoporous carbon products show high surface areas ranging from 1830 to 2820 m² g⁻¹, and clear bimodal pore-size distributions: 2–6 nm of mesopores and 0.5–1.3 nm of micropores (Fig. 4b). The large surface areas, high pore volumes, uniform bimodal meso-/micropore features make the porous carbons as an excellent candidate for catalyst supports, gas adsorbents, and high-rate electrochemical capacitors. ⁹¹⁻⁹⁳ The ordered mesopores allow fast ionic transport into the bulk particles, leading to excellent frequency response; and the abundant micropores provide high accessible surface, resulting in a high specific capacitance up to 170 F g⁻¹ in electrical double layer capacitor (EDLC).

A direct synthesis of ordered mesoporous SiC materials by pyrolyzing a self-assembled lab-made diblock copolymer...
Si₃N₄ materials have low density, high temperature strength, wear resistance, chemical inertness, bio-compatibility and basic good fracture toughness, mechanical fatigue and creep properties. The chemical compositions of silicon nitrides are diverse, e.g. Si₃N₃, Si₅N₇, Si₃N₄, SiN, while the most important one is Si₃N₄. Si₃N₄ materials have low density, high temperature strength, superior thermal shock resistance, excellent wear resistance, good fracture toughness, mechanical fatigue and creep resistance, chemical inertness, bio-compatibility and basic property, featuring many applications in reciprocating engines, bearings, metal cutting and shaping tools, arc welding nozzles, artificial articulation and solid base catalysis. Some applications, in particular the latter two, require high surface areas, as well as large and tunable pore sizes. These motives promote the development of mesoporous silicon nitrides to replace dense materials.

Silicon nitride can be directly synthesized via silicon nitridation (Si + N₂ → Si₃N₄). A high temperature above 1400 °C is required to activate nitrogen gas to produce pure phase Si₃N₄. However, the fact that silicon melted as a liquid above 1410 °C makes silicon nitridation unfeasible for the preparation of Si₃N₄ nanostructures.

Pyrolysis of silicon diimide at a high temperature above 1000 °C can produce silicon nitride. In general, the silicon diimide precursor is prepared by reacting silicon halides with ammonia at a low temperature (~0 °C). Kaskel and co-workers firstly adopted this method in the synthesis of disordered mesoporous silicon imido nitride with a high surface area (700 m² g⁻¹). After loading with potassium, it is an efficient superbase catalyst for alkene isomerization. The pore size of the mesoporous silicon nitrides can be tuned from 5.6 to 9.1 nm by changing silicon precursors (SiCl₄, SiBr₄ and SiI₄), solvents (pentane, toluene and tetrahydrofuran), as well as the calcination temperature. Mesoporous silicon nitride, silicon aluminum nitride, silicon boron nitride, etc. have been similarly synthesized by pyrolysis of silicon diimide gel, silicon aluminum imide and silicon boron imide gels precursors at 1000 °C in ammonia atmosphere. However, no surfactant template is presented in all these syntheses, leading to disordered mesostructures.

Carbothermal reduction of silica (SiO₂ + C + N₂ → Si₃N₄ + CO) has been industrially used to produce silicon nitride. Silica can be reduced to gas phase SiO by carbon as an intermediate at the first step. This is a non-in situ transformation process as mentioned above, and unsuitable for mesoporous pure phase Si₃N₄. Inagaki and Kapoor reported a synthesis of mesoporous silicon oxynitride via a direct nitridation with nitrogen gas using periodic mesoporous organosilicas (PMOs) as a precursor. It is found that the pyrolyzed PMO material can directly react with nitrogen to form Si-N bonds at 900–1050 °C. This process can be regarded as a special carbon thermal reduction. However, only less than 0.5 wt% nitrogen is detected by the XPS analysis in the final products, which much like a N-doped silica. Liu and co-workers reported a carbothermal reduction synthesis for mesoporous oxynitrides by using silica SBA-15 as a precursor. Carbon is filled inside the pore channels of the mesoporous silica via a conventional nanocasting process in advance. Then the mesostructured silica-carbon nanocomposite is heated at 1360 °C under nitrogen gas for carbothermal reduction. Residual carbon is finally removed by calcination in air at 600 °C. However, because nitrogen is not an efficient nitridation agent, only 16.5 wt% of nitrogen is incorporated into the silica networks. The calcination in air might further reduce the nitrogen content.

If ammonia serves as a nitridation agent, the oxygen atoms in the silica can be substituted by nitrogen atoms step by step at ~1450 °C (SiO₂ + NH₃ → Si₃N₄ + H₂O + N₂ + H₃). The partially nitridized intermediate contains silicon, oxygen and nitrogen, forming Si₅N₄O mixed covalently bonded
network, so called as silicon oxynitride.\textsuperscript{106–109} This process has been clearly tracked by $^{29}$Si NMR spectra, as shown in Fig. 5. The $^{29}$Si NMR spectrum of the silica precursor shows a strong resonance at about −109 ppm, attributed to the SiO$_4$ linkage units. During the ammonia treatment, the resonance signals gradually move to the high chemical shift direction, and finally centre at about −49 ppm, which can be attributed to the SiN$_4$ linkage units. The intermediate samples show broad signals because of involved linkage units: SiO$_4$, SiNO$_3$, SiN$_2$O$_2$, SiN$_3$O and SiN$_4$.

Marcos and Hauskuri firstly reported the synthesis of ordered mesoporous silicon oxynitrides by directly treating as-made silica MCM-41 with ammonia gas at 950 °C.\textsuperscript{110} The obtained silicon oxynitrides retain ordered mesostructures with high surface areas of 880–1100 m$^2$ g$^{-1}$ and narrow pore size distributions at mean value of ~2 nm, as well as contain 9.7–12.9 wt% of nitrogen. The surfactant-free MCM-41 could also result in ordered mesoporous silicon oxynitride. But the nitrogen content reduces to 7 wt%, due to the low reactivity of condensed silica. Subsequent research work was focused on the enhancement of nitrogen content, which was believed to be fundamental for improvement of alkalinity of silicon oxynitride. The attempts mainly included the increase of nitridation temperature and change of silica precursors. Xia and Mokaya synthesized mesoporous MCM-41- and MCM-48-type silicon oxynitride materials containing 8.6–25.1 wt% of nitrogen, by tuning the nitridation temperature from 850 to 1150 °C.\textsuperscript{111,112} SBA-15 has a much thicker wall than MCM-41 and MCM-48, endowing it higher thermal stability to survive ammonia nitridation. Liu and co-workers used SBA-15 as a precursor to produce mesoporous silicon oxynitride.\textsuperscript{113} Mesoporous products after ammonia nitridation at 1000, 1050 and 1100 °C contain 14.3, 20.6 and 24.3 wt% of nitrogen, respectively. Further increasing the temperature to 1150 °C results in a material containing 27.6 wt% of nitrogen; but the mesostructure partially collapses and the surface area decreases to 230 m$^2$ g$^{-1}$.\textsuperscript{114} Instead of the powder form, ordered mesoporous silicon oxynitride thin film was reported by using the mesoporous silica film as a precursor via a similar ammonia nitridation process.\textsuperscript{115,116}

The nitrogen content in silicon oxynitride products mainly depends on the ammonia treatment temperature.\textsuperscript{114,117–119} Previous works showed that non-porous silica could be completely converted to silicon nitride at above 1400 °C.\textsuperscript{106,107} However, the treatment temperature is higher than the thermal stability of mesoporous silica hard-template and silicon oxynitride product (about 1100–1150 °C in ammonia atmosphere).\textsuperscript{111,114} As a consequence, partial oxygen atoms are substituted by nitrogen atoms upon the nitridation. The mesoporous...
silicon oxynitride materials contains 10–25 wt% of nitrogen (the theoretical nitrogen content of Si3N4 is 39.94 wt%), and more than 20 wt% oxygen atoms in the final products.

Iwamoto and Ishizu reported the improvement of the nitrogen content to 33.8 wt% by simply increasing the ammonia flow rate and decreasing the weight ratio of the silica precursor in a plug flow reactor. More recently, a further increase of the nitrogen content up to 38.8 wt% was achieved, which is quite close to the theoretical value for pure phase Si3N4. The high nitridation degree is believed to be attributed to the use of plug-flow reactor. It is the alumina boat container that prevents the smooth diffusion of ammonia and water byproduct, and thus leads to a sufficient nitridation in previously published reports.

Shi et al. developed a nanocasting synthesis method to synthesize mesoporous silicon (oxy)nitrides by using PCS as a precursor and ordered mesoporous carbon (CMK-3) as a hard template. The PCS precursor is first filled into the pore channels and then converted to silicon nitride upon pyrolysis in ammonia atmosphere up to 900 °C. Almost all carbon atoms in the precursor can be gradually substituted by nitrogen atoms. The intermediate containing silicon, nitrogen and hydrogen atoms with trace amount of residue carbon is formed. The Si–N–H networks are not well cross-linked with lots of Si–NH2 and Si–NH–Si units. A following high-temperature (1400 °C) pyrolysis process is adopted to get a rigid Si–N network.

Considered that the carbon template was unstable in ammonia atmosphere above 900 °C, the high temperature treatment is conducted under nitrogen. Thereafter, the carbon template can be removed by ammonia gas at 1000 °C to avoid oxidation. The obtained ordered mesoporous silicon nitride has a 3D bicontinuous cubic mesostructure (Ia3d), a BET surface area of 384 m² g⁻¹, a pore volume of 0.71 cm³ g⁻¹ and a mean pore size of 5.7 nm. The formation of silicon nitrides is confirmed by FT-IR and 29Si NMR techniques. The Si, N, O, and C contents are 54, 32, 11, and 2.0 wt%, respectively. Although no oxygen-based chemicals are involved in the synthesis, the final product still contains 11 wt% of oxygen, which might be caused by the impurity in industry ammonia and the residual oxygen in the carbon template.

Ordered mesoporous silicon oxynitride materials can be used as a solid base catalyst, showing a good catalytic activity for Knoevenagel condensation. It is found that the base strength of the mesoporous silicon oxynitrides is stronger or at least comparable to that of MgO. Mesoporous silicon oxynitrides are stable in inert atmosphere during Knoevenagel condensation (without distinct basic site leaching); in H₂ atmosphere up to 800 °C, and in water, butanol and toluene at room temperature. But they are not stable in oxidation atmosphere. The incorporated nitrogen is almost entirely removed by calcination in air at 800 °C. This may limit their practical applications. Ordered mesoporous aluminosilica oxynitrides, borosilica oxynitrides and alumino-phosphate oxynitrides have also been prepared by using a similar ammonia nitridation method from the corresponding aluminosilica, borosilica and alumino-phosphate precursors. These materials show both acidic and basic catalytic activities in one.

2.3 Mesoporous SiOC materials

Introducing a third element, such as oxygen, nitrogen, boron, titanium, aluminum and zirconium, etc. into SiC-based materials can greatly affect their performance of the ceramics. For example, silicon oxy carbide (SiOC) and silicon carbo nitride (SiCN) both show better thermal stability against crystallization and phase separation, oxidation resistivity and mechanical strength than pure SiC materials owing to their complex-covalent chemical bond networks.

PMOs contain both Si–C and Si–O structure units in the framework, favouring the formation of SiOC materials. Babonneau and co-workers reported the synthesis of mesoporous SiOC materials by pyrolyzing PMOs at a high temperature of about 1000 °C under argon flow. If the PMO precursor has a 2D-hexagonal phase, all Si–C bonds are totally cleaved after calcination. The product is composed by phase separated free carbon and silica domains. No SiO2–C4–x structure units can be detected by 29Si NMR. Beginning with the 3D-cubic PMOs mesostructures, the same calcination process yields the formation of SiOC materials with the maintenance of the initial cubic mesostructure and particle morphology. 29Si NMR spectra clearly show the formation of SiOC1 and SiC2O2 tetrahedral units, suggesting a successful formation of ceramics SiOC frameworks. About 12 wt% of free carbon is presented in the final product.

It’s quite surprising that the 2D hexagonal and 3D cubic mesostructures synthesized from the same microstructure unit (O1.5Si–CH2–CH2–SiO1.5) (1000 °C) leads to totally different microstructure in final product upon the same argon protected pyrolysis, namely two phases SiO2/C nanocomposite and SiOC. This phenomenon can be observed both in small pore PMOs synthesized by using cetyltrimethylammonium chloride (CTAC) and large pore PMOs synthesized by using triblock copolymer P123 or F127 as a SDA. The reason is still unclear.

Kim and Nghiem heated an as-made surfactant-organic silica-silica nanocomposite in nitrogen, which was synthesized by using anionic surfactant as a SDA as reported by Che, to prepare ordered mesoporous SiOC materials. In this nanocomposite precursor, the mesoporous silica framework is functionalized with organic groups on their pore surface by R-(CH2)3-(Si–O–)3 units. The products show ordered mesostructure and the structure is stable in air up to 800 °C. 29Si NMR spectra show the presence of SiC2O4–x tetrahedral units, indicative of the formation of SiOC materials. The authors claimed that no free carbon was detected by 13C NMR. But the facts that weak SiC2O4–x signal in its 29Si NMR spectrum, the super high surface area (1762 m² g⁻¹) and its capability for H₂ sorption might suggest the present of some free carbon species on the pore surface.

Shi et al. reported an atmosphere-assisted in situ composition transformation for the ordered mesoporous SiOC materials by using PCS as a precursor and mesoporous carbon as a template. Firstly, Si/C nanocomposites are prepared by filling PCS precursors into the channels of the ordered mesoporous carbon CMK-3 template, and following pyrolysis at 900–1500 °C in an inert atmosphere. The carbon template is then removed by calcination in air at 500 °C.
Simultaneously, the SiC frameworks are converted to silicon oxy carbides because of partial oxidation. A typical product synthesized at 1400 °C is composed of Si: 46.2, O: 46.3, and C: 7.5 wt%. The TGA analysis clearly confirms the absence of free carbon; that is, all carbon atoms are connected with silicon and oxygen via covalent bond networks. The mesoporous SiO-C materials possess the BET surface area from 250 to 420 m² g⁻¹, pore volumes from 0.44 to 0.76 cm³ g⁻¹, and mean pore size distributions from 4.9 to 8.4 nm, depending on the synthesis parameters. Although the synthesis method adopts a repeat nanocasting process (from mesoporous silica hard template to carbon and then from carbon to the final SiC material), the final materials show some advantages: no free carbon in the final products, large pore size and tunable mesostructure.

Recently, Fuertes and Suárez used a sub-micrometre-size solid core/mesoporous shell (SCMS) silica particle as a hard template and polyacrylamide (PCMS, FW 800, Aldrich) as a ceramic precursor to fabricate mesoporous SiO-C capsules via nanocasting strategy. PCMS is firstly filled inside the channels of the SCMS shells and then converted to SiOC by heating to 1000 °C under nitrogen. Mesoporous SiOC with hollow spherical morphology is finally obtained by etching the silica template. The SiOC capsules contain Si, C, H, and O in the following amounts (wt%): Si 28.1, C 34.3, H 3.2 and O 34.4 and can be converted to mesoporous silica capsules by calcination at 700 °C in air.

2.4 Mesoporous SiCN and SiBCN materials

2.4.1 Nanocasting synthesis. Generally, SiCN materials are synthesized by pyrolyzing inorganic polymeric precursors those contain Si, C, and N on their molecular chains. For example, polyvinylsilazane (PVS) contains –Si–N– repeating units in its main chain and alkyl side groups connected to the main chain by Si–C bonds, and therefore can directly transform into SiCN materials in inert atmosphere. Kim and co-workers directly utilized PVS (from KION Corp.) as a precursor and mesoporous carbon as a hard template for nanocasting synthesis of ordered mesoporous amorphous SiCN materials. XPS spectra of the synthesized mesoporous SiCN product (Fig. 6) clearly show the presence of Si, N, Si-C, C-N and C-O, confirming the formation of SiCN materials. Two kinds of ordered mesoporous carbon, CMK-3 and CMK-8, are used as hard-templates to produce mesoporous SiCN materials with 2D-hexagonal and 3D-cubic gyroidal structures. The carbon template is removed by heating the SiCN/C at 650 °C for 2 h in air. EDX results reveal low oxygen contents (~3 wt%) in mesoporous SiCN products, implying that the products possess quite high oxidation resistivity. The mesostructures can be well retained upon reheating at 1000 °C in air, and the surface area of the 2D and 3D mesoporous SiCN structures slightly reduces from 247 and 472 to 235 and 427 m² g⁻¹, respectively. The oxygen contents of the samples after re-treatment at 1000 °C are not reported.

Shi et al. nanocast ordered mesoporous SiCN by using PCS as a precursor, which is much stable in air than PVS and thus benefits for manipulation. Ordered mesostructured SiC nanocomposites are obtained in the first step using mesoporous carbon CMK-3 as a hard template. The SiC/C intermediates are treated by ammonia gas flow at 1000 °C. During this treatment, mesoporous carbon templates are removed and the SiC frameworks are partially nitridized to form SiCN products. The mesoporous SiCN materials show an ordered mesostructure with surface areas about 200–300 m² g⁻¹ and pore sizes about 5–8 nm. The silicon, nitrogen, carbon and oxygen contents are 54.5, 11.6, 21.2 and 12.6 wt%. No free carbon is detected by TGA analysis. Oxygen might come from industry ammonia gas. The detailed elemental distribution profile is unclear in these products. The SiCN materials are probably a uniform mixture with more nitrogen on the pore surface and more carbon inside the framework.

Besides ternary SiOC, SiON and SiCN ceramics, mesoporous tetraarylsilicoboron nitride (SiBCN) materials were prepared by Miele and co-workers using a lab-made boron-modified polysilazane ([B(C₂H₄SiCH₃NCH₃)₃]ₙ) as a precursor and mesoporous carbon CMK-3 as a template via the nanocasting strategy. The obtained mesoporous SiBCN material has an ordered 2D-hexagonal mesostructure with amorphous framework, a high surface area of 600 m² g⁻¹ and a large pore volume of 0.61 cm³ g⁻¹. Elemental analysis shows the chemical molar ratio of Si : B : C : N being 3.0 : 1.0 : 4.2 : 3.5. Less than 2 wt% of oxygen is recorded in the final product, which could be contributed to the utilization of mesoporous carbon template and non-oxygen chemicals. IR, Raman and XPS analyses confirm the formation of Si-N, B-N, C-C and C-N bonds, and the absence of Si-C bond in the final frameworks. The complex covalently bonded networks show excellent thermal stability in both air and ammonia atmospheres.

2.4.2 Direct synthesis based on block copolymer self-assembly. Preceramic polymers have unique features, including lyotropic, easy shaping, and in situ conversion to non-oxide ceramics with the maintenance of the morphology. These features, together with the well-reported self-assembly of block-copolymers for ordered mesostructures via the microphase separation mechanism, endow them with the feasibility to directly fabricate ordered mesoporous ceramics. Several ordered mesoporous SiCN materials have been synthesized via direct assembly method by using pre-ceramic polymer as a precursor. This method has been proved to be feasible for mesoporous BN, BCN and SiC, as being described below.

Two synthesis pathways have been developed for the directly fabrication of ordered mesoporous non-oxide ceramics as shown in Fig. 7. The first pathway is based on the self-assembly of a single inorganic-block-organic copolymer (pathway I in Fig. 7), in which the inorganic segment serves as a ceramic precursor and the organic block as a mesopore template. Ordered mesostructure is formed due to the microphase separation. The inorganic domain is then cross-linked to fix the mesostructure by the cross-linking agent, as well as by heating or radiation induced self-cross-linkage. The mesostructures are pyrolyzed at high temperatures in inert atmosphere to convert the inorganic part to non-oxide ceramics, and remove the organic segments to open mesopores. In the second pathway, an organic block copolymer is used as a SDA and an inorganic polymer is used as a ceramic precursor.
Hierarchically porous PtSiCN catalysts with micrometre scale patterns can be similarly synthesized, by using PI-b-PDMAEMA as a mesostructure template, PS spheres as a macro pore template, polydimethylsiloxane (PDMS) mold as a micro-metre scale pattern producer, Ceraset as an inorganic precursor and dimethyl(1,5-cyclooctadiene) platinum as a crosslinking agent.\textsuperscript{163} The catalyst has homogeneous dispersion of Pt nanoparticles on the hierarchically porous SiCN frameworks, and show high activity and thermal stability up to 600 °C in methane oxidation.

Before the above successful synthesis of mesoporous SiCN, Wiesner and co-workers also reported a synthesis of similar nanocomposites with lamellar mesostructure from Ceraset and block copolymer polyisoprene-block-poly(ethylene oxide) (PI-b-PEO).\textsuperscript{162,164} But the mesostructure collapses upon pyrolysis due to the absence of support between the ceramic layers. Wan et al. reported a similar synthesis from preceramic polymer Ceraset and block copolymer polybutadiene-block-poly(ethylene oxide) (PB-b-PEO).\textsuperscript{165} The morphology of the pure block copolymer is hexagonally packed cylindrical mesophase in which the PEO cylinders are surrounded by the PB matrix. Incorporation of Ceraset leads to an increase in the volume of the PEO domain, and thus a mesophase transformation from the cylindrical to lamellar phase can be occurred. Disordered mesostructured product was achieved by a simple pyrolysis procedure (directly from room temperature to a high temperature using a constant rate) due to the unstable lamellar structure after pyrolysis.\textsuperscript{165} If an as-made high Ceraset containing (62 wt%) lamellar phase mixture was cured at 100 °C for 12 h and then at 200 °C for 5 h before the pyrolysis, an mesophase transition occurred, resulting in hexagonally packed PB cylinders surrounded by PEO/Ceraset matrix.\textsuperscript{166} In this case, the pyrolysis (500–800 °C) yields the mesopores due to the decomposition of PB and PEO species. However, mesoporosity is gradually destroyed once the temperature reaches 1400 °C.

Directly connecting the pre-ceramic segment to an organic polymer \textit{via} covalent bonds is a more simple strategy to avoid macrophase separation, as shown in Fig. 7 (pathway I). The key issue for the self-supported ceramic framework is the formation of a continuous inorganic segment matrix phase after microphase separation. In this case, the volume fraction of inorganic polymer should be considered. Otherwise isolated inorganic domains are formed, and surrounded by organic matrix mesophase or unstable lamellar phase. Accordingly, isolated ceramic particles, nanorods or layers are the products. For example, the mesostructure of the as-made thin films prepared by the self-assembly of polystyrene-b-polyferrocenylethylmethacrylate (PS-b-PFEMS) is PFEMS cylinder surrounded by PS matrix (its volume fraction is 0.8–0.6).\textsuperscript{167,168}
The final product was isolated ceramic SiC/C nanorods containing iron oxides. Similar phenomena were also observed in the self-assembly of polybutenylmethyl silacyclobutane-b-polystyrene (PBMSb-b-PS), polypentamethylenvinyl cyclodisilazane-b-polystyrene (PVSA-b-PS) diblock copolymers and PVSA-b-PSb-PVSA triblock copolymer.\(^\text{169,170}\) The inorganic cores with organic shell micelle structure lead to the formation of silicon carbide and silicon nitride based ceramic nanoparticles. Manners and Ozin prepared a PS-b-PFEMS with a high PFEMS volume fraction (0.52), which yielded an unstable lamellar mesophase.\(^\text{171}\)

The first successful direct synthesis of ordered mesoporous non-oxide ceramic (BN and BCN) materials via the pathway I was reported by Wan and co-workers.\(^\text{172}\) A lab-made diblock inorganic-organic copolymer polyboronorbornene-b-polyboronenedecaborane (PNB-b-PDB) is used to assemble ordered mesostructures via the EISA approach (Fig. 8). 2D Hexagonal mesophase is obtained when THF is used as a solvent. Upon pyrolysis at 1000 °C under nitrogen, ordered mesoporous BCN structure is obtained with a high surface area of 950 m\(^2\) g\(^{-1}\) and a narrow pore size distribution centered at ~20 nm, which could be directly observed in its SEM image (Fig. 8). When the nitrogen gas is replaced by ammonia during the pyrolysis at 1000 °C, the obtained material is primarily composed by BN. The carbon atoms in polycarbonare are substituted by nitrogen atoms similarly with the nitridation process from PCS to silicon nitride.\(^\text{125}\)

Afterwards, Kim and Nghiem used a lab-made polyvinilsilazane-b-polystyrene (PVSZ-b-PS) diblock copolymer with the volume fraction of PVSZ from 0.5–0.7 to synthesize ordered mesoporous SiCN ceramic materials.\(^\text{173}\) The mesostructure is controlled by the PVSZ/PS ratio as predicted in the phase diagram. A 2D-hexagonally mesostructured film is coated from a precursor with a high PVSA fraction, and converted to ordered mesoporous SiCN products by pyrolysis at 1400 °C under argon gas flow. The resulting material has a BET surface area of 428 m\(^2\) g\(^{-1}\) and a narrow pore size distribution with a mean pore size of ~5.6 nm. Elemental analysis shows the compositions of Si, C, N and O with 44.72, 25.68, 22.8 and 6.73 wt%.

To directly obtain ordered mesoporous SiC materials, poly-carbosilanes-b-polystyrene (PCS-b-PS) and polyborosilanes-b-polydimethylmethacrylate (PCS-b-PMMMA) diblock copolymers were prepared by Kim and co-workers.\(^\text{174,177}\) Self-assembly of PCS-b-PS results in the ordered mesoporous SiC materials with the 2D hexagonal structure, a mean pore size of 7.8 nm and a high surface area of 1325 m\(^2\) g\(^{-1}\).\(^\text{174}\) The high surface area is possibly caused by large amount of free carbon (Si(C\(_2\))\(_{7,7}\)O\(_{0,29}\)). Burning off free carbon at 1000 °C in air leads to a partially oxidized product (Si(C\(_{1,1}\))O\(_{0,3}\)) with a decrease in surface area (795 m\(^2\) g\(^{-1}\)) and a shrinkage in pore size (4.1 nm). The mesostructural regularity of the porous SiC thin film prepared from PCS-b-PMMMA self-assembly is quite low.\(^\text{174}\) In addition, abundant oxygen in PMMA may affect the purity of the final product. No data for the oxygen content was, however, provided in that paper.

### 2.5 Mesoporous BN, B\(_2\)C and BCN materials

Hexagonal phase of boron nitride (BN) has a similar crystal structure with graphite in which the C–C covalent-bond network is replaced by B–N.\(^\text{175,176}\) Differently, BN is an insulator with a band gap of 5.5 eV. Interestingly, zigzag-terminated BN ribbons exhibit an unexpected metallic behaviour because the dangling bonds located in specific location can cause some unoccupied states just above the Fermi energy level.\(^\text{177}\) Carbon doping can further adjust the hardness and electronic properties of the BN materials. These features, together with interesting physical and chemical properties such as high thermal conductivity, chemical durability and oxidation resistance, make BN a good candidate for high temperature and protective coating material, catalyst support under harsh conditions, molecular adsorption and separation, semiconductors and low dielectric devices.\(^\text{178,179}\)

It has been widely reported that carbon nanostructures can be converted to BCN and even pure BN materials by chemical substitution of B\(_2\)O\(_3\) under nitrogen gas at high temperatures.\(^\text{180–183}\) Zettl and Han treated activated carbon with B\(_2\)O\(_3\) under nitrogen gas flow to prepare disordered nanoporous BN materials with a surface area of 168 m\(^2\) g\(^{-1}\).\(^\text{181}\) Ordered mesoporous carbons was utilized as a source to prepare mesoporous BN and BCN by Vinu et al.\(^\text{184}\) Their results show that amorphous mesoporous carbon can be successfully converted to mesoporous crystalline BN and BCN without any distinctive change in particle morphology between 1400 and 1750 °C. However, the long-range mesostructure ordering loses. Murakami et al. carefully investigated the solid-state \(^1\)B magic-angle spinning NMR spectra of these mesoporous BN and BCN materials.\(^\text{185,186}\) It is found that some of boron atoms are four-coordinated and formed diamond-like structured domains, especially in the BCN samples. These 3D structured domains connect the layered 2D domains to form a “pillar and wall” structure, in good agreement with the HRTEM results reported by Vinu and co-workers.\(^\text{184}\)

Ordered mesoporous BN materials were firstly prepared using tri(methylamino)borazine (MAB) as a precursor and mesoporous carbon CMK-3 as a hard template via the nano-casting approach by Miele, Bios and co-workers.\(^\text{187}\) The synthesis involves the common impregnation-dry protocol, \textit{in situ} conversion from MAB to BN at 1000 °C in nitrogen, and elimination of the carbon template by ammonia treatment at 1000 °C. It is worthy to emphasize the template removal. This process is the first demonstration of the carbon template removal by ammonia in nanocasting synthesis.\(^\text{188}\) Air cannot be used to eliminate carbon in this case because of oxidation of boron nitride at 650 °C. The resultant mesoporous BN have the ordered 2D hexagonal mesostructure with a high specific surface area of ~540 m\(^2\) g\(^{-1}\), a pore volume of ~0.27 cm\(^3\) g\(^{-1}\) and a narrow pore size distribution (centered at 4.4 nm), and contain 35 wt% of boron, 37 wt% of nitrogen and 21 wt% of oxygen.\(^\text{187}\) The high oxygen content may be related to water adsorption usually expected in the compound with a high surface specific area or the carbon template. The ordered mesoporous BN powders can be further sintered into monoliths by spark plasma technique.\(^\text{189}\) The monoliths possess both mesoporosity and macroporosity, and have specific surface areas about 274–428 m\(^2\) g\(^{-1}\), depending on sintering temperature. The synthesis parameters had carefully been investigated: (1) the carbon template. Replacing the CMK-3 template to a 3D cubic mesostructured (\textit{Ia\(_3\)d}) carbon CMK-8 results in a
 BH3 synthesis of mesoporous BN (and BCN) materials by choosing micropores of the hard template. Therefore can well infiltrate into both the mesopores and reason is that MAB has an appropriate molecular size, and found that MAB is one of the best precursors. The possible volume of 0.16 cm$^3$ g$^{-1}$ (3) the precursor. Different precursors, including tri(methylamino)borazine and hexamethyldisilazane have been studied to borazine (MAB), polyMAB, and a mixture of tri(chloro)borazine (MAB)-PDB). The mesostructure can be tuned by the organic solvent and the composition is controlled by the pyrolysis atmosphere: nitrogen leads to BN and ammonia yields BCN. (Bottom) SEM image and high-magnification image (inset) of the obtained mesoporous BN. Reprinted with permission from ref. 172.

mesoporous BN with the cubic structure. The silica hard template. When mesoporous silica SBA-15 is used as a template, a partial filling of MAB occurs in the mesopore voids of SBA-15 due to the hydrophilic nature of the silica template. External pore blockage is probably involved during the synthesis. The product has a low surface area of 140 m$^2$ g$^{-1}$, a small pore volume of 0.16 cm$^3$ g$^{-1}$ and a broad pore size distribution. (3) the precursor. Different precursors, including tri(methylamino)borazine (MAB), polyMAB, and a mixture of tri(chloro)borazine and hexamethyldisilazane have been studied to impregnate into the mesoporous carbon template. It is found that MAB is one of the best precursors. The possible reason is that MAB has an appropriate molecular size, and therefore can well infiltrate into both the mesopores and micropores of the hard template.

Mokaya and Rushton reported a successful nanocasting synthesis of mesoporous BN (and BCN) materials by choosing BH$_3$NH$_3$ (and acetonitrile) as a precursor and SBA-15 as a hard template. The crystallinity is slightly improved relative to that of the above mesoporous BN synthesized by Miele and co-workers; but no small-angle XRD and TEM images are provided to show the mesostructural regularity. A soft-templating synthesis of mesoporous BN using cationic surfactant CTAB as a SDA was reported by Dibandjo et al. Only disordered mesoporous BN structure is obtained. While the materials have high surface areas of 200–800 m$^2$ g$^{-1}$ and moderate pore volumes of 0.59–0.74 cm$^3$ g$^{-1}$, the mesoporosity can be retained up to 1600 ºC under inert atmosphere. The direct fabrication of ordered mesoporous BN materials by using the pre-ceramic polymers as a precursor via the EISA route has been described in section 2.4.2.

More recently, Kaska and co-workers reported a nanocasting synthesis of ordered mesoporous boron carbides by using bisdecaboranyl-hexane as a precursor and mesoporous silica as a hard template. Bisdecaboranyl-hexane is filled inside the mesopore and in situ converted to B$_4$C at 800–1300 ºC. The sample pyrolyzed at 800 ºC shows the highest surface area of 778 m$^2$ g$^{-1}$, but the XRD result reveals its amorphous nature. Only the sample after being pyrolyzed at 1300 ºC features clear crystalline framework on the basis of the XRD pattern. However, the mesostructure collapses. The possible reason is that oxygen and silicon diffused from the silica template during the pyrolysis. The mesostructure therefore undergoes destruction. Elemental analysis indeed reveals that the sample synthesized at 1000 ºC contains 5 wt% of silicon and 9 wt% of oxygen even after six times washing by HF, giving an evidence on the oxygen and silicon diffusion.

2.6 Mesoporous carbon nitride materials

Theoretically, carbon nitrides have five different crystal structures: one is the 2D graphitic C$_3$N$_4$ and the other four are 3D structures, including $\alpha$-C$_3$N$_4$, $\beta$-C$_3$N$_4$, cubic-C$_3$N$_4$ and pseudocubic-C$_3$N$_4$. Carbon nitrides show great research interests because of their distinctively mechanical, conducting, field emission and energy-storage properties. The 3D structured carbon nitrides are super-hard materials whose properties are expected to be similar to or even better than those of diamond and $\beta$-Si$_3$N$_4$. Recently, it is reported that the melon-derived carbon nitride is a semiconductor material and can be used as a high efficient, low cost photocatalyst and solid basic catalyst.

Qiu and Gao prepared an organic polymer by refluxing ethylenediamine and carbon tetrachloride at 90 ºC, which could be directly converted to 2D graphitic carbon nitride at 600 ºC under nitrogen atmosphere. Vinu et al. filled this kind of polymer into SBA-15 to prepare ordered mesoporous carbon nitrides by the nanocasting method. The product has the 2D hexagonal ordered mesostructure, a pore size of ~2.9 nm, a specific surface area of 140 m$^2$ g$^{-1}$, and a pore volume of 0.16 cm$^3$ g$^{-1}$. The C/N ratio can be tuned from 4.5 to 3.5 by increasing ethylenediamine to carbon tetrachloride weight ratio from 0.3 to 0.9. An interesting finding is that the sample with a low nitrogen content exhibits a higher catalytic activity in Friedel-Crafts acylation of benzene than one with high nitrogen content (all catalysts give 100% selectivity). The possible reason is that more defect sites are formed in the pore walls caused from the incomplete polymerization of low amount of ethylenediamine. The 3D cubic mesoporous carbon nitride structure can also be replicated by using SBA-16 as a hard template. Recently, Vinu and co-workers prepared a mesoporous carbon nitride with very small particle size (< 150 nm) by using new mesoporous silica IBN-4 as a hard template (Fig. 9). The carbon to nitrogen atomic ratio (2.3) of this material is higher than those prepared from SBA-15 and KIT-6. The high nitrogen content is believed
to be related to the smaller particle size. This material shows excellent catalysis performance in transesterification of β-keto esters with 100% selectivity as a solid metal-free basic catalyst.\textsuperscript{210}

Antonietti and co-workers used cyanamide as a precursor and a cage-type mesoporous silica as a hard template for nanocasting synthesis of graphitic carbon nitride nanoparticles.\textsuperscript{211} Subsequently, a cage-type mesoporous carbon nitride material was prepared by the same group using silica nanoparticles as a hard template.\textsuperscript{212} Disordered mesoporous carbon nitrides are produced, which possess a pore diameter of \( \sim 12 \) nm and surface areas between 86 and 439 m\(^2\) g\(^{-1}\) depending on the precursor/silica weight ratio. An average value of 0.71 is determined for the C/N atomic ratio, which is quite close to the theoretical one of 0.75. The carbon nitride shows the absorption pattern on its UV-vis spectrum at \( \sim 420 \) nm.

Fig. 9  (a) XRD patterns and (b) nitrogen sorption isotherms of the mesoporous carbon nitride MCN-3 and its hard template mesoporous silica IBN-4; (b inset) FTIR spectrum. SEM image and EEL spectrum of MCN-3. Reprinted with permission from ref. 210.

Fig. 10  (a) The structure scheme and (b) optical properties of graphitic carbon nitride. (c) The SAXS image with their corresponding patterns, and (d, e) TEM images of ordered mesoporous carbon nitrides synthesized from SBA-15 template using cyanamide as a precursor. Reprinted with permission from ref. 204 and 218.
This behaviour is similar to a typical semiconductor with a pronounced band gap. Thomas and co-workers improved the synthesis by adopting silica SBA-15 as a hard template to fabricate ordered mesoporous carbon nitrides. The obtained carbon nitrides have a high surface area of 239 m² g⁻¹, a pore volume of 0.59 cm³ g⁻¹ and a mean pore size of 4.89 nm, as well as a C/N ratio of 0.72 with a residual hydrogen content of 1.88 wt%.

Cyanamide is one of carbon and nitrogen-rich organic compounds which is commonly applied to prepare carbon nitrides. This kind of compounds also include mellem [C₆N₅(NH₂)₃], melamine [C₃N₆(NH₂)₃], dicyandiamide (H₂C₄N₄), ammonium dicyanamide (NH₄[N(CN)₂]), cyanamide (H₂C₅N₂), polymeric melem was formed from the condensation of cyanamide at ~389 °C and converted to carbon nitrides at about 500 °C, that was carefully traced by Wang and co-workers. The condensed carbon nitrides possess an intrinsic semiconductor-like absorption in the blue region of the visible light spectra (Fig. 10). The band gap of the carbon nitride is estimated to be 2.7 eV, which is large enough to overcome the endothermic character of the water-splitting reaction for hydrogen production and oxygen production (1.23 eV). Calculation based on density-functional-theory (DFT) shows that the reduction level of H⁺ ions is well positioned in the middle of the band gap and the oxidation one is located slightly above the top of the valence band. This result indicates that carbon nitride has the potential to act as a photocatalyst for hydrogen production, as well as for oxygen generation but with less efficiency. A steady H₂ production from water can be achieved on condensed carbon nitride under visible light (> 420 nm).

The photocatalytic performance of water splitting on the mesoporous carbon nitrides under visible light were further tested. It shows a remarkable improvement in hydrogen production activity over the bulk material, which can be attributed to the high surface area and the short diffusion length of free carriers. The presence of small amount (3 wt%) of Pt in the mesoporous CN materials is efficient for promoting charge transfer and creating hydrogen desorption sites, can greatly enhance the hydrogen production activity by a factor of ~750.

Disordered mesoporous carbon nitrides have been used as an efficient catalyst, for example, in activation of CO₂ to oxidize benzene and form phenol and CO with 100% selectivity, in cyclotrimerisation of nitriles into triazine derivatives, in the cyclisation of functional alkynes, and in the Friedel-Crafts acylation of benzene by hexanoyl chloride. The acylation avoids the use of metal chlorides and halogenated compounds and is therefore environmentally sustainable. In particular, when formic acid serves as an electrophile, benzaldehyde is produced with a 100% yield. This process can be a very valuable alternative to the usual toluene oxidation route for the preparation of benzaldehyde. Antonietti and co-workers reviewed the application as catalysts in detail in 2008.

Mesoporous carbon nitrides can also be used as a hard template to produce metal nitride nanomaterials by directly heating a metal species loaded sample to 650–800 °C under nitrogen atmosphere. During the heat treatment, the melem-derived carbon nitrides decompose and reactive nitrogen-contained species are formed which can efficiently convert metal salts/oxides to nitrides. Thomas and co-workers developed this strategy and produced plenty of metal nitrides including TiN, GaN, VN and ternary Al–Ga–N and Ti–V–N nanoparticles by using the cage-like mesoporous carbon nitrides both as a hard template and a nitrogen source. Metal oxides such as TiO₂, V₂O₅, Ga₂O₃, Nb₂O₅ and Al₂O₃ can also be converted to corresponding nanostructured metal nitrides. Careful composition analysis reveals that in some cases, such as GaN, TaN and Al–Ga–N, no carbon is detected in the final products. While a large amount of residual carbon is found in some nitrides, for example 15–25 wt% in TiN, NbN, AlN and VN and about 50 wt% in Ti–V–N. The reason for the large difference in the carbon residual amount is still unclear. Domen and co-workers adopted this method to synthesize tantalum nitride nanoparticles using TaCl₅ as a precursor. It is found that TaN is produced under N₂ atmosphere. Pure phase high quality Ta₃N₅ is formed when N₂ is replaced by ammonia atmosphere. The obtained Ta₃N₅ nanoparticle catalyst exhibits a high performance in photocatalytic water splitting. Ordered mesoporous TiN/carbon composite has also been synthesized by using a similar procedure, which will be discussed in section 5.

2.7 Mesoporous phosphorus nitrides

Mohanty and Landskron synthesized an ordered mesoporous phosphorus(v) nitride via the nanocasting strategy, using SBA-15 or SBA-16 as a hard template and (PNCl₂)₃, as a precursor. The mesoporous phosphorus nitrides have the 2D hexagonal (P6₃mm) and 3D body centered cubic (Im3m) structure with amorphous frameworks, which are collected as the final products upon heating the (PNCl₂)₃/silica composite at 700 °C under ammonia gas.

3. Mesoporous metal chalcogenides

Metal chalcogenides, including sulfides, selenides and tellurides, are an important semiconductor family with outstanding electronic, catalytic, semiconducting, optical, and magnetic properties. Recently, sustained efforts have been made to prepare nanoporopus metal chalcogenides because of the promising potential applications based on their unique nature and ultra-high densities of interaction sites due to the high surface area. Among them, ordered mesoporous metal chalcogenides are mostly interested because their band gap may be finely adjusted by tuning the thickness of the uniform nano-sized pore walls to meet application requirements. Ordered mesoporous semiconductors with continuous frameworks and/or isolated pores are regarded as a negative image of an ordered arranged quantum dot/nanorod superlattice. It has been named as “exo-semiconductor” or “quantum antidot” and attracted considerable interests. The challenge is to find suitable synthetic approaches that can lead to high quality mesoporous crystalline metal chalcogenides.

Metal chalcogenides can be divided into two groups based on their chemical nature of the metals. The first group includes cadmium, zinc, indium and copper, and so on. Metal cations in this group can stably exist in aqueous solution and easily be precipitated by S⁻², Se⁻² and Te⁻². The second group includes
Ge, Sn, Sb, Mo, W and so on. The corresponding cations are unstable and tend to form stable metal anions in nature, such as MoO66−. Most of them can form metal–chalcogen cluster anions, which can be used as precursors for the synthesis of mesoporous metal chalcogenides.

3.1 Cadmium, zinc, indium, copper chalcogenides

3.1.1 Soft-templating synthesis. Stupp and Braun firstly reported a synthesis of ordered mesostructured CdS materials with 2D-hexagonal structure by using oligoethylene oxide oleyl ether surfactant [CnH2n+1(OCH2CH2)m–OH] as a SDA via the precipitation reaction route.233 CdS can be precipitated by flowing H2S gas over a hexagonal patterned liquid-crystal solution that is made of the surfactant and cadmium diacetate or cadmium chloride. The specific cation–ethylene oxide interaction is believed to be a key factor in the formation of ordered mesostructure. Cd2+ cations are confined in the hydrophilic region of the surfactant-H2O liquid-crystal mesophase and in situ transformed to CdS, without destroying the ordered mesostructure. The counterions of cadmium salts show significant effect on both ordering and crystal structure of the mesostructured CdS materials.234 The counterions of NO3− and ClO4− can result in an ordered mesostructure; while Cl− and CH3COO− lead to a relatively low regularity. The products in the above four cases are hexagonal wurtzite phase CdS. However, the counterion of SO42− fails in forming ordered mesostructure and the obtained CdS material possesses the cubic zinc blende crystal phase.235

The synthesis of ordered mesostructured ZnS and Cd0.5Zn0.5S is successful by replacing the cadmium salt to other metal salts; but Ag2S, CuS, HgS, CoS, NiS and PbS materials are failed.244 The behind reason is still unclear.

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Fig. 11 Proposed synthesis mechanism of the mesoporous CdS film (a) and CdTe film (b) by H2S deposition and electrodeposition approach, respectively, and their corresponding TEM images: (c) CdS, (d) CdTe. Reprinted with permission from ref. 241.
If H₂Se is used to precipitate cadmium salt in a similar system, ordered mesostructured CdSe can be obtained, in spite of some solid non-porous particles are simultaneously formed. The result implies a complicated process in the H₂Se precipitation. The synthesis of mesostructured ZnS with zinc blende crystalline framework using CTAB as a SDA was reported by Kessler and Li.

Ordered mesostructured CuS materials can be prepared by the cation-exchange method using the above synthesized mesostructured CdS as a precursor. The synthesis process is quite simple, that is immersing the mesostructured CdS powder into a concentrated Cu²⁺ aqueous solution. The Cd²⁺ ions can be then completely replaced by Cu²⁺ and the exchange causes negligible effect on both the crystalline nature and the mesostructural regularity of the composite materials.

In all above cases, the metal chalcogenide-surfactant mesostructures are composed of the inorganic nanoparticle aggregations supported by organic surfactant micelle arrays. The inorganic domains cannot form a self-supported continuous framework. As a result, the mesostructures collapse after the removal of the surfactant templates either by calcination or by solvent extraction. The mesoporosity in these hybrid nanocomposites is inaccessible by guest molecules.

Electrodeposition method can be applied to synthesize mesostructured CdTe films with a much condensed inorganic framework, and thus enable the framework to retain structural regularity after the surfactant template removal. Nandhakumar et al. firstly dissolved cadmium sulfate and tellurium dioxide in the hydrophilic domain of a 2D hexagonal liquid-crystal mesophase, and then electrodeposited CdTe onto a substrate. The obtained mesostructured CdTe film shows strong optical birefringence at energies above and below the band gap energy (1.5 eV), as predicted by the theoretical calculation. The surfactant template could be removed by isopropanol extraction without destroying the ordered mesostructure due to the much condensed framework (Fig. 11c), but no nitrogen sorption isotherms were presented. Stupp and co-workers also demonstrated the electrodeposition synthesis of mesostructured CdTe films by using Cd(NO₃)₂ and TeO₂ as precursors (Fig. 11b). The as-made sample is Te-rich CdTe (75% Te and 25% Cd), but the excess Te could be dissolved by NaOH solution, resulting in a stoichiometric CdTe product without losing mesostructure regularity (Fig. 11d).

### 3.1.2 Nanocasting synthesis

Compared to the soft-templating method, nanocasting synthesis has two notable advantages in the synthesis of mesoporous metal chalcogenides: (1) mesoporous silica is a quite stable template at high temperature, which can survive the calcination process at high temperatures (600–900 °C). Well crystallized metal chalcogenide products can be expected, which can not be achieved in the above described soft-templating synthesis. (2) The silica templates can be entirely eliminated by HF or NaOH without any detectable residues. As mentioned above, it is hard to completely remove all the organic part either by calcination or solvent extraction in the soft-templating synthesis.

The key issue for a successful nanocasting of ordered mesoporous metal chalcogenides is sufficient incorporation of both metal and chalcogen (S, Se, and Te) precursors into the template mesochannels. A precursor containing both metal and chalcogen elements is the first choice. A copper-tellurolate cluster [(Cu₅(TePh)₃)[(PPh₂Et)₃]] is loaded into MCM-41 and in situ converted to Cu₂Te, and a series of cadmium organochalcogenolates such as the type of Cd(XPh)₂TMEDA (X: S, Se, Te, TMEDA: tetramethylthelenediamine) are infiltrated into SBA-15 mesopores to produce CdS, CdSe and CdTe. However, only isolated dispersed nanoparticles are formed in the mesopores of the hard template due to the low yield. Gao et al. prepared a special lab-made cadmium thioiglycolate cluster [Cd₉₀(S₂C₅H₅)₈(N₄O₃)] by refluxing a mixture of Cd(NO₃)₂ and 2-mercaptoethanol solution at room temperature for 24 h. This special precursor can be easily loaded into the template channels because it has many –OH groups and then be in situ converted to crystalline CdS with a high yield (45 wt%) by heating in air at 160 °C. All these features lead to the first successful nanocasting synthesis of ordered mesoporous metal chalcogenides. The mesoporous CdS products possess the highly ordered 2D hexagonal mesostructure with the crystalline hexagonal wurztite phase. The average crystal size is ~6 nm, consistent with the pore diameter of the hard-template SBA-15, and the BET surface area is 101 m² g⁻¹. A blue shift in the PL spectra relative to bulk CdS material is observed due to the quantum size effect.

The above strategy is unfeasible to other compositions due to the use of the special lab-made precursor. An alternative pathway is the use of two precursors to synthesize metal chalcogenides inside the mesopore channels: one is the metal source and another is the chalcogen agent. Metal ions, including Cu²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Hg²⁺ and Ag⁺, are firstly introduced into the mesopores channels by adsorption or ion exchange. The subsequent treatment with H₂S or Na₂S converts the metal ions into sulfides inside the mesopores. However, this synthesis strategy fails in the replication of the ordered mesostructure because only small amount of metal ions are loaded inside the pores. Increasing the loading amount causes serious pore blockage due to the fast precipitation between metal ions and S²⁻.

Liu et al. developed a one-step impregnation method to replicate mesoporous CdS, ZnS and In₂S₃ materials by using thiourea as a sulfur source to replace H₂S and Na₂S. A clear solution is firstly made by mixing thiourea and metal nitrate in ethanol solvent, then impregnated into the channels of SBA-15 template and directly converted to corresponding metal sulfides by pyrolysis at about 150–170 °C in air. Thiourea can well mix with metal ions without forming insoluble precipitation which facilitates one-step introduction of two precursors. It should be mentioned that the UV-vis spectra of the mixture of thiourea and metal nitrates are clearly different from that of their individual solution, suggesting that a complex cluster might be formed and acted as the real precursor. The obtained CdS, ZnS and In₂S₃ materials possess the ordered 2D hexagonal mesostructure with crystalline pore walls consisted of nanoparticles. The CdS nanocrystals are cubic zinc blende phase, different from the hexagonal wurztite obtained in Gao’s case. Since no obvious difference is presented in the synthesis temperature of the two methods, the possible reason for the distinct discrepancy in CdS crystal structure is related to the precursors. Thiruvenkathathan and
Regev dispersed the above mesoporous zinc blende phase CdS materials in water by using sodium dodecyl sulfate (SDS) as a stabilizer.255 Two emission bands are observed from the mesostructured CdS in its fluorescence spectra, a sharp excitonic emission locating near the absorption band edge (513 nm) and a broad weak around 575–675 nm due to surface states and/or defects. The full width half-maximum (FWHM) of the intense emission at 513 nm is as low as 20 nm. The low FWHM and the insignificant surface defect/long wave emission indicate a high spectroscopic quality of mesoporous CdS, even when it is dispersed in water with SDS.

3.2 Sn, Ge, Sb, Mo, W chalcogenides

3.2.1 Soft-templating synthesis. Unlike the metal chalcogenides discussed in section 3.1, this group prefers to form cluster anions other than cations in aqueous solution, making the direct precipitation between metal cations and chalcogenide anions impossible. Alternatively, this group of mesoporous chalcogenides could be prepared via coordination reaction of their cluster anions with the metal cations, which was reviewed in detail by Kanatzidis in 2007.229 Here we would like to give a brief introduction and review the recent progress.

The most common used cluster anions included the tetra-hedral [MQ₄]⁴⁻, the adamantane [M₄Q₁₀]⁴⁻ and the dimeric [M₂Q₆]¹⁻ (M = Ge, Sn, Sb, Mo; Q = S, Se, Te), as shown in Fig. 12. In a typical synthesis, cation surfactant, such as cetylpyridinium bromide (CPBr) and CTAB, is used as a SDA. The surfactant and a salt containing those cluster anions is added as a linking agent. A precipitation is formed at a low temperature. Shi et al. demonstrated an Ordered mesoporous germanium-linked chalcogenide frameworks. Ion exchange with ammonia nitrate is applied to remove EDMHEAB template. Both the 2D hexagonal (P6mm) and 3D cubic (Ia3d) mesostructures can be obtained. Nitrogen sorption analyses show specific surface areas of 400–700 m² g⁻¹, pore sizes of ~3 nm and pore volumes of 0.23–0.32 cm³ g⁻¹. The atomic ratios between Ge and chalcogen can be 9:2 or 9:4, determined by the adding amount of chalcogenes. The band gaps of these semiconductors strongly depend on the chemical compositions, which continuously decrease from the sulfide to selenide, and further to telluride from 1.87 to 1.20 eV. The mesoporous germanium chalcogenides show much high adsorption ability for CO₂ and CH₄ than H₂, indicating that they can selectively separate CO₂ and CH₄ from their mixture with H₂ and thus be potentially used for H₂ purification. In particular, a high CO₂/H₂ separation factor of 39 and CH₄/H₂ one of 28 are achieved on the mesoporous germanium telluride. By replacing the [Ge₉]⁴⁺ cluster by isosctructural [Ge₉Pb₃]⁴⁺, the mesoporous germanium lead tellurides can also be obtained, which are expected to have high separation factor of CO₂/H₂ and CH₄/H₂ due to the more polarizable nature of Pb than that for Ge. Actually, the products exhibit an excellent separation performance of CO₂ and CH₄ over H₂ with respective separation factors of ~88 and 70, greatly higher than organic polymeric membranes and comparable to high-performance ceramic membranes. The excellent behaviour is strongly related to the polarizability of probe molecules (CO₂ > CH₄ > CO > H₂). The adsorbents can be completely recovered by nitrogen flowing at 30 °C and the selective adsorption is repeatable, revealing that they have promising potentials in gas separation.

The remaining disadvantages in the solution synthesis of metal chalcogenides are organic surfactant residual and poor crystallinity. The organic SDAs in mesostructured metal chalcogenides can not be eliminated by calcination in air due to the oxidation trend of these materials. Calcination in inert atmosphere leads to carbon residuals.246 Solvent extraction may destroy the ordered mesostructures in most cases, which only works for the electrodeposition derived samples.241,248,249 Ion exchange method can partially remove the organic surfactant template, but it introduces other cations such as NH₄⁺ into the final products. Even in this case about 6 wt% of organic surfactant is residual in final products.256

3.2.2 Nanocasting synthesis. As mentioned in section 3.1.2, a one-step impregnation method was reported by Liu et al. for the synthesis of ordered mesoporous CdS, InS₂ and ZnS.254 However, the fact that sulfur source, thiourea, decomposed at ~160 °C, limits its use for metal sulfides which can be formed at a low temperature. Shi et al. demonstrated an atmosphere-assisted high temperature reductive sulfuration method for the synthesis of ordered mesoporous metal sulfides.257 Highly ordered mesoporous WS₂ and MoS₂ with 2D hexagonal (P6mm) and 3D cubic double gyroid (Ia3d) mesostructures are successfully synthesized by using the silica SBA-15 and KIT-6 as hard-templates, phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) as tungsten and molybdenum precursors, and a mixture gas of H₂S and H₂ as a sulfur source.257 The ordered mesoporous WS₂ and MoS₂...
materials have a high surface areas of 90–120 m$^2$ g$^{-1}$, pore volumes of 0.15–0.21 cm$^3$ g$^{-1}$ and mean pore size of 4.6–5.0 nm. The high-temperature sulfuration treatment by H$_2$S gas is one of the key issues for this synthesis, because PTA precursor is stable above 300 °C both in air and in hydrogen atmosphere.257,258 High yields (>96 vol%) of metal sulfides from heteropoly acid PTA and PMA should also be mentioned. Consequently, mesoporous WS$_2$ and MoS$_2$ not only replicate the ordered mesostructures from the mother silica hard-templates, but also their particle morphologies.

Ordered mesoporous WS$_2$ and MoS$_2$ replicas show unique crystal orientation: the c-axis of the WS$_2$ and MoS$_2$ layered crystals is always perpendicular to the original mesopore long-direction, which can be observed in the TEM images and confirmed by SAED patterns (Fig. 13, inset a).257 A simple calculation demonstrates that this kind of crystal orientation can lower the surface energy by reducing the unsaturated dangling bonds. The correlation between the crystal and mesostructure orientation is quite interesting. The long range periodically arranged crystal boundary may dramatically affect the transportation behaviour of electron and phonon and thus bring novel properties.

Due to the lack of appropriate selenium and tellurium precursors, mesoporous selenides and tellurides have been rarely reported.

4. Mesoporous metal nitrides, carbides and fluorides

4.1 Mesoporous metal nitrides

The first synthesis of metal nitrides inside the channels of mesoporous silica templates was reported by Fischer and co-workers in 1999.259 A lab-made cluster triazido(trimethylamine)gallium is used as a precursor and in situ converted to gallium nitrides inside the mesopores upon heating at 500 °C under an ammonia flow. Huang and co-workers reported a synthesis of titanium nitrides (TiN) inside the mesochannels of SBA-15 by using Ti(NMe$_2$)$_4$ as a precursor in 2005.260 Before the impregnation of Ti(NMe$_2$)$_4$, the mesopore surface of SBA-15 is modified with methyl groups to minimize reactions between the precursor and the silanol groups. This modification is also believed to benefit the impregnation process. Ti(NMe$_2$)$_4$ is converted to crystalline TiN by heating up to 700–750 °C under an ammonia flow. They also synthesized gallium nitride (GaN)261 and indium nitride (InN)262 nanorods within SBA-15 by using GaCl$_3$ or In(NO$_3$)$_3$ as a precursor and ammonia as a nitrogen source. Crystalline GaN and InN nanorods are collected as products after the removal of the silica template, indicating an insufficient mesostructure replication. The direct band gap of InN nanorods is estimated by UV-vis spectra to be ~1.5 eV, distinctively larger than that of the bulk InN (0.7–0.8 eV). The band gap widening is believed to be mainly caused by the oxygen incorporation.262 The oxygen might be originated from the silica template, which will be discussed later.

Mokaya and co-workers have recently reported the synthesis of mesoporous GaN by using GaCl$_3$ as a precursor and mesoporous carbon CMK-3 as a hard-template via nanocasting synthesis.263 Carbon template is simultaneously removed during the ammonia nitridation of GaN. However, the ordered mesostructure collapses upon the nitridation due to the crystal growth.

Self-supported ordered mesoporous metal nitrides had not been achieved until recently. The synthesis strategy is illustrated in Fig. 14.45 Firstly, the metal precursor is incorporated into the channels of mesoporous silica hard-templates and transformed to mesostructured metal oxides inside the pores upon calcination in air. Then it can be converted to corresponding nitrides by high-temperature ammonia treatment. The silica template is removed before (route A) or after (route B) the ammonia nitridation process, depending on the thermal and chemical stabilities of the aimed metal nitrides.

Route A: the key issue for this route is that the mesostructure of the metal oxides should be stable enough to survival the ammonia nitridation treatment without the support of the silica templates. Mesoporous CoN is a good example.45 Mesoporous Co$_3$O$_4$ is firstly nanocast from the silica SBA-15 hard-template and then nitridizes to CoN by ammonia gas. Products synthesized at 275–350 °C show pure phase of CoN based on their XRD patterns (Fig. 15). The structural regularity of the mesoporous CoN products is almost as well as that of ordered mesoporous Co$_3$O$_4$. The BET surface area (~89 m$^2$ g$^{-1}$) and pore volume (~0.20 cm$^3$ g$^{-1}$) for the ordered mesoporous CoN are similar to that of the oxide. When the reaction temperature is above 375 °C, metallic coalt is formed due to the thermally unstable nature of CoN and the mesostructure totally collapses.264

It is quite interesting that the ordered mesostructure can be perfectly retained, accompanied with the composition transformation from Co$_3$O$_4$ to CoN. The theoretical volume shrinkage from Co$_3$O$_4$ to CoN is about 9.7%, corresponding to a small shrinkage of 3.4% in the domain size. Such a small volume change is believed to be the key factor for a successful pseudomorphic transformation process. Similar phenomena have been observed for in situ transformation and mesostructure inheritance from α-Fe$_2$O$_3$ to Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ materials.265 Mn$_3$O$_4$ to Mn$_2$O$_3$,266 and Co$_3$O$_4$ to CoO.267 The volume change ratios are all quite low: α-Fe$_2$O$_3$ to Fe$_3$O$_4$ (2.2%), Fe$_3$O$_4$ to γ-Fe$_2$O$_3$ (10.3%), Mn$_3$O$_4$ to Mn$_2$O$_3$ (10.5%), Co$_3$O$_4$
to CoO (−11.4%), corresponding to a domain size change of 0.74, 3.56, 3.63 and 3.95%, respectively. Once a large change ratio occurs, the mesostructure inevitably collapses upon the composition transformation. For example, a volume shrinkage of 49.6% is estimated from Co$_3$O$_4$ to Co. As a result, the mesostructure collapses once metal cobalt is formed from mesoporous Co$_3$O$_4$ either by hydrogen reduction at 320 °C or by ammonia reduction at 375 °C.

Route B: mesostructured metal oxide is converted to metal nitrides under the support of the silica template. The key issue in this route is the chemical stability of the product. The aimed products should be stable enough either in NaOH or HF aqueous solution to survive the silica template removal process. Hu and Zhang synthesized a mesostructured Cu$_3$N by using SBA-15 as a hard-template and copper(II) acetylacetone as a precursor. However, because Cu$_3$N is unstable in HF acid or basic solution, only mesostructured Cu$_3$N/silica composites can be obtained as final products. The synthesis of ordered mesoporous CrN reported by Shi et al. was a successful example. Literature results showed that a full nitridation of Cr$_2$O$_3$ to CrN by ammonia gas could only be achieved at a temperature above 800 °C. However, both Cr$_2$O$_3$ and CrN mesostructures are not stable at the high temperature. Therefore, the ammonia nitridation treatment has to be carried out with the support of the silica template. CrN is quite stable in base solution and thus the silica hard-template can be finally removed to obtain pure phase CrN products with ordered mesostructure.

It should be mentioned that the mesoporous silica template is simultaneously nitridized by ammonia above 700 °C in route B, as described in section 2.2. Water is a byproduct and affects the purity of the metal nitrides. Shi et al. carefully investigated the process and found that trace Cr$_2$O$_3$ was always detected in the final products in the nitridation process with a simple linear temperature increasing step followed with a platform step, which was adopted in most syntheses. Therefore, most of previously nanocast metal nitrides might be affected by the impurity byproduct, the steam from the nitridation of mesoporous silica. The incorporation of oxygen in the final metal nitride products had been noticed by Huang and co-workers, but it was not been ascribed to the nitridation of the silica template. Shi et al. demonstrated that a special temperature program could be helpful to prepare ordered mesoporous CrN with high purity on consideration of silica nitridation. The Cr$_2$O$_3$@SBA-15 nanocomposite is firstly heated to 950 °C in ammonia atmosphere and maintained for 500 min to ensure deep nitridation of Cr$_2$O$_3$ and the silica template. Then, the temperature is slowly decreased to 700 °C.

**Fig. 13** TEM images (a, b) and SAED pattern (inset a) of the mesoporous WS$_2$ prepared by the high-temperature reductive sulfuration method, showing the orientation correlation between the WS$_2$ crystal layers and the mesochannels of the silica template: the c-axis of the WS$_2$ layered crystals is always perpendicular to the original mesopore long-direction, as schemed in the inset of (a). Reprinted with permission from ref. 257.

**Fig. 14** The scheme of two pathways for the synthesis of self-supported mesoporous metal nitrides. Reprinted with permission from ref. 45. For simplification, the small rods which connect the adjacent nanowires to support the reversed mesostructure are not presented.

**Fig. 15** Small-angle and wide-angle XRD patterns of the ordered mesoporous Co$_3$O$_4$ and its derived mesoporous CoN materials functioned with the ammonia treatment temperature at 225 to 400 °C. Reprinted with permission from ref. 45.
with a ramp of 0.5 °C min⁻¹. Since the silica template would not further react with ammonia at this temperature, water is negligible in this step because the nitridation of the silica template with ammonia has been accomplished at the high temperature at above 950 °C. Chemical analysis shows that the product contained as low as 2.1 wt% of oxygen. While mesoporous CrN synthesized at 950 °C for 1000 min without the temperature-decreasing process contained >6.7 wt% of oxygen.

Domen and co-workers prepared a mesoporous Ta₂O₃/C₃N₄ material via an EISA route and used it as a precursor to obtain mesoporous Ta₂N₅ by ammonia nitridation at 800–900 °C.²⁷⁸ In order to prevent the mesostructure collapse during the high temperature treatment, the mesoporous Ta₂O₃ precursor is coated with a layer of silica as a support before the nitridation via a CVI method. The silica can be dissolved in a basic solution after nitridation. The ordered mesoporous crystalline Ta₂N₅ product shows a high surface area of 114 m² g⁻¹ and a mean pore size of 3.7 nm. No nitrogen and oxygen content data were provided in their report. After loading Pt, the mesoporous Pt/Ta₂N₅ catalyst shows higher photocatalytic activity for the visible light-driven H₂ evolution than conventional bulk Pt/Ta₂N₅, because the nanosized mesopore framework can promote the charge transfer to active surface sites.

As mentioned before in section 2.6, the melon-derived carbon nitrides can yield some nitrogen-containing species during decomposition at 800 °C, which can nitridize metal oxides to form crystalline nitrides.²²²–²²⁵ Very recently, Thomas and co-workers have adopted this strategy to synthesize ordered mesoporous TiN/carbon composites by using Ti(OEt)₄ as a metal source.²¹⁴ Ti(OEt)₄ is filled into the pre-synthesized ordered mesoporous carbon nitride template and converted to TiO₂, forming TiO₂/C₃N₄ mesostructured nanocomposites in the first step. The TiO₂/C₃N₄ nanocomposite is then heated up to 800 °C in a nitrogen flow for the nitridation. The final product is an ordered mesoporous TiN/C nanocomposite with about 30 wt% of residual carbon. Nitrogen sorption analysis show a high surface area of 439 m² g⁻¹, a large pore volume of 1.01 cm³ g⁻¹ and a uniform pore size distribution at around 7 nm. Other ordered mesoporous metal nitrides can be expected on the basis of established methods for metal oxides.²²²–²²⁵ The limitation lies in that the aimed materials should possess a thermal stability at least above 800 °C.

4.2 Mesoporous metal fluoride materials

Metal fluorides, especially the rare earth metal fluorides, show promising applications in optics, microelectronic and optoelectronic devices used as ultraviolet absorbents, solid-state laser components, optical amplifiers, lighting elements and sensitive bioprobes.²⁷¹–²⁷⁴ Most established synthetic approaches for metal fluorides are based on the precipitation reaction between metal cations and F⁻ anion. However, the precipitation is too fast to be controlled for the soft-templating synthesis of mesoporous metal fluorides. Rare-earth metal fluorides can also be fabricated by thermal decomposition of trifluoroacetate (TFA) complexes such as La(CF₃COO)₃.²⁷⁵ This kind of precursors contains both metal and fluorine elements and can be directly converted to metal fluorides without producing F⁻ ions. This advantage makes these complex precursors promising in the synthesis of metal fluoride nanostructures.²⁷⁶–²⁷⁸

Zhang et al. reported a nanocasting synthesis for ordered mesoporous metal fluorides including LaF₃, CeF₃, PrF₃, NdF₃, EuF₃, TbF₃, FeF₃ and MnF₂ by using their corresponding metal trifluoroacetates as precursors.²⁷⁹ The atomic ratios of fluorine to metal in precursors are much higher than that in the metal fluorides, implying that fluorine-contained byproducts are released during the decomposition. However, this process is interesting, with undetectable erosion on the mesoporous silica template. The final products show ordered mesostructure after removal of the silica template. This facile one-step nanocasting route can be extended to the preparation of ordered mesoporous metal fluorides doped with other rare-earth metals.²⁷⁹ Mesoporous Yb/Er or Yb/Tm (10 wt% Yb³⁺ and 2 wt% Er³⁺ or 2 wt% Tm³⁺) co-doped LaF₃ materials are fabricated by using La(CF₃COO)₃, Yb(CF₃COO)₃, Er(CF₃COO)₃ and/or Tm(CF₃COO)₃ as precursors, and exhibit strong upconversion emissions in visible range under infrared excitation (800 mW, 978 nm). The mesoporous Yb and Er co-doped LaF₃ materials show a green luminescence between 520 and 570 nm and a red luminescence between 630 and 680 nm at the same time. The luminescence intensity of red emission to green emission can be tuned by the specific surface areas of the samples: materials with high surface areas emitted large percentages red luminescence. This phenomenon is ascribed to the high surface defects density and accordingly, the high nonradiative relaxation rates in the samples with high surface areas.²⁷⁹

4.3 Mesoporous metal carbides

Transition metal carbides are interstitial compounds which are formed by incorporating carbon atoms into the sites of their parent metals. These materials possess unique physical and chemical properties, including extreme hardness, high melting temperature, excellent electric and thermal conductivity.²⁸⁰,²⁸¹ Early transition metal carbides show strong similarity of catalytic performance to those of the expensive Pt-group metals (Ru, Rh, Pd, Os, Ir, and Pt), especially in reactions involving the transformation of C–H bonds of hydrocarbons,²⁸¹–²⁸⁴ and therefore potential applications as alternative electrocatalysts in hydrogen and methanol fuel cells.²⁸⁵–²⁸⁷ For example, porous tungsten carbides with high surface areas show excellent catalytic performance on methanol oxidation.²⁸⁸

A soft-templating method was adopted to prepare disordered mesoporous WC materials by using resorcinol formaldehyde resin as a carbon source, ammonium metatungstate salt as a source and CTAB as a SDA.²⁸⁹ The resulting materials possess high surface areas up to 294 m² g⁻¹, showing higher activity for electrochemical oxidation of methanol than a commercial Pt-Ru/C catalyst. However, the absence of strong interaction between the precursors and CTAB templates results that the mesoporous WC products have no any long-range mesostructure ordering.

Yu et al. reported a synthesis of ordered mesoporous TiC/C nanocomposite materials by using a lab-made titanium citrate.
complex as a precursor, phenolic resol as a carbon source, and triblock copolymer Pluronic F127 as a SDA via the EISA route. During the synthesis, mesoporous amorphous TiO₂/carbon nanocomposites are formed in the first step, and subsequently converted to crystalline cubic phase TiC/carbon nanocomposites via carbothermal reduction above 950 °C. The products possess the highly ordered 2D hexagonal mesostructure, and the framework is composed of amorphous carbon and crystalline TiC nanoparticles. The Ti weight percentage can reach as high as about 32 wt%. Doong and co-workers reported a similar synthesis, however, in which TiCl₄ was used as titanium source. Ordered mesoporous crystalline TiO₂/amorphous carbon nanocomposite is the intermediate. Mesoporous TiC/C composites are obtained by heating the intermediate at 1000 °C for in situ carbothermal reduction. However, the long range ordering loses due to the crystal growth of TiO₂ below 1000 °C.

As for nanocasting synthesis, most of metal precursors have extremely low volume conversion yields to metal carbides. Isolated metal carbide nanoparticles have mainly been resulted which randomly distribute inside the mesopore channels of the silica templates. Shi and co-workers synthesized an ordered mesoporous tungsten carbide by a so-called impregnation-compaction nanocasting method. PTA is firstly impregnated into the channels of mesoporous silica template KIT-6. The intermediate composite is then pressed into compacted discs under 10 MPa. It is believed that the compacted process can block the mesopore entrance. The precursors can be therefore sealed inside the mesochannels to avoid volatilization of tungsten species during the high-temperature treatment at 700 °C under a mixed gas flow of Ar, H₂ and CO (1 : 0.05 : 1). The obtained ordered mesoporous tungsten carbide has a surface area of 138 m² g⁻¹ and shows a high and stable catalytic activity for the decomposition of ammonia. Complete ammonia decomposition can be achieved at about 500 °C, which is lower than that for the bulk material.

More recently, ordered mesoporous WC/C nanocomposites was replicated from mesoporous silica hard-templates by using PTA as a precursor and CH₄ as a carbon source. PTA is impregnated into the mesopore channels of SBA-15 or KIT-6 and then converted to tungsten carbide by CH₄ at a high temperature of 700–1000 °C. The ordered mesostructure can be retained upon the silica template removal. However, the final product contains about 46.4 wt% of free carbon. The extra carbon is believed to be the substantial role for supporting mesostructure, which occupies the mesopore voids beyond WC. By comparison, pure tungsten carbide material can be obtained when hydrogen is fed into the reduction gas. However, the mesostructural regularity is partially lost upon the silica removal in this case.

5. Summary and outlook

Ordered mesoporous inorganic non-oxide materials attract increasing interest due to their plenty of unique properties and functionalities and potential applications. Lots of achievements have been made on their synthesis and structural characterization, especially in the last five years. In this review, the ordered mesoporous inorganic non-oxide compound materials are categorized by compositions, including non-oxide ceramics, metal chalcogenides, metal nitrides, carbides and fluorides, and summarized on the basis of their synthesis approaches and mechanisms, as well as properties. We hope that related scientists can get information about the synthesis, properties and potential applications of these materials, and thus promote them and the related research.

Ordered mesoporous inorganic non-oxide materials can be prepared from the nanocasting and the soft-templating routes, in which nanocasting is a common one. The principal issues in the nanocasting synthesis include the template composition and mesostructure, pore surface chemistry, precursor selection, processing and template removal. It should be emphasized on the template composition and removal, precursor and processing, which are little important for most cases of the nanocast carbon or metal oxides. On the basis of the stability of the final product and the template, the nanocasting mesoporous non-oxides mainly originate from well reported large-pore mesoporous silica SBA-15 and KIT-6 with 2D hexagonal and 3D cubic gyroidal mesostructures, and their carbon derivation CMK-3 and CMK-8. For example, the oxygen in silica and air may bring impurity into the mesoporous silicon nitride and boron nitride products. Therefore, when the ordered mesoporous carbon is used as a template, ammonia gas should be adopted to remove carbon. The precursors that can be easily liquefied and dissolved, and more importantly have all elements in the aimed materials and a small volume shrinkage during the conversion, are good choices, for example, pre-ceramic polymers for SiC, Si₃N₄, SiCN, BN, BCN and carbon nitrides. The high volume yield of the target material facilitates the faithful replication of both the mesostructure, and in some cases, the particle morphology. However, in many cases, a simple decomposition of a precursor is unfeasible for mesoporous non-oxide semiconductors with ordered negative mesostructure. A widely adopted and effective method for nanocasting conversion is vapour–solid reaction. The reaction can be introduced at different steps to in situ tune the components and hence realize the change of the compositions, including (i) during the decomposition and conversion step (with templates); (ii) before and (iii) after the removal of mesoporous hard-template. At last, the processing temperature and atmosphere should be thoroughly considered. By comparison, the soft-templating method is limited in the synthesis of ordered mesoporous silicon nitrides, carbon nitrides, metal nitrides and fluorides, etc. The successful cases are the block-copolymer self-assembling non-oxide ceramics using inorganic-block-organic polymers as precursors via the EISA route. Besides that, mesostructured metal chalcogenide/SDA composites with different mesophases and various compositions have been synthesized by solution process. The poor crystallinity and template removal difficulty are always bottleneck issues due to the weak connection and the poor oxidation resistance of the pore walls.

Despite of great progress on the synthesis of the ordered mesoporous non-oxide materials, until now, a simple, facile and easy repeatable synthesis method from all commercial available chemicals, like that for mesoporous silica, has not been achieved. New and general approach is still required to extend compositions, improve crystallinity and purity, control
morphology, and achieve low-cost large-scale preparation. For example, a large number of non-oxide materials are semiconductors, such as SiC, ZnS, CdSe, MoS2. Their conductivities, optical properties and band structures are greatly dependent on their composition purities and nanostructures. High quality mesoporous semiconductor materials with uniform nanostructure are still a great challenge. Most reported mesoporous non-oxide materials are nanoparticles’ aggregation and possess a nanocrystalline framework structure. The properties are mainly dependent on the crystal size but not the mesostructure. By comparison, mesoporous metal oxide single-crystals can be synthesized, in which each mesoporous particle is a single crystal without any boundary inside the pore walls. If mesoporous non-oxide semiconductor single crystals could be fabricated, quite interesting properties would be expected, especially when the orientation of the crystal lattice and the mesostructure pattern could be well controlled, because the corresponding band structures are modulated by periodically arranged nanovoids. In addition, the majority of mesoporous non-oxide products are irregular-shaped powders, which are unfavourable for functional devices. The fabrication of mesoporous non-oxide semiconductor thin films or monoliths may be a new direction for the future research.

Investigation on the characteristic physicochemical properties of the mesoporous non-oxide materials should be performed in the near future for the sake of practical applications. Some non-oxide materials show relatively high oxidation resistivity in bulk state because a condensed oxide layer forms in the early stage and acts as the protection layer. However, mesoporous non-oxide materials have a nanosized (< 10 nm) pore wall structure, which is too thin to form an efficient protection layer. At the same time, the amorphous and high-surface-area features make them quite active. As a result, most of these materials start to be oxidized at as low as 400–500 °C in air. The poor oxidation resistivity greatly inhibits their application in oxidative environment. Up to now, acid and base resistivity of the mesoporous non-oxide ceramics has not been systematically evaluated. Finding a new strategy to increase the chemical stability is still a challenge.

The practical application lacks far behind the synthesis of the ordered inorganic mesoporous non-oxide materials. Exploring applications becomes the most important issue in this area, such as catalyst (carrier), luminescent sensors, solar cells and thermoelectric devices. We believe that the ordered mesoporous non-oxide materials are a promising research field and much more efforts should be put on them in the future.

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