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Supplementary Materials for

Polymer blend directed anisotropic self-assembly toward mesoporous inorganic bowls and nanosheets

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SUPPLEMENTARY RESULTS AND DISCUSSION



 λ_{ijk} : spreading coefficient γ_{ij} : interfacial tension

fig. S1. Morphologies in ternary phase blends. Possible morphologies in ternary phase blends composed of two minor phase 1 and 3 and a continuous matrix phase 2 predicted by the spreading coefficient (31, 32). (A) Complete wetting: 1/2 interfacial energy is larger than sum of 1/3 and 2/3 interfacial energies ($\lambda_{132} > 0$). To eliminate the high energy 1/2 interfaces, phase 3 intercalates at the 1/2 interface, thereby resulting in formation of 1@3 core-shell morphology (31). (B) Partial wetting: in contrast to complete wetting and non-wetting, there

is no specific high interfacial tension that overwhelms the sum of the others. Phase 3 only partially covers phase 1 to reduce the relatively high energy 1/2 interfaces but cannot fully encapsulate phase 1, because the difference in interfacial energy of 1/2 and 3/2 is not significant (interfacial energies of both minor phases/major matrix are similar each other). At this condition, the interfacial tensions are comparable and relatively well-balanced among the all three phases (34). (C) Non-wetting: 1/3 interfacial energy is larger than sum of 1/2 and 2/3 interfacial energies ($\lambda_{123} > 0$). To eliminate the high energy 1/3 interfaces, phase 1 and 3 tend to form separate dispersed domains within the matrix phase 2.



fig. S2. Procedure for bowl-like mesoporous inorganic particles. (A) Schematic representation of anisotropic self-assembled particle (ASAP) approach to prepare bowl-like mesoporous inorganic particles and (B) as-made anisotropic Janus hybrid in the hPMMA matrix with its predicted spreading coefficients.

To generate anisotropically self-assembled Janus domains (partial wetting; fig. S2B), there should be no specific high interfacial tension that overwhelms the sum of the other two, *i.e.*, all spreading coefficients are negative, and each phase partially spreads at the interfaces

of the other two. At this condition, the difference in interfacial tensions is not significant each other.

In general, the increase of the molar mass leads to the increase of the interfacial tension, and thus the interfacial tension between high molar mass pair of hPMMA/hPS ($\gamma_{PMMA/PS}$) is higher than that of hPMMA/BCP ($\gamma_{PMMA/BCP}$). However, since the PS blocks of BCP and hPS are chemically identical, hPMMA matrix has similar enthalpic interactions with both BCP and hPS phases. Therefore, $\gamma_{PMMA/PS}$ could be only slightly higher than $\gamma_{PMMA/BCP}$, and the difference is not significant (i.e., $\gamma_{PMMA/PS} \ge \gamma_{PMMA/BCP}$). Considering the fact that PS-blocks of BCPs can partially lower the interfacial tension between hPS and BCP ($\gamma_{PS/BCP}$) through favorable enthalpic interaction, $\gamma_{PS/BCP}$ should be the smallest. Therefore, the relation $\gamma_{PMMA/PS} \ge \gamma_{PMMA/BCP} > \gamma_{PS/BCP}$ can be inferred, which leads to negative spreading coefficients in all cases (note that all γ_x are positive). BCP-phase only partially covers hPS to reduce the relatively high energy hPS/hPMMA interfaces, but cannot fully encapsulate hPS, because the difference between $\gamma_{PMMA/PS}$ and $\gamma_{PMMA/BCP}$ is not significant.



fig. S3. Solution states of ternary phase blends. Transparent homogeneous solution turned opaque upon solvent removal at 50 °C due to visible light scattering by macrophase-separated domains. (Photo Credit: S. Kim, KAIST)

(A-b-B) BCP + B homopolymer blends



fig. S4. Phase behaviors of BCP and homopolymer blends. Schematic representations of the phase behaviors of A-*b*-B block copolymer and B homopolymer (hB) binary blends.

The phase behavior of the A-*b*-B/hB binary blends is greatly affected by the relative molar mass ratio of B block of BCP (MW_{B,BCP}) to that of B homopolymer (MW_{B,homo}). When MW_{B,homo} is much lower than MW_{B,BCP}, hB chains were solubilized into the B microdomains at the molecular level (*i.e.*, uniform solubilization). As MW_{B,homo} increases, hB is gradually expelled from the B microdomains and tends to swell the middle of the B microdomains without macrophase separation (*i.e.*, localized solubilization). When MW_{B,homo} is much larger than MW_{B,BCP}, BCP and hB phases were entirely segregated each other, forming independent BCP domains and and hB domains (*i.e.*, macrophase separation).



fig. S5. The contact angle images of water and diiodomethane on different polymer phases (hPMMA, hPS, and BCP).

Interfacial tensions between the two polymer phases (*i.e.*, hPMMA/hPS, hPMMA/BCP, and hPS/BCP) were determined by the harmonic mean equation:

$$\gamma_{ij} = \gamma_i + \gamma_j - 4 \left[\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \right]$$
(S1)

$$\gamma_i = \gamma_i^d + \gamma_i^p \tag{S2}$$

where γ_{ij} is the interfacial tension; γ_i is the surface tension; γ_i^d and γ_i^p are the dispersion and polar components of the surface tension γ_i of the solid polymers, respectively. The surface tension γ_i was calculated by using the measured contact angle θ of polar (*i.e.*, water) and nonpolar (*i.e.*, diiodomethane) liquids on the polymer films at 20 °C (fig. S5). The calculated results are listed in table S1.



fig. S6. Characterization of oblate mesoporous AS particles. (A) Schematic representation for synthesis and orientation of microdomains at the interface of oblate mesoporous AS particles. The oblate-ellipsoidal mesoporous particles were prepared in the absence of hPS. (B and C) SEM and (D and E) TEM images of oblate mesoporous AS with perpendicular mesopores after calcination at 550 °C. (F) N₂ physisorption isotherm and (G) corresponding pore size distribution. Oblate mesoporous AS particles have surface area of 307 m² g⁻¹ and mesopores of 15.3 nm.



fig. S7. TEM images of *bm*-AS particles. (A and B) The tilted and the top view of TEM images of *bm*-AS particles.



fig. S8. Cross-sectional TEM images of *bm*-AS-0.2. (A) Low magnification of TEM image and (B and C) enlarged TEM images inside the dotted boxes. *bm*-AS-0.2 particles had smaller particle size and hPS domain size and even some particles did not have hPS domains due to the low r_M .



fig. S9. Structural characterization of *bm*-AS-0.2. (A) Low magnification SEM image, (B) N_2 physisorption isotherm and (C) corresponding pore size distribution. *bm*-AS-0.2 particles have surface area of 279 m² g⁻¹ and mesopores of 15.1 nm.



fig. S10. Structural characterization of *bm*-AS-2. (A) Low magnification SEM image, (B) N_2 physisorption isotherm and (C) corresponding pore size distribution. *bm*-AS-2 particles have surface area of 291 m² g⁻¹ and mesopores of 15.3 nm.



fig. S11. Tunable mesopore size of *bm*-AS particles. (A to D) SEM images and the corresponding pore size distribution by changing molar mass of BCP.



fig. S12. Characterization of bowl-like mesoporous carbon (*bm*-carbon) particles. (A) The molecular structure of phenol-formaldehyde resin (resol). (B) TGA profiles of the organic components in the blends for synthesis of *bm*-carbon. Condensed resol converted into carbon materials with 57 wt% yield, whereas the other organic components (*e.g.*, PEO-*b*-PS, hPS, and hPMMA) were mostly decomposed during heat treatment at 900 °C under Ar. (C and D) SEM images of *bm*-carbon after carbonization at 900 °C. (E) N₂ physisorption isotherm and (F) the corresponding pore size distribution of *bm*-carbon particles. *bm*-carbon has surface area of 920 m² g⁻¹ and mesopores of 33 nm.



fig. S13. Characterization of bowl-like mesoporous TiO₂ (*bm*-TiO₂) particles. (A) TEM and (B) SEM images of *bm*-TiO₂ after heat treatment at 550 °C. (C) XRD pattern consistent with anatase TiO₂ (JCPDS No. 78-2486), (D) N₂ physisorption isotherm and (E) the corresponding pore size distribution of *bm*-TiO₂. *bm*-TiO₂ has surface area of 56.8 m² g⁻¹ and uniform mesopores of 15 nm.



fig. S14. Characterization of bm-Nb₂O₅/C. (A) Cross sectional TEM images of as-made bm-Nb₂O₅/C. (B) SAXS pattern of bm-Nb₂O₅/C after heat treatment at 700 °C under Ar, indicating periodic mesoporous structures. (C) TGA profile for bm-Nb₂O₅/C particles measured under constant artificial air flow.



fig. S15. Characterization of *mns*-AS. (A) Cross-sectional TEM image of as-made *mns*-AS.(B) Elemental mapping images of the O, Al, and Si.



fig. S16. Characterization of non-porous AS particles. (**A** and **B**) TEM images of as-made AS particles and hPS macrodomains in the hPMMA matrix in the absence of BCP. The samples were sectioned with 100 nm thickness by ultra-microtome. AS particles and hPS are separated and dispersed in the matrix. (C) EELS mapping images of the O, Si, and Al of as-made non-porous AS particles. The element distribution indicates that the AS nanoparticles and hPS domains were completely separated. (**D** and **F**) SEM images of AS particles without mesopores after calcination at 550 °C



fig. S17. Characterization of *meso*-Nb₂O₅/C. SEM images with (A) low and (B) high magnification, (C) XRD pattern, (D) N₂ physisorption isotherm, (E) pore size distribution, and (F) TGA profile for *m*-Nb₂O₅/C measured under constant artificial air flow.

Bulk mesoporous Nb₂O₅/carbon composite (*meso*-Nb₂O₅/C) was synthesized in absence of hPS and hPMMA (fig. S17). In contrast to *bm*-Nb₂O₅/C, *meso*-Nb₂O₅/C shows monolithic and irregular morphologies with a few tens of micrometer size (fig. S17, A and B). XRD pattern of *meso*-Nb₂O₅/C corresponds to orthorhombic phase with average crystallite size of 13.8 nm (fig. S17C). Specific surface area of 124 m² g⁻¹ (fig. S17D) and the pore size is 23 nm (fig. S17E). Carbon content of *meso*-Nb₂O₅/C is 12 wt% that is similar to *bm*-Nb₂O₅/C (fig. S17F).

The initial discharge and charge capacity of *meso*-Nb₂O₅/C electrode are 316 and 122 mA h g⁻¹ with CE of 38.6%. *meso*-Nb₂O₅/C exhibits reversible capacity of 153, 131, 110, 94, 76, 57 and 45 mA h g⁻¹ at 10, 25, 50, 100, 200, 500 and 1000 mA g⁻¹, respectively (Fig. 6D).



fig. S18. Characterization of commercial Nb₂O₅ (c-Nb₂O₅). (A) SEM mage, (B) XRD pattern consistent with orthorhombic phase (JCPDS No. 30-0873), (C) N₂ physisorption isotherm and (D) the corresponding pore size distribution of c-Nb₂O₅

SEM image of c-Nb₂O₅ shows that it has non-porous structures and irregular particle morphologies (fig. S18A). XRD pattern of c-Nb₂O₅ corresponds orthorhombic phase and the average crystallite size is 46.5 nm (fig. S18B). N₂ physisorption analysis shows specific surface area of 5 m² g⁻¹ (fig. S18C) and the pore size distribution indicates that c-Nb₂O₅ does not have pores (fig. S18D).

The initial discharge and charge capacity of c-Nb₂O₅ electrode are 121 and 67 mA h g⁻¹ with coulombic efficiency of 55%. c-Nb₂O₅ shows reversible capacity of 58, 55, 51, 45, 39, 33 and 27 mA h g⁻¹ at 10, 25, 50, 100, 200, 500 and 1000 mA g⁻¹, respectively (Fig. 6D).



fig. S19. Capacity retention of *bm*-Nb₂O₅/C electrode at various current densities.



fig. S20. The comparison of the electrochemical performance. (A) Rate capability and (B) capacity retention after long-term cycling of bm-Nb₂O₅/C with the reported results of metal oxide-based anode materials. The electrochemical performance of bm-Nb₂O₅/C is one of the best among intercalation-type materials, and even comparable to conversion-type materials.



fig. S21. Long-term cyclability of bm-Nb₂O₅/C. Cycling performance of bm-Nb₂O₅/C electrode at 500 mA g⁻¹ and the coulombic efficiency.



fig. S22. The thickness of electrodes. (A and B) Cross-sectional SEM images of bm-Nb₂O₅/C and meso-Nb₂O₅/C electrodes. (C) Volumetric capacities of bm-Nb₂O₅/C and meso-Nb₂O₅/C electrodes at different current densities.

bm-Nb₂O₅/C electrode shows dense packing with the thickness of ~11 μ m (fig. S22A) and has the electrode density of 0.86 g cm⁻³. On the other hand, the thickness of *meso*-Nb₂O₅/C electrode is ~24 μ m which is thicker than that of *bm*-Nb₂O₅/C due to its irregular particle morphology and large particle size (fig. S22B), thereby leading to the lower electrode density (0.35 g cm⁻³). The closely packing behavior of bowl-like morphologies contributes the higher volumetric capacity of *bm*-Nb₂O₅/C electrode than that of *meso*-Nb₂O₅/C at all current densities (fig. S22C). In particular, *bm*-Nb₂O₅/C (89.6 mA h cm⁻³) electrode demonstrated about 5.4 times higher volumetric capacity that *meso*-Nb₂O₅/C (16.4 mA h cm⁻³) at high current density of 1000 mA g⁻¹.

table S1. Interfacial tensions of pairs of polymers and spreading coefficients of PMMA/PS/PEO-*b*-PS blends system.

Interfacial tensions	$\gamma \ (mN \ m^{-1})$	Spreading coefficients	$\lambda \ (mN \ m^{-1})$
γρμμα/ps	1.63	$\lambda_{ m PMMA/PS/BCP}$	-0.66
Ŷ рмма/вср	1.60	$\lambda_{ m PMMA/BCP/PS}$	-0.60
<i>Υ</i> ΡS/BCP	0.63	$\lambda_{ extsf{ps/pmma/bcp}}$	-2.60

Block copolymer	r_M (M_{hPS}/M_{BCP})	Resultant shape	Concavity/particle size or thickness (nm)	Mesopore size (nm)
	0	Oblate	-/230	15.3
	0.2	Bowl	70/180	15.1
PEO- <i>b</i> -PS (26.1 kg mol ⁻¹)	1	Bowl	240/410	15.5
	2	Bowl	370/600	15.3
	40	Nanosheet	8.7 (thickness)	16.2
PEO- <i>b</i> -PS $(52.0 \text{ kg mol}^{-1})$	1	Bowl	280/460	39.8
No BCP	1	Sphere	100-300	No mesopore

table S2. The relation between synthetic conditions and physical properties of anisotropic AS materials prepared by ASAP approach.

Sample	Surface area $(m^2 g^{-1})$	Mesopore size (nm)
bm-AS	300	15.5
mns-AS	268	16.2
<i>bm</i> -carbon	920	33
<i>bm</i> -TiO ₂	56.8	15
<i>bm</i> -Nb ₂ O ₅ /C	50	21.5
meso-Nb ₂ O ₅ /C	124	23
c-Nb ₂ O ₅	5	No mesopore

table S3. The physicochemical properties of bowl-like inorganic particles.

table S ²	I. Electrochemical	performance	comparison	of bm -Nb ₂ O ₅ /C	with previous	ly reported
metal ox	tide-based anode r	naterials for K	IBs.			

Anode materials	Rate capability	Cyclability	References
	Intercalation-type	e materials	
<i>bm</i> -Nb ₂ O ₅ /C	245 mA h g ⁻¹ @10 mA g ⁻¹ 220 mA h g ⁻¹ @25 mA g ⁻¹ 198 mA h g ⁻¹ @50 mA g ⁻¹ 176 mA h g ⁻¹ @100 mA g ⁻¹ 157 mA h g ⁻¹ @200 mA g ⁻¹ 127 mA h g ⁻¹ @500 mA g ⁻¹ 103 mA h g ⁻¹ @1000 mA g ⁻¹	189 mA h g ⁻¹ @50 mA g ⁻¹ after 100 cycles 106 mA h g ⁻¹ @500 mA g ⁻¹ after 1000 cycles	This work
Nb ₂ O ₅ nanowires	152 mA h g ⁻¹ @100 mA g ⁻¹ 127 mA h g ⁻¹ @200 mA g ⁻¹ 104 mA h g ⁻¹ @400 mA g ⁻¹ 90 mA h g ⁻¹ @600 mA g ⁻¹ 81 mA h g ⁻¹ @800 mA g ⁻¹ 74 mA h g ⁻¹ @1000 mA g ⁻¹	75 mA h g ⁻¹ @400 mA g ⁻¹ after 400 cycles	[46]

Black Nb ₂ O _{5-x}	$72 \text{ mA h g}^{-1} @ 20 \text{ mA g}^{-1}$		
	$62 \text{ mA h g}^{-1}@40 \text{ mA g}^{-1}$	40.4 mA h g ⁻¹ @100 mA g ⁻¹	
	57 mA h g ⁻¹ @60 mA g ⁻¹		[47]
	51 mA h g ⁻¹ @100 mA g ⁻¹	after 270 cycles	
	44 mA h g^{-1} @200 mA g $^{-1}$		

KTO microscaffolds $(K_2Ti_6O_{13})$	95 mA h g ⁻¹ @20 mA g ⁻¹ 89 mA h g ⁻¹ @50 mA g ⁻¹ 82 mA h g ⁻¹ @100 mA g ⁻¹ 72 mA h g ⁻¹ @200 mA g ⁻¹ 64 mA h g ⁻¹ @500 mA g ⁻¹	59 mA h g ⁻¹ @500 mA g ⁻¹ after 1000 cycles	[48]
	57 mA h g ⁻¹ @1000 mA g ⁻¹		

	150 mA h g ⁻¹ @20 mA g ⁻¹		
	119 mA h g ⁻¹ @50 mA g ⁻¹		
KTO nanoribbons	105 mA h g ⁻¹ @100 mA g ⁻¹	$46 \text{ mA h g}^{-1} @ 200 \text{ mA g}^{-1}$	[40]
$(K_2Ti_4O_9)$	97 mA h g ⁻¹ @150 mA g ⁻¹	after 900 cycles	[49]
	89 mA h g ⁻¹ @200 mA g ⁻¹		
	81 mA h g ⁻¹ @300 mA g ⁻¹		

$$\begin{array}{c} 228 \text{ mA h g}^{-1} @ 100 \text{ mA g}^{-1} \\ 162 \text{ mA h g}^{-1} @ 200 \text{ mA g}^{-1} \\ 162 \text{ mA h g}^{-1} @ 2000 \text{ mA g}^{-1} \\ 116 \text{ mA h g}^{-1} @ 500 \text{ mA g}^{-1} \\ 84 \text{ mA h g}^{-1} @ 1000 \text{ mA g}^{-1} \\ 84 \text{ mA h g}^{-1} @ 1000 \text{ mA g}^{-1} \\ 75 \text{ mA h g}^{-1} @ 2000 \text{ mA g}^{-1} \end{array}$$

$$\begin{array}{c} 117 \text{ mA h g}^{-1} @ 20 \text{ mA g}^{-1} \\ 100 \text{ mA h g}^{-1} @ 40 \text{ mA g}^{-1} \\ 90 \text{ mA h g}^{-1} @ 40 \text{ mA g}^{-1} \\ 90 \text{ mA h g}^{-1} @ 80 \text{ mA g}^{-1} \\ 83 \text{ mA h g}^{-1} @ 100 \text{ mA g}^{-1} \\ 83 \text{ mA h g}^{-1} @ 100 \text{ mA g}^{-1} \\ 74 \text{ mA h g}^{-1} @ 200 \text{ mA g}^{-1} \\ 50 \text{ mA h g}^{-1} @ 400 \text{ mA g}^{-1} \\ 44 \text{ mA h g}^{-1} @ 500 \text{ mA g}^{-1} \end{array}$$

$$97 \text{ mA h g}^{-1}@30 \text{ mA g}^{-1}$$

$$80 \text{ mA h g}^{-1}@100 \text{ mA g}^{-1}$$

$$65 \text{ mA h g}^{-1}@250 \text{ mA g}^{-1}$$

$$65 \text{ mA h g}^{-1}@250 \text{ mA g}^{-1}$$

$$56 \text{ mA h g}^{-1}@500 \text{ mA g}^{-1}$$

$$50 \text{ mA h g}^{-1}@1000 \text{ mA g}^{-1}$$

$$42 \text{ mA h g}^{-1}@1500 \text{ mA g}^{-1}$$

$$20 \text{ mA h g}^{-1}@2000 \text{ mA g}^{-1}$$

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[52]

[50]

	38 mA h g^{-1} @50 mA g $^{-1}$		
TiO	29 mA h g ⁻¹ @100 mA g ⁻¹	15 mA h g^{-1} @200 mA g $^{-1}$	[52]
110_2	20 mA h g ⁻¹ @200 mA g ⁻¹	after 500 cycles	[33]
	9 mA h g ⁻¹ @500 mA g ⁻¹		

	Conversion-type	materials	
β-FeOOH	218 mA h g ⁻¹ @100 mA g ⁻¹ 175 mA h g ⁻¹ @200 mA g ⁻¹ 145 mA h g ⁻¹ @500 mA g ⁻¹ 115 mA h g ⁻¹ @1000 mA g ⁻¹	60 mA h g ⁻¹ @1000 mA g ⁻¹ after 1000 cycles	[54]
	83 mA h g^{-1} @2000 mA g^{-1}		

	225 mA h g ⁻¹ @200 mA g ⁻¹
	100 mA h g ⁻¹ @400 mA g ⁻¹
CuO particle	52 mA h g^{-1} @800 mA g $^{-1}$
	40 mA h g ⁻¹ @1000 mA g ⁻¹
	32 mA h g^{-1} @2000 mA g $^{-1}$

 $\begin{array}{c} 230 \text{ mA h g}^{-1} @ 50 \text{ mA g}^{-1} \\ 220 \text{ mA h g}^{-1} @ 100 \text{ mA g}^{-1} \\ 210 \text{ mA h g}^{-1} @ 100 \text{ mA g}^{-1} \\ 210 \text{ mA h g}^{-1} @ 200 \text{ mA g}^{-1} \\ 195 \text{ mA h g}^{-1} @ 300 \text{ mA g}^{-1} \\ 195 \text{ mA h g}^{-1} @ 300 \text{ mA g}^{-1} \\ 180 \text{ mA h g}^{-1} @ 500 \text{ mA g}^{-1} \\ 160 \text{ mA h g}^{-1} @ 1000 \text{ mA g}^{-1} \\ 130 \text{ mA h g}^{-1} @ 1000 \text{ mA g}^{-1} \\ 130 \text{ mA h g}^{-1} @ 3000 \text{ mA g}^{-1} \\ 105 \text{ mA h g}^{-1} @ 3000 \text{ mA g}^{-1} \\ 60 \text{ mA h g}^{-1} @ 5000 \text{ mA g}^{-1} \end{array}$

106 mA h g⁻¹@500 mA g⁻¹ [56] after 1000 cycles

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[55]

S32

α-Fe ₂ O ₃ /NC	320 mA h g^{-1} @50 mA g $^{-1}$	103 mA h g ⁻¹ @500 mA g ⁻¹ after 1000 cycles	[57]
	260 mA h g ⁻¹ @100 mA g ⁻¹		
	193 mA h g^{-1} @200 mA g^{-1}		
	157 mA h g ⁻¹ @500 mA g ⁻¹		
	136 mA h g^{-1} @1000 mA g $^{-1}$		
	113 mA h g^{-1} @2000 mA g^{-1}		
	87 mA h g ⁻¹ @5000 mA g ⁻¹		