Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

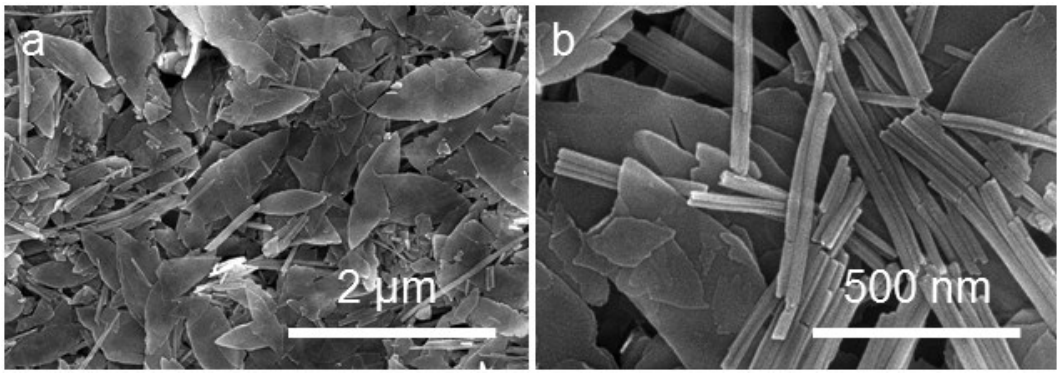

Figure S1. SEM images of B-MnP52 exhibiting its irregular morphology.

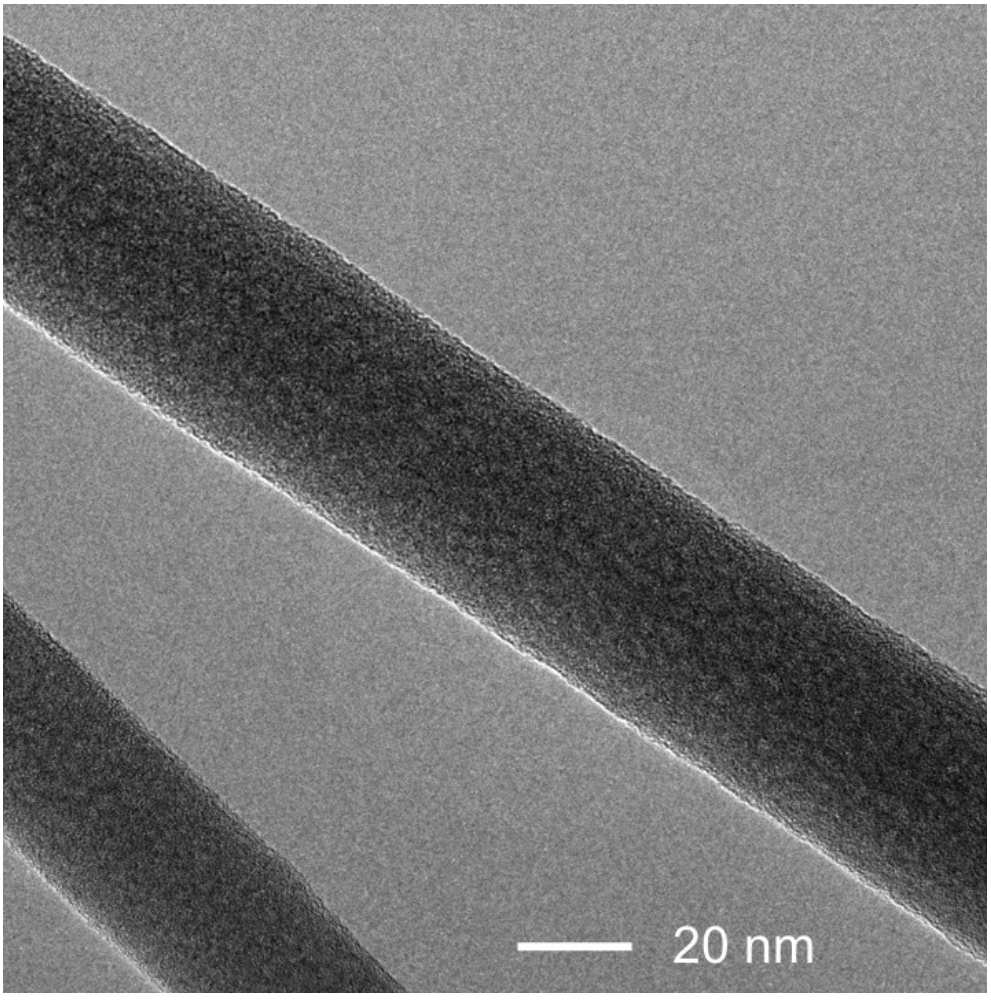

Figure S2. Enlarged view of the mesostructure of M-MnP52.

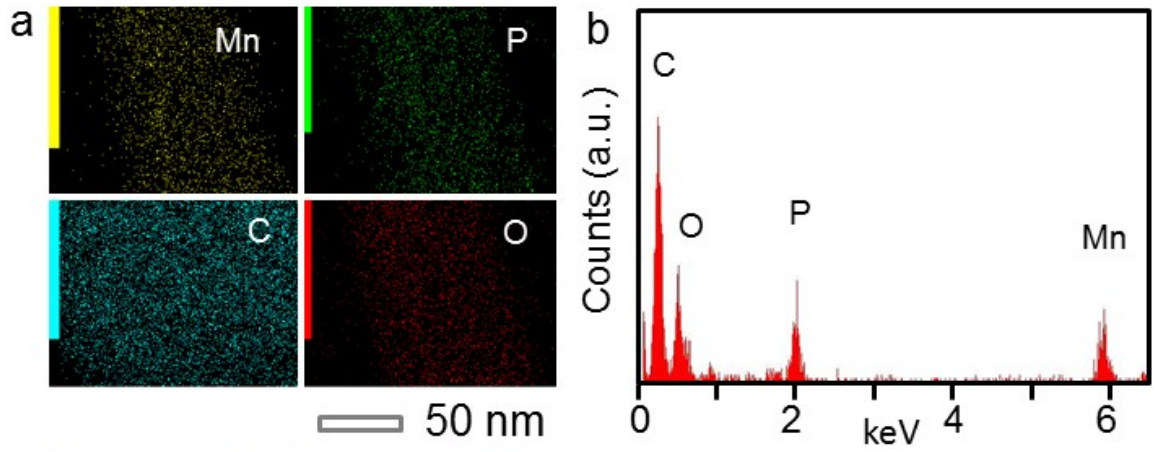

Figure S3. Elemental mapping (a) with EDX spectrum (b) of M-MnP52.

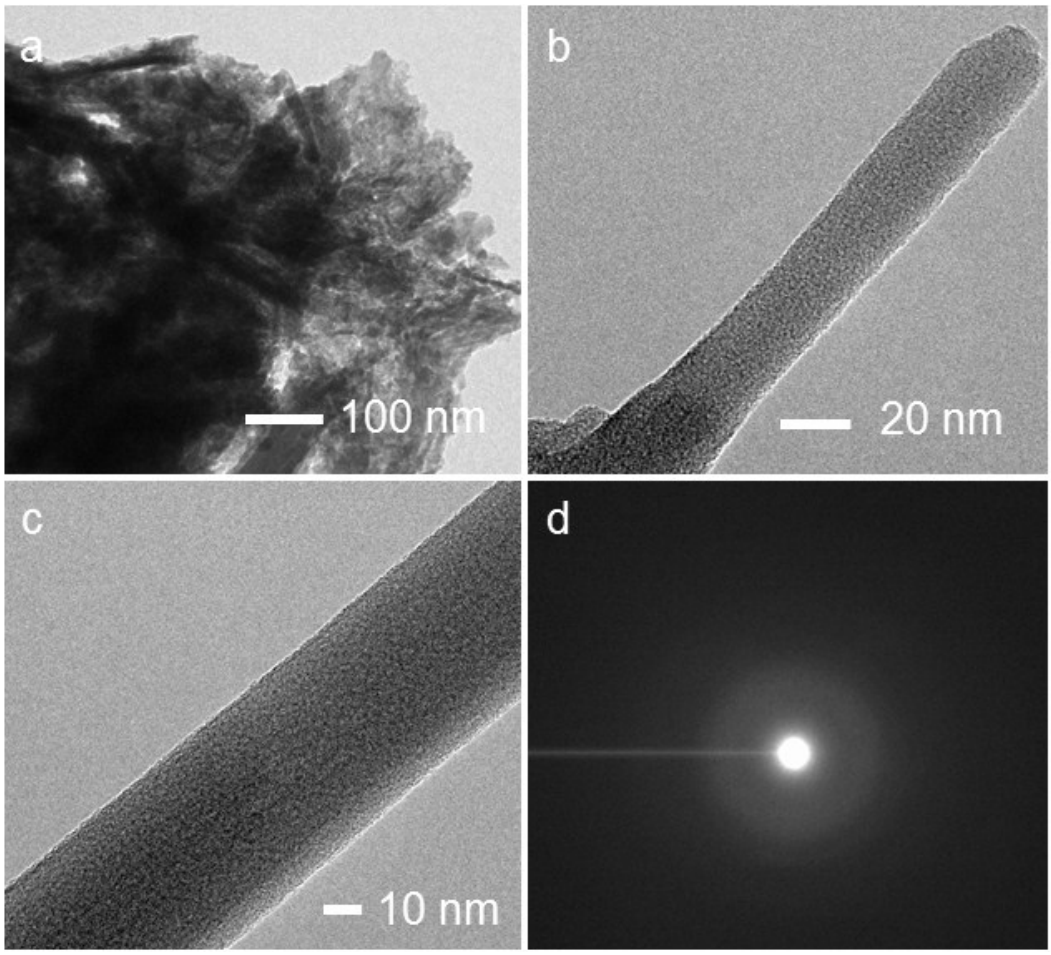

Figure S4. (a–c) TEM images and (d) SAED pattern of B-MnP52, showing non-porous structure with an amorphous framework.

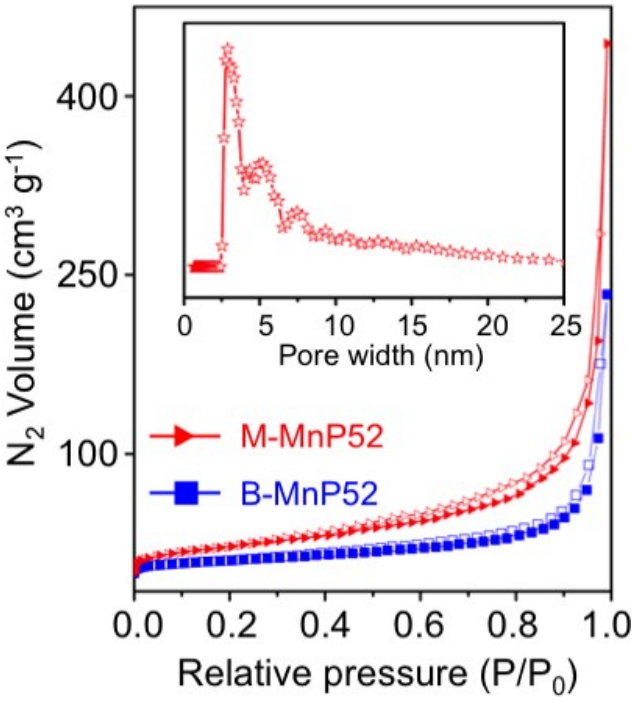

Figure S5. N_2 adsorption-desorption isotherms of M-MnP52 and B-MnP52. Pore size distribution curve of M-MnP52 is shown as an inset.

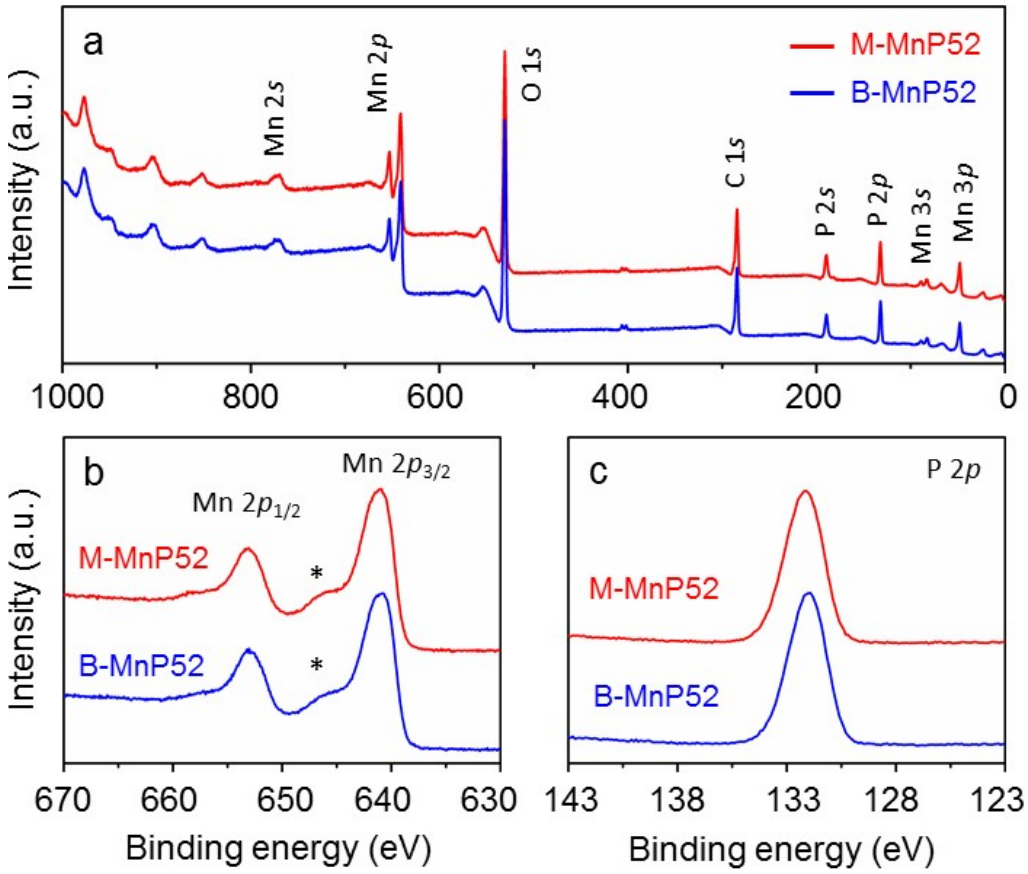

Figure S6. XPS spectra of M-MnP52 and B-MnP52: (a) survey spectra; (b) Mn 2p spectra; and (c) P 2p spectra. The satellite peaks are indicated by *.

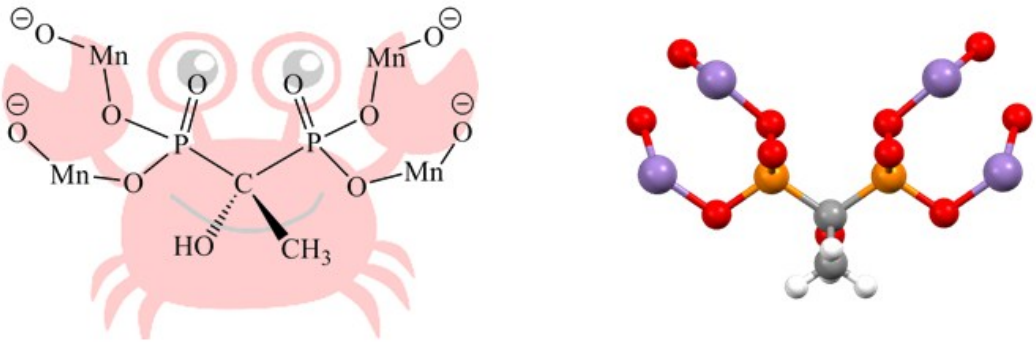

Figure S7. Proposed connection mode between phosphonic linkages and manganese moieties for M-MnP52.

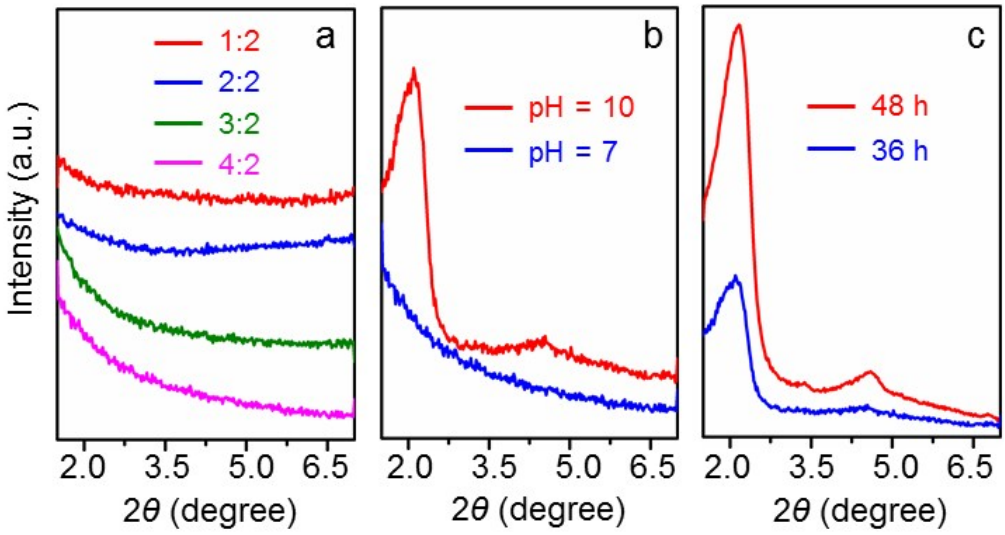

Figure S8. Low-angle XRD patterns of MnP samples prepared under different synthetic conditions: (a) Mn/P ratios of 1:2 to 4:2 at pH ~ 7, with aging time of 36 h; (b) Mn/P ratio of 1:2 at different pH, with aging time of 36 h; and (c) Mn/P ratio of 1:2 at pH ~ 10, with aging time of 36 and 48 h.

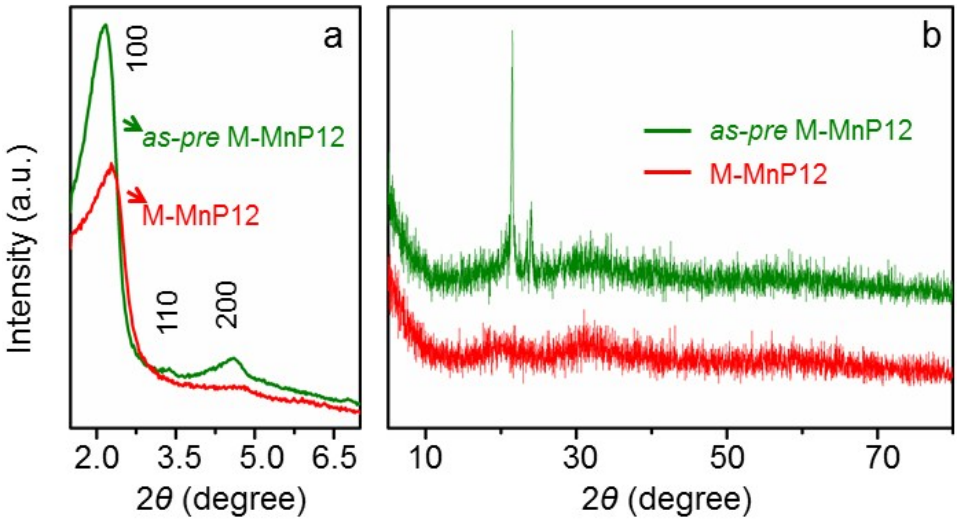

Figure S9. (a) Low-angle and (b) wide-angle XRD patterns of *as-pre* M-MnP12 and M-MnP12.

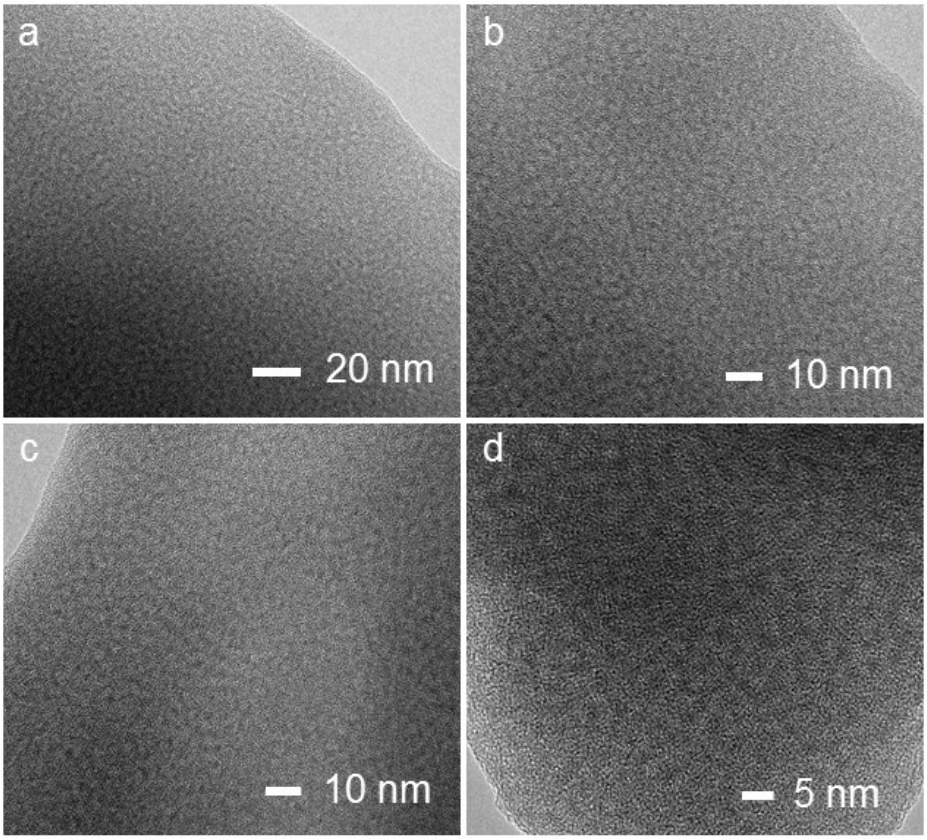

Figure S10. TEM images of M-MnP12 showing clearly visible mesostructure.

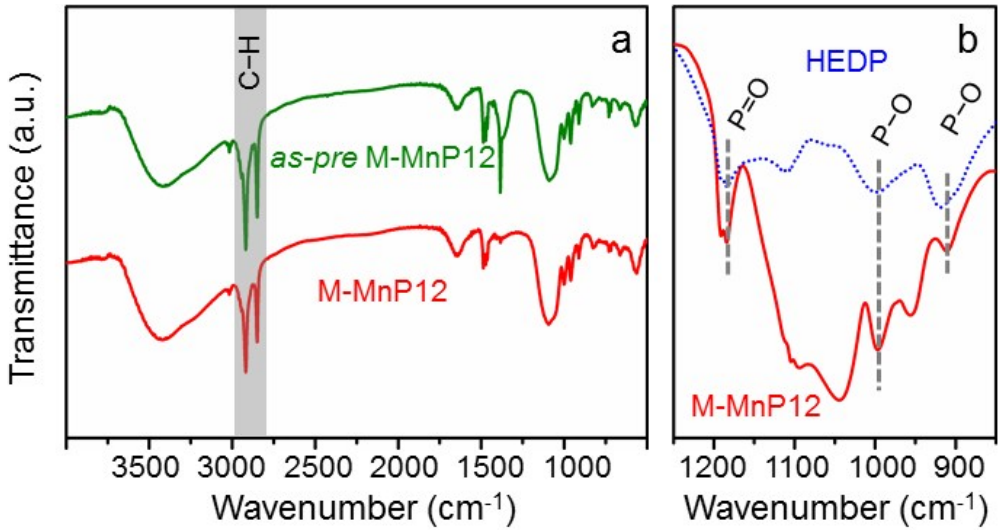

Figure S11. FT-IR spectra of (a) MnP samples (*as-pre* M-MnP12, M-MnP12) and (b) free phosphonic acid (HEDP).

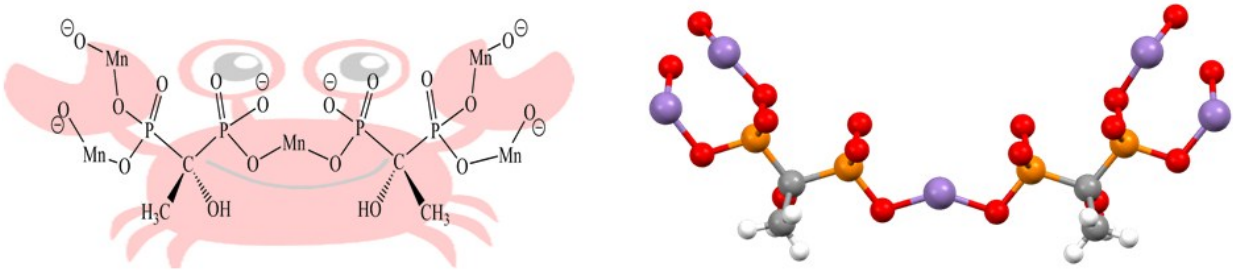

Figure S12. Proposed connection mode between phosphonic linkages and manganese moieties for M-MnP12.

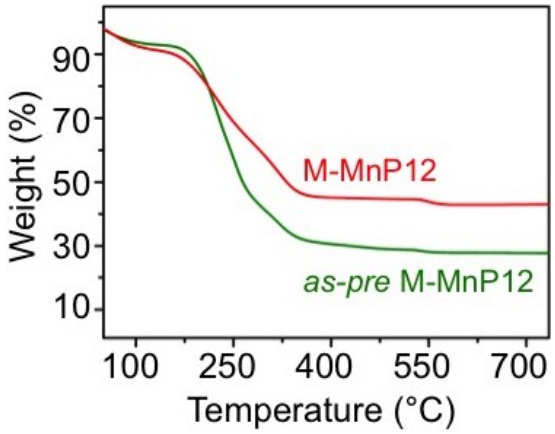

Figure S13. TGA curves of *as-pre* M-MnP12 and M-MnP12.

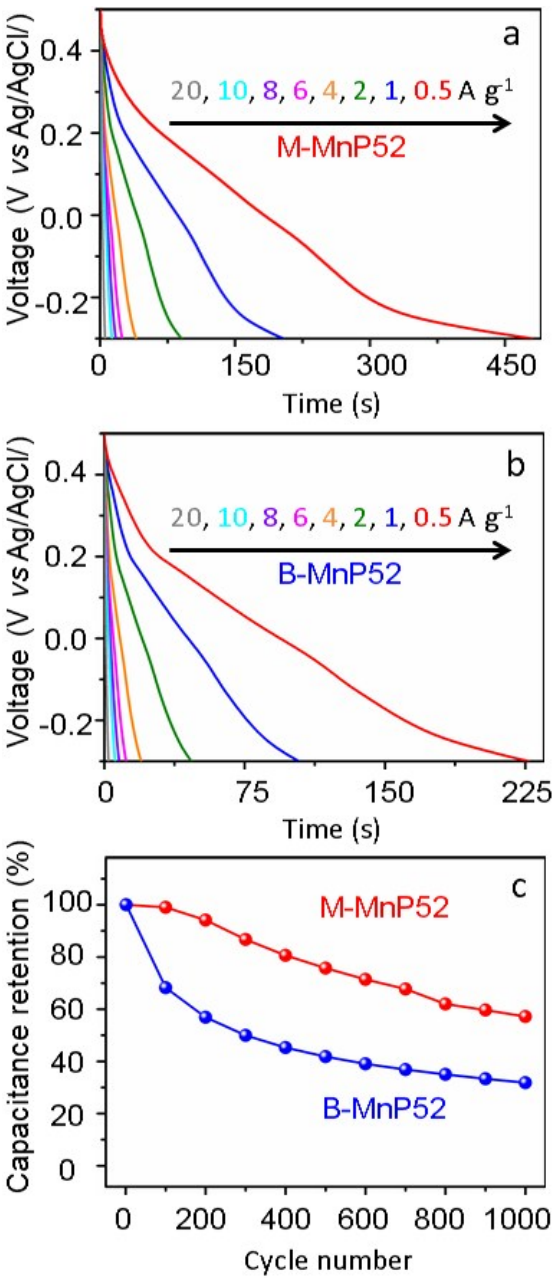

Figure S14. The galvanostatic discharge curves of (a) M-MnP52 and (b) B-MnP52 at various current densities, and (c) their cycling stability.

Table S1 Comparison of capacitive performance with previously reported phosphate materials.

Sample	Potential window (V)	Electrolyte	Scan rate (mV s^{-1})	Current density (mA cm^{-2})	Capacitance (F g^{-1})	Retention[a] (%)	Retention calculation range (A g^{-1})	Ref.
$NaMnPO_4$	-0.6 - 0.4	1 M NaOH	2	-	219	46	2-10	R1
M-MnP52	-0.3 - 0.5	3 M KOH	5	-	269	67.5	2-10	This work
$NaMnPO_4$	-0.6 - 0.4	1 M NaOH	-	2	163	-	-	R1
M-MnP52	-0.3 - 0.5	3 M KOH	-	2	243	-	-	This work
$Mn_3(PO_4)_2$/ graphene composite	0.0-0.4 V	6 M KOH	-	0.5	270	-	-	R2
M-MnP52	-0.3 - 0.5	3 M KOH	-	0.5	299	-	-	This work
$Mn_3(PO_4)_2$ nanosheets	-0.3 - 0.5	2 M KOH	-	-	-	40-44.5	0.5-5	R3
M-MnP52	-0.3 - 0.5	3 M KOH	-	-	-	60.5	0.5-6	This work

[a] *The retention is calculated by changing the applied current density (A g^{-1}).*

References

R1 B. Senthilkumar, K. V. Sankar, L. Vasylechko, Y. S. Lee, R. K Selvan, *RSC Adv.* 2014, **4**, 53192-53200.

R2 A. M. Abdulmajid, J. M. Moshawe, M. M. Tshifhiwa, O. O. Kabir, B. Abdulhakeem, M. Ncholu, *J. Colloid Interface Sci.* 2017, **494**, 325-337.

R3 Y. H. Dai, L. B. Kong, K. Yuan, M. Shi, Y. C. Luo, L. Kang, *Ionics,* 2016, **22**, 1461-1469.