

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

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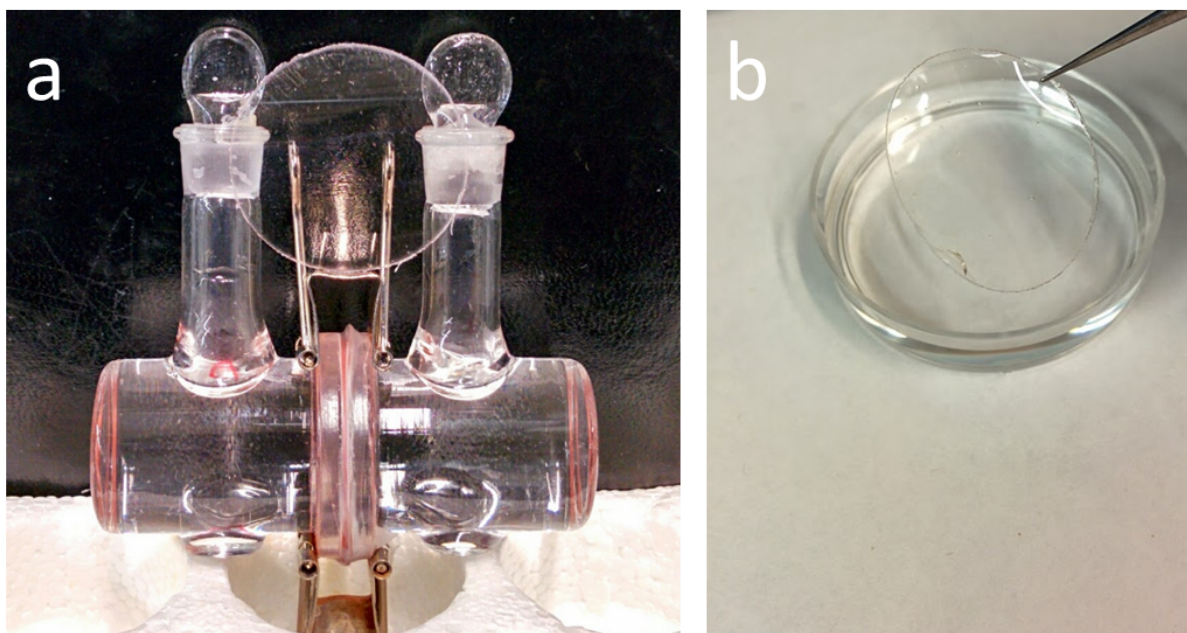
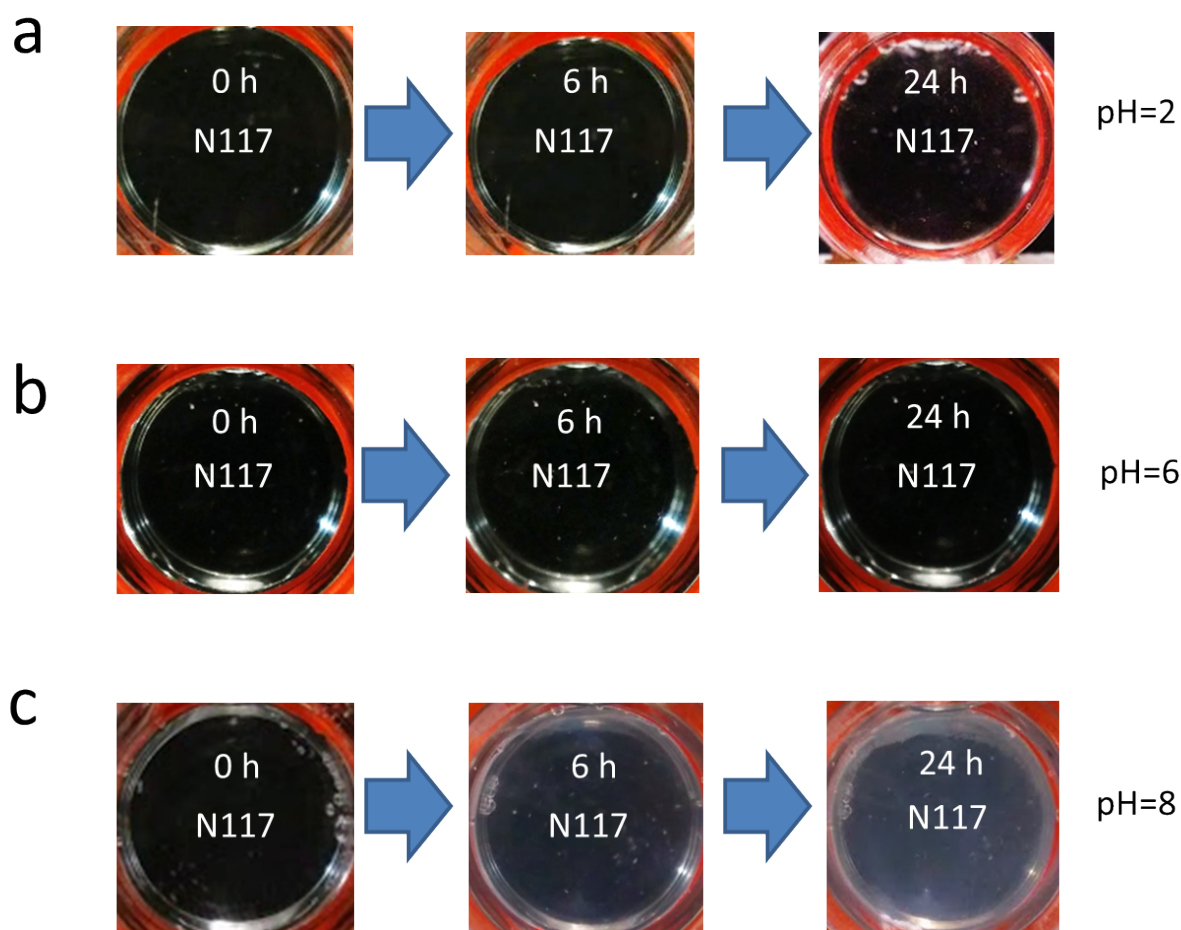


Figure S1. Optical images of (a) a reactor with two chambers with two precursor solutions separated by a piece of Nafion membrane sealed with two O-rings, and (b) a piece of transparent Nafion N117 membrane rinsed in water **before** use.

**Figure**

re S2. Optical images of the color changes vs time of the Nafion membrane inside the reactors with one chamber filled with $[\text{PO}_4^{3-}]$ solution adjusted to different pH values of (a) 2; (b) 6; (c) 8, keeping all other conditions unchanged.

We would like to highlight that the formation of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ is highly sensitive to the pH of solution.¹ In the design of our experiments, we are aware of that under acid conditions, Mn^{2+} could not form any solid precipitate with PO_4^{3-} .² In contrast, in alkali solution, Mn^{2+} could be partially oxidized to Mn^{3+} in the presence of oxygen in air forming Mn_3O_4 .³ Practically, we found that in the case that pure 0.1 M H_3PO_4 solution without pH adjustment, no solid formation was observed after 7 days under the same typical experimental conditions due to the acidic

environment. A series of controlled $[\text{PO}_4^{3-}]$ solutions with different pH values adjusted by LiOH were systematically investigated. We observed that no $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ white solid formed even till the pH value was adjusted to 6. White colored $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ could be observed when the pH value of the $[\text{PO}_4^{3-}]$ solution was adjusted to 8. The changes by color during reactions in chambers with different pH values (pH= 2, 6, 8, respectively) of $[\text{PO}_4^{3-}]$ solution were recorded throughout the process of 24 h (Figure S2 in SI). However, in the case of an excessive amount of LiOH was used to adjust the pH value of $[\text{PO}_4^{3-}]$ solution to 10, precipitation of white-colored Li_3PO_4 ($3\text{Li}^+ + \text{PO}_4^{3-} \rightarrow \text{Li}_3\text{PO}_4$) occurred during the process of adjusting the pH value (Figure S3 in SI).

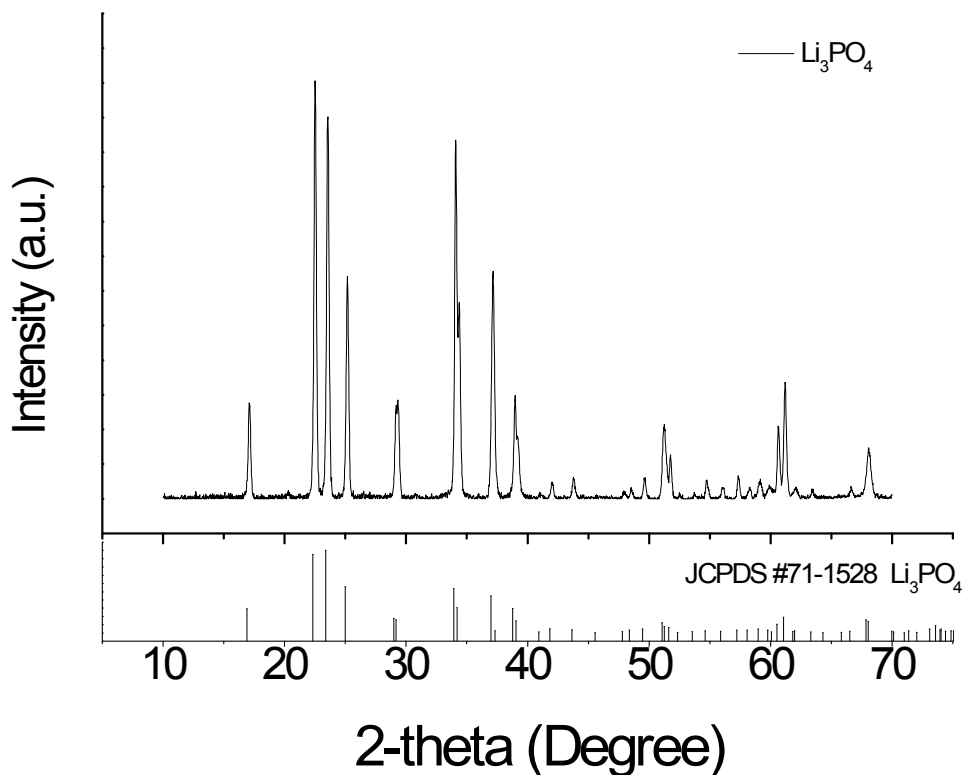


Figure S3. XRD pattern of Li_3PO_4 obtained in $[\text{PO}_4^{3-}]$ solution by adjusting pH to 10.

We tried to preliminarily assess the stability of nanoflakes in water (Figure S4 in SI). For nanoflakes obtained with shorter reaction time of 6 h and 24 h, they could be dissolved in DI water which suggests poor stability. It could be attributed to the exposure of early formed $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflakes in unsaturated environment.^{4,5} The possible mechanism of dissolution could be explained as follows: In DI water or unsaturated conditions, a new equilibrium between solid and solution must be reached which lead to the release of ions from the solid nanoflakes or dissolution. Besides, the pH value of DI water (pH = 6) is much lower than that in the original adjusted $[\text{PO}_4^{3-}]$ solution (pH = 8), which could accelerate the dissolution in DI water as well.⁶ Besides, the precursors might involve less crystalline and amorphous structures. The high solubility of amorphous structures are well documented.⁷ In the case of $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflakes obtained after 7 days of reaction, there are still significant amounts nanoflakes remained on the surface after 24 h immersion in water suggesting relatively good stability. The observation could be attributed to the large amount of solid $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ nanoflakes available for dissolution. Additionally, the higher degree of crystallinity also can enhance its stability in water. However, further studies are required to gain better understanding.

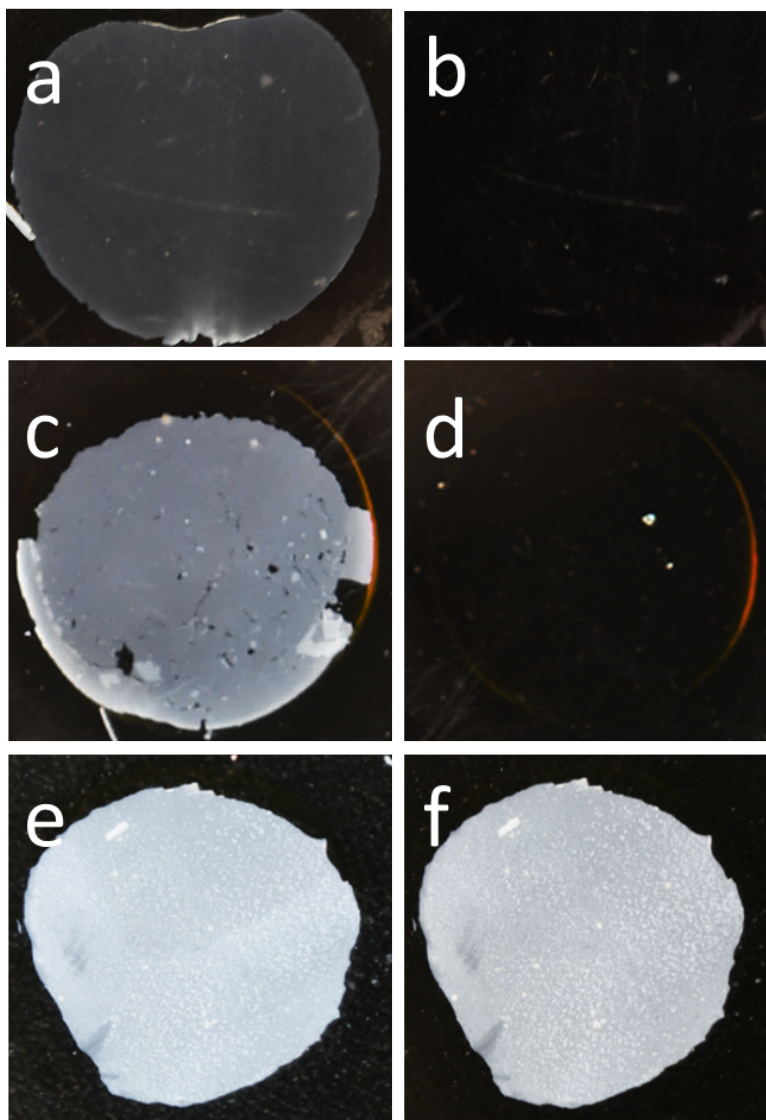


Figure S4. Optical images of Nafion N117 membranes coated with $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ obtained after various times of reaction: (a) the 6 h sample after immersed in **deionized** water for 1 min and (b) 6 h; (c) the 24 h sample after immersed in fresh water for 1 min and (d) 24 h; (e) the 7 d sample after immersed in fresh water for 1 min and (f) 24 h.

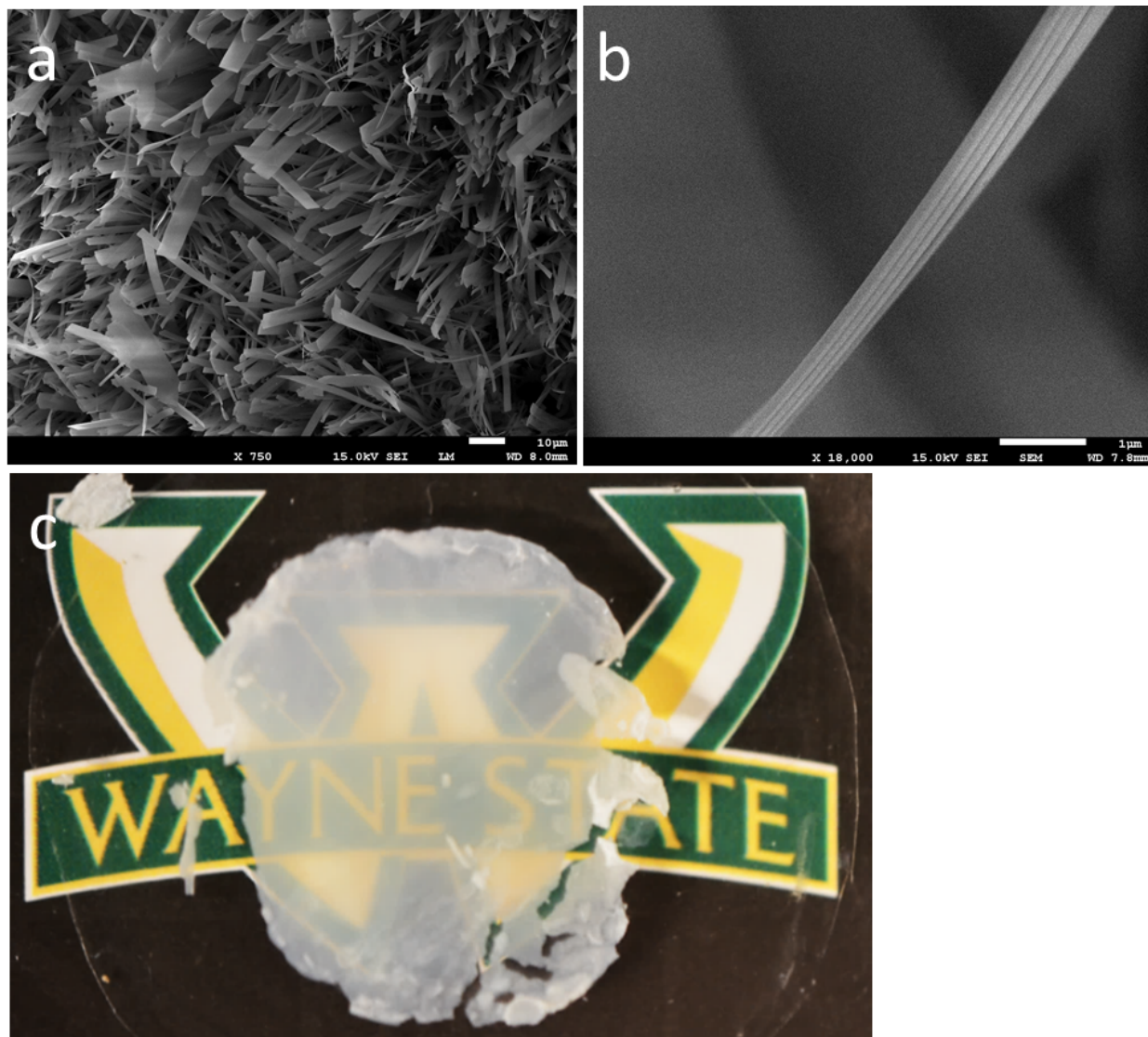


Figure S5. Mn₃(PO₄)₂·3H₂O nanobelt arrays prepared on Nafion N117 membrane after a reaction time of 24 h at 50 °C keeping other experimental conditions unchanged as those typical condition: (a) low-magnified FESEM image; (b) high-magnification view of a section of a nanobelt with layer-like structure; (c) optical images of the Mn₃(PO₄)₂·3H₂O nanobelt arrays prepared on Nafion N117 membrane immersed in water.

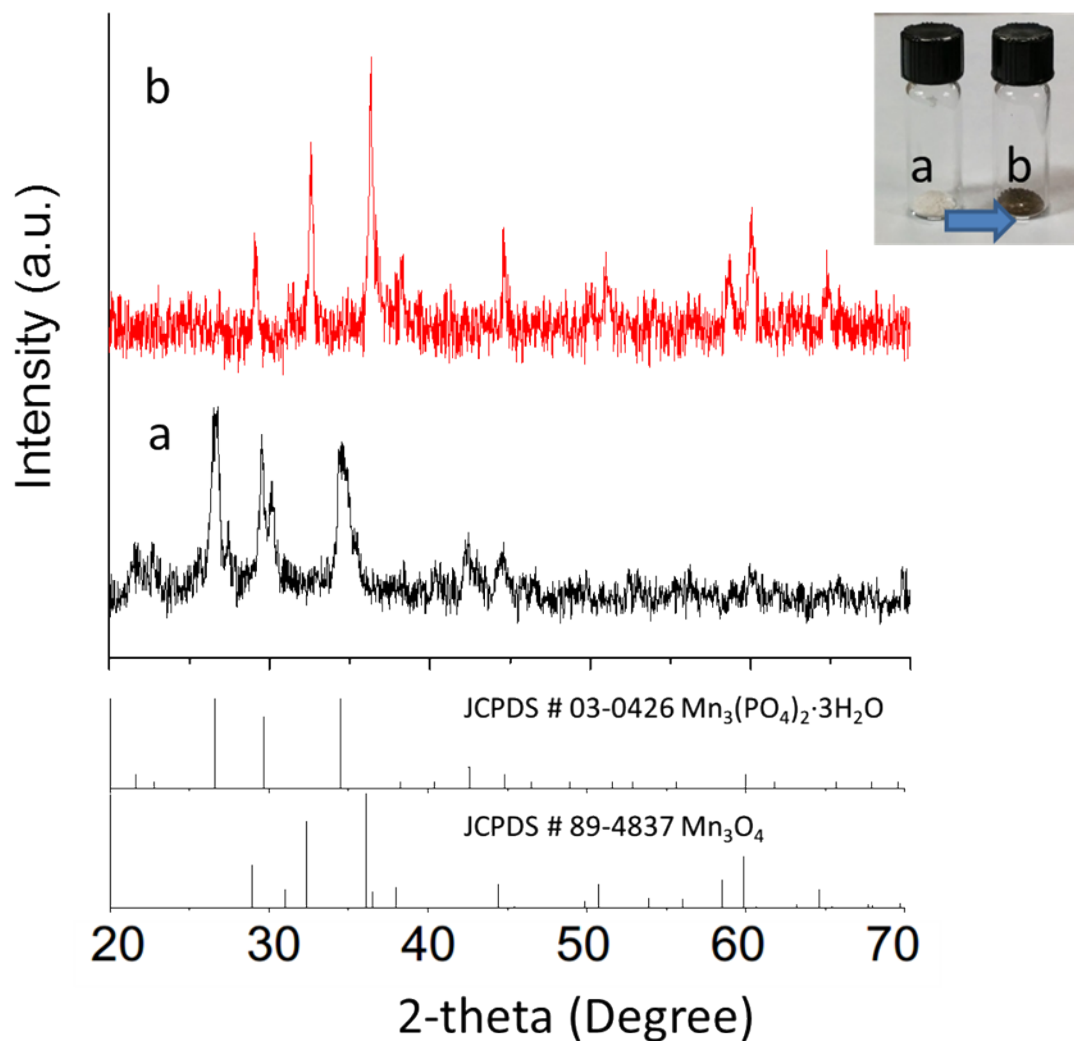


Figure S6. The XRD patterns of samples of (a) Mn₃(PO₄)₂·3H₂O nanoflake obtained after a typical reaction, (b) Mn₃O₄ after sample (a) was immersed in 1 M KOH solution for 24 h. The inset is the optical image of the color change from white (a) to black (b) corresponding to Mn₃(PO₄)₂·3H₂O and Mn₃O₄, respectively. The possible reaction involved in the transfer could be: $2\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O} + 12\text{KOH} + \text{O}_2 \rightarrow 2\text{Mn}_3\text{O}_4 + 4\text{K}_3\text{PO}_4 + 12\text{H}_2\text{O}$

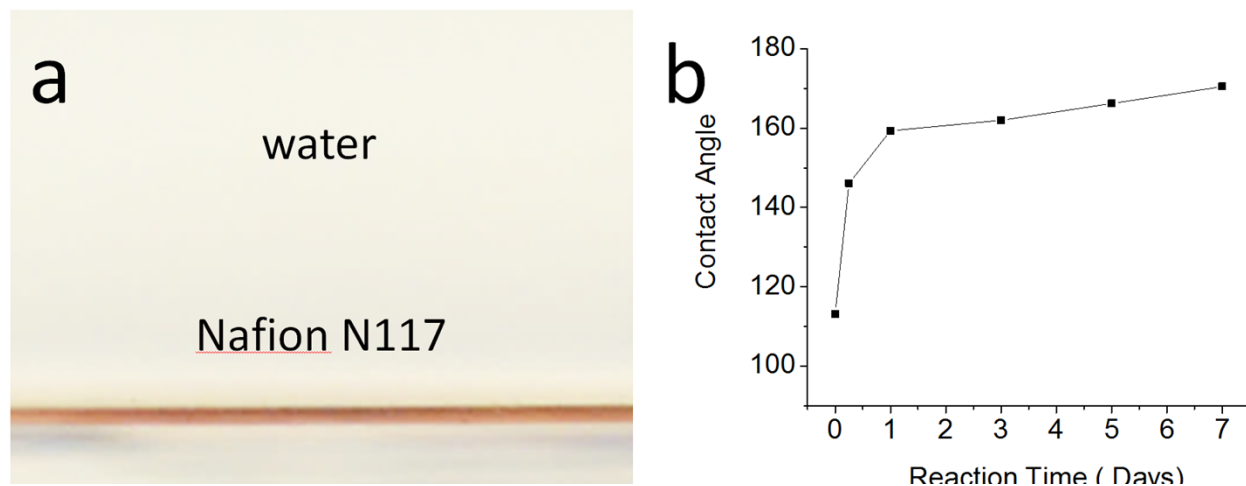


Figure S7. (a) Optical image of bared Nafion N117 membrane in water showing flat nature; (b) The underwater oil contact angles of the oil droplets sitting on $2\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ covered Nafion membranes obtained after different reaction periods of 6 h, 24 h, 3 d, 5 d, and 7 d. The 0 h data is from bare Nafion membrane.

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