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

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Table of contents entry

Bio-inspired synthesis of nanoarrays on flexible substrate using Mn$_3$(PO$_4$)$_2$·3H$_2$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 Mn$_3$(PO$_4$)$_2$·3H$_2$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 Mn$_3$(PO$_4$)$_2$·3H$_2$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;\textsuperscript{13} CVD synthesis needs expensive CVD reactors and typically operates at high temperature;\textsuperscript{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.\textsuperscript{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,\textsuperscript{18} high visual efficiency of fly eyes,\textsuperscript{19} iridescent colors of butterflies,\textsuperscript{20} low drag of shark skin,\textsuperscript{21} mechanically robust egg shells,\textsuperscript{22} strong surface adhesion of gecko’s feet,\textsuperscript{23} bacterial biofilms with resistance to liquid wetting and gas penetration,\textsuperscript{24} water collection capability of Namib dessert beetle,\textsuperscript{25} antifogging properties of mosquito compound eyes,\textsuperscript{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%).\textsuperscript{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 (\(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\)) as a model to explore the general application of bio-inspired membrane-assisted synthesis of nanostructures on flexible substrates. \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) 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 \(\text{LiMnPO}_4\) 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 \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) could be used as a catalyst for water oxidization.\(^{37}\) Precipitation and solid state reactions are typically used to synthesize \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\).\(^{33,36-37}\) Therefore, it will be very interesting to explore bio-inspired membrane-assisted methods to prepare \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) nanostructures at room temperature, in particularly, forming nanoarrays on flexible substrates.

Herein, we present a bio-inspired membrane-assisted approach to fabricate \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) 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 Mn$_3$(PO$_4$)$_2$·3H$_2$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 ~170° 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 MnSO$_4$·H$_2$O aqueous solution and 0.1 M of H$_3$PO$_4$ aqueous solution were prepared in beakers first. The pH value of H$_3$PO$_4$ 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 Mn$_3$(PO$_4$)$_2$·3H$_2$O nanoflake arrays only formed on the side of the membranes exposed to [PO$_4^{3-}$] solution, not the side exposed to [Mn$^{2+}$] solution.

*Materials Characterization.* X-ray diffraction analysis was carried out on a XRD instrument (Rigaku with Cu Kα 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 °C min$^{-1}$
from room temperature to 700 °C in air. For underwater oil contact angle analysis, 1, 2-
dichloroethane (C₂H₄Cl₂) dyed with Oil Red O was selected as the model oil due to that its
density is higher than that of water. 5 μL oil droplets were directly dropped on to
Mn₃(PO₄)₂·3H₂O 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
Mn₃(PO₄)₂·3H₂O 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 Mn₃(PO₄)₂·3H₂O nanoflake arrays in water. The uniform
white color suggests the even distribution of Mn₃(PO₄)₂·3H₂O nanoflake arrays on the Nafion
surface. Note that Nafion without Mn₃(PO₄)₂·3H₂O nanoarrays are totally transparent in water.
The formation of Mn₃(PO₄)₂·3H₂O was observed only on the side of the Nafion exposed to
[PO₄³⁻] solution. The other side of the Nafion membrane in contact with [Mn²⁺] solution
remained clean without any solid formation. This phenomenon, as expected, might be attributed
to the cation-exchange nature of Nafion membrane.

Nafion has a unique structure of fluorocarbon backbones attached with a high concentration of negatively charged sulfonate
groups (-SO₃⁻) at 1.13 mol/L. The unique property of Nafion only allows cations to be
exchanged but not anions or electrons. Thus, the Mn²⁺ cations transferred via Nafion can
react with PO₄³⁻ anions forming insoluble Mn₃(PO₄)₂·3H₂O nanoarrays only on the side of the
membrane exposed to [PO₄³⁻] solution. On the other side, the Li⁺ cations transferred are fully
dissolved without any solid formed as Li₂SO₄ are very soluble at room temperature in water.
Figure 1. Mn₃(PO₄)₂·3H₂O nanostructures grown on Nafion N117 substrates: (a) optical image of white color Mn₃(PO₄)₂·3H₂O formed on a piece of Nafion membrane, (b) XRD pattern assigned to Mn₃(PO₄)₂·3H₂O, (c) TGA profile, and (d) EDS analysis of the collected Mn₃(PO₄)₂·3H₂O to double confirm chemical composition.

Optical image clearly shows that Mn₃(PO₄)₂·3H₂O 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 Mn₃(PO₄)₂·3H₂O. The XRD diffraction peaks could be matched relatively well to that of Mn₃(PO₄)₂·3H₂O according to the JCPDS #003-0426. Mn₃(PO₄)₂·3H₂O 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 Mn₃(PO₄)₂·3H₂O. 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 Mn₃(PO₄)₂·3H₂O crystals. Experimentally observed mass loss (13.8 wt%) is well agreed with the theoretical value of structural water in Mn₃(PO₄)₂·3H₂O (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 Mn₃(PO₄)₂·3H₂O. Interestingly, the structural water in Mn₃(PO₄)₂·3H₂O can only be fully eliminated at much higher temperature (500 °C) than other regular hydrated compounds, such as FePO₄·2H₂O at 200 °C, CaHPO₄·2H₂O at 165 °C, and CaSO₄·2H₂O at 220 °C.⁴¹-⁴³ It could be attributed to the triclinic crystal structure of Mn₃(PO₄)₂·3H₂O, 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 Mn₃(PO₄)₂·3H₂O using our room-temperature method is confirmed.
Figure 2. (a) Low-magnification FESEM image to show the overview morphology of nanoflake arrays of Mn$_3$(PO$_4$)$_2$·3H$_2$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 Mn$_3$(PO$_4$)$_2$·3H$_2$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 theirs 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 Mn$_3$(PO$_4$)$_2$·3H$_2$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 $\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}$ 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, $\text{Mn}^{2+}$ ions are easily transferred from $[\text{Mn}^{2+}]$ solution chamber to $[\text{PO}_4^{3-}]$ solution chamber via the cation-exchange membrane. At the same time, $\text{Li}^+$ and $\text{H}^+$ 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. $\text{Li}^+$ and $\text{H}^+$ 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 $\text{Mn}^{2+}$ ions toward $[\text{PO}_4^{3-}]$ solution chamber could initiate nucleation due to low solubility of $\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}$ in water. Note: $\text{Mn}_3(\text{PO}_4)_2\cdot\text{nH}_2\text{O}$ has a
Solubility Product Constant $K_{sp} = 6.13 \times 10^{-32}$,\textsuperscript{44} and Mn$_3$(PO$_4$)$_2$ has a $K_{sp} = 1 \times 10^{-27}$.\textsuperscript{45} The formation of Mn$_3$(PO$_4$)$_2$·3H$_2$O 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,\textsuperscript{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$_4$)$_2$·3H$_2$O 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$_4$)$_2$·3H$_2$O on the surface.\textsuperscript{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$_4$)$_2$·3H$_2$O nanoflake arrays on flexible Nafion, unique surface property was investigated. Mn$_3$(PO$_4$)$_2$·3H$_2$O 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 tetrafluroethylene with hydrophilic sulfonic acid groups (−H$^+$SO$_3^-$) in its side chain.\textsuperscript{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.\textsuperscript{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 Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O nanoflake arrays obtained from 6 h reaction, the exposed surface in contact with oil droplet is only from Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O not Nafion. Thus, as shown in Figure 5b, the OCA increased significantly to 146\(^\circ\), and the oil droplet easily moved around. No Nafion deformation was observed at the interface between the oil droplet and the Nafion, indicating the Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)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\(^\circ\) 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 (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.\textsuperscript{50-53}
**Figure 5.** Shape change of an oil droplet (1, 2-dichloroethane dyed with Oil Red O, 5 μL) under water on the surface of (a) bare Nafion membrane, and as-deposited Nafion N117 membrane with Mn$_3$(PO$_4$)$_2$·3H$_2$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, \(\theta_{ow}\) 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 \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) nanoflake arrays, as expected (Figure S7b in SI).

We would like to highlight that the self-assembled nanostructured \(\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O}\) on Nafion membrane as a robust and flexible material may find other applications, including solid
supercapacitors, water oxidation, electrochemical biosensors and battery positive electrodes.\textsuperscript{37, 55-58} Moreover, Mn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·3H\textsubscript{2}O can be facilely transformed to Mn\textsubscript{3}O\textsubscript{4} which can find other applications (Figure S6 in SI).\textsuperscript{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 Mn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·3H\textsubscript{2}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 Mn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·3H\textsubscript{2}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\textsubscript{3}PO\textsubscript{4} and Mn\textsubscript{3}O\textsubscript{4}; FESEM and optical images of Mn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·3H\textsubscript{2}O prepared at 50 °C.

AUTHOR INFORMATION

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Author Contributions

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

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