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Controlling the Periodically Ordered Nanostructures in Ceramics: A Macromolecule-Guided Strategy

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Microscopic structures have a significant influence on the properties of ceramics. The development of macromolecular self-assembly has allowed for control over microscopic structures of ceramics to prepare ceramics with diverse compositions and ordered nanostructures. Herein, recent progress in the preparation of ceramics with periodically ordered nanostructures guided by phase-separated macromolecules are reviewed, which can be summarized as a general strategy termed the "macromolecule-guided strategy." Moreover, two different subcategories, namely, the macromolecule-templated method and the macromolecule-precursor method, are illustrated. In the former method, amphiphilic macromolecules are used as templates to guide the assembly of inorganic species into ordered nanostructures, which are subsequently converted into ceramics; in the latter method, amphiphilic macromolecules containing non-volatile elements are used as the single-source precursors for ordered ceramics. It is believed that the unique diversity and tunable features of macromolecular self-assembly might offer unprecedented opportunities in the development of functional ceramics for various applications.

1. Introduction

Ceramics have been utilized by human beings for thousands of years. Traditionally, porcelains were produced from naturally occurred clays.[1] This process was developed much earlier than the discovery of modern chemical science. Progresses of modern chemistry in the past two centuries contributed to a more fundamental understanding in the composition–property relationships of ceramics, which in turn, allow the rational design and efficient preparation of novel ceramic materials, including structural ceramics (e.g., Al_2O_3, mullite, ZrO_2, SiC, and Si_3N_4), high temperature-resistant ceramics (e.g., ZrC, HfC, WC, and Ta_4HfC_5), functional ceramics (e.g., TiO_2 for photocatalysis,[2] $BaTiO_3$ for ferroelectricity,[3] and GaN for semiconductivity[4]), among many others. Compared with the traditional aluminosilicate-type ceramics, these modern ceramics demonstrated not only largely improved mechanical properties and high-temperature stability, but also sensitive responses to external stimuli, such as pressure, temperature, light, or electricity, which have enabled numerous applications in modern industry and our daily life.[1]

Powder technology is the most widely applied technology in modern ceramic industry, in which various kinds of ceramic powders can be fabricated into ceramic products following a series of processes including mixing, shaping, drying, dewaxing, and sintering. Besides, the sol-gel technique is another frequently adopted method. In a typical sol-gel process, solid ceramic materials are produced from silicon- or metal-containing small molecules. First, these small molecules, like tetraethyl orthosilicate (TEOS), are dissolved in an organic solvent. Hydrolyzation is then carried out at suitable pH conditions to generate the colloidal solution, or a "sol." Such a fluidic "sol" is further processed into a "gel," which refers to the inorganic networks containing a liquid phase, with tunable morphologies by heating, adjusting pH condition, or long-time aging. Finally, followed by drying and sintering, the ceramic products with fine structures can be obtained.

On the other hand, preparation of ceramics from polymeric precursors has become increasingly attractive since the 1960s.[5] Compared with the traditional powder and sol-gel technologies, the "polymer-derived ceramics" method greatly broadens the scope of application scenarios and enables more processing technologies. As a result, many morphologies, like nanofibers, thin coatings, and composites, which were traditionally difficult to achieve, could be fabricated by electrospinning, solution casting, polymer infiltration pyrolysis (PIP), or resin transfer molding (RTM). Another benefit lies in the processing temperature. Taking the fabrication of carbide ceramics as an example, the processing temperature required for the powder technology

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is usually as high as 1500 °C, while it could be substantially lowered to 1100–1300 °C using the polymer-based method.[6] In practice, silicon-based polymers commonly serve as precursors because of the mature synthetic chemistry and low cost. The composition of the resulted ceramics could be accurately adjusted by tuning the chemical structure of silicon-based precursor polymers. Moreover, the polymer-based method also allows the preparation of ceramics with complicated compositions and complex microscopic structures. For example, pyrolysis of polymers containing silicon, nitrogen, boron, and carbon elements in the repeating units could lead to the formation of silicon boron carbonitride ceramic (SiBCN), which showed ultrahigh thermal stability.[7] Such ultrahigh thermal stability is originated from the high entropy of the disordered and multi-component nature of the SiBCN ceramics. For thermodynamic reasons, these multi-component ceramics are difficult to produce by traditional technologies.[7a]

Diverse types of silicon-containing preceramic polymers were synthesized, including polysilanes,[6b] polysiloxanes,[8] polycarbosilanes,[6a,9] polysilazenes,[6c,10] and polyborosilanes.[11] In general, pyrolysis of different silicon-containing polymers results in different silicon-based ceramics. For instance, pyrolysis of polycarbosilanes results in the formation of SiC, while pyrolysis of polysiloxanes and polysilazenes results in nonstoichiometric $Si_xC_yO_z$ and $Si_xC_yN_z$ ceramics, respectively (**Figure 1**). These polymer-derived ceramics have been applied in a variety of fields, including high-temperature ceramics, superhard materials, and special ceramics for chemical engineering and microelectronic engineering.[5]

Besides chemical compositions, microscopic structures also have significant influences on the properties of ceramics. For example, studies showed that the high-temperature stability of polymer-derived ceramics majorly originated from delicate controllability on the composition and distribution of different components.[12] Small-angle X-ray scattering (SAXS) experiments confirmed the existence of carbon-rich nanodomains with sizes of 1–3 nm. These carbon-rich nanodomains persisted even at high temperatures, which could inhibit the crystallization of the ceramic matrix and thus maintain the high entropy of the system. Therefore, controlling the microscopic structure of ceramics and studying the structure–property relationships would be meaningful to design high-performance ceramics with desired properties. To this end, studies on self-assembly of amphiphilic macromolecules provide a unique platform to realize the accurate control over microscopic structures of ceramics.

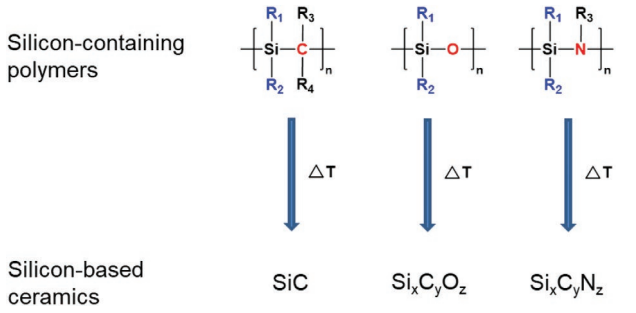

Figure 1. Preparation of silicon-based ceramics from silicon-containing preceramic polymers.

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Simply put, strategies to control the microscopic structures of ceramics based on self-assembly of amphiphilic macromolecules can be categorized into two types.[13] One is to blend amphiphilic macromolecules with ceramic precursors, which undergo co-assembly toward phase separation. Once that occurs, the ceramic precursors would preferably stay in only

one phase. Through chemical crosslinking (covalent bonding) or physical crosslinking (hydrogen bonding), the microstructure could be fixed and maintained upon high-temperature treatment. The following pyrolysis could remove the macromolecular components and transfer the phase-separated nanostructures to the resulting ceramics. In this method, the phase-separated macromolecules play the role as a template and we thus suggest naming it as the "macromolecule-templated method." On the other hand, when containing non-volatile inorganic elements, the phase-separated macromolecule itself could serve as the ceramic precursors, guiding the formation of ordered ceramic structures without any additional sacrificial templates. In this sense, it was referred to as the "macromolecule-precursor method." Combining these two methods, we term them as the "macromolecule-guided strategy," which has been extensively adopted to control the microscopic structures of ceramics.

In this article, we aim to present the recent progresses on the preparation of ceramics with periodically ordered nanostructures using the macromolecule-guided strategy. We mainly focus on the bulk ceramic materials, since the thin film cases, which closely relates to studies of the block copolymer lithography, have been systematically reviewed.[14] Two large types of ceramics, namely silicon-based ceramics and metal oxide ceramics, are covered. In the following sections, we first give a brief introduction to the basic principles of macromolecular self-assembly. Then, ordered mesoporous silica and metal oxide ceramics prepared from block copolymers templates will be discussed, including early examples using Pluronics, as well as the subsequent developments using block copolymers containing sp^2-hybridized carbon. In the next section, to exemplify the macromolecule-precursor method, ordered mesoporous ceramics pyrolyzed from single-source macromolecular precursors will be reviewed. Applications of such ordered ceramics as functional materials will also be briefly illustrated by several examples. Notably, limited by the scope of this feature article, we can only cover some pivotal works to illustrate the design rationale and principles, rather than showcasing all the details in this field.

2. Self-Assembly of Amphiphilic Macromolecules

Self-assembly of amphiphilic macromolecules provides a unique platform for controlling the periodic or quasiperiodic order on the nanometer scale. One of the most broadly investigated types of amphiphilic macromolecules is block copolymers, which are composed of two or more polymer blocks with chemically distinct repeating units connected by covalent bonds.[15] In some cases, the chemically distinct blocks are immiscible with each other and thus tend to undergo phase separation. However, the covalent bonds that connect the blocks do not allow the macroscopic phase separation. Instead, phase-separated block copolymers tend to form a wide range of ordered nanostructures with the balance of interface energy and polymer chain conformation entropy.[16]

There are three key factors determining the self-assembly behavior of block copolymers, namely, segregation strength, volume fraction, and molecular topology.[15] The segregation strength could be described by the Flory–Huggins parameter χ. A larger χ value means a stronger driving force for the microphase separation. The product of χ and N, where N represents the number of segments per polymer chain, determines the capability of phase separation. A second key parameter is the volume fractions of different blocks, which is denoted as f. The relative volume ratios of different immiscible blocks could lead to the formation of different periodically ordered nanostructures. For diblock copolymers, self-consistent field theory (SCFT) predicted that the phase diagram depended on the Flory–Huggins interaction parameter χ, number of segments per chain N, and volume fractions of two blocks f_A and f_B. When χN value is larger than 10.5, the diblock copolymers can undergo microphase separation to generate lamellar (LAM), double gyroid (DG), hexagonal cylinder (HEX), and body-centered cubic (BCC) supramolecular nanostructures (**Figure 2**a,b).[15,17] This prediction is consistent with various experimental observations.[18] For example, Bates and coworkers[18] investigated the self-assembly behaviors of polyisoprene-*b*-polystyrene (PI-*b*-PS) diblock copolymers and concluded that the experimental results could correspond well with the theoretical prediction (Figure 2c). Experimentally, all these periodically ordered nanostructures could be characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Besides this classical phase diagram, unusual supramolecular nanostructures, like Frank-Kasper A15 phase,[19] σ phase,[20a] dodecagonal quasicrystal phase,[20a] C14 and C15 phases,[21] were also observed in various systems such as polyisoprene-*b*-poly(lactic acid) (PI-*b*-PLA)[20a,b,21] and poly(dodecyl acrylate)-*b*-polylactide diblock copolymers.[19] In addition, molecular topology also plays an important role in the self-assembly of block copolymers.[22] In general, self-assembly of tri- or multi-block copolymers would lead to the formation of even more complicated supramolecular nanostructures,[14c,23] due to the presence of more compositional and interactional variables in these systems.

During the past three decades, the formation of ordered phase structures have also been extended to other amphiphilic macromolecule systems, for example, dendron/dendrimers,[24] and giant molecules.[25] These precisely defined macromolecules can self-assemble into ordered nanostructures with sub-20-nm feature sizes, filling the gap between small molecules and block copolymers. Dendron/dendrimers are repetitively branched molecules. Typically they are chemically precise and highly branched.[26] These features give them unique self-assembly behaviors facilitating the formation of unusual supramolecular nanostructures[24] including Frank–Kasper A15 phase,[27] σ phase,[28] and dodecagonal quasicrystal phase.[29] Giant molecules are composed of chemically precise and shape-persistent molecular nanoparticles, like fullerene (C_{60}), polyhedral oligomeric silsequioxane (POSS), polyoxometalate (POM), protein domain, and so on.[25] Self-assembly of giant molecules can form well-ordered nanostructures, including commonly observed lamellar (LAM), double gyroid (DG), hexagonal (HEX) and body-centered cubic (BCC) phases,[30] and unusual spherical phases, like the Frank–Kasper A15 phase,[31] σ phase,[31b,d,e,32] Z phase,[33] and the dodecagonal quasicrystal phase.[31b,e,f,32]

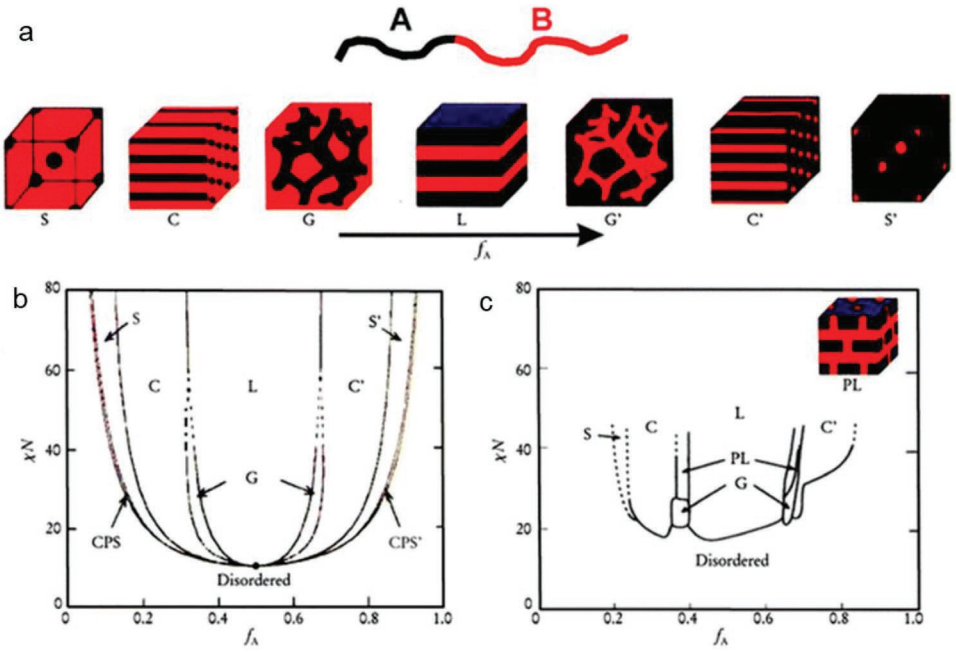

Figure 2. a) Morphologies of self-assembly of diblock copolymers in bulk: S and S' = body-centered cubic spherical phase, C and C' = hexagonal cylindrical phase, G and G' = bicontinuous double gyroid phase, L = lamellar phase; b) phase diagram of diblock copolymer self-assembly predicted by self-consistent field theory; c) experimental phase diagram of self-assembly of PI-*b*-PS diblock copolymers. Reproduced with permission.[78] Copyright 2012, Royal Society of Chemistry.

3. Ordered Mesoporous Ceramics from the Macromolecule-Templated Method

Synthesis of mesoporous silica, a type of ceramic material,[34] has become a hot research topic since the early 1990s.[35] Compared with crystalline zeolite frameworks, the presence of larger pores in mesoporous silica allows diverse applications including bioadsorption,[36] catalysis,[37] and drug delivery.[38] One of the most classical methods to prepare mesoporous silica is the template synthesis using small-molecule surfactants like cetyltrimethyl bromide (CTAB).[35a] When such small-molecule surfactants were mixed with a silicon source (e.g., tetraethyloxysilane, or TEOS), the resulting self-assembled micelles offer a structural template for hydrolysis of TEOS, thus achieving control over morphologies and pore sizes of the ordered mesoporous silica (**Figure 3**).[35a] Varying the molecular architectures and chemical compositions of the template surfactants could afford ordered mesoporous silica with diverse nanostructures.[39] However, limited by the short lengths of the hydrophobic chains in small-molecule surfactants, the pore sizes of mesoporous silica prepared by this method are typically smaller than 10 nm.[40]

The emerging studies on the self-assembly of macromolecules in the late 1990s, especially on amphiphilic block copolymers, provided a versatile platform for controlling the periodically ordered nanostructures, which, in principle, could be used to guide the assembly of inorganic components. Importantly, due to the high molecular weights of polymer blocks, the templates from amphiphilic macromolecules might break the pore size limit in the small-molecule surfactant systems. In 1998, Stucky and coworkers[41] first reported the preparation of ordered mesoporous silica using Pluronic templates

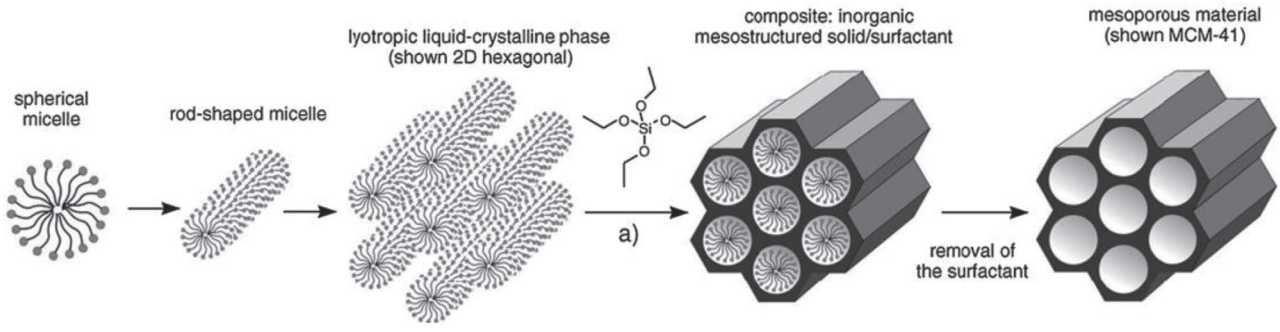

Figure 3. Preparation of ordered mesoporous silica templated by small-molecule surfactants. Reproduced with permission.[79] Copyright 2014, Royal Society of Chemistry.

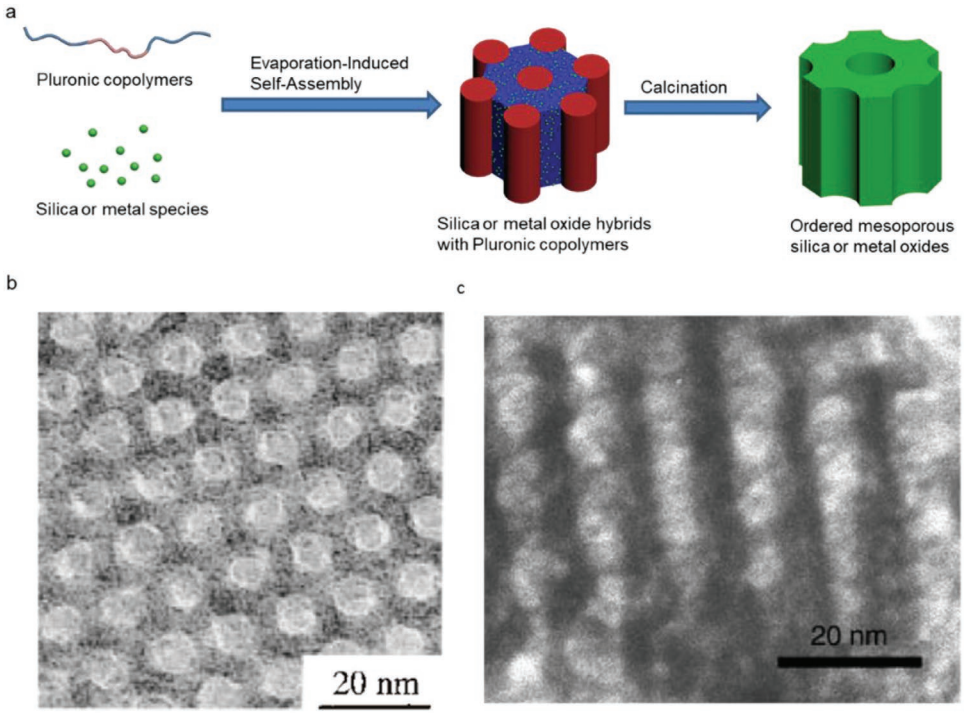

Figure 4. a) Schematic illustration of Pluronic-templated synthesis of ordered mesoporous silica and metal oxides. b,c) TEM images of hexagonally ordered mesoporous b) silica and c) ZrO_2 prepared by Pluronic-templated syntheses. Reproduced with permission.[41,44] Copyright 1998, American Association for the Advancement of Science; Copyright 1998, Springer Nature.

(**Figure 4**a). Pluronic is the brand name of a commercially available amphiphilic triblock copolymer poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO), in which the PEO blocks are hydrophilic and the PPO block is hydrophobic. The preparation procedure was quite similar. TEOS was co-assembled with the triblock copolymer, hydrolyzed to form the silicon-containing ordered nanostructures, followed by a thermal treatment to remove the organic components and lead to the formation of ordered mesoporous silica (Figure 4). Using Pluronic polymers of different molecular weights as the template, the resulting pore sizes could vary from 4 to 12 nm. In addition, by adding trimethylbenzene (TMB) as the pore expanding agent,[42] the largest pore size obtained using this method could reach 60 nm.[42b] Other types of amphiphilic block copolymers, like poly(ethylene oxide)-*b*-poly(butylene oxide) (PEO-*b*-PBO), could also be used as the guiding template to replace small-molecule surfactants for preparation of mesoporous silica.[43]

Following the same Pluronic-templated method, nanostructured metal oxides could also be obtained, including ZrO_2, TiO_2, Nb_2O_5, Ta_2O_5, SnO_2, HfO_2, Al_2O_3, and WO_3 (Figure 4c).[44] To achieve this, different metal chlorides were adopted to replace the silicon precursor and co-assembled with Pluronic polymers. Further pyrolysis of these metal-containing hybrids could convert them into diverse periodically ordered functional metal oxides with tunable pore sizes.[44,45]

In Pluronic-templated synthesis, the PEO blocks interact with the inorganic precursors presumably via hydrogen bonding[41,44] or coordination interactions[44] due to the presence of oxygen atoms. As a result, the wall thicknesses and pore sizes of the mesoporous nanostructures depend on the chain lengths of the PEO and PPO blocks and commercial availability of the Pluronic copolymers of a specific composition.[40] Another limitation is the poor thermal stability of the Pluronic copolymers, which could not allow high temperature annealing to improve crystallinity of the ceramics. If the annealing temperature is too high, decomposition of the Pluronic copolymer would lead to disordered domains.

To solve these problems, other amphiphilic block copolymers were synthesized via different living polymerization techniques to expand the applicability of the macromolecule-templated method.[18,46] In 1997, Wiesner and coworkers first reported the use of polyisoprene-*b*-poly(ethylene oxide) (PI-*b*-PEO) as the template to direct the assembly of silicon- and aluminum-containing colloidal particles via a typical sol-gel process (**Figure 5**a).[47] Varying the amounts of inorganic components could tune the self-assembled nanostructures from lamellar, hexagonal to body-centered cubic phases via an "evaporation-induce self-assembly" (EISA) step, due to the change in the relative volume ratios of two phases. Similarly, the inorganic species stay in the PEO phase because of the existence of hydrogen bonds. Calcination of the co-assembled nanostructured hybrids could remove the PI blocks and produce mesoporous aluminosilicate-type ceramics (Figure 5b).[48]

Brinkle and coworkers[49] reported the preparation of hexagonally ordered mesoporous silica using polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) as the template. By varying the volume fractions of the two blocks, spherical phases could be obtained, which allowed the preparation of ordered mesoporous silica with isolated spherical pores.[50] PS-*b*-PEO

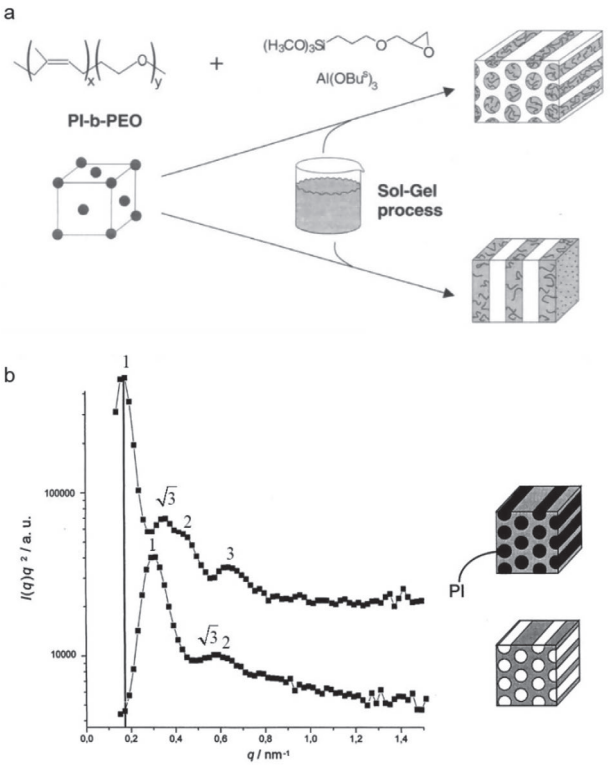

Figure 5. a) Sol-gel preparation of periodically ordered organically modified aluminosilicate-type ceramics; b) SAXS data of hexagonally ordered hybrid materials before (top) and after (bottom) calcination. Reproduced with permission.[47,48] Copyright 1997, American Association for the Advancement of Science; Copyright 2001, American Chemical Society.

can be synthesized through atom transfer radical polymerization (ATRP) conveniently with tunable molecular weights taking advantage of the development of controlled radical polymerization technology since the 1990s.[51] Impressively, mesoporous silica with ultra-large pores (up to 30.8 nm) and an ordered face-centered cubic (FCC) structure was reported by Zhao and coworkers.[52] Moreover, a hydrothermal recrystallization step was further applied to create nanopores (small than 4.0 nm) in the silica walls, making the isolated large spherical pores accessible (**Figure 6**). Compared with silica possessing cylindrical channels, the identical pore sizes in such mesoporous silica might enhance the specificity and selectivity in applications like gas adsorption and separation.

Other metal elements could also be incorporated to prepare composite ceramics by the macromolecule-templated method. For example, Wiesner and coworkers blended iron(III) ethoxide with aluminum- and silicon-containing species to co-assemble with PI-*b*-PEO. Calcination of the assembled hybrids leads to the formation of magnetic aluminosilicate-type ceramics with ordered hexagonal nanostructures (**Figure 7**).[53] In other studies, Ceraset, a type of polyureamethylvinylsilazane, was used to co-assemble with polyisoprene-*b*-poly(dimethylamino ethyl methacrylate)[34,54] or polybutadiene-*b*-poly(ethylene oxide)[55] to form organic-inorganic hybrids, which could further afford SiCN-type ternary ceramics after pyrolysis. These ternary ceramics showed ultrahigh stability at high temperature.[34] Besides the hexagonal structure, bicontinuous double gyroid phase, which showed many unique properties and often observed in block copolymers,[56] could also be obtained and maintained in the SiCN-type ternary ceramics after pyrolysis.[57]

Although successful in preparing nanostructured silica and composite silica, it was still difficult to target at highly crystalline metal oxide ceramics using the macromolecule-templated method. The co-assembled nanostructured hybrids are not stable at high temperatures, which, however, are required for thermal annealing to improve crystallinity. To tackle this challenge, Wiesner and coworkers[58] reported a "combined assembly of soft and hard chemistries" (CASH) strategy to prepare thermally stable, highly crystalline metal oxides with periodically ordered nanostructures (**Figure 8**). In this study, they co-assembled PI-*b*-PEO with various metal-containing molecules, including titanium chloride, titanium isopropyloxide, and niobium chloride to form hexagonally arranged polymer-metal oxide hybrids. After a high-temperature pyrolysis at higher than 500 °C in an argon atmosphere, the metal-containing PEO phase was converted into highly crystalline metal oxides, while the PI phase was converted into amorphous carbon (Figure 8a). The presence of the amorphous

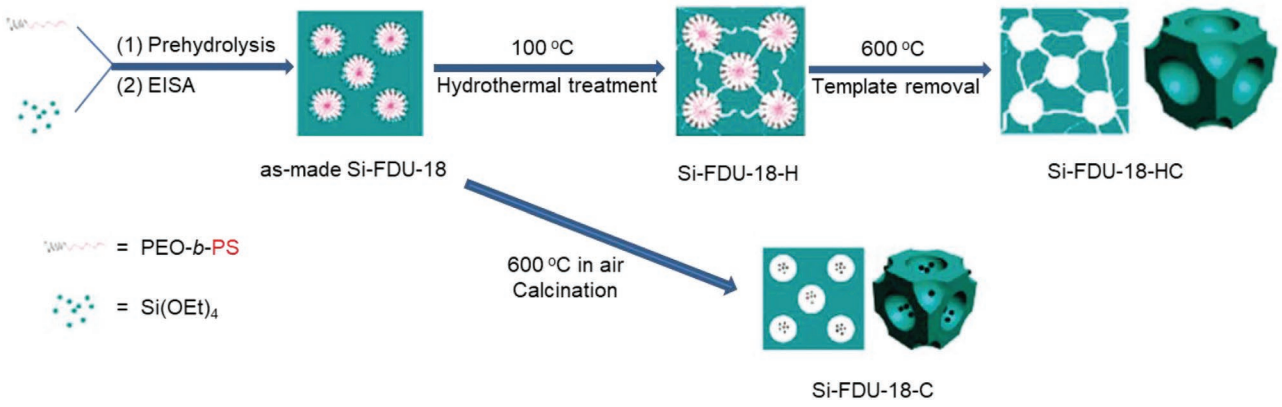

Figure 6. Synthesis of mesoporous silica with ordered FCC mesostructure and ultra-large accessible pores using PS-*b*-PEO as the template. Reproduced with permission.[52] Copyright 2001, American Chemical Society.

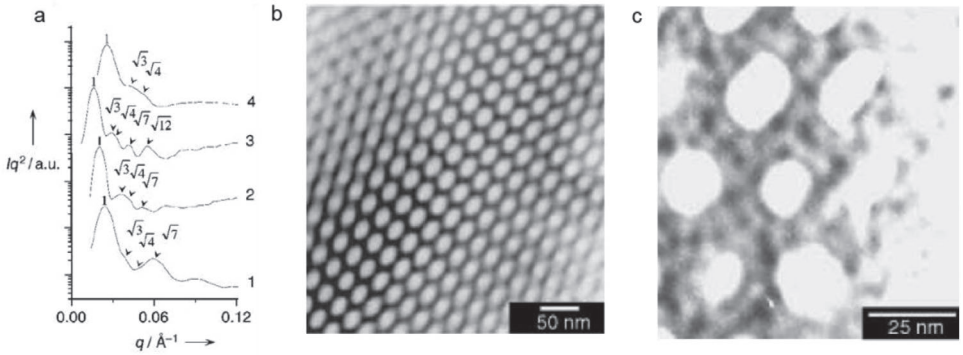

Figure 7. a) SAXS data of PI-*b*-PEO (trace 1), as-made iron-containing organic-inorganic composites (trace 2 and 3) and calcinated magnetic ceramics (trace 4); TEM image of b) as-made iron-containing organic-inorganic composites and c) calcinated magnetic ceramics. Reproduced with permission.[53] Copyright 2003, Wiley-VCH.

carbon layer largely improved the thermal stability of the mesostructure, which could thus be maintained even at such high temperatures. Further calcination in air could readily remove the residual amorphous carbon and afford the thermally stable, highly crystalline metal oxides with periodically ordered nanostructures.

This CASH strategy could be extended to other block copolymer templates and inorganic precursors as a general

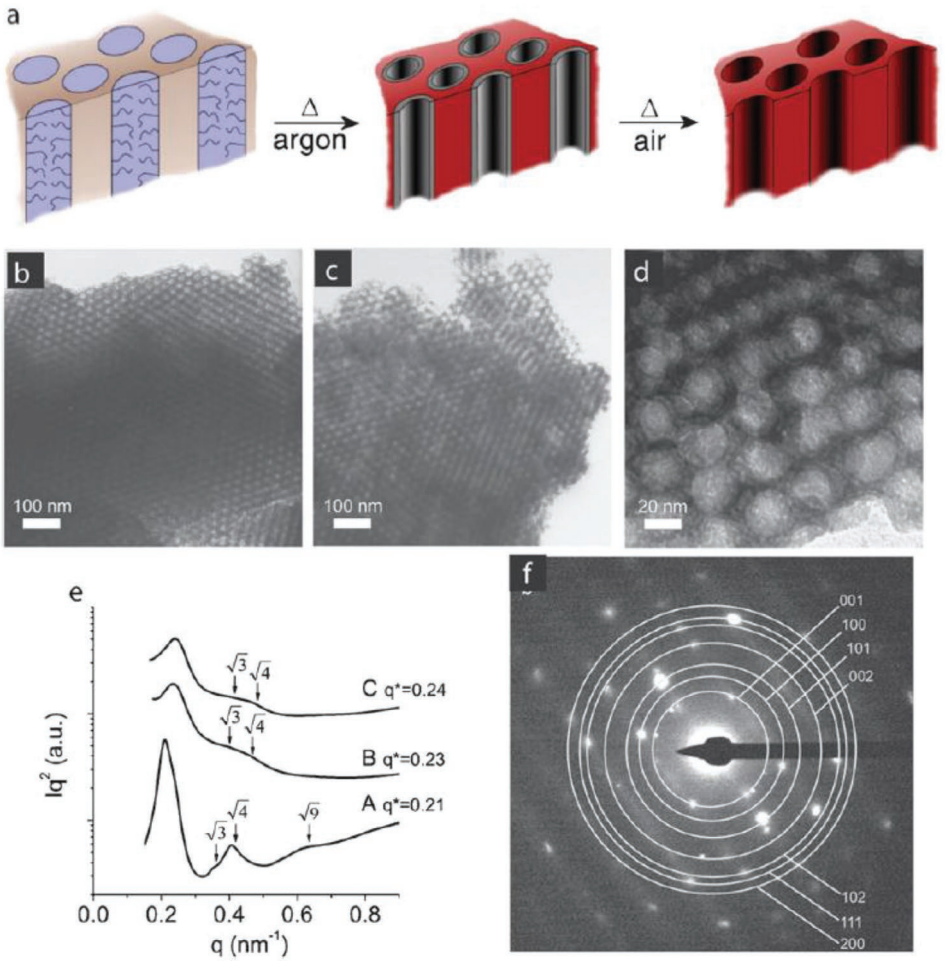

Figure 8. a) Schematic illustration of the CASH method for preparing highly crystalline metal oxides with ordered nanostructures; b–d) TEM images of b) as-made Nb_2O_5-polymer hybrid, c) pyrolyzed Nb_2O_5-carbon composite, d) highly crystalline Nb_2O_5 after calcination; e) SAXS data of A: as-made Nb_2O_5-polymer hybrid, B: pyrolyzed Nb_2O_5-carbon composite, and C: highly crystalline Nb_2O_5 after calcination; f) electron diffraction pattern of highly crystalline Nb_2O_5 after calcination. Reproduced with permission.[80] Copyright 2011, Royal Society of Chemistry.

way for the preparation of ordered mesoporous metal oxides with diverse functionalities. For examples, highly crystalline mesoporous TiO_2[59] and WO_3[60] with ordered mesostructures and identical pore sizes could be prepared using a PS-*b*-PEO template. The resulting nanostructured TiO_2 could be used as photocatalysts[59] and WO_3 could serve as sensors for detection of toxic H_2S gas[60a] and foodborne pathogens.[60b]

Although the macromolecule-templated method has made great achievements in preparing ceramics with periodically ordered nanostructures, several problems remained. First, this

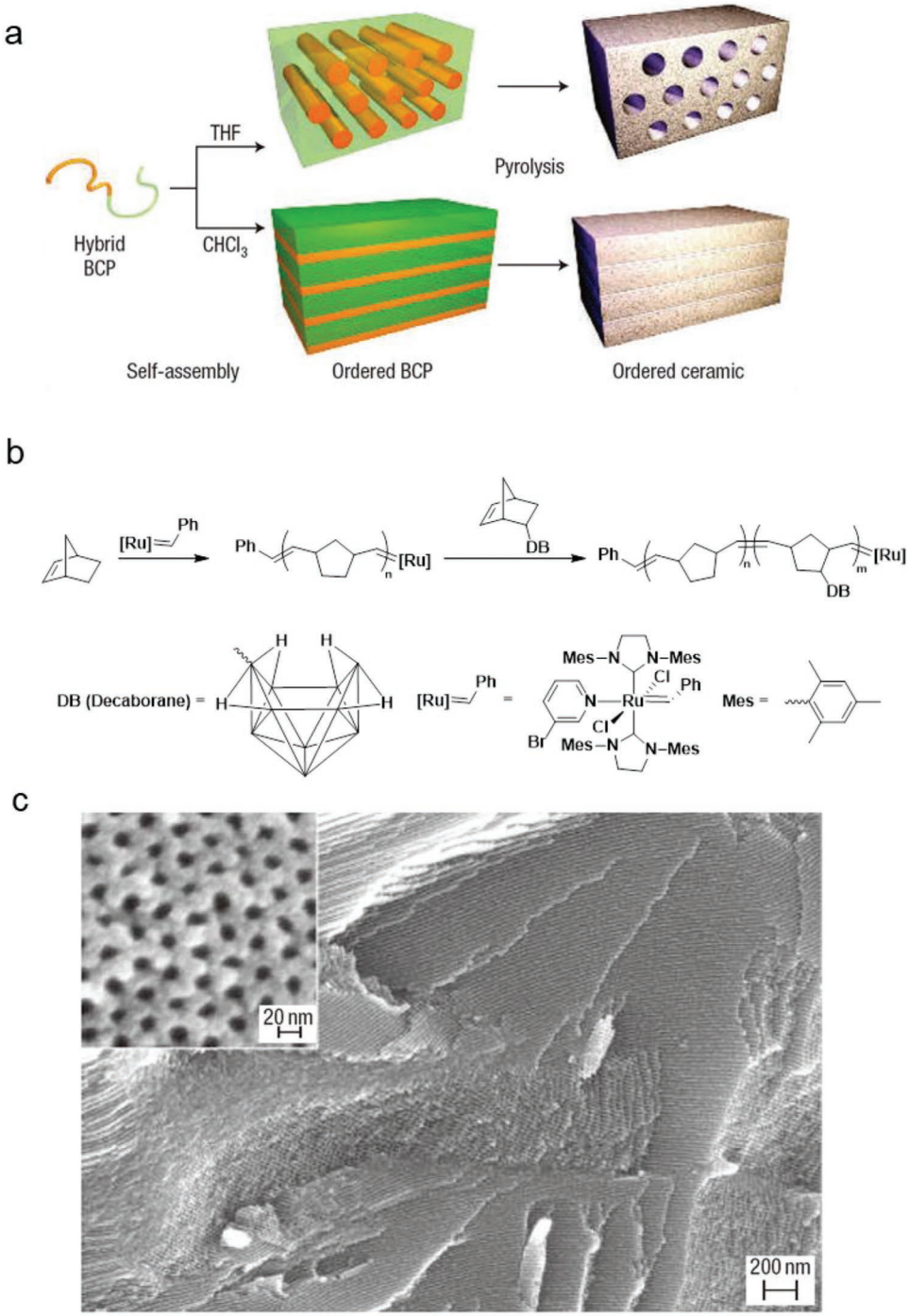

Figure 9. a) Schematic illustration of the self-assembly and pyrolysis of polynorbornene-*b*-polynorbornenedecaborane to afford ordered ceramics; b) synthetic route of the decaborane-containing diblock copolymer using ruthenium-catalyzed ring-opening metathesis polymerization; c) SEM image of pyrolyzed, ordered boron nitride ceramic coating. Reproduced with permission.[61] Copyright 2011, Springer Nature.

method stringently requires amphiphilicity of the macromolecule templates and ceramic precursors. If the ceramic precursor is immiscible with neither block of the amphiphilic macromolecule, macroscopic phase separation would take place instead of nanoscopic phase separation. Second, a tedious evaporation-induced self-assembly process is typically involved to assemble the components, which is time-consuming and costly. Third, the low dynamics of pre-hydrolyzed silica or metal oxide colloidal particles, typically involved in sol-gel process, resulted in relatively poor orders of the assembled nanostructures. These limitations require further development in this field.

4. Periodically Ordered Ceramics Prepared from the Macromolecule-Precursor Method

Besides the use of polymer templates, it is also possible to yield ceramics with periodically ordered nanostructures from a single block copolymer precursor, in which one of the blocks contains non-volatile inorganic elements (e.g., boron, silicon, iron, and so on). Self-assembly of such block copolymers produced ordered nanostructures with the inorganic elements enriched in certain domains. After pyrolysis, these non-volatile elements remain to form the nanostructured ceramics. Compared with macromolecule-templated method that typically involves a sol-gel process, this method eliminates the tedious evaporation and gelation steps and avoids the use of large amounts of flammable and expensive organic solvents. Moreover, the morphologies of pyrolyzed ceramics are determined by the morphologies of polymer precursors, which could be easily controlled by modern polymer processing techniques. This method also provides a potential route to prepare ceramics with complicated compositions that are difficult to prepare by macromolecule-templated method.

In 2007, Malenfant and coworkers[61] reported the preparation of boron nitride-based ceramics with ordered nanostructures using a decaborane-functionalized diblock copolymer precursor, which was synthesized by ruthenium-catalyzed ring-opening metathesis polymerization (ROMP).[62] This decaborane-functionalized diblock copolymer could self-assemble to form ordered lamellar and hexagonal nanostructures. Pyrolysis of these self-assembled ordered hybrids in nitrogen or ammonia atmosphere lead to the formation of boron nitride-based ceramics with ordered nanostructures (**Figure 9**). Since the decaborane building blocks in the block copolymer contributed significantly to the boron weight fraction, in this case the ceramic yield was high, and the supramolecular nanostructures remained stable during pyrolysis.

Silicon-containing diblock copolymers can also serve as single-source polymeric precursors to prepare silicon-based ceramics with ordered nanostructures. In 2007, Kim and coworkers[63] reported the synthesis of a poly(vinylsilazane)-*b*-polystyrene (PVSZ-*b*-PS) diblock copolymer by reversible addition-fragmentation chain transfer (RAFT) polymerization.[64] Pyrolysis of the hexagonally ordered PVSZ-*b*-PS result in the formation of ordered mesoporous SiCN-type ternary ceramic. When replacing the silicon-containing polyvinylsilazane block with a polycarbosilane block, ordered mesoporous SiC ceramic was obtained following the self-assembly and pyrolysis steps (**Figure 10**).[65]

Polyferrocenyldialkylsilane (PFS) is a novel type of organometallic polymer,[66] which can be synthesized by thermal

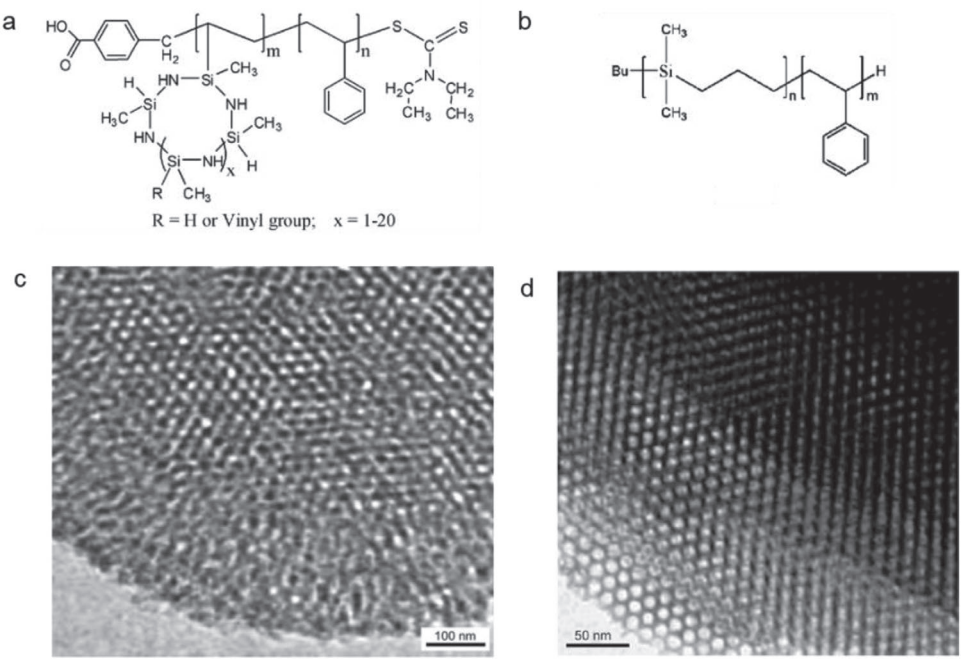

Figure 10. Chemical structures of a) poly(vinylsilazane)-*b*-polystyrene (PVSZ-*b*-PS) and b) polycarbosilane-*b*-polystyrene (PCS-*b*-PS); TEM images of c) pyrolyzed SiCN-type ternary ceramic from PVSZ-*b*-PS and d) pyrolyzed SiC ceramic from PCS-*b*-PS. Reproduced with permission.[63,65] Copyright 2007, Wiley-VCH; Copyright 2008, American Chemical Society.

ring-opening,[67] γ irradiation,[68] or living anionic polymerization.[69] Since the monomer of PFS contains iron and silicon elements, this type of ferrocene-containing polymer could be used as ceramic-forming precursors. As an early example, pyrolysis of a crosslinked polyferrocenyldimethylsilane (PFDMS) network resulted in the formation of shaped magnetic ceramics in high yields.[70] Microscopic characterization indicated that iron clusters, which brought in the magnetic property, were well dispersed in a SiC matrix. Later, pyrolysis of the thin films of a polystyrene-*b*-polyferrocenylethylmethylsilane (PS-*b*-PFEMS)[71] diblock copolymer with a hexagonal nanostructure resulted in ordered magnetic ceramic nanodots on the surface of a silicon wafer, while the pyrolysis of a nanostructured bulk sample of this block copolymer could maintain the fiber-like morphology of the silicon-containing block (**Figure 11**).[71a,72] According to the microscopy characterizations, small iron nanoparticles were dispersed on the surface of SiC cylinders, which explained the origination of the magneticity. In the thin film case, UV crosslinking of the polystyrene block was required to enhance the stability of the mesostructure before high-temperature pyrolysis.

Compared with the macromolecule-templated method, preparation of ordered ceramics from a single-source macromolecule precursor exhibits several advantages. First, the ceramic precursor species are covalently linked with the macromolecule backbones, which prevents the possible macroscopic phase separation in the cases of blends of macromolecule templates and ceramic precursors. Second, thermal annealing is the general way to process the self-assembling macromolecules into ordered supramolecular nanostructures, which could avoid the use of expensive and flammable organic solvents in the sol-gel process. Third, the dynamics of macromolecules are typically much faster than pre-hydrolyzed silica or metal oxide colloidal particles, which facilitates the formation of mesostructures with high order. Last, the processing techniques to make polymers into diverse morphologies have been well developed in modern polymer engineering, which makes it convenient to process ceramics with diverse morphologies. These features make the macromolecule-precursor method very promising in the future developments.

5. Applications of Ordered Ceramics Prepared from the Macromolecule-Guided Strategy

The unique characteristics of ordered ceramics prepared from the macromolecule-guided strategy are the high porosity and surface area, and in many cases, the compositional features of resulting ceramics, too. Applications of such ordered ceramics have emerged in diverse fields.

For example, mesoporous silica prepared from the macromolecule-templated method possesses larger pores compared with those templated from small-molecule surfactants, thus allowing the adsorption and transportation of large

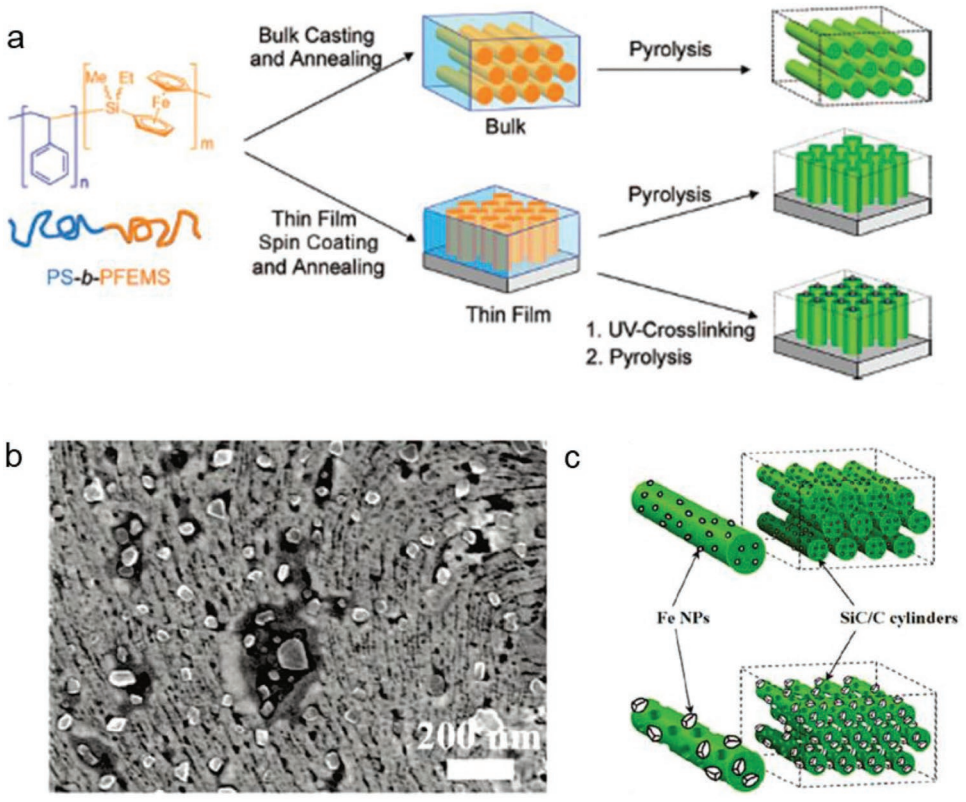

Figure 11. a) Pyrolysis of ferrocene-containing diblock copolymer in bulk and thin film; b) SEM image of pyrolyzed nanostructures ceramics; c) proposed structural model of magnetic ceramics with Fe nanoparticles present at the surfaces of the SiC cylinders. Reproduced with permission.[72] Copyright 2008, American Chemical Society.

nano-objects, such as biomacromolecules and nanoparticles.[40] In addition, new functions have been achieved by manipulating the compositions of ordered ceramics.[73] For example, nanostructured TiO_2 has been prepared for photocatalysis.[59] In these cases, the high surface area from the ordered nanostructures also played important roles, since the molecules in liquid or gaseous phases can only interact with the surface of functional ceramics.

Periodically ordered tungsten oxide (WO_3), a type of semiconducting transition metal oxides, was prepared following the macromolecule-templated method by Zhao and coworkers.[60a] Using the CASH method, a face-centered cubic mesostructured ceramic material with large accessible spherical pores and high crystallinity degree were achieved from a PS-*b*-PEO template (**Figure 12**a). The resulting crystalline WO_3 was applied as sensors for detection of toxic H_2S gas, showing sensitive and specific sensing performance (Figure 12b,c).[60a,74] Such ordered mesoporous WO_3 could also be used for sensing 3-hydroxyl-2-butanone,[60b] a metabolizing byproduct of foodborne pathogens (Figure 12d), which provided a useful and convenient

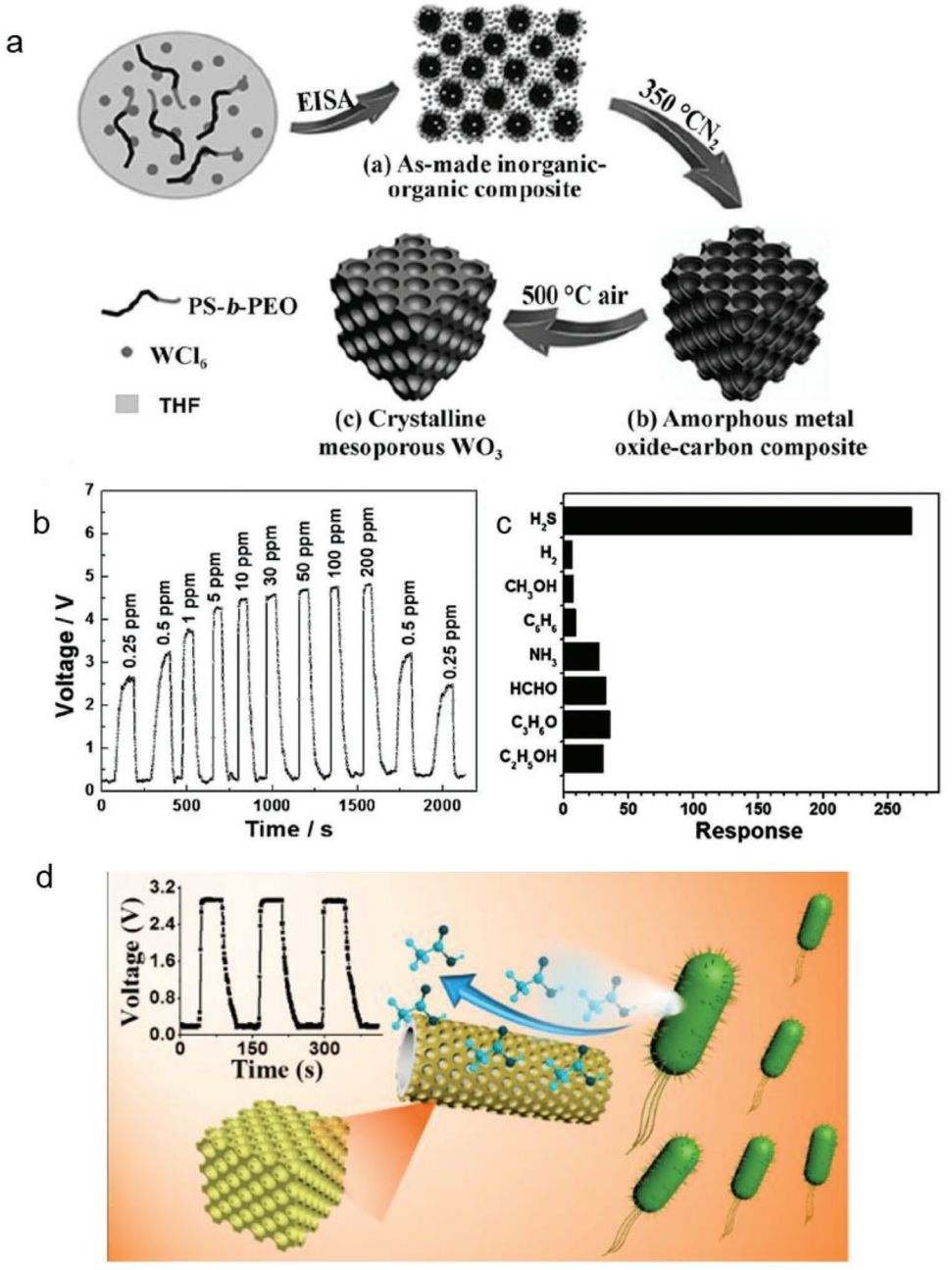

Figure 12. a) Schematic illustration of the preparation of ordered mesoporous tungsten oxide following the macromolecule-templated method; b) the response and recovery curve of ordered WO_3 to H_2S; c) responses of ordered WO_3 to different gases; d) detection of foodborne pathogens using nanostructurally ordered WO_3.[60] Copyright 2014, Wiley-VCH; Copyright 2017, American Chemical Society.

method for detection for foodborne pathogens with high specificity and sensitivity.

Interestingly, functional non-oxide ceramics with ordered nanostructures have also been demonstrated following the macromolecule-templated method. Wiesner and coworkers[75] prepared a highly ordered superconducting NbN templated by a polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) (PI-*b*-PS-*b*-PEO) triblock terpolymer. Through a sol-gel process, the Nb_2O_5 sol was assembled into the nanoscopic gyroidal morphology and stayed in the PEO phase. Calcination of the as-made organic–inorganic hybrid resulted in a single-gyroid Nb_2O_5 network. Further treatment of the single-gyroid Nb_2O_5 network with ammonia at high temperature could afford the superconducting single-gyroid NbN network (**Figure 13**). This work provided a unique platform to study the effect of nanostructures on the superconducting properties of materials.

By incorporating other metal elements into the assembled hybrids, ceramics with more complicated compositions and functionalities can also be prepared. Wiesner and coworkers[76] reported the one-pot preparation of Pt and Pt–Pb nanoparticles incorporated in ordered mesoporous niobium oxide–carbon composites. In this study, a PI-*b*-PEO diblock copolymer was used as the template to direct the assembly of metal species. Niobium chloride and niobium ethoxide were used as the niobium source, while platinum and lead complexes with organic ligands were used as the source of platinum and lead, respectively. During the co-assembly process, the niobium species stayed in the PEO phase, while the platinum and lead complexes stayed in the PI phase. After thermal treatment under inert atmosphere, the organic components were removed, forming the metal nanoparticle-niobium oxide composite ceramics (**Figure 14**). The amorphous carbon pyrolyzed from the PI block supported the mesostructures during the thermal treatment, and more importantly, the conductivity of such a carbon layer significantly enhanced the electrocatalytic performance in the electrooxidation of formic acid. Therefore, this composite niobium oxide ceramic was regarded as a promising candidate for fuel cell electrodes. Considering the complex and ordered nanostructures of such functional ceramics, the macromolecule-guided strategy holds great potential in developing novel ceramic materials with fine-tuned compositions, controllable structural orders, and functions.

6. Summary and Future Outlook

Self-assembly of macromolecules provides a unique and versatile strategy for controlling the periodically ordered nanostructures of materials. Based on this well-studied phenomenon, different methods have been developed to prepare nanostructured ceramics using macromolecules as the structural templates or precursors. In the macromolecule-templated method, amphiphilic macromolecules are used to direct the assembly of ceramic precursor species to form ordered hybrids. Pyrolyzing the ordered composites could afford ordered ceramics. Commercially available triblock Pluronic copolymers were first studied to guide the assembly of pre-hydrolyzed silica or metal oxide particles for the preparation of ordered mesoporous silica or metal oxides. Other amphiphilic block copolymers, such PI-*b*-PEO and PS-*b*-PEO,

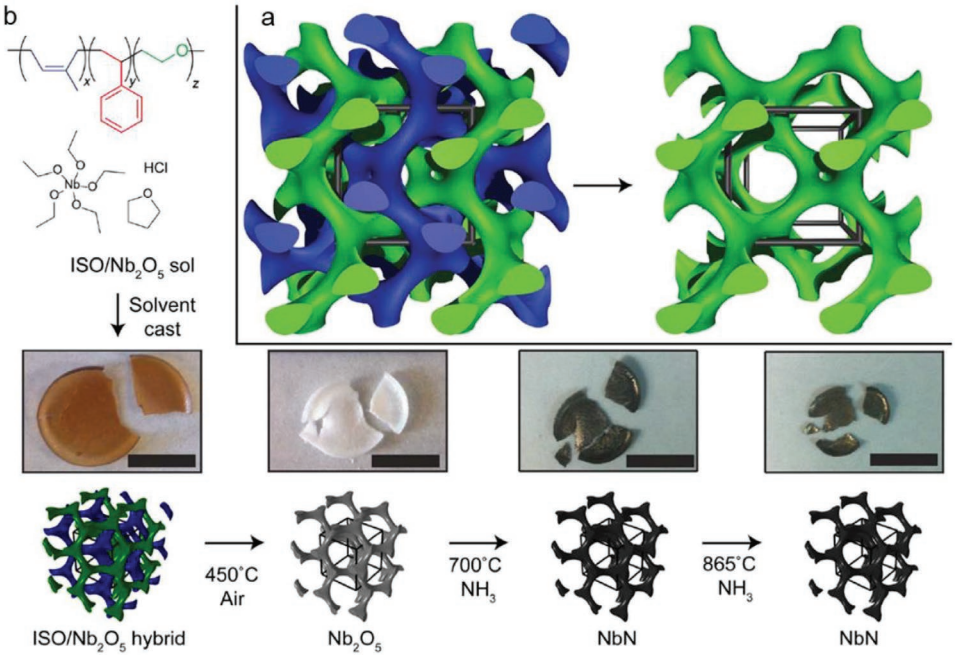

Figure 13. a) Gyroidal morphologies of the nanostructured hybrids before and after calcination; b) schematic illustration of the synthetic procedure of the nanostructured NbN ceramic along with the images showing changes in visual appearance. Reproduced with permission.[75] Copyright 2016, American Association for the Advancement of Science.

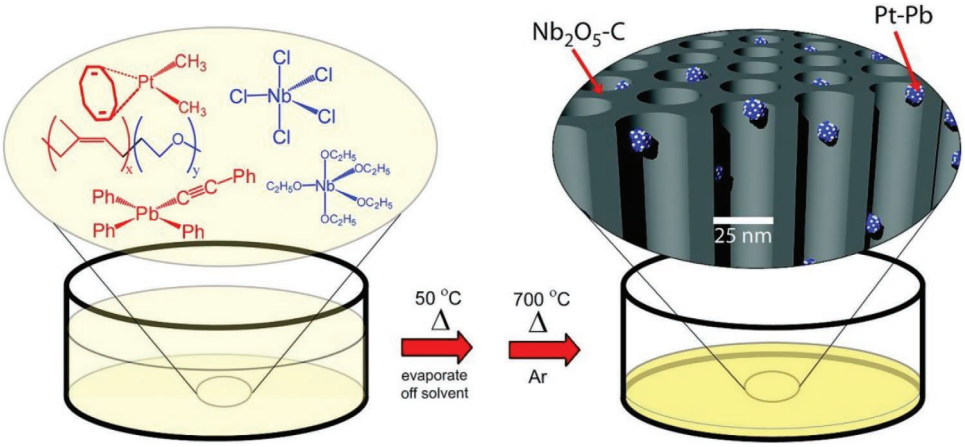

Figure 14. Preparation of ordered metal nanoparticle-carbon-niobium oxide ceramic composites templated from PI-*b*-PEO for catalytic electrochemical oxidation.[76] Copyright 2009, American Chemical Society.

have also been used to template the preparation of ordered mesoporous ceramics, which could adjust the pore sizes and wall thicknesses in a broader range, and could be adopted to prepare highly crystalline ceramics via high-temperature annealing. On the other hand, the macromolecule-precursor method uses block copolymers containing non-volatile inorganic elements (boron, silicon, iron, and so on) as the single precursor to produce ceramics with periodically ordered nanostructures. Several types of ordered ceramics, including BN, SiC, and SiCN ternary ceramics, have been prepared following this method.

Although significant progresses have been made in the past few decades, challenges and opportunities still remain in this field. First, the majority of ceramics prepared by the macromolecule-templated method are oxides, while the macromolecule-precursor method only succeeded in preparing limited types of non-oxide ceramics. The scarcity of ceramic-preparing methodology necessitates further exploration and expansion of compositional library, which largely depends on the new synthetic method to prepare novel macromolecule precursors containing various metal and other inorganic elements.[66,77] Second, currently, the ordered structures in ceramics prepared by the macromolecule-guided strategy are limited in certain classical mesostructures, such as lamellae, hexagonal columns, body-centered cubic, or face-centered cubic phases. Recent discoveries of unusual phases in soft matter could offer more opportunities toward novel ceramics with unprecedented nanostructures, which could further advance the study on the fundamental rules in their structure-property relationships. In such a way, new functions might be achieved by holding an enriched toolbox of fabrication methodologies and structural inventories.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

block copolymers, ceramics, functional materials, macromolecule-guided strategy, nanostructures

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