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Supplementary Information

Gradient substitution: an intrinsic strategy towards high performance sodium storage in Prussian blue-based cathodes

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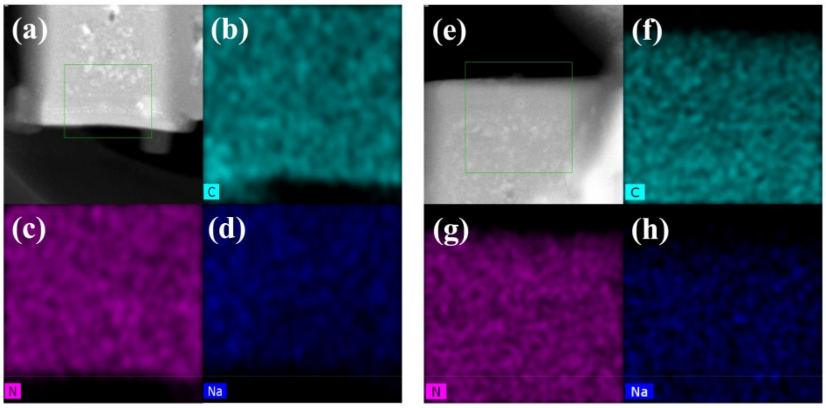

Figure S1. (a & e) STEM images of HNGPB and bare PB. (b-d) Element profiles for (b) carbon, (c) nitrogen and (d) sodium of HNGPB. (f-h) Element profiles for (f) carbon, (g) nitrogen and (h) sodium of LNGPB.

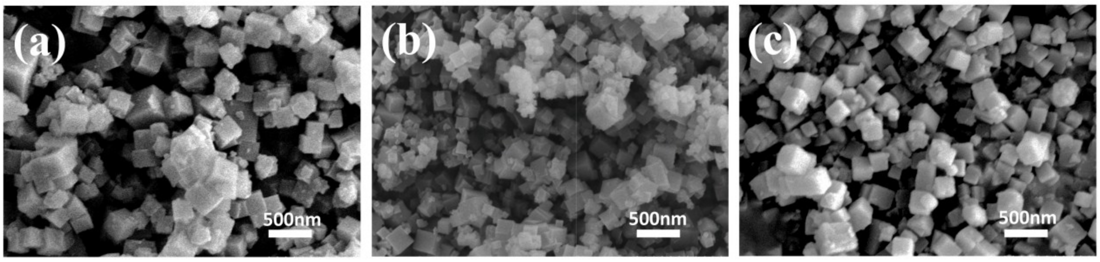

Figure S2. SEM images of (a) HNGPB, (b) LNPGB and (c) bare PB before cycling.

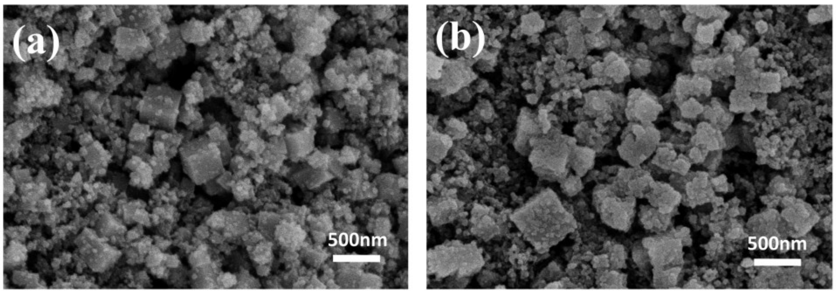

Figure S3. SEM images of (a) HNGPB and (b) bare PB after 600th cycling under current density of 100 mA g^{-1}.

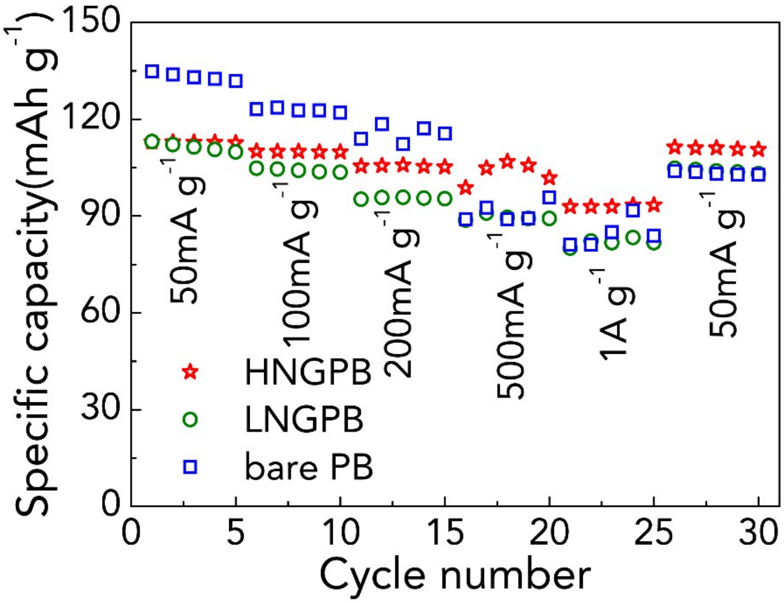

Figure S4. Rate performance of HNGPB, LNGPB and bare PB.

Table S1. Comparison of reported PB-based cathode materials for SIBs.

Composition	Capacity ($mAh\ g^{-1}$)	Cycle life	Reference
$FeFe(CN)_6$	120 @60 $mA\ g^{-1}$	87%@500th 240 $mA\ g^{-1}$	[19]
$Na_{1.70}FeFe(CN)_6$	120 @200 $mA\ g^{-1}$	73@100th 200 $mA\ g^{-1}$	[21]
FeHCF@CNT	170 @0.1 C	83%@1000th, 2.4 C	[24]
RGO-PB composite	163 @30 $mA\ g^{-1}$	90%@500th 200 $mA\ g^{-1}$	[25]
$Na_{0.61}Fe[Fe(CN)_6]_{0.94}$	170 @25 $mA\ g^{-1}$	100%@150th 25 $mA\ g^{-1}$	[26]
FeHCF@NiHCF	102 @25 $mA\ g^{-1}$	78%@800th 200 $mA\ g^{-1}$	[29]
FeHCF nanospheres @Graphene rolls	110 @150 $mA\ g^{-1}$	90%@500th 150 $mA\ g^{-1}$	[30]
FeHCF@Ketjen black	130 @50mA g^{-1}	90%@2000th 20C	[31]
RGO-coated $K_{0.33}FeFe(CN)_6$	160 @0.5 C	92.2%@1000th 0.5 C	[32]
3wt% Ni doped FeHCF	117 @10 $mA\ g^{-1}$	86.3@90th 200 $mA\ g^{-1}$	[33]
$Fe_{0.8}Ni_{0.2}$-HCF	106 @10 $mA\ g^{-1}$	96%@100th 10 $mA\ g^{-1}$	[34]
$Na_{1.70}Fe_{2.15}(CN)_6$	150 @8.54 $mA\ g^{-1}$	63.4@500th 85.4 $mA\ g^{-1}$	[36]
HNGPB	114 @100 $mA\ g^{-1}$	80%@600th 100 $mA\ g^{-1}$ 90%@1000th 1A g^{-1}	This work

Table S2 AAS results of HNGPB, LNGPB and bare PB.

Elements	**Na (mg L^{-1})**	**Fe (mg L^{-1})**	**Ni (mg L^{-1})**
HNGPB	0.34	1.26	0.14
LNGPB	0.19	0.73	0.14
Bare PB	0.52	1.98	-

Table S3 Elements analysis of HNGPB, LNGPB and bare PB.

Elements	**N (wt%)**	**C (wt%)**	**H (wt%)**
HNGPB	22.31	19.61	1.66
LNGPB	22.40	19.83	1.77
Bare PB	21.55	18.83	1.94

Calculation process of formulae:

$$n_{(CN)6} = \frac{N\ wt\%}{M_N * 6}$$

$$n_{Ni} = \frac{c_{Ni}/(c_{Ni} + c_{Fe} + c_{Na}) * (1 - C\ wt\% - N\ wt\% - H\ wt\% * 9)}{M_{Ni}}$$

$$n_{Fe} = \frac{c_{Fe}/(c_{Ni} + c_{Fe} + c_{Na}) * (1 - C\ wt\% - N\ wt\% - H\ wt\% * 9)}{M_{Fe}}$$

$$n_{Na} = \frac{c_{Na}/(c_{Ni} + c_{Fe} + c_{Na}) * (1 - C\ wt\% - N\ wt\% - H\ wt\% * 9)}{M_{Na}}$$

$$n_{Fe}^{1} = n_{Fe} - n_{(CN)6}$$

$$n_{H2O} = H\ wt\%/2$$

n_{Fe}^{1} stands for Fe ions in the M_1 site.

All the calculated results are then normalized on the basis that the sum of Fe and Ni in M_1 sites equals one in the final formulae.