Mesoporous titanium oxynitride monoliths from block copolymer-directed self-assembly of metal-urea additives

Li, Yun; Horia, Raymond; Tan, Wei Xin; Larbaram, Nathawat; Sasangka, Wardhana A.; Manalastas, William, Jr.; Madhavi, Srinivasan; Tan, Kwan Wee

2020

Li, Y., Horia, R., Tan, W. X., Larbaram, N., Sasangka, W. A., Manalastas, W., Jr., ... Tan, K. W. (2020). Mesoporous titanium oxynitride monoliths from block copolymer-directed self-assembly of metal-urea additives. *Langmuir*, 36(36), 10803-10810.
doi:10.1021/acs.langmuir.0c01729

<https://hdl.handle.net/10356/144044>

<https://doi.org/10.1021/acs.langmuir.0c01729>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Langmuir*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.langmuir.0c01729>

Downloaded on 26 Apr 2023 13:06:27 SGT

Mesoporous Titanium Oxynitride Monoliths from Block Copolymer–Directed Self-Assembly of Metal-Urea Additives

*Yun Li,[†] Raymond Horia,[†] Wei Xin Tan,[†] Nathawat Larbaram,[†] Wardhana A. Sasangka,[‡]
William Manalastas Jr.,[†] Srinivasan Madhavi,[†] and Kwan W. Tan^{†,*}*

[†]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.

[‡]Low Energy Electronic Systems, Singapore-MIT Alliance for Research and Technology Centre, Singapore 138602, Singapore.

*Corresponding Author: kwtan@ntu.edu.sg

ABSTRACT

This report describes a simple one-pot soft-templating and ammonolysis-free approach to synthesize mesoporous crystalline titanium oxynitride by combining block copolymer-directed self-assembly with metal sol and urea precursors. Pluronic F127 triblock copolymer was employed to structure-direct titanium-oxo-acetate sol nanoparticles and urea-formaldehyde into ordered hybrid mesostructured monoliths. The hybrid composites were directly converted into mesoporous crystalline titanium oxynitride and retained macroscale monolithic integrity up to 800 °C under nitrogen. Notably, the urea-formaldehyde additive provided nitrogen and rigid support to the inorganic mesostructure during crystallization. The resultant mesoporous titanium oxynitride exhibited good electrochemical catalytic activity toward hydrogen evolution reaction in 1 M KOH aqueous medium under applied bias. Our results suggest an inexpensive and safe pathway to generate ordered mesoporous crystalline metal oxynitride structures suitable for catalyst and energy-storage applications.

INTRODUCTION

Transition metal nitrides with multifunctional properties such as excellent electrical conductivity, corrosion resistance and thermal stability, are widely used in diverse applications, ranging from biocompatible coatings,¹ catalysis,^{2–7} energy storage,^{8,9} nanophotonics,¹⁰ and superconductors.¹¹ In particular, titanium nitride/oxy-nitride nanostructures with high surface area and three-dimensional (3D) porosity are appealing as high-temperature and corrosion-resistant electrodes and supports in catalysis, fuel cells and lithium-sulfur batteries.^{8,12–15}

Block copolymer-directed self-assembly provides a highly versatile pathway to generate a myriad of 2D and 3D periodically ordered and tunable morphologies for a wide range of functional materials, including carbon,^{16–20} semiconductors,^{21–25} metals^{26,27} and oxides,^{28–34} as well as nitrides.^{11,35–39} For example, Robbins et al. employed polyisoprene-*block*-polystyrene-*block*-polyethylene oxide (PI-*b*-PS-*b*-PEO) triblock terpolymers to structure-direct titanium-niobium oxide sol precursors into periodic 3D organic-inorganic mesostructures with the alternating gyroid lattice.³⁷ The hybrid nanocomposites were thermally annealed, first in air to form the metal oxide, and then converted into gyroidal mesoporous titanium-niobium nitride under ammonia.³⁷ Similar soft-templating approaches generating mesoporous boron nitride and niobium nitride structures had been reported.^{11,36,38} However, the requirement of multiple thermal annealing processes increase the overall complexity, time and cost, especially under hazardous ammonolysis conditions.⁴⁰

Alternative more benign approaches have been described, such as mixing metal salts with urea^{41,42} and using carbon nitride “reactive” templates⁴³ to generate metal nitride nanoparticles. For instance, Giodano and co-workers described an “urea-glass” method to form metal nitride and carbide nanoparticle clusters.^{44,45} They first dissolved metal chloride

salts in ethanol to form metal-orthoesters which then coordinated with urea into gel-like products. By varying the molar ratios of urea to metal, thermal annealing of the gel composites under nitrogen at 800 °C yielded crystalline metal nitride and carbide nanoparticle aggregates, albeit with wide distributions of nanoparticle size and porosity.^{44,45}

Here, we describe a facile one-pot and ammonolysis-free approach to synthesize monoliths of ordered mesostructured hybrid composite and mesoporous crystalline titanium oxynitride by block copolymer-directed self-assembly and thermal annealing under nitrogen. A commercially available structure-directing Pluronic F127 ABA triblock copolymer was mixed with titanium-oxo-acetate sol nanoparticles (metal source) and oligomeric urea-formaldehyde (nitrogen source) to form ordered mesostructured hybrid monoliths by solvent evaporation-induced self-assembly. The hybrid monoliths were heated under nitrogen at 800 °C, yielding mesoporous crystalline titanium oxynitride (TiON) monoliths. Notably, the urea-formaldehyde additive is essential to coordinate the tricomponent co-assembly as well as to provide nitrogen and structural support to the mesoporous crystalline TiON structures during thermal annealing. The resultant mesoporous TiON exhibited good catalytic activity toward hydrogen evolution reaction in 1 M KOH aqueous medium.

EXPERIMENTAL SECTION

Materials. Pluronic F127 polyethylene oxide-*block*-polypropylene oxide-*block*-polyethylene oxide (PEO-*b*-PPO-*b*-PEO, 12.6 kg/mol), urea (ACS reagent), formaldehyde solution (FA, ACS reagent, 37 wt% in H₂O), titanium isopropoxide ($\geq 97\%$), acetic acid (glacial, ACS reagent), sodium hydroxide (NaOH, $\geq 97\%$) and Nafion (5 wt%) were obtained from Sigma-Aldrich and used as received. Super P (ACS reagent) were bought from Alfa Aesar. Sulfuric

acid (98%), hydrochloric acid (HCl, 37%) and 200-proof ethanol (EtOH) were purchased from Merck and used as received.

Synthesis of Urea-Formaldehyde (Urea-FA) Derivatives. The base-catalyzed polymerization of urea-formaldehyde (urea-FA) derivatives were prepared using modified protocols as described elsewhere.^{18,46,47} In a typical synthesis, 2.02 g of urea was dissolved in 2.02 g of deionized water in a 100 ml round bottle flask. 0.2 g of NaOH was dissolved in 0.5 g of deionized water to form a 20 wt% NaOH solution. The NaOH solution was added dropwise into the urea solution and stirred for 10 min. 5 ml of FA solution (37 wt% in H₂O) was carefully added dropwise into the urea/NaOH solution over 10 min at room temperature. The molar ratio of urea/FA/NaOH was 10:20:1. The colorless transparent solution was heated to 70 °C and stirred for 1 h. After cooling to room temperature, the white-colored cloudy solution was neutralized with HCl (2 M) until pH of ~7. The suspension was freeze dried on a vacuum line for ~48 h at room temperature to extract water, followed by redissolving the white-colored urea-FA derivatives in EtOH. The resulting cloudy solution was filtered through PTFE syringe filters (0.2 µm) to remove the precipitated NaCl and freeze dried on the vacuum line overnight at room temperature. The EtOH washing and freeze drying steps were repeated a second time. Finally, the urea-FA derivatives were dissolved in EtOH as a 20 wt% solution.

Synthesis of Titanium Oxo-Acetate (Ti-AcHE) Nanoparticles. The titanium oxo-acetate (Ti-AcHE) nanoparticles were prepared using a previously described method.³¹ Briefly, 1 ml titanium isopropoxide (≥97%), 0.77 ml of acetic acid (glacial) and 0.671 ml of HCl (37 wt%) were added sequentially into 4 ml of ethanol, and stirred for 60 min. The resultant Ti-AcHE nanoparticles (~31 wt%) were used as synthesized.

Synthesis of F127/Urea-FA/Ti-AcHE Hybrid Monoliths. 0.10 g of F127 block copolymer was dissolved in 0.90 g of EtOH (10 wt%) in a scintillation vial. 2.08 g aliquot of urea-FA (20 wt%) was mixed with the F127 block copolymer solution and stirred for 15 min. The F127 to urea-FA mass ratio was about 1:4. 2.21 g aliquot of Ti-AcHE sol nanoparticles was added into the F127/urea-FA solution and stirred for another 15–30 min. The molar ratio of urea/Ti was about 2.7:1. The yellow-colored transparent hybrid solution was cast in 5 mL PTFE beakers set on a glass Petri dish covered with a hemispherical glass dome and heated at 45 °C on a hotplate under nitrogen. After ~48–72 h of hotplate heating to evaporate most of the solvent, the F127/urea-FA/Ti-AcHE hybrid monoliths were cured in a vacuum oven at 130 °C overnight.

Synthesis of All-Organic F127/Urea-FA Monoliths. 0.10 g of F127 block copolymer was dissolved in 0.90 g of EtOH (10 wt%). For the mass ratio of F127/urea-FA = 1:1, 0.50 g of urea-FA (20 wt%) was added into the F127 block copolymer solution (10 wt%) and stirred for 45 min. The all-organic hybrid monolith sample was formed by the evaporation induced self-assembly and curing procedures as described above.

Synthesis of Mesoporous Crystalline Titanium Oxynitride (TiON) Structures. The organic-inorganic F127/urea-FA/Ti-AcHE hybrid composites were heated in a tube furnace under flowing nitrogen at 350 °C (2 h) to remove the block copolymer and then at 800 °C (2–6 h) for TiON crystallization, with a ramp rate of 1 °C/min.

Synthesis of Mesoporous Titanium Dioxide (TiO₂) Structures. 1 g of F127 solution (10 wt% in EtOH) was mixed with 2.21 g aliquot of Ti-AcHE sol nanoparticles and stirred for 30 min. The yellow-colored transparent hybrid solution was cast in 5 mL PTFE beakers set on a glass Petri dish covered with a hemispherical glass dome and heated at 45 °C on a hotplate for 48–72 h under ambient conditions. The F127/Ti-AcHE hybrid monolith samples were

then cured in a vacuum oven at 130 °C overnight. Mesoporous TiO₂ samples were obtained under two different thermal annealing conditions. For X-ray characterization, mesoporous TiO₂ samples were obtained by thermal annealing in a tube furnace under flowing nitrogen at 350 °C (2 h) to remove the block copolymer and 800 °C (2 h) for TiO₂ crystallization, with a ramp rate of 1 °C/min. For the control TiO₂ catalyst, F127/Ti-AcHE hybrid samples were thermally annealed in a tube furnace under static air at 350 °C (2 h) to remove the block copolymer and 800 °C (2 h) for TiO₂ crystallization and complete removal of residual carbon, with a ramp rate of 1 °C/min.

Electrochemical Measurements. For the TiON working electrode, 4 mg of finely powdered mesoporous crystalline TiON, 50 µl of Nafion (5 wt%), 0.5 mg of Super P and 500 µl of EtOH were mixed and sonicated for 60 min to form a homogenous ink. The mass of a polished glassy carbon electrode (GCE) of 5 mm diameter (geometric area of 0.196 cm²) was first measured. 4 µl of the TiON catalyst ink was then loaded on the GCE by drop casting. The TiON working electrode was dried for 15 min under ambient conditions and then transferred into a low humidity dry box for additional drying of another 120 min. The dried TiON catalyst loading was calculated to be 0.13 mg after taking the mass difference between dried TiON-loaded GCE and bare GCE. For the control catalyst, the procedure was repeated to prepare a TiO₂ working electrode by loading the TiO₂/Nafion/Super P catalyst ink on a 5 mm diameter GCE, resulting in a dried TiO₂ catalyst loading of 0.10 mg. All electrochemical measurements were conducted using a standard three-electrode system comprising the catalyst-loaded GCE as working electrode, a Pt-metal counter electrode and a Hg/HgO reference electrode. The electrocatalytic activities of the working electrodes in hydrogen evolution reaction experiments were measured by linear sweep voltammetry in 1 M KOH electrolyte at 25 °C under stirring (1000 rpm) using a PARSTAT MC 1000 station. The scan rate was 2 mV/s. The electrochemical data were reported after calibration for the offset

potential against a reversible hydrogen electrode (RHE) and internal resistance correction. For the electrochemical stability experiments, 5000 cyclic voltammetry (CV) cycles were performed with the TiON-loaded GCE working electrode over the potential range of -1.0 to 0.4 V (versus RHE) with a scan rate of 100 mV/s in 1 M KOH electrolyte at 25 °C under stirring (1000 rpm).

Characterization. Small-angle X-ray scattering (SAXS) measurements were collected with a Xenocs Nano-inXider using Cu K_{α} radiation source and Dectris Pilatus 3 detectors. Using the Xenocs FOXTROT software, two-dimensional (2D) SAXS patterns were azimuthally integrated around the beam center into 1D scattering intensity curves plotted against the scattering vector magnitude $q = 4\pi \sin \theta / \lambda$, where θ is half of the total scattering angle and λ is the X-ray wavelength. Powder X-ray diffraction (PXRD) data were collected with a XRD Panalytical XPert Pro instrument using Cu K_{α} radiation.

Transmission electron micrographs and energy-dispersive spectroscopy (EDS) were obtained using a JEOL 2100F electron microscope operating at the accelerating voltage of 200 kV equipped with a EDAX EDS detector.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Supra spectrometer (Kratos Analytical, UK) equipped with a hemispherical analyzer and a monochromatic Al K_{α} source (1487 eV) operating at 15 mA and 15 kV. The XPS spectra were acquired from a sample area of 700×300 μm^2 at a take-off angle of 90° . A pass energy of 160 eV and 20 eV were used for survey and high-resolution scans, respectively. A 3.1 V bias was applied to prevent charge build up on the sample. The samples were prepared by pressing the powder material onto carbon tape.

Raman spectroscopy measurements were conducted using a WITec Alpha300 SR confocal Raman microscope with a 488 nm excitation laser source.

Thermogravimetric analysis (TGA) measurements were conducted using a TA Instruments Q500 under nitrogen with a heating rate of 5 °C/min.

Nitrogen sorption measurements were conducted using a Micromeritics ASAP 2020 at −196 °C. Samples were degassed at 130 °C overnight under vacuum before measurement. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method below 0.2 P/P_o .^{48,49} The mesopore size distribution was calculated by the Barret–Joyner–Halenda (BJH) method together with the improved Kruk–Jaroniec–Sayari (KJS) model using the desorption branch of nitrogen isotherm.^{49–51} The micropore size distribution was calculated using a non-local density functional theory (NLDFT) package based on the slit pore geometry model 255 (HS-2D-NLDFT- Carbon, N₂, 77 K)^{49,52} with a regularization parameter of 0.01, applied to the adsorption isotherm branch for the relative pressure range of 0 to 0.1, in the Micromeritics MicroActive Version 6.1 software.

RESULTS AND DISCUSSION

Tricomponent F127/Urea-FA/Ti-AcHE Hybrid Monoliths. The tricomponent co-assembly route to mesoporous TiON structures is shown schematically in Figure 1. We first synthesized oligomeric urea-formaldehyde derivatives (urea-FA) by the polymerization of urea and formaldehyde under basic conditions^{46,47} for three reasons: (1) Urea-FA exhibits enhanced solubility in ethanol compared to urea. (2) The hydroxymethyl groups in urea-FA derivatives are expected to promote selective interaction with the PEO blocks of F127 and titanium-oxo-acetate (Ti-AcHE) sol nanoparticles by hydrogen bonding.^{31,46} (3) Formaldehyde is a well-established crosslinking agent to stabilize the hybrid composite by thermal curing.^{17,18,46,47} The urea-FA derivatives were mixed stepwise with F127 block copolymer dissolved in ethanol and Ti-AcHE sol nanoparticles. Ordered F127/urea-FA/Ti-

AcHE mesostructured monoliths were obtained by evaporation induced self-assembly at 45 °C and thermal curing at 130 °C. Finally, the hybrid composite monoliths were thermally annealed at 800 °C under nitrogen, yielding highly crystalline mesoporous TiON structures.

Figure 1. Schematic of block copolymer-directed mesoporous titanium oxynitride structures. Optical images (middle row) show the freestanding monoliths of F127/urea-FA/Ti-AcHE hybrid composite (white colored) and thermally annealed mesoporous TiON (black colored), against 5 mm grid markings.

To investigate the interaction of block copolymer with urea-FA additives, we first prepared an organic-organic hybrid composite consisting of 1 part block copolymer to 1 part urea-FA by mass. Figure 2a shows the SAXS pattern of the all-organic composite (grey curve, sample (i)) has two well-resolved reflections consistent with the lamellar morphology (with scattering vectors of $(q/q^*)^2 = 1, 2$), thereby indicating the urea-FA additive selectively swelled F127 PEO blocks by hydrogen bonding and microphase separated into a well-ordered lattice.^{18,28} The first-order reflection corresponds to the domain spacing (d -spacing) of 15.5 nm, where $d = 2\pi/q^*$.

Figure 2. SAXS and PXRD patterns of (i) F127/urea-FA hybrid, (ii) F127/urea-FA/Ti-AcHE hybrid, and (iii, iv) mesoporous TiON samples annealed for 2 hours (iii) and 6 hours (iv) at 800 °C under nitrogen, respectively. Tick marks in (a) indicate the expected SAXS reflections for a lamellar (i) and hexagonal ($p6mm$) lattice (ii–iv). Peak markings and relative intensities for cubic rock salt TiN (sky blue, PDF 04-015-2441) and anatase TiO₂ (red, PDF 00-001-0562) are shown in (b).

We then mixed organic urea-FA with the block copolymer and inorganic Ti-AcHE sol nanoparticles in a stepwise manner, followed by solvent evaporation to generate the organic-inorganic mesostructured composite. Figure 1 shows a freestanding white-colored F127/urea-FA/Ti-AcHE hybrid monolith with F127/urea-FA mass ratio and urea/Ti molar ratio of 1:4 and 2.7:1, respectively. The SAXS pattern in Figure 2a (black curve, sample (ii)) is comprised of a significantly broader first-order and higher-order reflections with low

intensity, suggesting either short-range ordered hexagonal ($p6mm$) lattice (with scattering vectors of $(q/q^*)^2 = 1, 3, 4$) or wormhole-like structure.^{30,32} The first order reflection represents a d -spacing of 14.7 nm. The broader SAXS pattern may be attributed to reduced weak charge interactions between the urea-FA and Ti-AcHE additives with the block copolymer, thereby hindering mesophase ordering in the organic-inorganic system.³¹ We speculate the simultaneous incorporation of urea-FA and Ti-AcHE nanoparticles within the PEO blocks could have significantly perturbed the chain conformations and inhibited formation of well-defined mesophases during solvent evaporation.⁵³ We further explored hybrid composites with different urea/Ti molar ratios ranging from 4:1 to 6:1, however, SAXS patterns indicate the mesostructures were largely disordered (see Figure S1).

Mesoporous Crystalline TiON Structures. Thermal annealing at 800 °C under nitrogen resulted in the decomposition of block copolymer and conversion of urea-FA/Ti-AcHE into mesoporous crystalline TiON structures. The optical image in Figure 1 shows that the mesoporous crystalline TiON monolith retained the freestanding macroscopic shape. SAXS patterns of mesoporous TiON annealed at 800 °C for 2 hours (orange curve, sample (iii)) and 6 hours (blue curve, sample (iv)) in Figure 2a, respectively, exhibit even broader principal peaks at higher q values and disappearance of higher order reflections. The shifting of the primary peaks to higher q and loss in some degree of order were attributed to removal of organics and crystallization induced effects.³³ The d -spacing values of mesoporous crystalline TiON annealed for 2 and 6 hours are 9.8 and 9.7 nm, respectively. From SAXS the mesoscale contraction is approximately 34%, consistent with the 36% macroscopic shape shrinkage (Figure 1). Bright-field TEM micrograph in Figure 3a corroborated the retention of wormhole-like mesostructure after pyrolysis. The grainy texture of the TEM image suggests presence of carbonaceous residues (*vide infra*).

Figure 3. (a) Bright-field TEM and (b) HR-TEM images of mesoporous crystalline TiON with wormhole-like structure. (c) N₂ sorption isotherm and (d) BJH pore size distribution of mesoporous crystalline TiON.

The PXRD patterns of thermally annealed samples for 2 and 6 hours in Figure 2b display reflections and intensities that are consistent with cubic rock salt TiN and anatase TiO₂, indicating the TiON phase.¹⁵ However, the relatively broad PXRD peaks and similar lattice parameters⁵⁴ make it difficult to differentiate between the mixed TiON compositions, as well as pure TiN and TiO₂ phases. By applying the Scherrer Equation to the two prominent reflections at 2θ values of 43° and 62° , we estimated the size of crystallites oriented to the (2 0 0) and (2 2 0) planes of rock salt TiN to be about 2.3 nm after annealing for 2 hours at 800 °C. Increasing the annealing duration to 6 hours enabled growth of crystallites to ~2.5 nm. The high-resolution TEM (HR-TEM) micrograph in Figure 3b reveals the lattice fringes

of various crystallite orientations, confirming conversion of F127/urea-FA/Ti-AcHE hybrids into highly crystalline mesoporous structures.

Fast Fourier transform (FFT) analysis⁵⁵ of the HR-TEM image (Figure 3b) identified crystallites with average lattice spacing of 0.352 nm and 0.358 nm, matched with the (1 0 1) plane of anatase TiO₂ (Figure S2 and S3). We also observed crystallites with lattice spacing of 0.231 nm that could be matched with either (1 1 1) and (2 0 0) planes of rock salt TiN (Figure S4). However, the mixed compositions³⁷ and a relatively low nitrogen content (~7 at%, Figure S5) suggesting sparsely distributed TiON crystallites within the mesoscale framework, made it hard to find similar crystallites for accurate lattice spacing comparison. Together the XRD and HR-TEM analysis suggest formation of TiON crystallites amidst the dominant anatase TiO₂ phase. We speculate upon thermal annealing, the block copolymer decomposed to form the mesopores and amorphous Ti-AcHE sol precursors crystallized into tetragonal anatase TiO₂.^{31,45} Nitrogen atoms of urea-FA additive then diffused into the anatase TiO₂ crystallites, substituting oxygen to form the cubic TiON phase.^{15,45,54}

Energy-dispersive spectroscopy and mapping analysis of mesoporous crystalline TiON structures indicate uniform elemental distribution with the composition of 30.7 at% Ti, 33.3 at% O, 7.4 at% N, 23.2 at% C and 5.4 at% Cu (Figure S5). The high O content was likely derived from the Ti-AcHE sol nanoparticles and surface oxidation.⁴³ C and Cu were attributed to the carbon-coated TEM grid as well as pyrolyzed carbonaceous residues from urea-FA derivatives.⁵⁶ High-resolution X-ray photoelectron spectroscopy (XPS) measurements provided information on the chemical state of Ti, N, O and C (Figure S6). The Ti 2p spectrum in Figure S6a shows several component peaks assigned to TiN (2p_{3/2} at 455.6 eV and 2p_{1/2} at 461.2 eV), TiON (2p_{3/2} at 457.2 eV and 2p_{1/2} at 463.8 eV) and TiO₂ (2p_{3/2} at 458.8 eV and 2p_{1/2} at 464.6 eV), similar to literature values.^{57–59} The strongest component

peaks supported the dominance of anatase TiO₂ phase. The main peaks in the N 1s spectrum were assigned to TiN and TiON at 398.4 eV and 400.9 eV, respectively (Figure S6b).^{58,60} The minor peak at 396.4 eV was assigned to the CN bond, suggesting parts of the nitrogen-rich urea-FA converted into N-doped carbon residues.⁵⁸ The O 1s spectrum displays two main components peaks at 529.6 eV and 527.6 eV ascribed to TiON and TiO₂, respectively (Figure S6c).^{60–62} The component peak at 533.2 eV was attributed to hydroxyl groups on the sample surface.⁵⁹ XPS spectrum of C 1s with a peak at ~284.8 eV (Figure S6d), together with the D and G bands at 1350 cm⁻¹ and 1588 cm⁻¹ in the Raman spectrum (Figure S6e), respectively, indicate the residual carbon structure was disordered.^{19,63} Thermogravimetric analysis (TGA) of mesoporous crystalline TiON annealed for 2 and 6 hours at 800 °C reveals the residual carbon comprised ~22–24 wt% of the total sample mass (Figure S7).

The pore and porosity characteristics of mesoporous crystalline TiON structures were determined by nitrogen sorption measurements. The isotherm in Figure 3c exhibits two sharp adsorption steps at the relative pressure ranges of 0 to 0.02 and 0.8 to 0.9, attributed to capillary condensation of nitrogen in the micropores and mesopores, respectively. The Barret–Joyner–Halenda (BJH) pore size distribution plot in Figure 3d gives an average mesopore diameter of 9.5 nm, while non-local density functional theory (NLDFT) calculation denotes a micropore size distribution between 1 and 2 nm attributed to urea-FA–converted carbon residues (Figure S8).^{48,52} It is likely nitrogen remained dissolved in the residual carbon resulting in the “open” adsorption–desorption isotherm.⁶⁴ Based on the Brunauer–Emmett–Teller (BET) method⁵⁰ the specific surface area is 24 m²/g.

Urea-FA plays several essential roles in the F127/urea-FA/Ti-AcHE hybrid system to form mesoporous crystalline TiON structures. Firstly, it acts as a co-additive in the co-assembly of F127 block copolymer and Ti-AcHE nanoparticles, generating ordered mesostructured hybrid

composites. Secondly, it is an *in situ* nitrogen source enabling transformation of amorphous titanium-oxo-acetate sol precursors into crystalline TiON structures. Thirdly, urea-FA partially converts into residual carbon within the TiON mesostructure⁵⁶ and provides structural support during thermal annealing.^{26,32,33} We postulate the residual carbon reduced atomic mobility of Ti, N and O atoms at the surface and drastically inhibited growth of crystallites (<1 nm) even as the annealing duration was increased from 2 to 6 hours at 800 °C (*vide supra*). The residual carbon was also likely responsible for the delayed phase transformation of anatase TiO₂ into rutile TiO₂ that usually occurred above 700 °C.^{32,65} To test our hypothesis, control samples of mesoporous TiO₂ were synthesized by co-assembly of F127 block copolymer and Ti-AcHE sol nanoparticles, i.e., without urea-FA, and thermally annealed at 800 °C for 2 hours under nitrogen. SAXS and PXRD confirmed loss of mesostructure in the control TiO₂ samples due to the extensive growth of rutile crystals (Figure S9).^{30,32,65} Immersion in sulfuric acid to remove the carbonaceous residues similarly resulted in TiON mesostructure collapse (Figure S10).^{22,26}

Electrochemical Hydrogen Evolution Reaction. Finally, we conducted hydrogen evolution reaction (HER) experiments to probe the electrocatalytic activity of mesoporous crystalline TiON in alkaline medium. Figure 4 presents the polarization curves of mesoporous TiON, mesoporous TiO₂ and glassy carbon electrode, obtained from linear sweep voltammetry using a standard three-electrode setup in 1 M KOH electrolyte. Mesoporous TiO₂ were employed as a control catalyst for comparison.³¹ First, it is clear that the glassy carbon electrode (solid black curve) was not catalytically active towards HER. The mesoporous TiO₂ control catalyst (solid green curve) exhibited an almost negligible HER behavior⁶⁶ in contrast to the mesoporous TiON catalyst (solid orange curve) in the alkaline medium. The onset potential of mesoporous TiON catalyst was about -0.10 V and required an overpotential of -0.54 V to drive a current density of 10 mA/cm², comparable to the work by Pan and coworkers using

TiN nanoparticles on carbon cloth as catalyst for HER.⁶⁷ To investigate electrochemical stability, we performed a total of 5000 cyclic voltammetry (CV) cycles with the TiON catalyst as working electrode. The required overpotential of the TiON catalyst after 5000 CV cycles was increased to -0.64 V (compare the dashed and solid orange curves). We speculate the increase of HER overpotential ($\sim 19\%$) could be attributed to either oxidation on the mesoporous TiON catalyst surface⁶⁸ or inhibited diffusion of hydrogen gas in the micropores. We further note the nitrogen-doped residual carbon in the mesoporous structure may contributed to HER activity as an additional conducting pathway for charge transfer to the TiON catalyst.⁶⁹

Figure 4. Polarization curves of glassy carbon electrode (GCE, solid black), mesoporous TiO_2 (solid green), and mesoporous crystalline TiON before (solid orange) and after 5000 CV cycles (after CV, dashed orange), in 1 M KOH with internal resistance correction.

CONCLUSION

In conclusion, we demonstrated the first one-pot type soft-templating and ammonolysis-free approach to synthesize monoliths of highly crystalline and electrocatalytically active block copolymer-directed mesoporous TiON. The short-range ordered hybrid composites were formed by co-assembly of F127 block copolymer, urea-FA oligomers and titanium-oxo-acetate sol nanoparticles. Mesoporous crystalline TiON wormhole-like structures were obtained by thermal annealing under benign nitrogen at 800 °C whilst retaining the macroscopic monolith shape. In particular, the urea-FA additive is essential as an *in situ* nitrogen source as well as partially converting into residual carbon to provide structural support for TiON crystallization. The resultant mesoporous crystalline TiON catalyst exhibited higher electrocatalytic activity towards HER in alkaline medium compared to urea-free TiO₂ control catalyst.

Block copolymer self-assembly is a highly versatile tool to direct the periodic morphology, structural features, porosity and functional properties of both organic and inorganic mesostructures. Ordered mesoporous metal nitrides with desirable morphology and dimensionality could be achieved by employing structure-directing block copolymers of larger molar mass and higher amphiphilicity.^{28,33} Alternative nitrogen-rich additives that own a larger number of available –NH₂ functional groups (e.g., melamine^{70,71}) could promote enhanced hydrogen bond interactions with the block copolymers and metal sols to form long-range ordered mesoporous oxynitrides/nitrides after thermal annealing. Multi-metallic nitride mesoporous structures could further improve electrocatalyst performance via tailored composition-dependent catalytic activities and enhanced stability.^{7,37,43,68,72} Finally, the block copolymer soft-templating strategy shown in this work for oxynitrides may be expanded to other catalytic active inorganic systems such as phosphides⁷² and sulfides⁷³ for use in advanced energy storage applications.⁷⁴

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at

<https://pubs.acs.org/doi/10.1021/acs.langmuir>.

SAXS and PXRD patterns of hybrids with different urea/Ti molar ratios, TiO₂ and TiON after sulfuric acid treatment; Analysis of crystallite lattice spacing; Electron dispersive spectroscopy; X-ray photoelectron spectroscopy; Thermogravimetric analysis plots of mesoporous TiON; NLDFT analysis of micropore size distribution

AUTHOR INFORMATION

Corresponding Author

Kwan W. Tan – E-mail: kwtan@ntu.edu.sg

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.langmuir>.

Author Contributions

K.W.T., Y.L. and R.H. conceived the study and designed the experiments. Y.L. synthesized all the samples and performed most of the characterization with contributions from R.H., W.X.T. and N.L. W.A.S. conducted the TEM characterization. W.M.Jr. and S.M. performed the HER experiments. Y.L. and K.W.T analyzed the data with contributions from W.A.S. and W.M.Jr. K.W.T. supervised the work. Y.L. and K.W.T. wrote the manuscript and all authors contributed to revisions. All authors gave approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work was supported by a startup grant from Nanyang Technological University, Singapore. S.M. and W.M.Jr. wish to acknowledge financial support from the National Research Foundation of Singapore (NRF) Investigatorship Award (NRFI 2017-08). This work made use of research facilities at the Facility for Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore. The authors gratefully acknowledge J. C. Kuan, R. Lee, T. Salim, G. L. Seah and Y. Y. Tay for kind experimental assistance and discussion.

REFERENCES

- (1) Subramanian, B.; Muraleedharan, C. V.; Ananthakumar, R.; Jayachandran, M. A. Comparative Study of Titanium Nitride (TiN), Titanium Oxy Nitride (TiON) and Titanium Aluminum Nitride (TiAlN), as Surface Coatings for Bio Implants. *Surf. Coat.* **2011**, *205*, 5014–5020.
- (2) Ramanathan, S.; Oyama, S. T. New Catalysts for Hydroprocessing: Transition Metal Carbides and Nitrides. *J. Phys. Chem.* **1995**, *99*, 16365–16372.
- (3) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science* **2001**, *293*, 269–271.
- (4) Burda, C.; Lou, Y.; Chen, X.; Samia, A. C. S.; Stout, J.; Gole, J. L. Enhanced Nitrogen Doping in TiO₂ Nanoparticles. *Nano Lett.* **2003**, *3*, 1049–1051.
- (5) Ma, L.; Ting, L. R. L.; Molinari, V.; Giordano, C.; Yeo, B. S. Efficient Hydrogen Evolution Reaction Catalyzed by Molybdenum Carbide and Molybdenum Nitride Nanocatalysts Synthesized via the Urea Glass Route. *J. Mater. Chem. A* **2015**, *3*, 8361–8368.
- (6) Xie, J.; Xie, Y. Transition Metal Nitrides for Electrocatalytic Energy Conversion: Opportunities and Challenges. *Chem. Eur. J.* **2016**, *22*, 3588–3598.
- (7) Han, N.; Liu, P.; Jiang, J.; Ai, L.; Shao, Z.; Liu, S. Recent Advances in Nanostructured Metal Nitrides for Water Splitting. *J. Mater. Chem. A* **2018**, *6*, 19912–19933.
- (8) Dong, S.; Chen, X.; Zhang, X.; Cui, G. Nanostructured Transition Metal Nitrides for Energy Storage and Fuel Cells. *Coord. Chem. Rev.* **2013**, *257*, 1946–1956.
- (9) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. *Nat. Rev. Mater.* **2017**, *2*, 1–17.
- (10) Braic, L.; Vasilantonakis, N.; Mihai, A.; Villar Garcia, I. J.; Fearn, S.; Zou, B.; Alford, N. McN.; Doiron, B.; Oulton, R. F.; Maier, S. A.; Zayats, A. V.; Petrov, P. K. Titanium Oxynitride Thin Films with Tunable Double Epsilon-Near-Zero Behavior for Nanophotonic Applications. *ACS Appl. Mater. Interfaces* **2017**, *9*, 29857–29862.
- (11) Robbins, S. W.; Beaucage, P. A.; Sai, H.; Tan, K. W.; Werner, J. G.; Sethna, J. P.; DiSalvo, F. J.; Gruner, S. M.; Dover, R. B. V.; Wiesner, U. Block Copolymer Self-Assembly-Directed Synthesis of Mesoporous Gyroidal Superconductors. *Sci. Adv.* **2016**, *2*, e1501119.
- (12) Cui, Z.; Zu, C.; Zhou, W.; Manthiram, A.; Goodenough, J. B. Mesoporous Titanium Nitride-Enabled Highly Stable Lithium-Sulfur Batteries. *Adv. Mater.* **2016**, *28*, 6926–6931.
- (13) Lim, W.-G.; Jo, C.; Cho, A.; Hwang, J.; Kim, S.; Han, J. W.; Lee, J. Approaching Ultrastable High-Rate Li-S Batteries through Hierarchically Porous Titanium Nitride Synthesized by Multiscale Phase Separation. *Adv. Mater.* **2019**, *31*, 1806547.
- (14) Fritz, K. E.; Beaucage, P. A.; Matsuoka, F.; Wiesner, U.; Suntivich, J. Mesoporous Titanium and Niobium Nitrides as Conductive and Stable Electrocatalyst Supports in Acid Environments. *Chem. Commun.* **2017**, *53*, 7250–7253.
- (15) Wang, W.; Savadogo, O.; Ma, Z.-F. Preparation of New Titanium Oxy Nitride Based Electro Catalysts Using an Anhydrous Sol-Gel Method for Water Electrolysis in Acid Medium. *Int. J. Hydrogen Energy* **2012**, *37*, 7405–7417.
- (16) Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. Ordered Nanoporous Arrays of Carbon Supporting High Dispersions of Platinum Nanoparticles. *Nature* **2001**, *412*, 169–172.
- (17) Liang, C.; Hong, K.; Guiochon, G. A.; Mays, J. W.; Dai, S. Synthesis of a Large-Scale Highly Ordered Porous Carbon Film by Self-Assembly of Block Copolymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 5785–5789.

- (18) Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Yang, H.; Li, Z.; Yu, C.; Tu, B.; Zhao, D. Ordered Mesoporous Polymers and Homologous Carbon Frameworks: Amphiphilic Surfactant Templating and Direct Transformation. *Angew. Chem., Int. Ed.* **2005**, *44*, 7053–7059.
- (19) Werner, J. G.; Hoheisel, T. N.; Wiesner, U. Synthesis and Characterization of Gyroidal Mesoporous Carbons and Carbon Monoliths with Tunable Ultralarge Pore Size. *ACS Nano* **2014**, *8*, 731–743.
- (20) Zhang, Q.; Matsuoka, F.; Suh, H. S.; Beaucage, P. A.; Xiong, S.; Smilgies, D.-M.; Tan, K. W.; Werner, J. G.; Nealey, P. F.; Wiesner, U. B. Pathways to Mesoporous Resin/Carbon Thin Films with Alternating Gyroid Morphology. *ACS Nano* **2018**, *12*, 347–358.
- (21) Arora, H.; Du, P.; Tan, K. W.; Hyun, J. K.; Grazul, J.; Xin, H. L.; Muller, D. A.; Thompson, M. O.; Wiesner, U. Block Copolymer Self-Assembly-Directed Single-Crystal Homo- and Heteroepitaxial Nanostructures. *Science* **2010**, *330*, 214–219.
- (22) Tan, K. W.; Jung, B.; Werner, J. G.; Rhoades, E. R.; Thompson, M. O.; Wiesner, U. Transient Laser Heating Induced Hierarchical Porous Structures from Block Copolymer-Directed Self-Assembly. *Science* **2015**, *349*, 54–58.
- (23) Tan, K. W.; Werner, J. G.; Goodman, M. D.; Kim, H. S.; Jung, B.; Sai, H.; Braun, P. V.; Thompson, M. O.; Wiesner, U. Synthesis and Formation Mechanism of All-Organic Block Copolymer-Directed Templating of Laser-Induced Crystalline Silicon Nanostructures. *ACS Appl. Mater. Interfaces* **2018**, *10*, 42777–42785.
- (24) Tan, K. W.; Wiesner, U. Block Copolymer Self-Assembly Directed Hierarchically Structured Materials from Nonequilibrium Transient Laser Heating. *Macromolecules* **2019**, *52*, 395–409.
- (25) Yu, F.; Zhang, Q.; Thedford, R. P.; Singer, A.; Smilgies, D.-M.; Thompson, M. O.; Wiesner, U. B. Block Copolymer Self-Assembly-Directed and Transient Laser Heating-Enabled Nanostructures towards Phononic and Photonic Quantum Materials. *ACS Nano* **2020**.
- (26) Warren, S. C.; Messina, L. C.; Slaughter, L. S.; Kamperman, M.; Zhou, Q.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U. Ordered Mesoporous Materials from Metal Nanoparticle-Block Copolymer Self-Assembly. *Science* **2008**, *320*, 1748–1752.
- (27) Cowman, C. D.; Padgett, E.; Tan, K. W.; Hovden, R.; Gu, Y.; Andrejevic, N.; Muller, D.; Coates, G. W.; Wiesner, U. Multicomponent Nanomaterials with Complex Networked Architectures from Orthogonal Degradation and Binary Metal Backfilling in ABC Triblock Terpolymers. *J. Am. Chem. Soc.* **2015**, *137*, 6026–6033.
- (28) Templin, M.; Franck, A.; Chesne, A. D.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädler, V.; Wiesner, U. Organically Modified Aluminosilicate Mesostructures from Block Copolymer Phases. *Science* **1997**, *278*, 1795–1798.
- (29) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **1998**, *279*, 548–552.
- (30) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. Generalized Syntheses of Large-Pore Mesoporous Metal Oxides with Semicrystalline Frameworks. *Nature* **1998**, *396*, 152–155.
- (31) Fan, J.; Boettcher, S. W.; Stucky, G. D. Nanoparticle Assembly of Ordered Multicomponent Mesostructured Metal Oxides via a Versatile Sol-Gel Process. *Chem. Mater.* **2006**, *18*, 6391–6396.
- (32) Lee, J.; Orilall, M. C.; Warren, S. C.; Kamperman, M.; DiSalvo, F. J.; Wiesner, U. Direct Access to Thermally Stable and Highly Crystalline Mesoporous Transition-Metal Oxides with Uniform Pores. *Nat. Mater.* **2008**, *7*, 222–228.

- (33) Tan, K. W.; Sai, H.; Robbins, S. W.; Werner, J. G.; Hoheisel, T. N.; Hesse, S. A.; Beaucage, P. A.; DiSalvo, F. J.; Gruner, S. M.; Murtagh, M.; Wiesner, U. Ordered Mesoporous Crystalline Aluminas from Self-Assembly of ABC Triblock Terpolymer–Butanol–Alumina Sols. *RSC Adv.* **2015**, *5*, 49287–49294.
- (34) Yamauchi, Y.; Nagaura, T.; Ishikawa, A.; Chikyow, T.; Inoue, S. Evolution of Standing Mesochannels on Porous Anodic Alumina Substrates with Designed Conical Holes. *J. Am. Chem. Soc.* **2008**, *130*, 10165–10170.
- (35) Malenfant, P. R. L.; Wan, J.; Taylor, S. T.; Manoharan, M. Self-Assembly of an Organic–Inorganic Block Copolymer for Nano-Ordered Ceramics. *Nat. Nanotechnol.* **2007**, *2*, 43–46.
- (36) Maleki, M.; Beitollahi, A.; Lee, J.; Shokouhimehr, M.; Javadpour, J.; Park, E. J.; Chun, J.; Hwang, J. One Pot Synthesis of Mesoporous Boron Nitride Using Polystyrene-*b*-Poly(Ethylene Oxide) Block Copolymer. *RSC Adv.* **2014**, *5*, 6528–6535.
- (37) Robbins, S. W.; Sai, H.; DiSalvo, F. J.; Gruner, S. M.; Wiesner, U. Monolithic Gyroidal Mesoporous Mixed Titanium–Niobium Nitrides. *ACS Nano* **2014**, *8*, 8217–8223.
- (38) Beaucage, P. A.; Susca, E. M.; Gruner, S. M.; Wiesner, U. B. Discovering Synthesis Routes to Hexagonally Ordered Mesoporous Niobium Nitrides Using Poloxamer/Pluronics Block Copolymers. *Chem. Mater.* **2017**, *29*, 8973–8977.
- (39) Susca, E. M.; Beaucage, P. A.; Thedford, R. P.; Singer, A.; Gruner, S. M.; Estroff, L. A.; Wiesner, U. Preparation of Macroscopic Block-Copolymer-Based Gyroidal Mesoscale Single Crystals by Solvent Evaporation. *Adv. Mater.* **2019**, *31*, 1902565.
- (40) Yang, M.; MacLeod, M. J.; Tessier, F.; DiSalvo, F. J. Mesoporous Metal Nitride Materials Prepared from Bulk Oxides. *J. Am. Ceram. Soc.* **2012**, *95*, 3084–3089.
- (41) Buha, J.; Djerdj, I.; Antonietti, M.; Niederberger, M. Thermal Transformation of Metal Oxide Nanoparticles into Nanocrystalline Metal Nitrides Using Cyanamide and Urea as Nitrogen Source. *Chem. Mater.* **2007**, *19*, 3499–3505.
- (42) Gomathi, A. Ternary Metal Nitrides by the Urea Route. *Mater. Res. Bull.* **2007**, *42*, 870–874.
- (43) Fischer, A.; Müller, J. O.; Antonietti, M.; Thomas, A. Synthesis of Ternary Metal Nitride Nanoparticles Using Mesoporous Carbon Nitride as Reactive Template. *ACS Nano* **2008**, *2*, 2489–2496.
- (44) Giordano, C.; Erpen, C.; Yao, W.; Antonietti, M. Synthesis of Mo and W Carbide and Nitride Nanoparticles via a Simple “Urea Glass” Route. *Nano Lett.* **2008**, *8*, 4659–4663.
- (45) Giordano, C.; Erpen, C.; Yao, W.; Milke, B.; Antonietti, M. Metal Nitride and Metal Carbide Nanoparticles by a Soft Urea Pathway. *Chem. Mater.* **2009**, *21*, 5136–5144.
- (46) Christjanson, P.; Pehk, T.; Siimer, K. Hydroxymethylation and Polycondensation Reactions in Urea–Formaldehyde Resin Synthesis. *J. Appl. Polym. Sci.* **2006**, *100*, 1673–1680.
- (47) Bezbozhnaya, T. V.; Zamashchikov, V. V.; Lutsyk, A. I. Synthesis of Urea-Formaldehyde Oligomers without a Solvent. *Russ. J. Appl. Chem.* **2004**, *77*, 1544–1546.
- (48) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
- (49) Kruk, M.; Jaroniec, M. Gas Adsorption Characterization of Ordered Organic–Inorganic Nanocomposite Materials. *Chem. Mater.* **2001**, *13*, 3169–3183.
- (50) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.

- (51) Kruk, M.; Jaroniec, M.; Sayari, A. Application of Large Pore MCM-41 Molecular Sieves To Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. *Langmuir* **1997**, *13*, 6267–6273.
- (52) Jagiello, J.; Olivier, J. P. 2D-NLDFT Adsorption Models for Carbon Slit-Shaped Pores with Surface Energetical Heterogeneity and Geometrical Corrugation. *Carbon* **2013**, *55*, 70–80.
- (53) Jain, A.; Wiesner, U. Silica-Type Mesostructures from Block Copolymer Phases: Formation Mechanism and Generalization to the Dense Nanoparticle Regime. *Macromolecules* **2004**, *37*, 5665–5670.
- (54) Zukalova, M.; Prochazka, J.; Bastl, Z.; Duchoslav, J.; Rubacek, L.; Havlicek, D.; Kavan, L. Facile Conversion of Electrospun TiO₂ into Titanium Nitride/Oxynitride Fibers. *Chem. Mater.* **2010**, *22*, 4045–4055.
- (55) Hudak, B. M.; Depner, S. W.; Waetzig, G. R.; Talapatra, A.; Arroyave, R.; Banerjee, S.; Guiton, B. S. Real-Time Atomistic Observation of Structural Phase Transformations in Individual Hafnia Nanorods. *Nat. Commun.* **2017**, *8*, 15316.
- (56) Jiang, X.; Li, C.; Chi, Y.; Yan, J. TG-FTIR Study on Urea-Formaldehyde Resin Residue during Pyrolysis and Combustion. *J. Hazard. Mater.* **2010**, *173*, 205–210.
- (57) Yan, L.; Chen, G.; Tan, S.; Zhou, M.; Zou, G.; Deng, S.; Smirnov, S.; Luo, H. Titanium Oxynitride Nanoparticles Anchored on Carbon Nanotubes as Energy Storage Materials. *ACS Appl. Mater. Interfaces* **2015**, *7*, 24212–24217.
- (58) Han, Y.; Yue, X.; Jin, Y.; Huang, X.; Shen, P. K. Hydrogen Evolution Reaction in Acidic Media on Single-Crystalline Titanium Nitride Nanowires as an Efficient Non-Noble Metal Electrocatalyst. *J. Mater. Chem. A* **2016**, *4*, 3673–3677.
- (59) Bharti, B.; Kumar, S.; Lee, H.-N.; Kumar, R. Formation of Oxygen Vacancies and Ti 3+ State in TiO₂ Thin Film and Enhanced Optical Properties by Air Plasma Treatment. *Sci. Rep.* **2016**, *6*, 32355.
- (60) Jaeger, D.; Patscheider, J. A Complete and Self-Consistent Evaluation of XPS Spectra of TiN. *J. Electron Spectrosc. Relat. Phenom.* **2012**, *185*, 523–534.
- (61) Chang, C.-C.; Nogan, J.; Yang, Z.-P.; Kort-Kamp, W. J. M.; Ross, W.; Luk, T. S.; Dalvit, D. A. R.; Azad, A. K.; Chen, H.-T. Highly Plasmonic Titanium Nitride by Room-Temperature Sputtering. *Sci. Rep.* **2019**, *9*, 15287.
- (62) Nasim, F.; Ali, A.; Hafizuddin, M.; Bhatti, A. S. Role of Ti Phases in the Modulation of Border Traps at the TiO₂/n-Si Interfaces. *J. Appl. Phys.* **2012**, *112*, 044513.
- (63) Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. *Phys. Rev. B* **2000**, *61*, 14095–14107.
- (64) Seo, M.; Hillmyer, M. A. Reticulated Nanoporous Polymers by Controlled Polymerization-Induced Microphase Separation. *Science* **2012**, *336*, 1422–1425.
- (65) Guldin, S.; Hüttner, S.; Tiwana, P.; Orilall, M. C.; Ülgüt, B.; Stefik, M.; Docampo, P.; Kolle, M.; Divitini, G.; Ducati, C.; Redfern, S. A. T.; Snaith, H. J.; Wiesner, U.; Eder, D.; Steiner, U. Improved Conductivity in Dye-Sensitised Solar Cells through Block-Copolymer Confined TiO₂ Crystallisation. *Energy Environ. Sci.* **2011**, *4*, 225–233.
- (66) Wang, Y.; Zhu, Q.; Xie, T.; Peng, Y.; Liu, S.; Wang, J. Promoted Alkaline Hydrogen Evolution Reaction Performance of Ru/C by Introducing TiO₂ Nanoparticles. *ChemElectroChem* **2020**, *7*, 1182–1186.
- (67) Zhu, Q.; Yao, L.; Tong, R.; Liu, D.; Ng, K. W.; Pan, H. Cobalt/Titanium Nitride@N-Doped Carbon Hybrids for Enhanced Electrocatalytic Hydrogen Evolution and Supercapacitance. *New J. Chem.* **2019**, *43*, 14518–14526.
- (68) Choi, D.; Kumta, P. N. Nanocrystalline TiN Derived by a Two-Step Halide Approach for Electrochemical Capacitors. *J. Electrochem. Soc.* **2006**, *153*, A2298.

- (69) Lu, X.; Liu, T.; Zhai, T.; Wang, G.; Yu, M.; Xie, S.; Ling, Y.; Liang, C.; Tong, Y.; Li, Y. Improving the Cycling Stability of Metal–Nitride Supercapacitor Electrodes with a Thin Carbon Shell. *Adv. Energy Mater.* **2014**, *4*, 1300994.
- (70) Kailasam, K.; Jun, Y.-S.; Katekomol, P.; Epping, J. D.; Hong, W. H.; Thomas, A. Mesoporous Melamine Resins by Soft Templating of Block-Co-Polymer Mesophases. *Chem. Mater.* **2010**, *22*, 428–434.
- (71) Yu, J.; Guo, M.; Muhammad, F.; Wang, A.; Yu, G.; Ma, H.; Zhu, G. Simple Fabrication of an Ordered Nitrogen-Doped Mesoporous Carbon with Resorcinol–Melamine–Formaldehyde Resin. *Microporous Mesoporous Mater.* **2014**, *190*, 117–127.
- (72) Fu, S.; Zhu, C.; Song, J.; Engelhard, M. H.; Li, X.; Du, D.; Lin, Y. Highly Ordered Mesoporous Bimetallic Phosphides as Efficient Oxygen Evolution Electrocatalysts. *ACS Energy Lett.* **2016**, *1*, 792–796.
- (73) Guo, Y.; Park, T.; Yi, J. W.; Henzie, J.; Kim, J.; Wang, Z.; Jiang, B.; Bando, Y.; Sugahara, Y.; Tang, J.; Yamauchi, Y. Nanoarchitectonics for Transition-Metal-Sulfide-Based Electrocatalysts for Water Splitting. *Adv. Mater.* **2019**, *31*, 1807134.
- (74) Li, C.; Li, Q.; Kaneti, Y. V.; Hou, D.; Yamauchi, Y.; Mai, Y. Self-Assembly of Block Copolymers towards Mesoporous Materials for Energy Storage and Conversion Systems. *Chem. Soc. Rev.* **2020**, *49*, 4681–4736.