Supplementary Information

3D Graphene current collector boost ultrahigh specific capacity in a highly uniform Prussian blue @ graphene composite as a freestanding cathode for Sodium ion batteries

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Table S1. The active mass content, initial capacity and capacity retention (after 100cycles at 0.5C) of xPBGA (x=10, 20, 50, 100, 150)

	Active mass content	Initial capacity [mAh g⁻¹)	capacity retention ratio [mAh g⁻¹]
10PBGA	20.4%	214.3	84.3%
20PBGA	33.8%	130.6	84.9%
50PBGA	56.1%	79.3	75.9%
100PBGA	71.9%	75.0	58.7%
150PBGA	79.3%	38.0	71.8%

Table S1 shows the corresponding relation between the active mass lading, initial capacity, capacity retention ratio and the sample name. Due to the activated process, the initial capacity is counted as the highest discharge capacity in the first 10 circle. The capacity retention ratio is calculated after 100 cycles at a current density of 0.5C (85 mAh g⁻¹).

Calculation of the accurate chemical formula of PB: We suggest that the chemical formula should be $K_xFe_{4-0.33x}[Fe(CN)_6]_3 \cdot nH_2O$ due to previous work[1]. We found equations which are not linear correlate each other to find the unknow value

The first one is. The value of **n** can be calculated by the second mass loss stage in TGA (**Figure S4**), where the mass loss is 9.0%, while the integral mass (without calculating absorbed water) is 93.4%. So the zeolitic water contributed 9.64% of weight in the molecule.

The second one is. From the EDX spectrum(**Figure S10**), Although as we known, the EDX spectrum cannot be used to quantitative analyses all the light element (like C, O, N), but we can still get a molecule ratio of K: Fe, which is about 62.2%, so we can get the value of **x**.

$$\frac{18n}{39x + 56 * (7 - 0.33x) + 26 * 18} = \frac{9.64\%}{1 - 9.64\%} \tag{1}$$

$$\frac{x}{7 - 0.33x} = 62.2\% \tag{2}$$

Finally we calculated the relatively accurate chemical formula is $K_{5.49}Fe_{2.17}[Fe(CN)6]_3 \cdot 5.87H_2O$, also $K_{1.83}Fe_{0.72}[Fe(CN)6] \cdot 1.96H_2O$.

CV data processing details: We separated the EDLC capacitance from Graphene aerogel and the capacity from Prussian blue by processing the CV data at different sweep rate (0.25, 0.5, 0.75, 1, 1.5mV/s) as the main body says. The linear regression was conducted by Origin 8.0. The k_1v curve was drawn by connecting the feature points.

In addition, the k_1v curve surpassed the CV curve at the charge interval between 3.7 V and 4.2 V at a sweep rate of 0.25mV/s. This phenomenon is mainly due to the polarization at high sweep rate. In order to keep the rationality of the data, we reduce the k_1v curve to fully cover the raw CV curve in Figure 6c. However, the contribution ratio was still calculated by the initial data
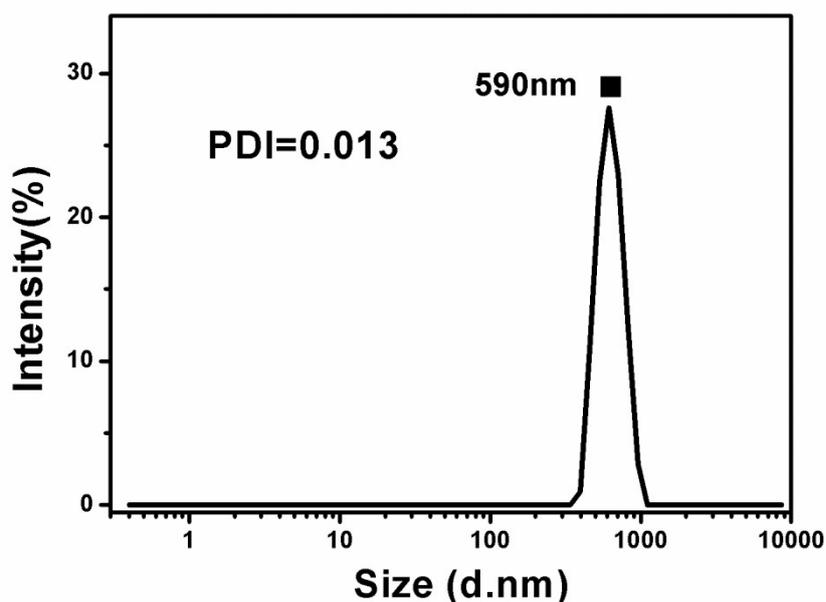
Figure S1 Dynamic Light Scattering (DLS) test result of PB nanocube

(dispersed in DI water)
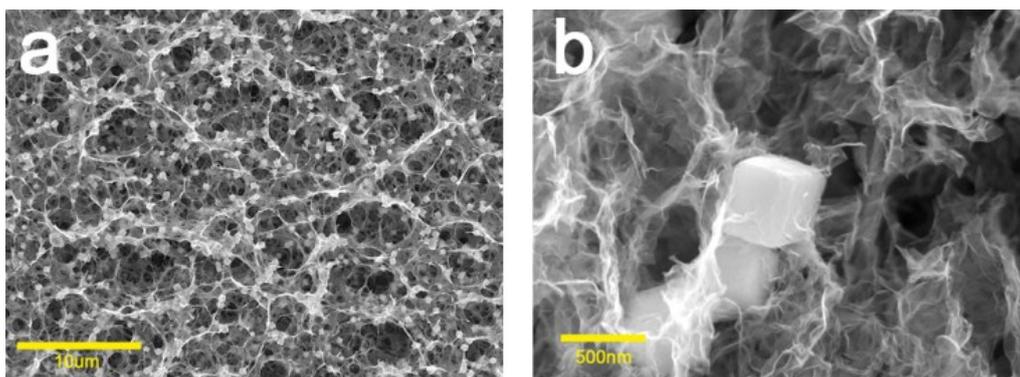
Figure S2 SEM images of PBGA sample after annealing
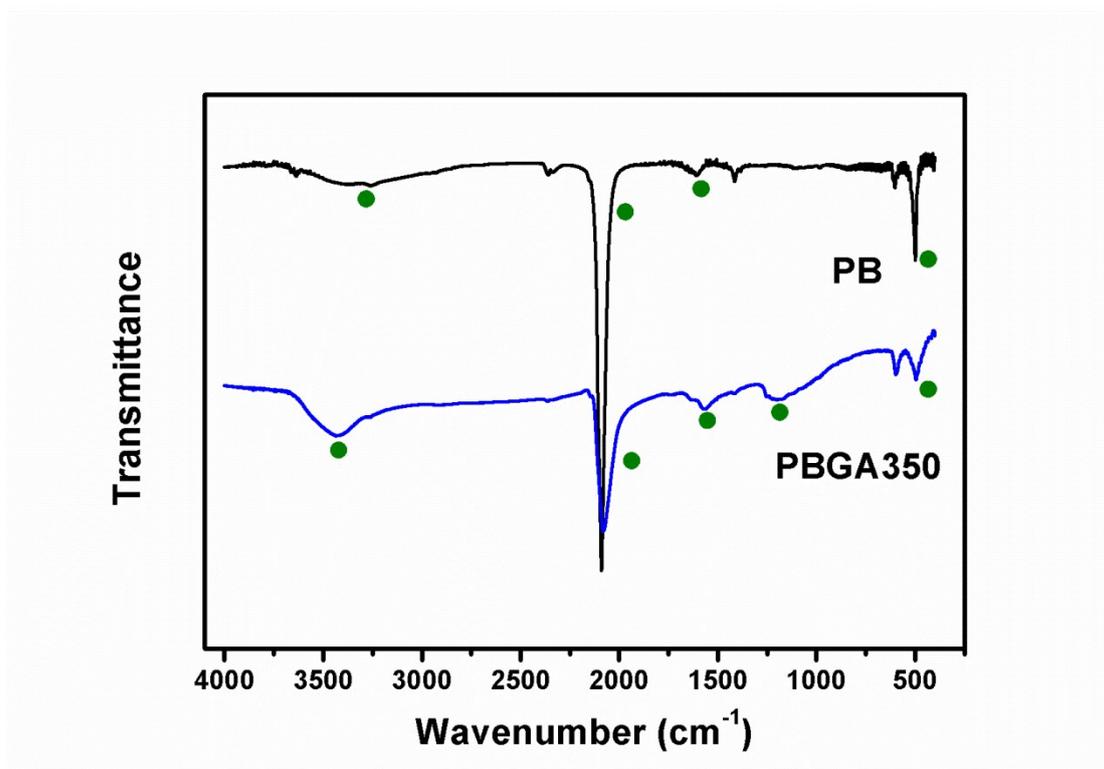
Figure S3 Fourier transform infrared spectrums (FTIR) of PB and 50PBGA (after

annealing).
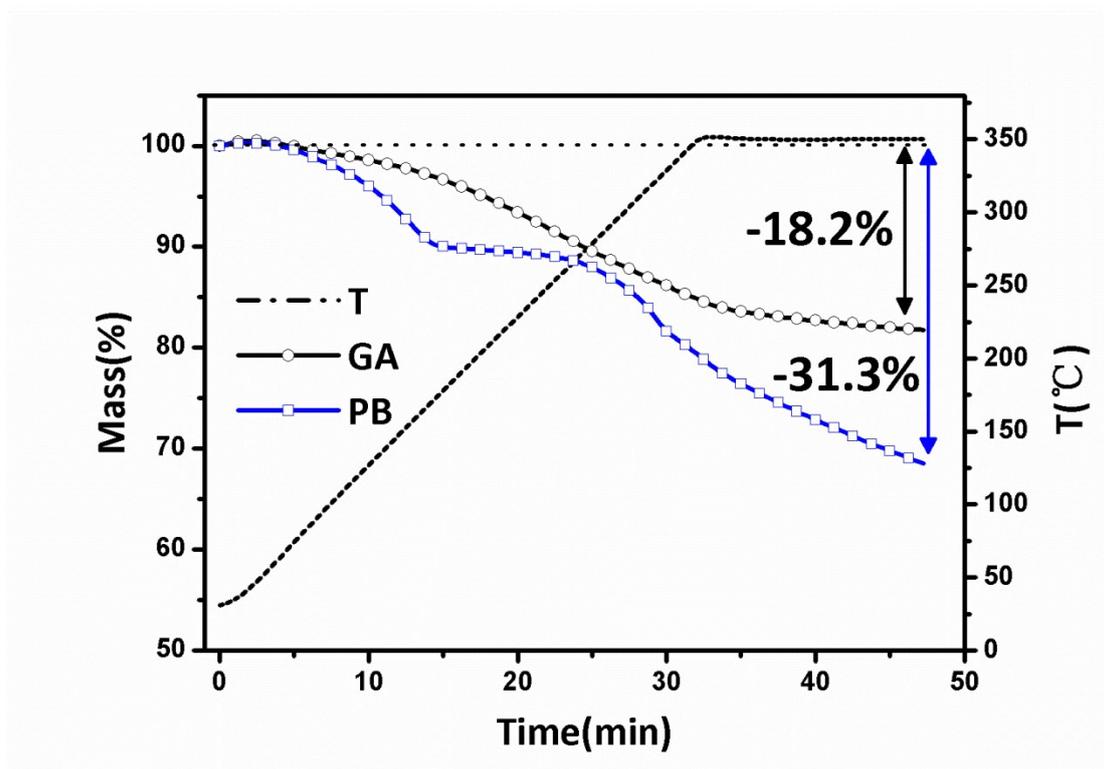
Figure S4 Thermogravimetric Analysis (TGA) curves of Prussian blue and Graphene

aerogel
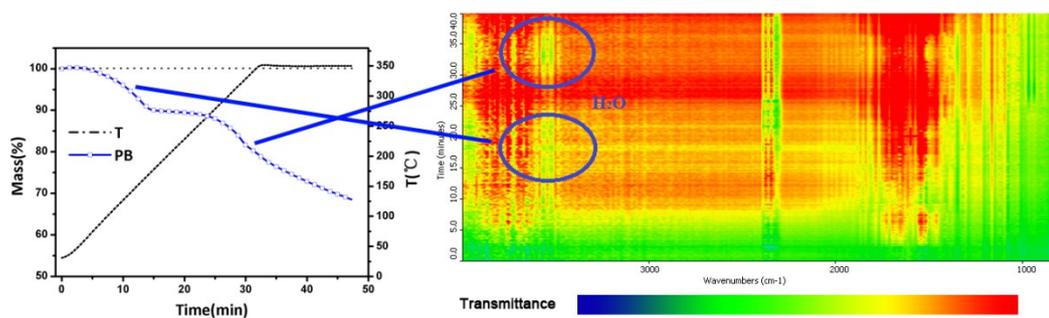
Figure S5 TG-IR spectrum of PB sample.
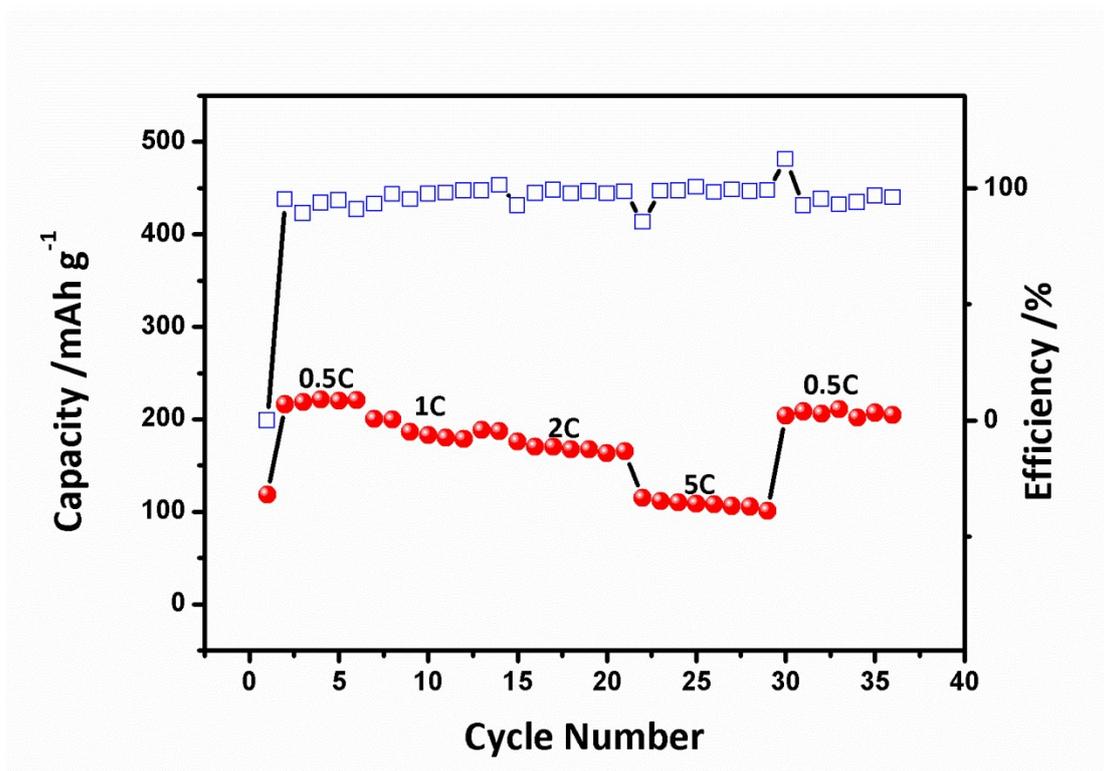
Figure S6. Rate performance of 10PBGA
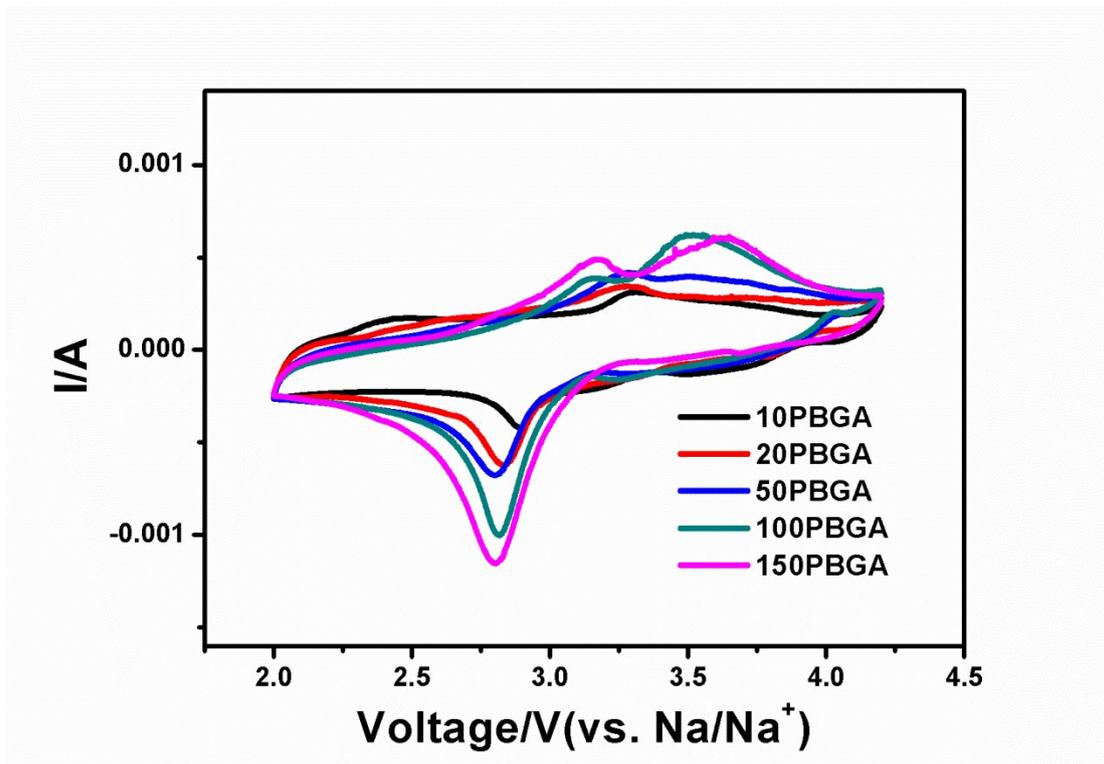
Figure S7 CV curves of xPBGA with different x value
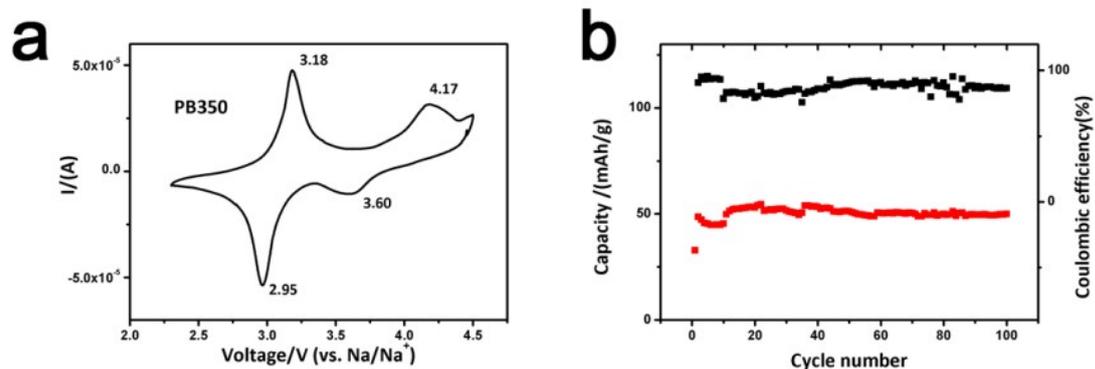
Figure S8 (a) CV curve and (b) cycles performance of PB fabricated by direct smear method.
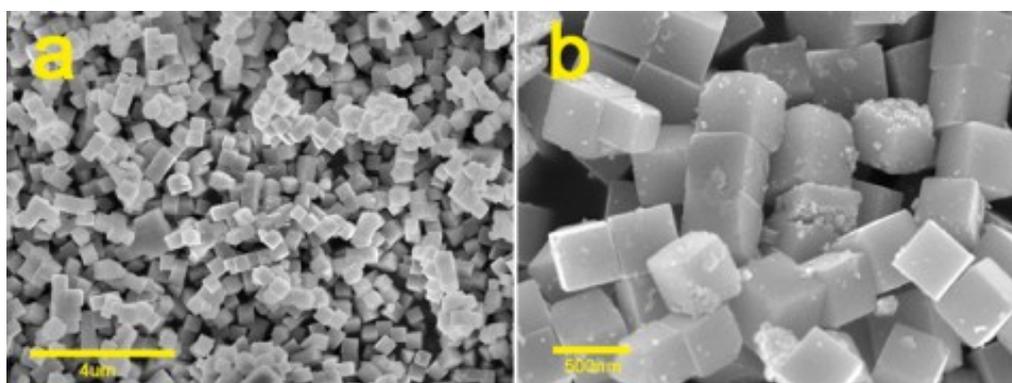
Figure S9 SEM images of PB after annealing
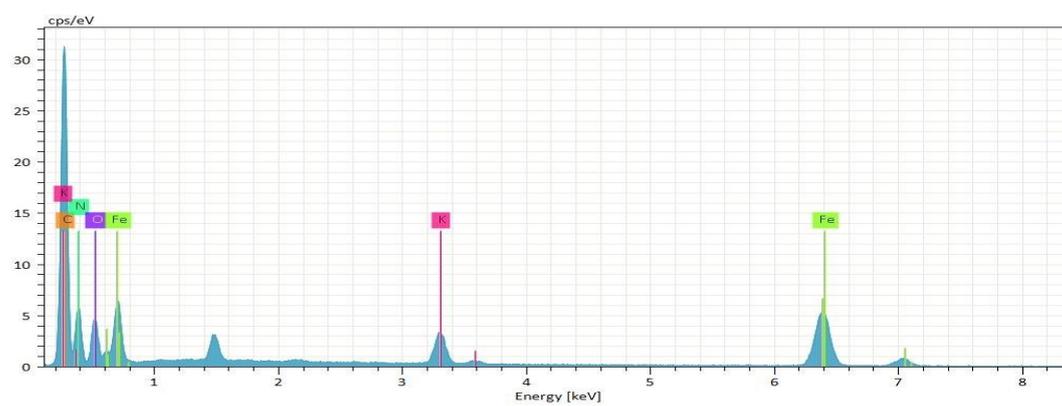
Figure S10 EDX spectrum of PB

1. L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng and X. W. Lou, *Journal of the American Chemical Society*, 2012, **134**, 17388-17391.