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Discovering Synthesis Routes to Hexagonally Ordered Mesoporous Niobium Nitrides Using Poloxamer/Pluronics Block Copolymers

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Supporting Information

Transition metal nitrides such as niobium nitride have been the subject of increasing scientific and technological interest in areas as diverse as supports for electrochemical catalysts,[1] energy storage devices,[2] and high critical field superconductors.[3] In such applications, ordered mesoscale porosity has been shown to have a beneficial effect on material performance, e.g., by increasing the surface area for a catalyst support,[4] by improving the performance of lithium−air batteries,[5] or by enabling studies of emergent properties such as flux pinning and angle-dependent magnetoelectric coupling in superconductors.[6] Block copolymer−inorganic hybrid coassembly[7,8] is a reproducible, convenient, and tunable route to produce such ordered mesoporous structures in a wide variety of functional materials, ranging from highly crystalline transition metal oxides[9,10] to single-crystal silicon nanostructures.[11] However, only a handful of studies to date have examined the use of block copolymers to structure-direct transition metal nitrides,[5,6,12,13] and most have made use of custom synthesized triblock terpolymers based on poly(isoprene-*b*-styrene-*b*-ethylene oxide) to generate complex cocontinuous gyroidal block copolymer network morphologies. These materials, which are available commercially only from a single vendor at extreme cost, represent a substantial impediment to the expanded study and application of ordered mesoporous transition metal nitrides. In contrast, poloxamer/Pluronics family poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (PEO−PPO−PEO) ABA triblock copolymers are widely commercially available. These ABA triblocks have been widely used to produce ordered mesoporous silica and transition metal oxides with varying mesostructures and degrees of crystallinity,[14,15] but as reviewed recently, their use in controlling the mesostructure of other families of functional inorganic materials such as carbides, sulfides, and nitrides has remained challenging.[16] Indeed, the sole report of a mesoporous transition metal nitride from a Pluronics ABA triblock involved a titanium nitride material produced as a composite with carbon as support,[13] substantially limiting opportunities for further processing and application in areas requiring the mechanical, electrochemical, and superconducting properties of the pure nitrides. Furthermore, to the best of our knowledge, no report exists to date of any block copolymer-directed pure mesoporous transition metal nitride with hexagonal morphology, the most common structure in studies of mesoporous materials.

One route to the synthesis of transition metal nitrides is treatment of transition metal oxides at high temperatures in flowing ammonia gas.[17] This process has been used to produce niobium nitride from fibers of niobium oxide[18] and from both monolithic[6] and thin film[4] ABC triblock terpolymer-derived niobium oxides with strut sizes around 30 nm. In the micrometer-scale fibers, nitride formation was first reported at 800 °C, while in the terpolymer-derived materials nitride formation was first observed at 600 °C. This decrease is correlated with the dramatically decreased solid-state diffusion length and increased accessibility to gas flow in mesostructured materials, suggesting that further increasing porosity and/or lowering wall thickness may enable oxide−nitride conversion at even lower temperatures, thereby allowing use of the relatively low molar mass Pluronics copolymers.

The synthesis of mesoporous structures consisting of atomically crystalline materials generally relies on either confining crystallization with a mechanical support such as carbon[9] or on optimizing the kinetics of crystal growth so that individual crystal grains do not grow larger than the size of the mesostructured pore walls.[19] The first route is multistep and requires optimization of chemistries to remove the support material without degradation to the underlying functional material (e.g., oxidation of a nitride), while the second route is direct but requires careful choice of reaction parameters to balance the competing kinetically limited processes of formation of the phase of interest with isotropic grain growth. For inorganic materials derived from poloxamer/Pluronic triblock copolymers, typical pore wall thickness is between 50 and 100 Å,[20] only slightly larger than the first supercritical crystalline nuclei which form in classical nucleation theory. Any synthetic approach based on the latter route must therefore reach a temperature high enough to nucleate the phase of interest but remain at a temperature low enough and for a time short enough that grains do not continue to grow significantly. The challenging combination of small wall thickness and high formation and crystallization temperatures have prevented access to poloxamer/Pluronics copolymer derived pure mesoporous nitrides in the past.[14]

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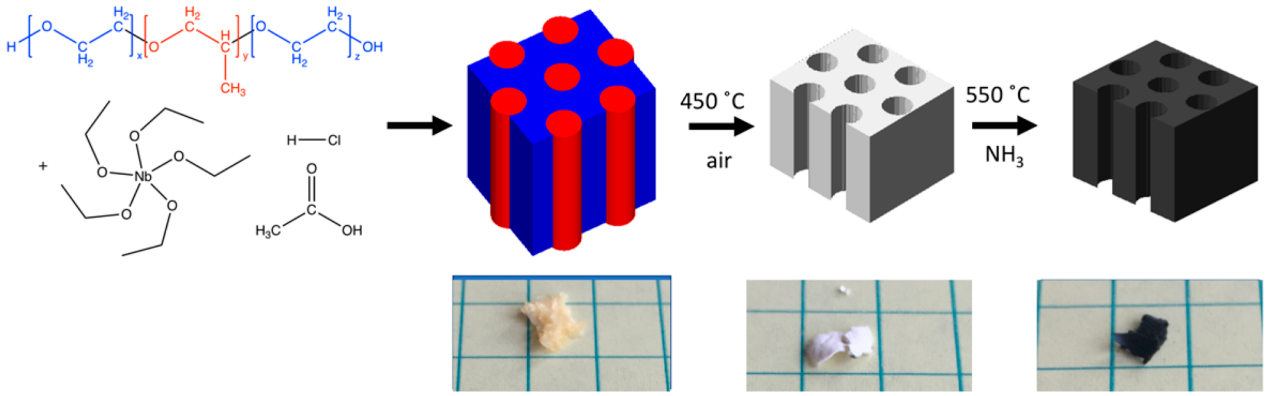

Figure 1. Schematic of synthetic route to mesoporous niobium nitride (tow row) and photographs (bottom row) of corresponding oxide−polymer hybrid, freestanding oxide, and freestanding nitride against quarter-inch gridlines.

Based on these considerations, we developed synthetic routes (Figure 1) to hexagonally ordered, mesoporous niobium nitrides with sub-10 nm pores using poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) ABA triblock copolymers (BASF Pluronic F127) and carefully tuned thermal processing conditions. First, a mesostructured oxide−polymer hybrid composite is prepared by a sol−gel condensation of niobium(V) ethoxide catalyzed by a combination of acetic and hydrochloric acid in ethanol, followed by solvent evaporation. The resulting hybrid films can then be calcined at 450 °C in air to remove the block copolymer and other organic species, producing an amorphous, white, ordered mesoporous niobium(V) oxide. This oxide is then treated in flowing ammonia gas, e.g., at a temperature of 550 °C for 90 min, to produce a visibly black, monolithic material. As revealed by ex situ as well as in situ small- and wide-angle X-ray scattering (SAXS/WAXS), small deviations from these processing conditions often result in either amorphous but mesostructured materials or highly crystalline materials with poor mesostructure retention due to the delicate balance between crystallization of the nitride phase of interest and growth of the crystalline domains beyond the pore wall thickness. The narrowness of this processing window is likely responsible for previous failures in the synthesis of Pluronics directed mesoporous nitrides.

To characterize the mesoporosity and crystallinity of the material after every processing step, we first used ex situ SAXS and WAXS; see Figure 2. SAXS patterns exhibited a strong main peak which, if assigned to a hexagonal lattice, represents d_{100} spacings of 13, 9.7, and 8.8 nm for the hybrid, oxide, and nitride, respectively (Figure 2A, bottom to top). Interestingly, the lattice order improves with each processing step, as determined by the sharpness of the smallest angle peak and appearance and increase in intensity of higher order peaks. The WAXS pattern for the freestanding oxide (Figure 2B, bottom) was indicative of an atomically amorphous material, consistent with past observations of mesoporous niobium(V) oxide treated at these temperatures.[6,20] The WAXS pattern for the nitride sample (Figure 2B, top) exhibited peaks consistent with a rock salt lattice (space group $Fm\overline{3}m$) with a lattice constant of 4.26 Å. This lattice constant is considerably lower than that of pure, bulk delta-phase niobium nitride samples grown by, e.g., magnetron sputtering[21] and is consistent with residual oxygen and cation site vacancies in the lattice, as observed in other mesoporous nitrides[12] as a result of incomplete interdiffusion of oxygen and nitrogen during ammoniolysis. This class of materials is also referred to as niobium oxynitrides, with formulas most accurately given by $NbN_xO_y[]_{1-x-y}$, where [] indicates vacancies. The material may also possess a significant fraction of cation vacancies driven by incomplete reduction of the Nb^{5+} to Nb^{3+} and incomplete densification of the material during ammoniolysis. Both factors—oxygen and anion site vacancies as well as cation site vacancies—may contribute to a reduced lattice parameter when compared with defect-free NbN.

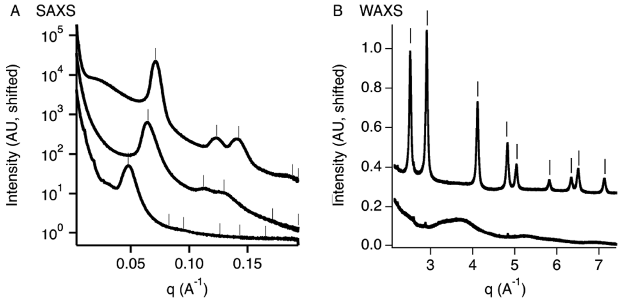

Figure 2. Material characterization by small- and wide-angle X-ray scattering (SAXS and WAXS). (A) SAXS traces of polymer−oxide hybrid (bottom, d_{100} = 13 nm), freestanding oxide (middle, d_{100} = 9.7 nm), and freestanding nitride (top, d_{100} = 8.8 nm). All markings indicate expected reflections for a hexagonal lattice with the given d_{100} spacings. (B) Synchrotron WAXS traces of mesoporous oxide (bottom) and nitride (top). Peak markings (|) are consistent with a NaCl-type lattice with a unit cell dimension of 4.26 Å. This material was nitrided at 550 °C for 90 min.

Debye−Scherrer analysis of the WAXS data gives an upper bound for the coherent scattering domain size of 6.5 nm. This is smaller than reported pore wall sizes in similar F127-derived mesoporous materials,[20] consistent with crystallization within the bounds of the mesostructured material wall. We suspect that the relatively low temperature of 550 °C for formation of the nitride allows extremely little grain growth, essentially trapping the first supercritical nuclei and producing a highly nanocrystalline material, thereby enabling retention of the mesostructure.

To corroborate the SAXS structure assignment and confirm that the materials had open and accessible mesopores, we used a combination of transmission electron microscopy (TEM) and nitrogen physisorption (Figure 3). The TEM images were consistent with mesoporous structures with repeat distances of 9 nm for the oxide and 8 nm for the nitride, comparable to lattice parameters observed by SAXS (vide supra). The nitride image (Figure 3B) clearly shows both face-on (along the

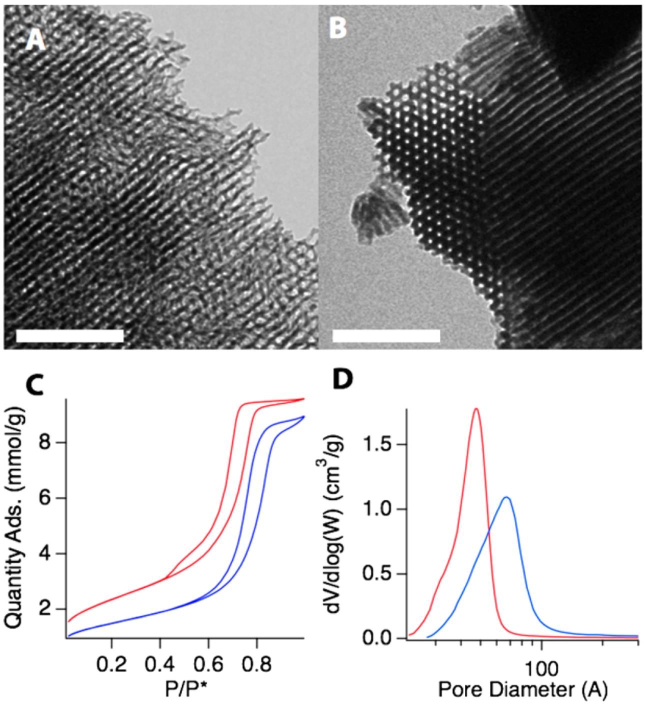

Figure 3. Material characterization by transmission electron microscopy and nitrogen physisorption. (A) TEM of freestanding mesoporous oxide and (B) of freestanding mesoporous nitride. All scale bars are 100 nm. (C) Nitrogen sorption isotherms of oxide (red) and nitride (blue). (D) Nitrogen sorption-derived pore size distributions of oxide (red) and nitride (blue).

cylinders' long axis) and edge-on (normal to the cylinders' long axis) views consistent with hexagonal symmetry. The nitrogen physisorption data (Figure 3C) exhibited a type IV(a) behavior with a H1 type hysteresis,[22] consistent with other block copolymer-derived mesoporous materials. The physisorption patterns were analyzed[23,24] to determine the pore size distribution and overall pore surface area (Figure 3D). The oxide sample had a surface area of 183 m^2 g^{-1}, while the nitride sample had a surface area of 117 m^2 g^{-1}. Both values are consistent with those reported for mesoporous oxides,[20] with the lower surface area in the nitride likely being due to shrinkage and densification of the material overall.[6] The oxide pore size distribution included a pronounced tail toward smaller pore sizes, while the nitride pore size distribution exhibited a more uniform behavior. This may be a result of micropores collapsing or access to the pores closing over as the structure shrinks during processing. Further, the pore size distribution shows an increase in pore diameter from 48 Å in the oxide to 68 Å in the nitride. This is consistent with observation of the micrographs and with the expected densification of the material (ca. 50% based on comparison of bulk densities[25]).

The combination of SAXS and N_2 sorption data suggests that the overall mesoscale lattice shrinks slightly, but the densification of the material is so dramatic that the pore size increases despite the overall structure shrinkage. In other words, the material deforms as it undergoes solid-state chemical reaction to accommodate a 50% or greater volume shrinkage by a combination of direct densification of the pore walls (leading to larger BET-measured pore sizes) and by shrinkage of the entire mesoscale lattice (leading to smaller SAXS-measured lattice parameters). Specifically, the SAXS lattice parameter decreases by 10% indicating overall material volume shrinkage of 25% (based on SAXS-measured lattice parameters), yet the pore wall diameter shrinks by 24% (TEM analysis, data not shown), indicating a pore wall volume shrinkage of ca. 40%. The 20% increase in pore diameter observed by N_2 sorption is thus reasonable in the context of the SAXS and TEM measurements.

The optimization of crystallinity in block copolymer-derived mesoporous materials has been a significant challenge. Since the reported heat treatment at 550 °C for 90 min produces materials on the edge of the first observable crystalline nitride grains, small variations in processing conditions substantially influence the crystallinity of the resulting nitride and/or retention of the mesostructure. For example, ex situ SAXS and WAXS on a material treated for a slightly longer time of 120 min (Figure 4, top traces) instead of 90 min at 550 °C (Figure 4, middle traces) show larger coherent scattering domain sizes and lattice parameters in WAXS indicative of lower oxygen and vacancy concentration but lower mesostructure quality as indicated by significantly lower intensity in the higher-order SAXS peaks. In contrast, SAXS and WAXS on samples treated for 90 min at a lower temperature of 500 °C indicate equivalent mesostructure retention to treatment at 550 °C for 120 min but a lack of any WAXS peaks (Figure 4, bottom traces), consistent with very limited or no crystal growth. Interestingly, despite having no detectable crystallinity in WAXS, the sample treated at 500 °C remained optically black, a feature typically associated with metallic conducting materials (e.g., NbN) and not with semiconductors and insulators (e.g., Nb_2O_5).

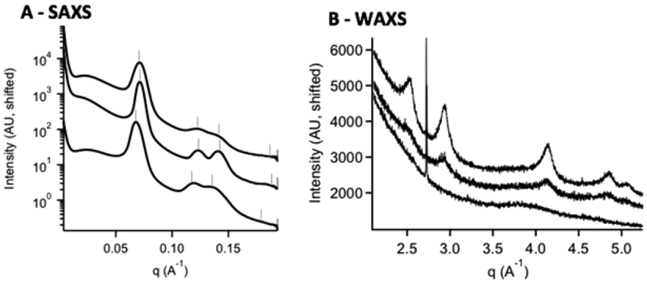

Figure 4. (A) SAXS patterns for nitrides produced at (top) 550 °C for 120 min, (middle) 550 °C for 90 min, and (bottom) 500 °C for 90 min. Tick marks indicate expected peak positions for a hexagonal morphology relative to the observed primary peak, with the top two traces having a d_{100} spacing of 8.8 nm. The bottom trace has a d_{100} spacing of 9.1 nm, indicative of a lower degree of shrinkage. (B) Lab source WAXS patterns from the materials in (A), showing a corresponding increase in crystallinity with increasing heating temperature or time (as in A). Mesostructure loss occurs concurrently with additional crystallization of the material at even slightly longer times, while materials treated at lower temperatures do not exhibit any resolvable WAXS peaks. The extremely sharp WAXS peak at ca. 2.65 Å^{-1} is a known instrument artifact. The lower intensities and increased widths relative to the synchrotron data are a result of lower signal and increased source broadening on the lab diffractometer.

To further probe the thermal conditions under which crystalline, mesoporous nitrides can be synthesized, we used *in situ* synchrotron SAXS/WAXS during annealing in ammonia in a custom flow furnace (see photo in Figure S1) during a 5 °C min^{-1} ramp from room temperature to 720 °C (Figure 5). Please note that because of the time constraints at a synchrotron, this thermal processing history is considerably different from the ex situ experiments described so far, where

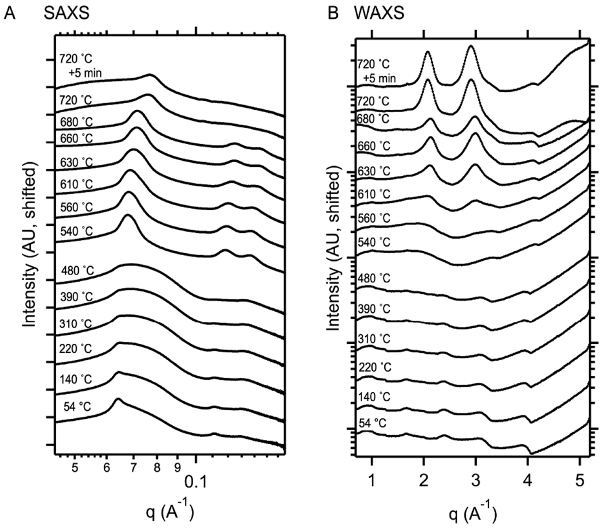

Figure 5. In situ SAXS (A) and WAXS (B) data collected from a mesoporous oxide sample during a 5 °C min^{-1} ramp from room temperature to 720 °C under flowing ammonia gas. The window from 560 to 660 °C in which both SAXS peaks (indicative of mesoporosity) and WAXS peaks (indicative of crystalline nitride) are observed can be used to guide processing.

the final temperatures of 500 or 550 °C were held between 90 and 120 min, vide supra, while here the temperature steadily increased at the 5 °C min^{-1} rate. Consistent with results in Figure 4A, in situ SAXS (Figure 5A) reveals (i) a hexagonal mesostructure at a temperature around 540 °C, which at the heating rate of 5 °C min^{-1} vanishes above 680 °C, as evidenced by the loss of higher-order SAXS reflections, and (ii) between 540 and 680 °C the first order peak steadily shifting to higher q values indicating continuous material densification, from a lattice parameter of 9.3 nm at 540 °C to a lattice parameter of 8.8 nm at 680 °C. The final pattern at 720 °C, if assigned to a hexagonal lattice, would have a lattice parameter of 8.4 nm. These parameters are consistent with ex situ observations, vide supra. In situ WAXS (Figure 5B) exhibited clear peaks consistent with the rocksalt NbN phase beginning at 610 °C, at which point the nitride lattice parameter is 4.12 Å. The first emergence of such peaks may occur at lower temperatures of ca. 540−560 °C, but at the ramp rate of 5 °C min^{-1} the peak widths are so high that unequivocal peak identification above the background is challenging. As the temperature increases, the WAXS peaks shift gradually toward increased lattice parameters, reaching a value of 4.23 Å at 680 °C, the last temperature where the sample exhibits clear higher order reflections in SAXS indicative of long-range hexagonal mesostructural order, and ultimately reaching a value of 4.32 Å at 720 °C. Compared to the lattice parameter of 4.26 Å attained after holding at 550 °C for 90 min, these results suggest alternative routes to similar quality nitrides (or even better, less defective materials) involving shorter anneals at higher temperatures.

These in situ studies corroborate the increase in intensity in the higher order SAXS peaks observed in the transition from oxide to nitride, with sharp higher-order reflections in SAXS appearing concurrently with the possible first crystallization of the nitride as observed in WAXS at 540 °C. We thus establish a minimum window for Pluronics directed formation of mesoporous nitrides, though it should be noted that the crystalline material may form for longer times at lower temperatures (as observed with the synthesis at 550 °C for 90 min) and may collapse if held at higher temperatures for longer times. We can infer from the relatively rapid growth of nitride domains in ∼minutes at temperatures above 600 °C that long dwell times at high temperature in conventional furnace anneals are not necessary, potentially opening the door to synthesis of nitrides with lower residual oxygen via, e.g., rapid thermal processing.[24,25] In situ annealing studies may further accelerate the translation of these Pluronics-based synthetic routes to other materials by allowing rapid screening of the coexistence window for crystallinity and mesoporosity.

In summary, we described routes to synthesize hexagonally ordered freestanding mesoporous niobium nitrides from ordered mesoporous niobium oxide structured by commercially available Pluronics ABA triblock copolymers based on treatment at moderate temperatures and times (e.g., 550 °C for 90 min) under flowing ammonia gas. We further demonstrated the sensitivity of mesostructural order and crystallinity of the resulting materials to relatively small variations of heat treatment temperature and duration, which likely is the reason Pluronics-based routes to mesoporous nitrides had previously been challenging. We expect the synthetic routes discussed will open the door to wider exploration of the impact of mesoscale order on the properties and applications of mesoporous transition metal nitrides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b03834.

Materials, methods, and photograph of custom in situ SAXS/WAXS apparatus (PDF)

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Author Contributions

P.A.B. and U.B.W conceived the project. P.A.B synthesized samples and performed and analyzed N_2 sorption, WAXS, and in situ SAXS/WAXS measurements. P.A.B. performed and P.A.B and S.M.G analyzed SAXS measurements. E.M.S. performed and analyzed TEM measurements. P.A.B. and U.B.W. wrote the manuscript with input from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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