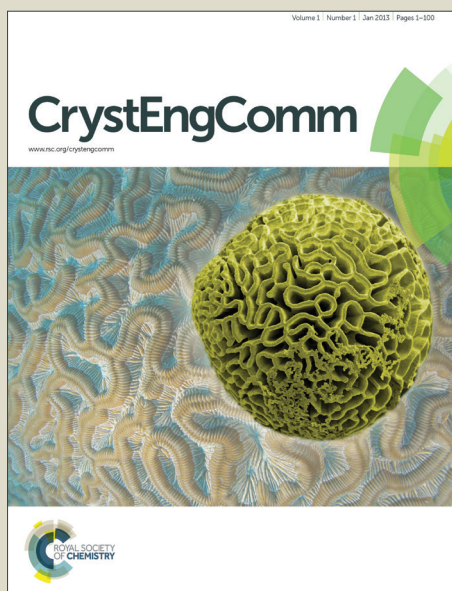


CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Bio-Inspired Formation of Nanostructured Arrays on Flexible Substrates with Superoleophobicity

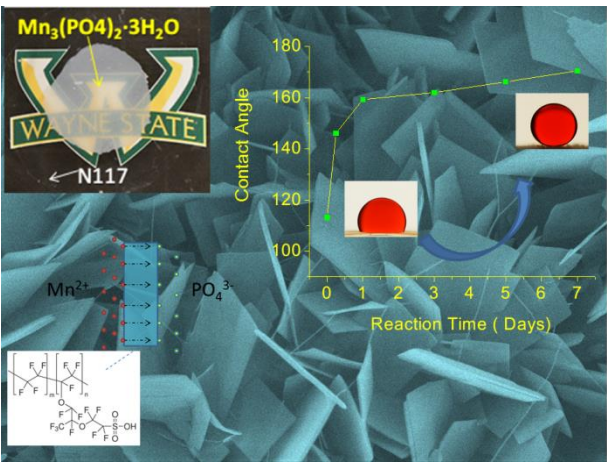
*Xinghua Meng, Da Deng**

Department of Chemical Engineering and Materials Science, Wayne State University,

5050 Anthony Wayne Dr. Detroit, MI, United States, 48202

KEYWORDS: Bio-Inspired, Cation-exchange membrane, $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, Nanoarray, Superoleophobicity.

Table of contents entry



Bio-inspired synthesis of nanoarrays on flexible substrate using $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ as model is demonstrated and achieves superoleophobicity.

ABSTRACT: Nanomaterials with size and structure-dependent properties are attracting much attention recently. However, it is still challenging to achieve large-scale fabrication of nanostructured arrays on flexible substrates at room temperature. Here, we report a facile procedure, inspired by eggshell formation, to synthesize high-order nanostructured flake arrays on a flexible Nafion membrane. We demonstrated, using $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ as a model, that cation exchange Nafion membrane can function as a controller of cations and pH to provide the right reaction environment for the nucleation and formation of rectangle shaped $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays directly grown on the substrate of Nafion membrane at room temperature. The bio-inspired approach offers a facile procedure for large scale synthesis of various nanostructures, in principle, at room temperature. The formation mechanism was investigated by tuning experimental parameters. Interestingly, we also demonstrated that the hierarchical structures of nanoflake arrays on flexible substrates shown impressive underwater superoleophobicity, similar to that of fish scales.

1. INTRODUCTION

Functional nanostructured materials have been attracting much attention in the past few decades. Nanostructured materials can find many important applications, including catalysis,¹ sensors,²⁻³ energy storage,⁴ self-cleaning surface,⁵ drug delivery,⁶ water splitting,⁷ and solar cells.⁸ Nanostructures are typically synthesized by hydrothermal methods,⁹ co-precipitation,¹⁰ chemical vapor deposition (CVD),¹¹ and template-assisted deposition.¹² The existing methods have certain limitations, such as the needs of extreme experimental conditions, expensive instruments and the lack of feasibility to synthesize nanostructures on flexible substrates (e.g., polymers) at room

temperature on a large scale. For instances, hydrothermal methods require high temperature and high pressure conditions;¹³ CVD synthesis needs expensive CVD reactors and typically operates at high temperature;¹⁴⁻¹⁵ it is generally difficult to fabricate high-order nanostructured arrays on substrates by co-precipitation methods in solution; template-assisted synthesis requires the use of expensive sacrificed templates that have to be removed.¹⁶⁻¹⁷ Therefore, it is always intellectually interesting and technically challenging to develop new approaches for facile synthesis of ordered nanostructures on given flexible substrates at room temperature.

Nature, with nearly four billion years of evolution, offers many inspirations to develop facile approaches to synthesize nanostructures on substrates at room temperature. Numerous hierarchical nanostructures are synthesized by various species in nature, providing unique features. Few interesting examples are: self-cleaning lotus leaves,¹⁸ high visual efficiency of fly eyes,¹⁹ iridescent colors of butterflies,²⁰ low drag of shark skin,²¹ mechanically robust eggshells,²² strong surface adhesion of gecko's feet,²³ bacterial biofilms with resistance to liquid wetting and gas penetration,²⁴ water collection capability of Namib desert beetle,²⁵ antifogging properties of mosquito compound eyes,²⁶ and robust eggshells. Bio-inspired synthesis of functional nanostructures is attracting much attention recently. Taking eggshell for example, the inorganic eggshell is formed by a sophisticated strategy: the carbonate ions from metabolism of embryo could pass through the eggshell membrane and react with calcium ions from uterus forming calcium carbonate structures on only external surface of eggshell membrane to form a protective eggshell of calcium carbonate (~95%) stabilized by a protein matrix (~5%).²⁷⁻²⁸ The robust shell can protect the embryo inside, and also controls the passage of air in and out of the egg through tiny pores. It will be interesting to learn from this sophisticated strategy of eggshell membrane assisted synthesis of eggshell and develop artificial membrane assisted synthesis of

nanostructures on a large scale. Another interesting example would be fish scales with superoleophobicity that could provide protection towards pollutants and toxins in rivers.²⁹ Artificial fish scales with superoleophobicity can find many applications, including antifouling coating, pollutants and toxins prevention, and oil spill recovery. However, bio-inspired membrane-assisted synthesis of functional nanostructures is still in its infancy. It would be interesting to learn the strategy from the eggshell formation mechanism to synthesize superoleophobic materials. There are only few reports on membrane-assisted synthesis of calcium based materials.³⁰⁻³¹ We believe that bio-inspired synthesis could be applied, in principle, to prepare many different kinds of nanostructures, beyond calcium based materials, with unique morphologies, desired structures and compositions, therefore functional properties, opening up opportunities of low cost and green production of nanostructures.

We have identified hydrated manganese (II) phosphate ($\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$) as a model to explore the general application of bio-inspired membrane-assisted synthesis of nanostructures on flexible substrates. $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ mineral, existing as Reddingite mineral in nature, is a functional material with many important applications. For example, it could be used as coating materials to enhance wear,³² a precursor to synthesize LiMnPO_4 cathode materials for lithium-ion batteries,³³⁻³⁴ and additive in flame retardant systems.³⁵ Additionally, it also demonstrated interesting ferromagnetic properties.³⁶ In the preparation of this manuscript, we also learned that $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ could be used as a catalyst for water oxidization.³⁷ Precipitation and solid state reactions are typically used to synthesize $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$.^{33, 36-37} Therefore, it will be very interesting to explore bio-inspired membrane-assisted methods to prepare $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanostructures at room temperature, in particular, forming nanoarrays on flexible substrates.

Herein, we present a bio-inspired membrane-assisted approach to fabricate $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays on flexible polymer substrates at room temperature for the first time. Cation-

exchange membrane (Nafion N117) was selected as the semi-permeable membrane to control the diffusion direction of Mn^{2+} ions as well as the cations concentration for controlled crystallization to form a unique 2-D rectangle shape. At the same time, hydrophilic groups on the Nafion membrane facilitate nucleation and growth of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflakes on the Nafion membrane, forming a robust nanoflake arrays coated membrane as a piece of material with flexibility. The flake-like nanostructures formed on a substrate and hydrophilic nature of the hydrate can achieve impressive underwater hydrooleophobicity with oil contact angle at $\sim 170^\circ$ and extremely low oil-adhesion, which is similar to that of fish scales.

2. EXPERIMENTAL SECTION

Materials Synthesis. All chemicals were used as received. In a typical procedure, 0.1 M of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ aqueous solution and 0.1 M of H_3PO_4 aqueous solution were prepared in beakers first. The pH value of H_3PO_4 solution was adjusted to 8 by a LiOH aqueous solution. Then 8 ml each of the two solutions were put into two chambers of the reactor separated by a piece of cation exchange membrane (Nafion N117) and sealed with two o-rings (Figure S1a in Support Information-SI). The membrane was rinsed and saturated in deionized water before use. The reactors were maintained at room temperature for different time intervals, ranging from 6, 24 h, 3, 5 to 7 d. It was observed that $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays only formed on the side of the membranes exposed to $[\text{PO}_4^{3-}]$ solution, not the side exposed to $[\text{Mn}^{2+}]$ solution.

Materials Characterization. X-ray diffraction analysis was carried out on a XRD instrument (Rigaku with Cu K α radiation). The morphology was characterized by a field emission scanning electron microscope (FESEM, JEOL 7600) coupled with energy dispersive x-ray spectroscopy (EDS) for elemental analysis. A transmission electron microscope (TEM, JEOL 2010) was also used. A thermogravimetric analysis (TGA, TA Q600) was carried out at ramp rate of $10^\circ\text{C min}^{-1}$

from room temperature to 700 °C in air. For underwater oil contact angle analysis, 1, 2-dichloroethane ($C_2H_4Cl_2$) dyed with Oil Red O was selected as the model oil due to that its density is higher than that of water. 5 μ L oil droplets were directly dropped on to $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoflake arrays covered Nafion membrane under water. The optical images of the bead-like oil droplets were taken by a camera with a micro lens (Nikon 85mm f/3.5G). The static oil contact angles were measured based on optical images using ImageJ software.

3. RESULTS AND DISCUSSION

Figure 1 shows the optical image and chemical composition characterization of the $Mn_3(PO_4)_2 \cdot 3H_2O$ nanostructures formed by bio-inspired membrane-assisted synthesis after 7 days of reaction at room temperature. Figure 1a is the optical image of a piece of Nafion membrane covered with white color $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoflake arrays in water. The uniform white color suggests the even distribution of $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoflake arrays on the Nafion surface. Note that Nafion without $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoarrays are totally transparent in water. The formation of $Mn_3(PO_4)_2 \cdot 3H_2O$ was observed only on the side of the Nafion exposed to $[PO_4^{3-}]$ solution. The other side of the Nafion membrane in contact with $[Mn^{2+}]$ solution remained clean without any solid formation. This phenomenon, as expected, might be attributed to the cation-exchange nature of Nafion membrane.^{30-31, 38} Nafion has a unique structure of fluorocarbon backbones attached with a high concentration of negatively charged sulfonate groups ($-SO_3^-$) at 1.13 mol/L.³⁹ The unique property of Nafion only allows cations to be exchanged but not anions or electrons.^{38, 40} Thus, the Mn^{2+} cations transferred via Nafion can react with PO_4^{3-} anions forming insoluble $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoarrays only on the side of the membrane exposed to $[PO_4^{3-}]$ solution. On the other side, the Li^+ cations transferred are fully dissolved without any solid formed as Li_2SO_4 are very soluble at room temperature in water.

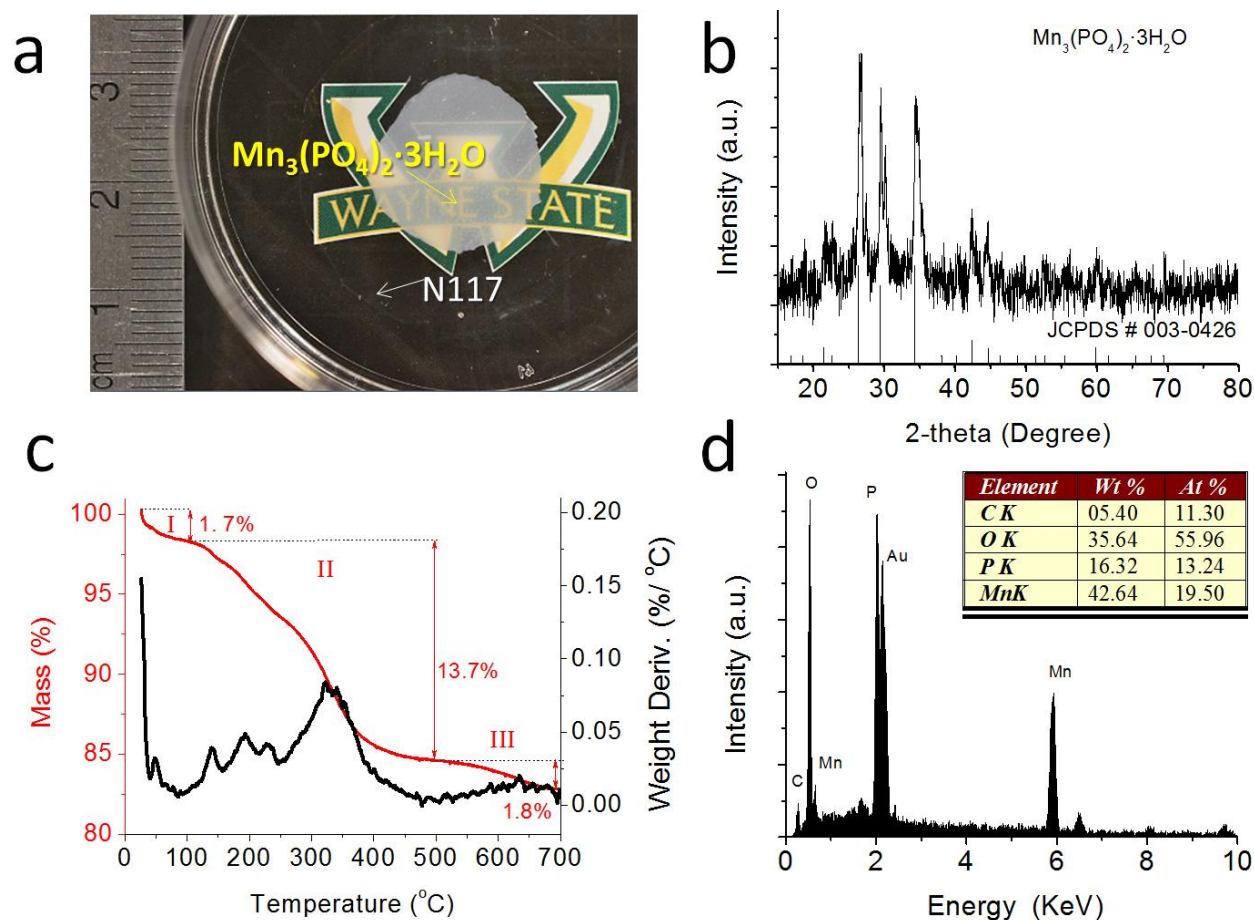


Figure 1. $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanostructures grown on Nafion N117 substrates: (a) optical image of white color $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ formed on a piece of Nafion membrane, (b) XRD pattern assigned to $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, (c) TGA profile, and (d) EDS analysis of the collected $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ to double confirm chemical composition.

Optical image clearly shows that that $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ forms a uniform white film on the Nafion membrane surface (Figure 1a). The part of Nafion membrane not exposed to reactants (covered by O-rings) is colorless. The XRD result (Figure 1b) confirms that the white sample is $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. The XRD diffraction peaks could be matched relatively well to that of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ according to the JCPDS #003-0426. $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ should have triclinic crystal structure, and the lattice constants generally agreed with that in literature.³⁷ Figure 1c

shows TGA profile of the as-prepared $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. There are three stages. Firstly, from room temperature to 87 °C, the 1.6% mass drop could be attributed to the removal of physically adsorbed water molecules on the surface. Then, the weight loss continued to drop 13.8wt% up to 500 °C, which suggests the removal of structural water in $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ crystals. Experimentally observed mass loss (13.8 wt%) is well agreed with the theoretical value of structural water in $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (13.2 wt%). After 500 °C, there is still slight decrease (1.8 wt%) from 500 to 700 °C, which could be assigned to the decomposition of trace impurities. The profile of the TGA curve is consisted with references reported,^{33, 35, 37} once again confirming its chemical composition as $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. Interestingly, the structural water in $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ can only be fully eliminated at much higher temperature (500 °C) than other regular hydrated compounds, such as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ at 200 °C, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at 165 °C, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 220 °C.⁴¹⁻⁴³ It could be attributed to the triclinic crystal structure of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, which could form strong intermolecular attraction.³⁶⁻³⁷ As shown in Figure 1d, EDS analysis shows the presence of elements of Mn, P and O. The atomic ratio of Mn and P is 1.47, which is very close to the theoretical ratio 1.5. Therefore, based on TGA, XRD, EDS analysis, the formation of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ using our room-temperature method is confirmed.

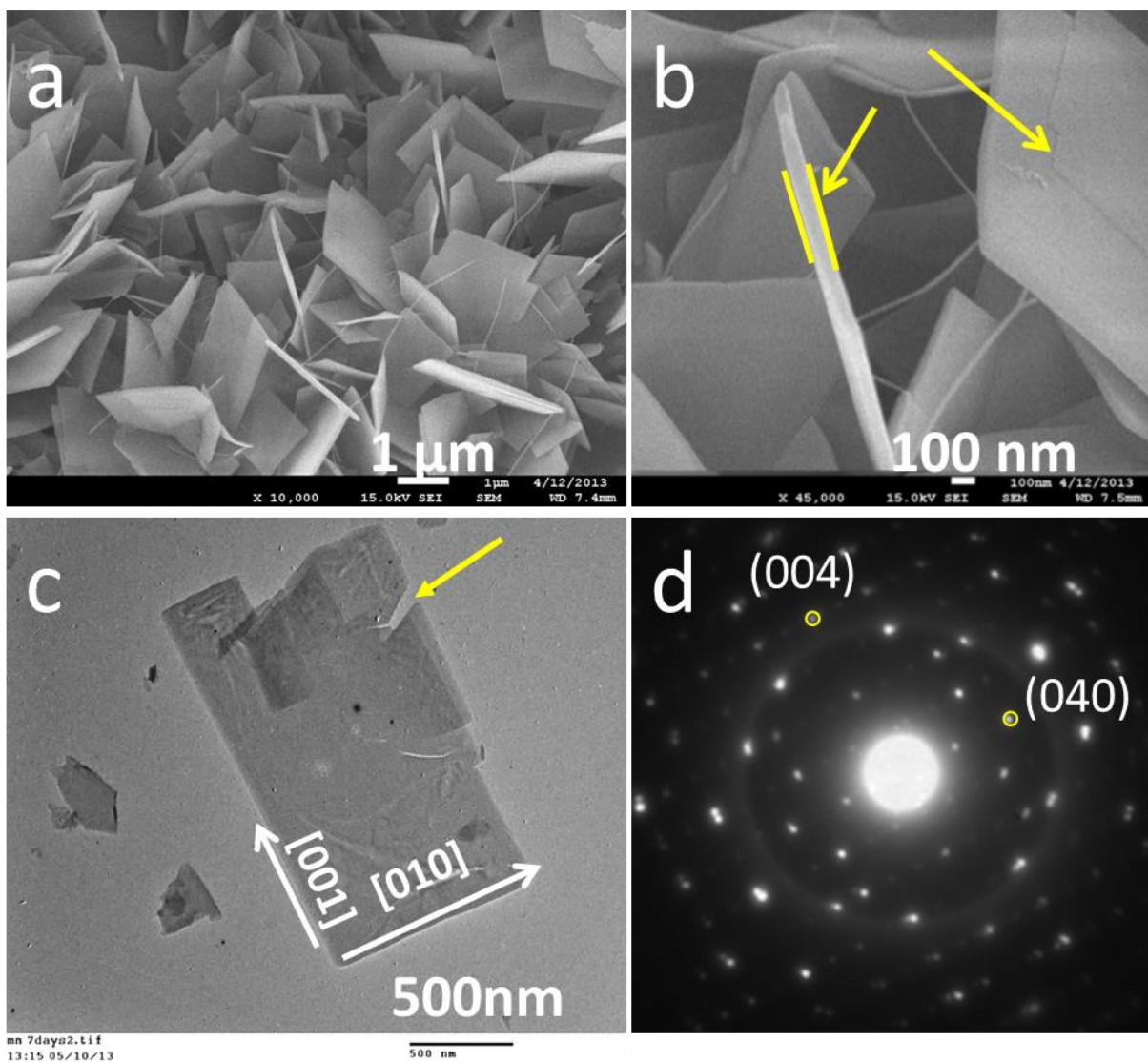


Figure 2. (a) Low-magnification FESEM image to show the overview morphology of nanoflake arrays of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ grown on Nafion N117 membrane at room temperature after 7 days of reaction; (b) high-magnification FESEM image of few typical flakes tilted at different degrees, and the “edge” and “face” are defined as highlighted, and nanowires and multilayers are observed; (c) TEM image of one typical rectangle flake; the yellow arrow highlights the edge where the defect and multilayers observed; (d) the corresponding SAED pattern of a section of a typical flake showing in (c).

The structure of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays was characterized by both FESEM and TEM (Figure 2). The low-magnification overall view (Figure 2a) shows that nanoflake arrays were formed on the surface of Nafion substrates. The nanoflakes are interlaced and intercrossed with each other to form continuing 3D structures on the surface of the membrane substrate, with each nanoflake growing outwards against the Nafion substrate. The intercrossed network could enhance the mechanical stability of the nanoflakes standing on the substrate forming arrays. The nanoflakes are rectangle in shape with width at 500 nm to 2 μm and the length at 1-3 μm . The thickness of nanoflakes is about 80-100 nm (Figure 2b). The nanoflakes were formed by stacked layered-structures, as evidenced by thin layers on the surface of the nanoflake (highlighted by yellow arrow in Figure 2b). Surprisingly, there are nanowires and branched nanowires linking the nanoflakes observed (Figure 2a-b). The Y-shaped nanowires connecting three nanoflakes are particularly interesting. The by-products of nanowires might find potential applications utilizing their function as linkers for electron, mass and energy transfer in the future. Our on-going effort is to further investigate the byproduct of nanowires. For the scope of this current paper, we will focus on the main product of nanoflake arrays. The as-grown $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ in rectangle shape was double-confirmed by TEM image (Figure 2c). The layered-structure more clearly observed with uniform projection of two layers with different contrast at the upper right side as highlighted by the yellow arrow. Based on SAED analysis, these rectangle flakes have extended length along [001] direction and extended width along [010]. The flakes have dominantly exposed {100} facets, which could be thermodynamically stable under the experimental conditions. Notably, the mouth-like defect in the top right of the flake highlighted by a yellow arrow suggests an intercrossed flake was “locked” by it but broken off under intensive mechanical vibration in the preparation of sample for TEM. The interlocked nanoflakes could

enhance their stability as an integrated piece of materials on a macro scale. The SAED pattern shows the clear diffraction spots indicating good crystallinity and all the spots can be assigned to $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$.

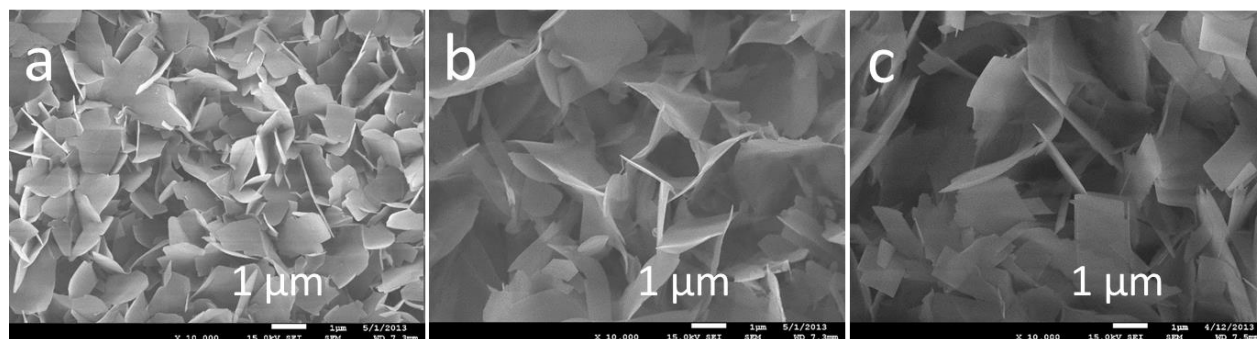


Figure 3. FESEM images of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ formed on Nafion N117 membrane after different reaction periods of (a) 6 h, (b) 24 h, and (c) 5 d, keeping all other experimental parameters constant.

In order to explore the mechanism of formation of nanoflake arrays of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, the effect of different reaction time and temperature on nanoflakes were studied. The evolution in the morphologies of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ over time is presented in Figure 3. After 6 h, a large number of flakes without regular shapes formed on the surface, and the color of the membrane started to change from transparent to translucent (Figure S2c, 6 h in SI). The flakes were not in rectangle shape yet at this stage (Figure 3a). When the reaction time was extended to 24 h, the size increased as compared to those obtained after 6 h of reaction and the color changed to light white (Figure S2c, 24h in SI). We also observed that, at 50 °C instead of room temperature, nanobelt arrays instead of nanoflakes would be formed after 24 h of reaction (Figure S5a in SI), which suggests that high temperature could significantly accelerate the oriented growth of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ arrays along [001] direction. The formation of belt could be considered as the extended rectangle shape flakes with faster growth in [001] direction under higher temperature.

Two factors, namely cation mobility in Nafion and crystallization rate, are significantly affected by temperature, leading to the formation of layered nanobelts on the flexible substrate (Figure S5 in SI).

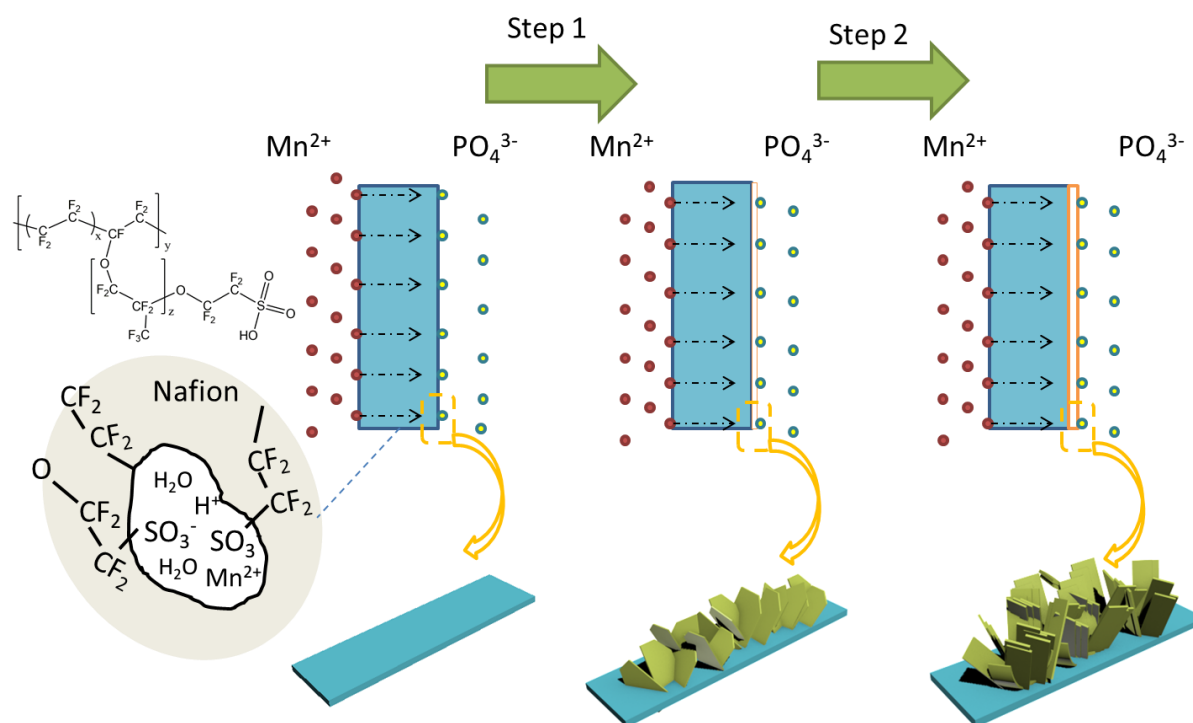


Figure 4. The schematic to illustrate the formation of nanoflake arrays $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ on a Nafion membrane.

Based on our experimental evidences and understanding on the properties of Nafion, we propose a possible formation mechanism (Figure 4). At the beginning, Mn^{2+} ions are easily transferred from $[\text{Mn}^{2+}]$ solution chamber to $[\text{PO}_4^{3-}]$ solution chamber via the cation-exchange membrane.³⁸ At the same time, Li^+ and H^+ as counter ions are also carried from $[\text{PO}_4^{3-}]$ solution chamber and Nafion to $[\text{Mn}^{2+}]$ solution chamber to balance the charge. Li^+ and H^+ ions in the $[\text{Mn}^{2+}]$ solution chamber are fully dissolved with the presence of $[\text{SO}_4^{2-}]$ anions without solid formation. In contrast, the transfer of Mn^{2+} ions toward $[\text{PO}_4^{3-}]$ solution chamber could initiate nucleation due to low solubility of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ in water. Note: $\text{Mn}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ has a

Solubility Product Constant $K_{sp}=6.13 \times 10^{-32}$,⁴⁴ and $Mn_3(PO_4)_2$ has a $K_{sp}=1 \times 10^{-27}$.⁴⁵ The formation of $Mn_3(PO_4)_2 \cdot 3H_2O$ crystals on the surface of Nafion might experience a typical nucleation and growth process. In this process, Nafion played an important role. Firstly, Nafion has ion channels,⁴⁶ which assist the continuous transfer of Mn^{2+} ions in $[PO_4^{3-}]$ solution side due to the presence of concentration gradient between the two sides of the membrane. Secondly, Nafion provides pre-existing interface, reducing the activation energy for nucleation of $Mn_3(PO_4)_2 \cdot 3H_2O$ to initiate heterogeneous nucleation and growth. Thirdly, the large amounts of sulfonate groups with negative charge can bind with Mn^{2+} ions to keep the initial heterogeneous nucleation of $Mn_3(PO_4)_2 \cdot 3H_2O$ on the surface.⁴⁷⁻⁴⁸ Eventually, the nanoflake arrays were formed on the flexible substrate. However, the exact mechanism of formation is still not fully understood which will require additional studies.

To demonstrate the possible application of the as-prepared $Mn_3(PO_4)_2 \cdot 3H_2O$ nanoflake arrays on flexible Nafion, unique surface property was investigated. $Mn_3(PO_4)_2 \cdot 3H_2O$ is a typical oleophobic material due to its hydrate nature and the existence of hydrophilic groups. After introducing hierarchical nanostructures, its oleophobicity could transform into superoleophobicity under water, like fish scales. To explore the effect of the structures to its wettability underwater, we measured the oil contact angles (OCAs) on the as-deposited Nafion membrane based on different reaction time (0 to 7 days). Bare Nafion membrane has OCA of 113° (Figure 5a). Comparing with the flatten surface of Nafion N117 in water (Figure S7a in SI), the bottom of Nafion detached from the glass slides and deformed slightly after being exposed to oil droplet. The oil droplet was stuck to Nafion surface. The observed phenomenon might be ascribed to the nature of Nafion membrane. Nafion has a backbone of hydrophobic tetrafluoroethylene with hydrophilic sulfonic acid groups ($-H^+SO_3^-$) in its side chain.³⁸ Goswami

et al. studied the behavior of the deformation of Nafion in contacting with water and observed a transformation from hydrophobicity to hydrophilicity due to the movement of polar groups.⁴⁹ Therefore, the slightly deformed surface observed could be caused by partly restructuring surface group in responding to changes in surface energy (from water to oil locally) and the induced mechanical stress. After the surface of the Nafion was covered by $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays obtained from 6 h reaction, the exposed surface in contact with oil droplet is only from $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ not Nafion. Thus, as shown in Figure 5b, the OCA increased significantly to 146° , and the oil droplet easily moved around. No Nafion deformation was observed at the interface between the oil droplet and the Nafion, indicating the $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ with hierarchical micro/nanostructures have isolated the surface of Nafion from the oil droplet. As the reaction time extended with further nanostructure growth, the OCA was higher at 166° after 5 days (Figure 5c). Finally, it was totally superoleophobic and oil-adhesion was ultralow for the 7 d sample (Figure 5d). Here, the oil droplet demonstrates a nearly spherical shape ($\text{OCA} = 171^\circ$). The extremely low oil-adhesion also was achieved, where the oil droplets rolled off easily (see the video in SI). The interesting superoleophobicity underwater with the assistance of hierarchical micro/nanostructure could find many applications, including pollutants and toxins prevention, oil/water separation, microscale transfer.⁵⁰⁻⁵³

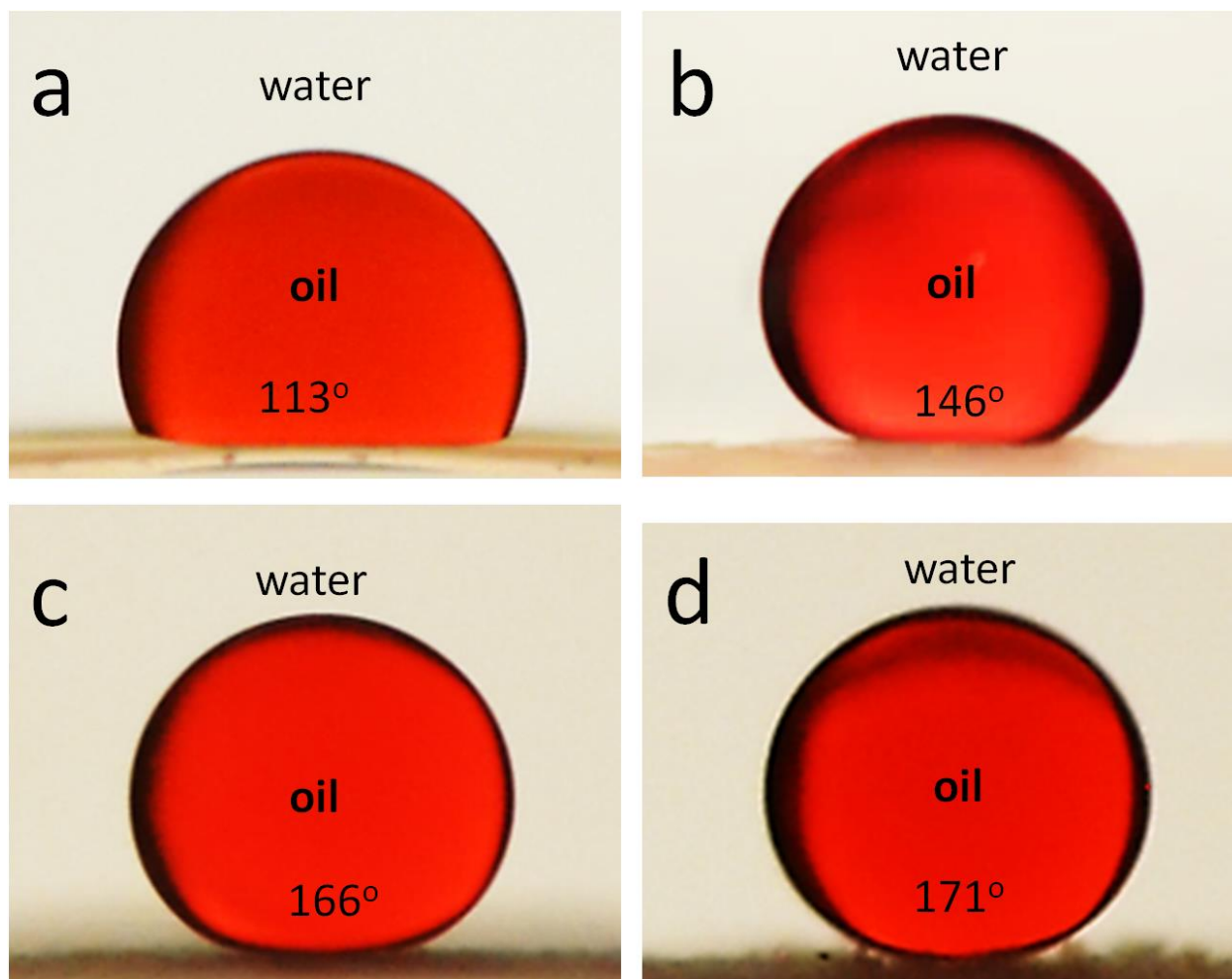


Figure 5. Shape change of an oil droplet (1, 2-dichloroethane dyed with Oil Red O, 5 μ L) under water on the surface of (a) bare Nafion membrane, and as-deposited Nafion N117 membrane with $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays after reaction time of (b) 6 h, (c) 5 d, (d) 7 d.

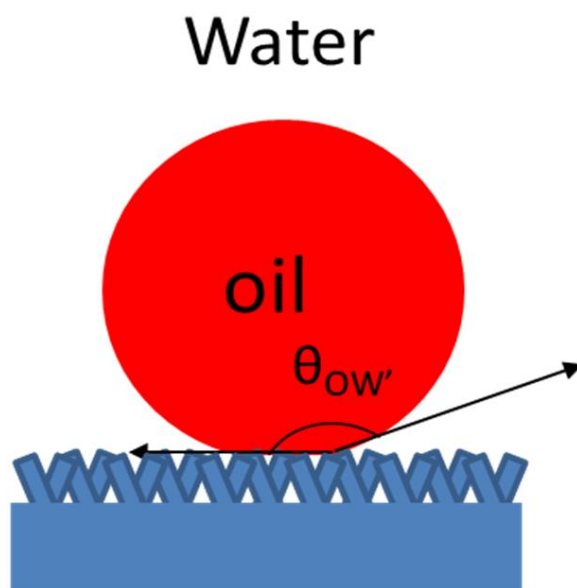


Figure 6. The schematic to demonstrate the nanoflake arrays induced roughness and superoleophobicity underwater.

The observed superoleophobicity underwater can be interpreted by Cassie model (Figure 6). The Cassie equation is:⁵⁴

$$\cos\theta_{OW'} = f\cos\theta_{OW} + f - 1$$

where f is the area fraction of solid, θ_{OW} and $\theta_{OW'}$ are the contact angles of oil droplet sitting on a smooth and rough surface, respectively, in water. When the rough surface was immersed in water, the space and voids between hierarchical micro/nanostructures were occupied by water, or f is extremely small. Consequently, the nanoflake arrays filled with water could prevent the oil droplet from touching the Nafion membrane. The superoleophobicity, measured based on the oil droplet contact angle underwater, increases with the decrease of f or the increase of roughness at micro/nanoscale induced by $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays, as expected (Figure S7b in SI).

We would like to highlight that the self-assembled nanostructured $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ on Nafion membrane as a robust and flexible material may find other applications, including solid

supercapacitors, water oxidation, electrochemical biosensors and battery positive electrodes.^{37, 55-}

⁵⁸ Moreover, $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ can be facily transformed to Mn_3O_4 which can find other applications (Figure S6 in SI).⁵⁹⁻⁶¹ Our on-going efforts are focusing on those directions and results will be reported once available.

4. Summary

We demonstrated a bio-inspired membrane-assisted approach to fabricate nanoflake arrays on flexible Nafion membrane at room-temperature. Nafion N117 membrane not only controlled the transportation of ions and their reactions, but also was used as a flexible substrate to support the growth of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays. We believe our approach outlined in this paper could be applied to achieve room-temperature and bio-inspired synthesis of many different kinds of functional nanostructures, including but not limited to metal hydroxides, metal phosphates, etc. The hierarchical nanostructures of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflake arrays demonstrated interesting superoleophobicity underwater similar to fish scales and they could find important applications.

ASSOCIATED CONTENT

Supporting Information. Optical images of the reactor and Nafion membranes under various conditions. XRD patterns to show Li_3PO_4 and Mn_3O_4 ; FESEM and optical images of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ prepared at 50 °C.

AUTHOR INFORMATION

Corresponding Author

[*da.deng@wayne.edu](mailto:da.deng@wayne.edu)

Author Contributions

DD designed the research; XH carried out the experiments; DD&XH analyzed the results and wrote the paper.

ACKNOWLEDGMENT

The authors thank the Lumigen Instrument Center, Wayne State University, Detroit, MI.

REFERENCES

1. Zhou, Z. Y.; Tian, N.; Li, J. T.; Broadwell, I.; Sun, S. G. Nanomaterials of High Surface Energy with Exceptional Properties in Catalysis and Energy Storage. *Chem. Soc. Rev.* **2011**, *40*, 4167-4185.
2. Sun, Z. Y.; Yuan, H. Q.; Liu, Z. M.; Han, B. X.; Zhang, X. R. A Highly Efficient Chemical Sensor Material for H₂S: Alpha-Fe₂O₃ Nanotubes Fabricated Using Carbon Nanotube Templates. *Adv. Mater.* **2005**, *17*, 2993-2997.
3. Jiang, H. J. Chemical Preparation of Graphene-Based Nanomaterials and Their Applications in Chemical and Biological Sensors. *Small* **2011**, *7*, 2413-2427.
4. Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W. Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat. Mater.* **2005**, *4*, 366-377.
5. Bhushan, B.; Jung, Y. C. Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-cleaning, Low adhesion, and Drag Reduction. *Prog. Mater. Sci.* **2011**, *56*, 1-108.
6. Farokhzad, O. C.; Langer, R. Impact of Nanotechnology on Drug Delivery. *Acs Nano* **2009**, *3*, 16-20.
7. Osterloh, F. E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* **2013**, *42*, 2294-2320.
8. Zhang, Q. F.; Cao, G. Z. Nanostructured photoelectrodes for dye-sensitized solar cells. *Nano Today* **2011**, *6*, 91-109.
9. Lak, A.; Mazloumi, M.; Mohajerani, M.; Kajbafvala, A.; Zanganeh, S.; Arami, H.; Sadrnezhaad, S. K. Self-Assembly of Dandelion-Like Hydroxyapatite Nanostructures Via Hydrothermal Method. *J. Am. Ceram. Soc.* **2008**, *91*, 3292-3297.
10. Chang, Y.; Zeng, H. C. Controlled Synthesis and Self-assembly of Single-crystalline CuO Nanorods and Nanoribbons. *Cryst. Growth Des.* **2004**, *4*, 397-402.
11. Kamins, T. I.; Williams, R. S.; Chen, Y.; Chang, Y. L.; Chang, Y. A. Chemical Vapor Deposition of Si Nanowires Nucleated by TiSi₂ Islands on Si. *Appl. Phys. Lett.* **2000**, *76*, 562-564.

12. Pan, H.; Liu, B. H.; Yi, J. B.; Poh, C.; Lim, S.; Ding, J.; Feng, Y. P.; Huan, C. H. A.; Lin, J. Y. Growth of Singlecrystalline Ni and Co Nanowires via Electrochemical Deposition and Their Magnetic Properties. *J. Phys. Chem. B* **2005**, *109*, 3094-3098.
13. Byrappa, K.; Adschiri, T. Hydrothermal Technology for Nanotechnology. *Prog. Cryst. Growth Charact. Mater.* **2007**, *53*, 117-166.
14. Cassell, A. M.; Raymakers, J. A.; Kong, J.; Dai, H. J. Large scale CVD synthesis of single-walled carbon nanotubes. *J. Phys. Chem. B* **1999**, *103*, 6484-6492.
15. Obratsov, A. N.; Obratsova, E. A.; Tyurnina, A. V.; Zolotukhin, A. A. Chemical vapor deposition of thin graphite films of nanometer thickness. *Carbon* **2007**, *45*, 2017-2021.
16. Xia, X. H.; Tu, J. P.; Zhang, Y. Q.; Chen, J.; Wang, X. L.; Gu, C. D.; Guan, C.; Luo, J. S.; Fan, H. J. Porous Hydroxide Nanosheets on Preformed Nanowires by Electrodeposition: Branched Nanoarrays for Electrochemical Energy Storage. *Chem. Mater.* **2012**, *24*, 3793-3799.
17. Singh, K. V.; Martinez-Morales, A. A.; Andavan, G. T. S.; Bozhilov, K. N.; Ozkan, M. A simple way of synthesizing single-crystalline semiconducting copper sulfide nanorods by using ultrasonication during template-assisted electrodeposition. *Chem. Mater.* **2007**, *19*, 2446-2454.
18. Cheng, Y. T.; Rodak, D. E.; Wong, C. A.; Hayden, C. A. Effects of Micro- and Nanostructures on The Self-cleaning Behaviour of Lotus Leaves. *Nanotechnology* **2006**, *17*, 1359-1362.
19. Huang, J. Y.; Wang, X. D.; Wang, Z. L. Bio-inspired Fabrication of Antireflection Nanostructures by Replicating Fly Eyes. *Nanotechnology* **2008**, *19*.
20. Vukusic, P.; Sambles, J. R.; Lawrence, C. R.; Wootton, R. J. Quantified Interference and Diffraction in Single Morpho Butterfly Scales. *P Roy Soc B-Biol Sci* **1999**, *266*, 1403-1411.
21. Bixler, G. D.; Bhushan, B. Fluid Drag Reduction with Shark-Skin Riblet Inspired Microstructured Surfaces. *Adv. Funct. Mater.* **2013**, *23*, 4507-4528.
22. Imai, H.; Oaki, Y. Bioinspired Hierarchical Crystals. *MRS Bull.* **2010**, *35*, 138-144.
23. Autumn, K.; Peattie, A. M. Mechanisms of Adhesion in Geckos. *Integr. Comp. Biol.* **2002**, *42*, 1081-1090.
24. Epstein, A. K.; Pokroy, B.; Seminara, A.; Aizenberg, J. Bacterial Biofilm Shows Persistent Resistance to Liquid Wetting and Gas Penetration. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 995-1000.
25. Zhai, L.; Berg, M. C.; Cebeci, F. C.; Kim, Y.; Milwid, J. M.; Rubner, M. F.; Cohen, R. E. Patterned Superhydrophobic Surfaces: Toward a Synthetic Mimic of the Namib Desert Beetle. *Nano Letters* **2006**, *6*, 1213-1217.
26. Gao, X. F.; Yan, X.; Yao, X.; Xu, L.; Zhang, K.; Zhang, J. H.; Yang, B.; Jiang, L. The Dry-style Antifogging Properties of Mosquito Compound Eyes and Artificial Analogues Prepared by Soft Lithography. *Adv. Mater.* **2007**, *19*, 2213-2217.
27. Arias, J. L.; Fernandez, M. S. Biomimetic Processes through the Study of Mineralized Shells. *Mater. Charact.* **2003**, *50*, 189-195.
28. Toro, P.; Quijada, R.; Yazdani-Pedram, M.; Arias, J. L. Eggshell, A New Bio-filler for Polypropylene Composites. *Mater. Lett.* **2007**, *61*, 4347-4350.
29. Waghmare, P. R.; Gunda, N. S. K.; Mitra, S. K. Under-water superoleophobicity of fish scales. *Sci. Rep.* **2014**, *4*.
30. Takiguchi, M.; Igarashi, K.; Azuma, M.; Ooshima, H. Tubular Structure Agglomerates of Calcium Carbonate Crystals Formed on a Cation-exchange Membrane. *Cryst. Growth Des.* **2006**, *6*, 1611-1614.

31. Zhang, Y.; Liu, Y.; Ji, X. B.; Banks, C. E.; Zhang, W. Sea Cucumber-Like Hydroxyapatite: Cation Exchange Membrane-assisted Synthesis and Its Application in Ultra-sensitive Heavy Metal Detection. *Chem. Commun.* **2011**, 47, 4126-4128.
32. Shi, W. K.; Jiang, H. W.; Qin, D. T.; Chen, Y. Friction and Wear Performance of Superfine Manganous Phosphate Conversion Coating. *Tribology* **2009**, 29, 267-271.
33. Zhu, H. J.; Zhai, W.; Yang, M.; Liu, X. M.; Chen, Y. C.; Yang, H.; Shen, X. D. Synthesis and Characterization of LiMnPO_4/C Nano-composites from Manganese(II) Phosphate Trihydrate Precipitated from a Micro-channel Reactor Approach. *RSC Adv.* **2014**, 4, 25625-25632.
34. Su, K.; Liu, F.; Chen, J. T. Preparation of High Performance Carbon-coated LiMnPO_4 Nanocomposite by an Acetate-assisted Antisolvent Precipitation Method. *J. Power Sources* **2013**, 232, 234-239.
35. Zhang, P.; Song, L.; Lu, H. D.; Hu, Y.; Xing, W. Y.; Ni, J. X.; Wang, J. Synergistic Effect of Nanoflaky Manganese Phosphate on Thermal Degradation and Flame Retardant Properties of Intumescent Flame Retardant Polypropylene System. *Polym. Degrad. Stab.* **2009**, 94, 201-207.
36. Peng, S.; Huang, J. W.; Wu, W. W.; Wu, X. H.; Liao, S.; Fan, Y. J. Synthesis Via Solid-State Reaction at Room Temperature and Characterization of Layered Nanocrystalline $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. *Applied Chemical Industry* **2009**, 12, 8.
37. Jin, K.; Park, J.; Lee, J.; Yang, K. D.; Pradhan, G. K.; Sim, U.; Jeong, D.; Jang, H. L.; Park, S.; Kim, D.; Sung, N. E.; Kim, S. H.; Han, S.; Nam, K. T. Hydrated Manganese(II) Phosphate ($\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$) as a Water Oxidation Catalyst. *J. Am. Chem. Soc.* **2014**, 136, 7435-7443.
38. Mauritz, K. A.; Moore, R. B. State of Understanding of Nafion. *Chem. Rev.* **2004**, 104, 4535-4585.
39. Rozendal, R. A.; Hamelers, H. V. M.; Buisman, C. J. N. Effects of membrane cation transport on pH and microbial fuel cell performance. *Environ. Sci. Technol.* **2006**, 40, 5206-5211.
40. Okada, T.; Xie, G.; Gorseth, O.; Kjelstrup, S.; Nakamura, N.; Arimura, T. Ion and water transport characteristics of Nafion membranes as electrolytes. *Electrochim. Acta* **1998**, 43, 3741-3747.
41. Wu, Y. S.; Chen, L.; Xie, K. W.; Li, J. P.; Chen, Y.; Tang, Y. W.; Zhou, Y. M.; Lu, T. H. Synthesis and Characterization of Multi-wall Carbon Nanotubes Supported-Hydrated Iron Phosphate Cathode Material for Lithium-ion Cells by A Novel Homogeneous Precipitation Method. *Ionics* **2012**, 18, 721-729.
42. Miyazaki, T.; Sivaprakasam, K.; Tantry, J.; Suryanarayanan, R. Physical Characterization of Dibasic Calcium Phosphate Dihydrate and Anhydrate. *J. Pharm. Sci.* **2009**, 98, 905-916.
43. Wullschlegel, L.; Ghazi Wakili, K. Numerical parameter study of the thermal behaviour of a gypsum plaster board at fire temperatures. *Fire Mater.* **2008**, 32, 103-119.
44. Latutova, M. N.; Makarova, E. I.; Suleimanova, S. V.; Smirnov, M. A. Strengthening and simultaneous neutralization of aluminosilicate soils contaminated with heavy metals and petroleum products. *Soil Mech Found Eng* **2008**, 45, 59-63.
45. Kim, T.-H.; Park, H.-S.; Lee, M.-H.; Lee, S.-Y.; Song, H.-K. Restricted growth of LiMnPO_4 nanoparticles evolved from a precursor seed. *Journal of Power Sources* **2012**, 210, 1-6.

46. Schmidt-Rohr, K.; Chen, Q. Parallel cylindrical water nanochannels in Nafion fuel-cell membranes. *Nat. Mater.* **2008**, *7*, 75-83.
47. Mann, S. Molecular Recognition in Biomineralization. *Nature* **1988**, *332*, 119-124.
48. Nasef, M. M.; Yahaya, A. H. Adsorption of some heavy metal ions from aqueous solutions on Nafion 117 membrane. *Desalination* **2009**, *249*, 677-681.
49. Goswami, S.; Klaus, S.; Benziger, J. Wetting and absorption of water drops on nafion films. *Langmuir* **2008**, *24*, 8627-8633.
50. Zhang, F.; Zhang, W. B.; Shi, Z.; Wang, D.; Jin, J.; Jiang, L. Nanowire-Haired Inorganic Membranes with Superhydrophilicity and Underwater Ultralow Adhesive Superoleophobicity for High-Efficiency Oil/Water Separation. *Adv. Mater.* **2013**, *25*, 4192-4198.
51. Tian, D. L.; Zhang, X. F.; Tian, Y.; Wu, Y.; Wang, X.; Zhai, J.; Jiang, L. Photo-induced water-oil separation based on switchable superhydrophobicity-superhydrophilicity and underwater superoleophobicity of the aligned ZnO nanorod array-coated mesh films. *J. Mater. Chem.* **2012**, *22*, 19652-19657.
52. Wang, B.; Guo, Z. G. pH-responsive bidirectional oil-water separation material. *Chem. Commun.* **2013**, *49*, 9416-9418.
53. Xue, Z. X.; Wang, S. T.; Lin, L.; Chen, L.; Liu, M. J.; Feng, L.; Jiang, L. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Adv. Mater.* **2011**, *23*, 4270-4273.
54. Liu, M. J.; Wang, S. T.; Wei, Z. X.; Song, Y. L.; Jiang, L. Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. *Adv. Mater.* **2009**, *21*, 665-669.
55. Brimblecombe, R.; Koo, A.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. Solar Driven Water Oxidation by a Bioinspired Manganese Molecular Catalyst. *J. Am. Chem. Soc.* **2010**, *132*.
56. Yang, C.; Dong, L.; Chen, Z. X.; Lu, H. B. High-Performance All-Solid-State Supercapacitor Based on the Assembly of Graphene and Manganese(II) Phosphate Nanosheets. *J. Phys. Chem. C* **2014**, *118*, 18884-18891.
57. Gao, H.; Lian, K. Proton-Conducting Polymer Electrolytes and Their Applications in Solid Supercapacitors: A Review. *RSC Adv.* **2014**, *4*, 33091-33113.
58. Zhang, Z.; Zhang, Y.; Song, R.; Wang, M.; Yan, F.; He, L.; Feng, X.; Fang, S.; Zhao, J.; Zhang, H. Manganese (II) phosphate nanoflowers as electrochemical biosensors for the high-sensitivity detection of ractopamine. *Sensors and Actuators B: Chemical* **2015**, *211*, 310-317.
59. Wang, H. L.; Cui, L. F.; Yang, Y. A.; Casalongue, H. S.; Robinson, J. T.; Liang, Y. Y.; Cui, Y.; Dai, H. J. Mn₃O₄-Graphene Hybrid as a High-Capacity Anode Material for Lithium Ion Batteries. *J. Am. Chem. Soc.* **2010**, *132*, 13978-13980.
60. Lee, J. W.; Hall, A. S.; Kim, J. D.; Mallouk, T. E. A Facile and Template-Free Hydrothermal Synthesis of Mn₃O₄ Nanorods on Graphene Sheets for Supercapacitor Electrodes with Long Cycle Stability. *Chem. Mater.* **2012**, *24*, 1158-1164.
61. Yao, Y. J.; Xu, C.; Yu, S. M.; Zhang, D. W.; Wang, S. B. Facile Synthesis of Mn₃O₄-Reduced Graphene Oxide Hybrids for Catalytic Decomposition of Aqueous Organics. *Industrial & Engineering Chemistry Research* **2013**, *52*, 3637-3645.