

Electronic Supporting Information (ESI) for:

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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Experimental section

Materials: Cobalt (II) nitrate hexahydrate (ACS reagent, $\geq 98\%$), copper (II) nitrate trihydrate (purum p.a., 98.0-103% (RT)), zinc nitrate hexahydrate (reagent grade, 98%), manganese (II) nitrate tetrahydrate (purum p.a., $\geq 97.0\%$ (KT)), citric acid ($\geq 99.5\%$), ethylene glycol (reagent plus, $\geq 99\%$), ethanol ($\geq 99.5\%$), methanol ($> 98.5\%$), tetrahydrofuran ($\geq 99.0\%$), hexane ($>98.5\%$), 2,2-azobis(2-methylpropionitrile) (AIBN), poly(ethylene glycol) methyl ether (PEO₄₅₅-OH, $M_n = 20000$), tetrahydrofuran ($>99.0\%$, contains 250 ppm BHT as inhibitor), dichloromethane ($>99.5\%$, contains 50 ppm amylene as stabilizer), toluene ($>99.5\%$) were all purchased from Sigma-Aldrich. N,N'-dicyclohexylcarbodiimide (DCC, $>99\%$), 4-dimethylaminopyridine (DMAP, $>99\%$), and *n*-butyl acrylate ($\geq 98\%$, contains 10-20 ppm monomethyl ether hydroquinone as inhibitor) were purchased from Alfa Aesar. Alumina Basic was purchased from Dynamic Adsorbents Inc. Nitrogen gas ($>99\%$) was purchased from Praxair. S-1-dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (RAFT-COOH) was synthesized according to previous report.^[1] CH₂Cl₂ was dried using a column of basic alumina. The *n*-butyl acrylate was purified through a column of basic alumina for removing the inhibitor. AIBN was purified by re-crystallization from ethanol solution. All chemicals were used as received unless otherwise noted. Double side polished silicon wafers (high resistivity ($> 10 \Omega \cdot \text{cm}$) and 500 μm thick) were purchased from Silicon Inc.

Syntheses and fabrication:

A. Synthesis of PEO-RAFT: For the synthesis of macroinitiator (PEO-RAFT), the PEO₄₅₅-OH (26g, 1.3mmol) was first dissolved in toluene and subsequently dried by azeotropic distillation at 180 °C for 1 h using a Dean Stark trap and a condenser in order to remove the residual water. After distillation, the toluene was removed by rotary evaporation and the product was dried in a vacuum oven overnight at room temperature. 0.94 g of DCC (4.6 mmol) and 0.09 g DMAP (0.78 mmol) were dried in a two port round bottom flask with a stir bar on the Schlenk line overnight. 25 mL of CH₂Cl₂ was dried by passing through a basic alumina column and directly added into the two port round bottom flask, followed by adding 0.71 g of RAFT-COOH (1.95 mmol) and 26 g dried PEO into the same reaction flask. The solution was purged with nitrogen gas for 30 min and stirred at room temperature for 55 h. The insoluble salts were removed by filtration and the filtrate was subsequently concentrated using rotary evaporation and the PEO-RAFT was precipitated by in excess of cold hexane (200 mL, 0 °C). The unreacted RAFT-COOH was removed through recrystallization of the precipitate by dissolving in hexane at 80 °C and then cooling to room temperature and filtering the recrystallized PEO-RAFT with a Buchner funnel. This recrystallization step was repeated a total of three times producing a yellow, crystalline PEO-RAFT and a colorless filtrate. Finally, the PEO-RAFT was dried in vacuum oven for 12 h at room temperature.

B. Synthesis of poly(ethylene oxide)-*b*-poly(*n*-butyl acrylate) (PEO-*b*-PBA): For the synthesis the block copolymer (BCP)PEO-*b*-PBA, PEO-RAFT (1 g), *n*-butyl acrylate (4.5 g), and AIBN (0.0058 g) were dissolved in 12.5 g chloroform in a 100 mL flask. The flask was subsequently purged with nitrogen gas for 20 min. The stirred solution was heated to 70 °C and allowed to polymerize for 8 h. After polymerization, the reaction was stopped by quenching the flask into the ice water. A rotary evaporator was used for removing the solvent and concentrating the product. The concentrated product was diluted with 5 mL THF. The THF solution was added slowly into 100 mL of cold hexane (0 °C) in order to precipitate the PEO-*b*-PBA. This precipitation procedure was repeated for 3 times in order to remove the residual BA monomer. The final product (PEO-*b*-PBA) was then dried under vacuum for 12 h at room temperature.

C. Microwave processing: Microwave heating was used to convert the nitrate precursors into the corresponding metal carbonates and/or metal oxides and for the thermal decomposition of PEO-*b*-PBA templates. This step was

carried out using a CEM Discover reactor (explorer hybrid 12), which operates at a fixed frequency of 2.45 GHz with a variable microwave power ranging from 0 to 300 W. The films were placed at the bottom of a sealed 35 mL glass tube and purged with nitrogen gas for 10 min prior to the microwave heating in order to prevent premature block copolymer decomposition in the air atmosphere. For assessing the temperature of the films during microwave heating, the open vessel attenuator was utilized for monitoring the *in-situ* temperature profile of the DSP silicon wafers (1.5 cm × 1.5 cm) at different microwave power (5-150 W) for up to 5 min using an infrared thermometer (TESTO 875) with calibrated emissivity of the DSP silicon wafers.

D. Film fabrication: DSP silicon wafers (Silicon Inc.) were cut into 1.5 cm × 1.5 cm pieces; cleaned with piranha solution (3:7 v/v mixture of 30 vol% H₂O₂ and 70 vol% H₂SO₄ (> 48%)) at 90 °C for 45 min and followed by rinsing with deionized water for three times. BCP micelle-templated films were fabricated by following procedure: first, 70 mg of PEO-*b*-PBA was dissolved into 1.8 g THF and 437 mg cobalt (II) nitrate hexahydrate with 144 mg citric acid were dissolved into 0.6 g of ethanol. Subsequently, the ethanolic solution was added drop-wisely into the BCP-THF solution under vigorous stirring (1000 rpm) and this solution was stirred for 12 h at 1000 rpm prior to casting the films. This solution was utilized to fabricate films on the cleaned silicon wafers by dip coating at 100 mm/min at 22 °C and 40-50% relative humidity. The films were allowed to dry at room temperature for at least 5 min prior to further processing. BCP micelle-templated cobalt carbonate films were fabricated by using a previously described microwave at 40 W for 1 min. For synthesizing mesoporous cobalt oxide thin films, the cast films were heated at 40W for 1 min first, cooled down to room temperature, followed by an additional heating step at 70W for 45 s. For the control experiment, BCP micelle-templated cobalt carbonate films were heated in a conventional preheated muffle furnace (Ney Vulcan 3-130) at 200 °C for 1 h followed by natural cooling to room temperature. Mesoporous cobalt oxide films required heating in a preheated furnace at 200 °C for 1 h, natural cooling to room temperature followed by additional heating at 300 °C for 45 min.

The dip-coating solution of copper-based films was prepared by first dissolving 70 mg PEO-*b*-PBA template in 1.8 g THF. In a separate vial, 210 mg copper (II) nitrate trihydrate along with 144 mg citric acid was dissolved in 0.6 g ethanol solvent. After 30 min, the ethanolic solution was added drop-wise under stirring (1000 rpm) into the solution containing PEO-*b*-PBA. This mixture was stirred at 1000 rpm for 12 h prior to film casting. To fabricate copper carbonate thin films, the cast films were microwave heated at 40W for 1 min. For mesoporous copper oxide, the thin films were microwave heated at 40W for 1 min, cooled down to room temperature followed by further heating at 70W for 45 s.

Micelle-templated thin films of zinc oxide and manganese oxide were prepared using similar protocols with processing conditions given below.

Table S1. Synthesis conditions employed for fabrication of micelle-templated carbonates and mesoporous oxides of Co, Cu, Zn and Mn by microwave processing

Precursor system	Solvent	Calcination to carbonate	Calcination to oxide
Co(NO ₃) ₂ ·6H ₂ O (437 mg), citric acid (144 mg) and PEO- <i>b</i> -PBA (70 mg)	THF (1.8 g) and ethanol (0.6 g)	40W for 1 min	40W for 1 min and 70W for 45 s
Cu(NO ₃) ₂ ·3H ₂ O (210 mg), citric acid (144 mg) and PEO- <i>b</i> -PBA (70 mg)	THF (1.8 g) and ethanol (0.6 g)	40W for 1 min	40W for 1 min and 70W for 45 s
Zn(NO ₃) ₂ ·6H ₂ O (450 mg), citric acid (144 mg) and PEO- <i>b</i> -PBA (70 mg)	THF (1.8 g) and ethanol (0.6 g)	40W for 1 min and 100W for 1 min	40W for 1 min and 100W for 1 min followed by 250W for 45 s
Mn(NO ₃) ₂ ·4H ₂ O (270 mg), citric acid (144 mg) and PEO- <i>b</i> -PBA (70 mg)	THF (1.8 g), ethanol (0.6 g) and ethylene glycol (15 mg)	40W for 1 min	40W for 1 min and 70W for 45 s

E. Characterization: To determine the carbonate and oxide formation temperatures for different metal nitrate-citric acid complexes, thermogravimetric analysis (TGA, TA Instruments, TGA-Q50) was performed on crushed metal nitrate-citric acid complex powders. The powders were heated under air purge of 60 ml/min with a heating ramp rate of

5 °C/min. Fourier transform infrared (FTIR, NICOLET iS50) were used to determine the changes in chemical structures of films after microwave processing, which is collected in transmission mode with using a DeuteratedTriGlycine Sulfate (DTGS) detector. For each measurement, 512 scans were taken at a resolution of 8 cm⁻¹. Baseline corrections to spectra were carried out in OMNIC software. To determine the crystal structure of porous copper oxide, zinc oxide and manganese oxide, thin film samples were scrapped from the silicon wafers to obtain powders. Powder x-ray diffraction (Bruker AXS Dimension D8 x-ray system) were performed at room temperature using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The thickness of the films through each stage of processing was determined using UV-Vis-NIR spectroscopic ellipsometry (M-2000, J.A. Woollam, Co.). The optical properties of the films were fit using a generalized oscillator mode (genosc from J.A. Woollam, Co.) with Lorentzian oscillators to ensure these optical properties were Kramers-Kronig consistent. Table S2 lists the thicknesses of the films fabricated in this study.

Table S2. Film thicknesses through MW processing determined by spectroscopic ellipsometry

Metal center	As cast film (nm)	Carbonate (nm)	Oxide (nm)
Cobalt	398	210	131
Copper	248	126	86
Zinc	583	341	228
Manganese	417	236	145

The surface morphology of the films was determined using Atomic Force Microscope (AFM) (Dimension Icon, Veeco). The micrographs were obtained under the tapping mode using PPP-NCC-50 tips (Nanosensor). The AFM micrographs were flattened and the FFT images were obtained using the Nanoscope Analysis software. Grazing incidence small angle x-ray scattering (GISAXS) was performed at X9 beamline of National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Thin film samples were irradiated with an incident X-ray beam of energy of 13.5 keV ($\lambda = 0.0918 \text{ nm}$) and scattering data were collected using a Pilatus detector at a distance of 4.73 m. All samples under vacuum ($\approx 40 \text{ Pa}$) were measured at multiple angles both below and above the critical angle. Grazing incidence X-ray diffraction (GIXD) was also performed on the thin films and scattered intensity data was collected on a charged couple device (CCD) WAXS detector to determine the crystal structure of the metal oxide films. The relative crystallinity of furnace and microwave heated cobalt oxide films were compared by determining the area and intensity of the most intense (311) diffraction peak according to the following equation;

$$\text{Relative Crystallinity} = \left(\frac{I_{furnace}(311)}{I_{microwave}(311)} \right) * \left(\frac{m_{microwave}}{m_{furnace}} \right)$$

where, $I_{furnace}$ is the intensity of diffraction peak (311) obtained from furnace calcined film, $I_{microwave}$ is intensity of diffraction peak (311) obtained from microwave heated film, and $m_{furnace}$ is the mass of furnace heated film, $m_{microwave}$ is mass of film on microwave heating. [2]

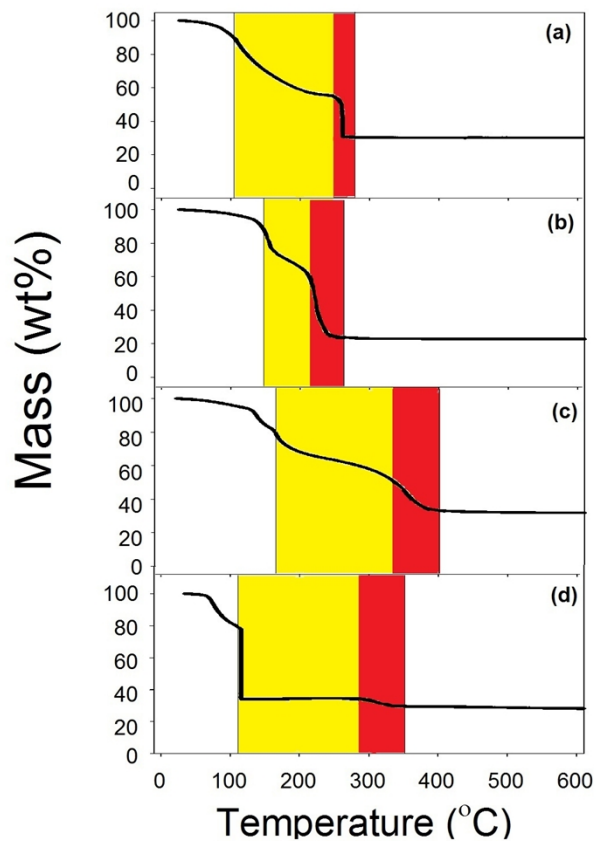


Figure S1. TGA traces for complex of (a) cobalt nitrate-citric acid (b) copper nitrate-citric acid (c) zinc nitrate-citric acid (d) manganese nitrate-citric acid. The decomposition onset for precursor complex into corresponding carbonate (yellow) and oxide formation (red) varies on the different metal nitrate precursors.

Microwave heating

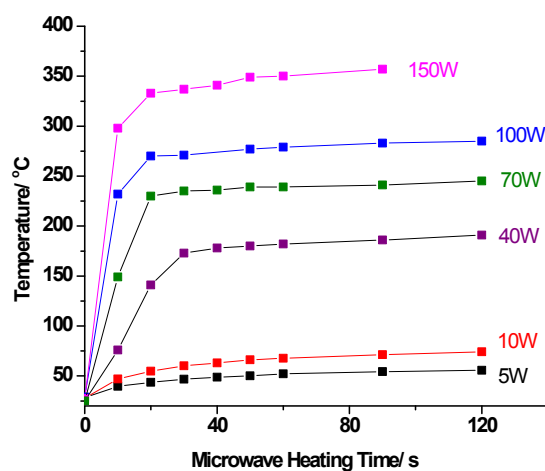


Figure S2. The temperature of DSP silicon substrates as a function of heat time under different microwave power treatment

Chemical evolution determined from FTIR

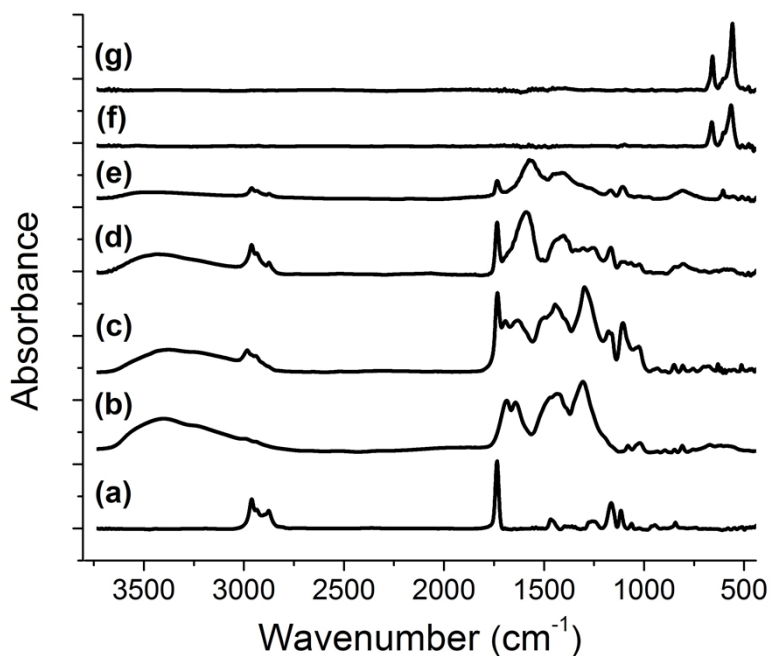


Figure S3. FTIR spectra of (a) poly (ethylene oxide)-b-poly (butyl acrylate) (PEO-*b*-PBA) block copolymer template (b) cobalt nitrate-citric acid complex (c) as-cast film of PEO-*b*-PBA micelle templated cobalt nitrate-citric acid complex (d) cobalt carbonate film with template remaining on heating at 200 °C for 1 h in conventional furnace (e) cobalt carbonate film with template remaining on microwave heating at 40 W for 1 min (f) mesoporous cobalt oxide on conventional furnace heating at 200 °C for 1 h and at 300 °C for additional 45 min (g) mesoporous cobalt oxide on microwave heating at 40 W for 1 min followed by 70 W for additional 45 s

Figure S3 shows the FTIR absorbance spectra of block copolymer templated cobalt nitrate-citric acid complex films at different processing stage. For the BCP films (spectrum (a)), the band from 3000 cm^{-1} to 2800 cm^{-1} arise from a series of symmetric and asymmetric stretching vibration of C-H bonds, which is contributed by both the PEO and PBA blocks. The strong sharp absorption at 1740 cm^{-1} arises from the stretching vibration of C=O in PBA. The band at 1470 cm^{-1} is contribution of C-H in-plane bending. The bands at 1260 cm^{-1} and 1170 cm^{-1} both arise from C-O stretching vibration in PBA while the band at 1120 cm^{-1} is a result of asymmetric vibration of the structure $-\text{CH}_2-\text{O}-\text{CH}_2-$ in PEO. Here, three regions can be used to track the existence of block copolymer template in the micelle templated films: 3000 cm^{-1} - 2800 cm^{-1} , 1740 cm^{-1} and 1170 cm^{-1} . Figure S3b shows the spectrum of cobalt nitrate-citric acid complex. Bands arising from the citric acid include the broad band from 3600 cm^{-1} to 2500 cm^{-1} due to the O-H stretching in $-\text{COOH}$ and $-\text{OH}$ groups respectively, the band at 3000 cm^{-1} - 2800 cm^{-1} arising from the $-\text{CH}_2-$ groups, the strong absorption at 1690 cm^{-1} corresponds to the C=O stretching vibration of $-\text{COOH}$ and a series of bands arising from CH_2 deformation from 1430 cm^{-1} to 1420 cm^{-1} . Cobalt nitrate also give out characteristic bands at 1640 cm^{-1} , corresponding anti-symmetric stretching of NO_2 . The NO_2 group has characteristic bands at 1497 cm^{-1} and 1290 cm^{-1} , which correspond to asymmetric and symmetric stretching vibration. The strong band at 1290 cm^{-1} corresponds to the symmetric stretching of NO_2 . Also, bands at 1024 cm^{-1} and 812 cm^{-1} are due to the NO stretching and non-plane deformation of nitrate group.

The spectrum of the as-cast BCP template film (Figure S3c) is basically a superposition of (a) and (b). In (d) and (e), several changes can be observed: A series of bands that arise from the nitrate groups and citric acid, including 1690 cm^{-1} , 1640 cm^{-1} , 1497 cm^{-1} , 1430 cm^{-1} to 1420 cm^{-1} and 1290 cm^{-1} , decreases dramatically. This indicates the deformation of the nitrate groups and citric acid. The broad bands in (d) and (e) between 1600 cm^{-1} and 1320 cm^{-1} , corresponding to inorganic carbonates, indicate the formation of cobalt carbonate. Comparing (d) and (e), the band at 1290 cm^{-1} is still visible in (d) while almost disappeared in (e). Thus, a higher conversion to carbonate is achieved by microwave treatment of 40 W for 1 min than the 1 h furnace heating at 200 °C. The block copolymer template also decomposed to a higher extent in microwave, as indicated by the disappearance of the bands at 1740 cm^{-1} . The sharp

bands at 661 cm^{-1} and 570 cm^{-1} indicates the formation of Co_3O_4 .^[3] The absence of bands at higher wavenumber indicates a thorough conversion from carbonate to oxide and the complete removal of block copolymer template.

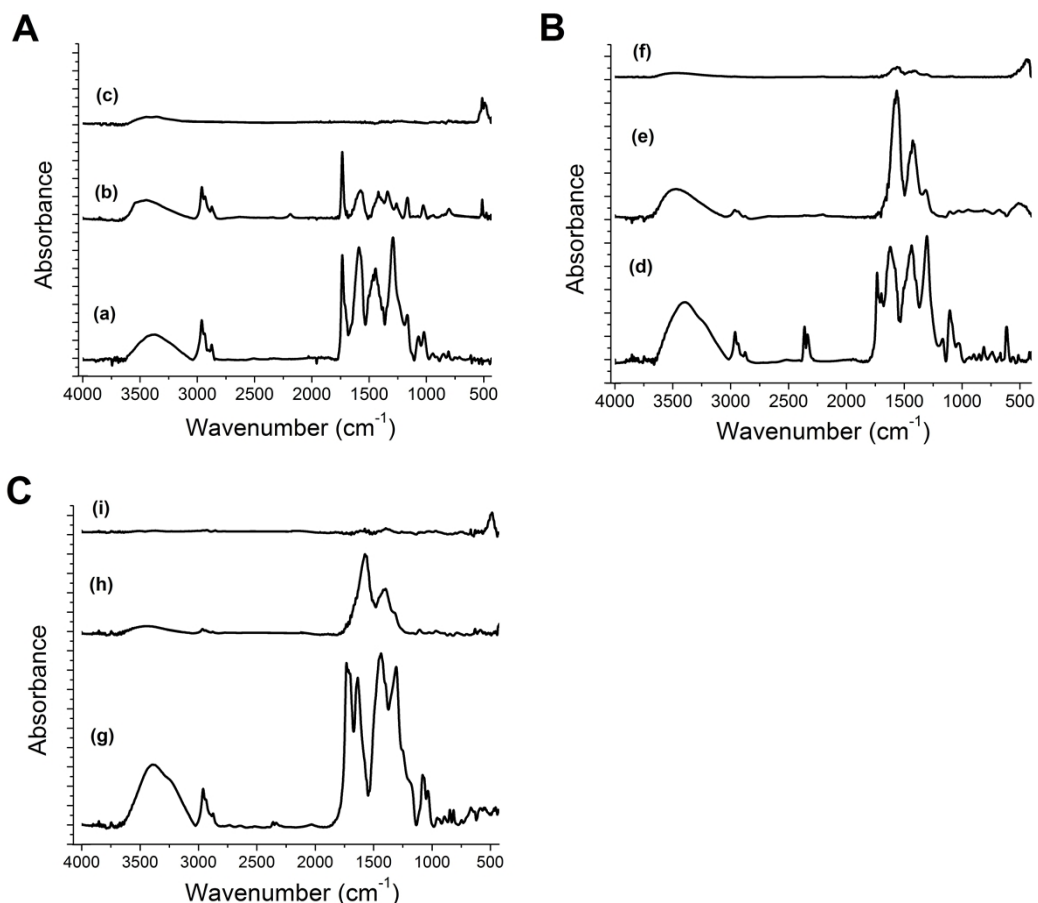


Figure S4. FTIR spectra for (A) PEO-*b*-PBA micelle templated (a) as-cast copper nitrate-citric acid complex (b) copper carbonate film (c) mesoporous copper oxide thin film; (B) PEO-*b*-PBA micelle templated (d) as-cast zinc nitrate-citric acid (e) zinc carbonate film (f) mesoporous zinc oxide film and (C) PEO-*b*-PBA micelle templated (g) as-cast manganese nitrate-citric acid thin film (h) mesoporous manganese carbonate film (i) mesoporous manganese oxide thin film

Figure S4 represents the FTIR spectra for micelle templated thin films of copper, zinc and manganese oxide respectively. In case of these micelle templated thin films, peaks arising due to PEO-*b*-PBA template and metal nitrate can again be tracked to study the conversion of nitrate-citric acid complex to metal carbonate and corresponding oxide. The FTIR spectra for micelle templated copper nitrate-citric acid film (Figure S4A) indicates a sharp peak at 1740 cm^{-1} corresponding to the stretching vibration of C=O in PBA while distinct copper nitrate peaks are visible at 1594 cm^{-1} and 1454 cm^{-1} . After microwave heating at 40W for 1 min, new peaks can be seen at 1578 cm^{-1} and 1422 cm^{-1} due to formation of copper carbonate. The peak at 1740 cm^{-1} is still visible, which indicates the presence of PEO-*b*-PBA template at this stage. Further heating at 70W for 45 s leads to totally decomposition of the template, which can be confirmed by the disappearance of peak at 1740 cm^{-1} . Similarly the peaks arising from carbonate disappears and a new broad peak at 520 cm^{-1} is visible indicative of stretching of Cu-O bond.^[4]

The FTIR spectra for micelle templated zinc nitrate-citric acid film (Figure S4B) is characterized by zinc nitrate peaks are visible at 1625 cm^{-1} and 1440 cm^{-1} . After microwave heating at 40W for 1 min followed by heating at 100W for another 1 min, new peaks can be observed at 1581 cm^{-1} and 1425 cm^{-1} due to formation of zinc carbonate. Upon further heating at 250W for 45 s, block copolymer template is completely removed and zinc carbonate transforms into zinc oxide. As a result, a broad peak centered around wavenumber 505 cm^{-1} arises due to Zn-O bond vibrational mode.^[5]

In case of manganese nitrate-citric acid complex, nitrate peaks are visible at 1642 cm^{-1} and 1441 cm^{-1} . Heating the films at 40 W for 1 min gives rise to formation of manganese carbonate peaks at 1578 cm^{-1} and 1410 cm^{-1} respectively. The peak at 1740 cm^{-1} disappears at this stage indicating removal of micelle template. Further heating at 70 W for 45 s leads to decomposition of manganese carbonate into corresponding oxide with a peak formed at 485 cm^{-1} corresponding to Mn-O stretching bond.^[6]

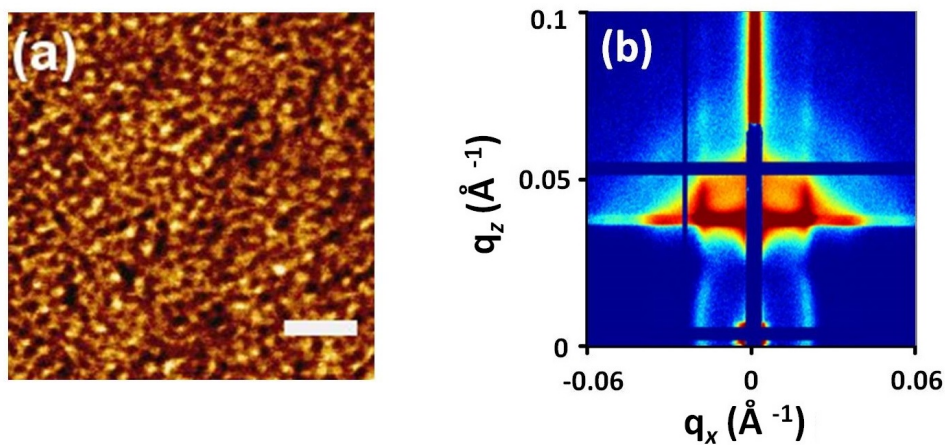


Figure S5. (a) AFM micrograph (scale bar- 200 nm) and (b) GISAXS of as-cast film of poly(ethylene oxide)-*b*-poly(butyl acrylate) templated cobalt nitrate-citric acid.

Figure S5 illustrates the morphology of a templated film using cobalt nitrate-citric acid and PEO-*b*-PBA as the template prior to conversion of the nitrate. The film exhibits short-range order from AFM and corresponding diffraction peaks in the GISAXS profile.

Surface morphology

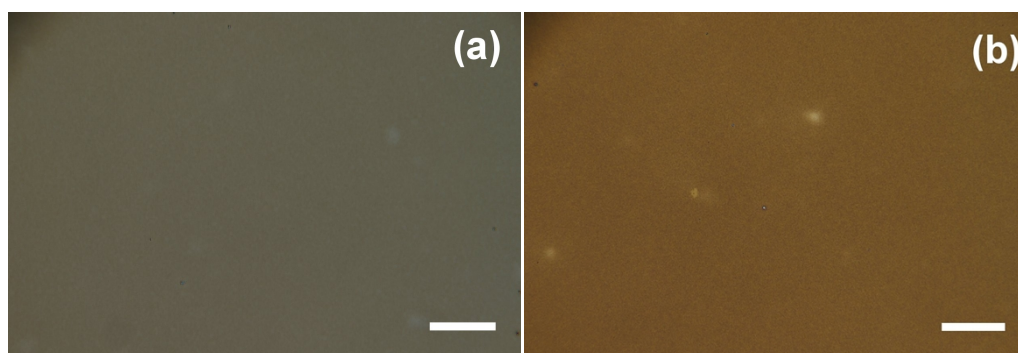


Figure S6. Optical micrographs of the surface of mesoporous cobalt oxide films fabricated using (a) furnace and (b) microwave heating protocols. A crack-free mesoporous thin film, similar to furnace calcined film, can be fabricated by the use of microwave heating protocols within 3 min . (Scale bar- $30\text{ }\mu\text{m}$)

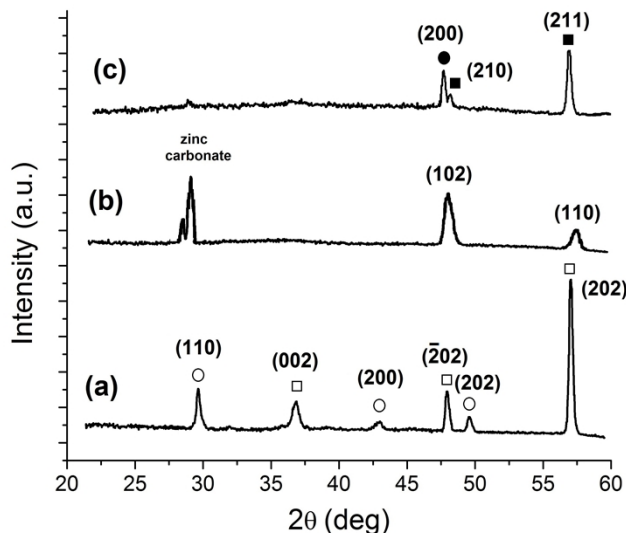


Figure S7. Powder XRD profiles for oxides of (a) copper (\square , CuO; \bullet , Cu_2O), (b) zinc, and (c) manganese (\blacksquare , $\beta\text{-MnO}_2$; \bullet , Mn_3O_4) prepared by microwave processing.

Figure S7 illustrates the powder x-ray diffraction obtained from scrapped films of mesoporous oxides of cobalt, zinc and manganese. The scattering data suggests that copper oxide obtained following microwave heating exists in cubic CuO^[7] and Cu₂O^[8] forms based on peak indexing. In case of zinc containing films, a distinct peak associated with zinc carbonate is obtained at 2θ of 28.7°. This matches well with the FTIR data (Figure S4) which indicated presence of some residual zinc carbonate in the zinc oxide. The peaks at 47.6° and 56.7° can be indexed to the (102) and (110) planes present in the hexagonal wurtzite structure of zinc oxide^[9]. Based on the diffraction patterns obtained in Figure S7(c), Mn₃O₄^[10] and $\beta\text{-MnO}_2$ ^[11] phases can be identified in mesoporous manganese oxide thin films.

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