A rechargeable iodine-carbon battery that exploits ion intercalation and iodine redox chemistry

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Graphitic carbons have been used as conductive supports for developing rechargeable batteries. However, the classic ion intercalation in graphitic carbon has yet to be coupled with extrinsic redox reactions to develop rechargeable batteries. Herein, we demonstrate the preparation of a free-standing, flexible nitrogen and phosphorus co-doped hierarchically porous graphitic carbon for iodine loading by pyrolysis of polyaniline coated cellulose wiper. We find that heteroatoms could provide additional defect sites for encapsulating iodine while the porous carbon skeleton facilitates redox reactions of iodine and ion intercalation. The combination of ion intercalation with redox reactions of iodine allows for developing rechargeable iodine–carbon batteries free from the unsafe lithium/sodium metals, and hence eliminates the long-standing safety issue. The unique architecture of the hierarchically porous graphitic carbon with heteroatom doping not only provides suitable spaces for both iodine encapsulation and cation intercalation but also generates efficient electronic and ionic transport pathways, thus leading to enhanced performance.
Over the past decades, Li-ion batteries (LIBs), consisting of a lithium-containing cathode and a graphite anode, have demonstrated great success for energy storage via the classic lithium intercalation process\textsuperscript{1,2}. However, the specific capacity of LIBs is limited by the cathode, which is still far below the theoretical capacity of graphite (372 mAh g\textsuperscript{-1}) and has to be significantly improved in order to meet the ever increasing energy storage demand\textsuperscript{3,4}. Along with intensive research on the exploitation of advanced cathode materials of novel chemical and/or physical structures\textsuperscript{5–11}, many other rechargeable batteries, such as Na-ion battery\textsuperscript{12,13}, Li-S battery\textsuperscript{14}, and Li-/Na-ion battery\textsuperscript{15–18} have been devised. Recent publications reported rechargeable Li–iodine batteries with a high theoretical energy density/discharge capacity of 612 Wh kg\textsuperscript{-1}/211 mAh g\textsuperscript{-1} based on the highly reversible electrochemical redox reaction between the lithium anode and iodine cathode (2Li + I\textsubscript{2} \rightarrow 2LiI)\textsuperscript{14,15}. Although the abundance of iodine resource in ocean\textsuperscript{14–18} makes the rechargeable Li–iodine batteries particularly interesting as low-cost, but efficient, alternatives to LIBs, inexpensive and highly conducting iodine-based cathodes with a stable and high iodine loading still need to be developed. So far, a few carbon hosts, including porous carbons, have been developed for Li–iodine batteries\textsuperscript{14,15,18,19}. However, the use of heteroatom-doped/functionalized carbon supports to enhance the iodine loading, and hence the battery performance, has been rarely discussed. As for LIBs, the practical application of Li–iodine batteries is also still hindered by the safety risk intrinsically associated with the metallic lithium electrode due to the lithium dendrite formation hindered by the safety risk intrinsically associated with the presence of phytic acid as the phosphorous source. The resultant free-standing and highly porous carbon matrix co-doped with nitrogen and phosphorus (HPCM-NP) through an interfacial polymerization of aniline on a cellulose wiper in the presence of phytic acid, followed by carbonization. The oxidative polymerization of aniline monomers in the presence of phytic acid led to the formation of porous polyaniline (PANI) along individual fibers in the cellulose wiper. The subsequent pyrolysis of PANi coated cellulose wiper at an elevated temperature resulted in the formation of HPCM-NP. The optimized condition for the formation of HPCM-NP was determined by adjusting the amount of aniline monomers (Supplementary Figs. 1, 2 and Supplementary Note 1). Then, iodine can be facilely loaded into the porous carbon matrix via surface adsorption from an iodine saturated aqueous solution (see Methods for detailed procedure). Large-scale of free-standing and highly flexible HPCM-NP scaffold can be prepared as its size is mainly determined by the size of the starting cellulose wiper (Fig. 1b). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the flexible HPCM-NP knits with flexible ligaments (Fig. 1c), and the individual carbon fibers are covered uniformly with the hierarchical porous carbon network (Figs. 1d, e). The high-resolution TEM image further reveals that the shells of these interconnected fibers contain a myriad of micropores (Fig. 1f, cf. Figs. 2b, c). For comparison, carbonized pure cellulose wiper and PANi aerogel were also prepared at the same elevated temperature (Supplementary Figs. 3, 4). To load iodine, these as-prepared carbon scaffolds were immersed into the iodine saturated aqueous solution at room temperature (Supplementary Fig. 5). The hierarchically porous structure with a large surface area facilitated the penetration of the iodine solution into the inside of carbon matrix, possibly by an energetic capillary action\textsuperscript{15,19,33}, and the adsorption of iodine species throughout the entire carbon matrix homogenously rather than accumulate on the outmost surface only\textsuperscript{1,3}. This was confirmed by the element mapping analysis along the whole carbon fiber (Fig. 1g) and the EDX spectrum for the bulk sample (Supplementary Fig. 6). The same procedure was used to load iodine into other carbon materials, including the pure porous carbon cloth (CC) (Supplementary Fig. 5), N and P co-doped porous carbon foam (NPCF) (Supplementary Fig. 4) and activated carbon (AC) (Supplementary Fig. 7 and Supplementary Note 2). It was noticed that the co-doping of HPMMC-NP with N and P could enhance the uploading of iodine species (cf. Fig. 2a)\textsuperscript{14,34}. The hierarchically porous frameworks of HPMMC-NP can act as effective physical barriers for preventing the dissolution of the adsorbed iodine (Supplementary Fig. 8), but efficient pathways for electron transfer via the highly conductive 3D

### Results

#### Structure characterization of iodine-carbon composite.

Figure 1a schematically illustrates the preparation process for HPCM-NP through an interfacial polymerization of aniline on a cellulose wiper in the presence of phytic acid, followed by carbonization. The oxidative polymerization of aniline monomers in the presence of phytic acid led to the formation of porous polyaniline (PANI) along individual fibers in the cellulose wiper. The subsequent pyrolysis of PANi coated cellulose wiper at an elevated temperature resulted in the formation of HPCM-NP. The optimized condition for the formation of HPCM-NP was determined by adjusting the amount of aniline monomers (Supplementary Figs. 1, 2 and Supplementary Note 1). Then, iodine can be facilely loaded into the porous carbon matrix via surface adsorption from an iodine saturated aqueous solution (see Methods for detailed procedure). Large-scale of free-standing and highly flexible HPCM-NP scaffold can be prepared as its size is mainly determined by the size of the starting cellulose wiper (Fig. 1b). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the flexible HPCM-NP knits with flexible ligaments (Fig. 1c), and the individual carbon fibers are covered uniformly with the hierarchical porous carbon network (Figs. 1d, e). The high-resolution TEM image further reveals that the shells of these interconnected fibers contain a myriad of micropores (Fig. 1f, cf. Figs. 2b, c). For comparison, carbonized pure cellulose wiper and PANi aerogel were also prepared at the same elevated temperature (Supplementary Figs. 3, 4). To load iodine, these as-prepared carbon scaffolds were immersed into the iodine saturated aqueous solution at room temperature (Supplementary Fig. 5). The hierarchically porous structure with a large surface area facilitated the penetration of the iodine solution into the inside of carbon matrix, possibly by an energetic capillary action\textsuperscript{15,19,33}, and the adsorption of iodine species throughout the entire carbon matrix homogenously rather than accumulate on the outmost surface only\textsuperscript{1,3}. This was confirmed by the element mapping analysis along the whole carbon fiber (Fig. 1g) and the EDX spectrum for the bulk sample (Supplementary Fig. 6). The same procedure was used to load iodine into other carbon materials, including the pure porous carbon cloth (CC) (Supplementary Fig. 5), N and P co-doped porous carbon foam (NPCF) (Supplementary Fig. 4) and activated carbon (AC) (Supplementary Fig. 7 and Supplementary Note 2). It was noticed that the co-doping of HPMMC-NP with N and P could enhance the uploading of iodine species (cf. Fig. 2a)\textsuperscript{14,34}. The hierarchically porous frameworks of HPMMC-NP can act as effective physical barriers for preventing the dissolution of the adsorbed iodine (Supplementary Fig. 8), but efficient pathways for electron transfer via the highly conductive 3D
carbon skeleton\textsuperscript{34, 35}, enhancing the electrochemical performance.

As shown in Fig. 2a, the adsorption of iodine on all the carbon materials investigated in this study followed the same trend: initially increased with increasing time and then leveled off at the equilibrium point. The time to reach the adsorption equilibrium was around 7, 7, 5, and 3 h for HPCM-NP, NPCF, CC, and AC, respectively, and the adsorption capacity at equilibrium decreased from 125 to 50 wt\% along the same order (The mass ratio of iodine is normalized to carbon). For AC, the equilibrium was reached rapidly due to the surface-dominated adsorption. In contrast, the adsorption process of iodine on hierarchically porous HPCM-NP is relatively slow\textsuperscript{15, 35}, but achieves a large adsorption capacity. X-ray diffraction (XRD) pattern reveals the presence of broad peaks at around 24.5° and 43.6° attributable to the (002) and (101) diffraction peaks of graphitic carbons (Supplementary Fig. 9a). However, no diffraction peak of the loaded iodine is observed, suggesting the formation of non-crystalline iodine\textsuperscript{34, 36}. The pronounced Raman D and G bands (~1355 and 1596 cm\textsuperscript{-1}, Supplementary Fig. 9b) are ascribed to the disordered carbon and graphitic sp\textsuperscript{2} carbon, respectively. The $I_D/I_G$ Raman peak intensity ratios were found to be 1.5, 1.4, 1.3, 1.2, and 1.0 for the I\textsubscript{2}-HPCM-NP, I\textsubscript{2}-NPCF, iodine-nitrogen doped porous carbon cloth (I\textsubscript{2}-NCC, see Methods), I\textsubscript{2}-CC, and I\textsubscript{2}-AC, respectively. Thus, it was evident that the formation of highly porous structure and the introduction of heteroatom dopings led to an increased number of edges and surface defects\textsuperscript{13}, which most likely improved the iodine adsorption and battery performance\textsuperscript{13, 25, 26}. In consistence with the XRD data, Raman spectroscopy reveals no iodine peak, indicating, once again, the formation of amorphous iodine\textsuperscript{34, 36}. Nitrogen adsorption-desorption isotherms show a sharp adsorption slope at $P/P_0 < 0.1$, suggesting the presence of micropores (Fig. 2b and Supplementary Fig. 10). The corresponding pore size distribution curve for HPCM-NP further confirms the presence of micropores with a narrow size distribution (centered at ~1.7 nm, Fig. 2c), attractive for iodine adsorption\textsuperscript{33, 35}. Nevertheless, the uptake of iodine led to a significantly decreased specific surface area (i.e., 973 m\textsuperscript{2} g\textsuperscript{-1}, vs. 1487 m\textsuperscript{2} g\textsuperscript{-1} for pure HPCM-NP). The same tendency was also observed for other carbon materials (1102, 478, 855, and 205 m\textsuperscript{2} g\textsuperscript{-1} for the NPCF, I\textsubscript{2}-NPCF, CC, and I\textsubscript{2}-CC, respectively). More importantly, the pore size gradually decreased with increasing amount of the adsorbed iodine (Fig. 2c). These results indicate the adsorption/infiltration/accumulation of iodine into the pores\textsuperscript{34, 36}. With the iodine loading increased up to ~48 wt\%, the specific surface area...
of HPCM-NP decreased from 1487 to 85 m² g⁻¹ (Fig. 2b) with a containment decrease in the volume fraction of micropores (Fig. 2c).

X-ray photoelectron spectroscopy (XPS) survey spectra reveal the presence of C, N, P (Supplementary Fig. 11a), confirming the formation of nitrogen and phosphorus co-doped carbon for HPCM-NP. As expected, the presence of some oxygen (5.1 %) cannot be ruled out.25 High-resolution N1s XPS spectrum of HPMC-NP (Fig. 2d) can be convoluted into four peaks centered at 396.0, 400.5, 401.3 and 402.0 eV corresponding to pyridinic N (N1), pyrrolic N (N2), graphitic (N3), and oxidized pyridinic N (N0) nitrogen, respectively. The fitted P2p peaks of HPMC-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds, respectively. The fitted P2p peaks of HPMC-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds, respectively. The fitted P2p peaks of HPMC-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds, respectively. The fitted P2p peaks of HPMC-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds, respectively. The fitted P2p peaks of HPMC-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds.25 Upon the iodine uploading, three peaks centered at 128, 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds.

The differential charge density was calculated from:

\[ E_{\text{ad}} = E_1 - E_{\text{ref}}(\rho_f) - E_{\text{ref}}(\rho_2) + E_{\text{ref}}(\rho_1) \]

The time-dependent profiles for the mass ratio of iodine adsorbed on various carbons (the mass ratio is normalized to the mass of carbon) and the corresponding pore size distribution curves of HPMC-NP with different mass loading of iodine. High-resolution XPS spectra of N1s, P2p, and I3d for I2-HPCM-NP samples. Thermodgravimetric analysis curves of various carbon (iodine content, 40 wt%), and I2-HPCM-NP composite with different iodine content. The bond lengths and heights of adsorbed I2 molecule are also listed in the figure, along with the corresponding adsorption energies.

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reveals that the strong interaction between iodine and graphene can be achieved via N and P doping (Fig. 2g, explained in detail in Supplementary Fig. 13 and Supplementary Note 4). Specifically, the synergic effect of N and P co-doping significantly improves the adsorption energy ($E_{ad}$), which will enhance the stability of iodine adsorbed. Furthermore, the strong interactions toward iodine would also benefit to the nucleation of iodine by lowering the surface tensile against the carbon substrate, leading to the high iodine loading $24, 40$. With increasing iodine loading, however, more and more iodine molecules aggregated in the pores without directly supported by the carbon surface, resulting in the poorer thermal stability (Supplementary Fig. 14). Therefore, hierarchically porous structure and heteroatom doping are crucial for the stability of adsorbed iodine, which would contribute to the battery performance and it’s cycling stability.

**Electrochemical performance of lithium-iodine battery.** Cyclic voltammogram (CV) curves show a support-dependent property for various iodine loaded carbon electrodes (Fig. 3a). The well-defined redox peaks in each CV curve indicate a two-step redox process of iodine-carbon composite electrodes. The sharp peak at about 3.0 V and a hump at around 3.4 V correspond to the oxidation of LiI to LiI$_3$ and then to higher-order elemental iodine, respectively. In contrast, the cathodic peaks centered at ~2.9 and 3.4 V arise from the reversible conversion pairs of LiI$_3$/LiI and I$_2$/LiI$_3$, respectively. The differential capacity plot (Supplementary Fig. 15) also confirms the two-step process for the redox reactions. The good linear relationship between the peak current ($i_p$) and the square root of scan rates for LiI$_3$/LiI redox pair (Supplementary Fig. 16) suggests a diffusion-controlled redox process $^{14}$. In contrast, the oxidation current of I$_2$ converted to elemental iodine is directly proportional to the value of the scan rates, and thus the ion diffusion is quick and its redox kinetic is only limited by electron transfer. Obviously, the pseudocapacitive character is involved in the redox process of iodine, which would be favorable for both high capacity and high-rate performance $^{14, 15, 18}$.

Notably, the I$_2$-HPCM-NP electrode shows the largest current density with good reversibility and the peak potential difference ($\Delta E_p$) of the redox peaks is only 88 mV (Fig. 3a). In contrast, the $\Delta E_p$ of I$_2$-NPCF, I$_2$-NCC, I$_2$-CC, and I$_2$-AC is around 91, 135, 170, and 220 mV, respectively. The observed remarkably large current density and good reversibility for the I$_2$-HPCM-NP could be attributed, once again, to the synergistic effect of N, P co-doping to introduce more edge/active defects with respect to other carbon hosts $^{25, 43, 44}$. As revealed by the experimental and theoretical results (Supplementary Figs. 13, 17, 18 and Supplementary Note 5), the strong anchoring effect could not only accelerate the nucleation of iodine and enable fast kinetics according to the basal growth behavior of nanostructures, but also stabilize iodine and LiI$_3$ to retard the shuttle effect, thus improving the reversibility and cycling stability $^{14, 15, 34}$. Therefore, a rational design and controllable construction of the carbon electrode is essential to enhance the overall performance of the electrode materials $^{13, 34}$.

The typical galvanostatic charge/discharge curves (Fig. 3b) of the Li–iodine battery using different iodine-carbon cathodes exhibit two voltage slopes at 3.3–3.5, 2.9–3.1 V for charging curves and 3.2–3.4, 2.8–3.0 V for discharging curves. The good symmetric charge/discharge profile for I$_2$-HPCM-NP electrode with high Coulombic efficiency (CE) suggests a good reversibility. At the current density of 100 mA g$^{-1}$, the I$_2$-HPCM-NP electrode delivered the largest initial discharge capacity of 386 mAh g$^{-1}$ and charge capacity of 391 mAh g$^{-1}$ with a high
CE of 98.7% and high symmetry (Fig. 3b and Supplementary Fig. 19). Such a high capacity is even larger than the theoretical capacity (211 mAh g⁻¹) for Li–iodine batteries. This is because the pure HPCM-NP would also contribute to the whole capacity of I₂-HPCM-NP due to the capacitive contribution (~56 mAh g⁻¹) in Supplementary Fig. 20, the details in Supplementary Note 8. Notably, the specific capacity of I₂-HPCM-NP decreased with increasing the iodine loading (Supplementary Fig. 21) since not all iodine participated in the redox reactions at high loadings. At the mass loading of 2 mg cm⁻², the calculated discharge capacities for I₂-HPCM-NP, I₂-NPCF, I₂-NCC, I₂-CC and I₂-AC at different current densities from 100 to 2000 mA g⁻¹ are summarized in Fig. 3c. The initial specific capacities for I₂-NPCF, I₂-NCC, I₂-CC, and I₂-AC cathodes are around 368, 331, 283, and 206 mAh g⁻¹, respectively, at a current density of 100 mA g⁻¹. These capacities decreased to 238, 179, 151 and 102 mAh g⁻¹ (Supplementary Fig. 21) since not all iodine participated in the redox reactions at high loadings. At the mass loading of 2 mg cm⁻², the calculated discharge capacities for I₂-HPCM-NP, I₂-NPCF, I₂-NCC, I₂-CC and I₂-AC at different current densities from 100 to 2000 mA g⁻¹ are summarized in Fig. 3c. The initial specific capacities for I₂-NPCF, I₂-NCC, I₂-CC, and I₂-AC cathodes are around 368, 331, 283, and 206 mAh g⁻¹, respectively, at a current density of 100 mA g⁻¹. These capacities decreased to 238, 179, 151 and 102 mAh g⁻¹ when the current density increased to 2000 mA g⁻¹, corresponding to a capacity fade of 35.3, 45.9, 46.6, and 50.5%. Notably, a good capacity retention of 70.7% was observed for I₂-HPCM-NP after a total of 100 cycles at the increased current density from 100, 200, 500, 1000 to 2000 mA g⁻¹ (20 consecutive cycles at each of the current densities; Fig. 3d). Thereafter, the capacity can be recovered to 375 mAh g⁻¹ with a capacity retention of 97.2% by switching the current density back to 100 mA g⁻¹, which is better than the corresponding values for other composite electrodes (96.7, 93.5, 95.4, and 91.3% capacity retention for I₂-NCC, I₂-NPCF, I₂-CC, and I₂-AC, respectively). The 3D hierarchical porous framework not only allows for the electrolyte to easily access into the inner surface but also ensures effective electronic transport along the conductive carbon skeleton (Supplementary Fig. 22 and Supplementary Note 7). Thus, the improved rate capability for the I₂-HPCM-NP can be achieved. Besides, I₂-HPCM-NP samples obtained at various temperatures 600-1000 °C exhibited increased specific capacity from 215 to 295 mAh g⁻¹ with increasing temperature (Supplementary Fig. 23), possibly due to the formation of graphitic carbon with a good electric conductivity at high pyrolysis temperatures. A long-term cycling stability test for I₂-HPCM-NP revealed a capacity retention of 84.5% after 2000 charge/discharge cycles (79.4% and 66.3% capacity retention after 2000 cycles for I₂-NCC and I₂-NPCF; 78.3 and 66.0% capacity retention after 1000 cycles for I₂-CC and I₂-AC), suggesting the good cycling stability (Fig. 3e). The cycling performance of I₂-HPCM-NP is thus comparable to many other similar iodine cathodes in the literature (Supplementary Table 1). It is revealed a slow dissolution of iodine into the electrolyte (Supplementary Fig. 24 and Supplementary Note 8) during the cycling test and no obvious side reaction of the electrolyte is observed except the reversible redox of iodine over the potential range tested (Supplementary Fig. 25 and Supplementary Note 9). However, the gradual formation of Li dendrites on the Li-metal electrode (Supplementary Fig. 26 and Supplementary Note 10) could slightly deteriorate the battery stability. In addition to the strong anchoring effect of heteroatom doping, the improved cycling stability should be attributed to the rational-designed porous carbon matrix prepared via the direct pyrolysis of 3D PANi aerogel on a carbon fiber substrate without nonconductive binders, which provides abundant electrode/electrolyte contact interfaces and reduces ion diffusion path for fast electrochemical kinetics (Supplementary Fig. 22). In contrast, for those reported binder-added electrodes, additional irreversible capacity loss and poor cycling stability are inevitable, arising from the insulating, inactive, and easily swelling polymeric binders. 

Electrochemical performance of sodium-iodine battery. To exploit the broad applications for the iodine-carbon cathodes, I₂-HPCM-NP electrode was also coupled with Na metal to fabricate a Na–I₂ battery. The CV curve (Fig. 4a) exhibits a two-step redox process. Typically, the two cathodic peaks located at 3.15 and 2.76 V could be ascribed to the sequential reduction
transitions of $\text{I}_2/\text{I}_3^-$ and $\text{I}_3^-/\text{I}^-$ with the insertion of Na$^+$ ions. In the reverse process, the two anodic peaks are ascribed to the oxidation of NaI to NaI$_3$ at 2.75 V and the subsequent oxidation to $\text{I}_2$ at 3.16 V$^{16}$. The typical charge/discharge curves (Fig. 4b) reveal that the specific capacity is 224, 200, 171, 156 and 137 mAh g$^{-1}$ at a current density of 100, 200, 300, 500 and 1000 mA g$^{-1}$, respectively. The specific capacity is smaller than that of Li–I$_2$ battery at the same current density (vide supra) due to the larger ionic radius and slower diffusion kinetics for Na$^+$ ions$^{12, 13, 16, 28}$. To gain deep insight into the energy storage process in a Na–I$_2$ battery, we performed in-situ Raman measurements at various discharging/charging stages (Figs. 4c, d). During the discharge process, a characteristic peak at about 115 cm$^{-1}$ emerged and gradually became more intense as the reaction progressed. This peak could be ascribed to the symmetric stretching mode of $\text{I}_3^-$, corresponding to the conversion of $\text{I}_2$ to $\text{I}_3^-$ along with the insertion of Na$^+$ ions$^{15, 16}$. With further decreasing potential to 2.0 V, the gradually disappeared peak indicated the reaction transformation of NaI$_3$ to NaI at the second reaction step. Therefore, it was evident that the reversible reactions occurred during the discharging/charging processes via $2\text{Na} + \text{I}_2 \leftrightarrow 2\text{NaI}$ with the formation of NaI$_3$ as an intermediate$^{14}$–$^{16}$. These results indicate that the redox behaviors of iodine and sodium couple is quite similar to those of Li–I$_2$ battery. When the current density was increased by ten times (100 to 1000 mA g$^{-1}$), a capacity retention of ~61.2% was obtained and ~93.8% of the capacity retained after 50 cycles at 1000 mA g$^{-1}$ (Fig. 5a).

![Fig. 5](image-url) Electrochemical performance of iodine–carbon hybrid full battery. Charge/discharge curves at different rates of I$_2$-HPCM-NP//HPCM-NP in a LiTFSI and b NaClO$_4$, respectively, and the corresponding discharge capacities (up: based on the weight of anode and cathode; down: based on the weight of carbon-based electrodes). c Surface pseudocapacitance (redox) contributions at different conditions. d Charge/discharge curves at different rates of I$_2$-HPCM-NP//Li$_4$Ti$_5$O$_12$ full battery and the corresponding discharge capacities (up: based on the weight of anode and cathode; down: based on the weight of carbon-based electrodes). e, f Rate capability and g, h cycling performance of different hybrid full batteries with e, g LiTFSI and f, h NaClO$_4$. i Ragone plot of full batteries, where power and energy densities are estimated based on the total mass of cathode and anode materials
initial discharge capacity (210 mAh g\(^{-1}\)) can be recovered when the current was restored to 100 mA g\(^{-1}\) (Supplementary Fig. 27a), suggesting a good rate-performance. Besides, the Na–I\(_2\) battery retained 85% of its initial discharge capacity over 500 charge/discharge cycles (Supplementary Fig. 27b), exhibiting also a good cycling stability\(^{14-16,19}\).

**Electrochemical performance of iodine–carbon full batteries.** As demonstrated above, the specific capacity of Li–I\(_2\) battery is larger than that of Na–I\(_2\) battery, though the same I\(_2\)-carbon cathode was used. Therefore, the ion intercalation at the carbon electrode should have a significant influence on its specific capacity, presumably due to the different sizes between Li and Na ions\(^{15,16}\). When used as anodes in LIBs, the first discharging capacities are around 388, 375, 369, 211, and 163 mAh g\(^{-1}\) for HPCM-NP, NPCF, NCC, CC, and AC (Supplementary Fig. 28), respectively. The observed good performance of the HPCM-NP anode (Supplementary Fig. 29 and Supplementary Note 11) is comparable to and even better than those of other carbon-based anodes (Supplementary Table 2), particularly coupled with LiMn\(_2\)O\(_4\) and Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C cathodes (Supplementary Fig. 30 and Supplementary Note 12) in full batteries using Li\(_i^+\)/Na\(_i^+\) containing electrolytes (Supplementary Fig. 31). These results indicate that HPCM-NP can also be used as anodes in Li/Na-ion batteries based on ion intercalation process, and, if coupled with the I\(_2\)-HPCM-NP cathode, a metal-electrode-free iodine-carbon full battery can be developed by using Li\(_i^+\)/Na\(_i^+\)-containing electrolytes.

To further incorporate the redox reactions of iodine with the intercalation process, a full battery is fabricated by coupling I\(_2\)-HPCM-NP cathode with HPCM-NP (I\(_2\)-HPCM-NP/HPCM-NP) anode in a Li- or Na-ion electrolyte, which is free from the Li or Na metal anode, and hence without the associated safety risk\(^7\). The charge/discharge curves of I\(_2\)-HPCM-NP//HPCM-NP exhibited relatively smooth profiles without obvious discharge plateaus for both the Li (LiTFSI, Fig. 5a)- and Na (NaClO\(_4\), Fig. 5b)- ion electrolyte. The discharge capacity at the current density of 50 mA g\(^{-1}\) is 217, 182 mAh g\(^{-1}\) in a Li-, Na-ion electrolyte, respectively. The typical CV curves with a couple of redox peaks (Supplementary Fig. 32) show the redox behaviour of iodine coupled with insertion/extraction of Li\(_i^+\) ions. To clarify the contributions of both processes, the fractions of redox capacitive and diffusion-controlled contributions to charge storage were determined (Fig. 5e)\(^{46,47}\). At a low scan rate of 0.1 mV s\(^{-1}\), the pseudocapacitive contribution was only 40%, indicating that ~60% of the total stored charge was on the basis of the ion intercalation process at a specific potential (e.g., 2.8 V). However, the ratio increased to ~57% at a high scan rate of 0.5 mV s\(^{-1}\). These results indicate that the higher pseudocapacitive contribution renders the better high-rate performance as the ion intercalation process needs a longer time to achieve\(^{46,47}\). The almost equal contributions (~50%) for the both processes seen in Fig. 5c suggests that the energy storage of a metal-electrode-free iodine-carbon full battery can be modulated by adjusting both redox reactions of iodine and cation intercalation - a plausible concept, but one which has not yet been realized. To further verify the feasibility, HPMC-NP was replaced with a typical zero-strain intercalative anode, Li\(_i^+\)Ti\(_5\)O\(_{12}\) (Supplementary Fig. 33), in the full cell (Fig. 5d). The CV curve of I\(_2\)-HPCM-NP exhibited a pair of redox peaks of iodine located at around 3.0 V whereas the peaks for Li\(_i^+\)Ti\(_5\)O\(_{12}\) located at around 1.5 V was ascribed to the reversible intercalation process of Li\(_i^+\) ions (Supplementary Fig. 34). When coupled both electrodes in a full cell, a pair of redox peaks at around 1.42/1.27 V could be ascribed to the overall electrochemical reaction (2Li\(_i^+\)Ti\(_5\)O\(_{12}\) + 2xLi\(_i\) ↔ 2Li\(_{4+x}\)Ti\(_5\)O\(_{12}\) + I\(_2\)), in which both redox reactions and the ion intercalation were coupled together, leading to a specific capacity of 240 mAh g\(^{-1}\) (Fig. 5d). The ratio of pseudocapacitive contribution over intercalative one at a given voltage is quantitatively determined according to the CV curves at various scan rates (Supplementary Fig. 35). The calculated capacity contribution from the surface pseudocapacitive is in the range of 41-64%. This result implies a dominating diffusion-limited ion-intercalative process at slow scan rates whereas the surface redox reaction is restricted at a specific potential. Further quantitative capacitive analyses on the hybrid ion storage behavior indicate that the surface pseudocapacitive contribution increased from 41% to 61% with increasing the scan rate at a fixed potential (1.45 V) as the high scan rate could facilitate the pseudocapacitive process (cf. Fig. 5e). These results support the concept to improve the performance of I\(_2\)-HPCM-NP//HPCM-NP full batteries by the combination of iodine ion intercalation with its redox reactions.

According to the rate capability tests (Figs. 5e, f), the capacity retentions of I\(_2\)-HPCM-NP//HPCM-NP and I\(_2\)-HPCM-NP//Li\(_i^+\)Ti\(_5\)O\(_{12}\) after 50 cycles at various current densities from 50 to 800 mA g\(^{-1}\) (about 16 times increase) were about 49.9% (108.3 mAh g\(^{-1}\)) and 48.0% (115.1 mAh g\(^{-1}\)), respectively (Fig. 5e). For the hybrid full battery in a Na-ion electrolyte, the capacity retentions of I\(_2\)-HPCM-NP//HPCM-NP was approximately 44.6% (81.1 mAh g\(^{-1}\)) after 50 cycles with the current densities increased by 10 times (increased from 50 to 500 mA g\(^{-1}\)) (Fig. 5f).

Furthermore, the hybrid full batteries exhibited good cycling stability with capacity retention of ~74% for I\(_2\)-HPCM-NP//HPCM-NP and 76% for I\(_2\)-HPCM-NP//Li\(_i^+\)Ti\(_5\)O\(_{12}\) after 500 cycles at a current density of 500 mA g\(^{-1}\) (Fig. 5g). In contrast, the battery in a Na-ion electrolyte can deliver discharge capacity of 58.9 mAh g\(^{-1}\) with the initial capacity retention of 55.0% after 300 cycles at a current density of 400 mA g\(^{-1}\) (Fig. 5h). The good battery performance in Li-ion electrolyte could be contributed to the smaller size and the fast diffusion kinetics of Li ions\(^{13,16,36}\). As can be seen from the Ragone plot (Fig. 5i), the power and energy densities of the metal-electrode-free iodine-carbon full batteries are comparable to and even better than recently reported Li-ion or Na-ion full batteries\(^{30,31,48}\). Specifically, energy densities of 165.6 Wh kg\(^{-1}\) for the iodine-carbon battery using a Li-ion electrolyte and 152.6 Wh kg\(^{-1}\) for that using a Na-ion electrolyte were achieved at the power densities of 37.4 and 40.4 W kg\(^{-1}\), respectively. When the electrolyte was included in the calculation, the energy density of full battery was around 27.8/27.0 Wh kg\(^{-1}\) in a Li-/Na-ion electrolyte at a power density of 6.5/7.3 W kg\(^{-1}\), respectively (Supplementary Fig. 36) because the weight ratio between the electrolyte and electrode materials was in the range of 4.5 ~ 5.0. As shown in Supplementary Fig. 37, a red LED was powered on by an iodine-carbon full battery, which demonstrates that the combination of redox reactions and ion intercalation as an effective approach for the development of high-performance iodine-carbon rechargeable batteries from low-cost heteroatom-doped 3D porous carbon electrodes for efficient energy storage.

**Discussion**

In this study, we have prepared 3D free-standing porous carbon matrix co-doped with N and P by a facile pyrolysis of polyaniline coated cellulose wipers generated from interfacial polymerization of aniline on the cellulose wiper in the presence of phytic acid. Owing to the heteroatom-doped hierarchically porous carbon structure, iodine can be efficiently loaded up to a high content (125 wt%), leading to the formation of free-standing iodine-carbon electrodes for fabricating rechargeable Li- and Na–I\(_2\) batteries with high performance. Typically, the rechargeable Li–I\(_2\) and
Na–I2 batteries manifested high discharge capacities of 386 and 253 mAh g⁻¹, excellent rate performances and excellent cycle stabilities (84.5%, 2000 cycles; 85.0%, 500 cycles). More importantly, the combination of the surface-dominated redox reactions of iodine with the intrinsic intercalative properties of such a porous graphitic carbon in a full metallic Li/Na-electrode-free batteries led to high reversible capacities of up to 217/182 mAh g⁻¹ for iodine–carbon full batteries with a Li-/Na-ion electrolyte, respectively, and good cycling stabilities (76.7%@500 cycles and 69.8%@300 cycles at a current density of 500 mA g⁻¹). The methodology developed in this study opens new avenues for the development of novel rechargeable batteries, even free from the metallic Li/Na anode and associated safety risk, from low-cost heteroatom-doped porous graphitic carbon via the combination of redox capacitive properties and ion intercalation.

Methods
Preparation of heteroatom doped porous carbon matrix. 1.2 ml aniline monomer was added into 30 ml phytic acid solution. 1.0 g of ammonium persulfate (APS) was dissolved into the 15 ml deionized (DI) water under stirring. After cooling down to about 4 °C, both solutions were mixed together. Cellulose wiper was immersed into above solution and kept at 4 °C for overnight. The resultant wiper was washed with a large amount of DI water and dried at 60 °C, followed by annealing at 800 °C in N2. In order to prepare nitrogen-doped carbon cloth (NCC), the as-prepared wiper was washed with 10% ammonia water (de-doping process) to remove phytic acid before thermal treatment. For comparison, polyaniline aerogel were also prepared by the same procedure and carbonized at 1000 °C for 2 h in N2. Pure carbon cloth was obtained by directly pyrolysis of cellulose cloth under same experimental condition.

The loading of iodine on various carbon scaffolds. Iodine was loaded on various carbon scaffolds according to a simple inside encapsulation method. Typically, 10 mg of iodine was added into 20 ml DI water. Notably, most of iodine particles remain undissolved at the bottom due to the low solubility. HPMC-NP and other carbon materials were immersed into the above solution for a certain time, respectively. During the inside encapsulation process, it can be seen that most of iodine particles disappeared gradually. Then, the obtained sample was dried at 80 °C. The iodine adsorbed on carbon scaffolds was measured according to the mass change before and after the encapsulation process. The mass loading of iodine was normalized to the total mass of carbon and iodine unless otherwise stated. Notably, the mass ratio in Fig. 2a was based on the mass of carbon.

Structural characterization. The phase purity and crystal structure of the products were determined by XRD measurements. XPS was recorded on an ESCALAB 250 X-ray photoelectron spectrometer. The Raman spectra were collected on a LabRAM HR 800 system using 514 nm laser. SEM images were measured on a FEI Tecnai G2 F20 (200 kV). The elemental mapping of the as-prepared wiper was performed on a NOVA NanoSEM 430 scanning electron microscope (SEM). The density functional theory (DFT) and molecular dynamics (MD) calculations were performed using the Vienna ab initio simulation package. The core-valence interaction was described by the projector augmented-wave (PAW) method. The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) was used to account for the exchange-correlation functional. The plane-wave energy cutoff was set to 400 eV. The Monkhorst-Pack scheme was used to sample the Brillouin zone (BZ). For the single layer, a grid of 21 × 21 × 1 was used. The van der Waals (vdW) corrections were used in the calculations of the iodine molecules (Li/I) adsorption for the systems of pure carbon used to describe the graphene doped with N and P. A vacuum region of 20 Å was employed for all the systems to avoid interaction of periodic images. The force convergence criterion was set to 0.01 eV Å⁻¹ for optimization.

Data availability. The relevant data are available within the article and its Supplementary Information file or from the corresponding authors on request.

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Author contributions
K.L. and J.Z. conceived and designed the experiments. K.L. performed sample characterization and electrochemical studies. Z.H. performed the density functional theory calculations. K.L., J.Z., J.M., H.M. and L.D. analyzed the experimental data and wrote the paper. All authors discussed the results and commented on the manuscript.

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