Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2020

# **Supporting Information**

# Design Principles of Pseudocapacitive Carbon Anode Materials for Ultrafast Sodium and Potassium-ion Batteries

Yong Gao<sup>a</sup>, Jing Zhang<sup>a</sup>, Nan Li<sup>a</sup>, Xiao Han<sup>a</sup>, Xian Luo<sup>a</sup>, Keyu Xie<sup>a</sup>, Bingqing Wei<sup>b</sup>, and Zhenhai Xia\*<sup>c</sup>

<sup>a</sup>State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China
<sup>b</sup>Department of Mechanical Engineering, University of Delaware, Newark DE 19716, United States
<sup>c</sup>Department of Materials Science and Engineering, Department of Chemistry, University of North Texas, Denton, TX 76203, USA
E-mail: <u>Zhenhai.xia@unt.edu</u>

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#### 1. Supplementary Calculation Methods

#### 1.1 Gibbs free energy of potassium ions (K<sup>+</sup>) and sodium ions (Na<sup>+</sup>) adsorption

According to the surface-induced pseudocapacitive mechanism for storage of sodium ions in SIBs and potassium ions in KIBs, when electrons move to the effective site of anode surface under potential U, Na<sup>+</sup> or K<sup>+</sup> in electrolyte are chemisorbed on active sites of anode surface, combining with the electrons. Therefore, this anode reaction for charging process in KIBs and SIBs can be expressed as

$$C^{+} + e^{-} + * \stackrel{Charging}{\rightleftharpoons}_{Discharging} C^{*}$$
(S1)

where \* represents the effective K<sup>+</sup> or Na<sup>+</sup> storage sites on the surface of the electrode and C<sup>+</sup> is the cation in electrolyte such as K<sup>+</sup> in 6M KOH and Na<sup>+</sup> in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The change of Gibbs free energy  $\Delta G$  before and after chemical reaction for Eq. S1 was given by  $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + \Delta G_U$  (S2)

where  $\Delta ZPE$  is the change of zero-point energy (ZPE) upon potassium (K) or sodium (Na) ions chemisorption on graphene/doped graphene substrates and is calculated to be 0.0182 eV for K and 0.023 eV for Na, respectively using DFT calculation.  $\Delta G_{U}=-eU$ , where U is the potential at the electrode, and e is the charge of electron.  $\Delta G_{pH}$  is the correction of H<sup>+</sup> free energy by the concentration dependence of the entropy. For alkaline environment such as 6 M KOH, the term  $\Delta G_{pH} = -k_BTln[H^+] = 0.828 eV$  and the term  $\Delta G_{pH} = -k_BTln[H^+] = 0.4166 eV$ . Also,  $\Delta E(K) = E(K^*) - E(*) - E(K)$  (S3a)

and

$$\Delta E(Na) = E(Na^*) - E(*) - E(Na)$$
(S3b)

where  $E(K^*)$  and  $E(Na^*)$  are the total energy of graphene substrates with K and Na adsorption, respectively, E(\*) is the total energy of a clean graphene surface and E(K) and E(Na) are the energies for a single potassium and sodium atom, respectively, and are calculated to be -1.0949 eV for K and -1.305 eV for Na in terms of the total energy of bulk potassium and sodium metal.

Based on the fact that the vibrational entropy in the adsorbed state is small, the entropy of adsorption of a potassium atom is  $\Delta S_K \approx -S_K^0$ , where  $S_K^0$  is the entropy of K<sup>+</sup> in the aqueous phase at the standard conditions and obtained to be 102.5 J mol<sup>-1</sup> K<sup>-1</sup>. Also,  $\Delta S_{Na} \approx -S_{Na}^0$ , where  $S_{Na}^0$  is the entropy of Na in the solid/liquid phase at the standard conditions and obtained to be 51.3 J

mol<sup>-1</sup> K<sup>-1</sup>. Thus,  $-T\Delta S_K$  and  $-T\Delta S_{Na}$  are equal to 0.319 eV and 0.160 eV, respectively, at T =

300 K. Accordingly, the change of Gibbs free energy  $\Delta G_{K^*}$  is given by

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_{pH} + \Delta G_U = \Delta G_{C*} + eU$$
(S4)

$$\Delta G = \Delta G_{C*} + eU \tag{S5}$$

$$\Delta G_{C*} = \Delta G_{K*} = \Delta E(K) + 1.1652 \tag{S6}$$

$$\Delta G_{C*} = \Delta G_{Na*} = \Delta E(Na) + 0.5996 \tag{S7}$$

In addition, with the increase of  $Na^+$  or  $K^+$  adsorbed on substrates, the external electric potential required for overcoming the potential barrier U, as a function of the number of  $K^+$  or  $Na^+$  chemisorbed on the surface of anode, is defined as

$$U = \left| \frac{\Delta G_{C*}}{ne} \right| \tag{S8}$$

Here, *n* is the number of  $K^+$  or  $Na^+$  chemisorbed on substrates, and *e* is the charge carried an electron.

#### **1.2 Energy density** ( $E_A$ or $E_{0/site}$ )

With the chemisorption of cations (K<sup>+</sup> and Na<sup>+</sup>) at active sites on electrodes, electric energy is stored in supercapacitors. For heteroatom-doped graphene electrode, the adsorption energy of a cation  $\Delta G_{C*}$  at different sites is different due to the doping effect. The lowest adsorption energy  $\Delta G_{C*}^{min}$ , of the absorbed cations that are able to desorb in discharging process must be positive while the highest one  $\Delta G_{C*}^{max}$ , should be equal to the free energy of phase transition  $\Delta G_T$  (i.e.,  $\Delta G_{C*}^{max} = \Delta G_T$ ). For a cation with chemical adsorption energy  $\Delta G_{C*}^{i}$ , the contribution of the cation to electric energy of supercapacitor is given by

$$E_{i} = \Delta G_{C*}^{i} \qquad (\Delta G_{C*}^{min} < \Delta G_{C*}^{i} < \Delta G_{C*}^{max} = \Delta G_{T} \text{ and } i = 1, 2, 3 \cdots)$$
(S8)

Assuming that the absorbing sites on electrode can be divided into N groups, each of which contains  $p_i$  active sites with the chemical adsorption energy and under cations coverage  $\theta_i$ , the total electric energy stored on the electrode can be expressed by<sup>[S1]</sup>

$$E_N = \sum_{i=0}^{N} \Delta G_{C*}^{\ i} p_i \theta_i \tag{S9}$$

where the number of the total sites of electrode surface M should be  $M = p_0 + p_1 + ... p_N$ . Therefore, the energy density, or electric energy stored on unit site  $E_{0/site}$  (unit, eV site<sup>-1</sup>), is given by

$$E_{0/site} = \frac{E_N}{M} = \frac{1}{M} \sum_{i=0}^{N} \Delta G_{C^*}^{\ i} p_i \theta_i$$
(S10)

Now, assuming that  $\Delta G_{C*}^{i}$ , increases from the minimum to the maximum with a very small increment *dG*, the chemical adsorption energy  $\Delta G_{C*}^{i}$ , can be given by<sup>[S1]</sup>

$$\Delta G_{C*}^{\ i} = \Delta G_{C*}^{\min} + \frac{i}{N} (\Delta G_{C*}^{\max} - \Delta G_{C*}^{\min})$$
(S11)

The coverage in Eq. S9 is related to the equilibrium constant  $K_i$  by

$$\theta_i = \frac{K_i}{1 + K_i} \tag{S12}$$

Thus,  $K_i$  can be associated with chemical adsorption energy by

$$K_i = e^{-\frac{\Delta G_C^i * (U)}{k_B T}}$$
(S13)

where  $\Delta G_{C^*}^i(U) = \Delta G_{C^*}^i - eU_{.}$ 

Thus, combining Eqs. S12-S13 yields

$$\theta_i = \frac{1}{\frac{\Delta G_C^i \cdot eU}{k_B T}}$$
(S14)

Assuming the number of sites  $p_i$  at each energy level is the same ( $p_i = M/N$ ), and combining Eqs. S10-S12 and S14, we have the energy density per site  $E_{0/site}$  (unit, eV site<sup>-1</sup>)

$$E_{0/site} = \frac{1}{N} \sum_{i=0}^{N} \Delta G_{C^{*}}^{i} \frac{1}{1 + e^{\frac{\Delta G_{C^{*}}^{i} - eU}{k_{B}T}}}$$
(S15)

or

$$E_{0/site} = \frac{1}{(\Delta G_{C*}^{max} - \Delta G_{C*}^{min})} \int_{\Delta G_{C*}^{min}}^{\Delta G_{C*}^{max}} \frac{x dx}{1 + e^{\frac{x - eU}{k_B T}}}$$
(S16)

$$E_{0/site} = 2.53E_A \tag{S17}$$

where  $E_A$  is the area specific energy (unit, J m<sup>-2</sup>), the geometric area of single carbon atom in graphene is calculated to be  $2.64 \times 10^{-20}$  m<sup>2</sup> and a hollow site includs 2.4 carbon atooms. Eq. S16 is a general expression, and it can be divided into three types according to the external electric potential *U* as follows.

1) For  $eU = \Delta G_{C*}^{max} = \Delta G_T$ , all the active sites are covered and thus the total coverage  $\theta = 1$ . The capacitor reaches its maximum capacity. Eq. S16 becomes

$$E_{0/site} = \frac{1}{2} (\Delta G_{C*}^{min} + \Delta G_{C*}^{max})$$
(S18)

This is the transition state for pseudocapacitive mechanism to metal battery-based charge storage mechanism.

2) For 
$$\Delta G_{C*}^{min} < eU < \Delta G_{C*}^{max} = \Delta G_T$$
, Eq. S16 can be given by  

$$E_{0/site} = \frac{eUk_BT}{eU - \Delta G_{C*}^{min}} ln \left[ \frac{1}{2} \left( 1 + e^{\frac{eU - \Delta G_{C*}^{min}}{k_BT}} \right) \right] - \frac{\frac{1}{2} (\Delta G_{C*}^{min} - eU)^2}{\Delta G_{C*}^{max} - \Delta G_{H*}^{min}} - \frac{k_BT (\Delta G_{C*}^{max} - eU + k_BT)}{(\Delta G_{C*}^{max} - eU + k_BT)} + \frac{(k_BT)^2}{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}}$$
(S19)

According to Eq. S19, energy density  $E_{0/site}$  can be enhanced by reducing the minimum adsorption  $\Delta G_{C*}^{min}$  or increasing the external electric potential U.

3) For  $eU < \Delta G_{C*}^{min}$ , none of the sites could absorb cations (Na<sup>+</sup> and K<sup>+</sup>), and therefore the energy density  $E_{0/site} = 0$ .

#### 1.3 Specific capacitance ( $C_A$ or $C_{0/site}$ )

Following the formula of electric energy stored in a capacitor ( $E=Q^2/2C$ ), and combining the energy density derived in Section 1.2, the total capacitance  $C_T$ , the capacitance per unit charge storage site  $C_{0/site}$  (unit, e V<sup>-1</sup> site<sup>-1</sup>) and the area specific capacitance  $C_A$  (unit, F m<sup>-2</sup>) of heteroatom-doped graphene supercapacitor can be calculated, respectively, by<sup>[S1]</sup>

$$C_{T} = \frac{\left(\sum_{i=0}^{N} p_{i}\theta_{i}e\right)^{2}}{2E_{N}} = \frac{\left(\frac{M}{N}e\sum_{i=0}^{N}\theta_{i}\right)^{2}}{2ME_{0/site}} = \frac{Me^{2}\left(\frac{1}{N}\sum_{i=0}^{N}\theta_{i}\right)^{2}}{2E_{0/site}}$$
(S20)

Thus, combining with Eq.S16 we have

$$C_{0/site} = \frac{C_T}{M} = \frac{e^2 \left(\frac{1}{N} \sum_{i=0}^{N} \theta_i\right)^2}{2E_{0/site}} = \frac{e^2 \left(\frac{1}{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}} \int_{\Delta G_{C*}^{min}} \frac{dx}{1 + e^{\frac{x - eU}{k_B T}}}\right)^2}{\frac{2}{(\Delta G_{H*}^{max} - \Delta G_{H*}^{min})} \int_{\Delta G_{C*}^{min}} \frac{dx}{1 + e^{\frac{x - eU}{k_B T}}}}$$
(S21)
  
(S21)
  
(S21)

$$C_{0/site} = 2.53C_A \tag{S22}$$

As mentioned above, the specific capacitance can also be classified into three cases:

1) For  $eU = \Delta G_{C*}^{max} = \Delta G_T$ , the coverage  $\theta$  is equal to 1, combining Eq. S18 with Eq. S21 yields

$$C_{0/site} = \frac{C_T}{M} = \frac{e^2 \left(\frac{1}{N} \sum_{i=0}^{N} \theta_i\right)^2}{2E_{0/site}} = \frac{e^2}{\Delta G_{C*}^{min} + \Delta G_{C*}^{max}}$$
(S22a)

This is the upper limit capacitance the capacitor could achieve. With decreasing the adsorption energy  $\Delta G_{C*}^{min}$ , the specific capacitance  $C_{0/site}$  increases. Since doping can reduce  $\Delta G_{C*}^{min}$ , it enhances the capacitance of the pseudocapacitors.

2) For  $\Delta G_{C*}^{min} < eU < \Delta G_{C*}^{max} = \Delta G_T$ , combining Eq. S16 with S19 and S21, we have the specific capacitance

$$C_{0/site} = \frac{e^{2} \left(\frac{1}{N} \sum_{i=0}^{N} \theta_{i}\right)^{2}}{2E_{0/site}} = \frac{\frac{1}{2} e^{2} \left[1 - \frac{k_{B}T}{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}} ln \left(\frac{1 + e^{\frac{\Delta G_{C*}^{max} - eU}{k_{B}T}}{\frac{1}{2} e^{2} \left(1 + e^{\frac{eU - \Delta G_{C*}^{min}}{k_{B}T}}\right)\right]^{2}}{\frac{1}{2} \left(\frac{1 + e^{\frac{eU - \Delta G_{C*}^{min}}{k_{B}T}}}{\frac{1}{2} \left(1 + e^{\frac{eU - \Delta G_{C*}^{min}}{k_{B}T}}\right)\right)^{2} - \frac{\frac{1}{2} (\Delta G_{C*}^{min} - eU)^{2}}{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}} - \frac{k_{B}T (\Delta G_{C*}^{max} - eU + k_{B}T)}{\frac{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}}{k_{B}T}} + \frac{(k_{B}T)^{2}}{\Delta G_{C*}^{max} - \Delta G_{C*}^{min}}}$$
(S22b)

In this case, the specific capacitance will increase with the reducing  $\Delta G_{C*}^{min}$  due to the fact that smaller barriers are need to overcome in charge storage.

3) For  $eU < \Delta G_{C*}^{min}$ , none of the sites can store protons, and therefore the specific capacitance,  $C_{0/site=0}$ .

#### **1.4 Power density** ( $P_{0/site}$ or $P_A$ )

Power density of a capacitor is defined as the change of energy per unit time, which involves charging/discharging time. The power density, or charging rate, is govern by both conductivity determining the number of electrons reaching the charge storage sites on the surface of electrode and energy barrier to be overcome for chemisorption of a cation C<sup>+</sup> on the site. For given external condition such as ohmic resistance or conductivity, chemisorption rate on site (or chemical reaction rate) would dominate the charging/discharging rate or the power density. Therefore, its power density per unit site is directly related to the chemical reaction rate. Using the similar procedure <sup>[S1]</sup>, the power density can be derived and related to the doping sites.

The forward reaction rate of Eq. S1 can be given by

$$r_i = k_i(U) \left(1 - \theta_i\right) c_{C^+}$$
(S23)

where  $k_i(U)$  and  ${}^{c}c^+$  are the rate constant and the concentration of cations namely Na<sup>+</sup> or K<sup>+</sup>, respectively, and  $\theta_i$  is the coverage of *i*-th cation. For  $\Delta G_{C*}^{i} > 0$  (endothermic process for cation adsorption), the rate constant  $k_i(U)$  in Eq. S23 is given by

$$k_i(U) = k_0 K_i \tag{S24}$$

Here,

$$K_i = \frac{\theta_i}{1 - \theta_i} = e^{-\frac{\Delta G(U)}{k_B T}}$$
(S25)

Thus, combining Eqs. S23-S25, the forward rate of Eq. S1 can be rewritten as

$$r_i = k_0 \theta_i \tag{S26}$$

where  $C_{Na+}=1$  and  $C_{K+}=12$ .

The current  $I_i$  resulting from per added or adsorbed a cation is then expressed by

$$I_i = er_i \tag{S27}$$

where *e* is the charge of an electron and  $r_i$  (unit, s<sup>-1</sup>site<sup>-1</sup>) is the forward rate of Eq. S1. On the other hand, the current *I*, can also be defined as

$$I_i = \frac{Q}{t_i} = \frac{e}{t_i} \tag{S28}$$

Finally, combining Eqs. S26-S28, we have the time taken for storing a cation on a graphene site,

$$t_i = \frac{1}{r_i} \tag{S29}$$

In addition, we assume that these charge storage sites with the same cation adsorption energy  $\Delta G_{C*}^{i}$  need the same time  $t_i$  in the charging process. Thus, the total time *t* required for a complete charging process is given by

$$\begin{split} t &= t_1 + t_2 + \dots + t_N = \frac{1}{r_1} + \frac{1}{r_2} + \dots + \frac{1}{r_N} = \frac{1}{k_0 \theta_1} + \frac{1}{k_0 \theta_2} + \dots + \frac{1}{k_0 \theta_N} = \frac{1}{k_0} \left( \frac{1}{\theta_1} + \frac{1}{\theta_2} + \dots + \frac{1}{\theta_N} \right) \\ &= \frac{1}{k_0} \left[ \left( 1 + e^{\frac{\Delta G_{C^*}^1 - eU}{k_B T}} \right) + \left( 1 + e^{\frac{\Delta G_{C^*}^2 - eU}{k_B T}} \right) + \dots + \left( 1 + e^{\frac{\Delta G_{C^*}^N - eU}{k_B T}} \right) \right] \end{split}$$

$$=\frac{\frac{N}{k_0}\int_{\Delta G_{C*}^{min}}^{\Delta G_{C*}^{max}}(1+e^{\frac{x-eU}{k_BT}})dx}{\Delta G_{C*}^{max}-\Delta G_{C*}^{min}}$$
(S29a)

Hence, the average charging time  $\bar{t}$ , required to storage a charge or cation, can be expressed approximately by

$$= t = \frac{\frac{N}{k_0} \int_{\Delta G_{C*}^{max}}^{M} (1 + e^{\frac{x - eU}{k_B T}}) dx}{M(\Delta G_{C*}^{max} - \Delta G_{C*}^{min})} = \frac{\frac{1}{k_0} \int_{\Delta G_{C*}^{min}}^{\Delta G_{C*}^{max}} (1 + e^{\frac{x - eU}{k_B T}}) dx}{M - \Delta G_{C*}^{max} - \Delta G_{C*}^{min}}$$
(S29b)
$$\frac{M}{M} = p$$

As mentioned above,  $\overline{N}^{-\nu}$  is a constant. Here, because it does not affect the trend of time change, it can be neglected.

Finally, combining Eqs. S23-S29, the power per charge storage site  $P_{0/site}$  (unit, eV site<sup>-1</sup> s<sup>-1</sup>) and area specific power  $P_A$  (unit, J m<sup>-2</sup> s<sup>-1</sup>) can be written as

$$P_{0/site} = \frac{E_{0/site}}{\bar{t}} = \frac{\sum_{0/site}^{\Delta G_{C*}^{max}} \frac{x \, dx}{1 + e^{\frac{x - eU}{k_B T}}} dx}{\frac{1}{k_0} \int_{\Delta G_{C*}^{max}}^{\Delta G_{C*}^{max}} (1 + e^{\frac{x - eU}{k_B T}}) dx}$$
(S30a)

$$P_{0/site} = 2.53P_A \tag{S30b}$$

It is worth noting that the rate constant  $k_0$ , as an unique unknown quantity in Eq. S30a is closely related to the whole process of cation transportation to electrode surface and recombination with electrons at charge storage sites.

For charging rate, considering only the case of  $\Delta G_{C*}^{min} < eU < \Delta G_{C*}^{max} = \Delta G_{T, \text{ thus Eq. S30a}}$  becomes

$$eUk_{B}Tln\left[\frac{1}{2}\left(1+e^{\frac{eU-\Delta G_{C*}^{min}}{k_{B}T}}\right)\right] - \frac{1}{2}(\Delta G_{C*}^{min} - eU)^{2} - \frac{k_{B}T\left(\Delta G_{C*}^{max} - eU + k_{B}T\right)}{\frac{\Delta G_{C*}^{max} - eU}{k_{B}T}} + (k_{B}T)^{2} - \frac{e^{\frac{\Delta G_{C*}^{max} - eU}{k_{B}T}}}{e^{\frac{\Delta G_{C*}^{max} - eU}{k_{B}T}}}$$

(S30c)

According to Eq. S30c, the charging rate will increase with decreasing of  $\Delta G_{C*}^{min}$ , or the increasing the external electric potential U. In particular, power density  $P_{0/site}$  is very sensitive to the external electric potential U.

# 2. Supplementary Figures 1-10



**Fig. S1** (a) Graphene sheet model, graphene nanoribbon models with (b) armchair and (c) zigzag edge and adsorption sites on graphene models for sodium (Na) and potassium (K) atoms. The green, while, yellow and purple balls in these graphene structures represent C, H, Na and K, respectively.



Fig. S2 Investigated possible charge storage sites and corresponding the change of Gibbs free energy ( $\Delta G_{K^*}$ ) upon adsorbing a potassium (K<sup>+</sup>) chemically on hollow sites (d) of (a) g-C, (b) z-C and (c) a-C graphene model. The possible charge storage sites investigated by us are indicated by Arabic numerals in different colors, and red represents the optimal charge storage site obtained by comparing the change of free energy of all possible sites. The green, while, yellow and purple balls in these graphene structures represent C, H, Na and K, respectively. (This marking and naming methods is the same in the following Supplementary Figs.).



Fig. S3 Investigated possible charge storage sites and corresponding the change of Gibbs free energy ( $\Delta G_{Na^*}$ ) upon adsorbing a sodium (Na<sup>+</sup>) chemically on hollow sites (d) of (a) g-C, (b) z-C and (c) a-C graphene model. The green, white and yellow balls in these graphene structures represent C, H and Na, respectively.



**Fig. S4** Investigated possible charge storage sites and corresponding the change of Gibbs free energy ( $\Delta G_{K^*}$ ) upon adsorbing a potassium (K<sup>+</sup>) chemically on (a) g-N, (b) pr-N, (c) py-N, (d) N-O, (d) py-N-site-4, and (f) N-O-site-2 graphene model. The green, while, blue, red and purple balls in these graphene structures represent C, H, N, O and K, respectively. py-N-site-4 represents such model where site 4 of py-N model adsorb spontaneously a potassium to form new stable structure according to negative value of  $\Delta G_{K^*}$  on site 4.



**Fig. S5** Distribution of change of Gibbs free energy ( $\Delta G_{Na^*}$ ) for (a) armchair graphene, (b) pr-N graphene nanoribbons, (c) g-N, and (d) B-3C graphene nanosheets, respectively. Green, while, blue and pink balls in these graphene structures represent C, H, N and B, respectively.



Fig. S6 (a) Doping structures with the different distance from dopant to edge. (b) Minimum chemical adsorption energy  $\Delta G_{K*}^{min}$  versus the distance from dopant to edge for K adsorption. The green, while, blue, red and purple balls in these graphene structures represent C, H, N, O and K, respectively.



**Fig. S7** Illustration of discharge profiles with combined capacitive and diffusion-controlled processes and pure capacitive-controlled process (inset).<sup>[S2]</sup>



**Fig. S8** Configurations of adsorbed ions versus the number of Na chemisorbed on B-3C graphene substrate. The number from 1 to 12 refers to the number of ions deposited on the surface of the graphene. The light black, green and yellow balls in these graphene structures represent C, B and Na, respectively.



**Fig. S9.** Anode design diagram of SIBs and KIBs based on bottom-up method. (a) configuration of SIBs or KIBs with 3D-doped carbon anode material. 3D carbon electrode material from doped carbon materials: (b) carbon nanotube-pillared graphene, (c) C60-graphene complex, and (d) wrinkled graphene structures.



**Figure S10.** Energy per unit site versus minimum K adsorption energy  $\Delta G_{K*}^{min}$  at a given potential of U=0.8 and 1.0 V.

**3. Supplementary Tables 1-7 Tables S1.** Overview of different types of storage charge mechanism for sodium ion batteries (SIBs)

	Charge storage mechanism	Features indicative of mechanism	Advantages	Disadvantages	Representative anode materials	Respective characteristics	Comments
Ion diffusion- controlled materials	Intercalation	In general, this is a process controlled by interlayer distance and ion size. Upon ions overcoming van der Waals intercalation pressure of interlayer to enter gap, with increase of intercalated Na+ ions, the structure of intercalation compounds will change. Commonly, Na+ ions between interlayer has lower energy than that of Na+ on surface due to larger contact area between interlayer <sup>[S3]</sup> .	High cycle stability	Low sodium ion storage capacity	Nature graphite <sup>[S4]</sup> , Expanded graphite <sup>[S5]</sup>	For the three charge storage mechanisms, phase transition even multistage phase transition will occur with increase of sodium ion storage. Gibbs phase rule can be used to determine whether charge/discharge can occur at	Conclusively , for any electrode materials of Na+ ions storage, their charge storage mechanism
	Conversion	In general, it is a multistep chemical reactions or multistage phase transition process to finally achieve theoretical maximum amount of Na+ ions storage.	High initial sodium ion storage capacity	Huge volume change leading to pulverization of electrode, lower rate performance resulting from high reaction overpotential	SnS2 <sup>[86]</sup> , FeSe2 <sup>[87]</sup> , MoS2/Graphene <sup>[88]</sup>	constant voltage. Of course, charge/discharge voltage can also be influenced by other factors such as polarization,	
	Alloying	Generally, these elements in groups IVA and VA can react with Na+ to form metal compounds. In theory, the more combination should be based on stoichiometric ratio.	High capacity	Lower rate performance	$\begin{array}{c} Ge \ (NaGe)^{[59]}, \\ Sn \\ (Na_{15}Sn_4)^{[510]}, \\ Pb \\ (Na_{15}Pb_4)^{[511]}, \\ Sb \ (Na_3Sb)^{[512]}, \\ P(Na_3P)^{[513]} \dots \end{array}$	filling of nanopore and so forth.	is almost not one, but several combinations . From the perspective of electrode design,
	Intercalation pseudocapacitive process	Charge storage does not occur on the surface but in the bulk material. The kinetics are not diffusion- limited and instead are limited by surface processes so that the overall behaviour seems capacitive <sup>[13]</sup> .			$TiO_{2}/graphene$ [S14], Nb <sub>2</sub> O <sub>5</sub> [S15]	Despite the distinction between intrinsic and non-intrinsic capacitive materials they	combining the merits of ion diffusion- controlled materials and capacitive process- controlled materials is the goal that it has achieved some successful experiences.
Capacitive process- controlled materials	Redox pseudocapacitive process	Charge storage does occur on the surface by reversible redox reaction.	High rate performance and superior cyclability.	Lower capacity	MoS <sub>2</sub> nanoflowers <sup>[S16]</sup> , RuO <sub>2</sub> <sup>[S17]</sup> , Nanocellular carbon foam (NCCF) papers <sup>[S18]</sup> , FeSe <sub>2</sub> microspheres <sup>[S7]</sup>	all exhibit capacitive properties, i.e. excellent charge- discharge efficiency and cycle stability. In addition, constant voltage	
	Underpotential pseudocapacitive process Electrical double layer (EDLC)	Charge storage does occur on the surface by reversible chemical adsorption/desorption. Charges are stored by electrostatic attraction on			N-doping graphene <sup>[S19]</sup> Porous	region is impossible for such capacitive process.	
Others	process Metal nanopore filling(nanoplating )	surface of electrode.	High cycle stability and capacity		Porous graphene networks (PGN) [S21]		

**Tables S2.** Summary of different types of heteroatom-doped carbon-based materials as anodes for sodium ion batteries (SIBs)

Dopants	Materials	Potential Range (V vs. Na <sup>+</sup> /Na)	Current Densities (mAg <sup>-1</sup> )	Capacity (mAhg <sup>-1</sup> )	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Width of interlayer gap (Å)	Main components of electrolyte	Mechanism (focusing on intercalation mechanism)	Ref.
В	<sup>a)</sup> BF-rGO	0.001-2	20	280	281	3.7	NaClO <sub>4</sub>	<ol> <li>enlarged interlayer spacing;</li> <li>more active sites resulting from the incorporation of B and O into rGO;</li> <li>2D structure shortening the Na<sup>+</sup> diffusion distance.</li> </ol>	S22
		0.001-2	20	200/1.0	034	5.4		1) F-doping: 2) large interlayer	
F	°)F-CP	0.001-2.8	50	230	46.4	4	NaClO <sub>4</sub>	distance; 3) disorder structure; 4) high electronegativity of F ( $\chi$ =3.98 higher than $\chi$ =2.55 for carbon) These contribute to a lowering of the sodium ion insertion-extraction barrier, thus promoting the Na <sup>+</sup> diffusion and providing more active sites for Na <sup>+</sup> storage.	S23
	<sup>d)</sup> BPC	0.001-2.8	50	149	763.3	4	NaClO <sub>4</sub>		
N	°)G-NCs	0.01-3	50	329	133.8	-	NaClO <sub>4</sub>	Benefiting from the synergistic effect of nitrogen-doped carbon and graphene, the G-NCs electrode possesses a high capacitive charge storage, which contributes to the fast sodium ion storage and superior cycle stability.	S24
	<sup>f)</sup> NC	0.01-3	50	250	73	-	NaClO <sub>4</sub>		
	<sup>g)</sup> G	0.01-3	50	300	-	-	NaClO <sub>4</sub>		
	<sup>h)</sup> rG	0.02-3	100	406.2	226	-	NaPF <sub>6</sub>		
	<sup>i)</sup> N-G	0.02-3	100	707.4	235	3.41	NaPF <sub>6</sub>		
	<sup>j)</sup> 3D-rGF	0.02-3	100	809.4	346	3.41	NaPF <sub>6</sub>		
N	<sup>k)</sup> 3D-N-rGF	0.02-3	100	1057.1	357	3.42	NaPF <sub>6</sub>	The observed superb to synergistic effects associated with the 3D mesoporous structure with a well-defined porosity, large surface area, and enlarged lattice spacing between graphene layers, coupled with the N-doping-induced defects and additional sites, to facilitate the diffusion of large-size sodium ions, enhance the storage of sodium ions, and minimize the effect of volume expansion during discharge-charge processes.	825
	<sup>1)</sup> NHCSs	0.005-3	50	334	182.6	3.87	NaClO <sub>4</sub>	The unique nitrogen-containing hollow carbon structure	
N	<sup>m)</sup> HCSs	0.005-3	50	163	-	-	NaClO <sub>4</sub>		S26
Р	<sup>n)</sup> P-CNSs	0.01-3	100	328	549.8	4.2	NaClO <sub>4</sub>	1) more active sites and short Na+ diffusion distance originated	S27

								from the ultrathin nanosheet and large surface area; 2) the enlarged interlayer space (4.2 Å), which can facilitate the insertion/extraction Na+; 3) the altered electronic state caused by the P-doping, which is beneficial to the adsorption of electrolyte ions.	
S	°) SC	0.01-2	100	482	39.8	3.9	NaClO <sub>4</sub>	The present work indicates that larger interlayer distance and low specific surface area are desirable to achieve high performance for the carbonaceous anode materials of SIBs	S28
	<sup>p)</sup> NC	0.01-2	-	-	139	3.6	NaClO <sub>4</sub>		
S	4) SGCNs	0.01-3	100	321.8	666.6- 898.8	3.8-4.1	NaClO4	Large reversible capacity is due to the expanded interlayer spacing of the carbon materials resulted from the S-doping, and superior rate capability is ascribed to the fast surface- induced capacitive behavior derived from its high surface area.	S29
S	r) SG	0.001-3	100	262	280	3.48	NaPF <sub>6</sub>	Unique nanoporous structure stemmed from the chemically S doping and larger interlayer gap spacing	S30
S	s) DC-S	0.01-3	20	516	117.3	3.66	NaPF <sub>6</sub>	Benefiting from the high sulfur doping level and the unique 3D coral-like structure, the as- prepared sulfur-doped carbon exhibits high reversible Capacity.	S31
	<sup>t)</sup> DC	0.01-3	20	126	14.8	3.62	NaPF <sub>6</sub>		1
N-S	<sup>u)</sup> NSC-SP	0.01-3	500	150	-	4.1	NaClO <sub>4</sub>	The first-principle calculations revealed that the expanded interlayer, defects and the doped N/S heteroatoms could not only favor the adsorption of Na-ion but also reduce its diffusion barrier and enhance its electronic conductivity, leading to the fast sodium storage in NSC-SP	S32
	v) C-SP	0.01-3	500	60	-	3.7	NaClO <sub>4</sub>		]
	w) NC-SP	0.01-3	500	115	-	-	NaClO <sub>4</sub>		
	x) SC-SP	0.01-3	500	90	-	-	NaClO <sub>4</sub>		
	y) HCS	0.01-3	500	120	503.6	3.88	NaClO <sub>4</sub>		
	z) N-HCS	0.01-3	500	150	499.7	3.89	NaClO <sub>4</sub>		
N-S	<sup>a1)</sup> NS-HCS	0.01-3	500	180	486.5	4.01	NaClO <sub>4</sub>	Nitrogen doped on the carbon surface predominantly alters the surface charge distribution, which is beneficial for capacity enhancement; sulfur doping changes the carbon structure and increases the carbon layer distance, which facilitates the sodium ion de-insertion/insertion process.	\$33

N-S	<sup>b1)</sup> S-N/C	0.01-3	50	350	379.4	3.82	NaClO4	The high capacity observed for S-N/C is attributed to S doping with enlarged interlayer distance and surface area to facilitate the insertion and diffusion of Na+, and to enhance the storage of Na+ by Faradaic reactions with tightly bound S.	S34
	<sup>c1)</sup> N/C	0.01-3	50	270	142.6	3.47	NaClO <sub>4</sub>		]
	d1) CM	0.05-2	100	305	431.7	5-10	NaClO <sub>4</sub>		
N-P	<sup>e1)</sup> NPCM	0.05-2	100	220	36.8	-	NaClO <sub>4</sub>	Excellent performance is attributed to synergetic effects of N, P co doping and porous structure for carbon spheres.	S35
N	<sup>fi)</sup> FN-CNFs	0.01-2	200	134	81.7	3.69	NaPF <sub>6</sub>	The superior performance can be attributed to N-doped sites and functionalized groups, which are capable of capturing sodium ions rapidly and reversibly through surface adsorption and surface redox reactions	S36

<sup>a)</sup> Boron-functionalized reduced graphene oxide (BF-rGO); <sup>b)</sup> Pure reduced graphene oxide(rGO); <sup>c)</sup> Fluorine-doped carbon particles (F-CP); <sup>d)</sup> Banana peels-derived carbon (BPC) resulting from carbonization of banana peels; <sup>e)</sup> Graphene-based nitrogen-doped carbon sandwich nanosheets(G-NCs); <sup>f)</sup> Nitrogen-doped carbon (NC); <sup>g)</sup> Graphene; <sup>h)</sup> Reduced graphene(rG); <sup>i)</sup>N-doped graphene(N-G); <sup>j)</sup> 3D reduced graphene foams(3D-rGF); <sup>k)</sup> 3D N-doped graphene foams(3D-N-rGF); <sup>1)</sup> Nitrogen-containing hollow carbon microspheres (NHCSs); <sup>m)</sup> Hollow carbon microspheres (HCSs, nitrogen-free); <sup>n)</sup> P-doped carbon nanosheets (P-CNSs); <sup>o)</sup>S-doped carbon (SC); <sup>P)</sup> N-doped carbon(NC); <sup>q)</sup> S-doped graphitic curly carbon nanosheets(SGCNs); r) Sulfur-doped graphene(SG); <sup>s)</sup> sulfur-doped disordered carbon (designated as DC-S); <sup>t)</sup> disordered carbon microsphere (C-SP); <sup>w)</sup> N-doped carbon microspheres (NC-SP); <sup>x)</sup> S-doped carbon microspheres (NSC-SP); <sup>v)</sup> Undoped carbon microsphere (C-SP); <sup>w)</sup> N-doped carbon microspheres (NC-SP); <sup>x)</sup> S-doped carbon microspheres (NC-SP); <sup>x)</sup> Hollow carbon sphere (HCS); <sup>z)</sup>N-doped hollow carbon sphere (N-HCS); <sup>a1)</sup> NS-codoped hollow carbon sphere (SNHCS); <sup>b1</sup> S-doped N-rich carbon nanosheets(S-N/C); <sup>c1)</sup> N-rich carbon nanosheets (N/C); <sup>d1)</sup> Carbon microspheres (CM), <sup>e1)</sup> N, P co-doped CM(NPCM); f1) Functionalized interconnected N-doped carbon nanofibers (FN-CNFs);

**Table S3** The crystal structure, lattice constant and lattice mismatch of Li, Na and K metals with graphene substrate. (the length of one carbon hexagon (2.478Å) along the graphene zigzag direction.)

Metal	Crystal structure	(110) spacing(Å)	п	$\delta = \frac{\begin{array}{c} \text{Lattice} \\ \text{mismatch} \\ s = \frac{a_s - n \times a_N}{a_N} \end{array}}{a_N}$	Ref.
Li		2.4815	1.0014	0.8%	S37
Na		3.034	1.2	2.44%	This work
K	8.320 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	3.762	1.5	1.82%	This work

**Table S4** Electron affinity and electronegativity of heteroatoms used to dope graphene structures and the optimal change of Gibbs free energy upon adsorbing a sodium atom (or a potassium atom) on the best site for these element-doped graphene models and corresponding structure for carbon-based anodes of SIBs and KIBs.

Doponto	Electron	Flootropogativity	Descriptor	ΔG <sub>Na*</sub>	ΔG <sub>K*</sub>	Optimal doping structure		
Dopants	(eV)	Electronegativity		(eV)	(eV)	Na	К	
C	1.2621	2.55	1.00	0.498	0.427	z-C	z-C	
В	0.2797	2.04	0.18	0.490	0.420	B-2C	B-2C	
Р	0.7466	2.19	0.51	0.272	0.310	P-2C	P-2C	
Sb	1.0474	2.05	0.68	0.250	0.280	py-Sb	py-Sb	
Si	1.3895	1.90	0.82	0.237	0.232	a-Si	a-Si	
N	1.4000	3.04	1.32	0.212	0.140	py-N	py-N	
0	1.4610	3.44	1.56	0.277	0.333	C=O	C=O	
S	2.0771	2.58	1.67	0.435	0.385	th-S-2O	th-S-2O	
Ι	3.0590	2.66	2.53	0.271	0.233	a-I	a-I	
Br	3.3636	2.96	3.09	0.372	0.316	z-Br	z-Br	
Cl	3.6127	3.16	3.55	0.416	0.347	z-Cl	z-Cl	
F	3.4011	3.98	4.21	0.472	0.394	z-F	z-F	

\* Here we used the absolute value of electron affinity for nitrogen. Source for electron affinity: <u>http://en.wikipedia.org/wiki/Electron\_affinity\_(data\_page)</u> Source for electronegativity: <u>http://en.wikipedia.org/wiki/Electroneegativity</u>

**Table S5** The optimal change of Gibbs free energy upon adsorbing a sodium atom on the best sites for these element-doped graphene models and capacity per charge storage site for carbon-based anodes of SIBs at U=0.7 V and KIBs at U=1.0V for the case of  $\Delta G_{c*}^{max} = 1.5 \ eV$ .

Donanta	Decovintor	$\Delta G_{Na^*}$	$\Delta G_{K^*}$	$C_{0/site}$ (eV <sup>-1</sup> site <sup>-1</sup> )		
Dopants	Descriptor	(eV)	(eV)	Na	K	
N-S	-	0.018	-	0.113	-	
F-N	-	-	0.128	-	0.212	
С	1	0.498	0.427	0.026	0.154	
В	0.18	0.490	0.420	0.027	0.155	
Р	0.51	0.272	0.310	0.067	0.179	
Sb	0.67	0.250	0.280	0.071	0.185	
Si	0.82	0.237	0.232	0.074	0.194	
Ν	1.32	0.212	0.140	0.078	0.210	
0	1.56	0.277	0.333	0.066	0.174	
S	1.67	0.435	0.385	0.037	0.163	
Ι	2.53	0.271	0.233	0.067	0.194	
Br	3.09	0.372	0.316	0.048	0.178	
Cl	3.55	0.416	0.347	0.040	0.171	
F	4.21	0.472	0.394	0.030	0.161	

**Tables S6.** Overview of different types of heteroatom-doped carbon-based materials as electrodes for sodium ion storage mainly based on capacitive charge storage mechanism.

Dopants	Materials	Potential Range (V vs. AgCl/Ag)	Current Densitie s (Ag <sup>-1</sup> )	Gravimetric capacitance (F g <sup>-1</sup> )	Surface area (m² g⁻¹)	Area specific capacitance (F m <sup>-2</sup> )	Normalized capacitance	Electrolyte	Ref.
N-S	<sup>1)</sup> GNRs	0-0.8	0.5	91	110	0.83	1	1 M Na <sub>2</sub> SO <sub>4</sub>	S38
	<sup>2)</sup> N-GNRs			289	245	1.18	1.42		
	<sup>3)</sup> S-GNRs			227	197	1.15	1.39		
	<sup>4)</sup> NS-GNRs			442	312	1.42	1.71		

<sup>1)</sup> Pristine graphene nanoribbons (GNRs); <sup>2)</sup> Nitrogen-doped graphene nanoribbons (N-GNRs); <sup>3)</sup> Sulfurdoped graphene nanoribbons (S-GNRs); <sup>4)</sup> Nitrogen-sulfur co-doped graphene nanoribbons (NS-GNRs);

**Tables S7.** Overview of different types of heteroatom-doped carbon-based materials as electrodes for  $K^+$  ion storage mainly based on capacitive charge storage mechanism.

Dopants	Materials	Potential Range (V)	Gravimetric capacitance (F g <sup>-1</sup> )	Surface area (m² g⁻¹)	Area specific capacitance (F m <sup>-2</sup> )	Normalized capacitance	Electrolyte	Ref.
	<sup>1)</sup> OMC	0.8.0 (113	117.8	620	0.19	1		
B	<sup>2)</sup> BMC-I	-0.8-0 (VS.	145.2	660	0.22	1.158	6M KOH	S39
	<sup>3)</sup> BMC-II	ng/ngO)	145.7	470	0.31	1.632		
D	<sup>4)</sup> OMCs	-1-0 (vs.	225.1	1257.8	0.18	1	6M KOH	
D	<sup>5)</sup> BOMC-0.02	Hg/HgO)	238.5	1157.0	0.21	1.167	ONI KUH	S40
	6)PC-800-2		336.0	1618	0.208	1		
р	<sup>7)</sup> PPC-700-2	-1-0 (vs.	308.0	1433	0.215	1.034	OU KOU	
P	PPC-800-2	Hg/HgO)	406.2	1581	0.257	1.236	OM KOH	S41
	PPC-900-2		265.4	1595	0.166	0.798		
	<sup>8)</sup> NCS		286	2779	0.103	1		
G	9)S-NCS-2	-1-0 (vs.	353	3022	0.117	1.136	ALVOU	
5	S-NCS-4	Hg/HgO)	405	3357	0.121	1.175		S42
	S-NCS-6		329	2935	0.112	1.087		
	10)PMC		169	304.3	0.555	1		
N	11)N-PMC	-1-0 (vs.	206	445.8	0.462	0.832	MKOU	
IN	12)PMNC	Hg/HgO)	192	494.7	0.388	1		S43
	13)N-PMNC		245	974.6	0.251	0.647		
	14)OMC		107	1127	0.095	1		
ND	<sup>15)</sup> N-OMC	-1-0 (vs.	148	1275	0.116	1.221	ALVOU	
IN-P	<sup>16)</sup> P-OMC	Hg/HgO)	162	2282	0.071	0.747	OM KOH	S44
	17)NP-OMC		210	1968	0.107	1.126		
D	<sup>18)</sup> T-rGO	-1-0 (vs.	135	50.4	2.679	1	OU KOU	
D	19)BT-rGO	Hg/HgO)	448	122.4	3.66	1.366	OM KOH	S45
	<sup>20)</sup> TRGO	0.0.0.1	75	355	0.211	1		
ND	<sup>21)</sup> N-TRGO	-0.9-0.1	82	234	0.35	1.659	ALVOU	
IN-P	<sup>22)</sup> P-TRGO	(vs.	131	215	0.61	2.89		S46
	23)N/P-TRGO	ng/ngO)	165	152	1.08	5.118		
N	<sup>24)</sup> PCS	-1-0 (vs.	339.9	2279	0.149	1	ALVOU	
IN	<sup>25)</sup> HPSCS	Hg/HgO)	407.9	2117	0.193	1.295	ONI KUH	S47
	<sup>26)</sup> MC-1.5-0		143	1147	0.125	1		
N	<sup>27)</sup> NMC-1.5-1	-1-0 (vs.	226	1573	0.144	1.152	ALVOU	C 10
IN	NMC-1.5-1.3	Hg/HgO)	229.4	1720	0.133	1.064		540
	NMC-1.5-2		229.7	1741	0.132	1.056		
	rGO-180		239	530	0.451	1		
	N-rGO-180		16	354	0.644	1.552		S49
N	GNS-700(10%O)	-1-0 (vs.	62	215	0.288	1.433	6M KOU	
	GNS-500(15%O)	Hg/HgO)	105	227	0.463	2.303	ONI KUH	
	GNS-400(18%O)		196	181	1.083	5.388		
	GNS-300(20%O)		226	97	2.330	11.592		

GNS-200(21%O)	261	72	3.625	18.035		
<sup>1)</sup> Ordered mesoporous carbon (OMC);	<sup>2)</sup> Boron-dop	ed mesopore	ous carbon v	with B conte	ent of I (BM	IC-I); <sup>3)</sup>
Boron-doped mesoporous carbon w	ith B content	of II (BMC-	II); <sup>4)</sup> 3D cub	ic-ordered n	nesoporous o	carbons
(OMCs); <sup>5)</sup> Boron-doped ordered me	soporous carl	oons (BOMC	Cs); <sup>6)</sup> Porous	s carbon(PC)	); 7) P-doped	porous
carbon(PPC); <sup>8)</sup> Nanoporous carbon	spheres (NCS	5); <sup>9)</sup> Sulfur d	loped nanopo	orous carbon	sphere (S-N	√CS); <sup>10)</sup>
Pomelo mesocarps-based carbon (P	MC); <sup>11)</sup> Nitro	ogen- doped	pomelo mes	ocarps-base	d carbon (N-	-PMC);
<sup>12)</sup> Pomelo mesocarps-based nano	sheet carbon	(PMNC); <sup>13)</sup>	Nitrogen-dop	bed pomelo	mesocarp	s-based
nanosheet carbon (N-PMNC); 14) O	rdered mesop	orous carbon	ns (OMC); 1:	5) N-doped o	ordered meso	oporous
carbons (N-OMC); 16) P-doped	ordered meso	porous carb	oons (P-OM	C); 17) N,	P-codoped	ordered
mesoporous carbons (NP-OMC);18	) Thermally r	educed grapl	hene oxide v	vithout boro	n oxide (T-r	:GO); <sup>19)</sup>
B-doped graphene nanoplatelets (BT	'-rGO); <sup>20)</sup> The	ermally redu	ced grapher	ne oxide (TR	(GO); 21) N	-doped
thermally reduced graphene oxid	e (N-TRGO)	; <sup>22)</sup> P-dope	d thermally	reduced g	raphene ox	ide (P-
TRGO); <sup>23</sup> N,P-codoped thermall	y reduced gi	aphene oxi	de (TRGO)	; 24) Poro	us carbon s	spheres
(PCSs); <sup>25)</sup> N-doped carbon sphere	es with hiera	rchical micr	opore-nano	sheet netwo	orks (HPSC	Ss); <sup>26)</sup>
Mesoporous carbons(MC);27)N-do	ped Mesopor	ous carbons	(NMC).			

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