BLOCK POLYMER PROCESSING FOR MESOSTRUCTURED INORGANIC OXIDE MATERIALS

Inventors: Galen D. Stucky, Goleta, CA (US); Bradley F. Chmelka, Golem, CA (US); Dongyuan Zhao, Shanghai (CN); Nick Melosh, Tucson, AZ (US); Qisheng Huo, East Amherst, NY (US); Jianlin Feng, Charlottesville, VA (US); Peidong Yang, Santa Barbara, CA (US); David Pine, Santa Barbara, CA (US); David Margolese, Montecito, CA (US); Wayne Lukens, Jr., Summerland, CA (US); Glenn H. Fredrickson, Santa Barbara, CA (US); Patrick Schmidt-Winkel, Russchlikon (CH)

Assignee: The Regents of the University of California, Oakland, CA (US)

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Field of Classification Search 516/111; 428/402; 501/12, 53; 523/209
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References Cited
U.S. PATENT DOCUMENTS
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6,541,539 B1 * 4/2003 Yang et al. 523/200
6,592,764 B1 * 7/2003 Stucky et al. 210/660
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ABSTRACT
Mesoscopically ordered, hydrothermally stable metal oxide-block copolymer composite or mesoporous materials are described herein that are formed by using amphiphilic block polymers which act as structure directing agents for the metal oxide in a self-assembling system.

32 Claims, 62 Drawing Sheets
**FIG. 1a**

**SUB-NANOPOROUS ZEOLITES: < 1 nm**

FAUJASITE

**FIG. 1c**

**MESOPOROUS MOLECULAR SIEVES: 2 - 10 nm**

MCM-41

**FIG. 1b**

**FIG. 1d**

**ULTRA LARGE PORE MATERIALS 5 - 50 nm**

SBA-15
FIG. 3a

FIG. 3b
FIG. 3c

FIG. 3d
**FIG. 4a**

VOL ADSORBED, (cm$^3$/g STP)

RELATIVE PRESSURE, ($P/\text{PO}$)

BET SURFACE AREA 850 m$^2$/g

**FIG. 4b**

PORE SIZE 89 (Å)

PORE VOLUME 1.17 cm$^3$/g

PORE DIAMETER (Å)
FIG. 7

![Graph showing XRD (100) spacing vs. TMB/surfactant (g/g) and pore size vs. TMB/surfactant (g/g).]
FIG. 11a

FIG. 11b
FIG. 14

OPTICAL DIELECTRIC CONSTANT

REFRACTIVE INDEX (n)

LORENTZ–LORENZ

OPTICAL DIELECTRIC CONSTANT

REFRACTIVE INDEX (n)

PORE VOLUME FRACTION
FIG. 27a

FIG. 27b
FIG. 41d

10 \mu m
3.0 kV x 1.300 10mm

FIG. 41e

10 \mu m

FIG. 41f

1 \mu m
3.0 kV x 5.500 11mm
FIG. 43a

FIG. 43b

FIG. 43c

FIG. 43d
FIG. 46a

FIG. 46b
FIG. 47b

PLOT FOR ADSORPTION IN CYLINDERS

POROSITY IN CYLINDRICAL PORES
Cylindrical Meniscus
Surface Area = 100 sq. m per g
Pore Volume = 0.17 cc per g

ADSORPTION IN CYLINDERS
DESORPTION FROM CYLINDERS
FIG. 52

INTENSITY RATIO (%)

CONCENTRATION (wt. %)

TIME (h)

SOLVENT

SOLID

SATURABLE

SOLIDIFIED

SATURATION CONCENTRATION OF LICI
BLOCK POLYMER PROCESSING FOR
MESOSTRUCTURED INORGANIC OXIDE
MATERIALS

CROSS REFERENCE TO RELATED
APPLICATIONS

This application is a divisional application of continuation
application Non-Provisional application Ser. No. 10/426,441
filed on Apr. 30, 2003, now U.S. Pat. No. 7,176,245 which
was a continuation of U.S. Non-Provisional application Ser.
No. 09/554,259 filed on Dec. 11, 2000 now U.S. Pat. No.
6,592,764 which claimed the benefit of PCT/U.S. 98/26201,
filed Dec. 9, 1998, and also claimed the benefit of U.S. Pro-
visional Application Nos. 60/069,143, filed Dec. 9, 1997, and
60/097,012, filed Aug. 19, 1998.

STATEMENT REGARDING FEDERALLY
FUNDED RESEARCH OR DEVELOPMENT

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invention.

BACKGROUND OF THE INVENTION

Large pore size molecular sieves are in high demand for
reactions or separations involving large molecules and have
been sought after for several decades. Due to their low cost,
ease of handling, and high resistance to photo induced corro-
sion, many uses have been proposed for mesoporous metal
oxide materials, such as SiO2, particularly in the fields of
catalysis, molecular separations, fuel cells, adsorbents, pat-
tered-device development, optoelectronic devices, and
chemical and biological sensors. One such application for
these materials is the catalysis and separation of molecules
that are too large to fit in the smaller 3-5 Å pores of crystalline
molecular sieves, providing facile separation of biomolecules
such as enzymes and/or proteins. Such technology would
greatly speed processing of biological specimens, eliminating
the need for time consuming ultracentrifugation proce-
dures for separating proteins. Other applications include sup-
ported-enzyme biosensors with high selectivity and antigen
expression capabilities. Another application, for mesoporous
TiO2, is photocatalytic water splitting, which is extremely
important for environmentally friendly energy generation.
There is also tremendous interest in using mesoporous Zr2,
SiO2-Al2O3, SiO2-TiO2, as acidic catalysts. Mesoporous WO3
can be used as the support for ruthenium, which currently
holds the world record for photocatalytic conversion of CH4
to CH3OH and H2. Mesoporous materials with semiconduct-
ing frameworks, such as SnO2 and WO3, can also be used in
the construction of fuel cells.

Mesoporous materials in the form of monoliths and films
have a broad variety of applications, particularly as thermally
stable low dielectric coatings, non-linear optical media for
optical computing and self-switching circuits, and as host
matrices for electrically-active species (e.g. conducting and
lasing polymers and light emitting diodes). Such materials are
of vital interest to the semiconductor and communications
industries for coating chips, as well as to develop optical
computing technology which will require optically transpar-
rent, thermally stable films as waveguides and optical
switches.

These applications, however, are significantly hindered by
the fact that, until this invention, mesoscopically ordered
metal oxides could only be produced with pore sizes in the
range (15-100 Å), and with relatively poor thermal stability.
Many applications of mesoporous metal oxides require both
mesoscopic ordering and framework crystallinity. However,
these applications have been significantly hindered by the fact
that, until this invention, mesoscopically ordered metal
oxides generally have relative thin and fragile channel walls.

Since mesoporous molecular sieves, such as the M41S
family of materials, were discovered in 1992, surfactant-
templated synthetic procedures have been extended to
include a wide variety of compositions and conditions for
exploiting the structure-directing functions of electrostatic
and hydrogen-bonding interactions associated with
amphiphilic molecules. For example, MCM-41 materials
prepared by use of cationic tetraethylammonium surfac-
tants commonly have d(100) spacings of about 40 Å with
uniform pore sizes of 20-30 Å. Cosolvent organic molecules,
such as trimethylbenzene (TMB), have been used to expand
the pore size of MCM-41 up to 100 Å, but unfortunately the
resulting products possess less resolved XRD diffraction
patterns. This is particularly the case concerning materials with
pore sizes near the high-end of this range (ca. 100 Å) for
which a single broad diffraction peak is often observed.
Pin-
navia and coworkers, infra, have used nonionic surfactants in
neutral aqueous media (S3+T) synthesis at pH≈7 to synthesize
worm-like disordered mesoporous silica with somewhat
larger pore sizes of 20-58 Å (the nomenclature S3+T or ST−
are shorthand notations for describing mesophase synthesis condi-
tions in which the nominal charges associated with the
surfactant species S and inorganic species I are indicated).
Extended thermal treatment during synthesis gives expanded
pore sizes up to 50 Å; see D. Khushalani, A. Kuperman, G. A.

The preparation of films and monolithic silicates using acidic sol-gel processing methods is an active research field,
and has been studied for several decades. Many studies have
focused on creating a variety of hybrid organic-silicate mate-
rials, such as Wojciech and Klein Apolyvinylic ete toughening
of TEOS monoliths (Wojciech, Klein; SPIE, Passive Materials
for Optical Elements II, 2018, 160-166 (1993)) or Lebeau et
al’s organic-inorganic optical coatings (B. Lebeau, Brasselet,
Zysy, C. Sanchez; Chem Mater., 9, 1012-1020 (1997)). The
majority of these studies use the organic phase to provide
toughness or optical properties to the homogeneous (non-
mesostructured) monolithic composite, and not as a struc-
ture-directing agent to produce mesoscopically ordered mate-
rials. Attard and coworkers have reported the creation of
monoliths with ≈40 Å pore size, which were synthesized with
low molecular weight nonionic surfactants, but did not com-
ment on their thermal stability or transparency; see G. S.
Attard; J. C. Glyde; C. G. G61tmer, C. G. Nature 378, 366
(1995). Dabadie et al. have produced mesoporous films with
hexagonal or lamellar structure and pore sizes up to 34 Å
using cationic surfactant species as structure-directing spe-
cies; see Dabadie, Ayral, Guizard, Cot, Lacan; J. Mater
Chem., 6, 1789-1794, (1996). However, large pore size
(>50 Å) monoliths or films have not been reported, and, prior
to our invention, the use of block copolymers as structure-
directing agents has not been previously explored.(after our
invention, Templin et al. reported using amphiphilic block
copolymers as the structure-directing agents, aluminosilicate
mesostructures with large ordering lengths (>15 nm); see
Templin, M., Franck, A., Chesne, A. D., Leist, H., Zhang, Y.,
5, 1997)).

While the use of low-molecular weight surfactant species has produced mesostructurally ordered inorganic-organic composites, the resulting materials have been in the form of powders, thin films, or opaque monoliths. Extension of prior art surfactant templating procedures to the formation of non-silica mesoporous oxides has met with only limited success, although these mesoporous metal oxides hold more promise in applications that involve electron transport and transfer or magnetic interactions. The following mesoporous inorganic oxides have been synthesized with small mesopore sizes (<4 nm) over the past few years:

MnO (Tian, Z., Tong, W., Wang, J., Duan, N., Krishnan, V.V., Suib, S. L. Science.


Nb2O5 (Antonelli, D. M., Ying, J. Y. Chem. Mater. 8, 874 (1996)).

Ta2O5 (Antonelli, D. M., Ying, J. Y. Chem. Mater. 8, 874 (1996)).


However these often have only thermally unstable mesostructures; see Ulagappan, N., Rao, C. N. R. Chem Commun. 1685 (1996), and Braun, P. V., Osenar, P., Stupp, S. I. Nature 380, 325 (1996).

Stucky and co-workers first extended the surfactant templating strategy to the synthesis of non-silica-based mesostructures, mainly metal oxides. Both positively and negatively charged surfactants were used in the presence of water-soluble inorganic species. It was found that the charge density matching between the surfactant and the inorganic species is very important for the formation of the organic-inorganic mesophases. Unfortunately, most of these non-silica mesostructures are not thermally stable. Pinnavaia and co-workers, supra, used nonionic surfactants to synthesize mesoporous alumina in neutral aqueous media and suggested that the wormhole-disordered mesoporous materials are assembled by hydrogen-bonding interaction of inorganic source with the surfactants. Antonelli and Ying, supra, prepared stable mesoporous titanium oxide with phosphorus in a framework using a modified sol-gel method, in which an organometallic precursor was hydrolyzed in the presence of alkylphosphate surfactants. Mesoporous zirconium oxides were prepared using long-chain quaternary ammonium, primary amines, and amphiphilic cocamidopropyl betaine as the structure-directing agents, see Kim, A., Bruinisma, P., Chen, Y., Wang, L., Liu, J. Chem. Commun. 161 (1997); Pochecho, G., Zhao, E., Garcia, A., Skylyarov, A., Fripiat, J. J. Chem. Commun. 491 (1997); and Pochecho G., Zhao, E., Garcia, A., Skylyarov, A., Fripiat, J. J. Mater. Chem. 8, 219 (1998).

A scaffolding process was also developed by Knowles et al. for the preparation of mesoporous ZrO2 (Knowles J. A., Hudson M. J. J. Chem. Soc., Chem. Commun. 2083 (1995)).

Porous HfO2 has been synthesized using cetyl trimethyl ammonium bromine as the structure-directing agent; see Liu, P., Liu, J., Sayari, A. Chem. Commun. 557 (1997). Suib et al., supra, prepared mixed-valent semiconducting mesoporous manganese oxide with hexagonal and cubic structures and showed that these materials are catalytically very active. A ligand-assisted templating approach has been successfully used by Ying and co-workers, supra, for the synthesis of Nb2O5 and Ta2O5. Covalent bond interaction between inorganic metal species and surfactant was utilized in this process to assemble the mesostructure. More recently, the surfactant templating strategy has been successfully extended to platinum by Attard, Barlett et al., supra.

For all these mesoporous non-silica oxides (except Pinnavaia’s alumina work, in which copolymers were used to produce mesoporous alumina in neutral aqueous conditions), low-molecular-weight surfactants were used for the assembly of the mesostructures, and the resulting mesoporous materials generally had small mesopore sizes (<4 nm), and thin (1–3 nm) and fragile frameworks. The channel walls of these mesoporous metal oxides were exclusively amorphous. There have been claims, based solely on the X-ray diffraction data, of mesoporous ZrO2 and MnO2 with crystalline frameworks; see Bagshaw and Pinnavaia, supra, and Huang, Y., McCarthy, T. J., Sachter, W. M. Appl. Catal. A 148, 155 (1996). However, the reported X-ray diffraction patterns cannot exclude the possibility of phase separation between the mesoporous and crystalline materials, and therefore their evidence has been inconclusive. In addition, most of the syntheses were carried out in aqueous solution using metal alkoxides as inorganic precursors. The large proportion of water makes the hydrolysis and condensation of the reactive metal alkoxides and the subsequent mesostructure assembly extremely difficult to control.

For an overview of the non-silica mesoporous materials prior to this invention, see the Sayari and Liu review article, Sayari, A., Liu, P. Microporous Mater. 12, 149 (1997).

There has also been a need for porous inorganic materials with structure function on different length scales, for use in areas as diverse as large-molecule catalysis, biomolecule separation, the formation of semiconductor nanostructure, the development of medical implants and the morphogenesis of skeletal forms. The use of organic templates to control the structure of inorganic solid has proven very successful for designing porous materials with pore size ranging from angstroms to micrometers. For example, mesoporous aluminosilicate and alumino-phosphate zeolite-type structures have been templated by organic molecules such as amines. Larger mesoporous (20–300 Å) materials have been obtained by using long-chain surfactant as structure-directing-agents. Recent reports illustrate that techniques such as surfactant emulsion or latex sphere templating have been used to create TiO2, ZrO2, SiO2 structures with pore sizes ranging from 100 nm to 1 μm. Recently, Nakamichi used a process that combined phase separation, solvent exchange with sol-gel chemistry to prepare macroscopic silica structures with random meso and macro-porous structure; see K. Nakamichi, J. Porous Mater. 4, 67 (1997). Mann and coworkers used bacterial threads as the templates to synthesize ordered macrostructures in silica-surfactant mesophases; see Davis, S. L., Burkett, N. H. Mendslson, S. Mann, Nature, 385, 420 (1997).

Researchers have commented on the assembly of inorganic composites directed by protein or organic surfactants, but little on the effect of inorganic salts on the self-assembly of macroscopic silica or calcium carbonate structures with diatom, coral morphologies; see Davis, S. L. Burkett, N. H. Mendelson, S. Mann, Nature, 385, 420 (1997); A. M. Beleber, X. H. Wu, R. J. Christensen, P. K. Hansma. G. D. Stucky,
BRIEF SUMMARY OF THE INVENTION

The present invention overcomes the drawbacks of prior efforts to prepare mesoporous materials and mesoscopic structures, and provides heretofore unattainable materials having very desirable and widely useful properties. These materials are prepared by using amphiphilic block copolymer species to act as structure-directing agents for metal oxides in self-assembling systems. Aqueous metal cations partition within the hydrophilic regions of the self-assembled system and associate with the hydrophilic polymer blocks. Subsequent polymerization of the metalate precursor species under strongly acidic conditions (e.g., pH 1), produces a densely cross-linked, mesoscopically ordered metal oxide network. Mesoscopic order is imparted by cooperative self-assembly of the inorganic and amphiphilic species interacting across their hydrophilic-hydrophobic interface.

By slowly evaporating the aqueous solvent, the composite mesostructures can be formed into transparent, crack-free films, fibers or monoliths, having two-dimensional hexagonal (p6 mm), cubic (I3 m), or lamellar mesostructures, depending on choice of the block copolymers. Heating to remove the organic template yields a mesoporous product that is thermally stable in boiling water. Calcination yields mesoporous structures with high BET surface areas. Unlike traditional sol-gel films and monoliths, the mesosopically ordered silicates described in this invention can be produced with high degrees of order in the 100-200 Å length scale range, extremely large surface areas, low dielectric constants, large anisotropy, can incorporate very large host molecules, and yet still retain thermal stability and the transparency of fully densified silicates.

In accordance with a further embodiment of this invention, inorganic oxide membranes are synthesized with three-dimension (3-d) meso-macro structures using simultaneous multiphase assembly. Self-assembly of polymerized inorganic oxide species/amphiphilic block copolymers and the concurrent assembly of highly ordered mesoporous inorganic oxide frameworks are carried out at the interface of a third phase consisting of droplets of strong electrolyte inorganic salts/water solution. The result is a 2-d or 3-d macroporous/mesoporous membranes which, with silica, are coral-like, and can be as large as 4 cm times 4 cm with a thickness that can be adjusted between 10 µm to several millimeters. The macropore size (0.5-100 µm) can be controlled by varying the electrolyte strength of inorganic salts and evaporation rate of the solvents. Higher electrolyte strength of inorganic salts and faster evaporation result in a thicker inorganic oxide a framework and larger macropore size. The mesoscopic structure, either 2-d hexagonal (p6 mm, pore size 40-90 Å) or 3-d cubic array, can be controlled by amphiphilic block copolymer templates. The resulting membranes are thermally stable and have large surface areas up to 1000 m²/g, and pore volume up to 1.1 cm³/g. Most importantly, these meso-macroporous coral-like planes provide excellent access to the mesopore surfaces for catalytic, sorption, catalysis, separation, and sensor arrays, applications.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a size comparison between two prior art porous inorganic materials, Faujasite and MCM-41, and SBA-15, prepared in accordance with this invention.

FIG. 2 shows powder X-ray diffraction (XRD) patterns of as-synthesized and calcined mesoporous silica (SBA-15) prepared using the amphiphilic polyoxyalkylene block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀.

FIG. 3 shows scanning electron micrographs (SEM’s) (a, b) of as-synthesized SBA-15 and transmission electron micrographs (TEM’s) (c, d) with different orientations of calcined hexagonal mesoporous silica SBA-15 prepared using the block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀.

FIG. 4 shows nitrogen adsorption-desorption isotherms plots (top) and pore size distribution curves (bottom) measured using the adsorption branch of the isotherm for calcined mesoporous silica SBA-15 prepared using the block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀, (a, b) without and (c, d) with TMB as an organic additive.

FIG. 5 shows transmission electron micrographs with different pore sizes and silica wall thicknesses for calcined hexagonal mesoporous silica SBA-15 prepared using the block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀, (a) pore size of 47 Å, silica wall thickness of 60 Å; (b) pore size of 89 Å, silica wall thickness of 30 Å; (c) pore size of 200 Å; (d) pore size of 260 Å.

FIG. 6 shows powder X-ray diffraction (XRD) patterns of as-synthesized and calcined mesoporous silica SBA-15.

FIG. 7 shows variation of the d(100) spacing (solid) and pore size (open) for mesoporous hexagonal SBA-15 calcined at 500° C. for 6 h in air (circles) and for mesoporous MCM-41 (squares) as functions of the TMB/ampiphile (copolym or surfactant) ratio (g/g).

FIG. 8 shows 29Si MAS NMR spectra of as-synthesized silica-copolymer mesophasic materials: (a) SBA-11 prepared by using Brij C₁₆EO₁₀ surfactant; (b) SBA-15 prepared using PE0₂₀₈PPO₉₀₆PPO₂₀ block copolymer.

FIG. 9 shows thermogravimetric analysis (TGA) and differential thermal analysis (DTA) traces for the as-synthesized SBA-15 prepared by using the block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀.

FIG. 10 shows powder X-ray diffraction (XRD) patterns of (a), as-synthesized and, (b) calcined MCM-41 silica prepared using the cationic surfactant C₁₆H₃₃N(CH₃)₃Br, and (c), calcined MCM-41 after heating in boiling water for 6 h; Calcined SBA-15 (d, e) prepared by using the block copolymer PE0₂₀₈PPO₉₀₆PPO₂₀ after heating in boiling water for (d), 6 h; (e), 24 h.

FIG. 11 shows photographs of transparent SBA-15 silica-copolymer monoliths incorporating (a) 27 wt % and (b) 34 wt % of the PEO-PPO-PEO structure-directing copolymer PLURONIC F127.

FIG. 12 shows a 200-keV TEM image of a 38 wt % SBA-15 silica-copolymer monolith prepared with PLURONIC F127.

FIG. 13 shows (a) a photograph of a transparent 50-µm thick SBA-15 silica-copolymer film prepared with PLURONIC P104. (b) an X-ray diffraction pattern of this film showing well resolved peaks that are indexable as (100), (110), (200), and (210) reflections associated with p6 mm hexagonal symmetry in which the one-dimensional axes of the aggregates lie horizontally in the plane of the film.

FIG. 14 shows the predicted variation of optical dielectric constant and refractive index as a function of silica porosity.

FIG. 15 shows low-angle and wide-angle X-ray diffraction (XRD) patterns of (a, c), as-made zincium/E0₂₀₈PPO₉₀₆PPO₂₀ composite mesostructure and (b, d) calcined mesoporous ZrO₂. The XRD patterns were obtained with a Scintag PADX diffractometer using Cu Kα radiation.

FIG. 16 shows TEM micrographs of 2-dimensional hexagonal mesoporous ZrO₂, (a) and (b) are recorded along the [110] and [001] zone axes, respectively. Inset in (b) is the
selected-area electron diffraction pattern obtained on the image area. The images were recorded with a 200 kV JEOL transmission electron microscope. All samples were calcined at 400° C. for 5 hr to remove the block copolymer surfactant species.

FIG. 17 shows TEM micrographs of 2-dimensional hexagonal mesoporous TiO₂, (a) and (b) are recorded along the [110] and [001] zone axes, respectively. Inset in (a) is the selected-area electron diffraction pattern obtained on the image area.

FIG. 18 shows TEM micrographs of 2-dimensional hexagonal mesoporous SnO₂(a) and (b) are recorded along the [110] and [001] zone axes, respectively. Inset in (a) is the selected-area electron diffraction pattern obtained on the image area.

FIG. 19 shows TEM micrographs of 2-dimensional hexagonal mesoporous WO₃(a) and (b) are recorded along the [110] and [001] zone axes, respectively.

FIG. 20 shows TEM micrograph of 2-dimensional hexagonal mesoporous Nb₂O₅ recorded along the [001] zone axis. Inset is selected-area electron diffraction pattern obtained on the image area.

FIG. 21 shows TEM micrograph of 2-dimensional hexagonal mesoporous Ta₂O₅ recorded along the [001] zone axis.

FIG. 22 shows TEM micrographs of disordered hexagonal mesoporous Al₂O₃.

FIG. 23 shows TEM micrograph of 2-dimensional hexagonal mesoporous HfO₂ recorded along the [110] zone axis.

FIG. 24 shows TEM micrographs of 2-dimensional hexagonal mesoporous SiAlO₃ recorded along the [001] zone axis.

FIG. 25 shows TEM micrographs of 2-dimensional hexagonal mesoporous SiAlO₅, (a) and (b) are recorded along the [110] and [001] zone axes, respectively.

FIG. 26 shows TEM micrograph of 2-dimensional hexagonal mesoporous ZrTiO₄ recorded along the [001] zone axis.

FIG. 27 shows (a) Bright field TEM image of a thin slice of the mesoporous TiO₂ sample. (b) Dark field image obtained on the same area of the same TiO₂ sample. The bright spots in the image correspond to TiO₂ nanocrystals.

FIG. 28 shows (a) Bright field TEM image of a thin slice of the mesoporous ZrO₂ sample. (b) Dark field image obtained on the same area of the same ZrO₂ sample. The bright spots in the image correspond to ZrO₂ nanocrystals.

FIG. 29 shows nitrogen adsorption-desorption isotherms and pore size distribution plots (inset) calculated using BJH model from the adsorption branch isotherm for calcined ZrO₂. The isotherms were measured using a Micromeritics ASAP 2000 system. The samples were outgassed overnight at 200° C. before the analyses.

FIG. 30 shows nitrogen adsorption-desorption isotherms (a) and pore size distribution plots (b) calculated using BJH model from the adsorption branch isotherm for calcined TiO₂. Inset in (b) is the EDX spectrum obtained on the mesoporous samples.

FIG. 31 shows nitrogen adsorption-desorption isotherms and pore size distribution plots (lower inset) calculated using BJH model from the adsorption branch isotherm for calcined Nb₂O₅. EDX spectrum obtained on the mesoporous samples is shown in the upper inset.

FIG. 32 shows nitrogen adsorption-desorption isotherms and pore size distribution plots (lower inset) calculated using BJH model from the adsorption branch isotherm for calcined Ta₂O₅. EDX spectrum obtained on the mesoporous samples is shown in the upper inset.

FIG. 33 shows nitrogen adsorption-desorption isotherms and pore size distribution plots (inset) calculated using BJH model from the adsorption branch isotherm for calcined Al₂O₃.

FIG. 34 shows nitrogen adsorption-desorption isotherms and pore size distribution plots (inset) calculated using BJH model from the adsorption branch isotherm for calcined WO₃.

FIG. 35 shows nitrogen adsorption-desorption isotherms (a) and pore size distribution plots (b) calculated using BJH model from the adsorption branch isotherm for calcined SnO₂.

FIG. 36 shows nitrogen adsorption-desorption isotherms (a) and pore size distribution plots (b) calculated using BJH model from the adsorption branch isotherm for calcined TiO₂.

FIG. 37 shows low-angle and wide-angle X-ray diffraction (XRD) patterns of (a, c), as-made titanium/EO₂₅PO₄₅O₂5 composite cubic mesostructure and (b, d) calcined mesoporous TiO₂.

FIG. 38 shows TEM micrograph of cubic mesoporous TiO₂.

FIG. 39 shows TEM micrograph of cubic mesoporous ZrO₂.

FIG. 40 shows SEM image of calcined mesoporous Al₂O₃ monolith thick film. The image was recorded on JEOL 6300 FX microscope.

FIG. 41 shows scanning electron micrographs (SEM) of (a, b) as-synthesized meso-macro silica membranes prepared by using P123 block copolymer (EO₂₅PO₄₅O₂5) in NaCl solution after washing out NaCl with de-ionic water; (c), small macropore size silica membrane prepared by adding a little amount ethylene glycol in P123 block copolymer and NaCl solution; (d), silica membrane prepared with fast evaporation by using P123 block copolymer in NaCl solution. (e), silica membrane with grape vine morphology prepared with high concentration of NaCl; (f), inorganic salt NaCl crystals co-grown with the silica membrane.

FIG. 42 shows scanning electron micrographs (SEM) of (a, b, c) as-synthesized meso-macro silica membranes prepared by using P123 block copolymer (EO₂₅PO₄₅O₂5) in (a), KCl; (b), NH₄Cl; (c), NaNO₃ solution after washing out inorganic salts with de-ionic water. (d), large macropore size silica membrane prepared by using P65 block copolymer (EO₂₅PO₄₅O₂5) in NaCl solution.

FIG. 43 shows SEM images of as-synthesized silica membranes after washed with water prepared by (a), using P127 block copolymer (EO₁₄₀PO₄₅O₁₄₀) in NaCl solution; (b, c, d), using P123 block copolymer in (b), MgSO₄ solution; (c), MgCl₂ solution; (d), Na₂SO₄ solution.

FIG. 44 shows powder X-ray diffraction (XRD) patterns of as-synthesized and calcined mesosilica membrane prepared using the amphiphilic polyoxyalkylene block copolymer (a), P123, EO₂₅PO₄₅O₂5; (b), P103, EO₁₄₀PO₄₅O₁₄₀; (c), P65, EO₂₅PO₄₅O₂5. The chemical composition of the reaction mixture was 1 g copolymer: 0.017 mol NaCl; 0.01 mol TEOS: 4 times 10⁻⁵ mol HCl: 0.72 mol H₂O: 0.33 mol H₂SO₄.

FIG. 45 shows transmission electron micrographs (TEM) of calcined silica membrane prepared using the block copolymer P123 in NaCl solution recorded in (a), (100); (b), (110) zone axes; (c, d) of calcined silica membrane prepared by adding a little amount of ethylene glycol. TEM were taken on a 2000 JEOL electron microscope operating at 200 kV.

FIG. 46 shows thermogravimetric analysis (TGA) and differential thermal analysis (DTA) traces for the as-synthesized meso-macroporous silica membranes prepared by using the
block copolymer P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) in NaCl solution, (top) after removal NaCl by washing with water, (bottom), without removal NaCl.

FIG. 47 shows nitrogen adsorption/desorption isotherm plots (a) and pore size distribution curves (b) for meso-macro silica membranes prepared using block copolymer P123 in NaCl solution without removal inorganic salt NaCl.

FIG. 48 shows nitrogen adsorption/desorption isotherm plots (top) and pore size distribution curves (bottom) for calcined meso-macro silica membranes prepared in NaCl solution using different block copolymers.

FIG. 49 shows nitrogen adsorption/desorption isotherm plots (a) and pore size distribution curves (b) for calcined meso-macro silica membranes prepared using block copolymer P127 in NaCl solution.

FIG. 50 shows nitrogen adsorption/desorption isotherm plots (a) and pore size distribution curves (b) for calcined meso-macro silica membranes prepared using non-ionic oligomeric surfactant Brij 76 (C<sub>18</sub>H<sub>37</sub>EO<sub>9</sub>OH) in NaCl solution.

FIG. 51 shows SEM images of (a)-(d), as-synthesized silica membranes prepared by using P123 block copolymer in LiCl solution without washing recorded at different region, (a), top region; (b) middle region; (c), same (b) with large magnification; (d), bottom region of the membrane. (e)-(h) as-synthesized silica membranes prepared by using P123 block copolymer in NiSO<sub>4</sub> solution without washing recorded at different region. (a), top region; (b) same (a) with large magnification; (c), bottom region of the membrane; (d), disk-like NiSO<sub>4</sub> crystal.

FIG. 52 shows the change of the compositions of the reaction mixture functioned with evaporation time. Change of the concentration in liquid phase of ethanol (open circle); water (solid circle); LiCl (open square); SiO<sub>2</sub> (solid square); Intensity ratio for (100) diffraction of silica-block copolymer mesophase (open triangle) and for (110) diffraction of LiCl crystal (solid triangle) at d spacing of 3.59 Å determined by XRD in solid phase.

FIG. 53 shows a schematic diagram of the simple procedure used to prepare coral-like meso-macro silica membranes.

FIG. 54 shows progressively higher magnifications of a section of a meso-macro silica membrane made in accordance with this invention.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides a simple and general procedure for the syntheses of ordered large-pore (up to 14 nm) mesoporous metal oxides, including TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, HfO<sub>2</sub>, and mixed oxides SiAlO<sub>2</sub>, SiAlO<sub>3</sub>, Al<sub>2</sub>SiO<sub>5</sub>, ZrTiO<sub>4</sub>, SiTiO<sub>2</sub>. Commercially available, low-cost, non-toxic, and biodegradable amphiphilic poly(alkylene oxide) block copolymers can be used as the structure-directing agents in non-aqueous solutions for organizing the network forming metal species. Preferably the block copolymer is a triblock copolymer in which a hydrophilic poly(alkylene oxide) such as poly(ethylene oxide) (EO<sub>2</sub>) is linearly covalent with the opposite ends of a hydrophobic poly(alkylene oxide) such as polypropylene oxide (PO<sub>2</sub>) or a diblock polymer in which, for example, poly(ethylene oxide) is linearly covalent with poly(butylene oxide) (BO<sub>2</sub>). This can variously be designated as follows:

poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)

HO(CH<sub>2</sub>CH=CH(CH<sub>3</sub>)O)n(CH<sub>2</sub>CH—CH<sub>2</sub>)O<sub>y</sub>H

PEO-PPO-PEO

EO<sub>x</sub>PO<sub>y</sub>EO<sub>x</sub>

or

poly(ethylene oxide)poly(butylene oxide)-poly(ethylene oxide)

HO(CH<sub>2</sub>CH=CH(CH<sub>2</sub>)O)n(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)O<sub>y</sub>H

PEO-PPO-PEO

EO<sub>x</sub>PO<sub>y</sub>EO<sub>x</sub>

where x is 5 or greater and y is 30 or greater, with no theoretical upper limit to either value subject to practical considerations. Alternatively, for particular applications, one can use a reverse triblock copolymer or a star block amphiphilic poly(alkylene oxide) block copolymer, for example, a star di-block copolymer or a reversed star di-block copolymer. Inexpensive inorganic salts rather than alkoxides or organic metal complexes are used as precursors. Both two-dimensional hexagonal (p6 mm) and cubic (Im3 m) mesostructures can be obtained, as well as lamellar mesostructures, depending on the choice of the block copolymers. Calcination at 400 °C yields mesoporous structures with high BET surface area (100-850 m<sup>2</sup>/g), porosity of 40-65%, large d spacings (60-200 Å), pore sizes of 30-140 Å, and wall thickness of 30-90 Å.

These novel mesoporous metal oxides are believed to be formed through a mechanism that combines block copolymer self-assembly with chelating complexation of the inorganic metal species. A unique aspect of these thermally stable mesoporous oxides is their robust inorganic framework and thick channel walls, within which a high density of nanocrystallite ses can be nucleated during calcination without disrupting the mesoscopic ordering. In addition, variations of this simple sol-gel process yield mesoporous oxides with technologically important forms including thin films, monoliths and fibers. The nanocrystalline framework, periodic large-pore structures, and high versatility of the inexpensive synthetic methodology make these mesoporous materials an excellent choice for applications including catalysis, molecular separations, fuel cells, adsorbents, optoelectronic devices, and chemical and biological sensors. For example, due to its low cost, ease of handling, and high resistance to photoinduced corrosion, one application for mesoporous TiO<sub>2</sub> is photocatalytic water splitting, which is extremely important for environmentally friendly energy generation. There is also tremendous interest in using mesoporous ZrO<sub>2</sub>, Si<sub>x</sub>xAl<sub>y</sub>O<sub>z</sub>, Si<sub>y</sub>x<sub>y</sub>O<sub>z</sub>, Ti<sub>x</sub>O<sub>y</sub> as acidic catalysts. Mesoporous WO<sub>3</sub> can be used as the support for ruthenium, which currently holds the world record for photocatalytic conversion of CH<sub>3</sub> to CH<sub>2</sub>OH and H<sub>2</sub>. Mesoporous materials with semiconducting frameworks, such as SnO<sub>2</sub> and WO<sub>3</sub>, can be also used in the construction of fuel cells.

Many applications of mesoporous metal oxides require both mesoscopic ordering and framework crystallinity. The mesoporous metal oxides of this invention are thermally stable and retain their mesoscopic ordering and structural integrity even after the nucleation of the high density of nanocrystallites within thick, robust channel walls. Develop-
ment of such thermally stable, large-pore mesoporous metal oxide materials with nanocrystalline frameworks using low-cost, non-toxic, and biodegradable polyalkylene oxide block copolymers has enormous potential for a variety of immediate and future industrial applications.

In practicing this invention, one can use any amphiphilic block polymer having substantial hydrophilic and hydrophobic components and can use any inorganic material that can form crown-ether-type complexes with alkyne oxide segments through weak coordination bonds. The inorganic material can be any inorganic compound of a multivalent metal species, such as metal oxides and sulphides, preferably the oxides. The metal species preferentially associates with the hydrophilic poly(ethylene oxide) (PEO) moieties. The resulting complexes then self-assemble according to the mesoscopic ordering directed principally by microphase separation of the block copolymer species. Subsequent crosslinking and polymerization of the inorganic species occurs to form the mesoscopically ordered inorganic block copolymer composites. The proposed assembly mechanism for these diverse mesoporous metal oxides uses PEO-metal complexation interactions, in conjunction with (for example) electrostatic, hydrogen bonding, and van der Waals forces to direct mesostructure formation.

As indicated above, one can carry out the assembly process in non-aqueous media using metal halides as the inorganic precursors, which effectively slows the hydrolysis/condensation rates of the metal species and hinders subsequent crystallization. Restricted hydrolysis and condensation of the inorganic species appears to be important for forming mesophases of most of the non-silica oxides, because of their strong tendency to precipitate and crystallize into bulk oxide phases directly in aqueous media.

The procedures of the present invention enable close control of the porosity of the final structure by varying the proportions of PEO and PPO or PBO and by adding an organic solvent to swell the PPO or PBO.

Because of their low cost, widespread use, and ease of preparation, we will first describe and exemplify the preparation of mesoporous silica, followed by the preparation of other metal oxides. We will then describe the multiphase assembly of meso-macro membranes, which we will exemplify with silica membranes.

Mesoporous Silicas

In accordance with this invention, we have synthesized a family of high quality, hydrothermally stable and ultra large pore size mesoporous silicas by using amphiphilic block copolymers in acidic media. One member of the family, to which we have assigned the designation SBA-15, has a highly ordered, two-dimensional hexagonal (p6 mm) honeycomb, hexagonal cage or cubic cage mesostructures. Calcination at 500° C. yields porous structures with high BET surface areas of 690-1040 m²/g, and pore volumes up to 2.5 cm³/g, ultra large d(100) spacings of 74.5-450 Å, pore sizes from 46-500 Å and silica wall thicknesses of 31-64 Å. SBA-15 can be readily prepared over a wide range of specific pore sizes and pore wall thicknesses at low temperature (35-80° C) using a variety of commercially available, low-cost, non-toxic, and biodegradable amphiphilic block copolymers, including triblock polyoxyalkylene, as described below. In general, all microphase-separating, domain-partitioning copolymer systems can be considered as candidates for the synthesis of such mesostructured materials, depending on solution composition, temperature, processing conditions, etc. The pore size and thickness of the silica wall is selectively controlled by varying the thermal treatment of SBA-15 in the reaction solution and by the addition of cosolvent organic molecules, such as 1,3,5-trimethylbenzene (TMB). The organic template can be easily removed by heating at 140° C. for 3 h, yielding the mesoporous SBA-15 product, which is thermally stable in boiling water.

Transparent films, fibers, and monolithic materials with mesoscopic order can also be prepared by a similar process utilizing the same family of triblock polyoxyalkylene copolymers, yielding mesoporous structure in bulk. These materials are similarly synthesized in acidic media at low temperatures (30-80° C.), and display a variety of well-ordered copolymer phases with mesostructures of about 100-500 Å. They can be processed (e.g., molded) into a variety of bulk shapes, which are also transparent. In addition, it is possible to use polymer processing strategies, such as shear alignment, spin casting, and fiber drawing to induce orientational order in these materials. After calcination at 350° C. these monoliths and films retain their macroscopic shape and mesoscopic morphology.

To our knowledge, these are the first reported thermally stable, transparent, monolithic, large-pore size materials with well-ordered mesostructure. Their dielectric constants can be varied to low values via the Lorentz-Lorenz relationship by tuning the pore volume fraction from 0.6 to as much as 0.86. The fluid solid processability, extraordinary periodic porous and cage structures, high pore volume fraction and inexpensive synthesis make them excellent low dielectric materials for inter-level dielectrics (ILD) for on-chip interconnects to provide high speed, low dynamic power dissipation and low cross-talk noise.

To produce the highly ordered, ultra large pore silica mesostructures we adopted an S"T"X"T" synthesis processing strategy. This synthesis methodology is distinctly different from the S"T"Y"T" route (pH=3) used to make the M4IS family of mesoporous materials: the two methods employ conditions that are on opposite sides of the isoelectric point of aqueous silica (pH=2). For example, mesoporous silica SBA-15 can be synthesized using block copolymers, which that have a polyoxyethylene-polyoxypropylene-polyoxyethyl-ylene (PEO-PPO-PEO) sequence centered on a (hydrophobic) polyoxypropylene glycol nucleus terminated by two primary hydroxyl groups; see Table 1 The synthesis is carried out in acidic (e.g., HCl, HBr, H₂SO₄, HNO₃, H₃PO₄) media at 35-80° C. using either tetraethylocthoro-silicate (TEOS), tetramethylthorsilicate (TMOS), or tetrapropoxysilane (TPOS) as the silico source.

Hexagonal SBA-15 has a wheat-like macroscopic morphogy, a highly ordered (four to seven peaks in the X-ray diffraction pattern), two-dimensional hexagonal (p6 mm) mesostructure, BET surface areas up to 1040 m²/g, pore volumes to 2.5 cm³/g, and thick silica walls (31-64 Å). The thick silica walls in particular are different from the thinner-walled MCM-41 mesostructures made with conventional low molecular weight cationic surfactants. The pore size and the thickness of the silica wall can be adjusted by varying the heating temperature (35-140° C) or heating time (11-72 h) of the SBA-15 in the reaction solution and by adding organic swelling agents such as 1,3,5-trimethylbenzene. The thick walls of the hexagonally ordered porous of these materials produce a novel combination of a high degree of both mesoscopic organization and hydrothermal stability. Based on the above properties, SBA-15 materials have potential applications in catalysis, separations, chemical sensors, and adsorbents.

Transparent films and monoliths have been synthesized with similar PEO-PPO-PEO copolymers as structure-directing agents in an acidic sol-gel reaction. These materials can be synthesized with various amounts of water, acid, silicate
source, and polymer to yield different mesophase structures depending upon the polymer and processing conditions used. The materials consist of a collection of aggregates of an organic polymer component, such as the amphiphilic copolymer PLURONIC F127, which for a hexagonal array that organizes a polymerized silica matrix in the interfaces between the polymer aggregates. Such morphologies are formed by interactions among the block copolymer and the oligomeric silicate species, and solidified as the silica polymerizes to form a monolithic structure. The polymer is not strongly incorporated into the silica walls, as inferred from the remarkably low temperature (150°C C) needed to remove the polymer, and supporting 1H nuclear magnetic resonance (NMR) relaxation measurements. These structures possess characteristic length scales of 100-200 Å and have very large domain sizes (>1 μm), yet retain good transparency. Upon calcination the monoliths become opaque, though retain their bulk shape and possess mesoscopically ordered, hexagonally arranged pores (100-200 Å diameter), which impart high internal surface areas to the materials (ca. 1000 m²/g).

Synthesis of Highly Mesoscopically Ordered Ultra-Large Pore and Hydrothermally Stable Mesoporous Silica.

Referring to FIGS. 1a, 1b, and 1c, there is shown, approximately to scale, two prior art inorganic oxide porous structures and the SBA-15 produced in accordance with this invention. As shown in FIGS. 1a and 1b, Faujasite, a subnanoporous zeolite has a pore size of less than 1 nm. MCM-41, a mesoporous molecular sieve material, shown at FIG. 1c, has a pore size of about 8 nm. In contrast, as shown in FIG. 1d, SBA-15, the ultra large pore mesoporous silica material produced by this invention, has a pore size of about 20 nm, in this particular example.

Mesoporous silica SBA-15 was synthesized at 35-80°C, using a hydrophilic-hydrophobic-hydrophilic PE0-PPO-PPO triloblock copolymer as the structure-directing-agent. 4.0 g of PLURONIC P123 (PE0-PPO-PPO) was dissolved in 30 g water and 120 g (2 M) HCl solution while stirring at 35°C. To the resulting homogeneous solution 8.5 g of TEOS was added while stirring at 35°C for 22 h. The mixture was then aged at 100°C without stirring for 24 h. The solid product was filtered, washed, and air-dried at room temperature. Calcination was carried out in air by slowly increasing the temperature (from room temperature to 500°C over 8 h) and heating at 500°C for 6 h.

X-ray diffraction is an important means for characterizing the SBA-15 family of materials. FIGS. 2a and 2b show small-angle XRD patterns for as-synthesized and calcined hexagonal mesoporous silica SBA-15 prepared by using the polyoxyalkylene triloblock copolymer PE0-PPO-PPO (PLURONIC 123). The chemical composition of the reaction mixture was 4 g of the copolymer: 0.041 M TEOS: 0.24 M HCl: 6.67 M H₂O. The XRD patterns were acquired on a Scintag PAD diffractometer equipped with a liquid nitrogen cooled germanium solid-state detector using Cu Kα radiation. The X-ray pattern of as-synthesized hexagonal SBA-15 (FIG. 2a) shows four well-resolved peaks that are indexable as (100), (110), (200), and (210) reflections associated with 6H hexagonal symmetry. The as-synthesized SBA-15 possesses a high degree of hexagonal mesosopic organization indicated by three additional weak peaks that are present in the 2Theta range of 1-3.5°, corresponding to the (300), (220), and (310) scattering reflections, respectively. The intense (100) peak reflects a d-spacing of 104 Å, corresponding to a large unit cell parameter (≈120 Å). After calcination in air at 500°C for 6 h, the XRD pattern (FIG. 2b) shows that the 6H morphology has been preserved, although the peaks appear at slightly higher 2Theta. values with d(100) = 95.7 Å and a cell parameter (a₀) of 110 Å. Six XRD peaks are still observed, confirming that hexagonal SBA-15 is thermally stable. A similarly high degree of mesoscopic order is observed for hexagonal SBA-15 even after calcination to 850°C.

SEM images (FIGS. 3a, 3b) reveal that as-synthesized hexagonal SBA-15 has a wheat-like morphology with uniform particle sizes of about 80 nm, and that these consist of many rope-like macrostructures. The SEM’s were obtained on a JEOL 6300-F microscope. Calcined hexagonal SBA-15 at 500°C in air shows a similar particle morphology, reflecting the thermal stability of the mesoscopic shape and structure. TEM images (FIGS. 3c, 3d) of calcined SBA-15 with different sample orientations show well ordered hexagonal arrays of mesopores (one-dimensional channels) and further confirm that SBA-15 has a two-dimensional p6 mm hexagonal structure. The TEM’s were acquired using a 2000 JEOL electron microscope operating at 200 kV. For the TEM measurements, samples were prepared by dispersing the powder products as a slurry in acetone and subsequently deposited and dried on a holey carbon film on a Ni grid. From high-dry contrast in the TEM images, the distance between mesopores is estimated to be about 110 Å, in agreement with that determined from XRD data.

Nitrogen adsorption-desorption isotherm plots and the corresponding pore-size distribution curves are shown in FIG. 4 for calcined hexagonal SBA-15 samples that were prepared using the copolymer PE0-PPO-PPO-PPO. The sample corresponding to the measurements shown in FIGS. 4a and 4b was prepared by reaction at 35°C for 20 h, heating at 100°C for 48 h, and subsequent calcination in air at 500°C, yielding a hexagonal SBA-15 product material with a mean pore size of 89 Å, a pore volume of 1.17 cm³/g, and a BET surface area of 850 m²/g. The sample corresponding to the measurements shown in FIG. 4c and 4d was prepared under identical conditions but additionally used TMB as an organic swelling agent to increase the pore size of the subsequent product material. Using TMB yields hexagonal mesoporous SBA-15 silica with a mean pore size of 260 Å, a pore volume of 2.2 cm³/g, and a BET surface area of 910 m²/g. The isotherms were measured using a Micromeritics ASAP 2000 system. Data were analyzed by the BJH (Barrett-Joyner-Halenda) method using the Halsey equation for multilayer thickness. The pore size distribution curve was obtained from an analysis of the adsorption branch of the isotherm. The pore volumes were taken at P/Po = 0.983 signal point. Prior to the BET measurements, the samples were pretreated at 200°C overnight on a vacuum line. In both FIGS. 4a and 4c, three well-distinguished regions of the adsorption isotherm are evident: (1) monolayer-multilayer adsorption, (2) capillary condensation, and (3) multilayer adsorption on the outer particle surfaces. In contrast to N2 adsorption results for MCM-41 mesoporous silica with pore sizes less than 40 Å, a clear type H1 hysteresis loop in the adsorption-desorption isotherm is observed for hexagonal SBA-15 and the capillary condensation occurs at a higher relative pressure (P/Po = 0.75). The approximate pore size calculated using the BJH analysis is significantly smaller than the repeat distance determined by XRD, because the latter includes the thickness of the pore wall. Based on these results, the thickness of the pore wall is estimated to be ca. 31 Å (Table 1) for hexagonal SBA-15 prepared using the PE0-PPO-PPO-PPO copolymer.

Heating as-synthesized SBA-15 in the reaction solution at different temperatures (80-140°C) and for different lengths of time (11.72 h) resulted in a series of structures with different pore sizes (47-89 Å) and different silica wall thicknesses.
(31-64 Å) (as presented in Table 1). The pore sizes and the wall thicknesses determined for hexagonal SBA-15 from TEM images (such as shown in FIGS. 5a, 5b) are in agreement with those estimated from X-ray and N₂ adsorption measurements. The walls are substantially thicker than those typical for MCM-41 (commonly 10-15 Å) prepared using alkyloammonium ion surfactants as the structure-directing agents. Higher temperatures or longer reaction times result in larger pore sizes and thinner silica walls, which may be caused by the high degree of protonation of the long hydrophilic PEO blocks of the copolymer under the acidic S¹⁺X⁻ synthesis conditions. EOH moieties are expected to interact strongly with the silica species and to be closely associated with the inorganic wall. Increasing the reaction temperature results in increased hydrophobicity of the PEO block group, and therefore on average smaller numbers of the EOH groups that are associated with the silica wall (see below) and thus increased pore sizes.

The pore size of hexagonal mesoporous SBA-15 can be increased to about 300 Å by the addition of cosolvent organic molecules such as 1,3,5-trimethylbenzene (TMB). In a typical preparation, 4.0 g of PLURONIC P123 was dissolved in 30 g water and 120 g (2 M) HCl solution with stirring at room temperature. After stirring to dissolve completely the polymer, 3.0 g TMB was added with stirring for 2 h at 35°C. 8.50 g TEOS was then added to the above homogeneous solution with stirring at 35°C for 22 h. The mixture was then transferred to a Teflon autoclave and heated at 100-140°C without stirring for 24 h. The solid product was subsequently filtered, washed, and air-dried at room temperature.

FIG. 6 shows the typical XRD patterns of hexagonal SBA-15 prepared by adding an organic swelling agent. The chemical composition of the reaction mixture was 4 g of the copolymer, 3 g TMB: 0.041 M TEOS: 0.24 M HCL: 6.67 M H₂O. The X-ray pattern of as-synthesized product (FIG. 6a) shows three well-resolved peaks with d spacings of 270, 154, and 133 Å at very low angle (20 of 0.2-1°), which are indexable as (100), (110), and (200) reflections associated with p6 mm hexagonal symmetry. The (210) reflection is too broad to be observed. The intense (100) peak reflects a d-spacing of 270 Å, corresponding to an unusually large unit cell parameter (a = 310 Å). After calcination in air at 500°C for 6 h, the XRD pattern (FIG. 6b) shows improved resolution and an additional broad (210) reflection with d spacing of 100 Å. These results indicate that hexagonal SBA-15 is thermally stable, despite its unusually large lattice parameter. The N₂ adsorption-desorption results show that the calcined product has a BET surface area of 910 m²/g, a pore size of 260 Å, and a pore volume of 2.2 cm³/g. TEM images confirm that the calcined products have highly ordered, hexagonal symmetry with unusually large pore sizes (FIGS. 5c, 5d).

FIG. 7 shows the change of the pore size and the d-spacing of the XRD d(100) peak as a function of the TMB/copolymer mass ratio for calcined hexagonal SBA-15. The pore sizes of calcined SBA-15 were measured from the adsorption branch of the N₂ adsorption-desorption isotherm curve by the BJH (Barrette-Joyner-Halenda) method using the Halsey equation for multilayer thickness. The pore size data for the MCM-41 sample were taken from ref. 4. The chemical compositions of the reaction mixture were 4 g of the copolymer: x g TMB: 0.041 M TEOS: 0.24 M HCl: 6.67 M H₂O for SBA-15 and NaAlO₂: 5.3 M TMACl: 2.27 TMAOH: 15.9 SiO₂: x g TMB: 0.15 TMAOH: 450H₂O for the MCM-41 (C₁₇₃₋₅TMACl = tetradecyltrimethylammonium chloride, TMAOH = tetraxethyldiammonium hydroxide). The ratios used in this study ranged from 0 to 3, with the d(100) spacing and pore size increasing significantly, up to 320 Å and 300 Å, respectively, with increasing TMB/copolymer ratio. The increased pore size is accompanied by retention of the hexagonal mesostructure, with the X-ray diffraction patterns of each of these materials exhibiting 3-4 peaks.

To the best of our knowledge, hexagonal SBA-15 has the largest pore dimensions thus far demonstrated for mesoscopically ordered porous solids. As shown in FIG. 7, the d(100) spacing and pore size of calcined MCM-41 prepared by using cationic surfactant species can also be increased, but compared to SBA-15, the change is much less. In addition, although MCM-41 pore sizes of ca. 100 Å can be achieved by adding auxiliary organic species (e.g., TMB), the resulting materials have significantly reduced mesostructural order. The XRD diffraction patterns for such materials are substantially less resolved, and TEM micrographs reveal less ordering, indicating that the materials possess lower degrees of mesoscopic order. This is particularly the case near the high-end of this size range (~100 Å) for which a broad single peak is often observed. These materials also tend to suffer from poor thermal stability as well, unless additional treatment with well TEOs (which reduces the pore size) is carried out. From our results, a family of highly ordered mesoporous SBA-15 silica can be synthesized with large uniform and controllable pore sizes (from 89-500 Å) by using PEO-PPO-PEO copolymer species as amphiphilic structure-directing agents, augmented by the use of organic swelling agents in the reaction mixture. The pore size for hexagonal SBA-15 determined by TEM images (FIGS. 5c, 5d) is in agreement with that established from separate N₂ adsorption measurements.

Magic-Angle Spinning (MAS) NMR spectra (FIG. 8) of as-synthesized hexagonal SBA-15 show three broad peaks at 99, 99, and 109 ppm, corresponding to Q₂, Q₃, and Q₄ silica species, respectively. From the relative peak areas, the ratios of these species are estimated to be Q₂:Q₃:Q₄ = 0.70:0.78:1. These results indicate that hexagonal SBA-15 possesses a somewhat less condensed, but similarly locally disordered, silica framework compared to MCM-41.

TGA and DTA analyses (FIG. 9) of hexagonal SBA-15 prepared using PEO₉₂PPO₇₀PEO₂₀ show total weight losses of 58 wt% apparently consisting of two apparent processes: one at 80°C (measured using TGA) yields a 12 wt% loss, accompanied by an endothermic DTA peak due to desorption of water, followed by a second 46 wt% weight loss at 145°C with an exothermic DTA peak due to desorption of the organic copolymer. A Netzsch Thermoanalyzer STA 409 was used for thermal analysis of the solid products, simultaneously performing TGA and DTA with heating rates of 5 K/min. in air.

The desorption temperature of the large block copolymer (~150°C) is much lower than that of cationic surfactants (~360°C), so that the organic copolymer species can be completely removed and collected without decomposition by heating SBA-15 in an oven (air) at 140°C for 3 h. (The possibility to recover and reuse the relatively expensive tri-block copolymer structure-directing species is an important economic consideration and benefit to these materials.) It should be noted that the pure block copolymer PEO₉₂PPO₇₀PEO₂₀ decomposes at 270°C, which is substantially lower than that of cationic surfactants (~360°C) during calcination. For comparison, the TGA of the copolymer PEO₉₂PPO₇₀PEO₂₀ impregnated in SiO₂ gel shows that the copolymer can be desorbed at 190°C, which is ~50°C higher than required for hexagonal SBA-15. Removal of the organic species from as-synthesized SBA-15 at these relatively low temperatures (e.g., 140°C) suggests the absence of strong electrostatic or covalent interactions between the copolymer species and the polymerized silica wall, together
with facile mass transport through the pores. The possibility to recover and reuse the relatively expensive triblock copolymer structure-directing species is an important economic consideration and advantage of these materials.

Hexagonal SBA-15 can be synthesized over a range of copolymer concentrations from 2-6 wt % and temperatures from 35-800°C. Concentrations of the block copolymer higher than 6 wt % yielded only silica gel or no precipitation of silica, while lower copolymer concentrations produced mesoporous silica. At room temperature, only amorphous silica powder or products with poor mesoporous order can be obtained, and higher temperatures (>80°C) yield silica gel. Like TEOS, tetramethyldisilicate (TMOS) and tetraethoxysilane (TPOS) can also be used as the silica sources for the preparation of hexagonal SBA-15.

SBA-15 can be formed in acid media (pH 1) using HCl, HBr, HNO₃, H₂SO₄, or H₃PO₄. Concentrations of HCl (pH 2-6) above the isoelectric point of silica (pH 2) produce no precipitation or yield unordered silica gel. In neutral solution (pH 7), only disordered or amorphous silica is obtained. We also measured the precipitation time (t) of the silica as a function of the concentration of HCl and Cl⁻. The [Cl⁻] concentration was varied by adding extra NaCl, while keeping the H⁺ concentration constant. From these measurements, log (t) is observed to increase linearly with log C (where C is the concentration of HCl or Cl⁻). Slopes of 0.31 for [Cl⁻] and 0.62 for HCl indicate that Cl⁻ influences the synthesis of SBA-15 to a lesser extent than does H⁺. Based on these results, we propose that the structure-directed assembly of SBA-15 by the polyykylxylene block copolymer in acid media occurs by a S²⁻X⁻ pathway. While both the EO and PO groups of the copolymer are positively charged in acid media, the PO groups are expected to display more hydrophobicity upon heating to 35-800°C, thereby increasing the tendency for mesoscopic ordering to occur. The protonated polyoxyalkylene (S¹), the anionic inorganic (X⁻) bonding, S¹-X⁻, and the positive silica species (I⁺) are cooperatively assembled by hydrogen bonding interaction forces. Assembly of the surfactant and inorganic species, followed by condensation of silica species, results in the formation of hexagonal SBA-15 mesophase silica. At high pH values (2-7), the absence of sufficiently strong electrostatic or hydrogen bonding interactions leads to the formation of amorphous or disordered silica.

One of the limitations of calcined MCM-41 materials prepared without additional treatment with TEOS is their poor hydrothermal stability. As shown in Fig. 10, both as-synthesized and calcined (500°C) 6 h MCM-41, prepared with C₉H₁₈N₄(CH₃)₃Br as previously described, show well resolved crystalline XRD patterns (Figs. 10a, 10b). However, after heating in boiling water for 6 h, the structure of calcined MCM-41 is destroyed and the material becomes amorphous, as evidenced by the absence of XRD scattering reflections in Fig. 10c. By contrast, all of the calcined hexagonal SBA-15 samples prepared using the PEO-PPO-PEO block copolymers are stable after heating in boiling water for 24 h under otherwise identical conditions. For calcined hexagonal SBA-15 prepared by using the PEO₁₀₀PPO₆₅PEO₁₀₀ copolymer and after calcination in air at 500°C and subsequent heating in boiling water for 6 h, the (210) reflection becomes broader, the (300), (220), and (310) peaks become weaker, while the (100) peak is still observed with similar intensity (Fig. 10d). After heating in boiling water for 24 h, the intensity of the (100) Bragg peak (Fig. 10e) is still unchanged. Nitrogen BET adsorption isotherm measurements carried out after such hydrothermal treatment shows that the monodispersity of the pore size, surface area, and pore volume are retained. The results confirm that calcined hexagonal SBA-15 silica is significantly more hydrothermally stable than calcined hexagonal MCM-41 silica, most likely because SBA-15 has a thicker silica wall. This is an improved one-step alternative to two-step post-synthesis treatments that use tetraethylorthosilicate (TEOS) to stabilize mesoporous MCM-41 by reforming and structuring the inorganic wall with additional silica.

Preparation of Mesoscopically Ordered Silica-Copolymer Monoliths and Films.

A typical preparation of monolithic silica-copolymer mesostructures is outlined below. A series of samples was made with varying amounts of PLURONIC F127 PEO₁₀₀PPO₆₅PEO₁₀₀ triblock copolymer, while holding other processing conditions constant. A calculated amount of a 20 wt % EtOH/PLURONIC F127 solution (between 0.7 and 3.5 ml) is transferred into a 50 ml vial. 0.72 ml of an acidic solution of HCl (pH 1.5) is added to the polymer solution while stirring, followed by addition of 1.0 ml of tetraethylorthosilicate (TEOS). The solution is stirred until homogeneous, and allowed to gel uncovered under ambient conditions. After gelation (~2 days) the samples are covered for 2 weeks at room temperature. At the end of this period the gels have shrunk, yet done so uniformly to retain the shape of the container. Further research has shown that addition of a small amount of 3-glycidoxypropyltrimethoxysilane can prevent shrinkage. The cover is removed and the materials are dried at room temperature to eliminate excess solvent. The F127 series materials produced are transparent up to 38 wt % polymer, after which the polymer macro-phase separates creating a white opaque material. Figs. 11a and 11b show optical photographs of two of the monoliths produced. These monoliths were produced using a 2:1 ratio of water to TEOS at pH 1.4 and room temperature, with aging for approximately 1 month. Note the high degree of transparency and only one crack in the 34 wt % sample. Subsequent research has allowed us to produce crack-free monoliths by varying the aging time and temperature. The monoliths pictured are approximately 3-mm thick; although thicker monoliths can be produced, the aging time for these samples increases significantly to eliminate cracking.

These monoliths were analyzed using XRD, TEM, and NIVIR to determine mesostructural morphology, as well as the mechanism of the structure formation. The F127 polymer series above showed an aggregation point of roughly 25 Wt % F127, below which the polymer was dispersed and homogeneously dispersed within the matrix and above which aggregation of the polymers led to silica-copolymer mesophases. The copolymer weight percent required to produce specific phases vary depending upon the exact conditions and copolymer used, however this example may be considered representative, though by no means all inclusive, of the results observed.

XRD patterns of powdered samples obtained from the monoliths show a single diffraction peak with increasing intensity for increasing polymer concentration with a maximum at 38 wt %. Below 27 wt % F127, no XRD intensity is observed. The d(100) peak is centered at 112 Å for 27-34 wt % and increases to 120 Å at the 38 wt % sample. The change in the location of the peak is due to phase changes in the material, as observed by TEM and NMR. TEM reveals well ordered silica-copolymer mesophases in the samples with higher copolymer concentration, such as the lamellar phase in the 38 wt % sample shown in Fig. 12. The image shows that the material has an extremely well ordered lamellar mesoscopic structure with a repeat distance of about 105 nm. The image region is 990 times 1200 nm. The large back-
ground stripes are artifacts produced by the microtome cutting process and are otherwise unrelated to the morphology of the material. Lower concentrations of copolymer produced hexagonal, gyroid, or micellar phases with spacings of about 110 Å. The domain sizes for these structures is quite large, well over 1 μm for the lamellar phase, which makes it surprising that only one XRD peak is observed, although others have shown that single XRD patterns do not always imply poorly ordered materials (F. Schuth). Below 27 wt% no mesostructural ordering is observed.

NMR spectroscopy was utilized to provide information about copolymer-silicate interactions on the molecular level. 1H T_{2} relaxation and two-dimensional 29Si—1H and 27Al—1H heteronuclear correlation NMR experiments reveal that the polymer is rigidly incorporated in the silicate at 11 wt% and begins to microphase separate at 20 wt%. At 27 wt% the PEO and PPO are 80% separated from the silicate, and at 38 wt% the PPO is fully separated (>10 Å) from the matrix. This indicates that a phase change has occurred in progressing from copolymer concentrations of 27 to 34 wt% in the samples, where some PPO—29Si correlation intensity is still observed. Some PEO was observed to be associated with the matrix at all concentrations, implying that the polymerizing silico and PEO blocks are compatible. This suggests that the material is produced by polymerization of silicate oligomers that selectively swell the PEO block of the composite mesostructure.

It is possible to use this chemistry and processing to produce thin SBA-15 silica-copolymer films by either spin-, drop-, or dip-casting. Such films can serve as robust permeable coatings for use in separation or chemical sensing applications or as host matrices for optically or electrically active guest molecules for use in optoelectronic devices. Fig. 13 shows a photograph and X-ray diffraction pattern of an optically transparent hexagonal SBA-15 polymer formed by drop-casting the reaction solution (2 ml TEOs, 0.6 ml H2O, 0.80 g PLURONIC P104, 1 ml dimethylformamide) onto a glass slide and drying at room temperature. The film is 50-μm thick, crack-free and transparent. The X-ray diffraction pattern of this film shows well resolved peaks that are indexable as (100), (110), (200), and (210) reflections associated with p6 mm hexagonal symmetry in which the one-dimensional axes of the ca. 20 Å aggregates are highly ordered horizontally in the plane of the film.

High quality films can be produced generally as follows. A mixture of 5 ml tetraethoxysilicate and 0.75-3.0 ml H2O (pH 1.4) is stirred for approximately 30 min or until the silicate has hydrolyzed sufficiently to become miscible with water and thereby form a homogeneous solution. An appropriate amount (generally between 1040 wt%) of block copolymer, such as PLURONIC P104 polylethyleneoxide-polypropyleneoxide-polyethyleneoxide copolymer, is dissolved in the solution. An additive such as ethanol, dimethyl formamide, or tetrahydrofuran can be added to vary the viscosity and coating properties. The mixture is allowed to age, then is dip-, drop-, or spin-coated onto a glass or Si wafer substrate. Thin films with variable thicknesses can also be produced using spin coating.

The XRD patterns confirm that these thin films have highly ordered hexagonal (p6 mm), cubic (1 m 3 m), or 3-d hexagonal (p6/mmm) mesostructures. They are highly ordered and can easily be shear aligned. BET measurements show that the thin films have narrow pore size distributions, pore sizes of 20-120 Å, pore volumes up to 1.7 cm3/g and BET surface areas up to 1500 m2/g. SEM images of these thin films show a uniformly flat surface. The thickness of the films can be adjusted from 100 nm-1 mm by varying the concentration of the solution, aging time and coating time.

The examples shown above use PEO20PPO70PEO20 copolymer species as the structure-directing agents. Highly ordered, ultra large pore size SBA-15 materials can also be synthesized by using PEO-PPO-PEO block copolymers with different ratios of EO to PO and without adding supplemental organic swelling agents, such as TMB. Table 1 summarizes the physicochemical properties of mesoporous silica prepared by using triblock and reverse triblock copolymers. The d(100)-spacings from X-ray diffraction measurements can be in the range of 74.5-118 Å, with pore sizes of 46-100 Å established by N2 adsorption measurements. The EO/PO ratio and intramolecular distribution and sizes of the corresponding blocks affects the formation of SBA-15. A lower EO/PO ratio with a symmetric triblock PEO-PPO-PEO copolymer architecture favors the formation of p6 mm hexagonal SBA-15. For example, PLURONIC L121, PEO90PPO30PEO90, at low concentrations (0.5-1 wt%) forms hexagonal SBA-15, while use of higher concentrations of this copolymer (2.5 wt%) leads to an unstable lamellar mesostructured silica phase. Higher EO/PO ratios of the block copolymer, e.g., PEO12PPO30PEO120, or PEO30PPO20PEO60, yield cubic SBA-15 silica, including an Im3 m morphology. These cubic mesophasic materials yield large 54-80 Å mesocopically ordered pores and high BET surface areas (up to 1000 m2/g). Hexagonal mesoporous silica SBA-15 can also be synthesized by using reverse PPO-PEO-PEO triblock copolymer configuration, for example, PEO10PPO30PEO10.

In general, any microphase-separating, domain-partitioning copolymer architecture can be considered promising for the synthesis of such mesostructured materials, according to the specifications imposed by processing conditions and ultimately the product properties desired. Additionally, cubic (Pm3 m) and hexagonal (p6 mm) mesostructures can be formed by using Brij 56, C18H35(OC2H5)2OH(C18H35O) surfactant species, with the pore sizes controllable from 25-40 Å and BET surface areas up to 1070 m2/g. Brij 76 (C18H35O) yields the three-dimensional hexagonal (P63/mmc) and two-dimensional hexagonal (p6 mm) mesostructures with similar pore sizes and surface areas; see Table 2.

Films and monoliths can be produced with several variations of the solution conditions and/or sol-gel parameters, such as the ratio of water to TEOS, aging time, acidity, additives, temperature, and choices of copolymer or nonionic surfactants. Materials for specific applications can be formulated by appropriate modification of these parameters. Heat treatment after gelation can also produce harder materials that are less likely to crack.

We have found that silica-surfactant mesophases and MCM-41-type mesoporous materials can be aligned using liquid crystal processing strategies, including imposition of magnetic, shear, or electric fields. Similarly, polymer processing of the silica-copolymer composites is expected to be equally advantageous for producing aligned ultra large mesopore hydrothermally stable materials. For example, it should be possible to induce orientational ordering of the silica-copolymer composites and resultant mesoporous materials by applying shear to the sol-gel/copolymer system as it dries. Concerning variations on processing SBA-15-copolymer thin films (0.1-100 μm), use of shear alignment strategies, including spin-coating and dip-casting (i.e., drawing a vertical line from a reservoir of the reaction solution), have been shown to induce larger degrees of orientational order than provided by drop-coat preparations. Moreover, guest molecules such as conducting or optically active organic spe-
cies can be introduced to the reaction solution(s) and incorporated into the silica-copolymer monoliths, films or powders prior to or during processing. We have demonstrated the efficacy of this for the inclusion of conducting polymer moieties, such as poly(3,4-ethylenedioxythiophene) in SBA-15 silica-copolymer monoliths and spin-, drop-, and dip-cast films.

Methods currently available for the preparation of inorganic-organic mesophases or mesoscopically ordered porous materials typically involve one of five pathways that rely on Coulombic or hydrogen-bonding interactions, represented by the shorthand notations $S^*$, $X^*$, $Y^*$, $S^*Y^*$, or $S^*Y$. The most popular route used in syntheses of mesoporous materials has been the $S^*$ approach in basic media, but the $S^*Y$ and $S^*X^*$ syntheses generally yield unstable non-silica based mesoporous materials. Furthermore, the surfactants used as the structure-directing agents in these cases (e.g., alkylammonium, alkylamine) are expensive and/or environmentally noxious. The $S^*Y^*$ synthesis route generally yields disordered or worm-like mesoporous solids due to the absence of strong electrostatic or hydrogen binding interactions. The materials and synthesis method described here are less expensive, non-toxic, and considerably more versatile than the cases described above. They can be used to tune material properties, such as mesoscopic ordering, pore size, hydrothermal stability, monolith shape, orientational alignment, and compatibility with a wide range of guest molecules to a significantly greater extent than possible with the current state-of-the-art.

The ultra large mesopores in calcined SBA-15 materials provide new opportunities in chromatographic separations of large molecules, such as proteins, enzymes, or polymers. In addition, these materials have promise for new applications in environmental remediation, such as the clean up of polycyclic aromatics, porphyrins, other large organics, and heavy metals from process streams or soils. These properties can be enhanced and tailored by functionalizing molecular moieties along the inorganic walls to provide chemical as well as size selective specificity of adsorption interactions.

To the best of our knowledge there have been no reports of mesoscopically ordered silica monoliths or films with large characteristic structural length scales (>50 Å). The large dimensions of the inorganic-copolymer aggregates and large pore sizes of the composite or mesoporous materials detailed herein are superior to conventional mesoporous solids due to their thermal stability, transparency, monolithic form, and ability to incorporate large guest molecules. SBA-15 mesoporous silica also has distinct advantages over dense silica, particularly for applications requiring a lower dielectric constant material. SBA-15 has much lower density, long range mesoscopic order and possibilities for obtaining materials with high degrees of structural anisotropy, compared to dense silica. The improvements substantially exceed those provided by MCM-type materials, as discussed earlier. This has attractive implications for the development of low dielectric constant materials, particularly for reducing the capacitance of interconnects, which are among the most severely limiting factors in improving integrated and optical circuit performance. As shown in FIG. 14, the quest for materials with dielectric constants significantly below 2 appears to be well within reach; calcined SBA-15 materials have been prepared with porosities of 0.6-0.86, which lead to calculated optical dielectric constants of 1.1-1.4. One can produce aligned morphologies or structures with unconnected spherical cavities to eliminate transverse channel connectivities, which are undesirable for dielectric materials applications.

Use of block copolymers with a hydrophobic core also produces the unique ability to stabilize hydrophobic guest molecules that would not otherwise be compatible with the hydrophilic sol-gel reaction, such as some optically active dyes and polymers. Before now all optical moieties incorporated into sol-gel materials were either water soluble or had to be chemically grafted onto a compatible polymer. The inclusion of a hydrophobic region within our silicates, yet still smaller then optical wavelengths, allows an entirely new area of monoliths and coatings to be developed using hydrophobic dyes and optically active organics while retaining optical transparency. Furthermore, inclusion of guest conducting or optically active species, such as polymers and/or metal nanoparticles, in the pores can create quantum-effect materials.

The controllability of the SBA-15 pore sizes, inorganic wall composition, organic composition, and guest species composition permit the properties (e.g., optoelectronic, mechanical, thermal, etc.) to be tuned over an enormous range. Indeed, sequential introduction of guest species, for example a conducting polymer coating on the interior of the inorganic wall, followed by a second polymer or metal-semiconductor species in the pore center, could lead to the first mesoscopically ordered arrays of nanosized coaxial quantum wires.

Generalized Block Copolymer Syntheses of Mesoporous Metal Oxides

Mesoporous metal oxides were synthesized at 30-70°C using poly(alkylene oxide) block copolymers HO(CH₂CH₂O)ₙ(CH₂═CHCH₂O)ₘ(HOCH₂CH₂O)ₙ∥PO₃—EO—PO₂—EO—∥PO₃—EO—PO₂—EO—∥PO₃—BO₃ block copolymers as the structure-directing agents. In a typical synthesis, 1 g of poly(alkylene oxide) block copolymer was dissolved in 10 g of ethanol (EtOH). To this solution, 0.01 mole of the inorganic chloride precursor was added with vigorous stirring. The resulting sol solution was gelled in an open petri dish at 40-60°C in air. The aging time differs for different inorganic systems. Alternatively, the sol solution can be used to prepare thin films by dip coating. The as-made bulk samples or thin films were then calcined at 400°C for 5 hours to remove the block copolymer surfactants. For the Al and Si-xAl₃ systems, calcination was carried out at 600°C for 4 hr. For WO₃, calcination at 300°C is sufficient to yield ordered mesoporous oxides.

X-ray diffraction (XRD) is an important technique for characterizing these metal oxide mesostructures. Table 3 summarizes the synthetic conditions, including the inorganic precursors and aging temperatures and times for the mesostructured inorganic/copolymer composites (before calcination) using E050PO50EO20 as the structure-directing agent. A broad array of mesostructured composites have been successfully prepared, covering the first-, second- and third-row transition metals and some main group elements as well. The ordering lengths shown in Table 3 correspond to the largest d value observed from the low-angle XRD patterns; it ranges from 70 to 160 Å for the different systems. High-order low-angle diffractions are also observed for most of these systems. Quantitative elemental analysis suggests that the frameworks of these mesostructured composites are made up of metal-oxygen-chlorine networks.

Upon calcination, mesoporous TiO₂, ZrO₂, Nb₂O₅, Ta₂O₅, Al₂O₃, WO₃, SiO₂, SnO₂, H₂O, and mixed oxides Siₓ-xTiₓYₙ, Zr₁-xTiₓO₂, Al₁-xTiₓO₂, Sn₁-xAlₓO₃, and Sn₁-xAlₓO₃ are obtained. X-ray diffraction, transmission and scanning electron microscopy imaging (TEM & SEM), and nitrogen adsorption/desorption are three crucial techniques for characterization of these materials. Table 4 summaries the analysis results, including the ordering length, pore size, wall thickness, wall structure, porosity and Brunauer-Emmett-Teller (BET) surface area.
FIG. 15 shows typical XRD patterns for mesostructured zirconium oxides prepared using $\text{EO}_2\text{PO}_{10}\text{EO}_2$ as the structure-directing agent before and after calcination. The as-made zirconium inorganic/polymer mesostructure (FIG. 15a) shows three diffraction peaks with $d=115, 65,$ and $59$ Å. After calcination, the diffraction peaks appear at higher 20 angles with $d=106, 60,$ and $53$ Å (FIG. 15b). Both sets of diffraction peaks can be indexed as the (100), (110), and (200) reflections from 2-dimensional hexagonal mesostructures with lattice constants of 132 and 122 Å, respectively. Similar XRD results are obtained in other mesoporous metal oxides. The ordering lengths of these mesoporous metal oxides (Table 4) are substantially larger than those of materials previously reported.

Thermogravimetric experiments indicate that the block copolymer is completely removed upon calcination at 400°C. The appearance of low-angle diffraction peaks indicates that mesoscopic order is preserved in the calcined metal oxide materials. This is confirmed by TEM images obtained from mesoporous samples. As examples, FIGS. 16-26 show TEM images of mesoporous $\text{ZrO}_2$, $\text{TiO}_2$, $\text{SnO}_2$, $\text{WO}_3$, $\text{Nb}_2\text{O}_5$, $\text{Ta}_2\text{O}_5$, $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, $\text{SiO}_2$, $\text{SnO}_2$, $\text{Al}_2\text{O}_3$, and $\text{ZrO}_2$ recorded along the [110] and [100] zone axes of the 2-dimensional hexagonal mesostructures. In each case, ordered large channels are clearly observed to be arranged in hexagonal arrays. The pore/channel walls are continuous and have thicknesses of 3.9-5.9 nm. They are substantially thicker than those typical of metal oxides prepared using alkylammonium ion surfactant species as the structure-directing agents. In addition, energy dispersive X-ray spectroscopy (EDX) measurements made on the calcined samples show the expected primary metal element signals with trace of C1 signal, which confirms that the inorganic walls consist predominantly of metal-oxygen networks.

Furthermore, selected area electron diffraction patterns (ED) recorded on mesoporous $\text{ZrO}_2$, $\text{TiO}_2$, $\text{SnO}_2$, and $\text{WO}_3$ show that the walls of these materials are made up of nano-crystalline oxides that show characteristic diffuse electron diffraction fringe patterns (FIGS. 16-18 and 20 insets). Wide-angle X-ray diffraction studies of calcined samples also clearly show broad peaks that can be indexed according to the corresponding oxide crystalline phase. FIG. 15b shows a wide-angle diffraction pattern for the calcined $\text{ZrO}_2$ sample. The sizes of the nanocrystals in the calcined materials are estimated to be about 2 nm using the Scherrer formula. In addition, bright-field and dark-field (BF/DF) TEM imaging were employed to study the distribution of these nanocrystals. FIGS. 27 and 28 show such images recorded on same area of one thin mesoporous $\text{TiO}_2$ and $\text{ZrO}_2$ sample. As can be seen in the dark field image (FIGS. 27b, 28b), the oxide nanocrystals are uniformly embedded in a continuous amorphous inorganic matrix to form mesocrystalline wall structures. This is the first time that the combination of electron diffraction, X-ray diffraction, and bright field/dark field TEM imaging has been used to conclusively demonstrate that our mesoporous metal oxides have mesocrystalline framework.

FIGS. 29-36 show BET isotherms that are representative of mesoporous hexagonal $\text{ZrO}_2$, $\text{TiO}_2$, $\text{Nb}_2\text{O}_5$, $\text{Ta}_2\text{O}_5$, $\text{Al}_2\text{O}_3$, $\text{WO}_3$, $\text{SiO}_2$, and $\text{ZrO}_2$. Barrett-Joyner-Halenda (BJH) analyses show that the calcined hexagonal mesoporous metal oxides exhibit pore sizes of 35-140 Å, BET surface areas of 100-850 $\text{m}^2/\text{g}$, and porosities of 40-60%. The pore sizes are again substantially larger than the previous reported values. For most of the isotherms obtained on these metal oxides, three well-distinguished regions of the adsorption isotherm are evident: (1) monolayer-multilayer adsorption, (2) capillary condensation, and (3) multilayer adsorption on the outer particle surfaces. In contrast to $\text{N}_2$ adsorption results obtained for mesoporous metal oxides prepared using low-molecular-weight surfactants with pore sizes less than 4 nm, large hysteresis loops that resemble typical H1- and H2-type isotherms are observed for these mesoporous metal oxides.

The foregoing examples used $\text{EO}_2\text{PO}_{10}\text{EO}_2$ copolymer species as the structure-directing agent. Mesoporous metal oxides with other mesostructures can be synthesized by using $\text{EO}_2\text{PO}_{10}\text{EO}_2$ or $\text{EO}_2\text{PO}_2\text{EO}_2$ block copolymers with different ratios of EO to PO or BO. For example, when $\text{EO}_2\text{BO}_2\text{EO}_2$ copolymer is used as the structure-directing agent, mesoporous $\text{TiO}_2$ with cubic mesostructure can be prepared. FIG. 37 shows typical XRD patterns for mesostructured titanium oxides prepared using $\text{EO}_2\text{BO}_2\text{EO}_2$ as the structure-directing agent, before and after calcination. The as-made titanium inorganic/polymer mesostructure (FIG. 38a) shows six diffraction peaks with $d=110, 70, 58, 44, 41, 25$ Å, which can be indexed as the (110), (200), (211), (310), (222), (440) reflections of an Im3 m mesophase. After calcination, the diffraction peaks appear at higher 20 angles with $d=76, 53,$ and $43$ Å (FIG. 38b). These diffraction peaks can be indexed as the (110), (200), and (211) reflections of Im3 m mesostructures. The cubic mesostructure is confirmed by the TEM imaging (FIGS. 38c, 39).

Films and monoliths (FIG. 40) can be produced by varying such synthetic conditions as the solvent, the ratio of inorganic/polymer, aging temperature, aging time, humidity, and choice of the block copolymer. Liquids that are common solvents for inorganic precursors and the block copolymers (e.g. methanol, ethanol, propanol, butanol) can be used during the synthesis. The temperature, the amount of water added, and the pH can adjusted to control formation of the mesostructures. Materials for specific applications can be formulated by appropriate modification of these parameters.

The advantages and improvements over existing practice can be summarized as follows:

1. Robust, thick channel walls (35-90 Å) which give enhanced thermal and chemical stabilities.
2. Very large pore sizes (3.5-14 nm)
3. Use of low-cost inorganic precursors
4. Versatile synthetic methodology using non-aqueous media that can be generally applied to vastly different compositions, among which mesoporous $\text{SnO}_2$, $\text{WO}_3$, and mixed oxides $\text{SiO}_2$, $\text{ZrO}_2$, $\text{Al}_2\text{O}_3$ are synthesized for the first time.
5. For the first time, conclusive demonstration of the nanocrystallinity of the framework in mesoporous $\text{ZrO}_2$, $\text{TiO}_2$, $\text{SnO}_2$, $\text{WO}_3$, using XRD, ED and BF/DF TEM imaging
6. Mesoporous metal oxides with various physical properties including semiconducting, low dielectric-constant, high dielectric-constant, and negative thermal expansion.

Crystallization of inorganic species during cooperative inorganic/organic self-assembly can lead to macroscopic phase separation of the inorganic and organic components. This is because crystallization energies often dominate the interaction energies that stabilize the inorganic-organic interface, thereby disrupting the establishment of mesostructural order. This is particular the case for non-lamellar phases. In the present invention, this situation is successfully circumvented by using conditions that initially produce a meso-copically ordered material with an amorphous inorganic wall structure (FIGS. 15c and 35c) within which a high density of nanocrystals can subsequently be nucleated upon calcination. The thick wall and the noncrystallized inorganic matrix prevent this partially crystalline structure from collapsing by
effectively sustaining the local strain caused by the nucleation of the nanocrystals. The coexistence of mesoscopic ordering and framework nanocrystallinity is extremely important for catalysis, sensor, and optoelectronic applications.

To the best of our knowledge, there has been no previous report of mesoporous metal oxide synthesis with such simplicity and versatility. The formation, with such unprecedented simplicity and generality, of large-pore mesopropically ordered metal oxides suggests that the same general inorganic/block polymer assembly mechanisms may be operating. In fact, it is well documented that alkylene oxide segments can form crown-ether type complexes with many inorganic ions, through weak coordination bonds. The multivalent metal species (M) can associate preferentially with the hydrophilic PEo moieties, as indicated in Scheme 1, because of their different binding capabilities with poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). The resulting complexes then self-assemble according to the mesoscopic ordering directed principally by the microphase separation of the block copolymer species, and subsequently cross-link and polymerize (Scheme 1) to form the mesopropically ordered inorganic/polymer composites.

The proposed assembly mechanism for these diverse mesoporous metal oxides uses PEo-metal chelating interactions in conjunction with electrostatics, van der Waals forces, etc., to direct mesostructure formation.

A unique feature of the current synthetic methodology is use of inorganic precursors in non-aqueous media. Because of the lower electronegativities of the transition metals compared to silicon, their alkoxides are much more reactive towards nucleophilic reactions such as hydrolysis and condensation. There has been some work on the nonhydrolytic sol-gel chemistry of inorganic oxides, a non-hydrolytic route involving carbon-oxygen bond cleavage instead of the metal-oxygen bond which has a general tendency to delay crystallization of the metal oxides, which is very important for the first step of our inorganic-copolymer cooperative self-assembly process. In addition, the hydrolytic route to metal oxides often leads to difficulties in controlling stoichiometry and homogeneity. Homogeneity depends on the rate of homocoagulation (i.e., formation of M-0-M and M-O-M) versus the rate of heterogeneous condensation, which can be hardly controlled in the hydrolytic process because of the different reactivities of the various precursors towards hydrolysis and condensation. However, in principle, the non-hydrolytic process should favor the formation of homogeneous binary oxides from different metal precursors because of the decreased difference in hydrolysis and condensation rates for different inorganic sources in non-aqueous media. This has been successfully demonstrated in the mesoporous mixed oxides syntheses using the methods of this invention.

This utilization of block copolymer self-assembly in conjunction with chelating complexation for inorganic/organic cooperative assembly in the non-aqueous media make it possible to synthesize mesoporous materials with vastly different compositions exemplified in Table 4.

Cooperative Multiphase Assembly of Meso-Macro Silica Membranes

Here we describe a novel procedure for the synthesis of artificial coral silica membranes with 3-d meso-macro structures. This process utilizes multiphase media while including microphase separation block copolymer/silica composite and macrophase separation between strong electrolytes and the composite in a single step. We find that strong electrolytes such as NaCl, HCl, KCl, NH4Cl, KNO3, or even transition metal cationic salts such as NiSO4, can be used to prepare meso-macro silica membranes that are formed at the interface of droplets of these inorganic salt solution. It is well known that in nature, macroscopic ordered silica structure such as diatom and coral are grown through a protein modified process in the ocean environments that are rich in inorganic salts such as NaCl. The process used in this study may be significant in understanding the formation of diatom and coral in nature which also can be considered as a 3-phase media process: the environment of the cell, the cell membrane and the aqueous media within the cell.

The silica membranes (size 4 cm x 4 cm, thickness 5 mm) with 3-d meso-macro silica network structures that we have prepared show oriented continuous rope, tyroid, and grape vine or dish pinwheel, and gyroid, morphologies dependent on the electrolyte strength of the inorganic salts or amphiphilic block copolymer templates. The macropore size (0.5-100 nm) can be controlled by inorganic salts and evaporation rate of the solvent. The mesoscopic structures can be highly ordered 2-d honeycomb (pore size 40-90 Å) or 3-d cubic packing, and controlled by the amphiphilic block copolymer templates. These artificial coral meso-macro silica membranes are thermally stable and exhibit a large surface areas up to 1000 cm²/g and pore volumes up to 1.5 cm³/g.

The silica membranes were prepared by the use of two-step sol-gel chemistry. First oligomeric silica sol-gel was obtained by pre-hydrolyzing of tetraethoxysilane (TEOS) in ethanol solution by an acid-catalyzed process. Second, the oligomeric silica sol-gel was added into a mixture solution of poly(ethylene oxide)-block-prene(ethylene oxide)-block-propylene oxide) (PEO-PPG-PEO) triblock copolymer and inorganic salts in water and ethanol. The final composition of this mixture was range of 1 TEOS: 6.8-34x10⁻⁵ copolymer 0.5-1.0 inorganic salt: 16-85H₂O. 0.002-0.04 HCl: 11-50 EtOH. The silica membranes with 3-d meso-macro structures were obtained after drying at room temperature, washing with water to remove the inorganic salts, and calcination to completely remove the organic block copolymer.

In a typical synthesis, 2.0 g TEOS (Aldrich) were added to 5 g ethanol, 0.4 g water and 0.4 g (0.1 M) of HCl solution with stirring at room temperature for 0.5 h, then heated at 70°C without stirring for 1 h. After cooling to room temperature, 1 g EO₂O₆EO₂O (PLURONIC P123, Aldrich/BASF, average molecular weight 5800), 1 g NaCl, 10 g ethanol and 10 g water were added to this solution with stirring at room temperature for 1 h. The resultant solution was transferred into an open petri dish, allowed to evaporate at room temperature. After complete drying, the solid membrane was removed from the dish, 20 g water added and then heated in a sealed container at 100°C for 3 days to dissolve the inorganic salts. After cooling to room temperature, the silica membranes were washed with de-ionized water and dried at room temperature. The as-synthesized silica membranes were calcined at 500°C for 3 h in air to completely remove all organic block copolymer.

FIG. 41 shows several representative scanning electron microscope (SEM) images, obtained on a JEOL 6300-F microscope, of the silica membranes and inorganic salt (NaCl) crystal co-grown with the membranes by sol-gel chemistry. The silica membranes prepared from NaCl solution show 3-d macroscopic network structures and a coral-like morphology (FIG. 41a). The reticular 3-d network (thickness of 1 M). The silica membrane is made up of continuous rope-like silica which exhibits highly mesoscopic ordering (see below). The silica membranes can be as large as 4 cm x 4 cm depended on the size of the container that is used.
The thickness of the silica membranes can be varied from 10 μm to 5 mm.

As shown in FIG. 41b, the whole silica membrane shows similar local macroscopic structure that is not long-range ordering. The average macropore size of the silica membranes is about 2 - 5 μm (± 0.5) (FIG. 41a) and can be varied from 0.5 - 100 μm by changing the evaporation rate or the electrolyte strength of the inorganic salts. For example, when a small amount of ethylene glycol is added into the sol-gel solution to slow the evaporation rate, a small macropore size (0.5 - 5 μm) is obtained as shown in FIG. 41c. Of interest is finding that when the evaporation rate is low, the thickness of the silica network is decreased several hundreds nanometer as shown in FIG. 41c. When the evaporation rate is high, the macropore size of the silica membranes can be as large as 10 - 50 μm, the framework thickness is increased (as shown in FIG. 41d) and the macroscopic structure of the silica membranes is changed to a 2-d honeycomb channel structure.

The electrolyte strength of the inorganic salts also can be used to control the macropore size. By using stronger electrolytes, for example, MgSO₄, the macropore size can be as much as 20 - 50 μm. In addition, the morphology of the silica membrane can be modified through changing the concentration of inorganic salts. Low concentrations of the inorganic salts result in an inhomogeneous silica membrane. While high concentrations, result in the grape vine morphology that makes up the silica membrane as shown in FIG. 41e.

The morphologies of the inorganic salt crystals are also affected by the organic block copolymer. For example, without the amphiphilic block copolymer, cubic crystals of NaCl as large as 100 μm can be grown in the solution of water and ethanol, however, in the presence of the surfactant under our synthesis conditions, most NaCl crystals show an acicular (±1 μm in diameter) morphology (FIG. 41f) with a length of as much as 1 cm. When NiSO₄ is used as the inorganic salts in our synthesis condition, a disk-like morphology of NiSO₄ crystal is observed at the bottom of the silica membranes. This suggests that the crystallization of the inorganic salts can be directly controlled by block copolymers.

Besides NaCl, other inorganic salts such as LiCl, KCl, NH₄Cl, Na₂SO₄, MgSO₄, NiSO₄, MgCl₂, chiral NaClO₄, and organic acids such as, malic acid, can be used to form the silica membranes. FIG. 42 shows several representative scanning electron microscope (SEM) images of the meso/macroporous silica membranes prepared by using block copolymer P123 (a-c), or P65 (d) in different inorganic salt solutions. The morphology of the silica membranes is dependent on the electrolyte strength of the inorganic salts. For example, when LiCl, KCl, and NH₄Cl are used, with electrolyte strengths comparable to that for NaCl, a similar corallike morphologies (FIGS. 42a, b, c) are observed, although the network morphology of the silica membranes is somewhat different. However, when the inorganic salts with stronger electrolyte strengths such as Na₂SO₄, MgSO₄, are used in the synthesis, the macroscopic structures consist silica networks made up of toroid, pinwheel, dish, and gyroid morphologies (FIG. 43).

The macroscopic structure is also affected by the block copolymer. When higher aver-age molecular weight block copolymers such as PLURONIC F127 (EO105PO75EO105) is used, cubic morphology is observed by SEM (FIG. 43a). This morphology results from silica grown around cubic NaCl crystals, suggesting a macroscopic inorganic crystal templating process for the mesoporous silica growth. When block copolymers such as PLURONIC P65 (EO90PO35EO26) is used, the silica membrane with large macropore size is obtained (FIG. 42d).

The mesoscopic ordering in these silica membranes formed by the cooperative self-assembly of inorganic silica species/amphiphilic block copolymer is mainly controlled by the block copolymer while can be characterized by the low-angle X-ray diffraction patterns (FIG. 44) and transmission electron microscopes (TEM) (FIG. 45). The XRD patterns of FIG. 44 were acquired on a Scintag PADX diffractometer using Cu Ka radiation. For the TEM of FIG. 45 measurements, the sample was prepared by dispersing the powder products as a slurry in acetone and subsequently deposited and dried on a hole carbon film on a Cu grid. As shown in FIG. 44a, the coral-like silica membranes synthesized by using P123 triblock copolymer after removal of NaCl by washing, shows a typical hexagonal (p6 mm) XRD pattern for mesoporuous materials with four diffraction peaks (a = 118 Å), which is similar to that of SBA-15 described above. After calcination at 500°C in air for 6 h, the four-peak XRD pattern is also observed and the intensity of the diffraction peaks is increased, suggesting that the p6 mm mesoscopic ordering is preserved and thermally stable, although the peaks appear at slightly larger 20 values, with a = 111 Å. The cell parameters of mesoscopic ordering on the silica membranes can be varied by using different triblock copolymers. For example, a = 101 Å for Pluronin P103 (EO125PO75EO125) (FIG. 44d) and a = 77.5 Å for Pluronin P65 (EO90PO35EO26) (FIG. 44c), these materials have 2-d hexagonal (p6 mm) mesoscopic highly ordered structures.

These results suggest that the presence of the inorganic salts such as NaCl does not greatly effect the cooperative self-assembly of block copolymer/silica to form highly ordered mesostructure. FIGS. 45a, b show TEM images of calcined silica membranes prepared by using P123 block copolymer in NaCl solution at different orientations, confirming that silica network of the membranes is made up of a 2-d p6 mm hexagonal mesostructure, with a well-ordered hexagonal array and one-dimensional channel structure. TEM images (FIGS. 45c, d) of the silica membranes with small macropore size (about 0.5 μm from SEM) prepared by adding a small amount of ethylene glycol show that the rope-like networks of the silica membranes is made up of loop-like mesoporous silica with oriented 1-d channel arrays parallel to the long axis. These rope-like silica form a 3-d network macroporous structure. It should be noted that when higher molecular weight block copolymer F127 is used as the mesoscopic structure-directing agents, a silica membrane with cubic mesostructure (a = 217 Å) can be obtained, based on XRD and TEM results.

SEM images of the silica membranes after calcination at 500°C in air show that the coral-like macrostructure is retained, demonstrating that the coral-like meso-macro silica membranes prepared with inorganic salts are thermally stable. Thermal gravimetric and differential thermal analyses (TGA and DTA) (FIG. 46) in air of the silica membranes prepared by using P123 block copolymer in NaCl solution after removal of the inorganic salts, show total weight losses of only 24 weight % (FIG. 46a). A Netzsch Thermoanalyzer STA 409 was used for thermal analysis of the solid products, simultaneously performing TGA and DTA with heating rates of 5 K/min in air. At 100°C, TGA registers a 18 weight % loss accompanied by an endothermic DTA peak caused from desorption of water, this is followed by a 6 weight % TGA loss at 150°C, which coincides with an exothermic DTA peak associated with decomposition of the organic block copolymer. By comparison, the silica mem-
branes obtained without removed the inorganic salts show
total weight losses of 50 weight % (FIG. 46 bottom). At 100°
C. TGA registers a 4 weight % loss from physical adsorption,
of water, followed by a 46 weight % TGA loss at 200° C. from
decomposition of the organic block copolymer.

The above observations confirm that the interaction
between silica species and block copolymer species is weak,
and after washing with water 84 weight % of the block
copolymer in the silica membranes is removed. After washing
by water and without calcination, these silica membranes
already show similar nitrogen sorption behavior to that for
calcined silica membranes, (FIGS. 47a, b) so that after wash-
ing, both macroporous (<2 µm) and mesoporous (60 Å)
channels are already accessible. The isotherms of FIG. 47
were measured using a Micromeritics ASAP 2000 system.
Data were calculated by using the BdB (Broekhoff and de
Boer) model. The pore size distribution curve was obtained
from an analysis of the adsorption branch of the isotherm.
The pore volume was taken at P/PG = 0.985 signal point. The BET
sample was pretreated at 200° C. overnight on the vacuum
line.

The representative nitrogen adsorption/desorption
isotherms and the corresponding pore size distribution
calculated by using Broekhoff and de Boer’s model are shown
in FIG. 48. The isotherms of FIG. 48. The isotherms were
measured using a Micromeritics ASAP 2000 system. Data were
calculated by using the BdB (Broekhoff and de Boer) model.
The pore size distribution curve was obtained from an analy-
sis of the adsorption branch of the isotherm. The pore volume
was taken at P/PG = 0.985 signal point. The BET sample
was pretreated at 200° C. overnight on the vacuum line. The coral-like silica membranes prepared using P123 block
copolymer in a NaCl solution show a typical isotherm (type
IV) of cylindrical channel mesoporous materials with H-type
hysteresis, and exhibit a narrow pore size distribution at the
mean value of 84 Å. This material has a Brunauer-Emmett-
Teller (BET) surface area of 660 m²/g, and a pore volume
of 1.1 cm³/g. The mesoporous pore size of the silica-membranes
prepared in NaCl solution depended on the amphiphilic block
copolymer, for example, the materials prepared by using
P103 and P65 show similar isotherms and exhibit pore sizes
of 77 and 48 Å, BET surface areas of 720 and 930 m²/g, and pore
volumes of 1.12 and 0.99 cm³/g respectively (FIG. 48).
When large molecular weight F127 block copolymer is used
as the templates, the silica membrane with cubic mesostruc-
ture shows the isotherms with a large H3-type hysteresis
(FIG. 49a) much different with that for hexagonal meso-
copony array silica membranes and does not fit to cylinders
model by using BdB model to calculate the pore size distri-
bution. (FIG. 49b) However, using spheres model, it shows
quite narrow pore size distribution at a mean of 10.5 nm, and
exhibit a BET surface area of 1003 m²/g, pore volume of 0.8
cm³/g (FIG. 49b). The silica membranes prepared by using
nonionic oligomeric surfactant C₁₆H₃₃EO₆₀ also high BET
surface area of 710 m²/g and pore volume of 0.64 cm³/g, but
slightly smaller a mean pore size of 3.6 nm (FIG. 50a, b).

In order to understand the formation of the coral-like meso-
macro silica membranes, we have carefully investigated the
macroscopic structures in different areas (FIG. 51) of the
as-made silica membranes prior to washing. As shown in
FIGS. 51a-d, without washing out the inorganic salt (LiCl)
the macroscopic coral-like structures of the membrane have
been already formed in the middle region of the silica mem-
brane. On the other hand, the image recorded in the top region
of the silica membrane is quite different than that from the
middle region and show disordered pillow windows that have
similar average macro-window size compared that in the
middle region. These results suggest that the silica membrane
grown at the air interface is different that water interface.
FIG. 51d shows the SEM image of the silica membrane pre-
bred by LiCl recorded at the bottom region, suggesting that
the mosaic-like inorganic salt LiCl crystals, which are con-
fined by XRD and chemical analysis, are formed in the bot-
tom of the silica membranes. The shape of the pillow-like
LiCl crystals is somewhat similar to the fenestrated mor-
phology observed at the top region of the silica membrane.
SEM images of the silica membrane prepared by using NiSO₄
as the inorganic salt recorded on the top, middle, bottom regions of
the membrane are shown in FIGS. 51e-h. Without washing out
the inorganic salt (NiSO₄) (FIGS. 51e-f) SEM images reveal a disk-like window morphology at the top of the mem-
brane, while inside this window, a coral-like morphology can
be seen (FIG. 46f). However, at the bottom of the membrane,
grape vine-like silica macrostructures with disk-like inor-
ganic salt-NiSO₄ crystals are observed (FIGS. 51g, h). The size
of disk-like NiSO₄ crystals is the same as the window size of
the silica membrane at the top. These results are consist
within initial phase separation between the coral-like silica
macrostructure and inorganic salts, followed by formation of
the silica macrostructure above the inorganic salts.

In order to further confirm the formation of the materials,
we investigate the change of composition as a function of the
evaporation time (FIG. 52). The chemical composition of the
starting reaction mixture was 1 g P123 block copolymer 0.01
mol TEOS: 1 g LiCl: 4×10⁻⁸ mol HCl: 0.55 mol H₂O : 0.33
mol ETOH. As shown in FIG. 52, in the beginning, the con-
centration (weight %) of ethanol is decreased rapidly, and the
concentration of water and SiO₂ and inorganic salt LiCl are
increased since a large amount of ethanol is evaporated. After
about 3 h, silica-block copolymer gel starts to form, in liquid
phase, the concentration of silica is rapidly decreased and the
concentration of LiCl is rapidly increased. When the silica
mesostructure is formed as determined by XRD, almost all
the ethanol has evaporated (in liquid phase, a concentration
lower than 1%) and only a trace amount of silica is found in
the liquid phase, suggesting that the silica/organic block
copolymer composition has been already solidified at this
time at the interface with salt water. When the concentration
of salt LiCl is near saturation concentration (45%), the crys-
tallization of the inorganic salt LiCl occurs. At this time,
the formation of mesostructured silica has been almost com-
pleted. These results further indicate that the macroscopic
silica structure is formed first at the interface of inorganic salt
water, and sequentially, when the solution of the inorganic
salt reaches saturation concentrations, crystalline inorganic
salts are formed in the bottom of the membrane.

Based on above results, we postulate that macroscopic
silica structure is formed around a droplet of inorganic salt
solution as illustrated in Scheme A (FIG. 53). Ethanol is first
evaporated, then water. As the inorganic salt solution
becomes more concentrated, two domains are formed, one a
water-rich domain, where most inorganic salt is located,
another a water-poor domain, where silica and block copoly-
mer compositions are located. The formation of two domains
results in tri-phase separation, a droplet of inorganic salt
solution phase separated by silica-block copolymer gel. The
droplet of the solution serves as a template for the growth of
silica-block copolymer composites. Once the macrostructure
is rigidified, the inorganic salt solution approaches to the
bottom of the container progressively. The cooperative self-
assembly of silica/block copolymer occurs at the interface of
the droplet, and results in coral-like mesomacrosopic silica
structure. On the other hand, when the silica is formed at the
interface of air and salt water, the droplet of the salt solution becomes flatters, resulting in the fenestrated membrane at the top.

Referring to FIG. 54, progressively higher magnifications are shown of a section of a meso-macro silica membrane made in accordance with this invention. The membrane is shown in FIG. 54a, which has a macropore structure, as shown in FIG. 54b. However the walls defining the macropores have a mesoporous structure.

In summary, artificial coral silica membranes with 3-d meso-macro structures have been synthesized by a novel process of an acidic catalyzed silicate sol-gel chemistry in the present of inorganic salts. Inorganic salts play an important role on the formation of meso-macro silica membranes that are grown at the interface of a droplet of inorganic salt solution. The results are of general important for understanding multiphase processes such as the formation of diatoms coral silica structures in nature. The silica membranes (size = 4 cm×4 cm, thickness = 5 mm) with 3-d meso-macro silica network structures show oriented continuous rope, toroid, and grape vine, or dish, pinwheel, gyroid, and cubic cage morphologies depending on the electrolyte strength of the inorganic salts or amphiilphic block copolymer templates. The macropore size (0.5-100 μm) can be controlled by inorganic salts and the evaporation rate of the solvent. The mesoscopic structures can be highly ordered 2-d honeycomb (pore size 40-90 Å) or 3-d cubic packing and are controlled by the amphiphilic block copolymer templates. The coral-like mesomacro silica membranes are thermally stable and exhibit large surface areas (to 1000 cm²/g) and pore volume (to 1.1 cm³/g). We anticipate that these new processes materials with structure and design on multiple length scales will have many applications in the areas, including separation, sorption, medical implant, catalysis, and sensor array applications.

The example shown above in forming meso-macro silica membranes used PLURONIC P123 block copolymer, EO₃₅PO₇₀EO₃₅ as the template to control mesoscopic ordering of the silica membranes. Besides P123, other surfactants can also be used in the synthesis. For example, one could use:

1) A diblock copolymer, poly(ethylene oxide)-block-poly(propylene oxide); poly(ethylene oxide)-block-poly(butylene oxide) (Dow Company); BS0-6600, BL30-1500;
2) A triblock copolymer, poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide); (BASF) poly(ethylene oxide)-block-poly(butylene oxide)-block poly(ethylene oxide) (Dow Company); such as PLURONIC L64, L121, L122, P65, P85, P103, P104, P123, PF20, PF40, PF80, F68, F88, F98, F108, F127;
3) A reversed triblock copolymer PLURONIC 25R8, 25R4, 25R2;
4) A star di-block copolymer (BASF), TETRONIC 901, 904, 908; and
5) A reversed star di-block copolymer TETRONIC 901R, 904R, 908R.

The inorganic salts can be electrolyte, such as KCl, NaCl, LiCl, NH₄Cl, MgCl₂, MgSO₄, KNO₃, NaClO₃, Na₂SO₄, NiSO₄, CoCl₂, water organic acid, such as DL tartaric acid, citric acid, malic acid. We claim that dissolvable alkali salts, alkali earth salts, transition metal, sulfate, nitrate, halide, chloride, per chorlate.

The preparation of meso-macro silica membrane are emulsion chemistry latex sphere template; phase separation and solvent exchanged; inorganic salts templating which was
developed by ourselves here. This discovery should have great significance for understanding the formation of the diatom and coral in nature. The macromesoporous materials would have many applications in the areas of sorption, catalysis, separation, sensor arrays, optoelectronic devices. The materials and synthesis method described here are very versatile in that they can be used for many fields of applications and for synthesis of any inorganic-surfactant composites, for example, aluminophosphate-based, TiO₂, ZrO₂, Al₂O₃, Nb₂O₅, Ta₂O₅, Cr₂O₃, Fe₂O₃, ZrTiO₄, Al₂SiO₅, HFO₂ meso-macroporous silica membranes. These materials would have many applications on sorption, catalysis, separation, sensor arrays, optoelectronic devices.

The invention claimed is:

1. A method of forming a mesoscopically structured material comprising the step of combining an amphiphilic block copolymer with an inorganic species in a solvent, wherein the block copolymer and the inorganic species are assembled and then the assembled inorganic species are polymerized to form a mesoscopically structured inorganic-organic composite, wherein said inorganic species combined with said block copolymer is a precursor inorganic species and said assembled inorganic species are hydrolyzed inorganic species, and

wherein said inorganic species is a mixture comprising at least two of M(OR)s₁-s₂-...-sₙ, R³⁻, R⁴⁻, R₅⁻, R₆⁻, and/or MXₚ, wherein:
M is at least one atom other than carbon, hydrogen, oxygen, or nitrogen;
S=I;
R³⁻, R⁴⁻, R₅⁻, and R₆⁻ are organic moieties;
while 0 = s₁, s₂, u, v, w, y ≥ 6;
s₁-u+v-w-y=1; and
X is a halogen atom.

2. The method of claim 1, wherein said inorganic species is selected from the group consisting of AlCl₃, SiCl₄, ZrCl₄, TiCl₄, AlCl₃/TiCl₄, SiCl₄/TiCl₄, ZrCl₄/WCl₆, SnCl₄/TiCl₄.

3. The method of claim 1, wherein said mesoscopically structured inorganic-organic composite has a macroscopic orientational order.

4. The method of claim 1, wherein said mesoscopically structured inorganic-organic composite has a framework in which there is located nanocrystallites.

5. The method of claim 1, wherein said mesoscopically structured inorganic-organic composite is in the form of (a) a powder, (b) a film, (c) a fiber, or (d) a monolith.

6. The method of claim 1, wherein said amphiphilic block copolymer and said inorganic species are combined under non-hydrolytic conditions.

7. The method of claim 1, wherein said amphiphilic block copolymer and said inorganic species are combined under non-aqueous conditions.

8. The method of claim 1, wherein said block copolymer and inorganic species are assembled and polymerized within an aligning field to form the mesoscopically structured inorganic-organic composite which has a macroscopic orientational order.

9. The method of claim 1, wherein said combined block copolymer and inorganic species are processed to induce orientational ordering before the assembled inorganic species are polymerized to form the mesoscopically structured inorganic-organic composite.

10. The method of claim 1, wherein said block copolymer and inorganic species are assembled and polymerized in the presence of electrically responsive molecules or optically responsive molecules to form the mesoscopically structured inorganic-organic composite.
11. The method of claim 1, including the step, after assembly of the block copolymer and the inorganic species and polymerization of the assembled inorganic species, of calcining said mesoscopically structured inorganic-organic composite to form a mesoscopically structured material.

12. The method of claim 1, including the step, after self-assembly of the block copolymer and the inorganic species and polymerization of the assembled inorganic species, of solvent extracting said mesoscopically structured inorganic-organic composite to form a mesoscopically structured material.

13. The method of claim 1, including the step, after self-assembly of the block copolymer and the inorganic species and polymerization of the assembled inorganic species, of removing the block copolymer from said mesoscopically structured inorganic-organic composite to form a mesoscopically structured material.

14. The method of claim 1, wherein said mesoscopically structured inorganic-organic composite is functionalized to impart responsiveness in at least one property including an optoelectronic property, a thermal property, an optical property, a separation property, or a reaction property to form a multi-functional mesoscopically structured inorganic-organic composite.

15. A method of making any of (a) a fuel cell material, (b) an opto-electronic material, (c) a quantum-effect material, or (d) a medical implant, from a mesoscopically structured inorganic-organic composite or a mesoporous inorganic oxide material which are formed by combining an amphiphilic block copolymer with an inorganic species in a solvent, wherein the block copolymer and the inorganic species are assembled and then the assembled inorganic species are polymerized to form said mesoscopically structured inorganic-organic composite.

16. The method of claim 15 in which mesoscopically structured material is formed by the following steps: placing the amphiphilic block copolymer in an aqueous solution of inorganic salt; combining the aqueous solution containing the block copolymer with the inorganic species to form a multiphase medium that enables microphase separation of inorganic species and the block copolymer, thereby forming an inorganic-block copolymer composite, wherein the block copolymer enables macrophase separation of the inorganic-block copolymer composite and the aqueous solution of inorganic salt; polymerizing the inorganic species to form a meso-macrostructured inorganic-organic composite; removing the block copolymer and aqueous solution from said meso-macrostructured inorganic-organic composite to form said mesoscopically structured material.

17. A mesoscopically structured material that was formed by combining an amphiphilic block copolymer with an inorganic species in a solvent, wherein the block copolymer and the inorganic species are assembled and then the assembled inorganic species are polymerized to form a mesoscopically structured inorganic-organic composite, wherein said inorganic species combined with said block copolymer is a precursor inorganic species and said assembled inorganic species are hydrolyzed inorganic species, and wherein said inorganic species is a mixture of $M(OR)_{x}$, $M(OR)_{y-2w-v}$, $R^{1}, R^{2}, R^{3}, R^{4}$, and/or $M X_{z}$, whereby:

$M$ is at least one atom other than carbon, hydrogen, oxygen, or nitrogen;

$S=1$ or 2;

$R^{1}, R^{2}, R^{3}, R^{4}$, and $R^{5}$ are organic moieties; while $0<s, t, u, v, w, y>6$ and $s+t+u+v+w+y>1$; and $X$ is a halogen atom.

18. The mesoscopically structured material of claim 17, wherein said inorganic species is selected from the group consisting of AlCl$_3$/SiCl$_4$, ZrCl$_4$/TiCl$_4$, AlCl$_3$/TiCl$_4$, SiCl$_4$/TiCl$_4$, ZrCl$_4$/WOCl$_6$, SnCl$_4$/InCl$_3$.

19. The mesoscopically structured material of claim 17 wherein said inorganic species includes at least two inorganic compounds.

20. The mesoscopically structured material of claim 17 wherein said mesoscopically structured inorganic-organic composite has macroscopic orientational order.

21. The mesoscopically structured material of claim 17 wherein said mesoscopically structured inorganic-organic composite has a framework in which there is located nanocrystallinity.

22. The mesoscopically structured material of claim 17 wherein said mesoscopically structured inorganic-organic composite is in the form of (a) a powder, (b) a film, (c) a fiber, or (d) a monolith.

23. The mesoscopically structured material of claim 17 wherein said amphiphilic block copolymer and said inorganic species are combined under non-hydrolytic conditions.

24. The mesoscopically structured material of claim 17 wherein said amphiphilic block copolymer and said inorganic species are combined under non-aqueous conditions.

25. The mesoscopically structured material of claim 17 wherein said block copolymer and inorganic species are assembled and polymerized within an aligning field to form the mesoscopically structured inorganic-organic composite which has a macroscopic orientational order.

26. The mesoscopically structured material of claim 17 wherein said combined block copolymer and inorganic species are processed to induce orientational ordering before the assembled inorganic species are polymerized to form the mesoscopically structured inorganic-organic composite.

27. The mesoscopically structured material of claim 17 wherein said block copolymer and inorganic species are assembled and polymerized in the presence of electrically responsive molecules or optically responsive molecules to form the mesoscopically structured inorganic-organic composite.

28. The mesoscopically structured material of claim 17 wherein said mesoscopically structured inorganic-organic composite is subjected to a calcining step to form a mesoscopically structured material.

29. The mesoscopically structured material of claim 17 wherein said mesoscopically structured inorganic-organic composite is subjected to a solvent extracting step to form a mesoscopically structured material.

30. The mesoscopically structured material of claim 17 wherein said block copolymer is removed from said mesoscopically structured inorganic-organic composite to form a mesoscopically structured material.

31. A product comprising any one of (a) a catalyst, (b) a separation material, (c) a semi-permeable coating, (d) a material for sensing an agent in a mixture that contact the product, (e) a fuel cell material, (f) an opto-electronic material, (g) a quantum-effect material, or (h) a medical implant, the product
including a mesoscopically structured inorganic-organic composite or a mesoporous inorganic oxide material which is formed by combining an amphiphilic block copolymer with an inorganic species in a solvent, wherein the block copolymer and the inorganic species are assembled and then the assembled inorganic species are polymerized to form said mesoscopically structured inorganic-organic composite.

32. The product of claim 31 formed by the following steps: placing an amphiphilic block copolymer in an aqueous solution of inorganic salt; combining the aqueous solution containing the block copolymer with an inorganic species in a solvent to form a multiphase medium that enables microphase separation of inorganic species and the block copolymer, thereby forming an inorganic-block copolymer composite, wherein the block copolymer enables macrophase separation of the inorganic-block copolymer composite and the aqueous solution of inorganic salt; polymerizing the inorganic species to form a meso-macrostructured inorganic-organic composite; removing the block copolymer and aqueous solution from said meso-macrostructured inorganic-organic composite to form said meso-macroscopically structured material.