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COMMUNICATION

Rapid (< 3 min) Microwave Synthesis of Block Copolymer Templated Ordered Mesoporous Metal Oxide and Carbonate Films using Nitrate-Citric Acid Systems

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Rapid chemical transformation from micelle templated precursors (metal nitrate and citric acid) to ordered mesoporous metal carbonates and oxides is demonstrated using microwave heating for cobalt, copper, manganese and zinc. Without aging requirements, < 3 min of microwave processing yields highly ordered mesoporous films.

Mesoporous materials are used in a vast array of applications ranging from batteries[1] to controlled DNA delivery[2] to solar cells.[3] Significant efforts have focused on developing efficient and facile synthesis methods to expand the diversity of materials and structures that are available for investigation. One common limitation in fabrication strategies is the time requirements associated with aging sol-gel materials and the need for a controlled temperature ramp for the calcination. For mesoporous silica, microwave (MW) processing rapidly (15 min) removes the template through a hydrothermal process,[4] but the sol gel must be initially aged. The MW-assisted synthesis method has been extended to other templated systems with a significant decrease in the processing time over conventional methods by as much as 40 h.[5-8] The resulting materials generally rely on hydrothermal processes invoked by the MWs. The hydrothermal environment has several drawbacks; most notably, the mesoporous framework material is limited by corrosion and the highly oxidizing environment limits the fabrication of non-oxide materials.

A recently reported "micelle-templating citric acid method," is promising for the synthesis of a wide variety of metal oxide and carbonate films without the need for extended aging.[9, 10] The method relies on the cooperative assembly of metal nitrate, citric acid, and block copolymers. The metal nitrate and citric acid form a complex that is thermally converted to a carbonate and subsequently to oxide

on calcination. Thus for the fabrication of a mesoporous oxide, two distinct heating steps are required, which extends the fabrication time to 4 h as a result of the thermal processing. As the synthesis is fully thermally driven, the rapid MW heating in the absence of water may be able to quickly drive the conversion from precursor film to mesoporous carbonate or oxide.

Herein, we report the fabrication of ordered mesoporous metal carbonates and oxides using non-hydrothermal, rapid microwave heating. This process relies on rapid and dramatic temperature increase originating from MW irradiation of the silicon wafer substrate.[11] This methodology is a solvent-free process, where the microwave heats only the substrate and film of interest to rapidly form the mesoporous film. We demonstrate this method to fabricate a variety of ordered mesoporous metal oxide and metal carbonate films using cobalt nitrate, copper nitrate, zinc nitrate and manganese nitrate precursors. A diblock copolymer, poly(ethylene oxide)-*b*-poly(n-butyl acrylate) (PEO-*b*-PBA), was synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization and used as the template. Details about the synthesis are noted in the electronic supporting information; the mass ratio of PEO-*b*-PBA to citric acid is held constant and the metal nitrate quantity is determined by stoichiometry with the citric acid (see Table S1 in Electronic Supplementary Information, ESI). Dip coated films from 3:1 (w/w) THF/ethanol solution of PEO-*b*-PBA (70 mg), cobalt (II) nitrate hexahydrate (437 mg), and citric acid (144 mg) on silicon wafers yield a poorly ordered mesostructure (Figure S5 in ESI) that evolves into a close packed spherical mesostructure using conventional furnace heating at 200 °C (preheated in all cases) for 1 h (Figure 1a). The as-cast films are approximately 500 nm thick, but the thickness decreases as the cobalt nitrate is converted into the carbonate and

subsequently to the oxide (see Table S2 for the thickness of the films through the different stages of MW processing). The temperature for conversion to carbonate or oxide is determined using TGA to illustrate the temperatures where significant mass loss occurs (Figure S1). The mesostructure is converted to primarily cobalt carbonate without removal of the template as determined by FTIR (Figure S3). Additional heating of this film at 300 °C for 45 min in a muffle furnace (Figure 1b), results in the complete removal of the template and transformation to mesoporous cobalt oxide (Figure S3). Using MW heating at 40 W, the same highly ordered cobalt carbonate can be obtained in less than 1 min as shown in Figure 1c, which corresponds to approximately 175 °C based on analogous microwave heating at the same power with the silicon wafers (Figure S2).
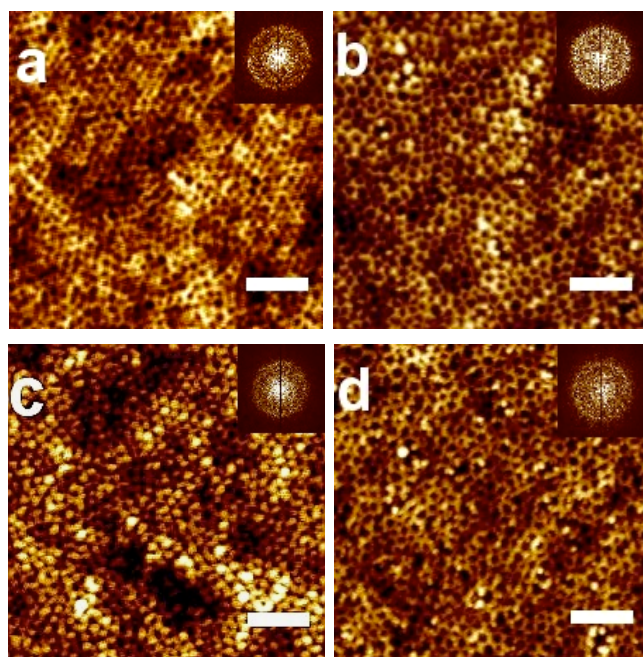
Figure 1. AFM micrographs of the surface topology of templated films for (a) cobalt carbonate with template remaining by heating to 200 °C for 1 h, (b) mesoporous cobalt oxide by heating (a) to 300 °C for additional 45 min, (c) cobalt carbonate by microwave heating at 40 W for 1 min, and (d) mesoporous cobalt oxide by heating (c) at 70 W for additional 45 s. (Scale bar- 200 nm) FFT of the micrographs are illustrated in the insets. These micrographs illustrate the highly uniform structure generated by the cooperative assembly. The pore size decreases on removal of the template.

Despite the reduced time and temperature conditions, the MW processing is more efficient at transformation to the carbonate based on the pyrolysis of the precursors determined from FTIR (Figure S3). The ability to control the morphology and resulting chemistry suggests that MW methods will be highly useful for processing mesoporous materials without adversely impacting the structure. To quantitatively compare the surface of these two carbonate materials, the FFT of these images are used. The d-spacing between thermal (32.3 nm) and microwave (33.4 nm) heating is nearly indistinguishable. Moreover, the peak width associated with the ordered structure is 11.5 μm^{-1} and 16.5 μm^{-1}, respectively. These data indicate that the structure is not significantly different between thermal and MW heating for the cobalt carbonate. Similar to the furnace heating, the carbonate can be transformed to the oxide

along with full pyrolysis of the template using MW methods, but the required time for this transformation is significantly decreased. Figure 1d illustrates the morphology of the mesoporous cobalt oxide after an additional 45 s of MW heating at 70 W. Again, this power is associated with a lower temperature (230 °C) then was used for the thermal process. The d-spacing between furnace (30.1 nm) and MW (28.5 nm) indicates significant shrinkage in the in-plane direction of the thin film on microwave heating. Moreover, the peak width associated with the ordered structure is 13.5 μm^{-1} and 15.5 μm^{-1}, respectively. Based on the AFM micrographs of cobalt oxide (Figure 1b and 1d), conventional oven heating yields an average pore diameter of 21 ± 3 nm, while MW heating leads to an average pore diameter of 19 ± 2 nm. These data indicate that the structure is not significantly different between thermal and microwave heating for the cobalt oxide as well.
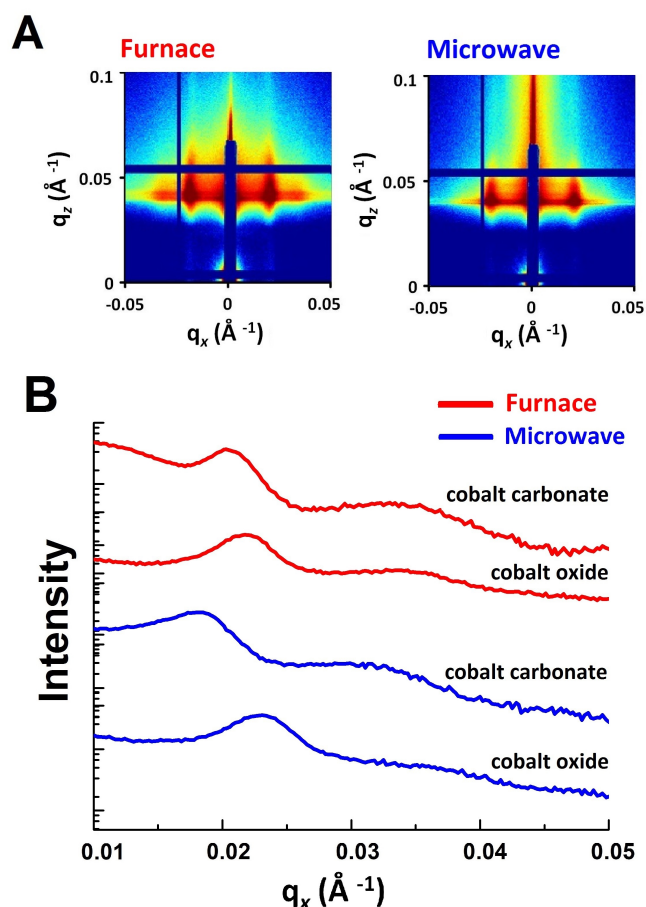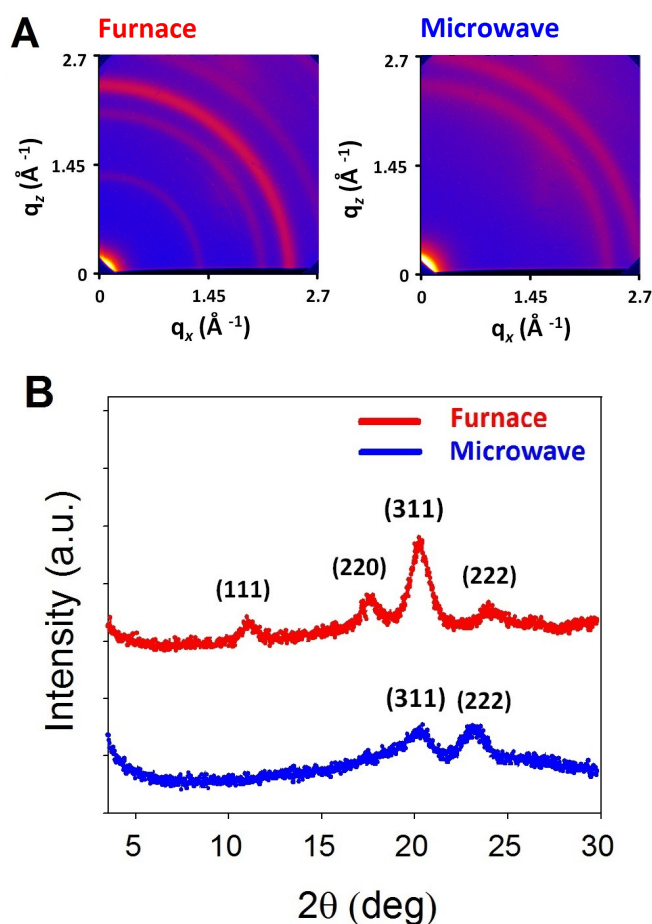

Figure 2. (A) 2-D GISAXS profiles for the mesoporous cobalt oxide films by furnace and microwave heating. (B) Comparison of the 1D scattering profiles from GISAXS for micelle templated films of cobalt carbonate and cobalt oxide using conventional furnace (top curves) and microwave heating (bottom curves). Two orders of diffraction from the templated structure are evident from the GISAXS profiles illustrating the presence of a highly ordered nanostructure.

To further illustrate the equivalence between microwave and thermal heating for the fabrication of ordered mesoporous cobalt oxide, the structure is quantified using grazing incidence small angle X-ray scattering (GISAXS). Figure 2 illustrates the 2D scattering profile for the different processing routes examined. These scattering

provides information on the in plane (q_x) and out of plane (q_z) correlations between the pores. Qualitatively, the difference between the profiles is limited with clear diffraction peaks corresponding to the ordered structure. This behavior is consistent with the AFM micrographs examined previously. Quantitatively, the in-plane d-spacing for mesoporous cobalt carbonate from thermal heating is 31.7 nm, while from the microwave heating is found to be 33.5 nm. On further heating to decompose the carbonate into the corresponding cobalt oxide, the in-plane d-spacing for thermally processed mesoporous cobalt oxide is found to be 29.0 nm, while that for the microwave processed thin film is 27.5 nm (Figure 2B).

Thus, there is increased domain contraction in the plane of the film in MW processing despite the lower temperature and shorter heating time. These differences suggest that the microwave process enables the nanostructure to contract more readily due to the volumetric contraction as the precursors are converted to oxide. This contraction can dissipate stresses that lead to cracks[12] and other structural defects. However, the crack density on the surface of microwave processed mesoporous cobalt oxide films is low (Figure S6). This rapid MW synthesis leading to a decrease, rather than an increase, in defect density, is similar to the improvements found for rapid thermal processing of zeolite membranes.[13] Such a crack-free nanoscale structure from MW synthesis can impact the macroscale properties and suitability of these films in a number of applications.


Figure 3. (A) GIXD profiles for the mesoporous cobalt oxide films by furnace and microwave heating. (B) Comparison of the azimuthally averaged diffraction profiles illustrating the decreased crystallinity from microwave processing (bottom curve) as compared to furnace heating (top curve) .The 1-D diffraction profiles have been offset along the y-axis

Crystallization of the framework can also lead to defects and drive crack formation due to the increase in density. Figure 3 illustrates the grazing incidence x-ray diffraction (GIXD) profiles for the mesoporous cobalt oxide films with the diffraction peaks indexed. The diffraction profiles are consistent with the normal spinel structure of Co_3O_4,[14] but the resolution (width^{-1}) of these peaks is significantly reduced for the microwave processed film. Examination of the width of the most intense (311) diffraction peak provides insight into the average size of the Co_3O_4 crystallite in the film through application of the Scherrer equation.[15] The average crystal size is 4.3 nm using thermal processing, but this significantly decreases to 2.9 nm with microwave processing. This agrees with microwave synthesis of silicalite where the crystal size was larger on thermal heating as compared to microwave heating.[16] The higher diffraction intensity from mesoporous cobalt oxide film calcined thermally suggests a higher degree of crystallinity as compared to microwave processing. Accounting for the thickness of these films and the area of the (311) diffraction peak, mesoporous cobalt oxide framework on thermal heating is estimated to be ~2.2 times more crystalline as compared to that obtained by microwave processing (see ESI for additional information). However, there is also a change in the relative intensity between the peaks, which suggests a change in the preferred orientation for the nanocrystal domains within the templated mesostructure. Additionally, there is a shift in the (222) peak position to lower 2θ, which we attribute to differences in the stress state of the crystal from the two processing protocols.

Combining the citric acid-mediated micelle templating strategy along with microwave approach, different metal carbonates and mesoporous oxides based on cobalt, zinc or manganese oxide can also be fabricated within 3 min. The onset of metal carbonate and corresponding metal oxide formation depends on the metal nitrate under consideration (Figure S1). Thus different microwave heating conditions are used for copper, zinc and manganese oxide syntheses as shown by FTIR analysis in Figure S4. These templated microwave syntheses yield ordered mesoporous films as shown in Figure 4. The average pore diameter for these metal oxides based on AFM micrographs is found to be 23 ± 4 nm in each case. Figure S7 illustrates that these mesoporous metal oxide films are partially crystalline after MW processing. A hexagonal wurtzite structure is observed for zinc oxide (with a minority peak associated with residual zinc carbonate). Copper oxide crystallizes into both cubic $Pn\overline{3}m$ (Cu_2O) and monoclinic $C2/c$ (CuO) structures. Similarly, manganese oxide appears to crystallize into both tetragonal hausmannite $I4_1/amd$ (Mn_3O_4) and tetragonal $P4_2/mnm$ β-MnO_2 structures. Traditionally, hard templating pathways involving multiple steps are used to fabricate mesoporous manganese or copper oxide due to difficulties associated with crystallization of these metal oxides during the calcination stage,[17] but some creative processing methodologies have been reported to enable the syntheses of these materials.[18] The microwave approach demonstrated here overcomes

these challenges and enables the direct soft templating of a wide variety of ordered mesoporous metal oxides.
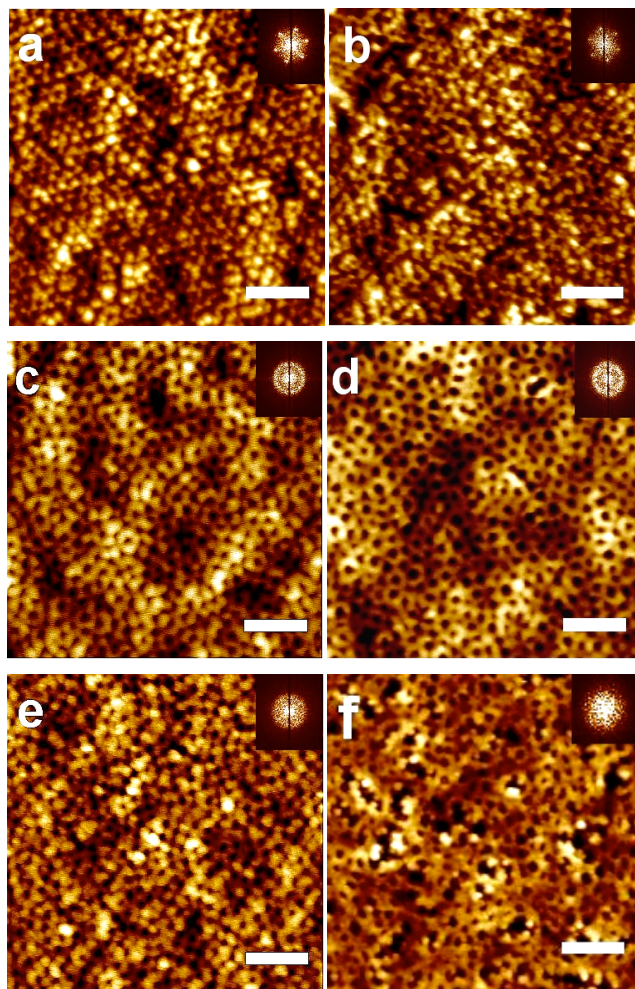
Figure 4. AFM micrographs of the surface topology of templated films for (a) copper carbonate on microwave heating at 40W for 1 min, (b) mesoporous copper oxide on heating (a) at 70 W for additional 45 s, (c) zinc carbonate on microwave heating at 70 W for 1 min and 100 W for 1 min, (d) mesoporous zinc oxide on microwave heating (c) at 250 W for additional for 45 s, (e) mesoporous manganese carbonate on microwave heating at 40 W for 1 min, (f) mesoporous manganese oxide on microwave heating (e) at 70 W for additional 45 s (Scale bar- 200 nm). FFTs of the images are shown in the insets. The micelle templated structure is well preserved for the carbonates, but the degradation in the quality of the templating is dependent on the metal center with the highly ordered nanostructure maintained in zinc oxide, while the pores collapse for copper oxide and the pore coalesce for manganese oxide.

Conclusions

The nitrate-citric acid route enables soft-templating of a variety of mesoporous metal carbonates and oxides that can be fabricated in less than 3 min using microwaves. It is expected that the microwave approach will provide a generalized and rapid route for the fabrication of a number of new carbonate and oxide-based mesoporous materials.

Notes and references

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