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## **Electronic Supplementary Information**

## Formation and Phase Evolution of Calcium Phosphates Modulated by Ion Exchange Ionomer Nafion

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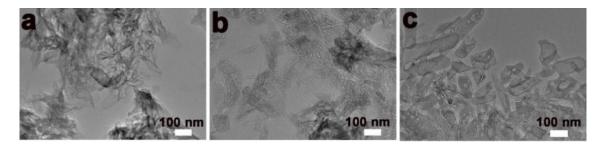
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$$\begin{array}{c} ---[(\mathsf{CFCF_2})(\mathsf{CF_2CF_2})_{\mathsf{m}}]_{\mathsf{n}} ---\\ |\\ \mathsf{OCF_2CFOCF_2CF_2SO_3H}\\ |\\ \mathsf{CF_3} \end{array}$$

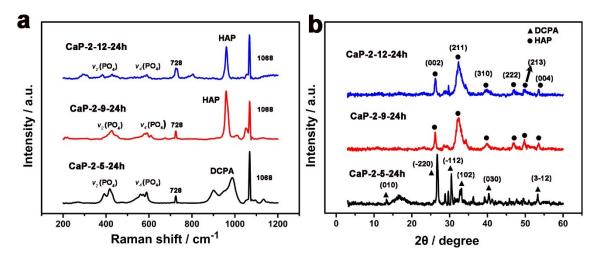
Figure S1. The chemical structure of Nafion.

Table S1. Preparation conditions of calcium phosphates (CaPs) in the assistance of Nafion.

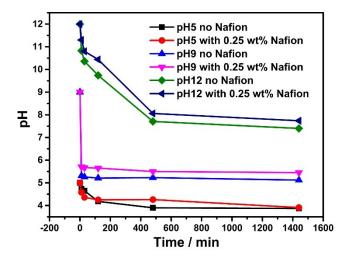
Sample	Nafion	[Ca <sup>2+</sup> ]	[PO <sub>4</sub> <sup>3-</sup> ]	pН	Incubating time (h)
	(by weight)	(M)	(M)		
CaP-1-9-2h	0.1 wt%	0.1	0.1	9	2
CaP-2-9-2h	0.25 wt%	0.1	0.1	9	2
CaP-3-9-2h	0.5 wt%	0.1	0.1	9	2
CaP-0-9-2h	0	0.1	0.1	9	2
CaP-4-9-10min	0.25 wt%	0.1	0.2	9	10min
CaP-5-9-10min	0.25 wt%	0.15	0.15	9	10min
CaP-6-9-10min	0.25 wt%	0.2	0.1	9	10min
CaP-0-5	0	0.1	0.1	5	Ranged from 10min to 24h
CaP-0-9	0	0.1	0.1	9	Ranged from 10min to 24h
CaP-0-12	0	0.1	0.1	12	Ranged from 10min to 24h
CaP-2-5	0.25 wt%	0.1	0.1	5	Ranged from 10min to 24h
CaP-2-9	0.25 wt%	0.1	0.1	9	Ranged from 10min to 24h
CaP-2-12	0.25 wt%	0.1	0.1	12	Ranged from 10min to 24h



**Fig. S2.** TEM images of the CaPs obtained from the dispersion containing 0.25 wt% Nafion with different initial Ca/P ratio (a) 0.2M/0.1M (CaP-6-9-10min); (b) 0.15M/0.15M (CaP-5-9-10min); (c) 0.1M/0.2M (CaP-4-9-10min). The dispersion mother solution pH is 9 and the incubating time is 10min.



**Fig. S3.** (a) Raman and (b) XRD spectra of formed CaPs in the presence of 0.25 wt% Nafion dispersion with the initial pH ranged from 5 to 12.



**Fig. S4.** pH shift of the incubating solutions before and after addition of 0.25 wt% Nafion with the initial pH of Ca<sup>2+</sup> and phosphate solution ranged from 5 to 12.