Supporting information

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Section I. Synthesis of Reference Samples

S1 Synthesis of the $Na_3V_2(PO_4)_3$ and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ reference samples

For $Na_3V_2(PO_4)_3$, stoichiometric amount of Na_2CO_3, $NH_4H_2PO_4$, NH_4VO_3 and desirable citric acid were dissolved into distilled water under vigorous stirring. Then the mixture was transferred to a water bath at 80 ^oC under continuously stirring for four hours. The resultant solution was dried overnight and the dry gel was grounded in a motor. Finally, the obtained powders were annealed at 750 ^oC for 8 hours at flowing argon atmosphere to achieve the $Na_3V_2(PO_4)_3$ reference sample.

For $Na_{3.12}Fe_{2.44}(P_2O_7)_2$, iron powder was firstly dissolved into citric acid solution under vigorously stirring until a clear sol was formed. Then the mixture of Na_2CO_3 and $NH_4H_2PO_4$ were added into above solution, and it was transferred to a water bath at 80 ^oC under vigorous stirring for four hours. The resultant solution was dried overnight. Then the obtained dry-gel was grounded in a motor. Finally, the obtained powders were annealed at 600 ^oC for 8 hours to achieve the $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ reference samples.

Section II. Calculation Process

S2 Calculation process for sodium intercalation coefficients based on the GITT results

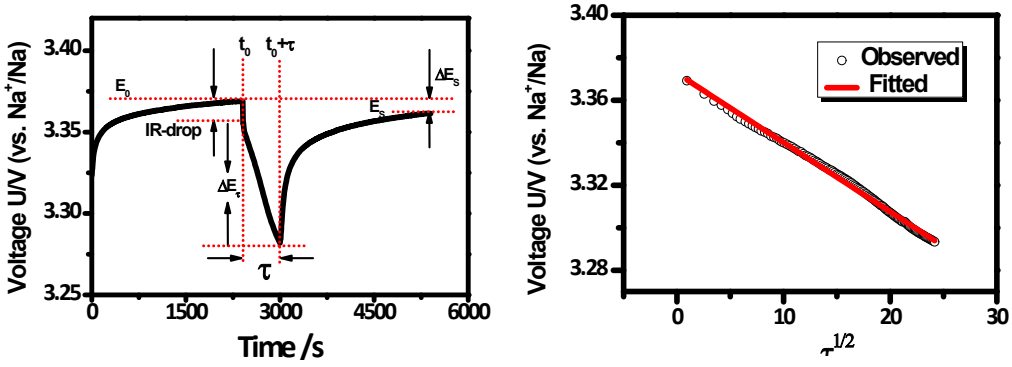
The sodium ion intercalation kinetics of the composites is investigated by GITT measurements. According to the Fick's second law of diffusion, D_{Na} can be calculated from the following equation:[S1]

$$D_{Na} = \frac{4}{\pi}\left(\frac{m_B V_m}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\tau\left(\frac{dE_\tau}{d\sqrt{\tau}}\right)}\right)^2 \quad (\tau << L^2/D_{Na}) \qquad (1)$$

where D_{Na} (cm^2s^{-1}) is the sodium diffusion coefficient; m_B, M_B and V_m are the mass, molecular weight and molar volume of the electrode material, respectively; A is the interfacial area between electrode and electrolyte; τ is duration of the current pulse. If the relationship between E and $\tau^{1/2}$ is linear, the equation (1) can be simplified as following:[S2]

$$D_{Na} = \frac{4}{\pi\tau}\left(\frac{m_B V_m}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \qquad (2)$$

The linear relationship between E and $\tau^{1/2}$ validates the applicability of the equation in this study. Therefore, the D_{Na} values are obtained based on the equation (2).



References:

[S1] W. Weppner, R. A. Huggins, *J. Electrochem. Soc.* **1977**, *124*, 1569.

[S2] E. Deiss, *Electrochimica Acta* **2005**, *50*, 2927.

Section III. Supporting Figures

Figure S1 Pore size analysis results of the biochemistry-directed $Na_3V_2(PO_4)_3$ hollow porous microspheres. The multiple peaks in the pore size analysis demonstrate the hierarchical porous architecture.

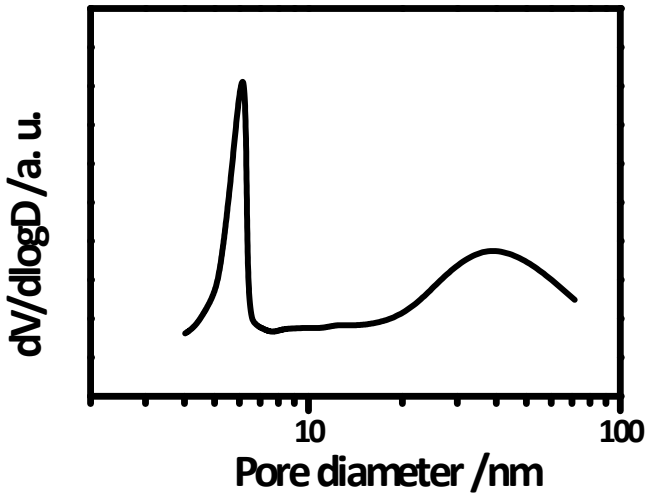


Figure S2 Morphology of bio-directed $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ hollow microsphere. (a,b) TEM image demonstrate the hollow microspherical architecture and porous shell in the $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ microsphere; (c) HRTEM image demonstrate the interplanar distance of ~0.835 nm, which coincides well with the (011) lattice planes of $Na_{3.12}Fe_{2.44}(P_2O_7)_2$. The results demonstrate the single-phase nature of the $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ crystal in the carbon-based framework of the hollow porous microsphere.

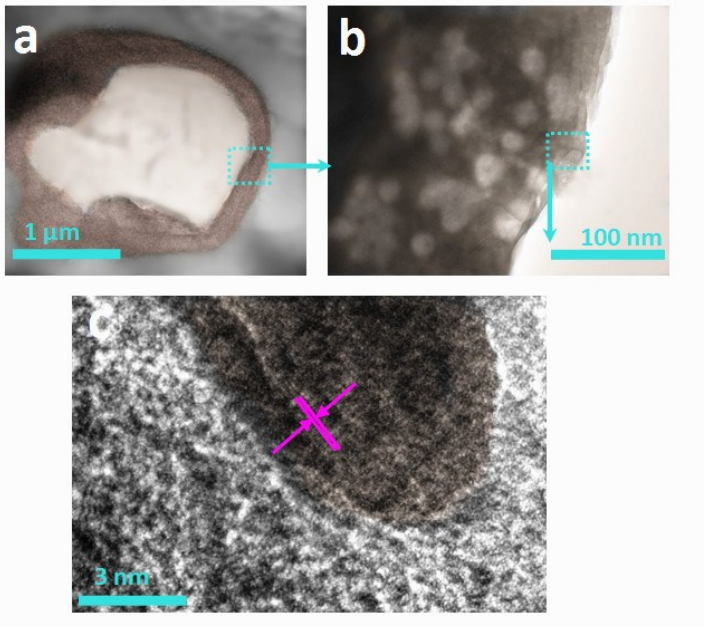


Figure S3 Morphology and physical characteristics of $Na_3V_2(PO_4)_3$ and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ reference samples. SEM (a, d) and TEM (b, e) images of $Na_3V_2(PO_4)_3$ (a, b) and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ (c, d) reference samples. Comparison of the pore volume (c) and carbon content (f) between the bio-directed and reference samples. Both reference samples have irregular and low porous microscale particles, which leads to their lower pore volumes and surface areas than the bio-directed samples.

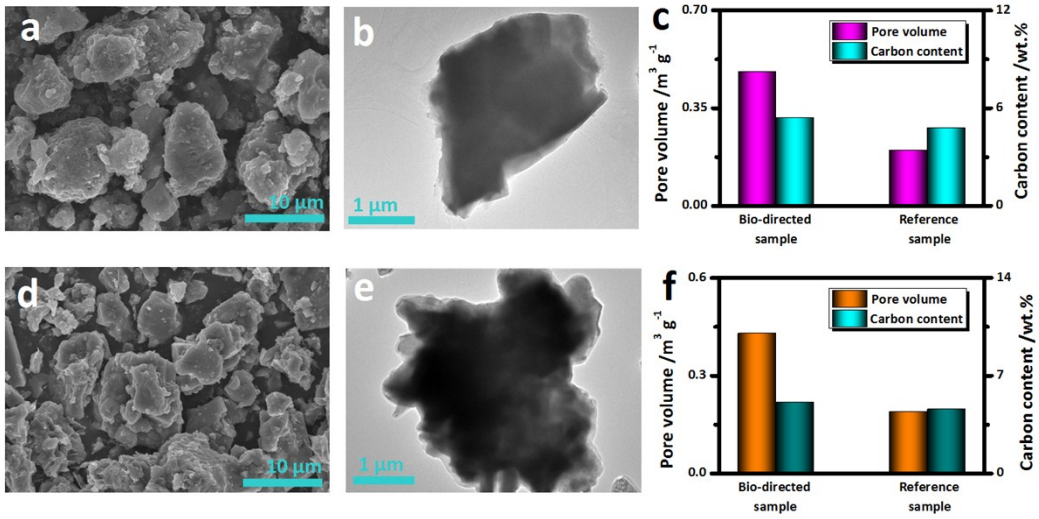


Figure S4 Comparison of R_{ct} values between the bio-directed and reference samples for the $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ composites. The bio-directed samples exhibit lower R_{ct} values than the reference one in the whole potential range, which indicates its faster reaction rates. The difference between both samples increase as potential decreases, which demonstrates the superior bulk react capability of bio-directed material than the reference one.

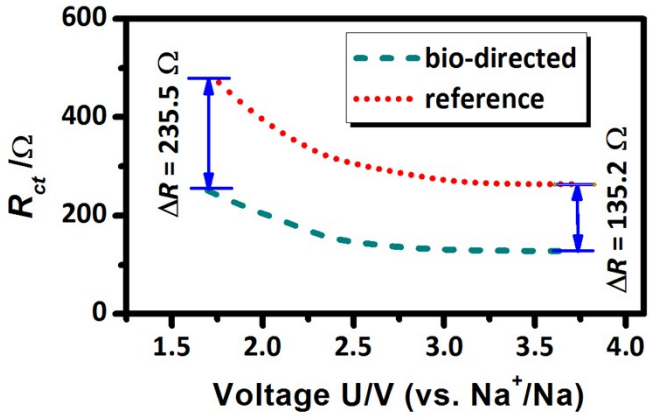
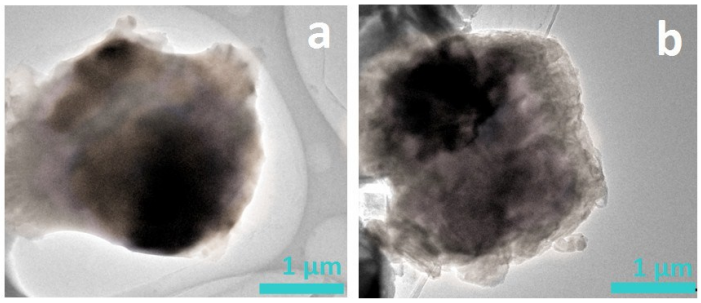


Figure S5 TEM images of cycled bio-directed $Na_3V_2(PO_4)_3$ (a) and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ (b) composites. Both materials maintain their spherical architecture after cycles.



Section VI. Supporting Tables

Table S1 Lattice parameters of the bio-directed and reference samples for the $Na_3V_2(PO_4)_3$ (a) and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ (b) composites.

(a) $Na_3V_2(PO_4)_3$

Materials	*a* /Å	*c* /Å
Bio-directed	8.7415(2)	21.8458(1)
Reference	8.7193(5)	21.8114(8)

(b) $Na_{3.12}Fe_{2.44}(P_2O_7)_2$

Materials	*a* /Å	*b* /Å	*c* /Å	α/°	β/°	γ/°
Bio-directed	6.4410(8)	9.4315(3)	11.0223(0)	64.4903(2)	85.9247(2)	72.9818(0)
Reference	6.4124(1)	9.4365(0)	11.0206(7)	64.2477(2)	85.6062(5)	73.2385(3)

Table S2 Atomic ratios of the $Na_3V_2(PO_4)_3$ and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ bio-directed hollow microspheres.

Atomic ratio	$Na_3V_2(PO_4)_3$	Atomic ratio	$Na_{3.12}Fe_{2.44}(P_2O_7)_2$
Na:V	1.4971	*Na:Fe*	1.2758
Designed value	1.5	Designed value	1.2787