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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.

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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^{1–4}. However, the specific capacity of LIBs is limited by the cathode, which is still far below the theoretical capacity of graphite (372 mAh g⁻¹) and has to be significantly improved in order to meet the ever increasing energy storage demand^{5–8}. Along with intensive research on the exploitation of advanced cathode materials of novel chemical and/or physical structures^{9–11}, many other rechargeable batteries, such as Na-ion battery^{12, 13}, Li–S battery⁴, and Li/Na-iodine battery^{14–16} have been devised. Recent publications reported rechargeable Li–iodine batteries with a high theoretical energy density/discharge capacity of 612 Wh kg⁻¹/211 mAh g⁻¹ based on the highly reversible electrochemical redox reaction between the lithium anode and iodine cathode ($2\text{Li} + \text{I}_2 \leftrightarrow 2\text{LiI}$)^{14, 15}. Although the abundance of iodine resource in ocean^{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^{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 and its high activity with moisture^{1, 3}.

Carbon-based electrodes have been widely used for energy storage/conversion with their performance being strongly dependent on the composition and microstructure of the carbon materials^{19–23}. In this context, heteroatom (e.g., B, N, P, and S) doping of graphitic carbons has been proven to significantly improve the electrocatalytic activities for metal-air batteries and enhance the capacity and cycling stability of Li–S batteries^{13, 24–26}. Specifically, three-dimensional (3D) conductive porous carbon networks, when used as the anode, have been demonstrated to improve the energy storage performance of lithium/sodium ion batteries by enhancing the ion intercalation²⁷. On the other hand, pre-lithiation/sodiation of a carbon anode provides a lithium/sodium reservoir to tune the cell potential^{28, 29}. However, it still remains a challenge to incorporate the ion intercalation with redox reactions, for example associated with iodine, to enhance the performance of rechargeable full batteries. Additionally, kinetic balance between anode and cathode still remains elusive. Therefore, it is highly desirable to rationally design electrode materials intercalated with redox active moieties^{28–32} to overcome the discrepancy between cathodic and anodic kinetics, in particular, and to enhance the battery performance, in general.

Herein, we report a free-standing hierarchically porous carbon matrix co-doped with nitrogen and phosphorus (HPCM-NP) prepared by pyrolysis of polyaniline coated cellulose wiper in the presence of phytic acid as the phosphorous source. The resultant free-standing conductive HPCM-NP renders the facile preparation of iodine-containing cathodes (i.e., iodine-carbon cathode) free from current collector, conductive additive, or any additional binder. The highly porous structure, coupled with the heteroatom co-doping, ensures a remarkably high iodine loading up to 125 wt%. Our results reveal that both the chemical and physical structures of HPCM-NP play important roles in regulating the iodine adsorption and subsequent electrochemical performance. Rechargeable Li–iodine and Na–iodine batteries based on the iodine-containing HPCM-NP cathodes exhibit a high discharge capacity of 386 and 253 mAh g⁻¹, respectively, along with a good rate-performance and good cycle stability with 84.5% capacity

retention after 2000 cycles for the Li–iodine battery and 85.0% capacity retention after 500 cycles for the Na–iodine battery. To avoid the use of the unsafe metallic Li and Na anode, we further constructs rechargeable batteries from the iodine-carbon cathode (I₂-HPCM-NP) and carbon cloth anode (HPCM-NP) with an electrolyte containing lithium (sodium) ions (e.g., LiTFSI, NaClO₄), which exhibits a reversible capacity of 217 (182) mAh g⁻¹, high energy density of 166 (153) Wh kg⁻¹ and good cycle performance with a 76.7% capacity retention after 500 cycles (69.8% @300 cycles) at a current density of 500 mA g⁻¹. Our kinetics and mechanistic studies reveal that proper encapsulation of iodine into the HPCM-NP electrodes with a hierarchically porous structure and a controllable heteroatom doping level could efficiently enhance the Li/Na-ion intercalation and electrolyte diffusion whilst restoring a kinetic balance between the anode and cathode electrodes, leading to the good battery performance.

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 easily 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^{15, 19, 33}, and the adsorption of iodine species throughout the entire carbon matrix homogeneously rather than accumulate on the outmost surface only^{4, 34}. 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 HPCM-NP with N and P could enhance the uploading of iodine species (cf. Fig. 2a)^{14, 34}. The hierarchically porous frameworks of HPCM-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

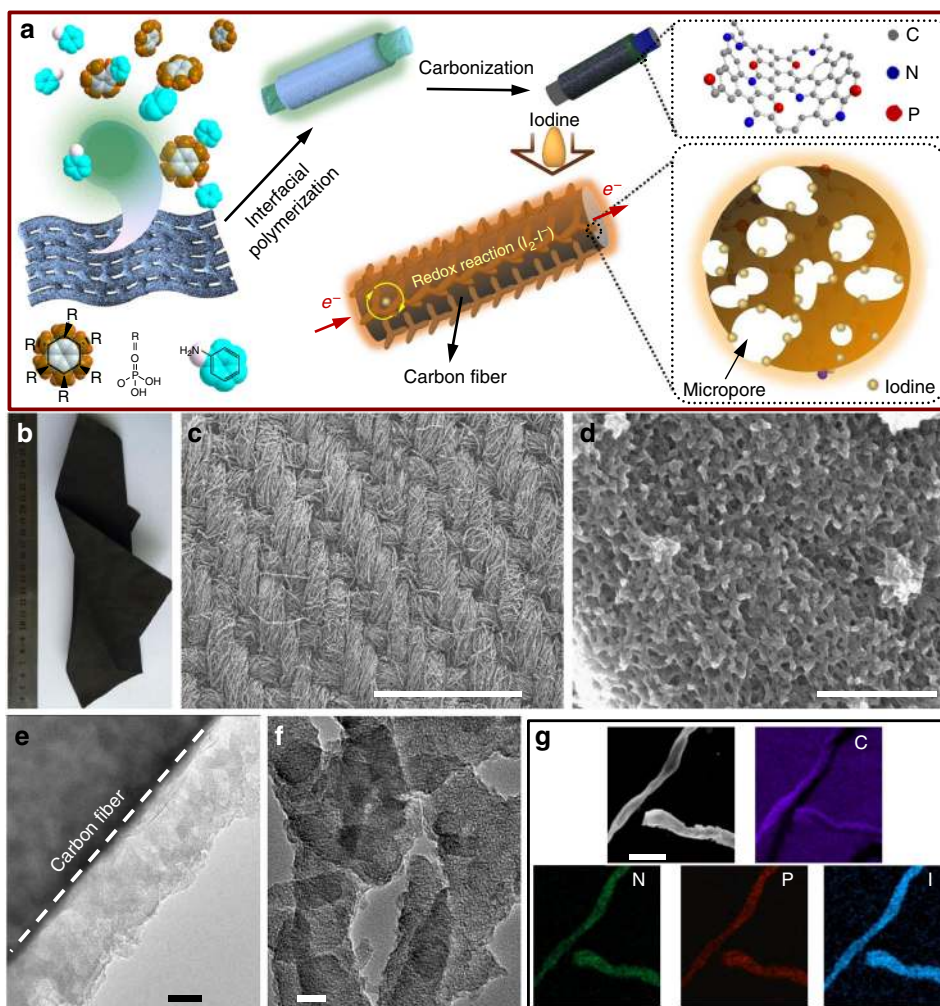


Fig. 1 Preparation of HPMC-NP and the loading iodine. **a** Interfacial deposition of PANi on the cellulose wiper via an oxidative polymerization in the presence of phytic acid and the subsequent carbonization in N_2 atmosphere. Then, iodine is escasulated into the as-prepared HPMC-NP from the iodine-saturated solution. **b** The digital photograph, **c, d** SEM images (Scale Bar, 1 mm and 500 nm, respectively), and **e, f** TEM images of the free-standing HPMC-NP (Scale Bar, 100 nm and 20 nm, respectively). **g** SEM image (Scale Bar, 15 μm) and the corresponding elemental mapping of the iodine loaded HPMC-NP

carbon skeleton^{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^{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^{15, 34, 35}. The pronounced Raman D and G bands (~ 1355 and 1596 cm^{-1} , Supplementary Fig. 9b) are ascribed to the disordered carbon and graphitic sp^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_2 -HPCM-NP, I_2 -NPCF,

iodine-nitrogen doped porous carbon cloth (I_2 -NCC, see Methods), I_2 -CC, and I_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 defects¹³, which most likely improved the iodine adsorption and battery performance^{13, 25, 26}. In consistence with the XRD data, Raman spectroscopy reveals no iodine peak, indicating, once again, the formation of amorphous iodine^{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^{33, 35}. Nevertheless, the uptake of iodine led to a significantly decreased specific surface area (i.e., $973\text{ m}^2\text{ g}^{-1}$, vs. $1487\text{ m}^2\text{ g}^{-1}$ for pure HPCM-NP). The same tendency was also observed for other carbon materials (1102 , 478 , 855 , and $205\text{ m}^2\text{ g}^{-1}$ for the NPCF, I_2 -NPCF, CC, and I_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^{34, 36}. With the iodine loading increased up to ~ 48 wt%, the specific surface area

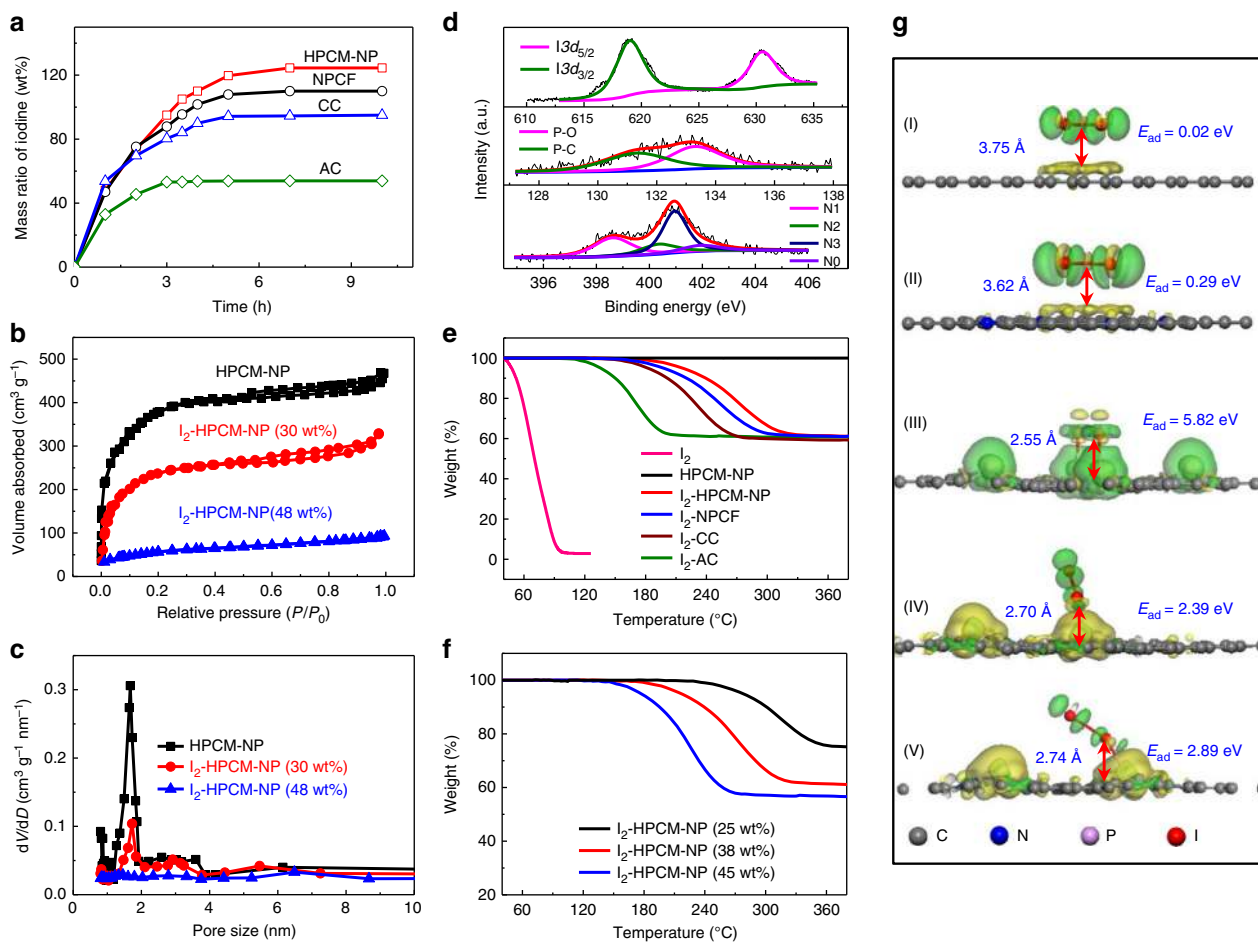


Fig. 2 Compositional characterization and stability analysis of iodine-carbon composites. **a** The time-dependent profiles for the mass ratio of iodine adsorbed on various carbons (the mass ratio is normalized to the mass of carbon). **b** N_2 adsorption-desorption isotherms and **c** the corresponding pore size distribution curves of HPCM-NP with different mass loading of iodine. **d** High-resolution XPS spectra of N1s, P2p, and I3d for I_2 -HPCM-NP samples. Thermogravimetric analysis curves of **e** pure iodine and iodine-carbon composites (iodine content, 40 wt%), and **f** I_2 -HPCM-NP composite with different iodine content. **g** The contour plots of the difference in charge density for the optimized structures of iodine molecule adsorbed on graphene I, graphene doped with N (II), P (III), isolated N and P (IV), and coupled N and P (V). The differential charge density was calculated from: $\Delta\rho = \rho_{I_2} - \rho_1 - \rho_2$, where ρ_1 , ρ_2 and ρ_{I_2} are the charge density of iodine, doped graphene with and without iodine adsorbed on the surface, respectively. Yellow and green color indicate the charge depletion and accumulation, respectively. The adsorption energies for I_2 molecule on these fragments were obtained using: $E_{ad} = -(E_1 + E_2 - E_{I_2})$, where E_{ad} is the adsorption energy of the I_2 molecule on the corresponding surfaces, E_1 is the total energy of the graphene (or heteroatom doped graphene), E_2 is the energy of one isolated I_2 molecule, and E_{I_2} is the energy of the optimized structures for I_2 molecules adsorbed on the graphene planes. The bond lengths and heights of adsorbed I_2 molecule are also listed in the figure, along with the corresponding adsorption energies

of HPCM-NP decreased from 1487 to 85 $m^2 g^{-1}$ (Fig. 2b) with an 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 out²⁵. High-resolution N1s XPS spectrum of HPCM-NP (Fig. 2d) can be convoluted into four peaks centered at ~398.6, 400.5, 401.3 and 402.0 eV corresponding to pyridinic (N1), pyrrolic (N2), graphitic (N3), and oxidized pyridinic (N0) nitrogen^{13, 25, 37}, respectively. The fitted P2p peaks of HPCM-NP located at 131.8 and 133.4 eV can be assigned to the P-C and P-O bonds^{25, 26}. Upon the iodine uploading, three peaks centered at 48.5, 619.2, and 630.6 eV were observed (Supplementary Fig. 11b), attributable to $I4d$, $I3d_{5/2}$ and $I3d_{3/2}$ of iodine (Fig. 2d)¹⁵. The obvious binding energy shift in comparison with the pure iodine suggests the strong interaction of iodine with the carbon substrate (Supplementary Fig. 12 and Supplementary Note 3). According to

the theoretical results (Supplementary Fig. 13), the charge modulation due to the nitrogen and phosphorus doping would contribute to the binding shift, which could also enhance the stability of iodine adsorbed^{15, 25, 38}.

The thermal gravimetric analysis (TGA) profile of pure iodine shows the evaporation of iodine below 80 °C due to its low sublimation temperature (Fig. 2e). Compared with pure iodine, iodine-adsorbed HPCM-NP (I_2 -HPCM-NP) sample shows an increased temperature range (120–200 °C) for iodine evaporation, indicating the strong interaction of iodine with the porous N, P co-doped carbon scaffold^{34, 39}. I_2 -HPCM-NP exhibited the highest on-set evaporation temperature at around 200 °C, suggesting the best thermal stability of adsorbed iodine on the HPCM-NP, followed by I_2 -NPCF (~180 °C), I_2 -CC (~150 °C), and I_2 -AC (~120 °C). The enhanced thermal stability for the uploaded iodine could lead to a better cycling stability of relevant batteries¹⁵. For I_2 -HPCM-NP, the on-set temperature for iodine evaporation significantly decreased from ~250 to 150 °C with increasing iodine loading (Fig. 2f). Our theoretical calculation

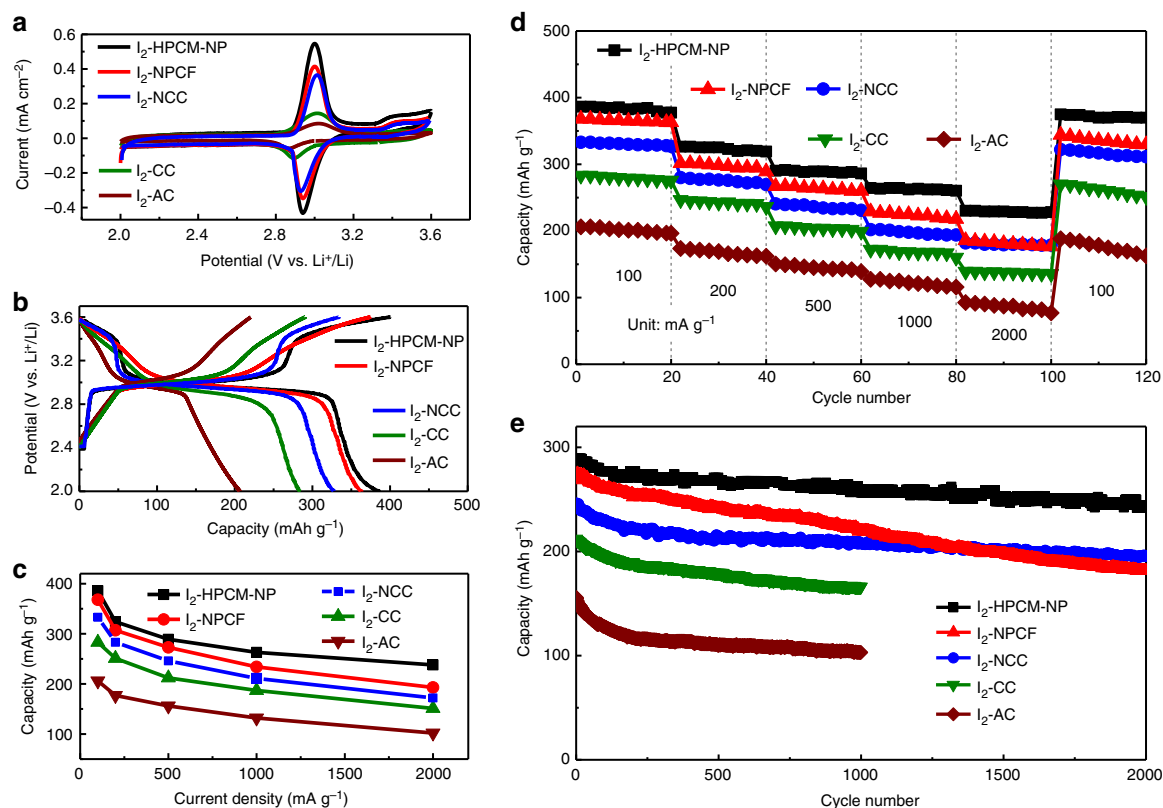


Fig. 3 Electrochemical performance of different iodine cathodes for Li-I₂ batteries. **a** Cyclic voltammograms (0.1 mV s⁻¹), **b** charge/discharge voltage profiles (100 mA g⁻¹), and **c** specific discharge capacities of different iodine-carbon cathodes between 2.0 and 3.6 V with the same iodine loading of 2.0 mg cm⁻². **d** Rate capability and **e** cycling stability tests of iodine-carbon cathodes at a current density of 500 mA g⁻¹

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 synergistic 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, 40–42}. 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 its 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 LiI₃ and then to higher-order elemental iodine, respectively. In contrast, the cathodic peaks centered at ~2.9 and 3.3 V arise from the reversible conversion pairs of LiI₃/LiI and I₂/LiI₃^{14, 15}. 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 LiI₃/LiI redox pair (Supplementary Fig. 16) suggests a diffusion-controlled redox process¹⁴. In contrast, the oxidation current of I₃⁻ 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 I₂-HPCM-NP electrode shows the largest current density with good reversibility and the peak potential difference (ΔE_p) of the redox peaks is only 88 mV (Fig. 3a). In contrast, the ΔE_p of I₂-NPCF, I₂-NCC, I₂-CC, and I₂-AC is around 91, 135, 170, and 220 mV, respectively. The observed remarkably large current density and good reversibility for the I₂-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 LiI₃ 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 I₂-HPCM-NP electrode with high Coulombic efficiency (CE) suggests a good reversibility. At the current density of 100 mA g⁻¹, the I₂-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^{14, 15}. This is because the pure HPCM-NP would also contribute to the whole capacity of I_2 -HPCM-NP due to the capacitive contribution ($\sim 56 \text{ mAh g}^{-1}$ in Supplementary Fig. 20, the details in Supplementary Note 6)^{14, 15}. Notably, the specific capacity of I_2 -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 I_2 -HPCM-NP, I_2 -NPCF, I_2 -NCC, I_2 -CC and I_2 -AC at different current densities from 100 to 2000 mA g^{-1} are summarized in Fig. 3c.

The initial specific capacities for I_2 -NPCF, I_2 -NCC, I_2 -CC, and I_2 -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 I_2 -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 I_2 -NCC, I_2 -NPCF, I_2 -CC, and I_2 -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 I_2 -HPCM-NP can be achieved. Besides, I_2 -HPCM-NP samples obtained at various temperatures 600 – $1000 \text{ }^\circ\text{C}$ 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^{13, 25}. A long-term cycling stability test for I_2 -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 I_2 -NCC and I_2 -NPCF; 78.3 and 66.0% capacity retention after 1000 cycles for I_2 -CC and I_2 -AC), suggesting the good cycling stability (Fig. 3e). The cycling performance of I_2 -HPCM-NP is thus comparable to many other similar iodine cathodes in the literature (Supplementary Table 1)^{14, 15, 18, 19}. 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)^{13, 24, 25, 34}. 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 binders⁴⁵.

Electrochemical performance of sodium-iodine battery. To exploit the broad applications for the iodine-carbon cathodes, I_2 -HPCM-NP electrode was also coupled with Na metal to fabricate a Na- I_2 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

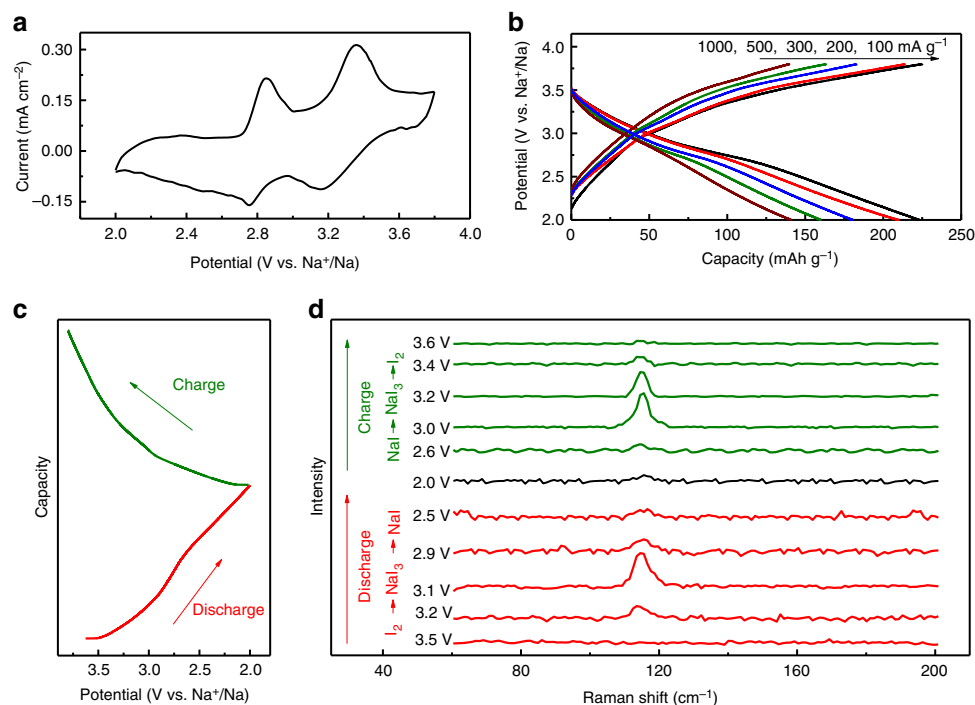


Fig. 4 Electrochemical performance of I_2 -HPCM-NP cathode for a Na- I_2 battery. **a** CV curve (0.1 mV s^{-1}) and **b** representative charge/discharge curves of I_2 -HPCM-NP cathode for Na- I_2 battery. **c** Discharge and charge curves with the test positions for analysis. **d** In situ Raman analyses of Na- I_2 batteries at different discharge and charge stages

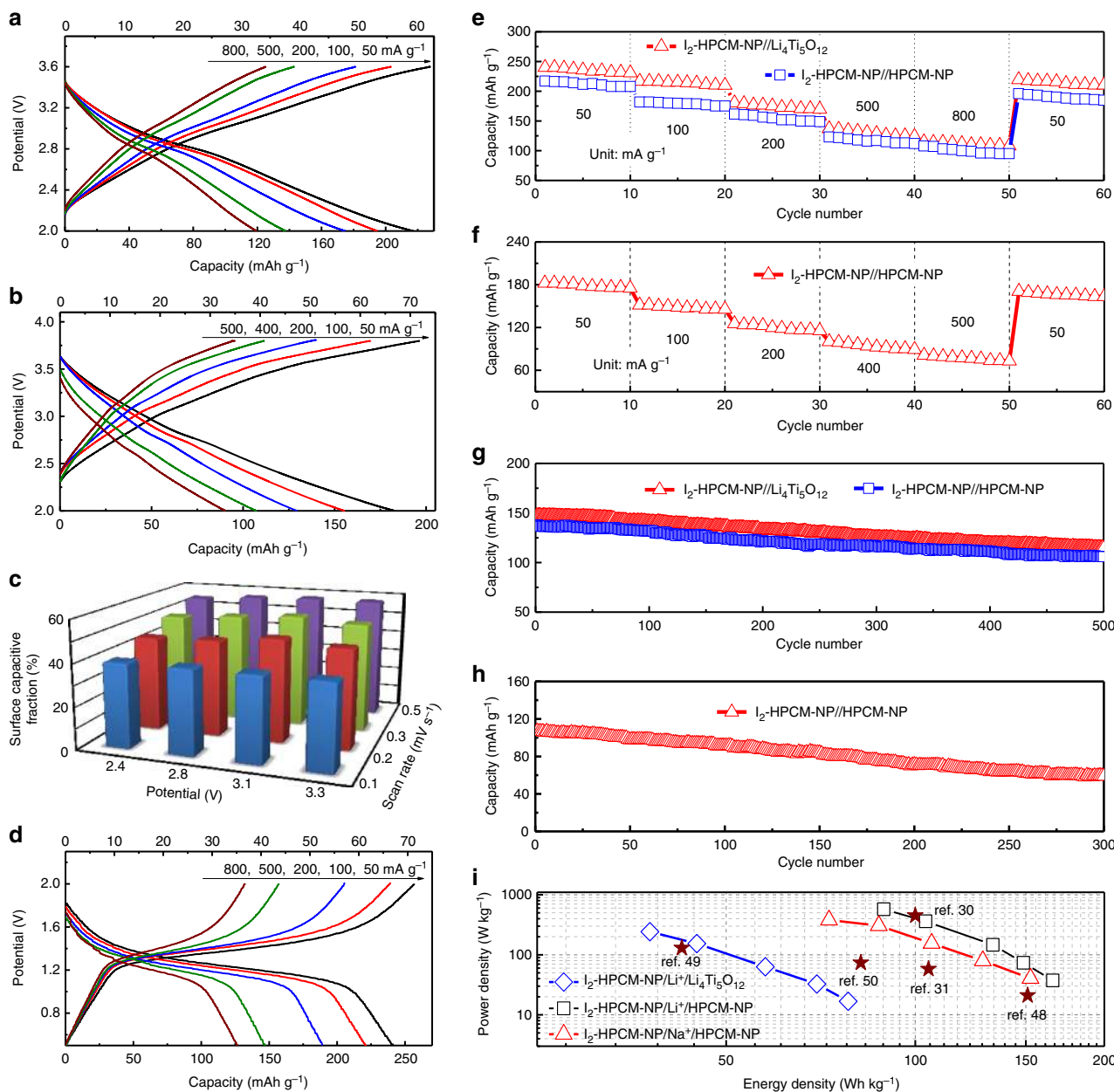


Fig. 5 Electrochemical performance of iodine-carbon hybrid full battery. Charge/discharge curves at different rates of I_2 -HPCM-NP//HPCM-NP in **a** LiTFSI and **b** $NaClO_4$, respectively, and the corresponding discharge capacities (up: based on the weight of anode and cathode; down: based on the weight of carbon-based electrodes). **c** Surface pseudocapacitive (redox) contributions at different conditions. **d** Charge/discharge curves at different rates of I_2 -HPCM-NP// $Li_4Ti_5O_{12}$ 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

transitions of I_2/I_3^- and I_3^-/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 I_2 at 3.16 V¹⁶. 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 ion 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 I_3^- , corresponding to the conversion of I_2 to 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 $2Na + I_2 \leftrightarrow 2NaI$ 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 $\sim 61.2\%$ was obtained and $\sim 93.8\%$ of the

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 (see Supplementary Table 2), particularly coupled with LiMn_2O_4 and $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathodes (Supplementary Fig. 30 and Supplementary Note 12) in full batteries using Li^+/Na^+ ion containing electrolytes (Supplementary Fig. 31). These results indicate that HPCM-NP can be also 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^+/Na^+ -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 risk⁷. 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^+ ions. To clarify the contributions of both processes, the fractions of redox capacitive and diffusion-controlled contributions to charge storage were determined (Fig. 5c)^{46, 47}. At a low scan rate of 0.1 mV s^{-1} , the pseudocapacitive contribution was only 40%, indicating that $\sim 60\%$ 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 $\sim 57\%$ at a high scan rate of 0.5 mV s^{-1} . These results indicate 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 ($\sim 50\%$) 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, HPCM-NP was replaced with a typical zero-strain intercalative anode, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (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 of 3.0 V whereas the peaks for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ located at around 1.5 V was ascribed to the reversible intercalation process of Li^+ 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 ($2\text{Li}_4\text{Ti}_5\text{O}_{12} + 2x\text{LiI} \leftrightarrow 2\text{Li}_{4+x}\text{Ti}_5\text{O}_{12} + \text{I}_2$),

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. 5c). 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// $\text{Li}_4\text{Ti}_5\text{O}_{12}$ after 50 cycles at various current densities from 50 to 800 mA g^{-1} (about 16 times increase) were about 49.9% ($108.3 \text{ mA h g}^{-1}$) and 48.0% ($115.1 \text{ mA h g}^{-1}$), 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 mA h 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 $\sim 74\%$ for I_2 -HPCM-NP//HPCM-NP and 76% for I_2 -HPCM-NP// $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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 mA h 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, 48–50}. 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 1000 °C for 2 h 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, poly-aniline 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 iodine and carbon 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 LabRAM HR 800 system using 514 nm laser. SEM images were measured on a Hitachi × 650 electron microscope. TEM images were presented on a JEOL JEM-2100 microscope. The thermostability of iodine-carbon composite was determined by Thermogravimetric analysis (TGA). The heating rate is 5 °C min⁻¹ from room-temperature to 400 °C under N₂. Brunauer-Emmett-Teller (BET) isotherms and specific surface area (i.e., BET surface area) were measured with a Kubo × 1000 instrument at 77 K. Prior to subsequent measurements, the I₂-loaded porous materials were firstly dried at 80 °C for 10 h to remove the surface adsorbed iodine and water. Then, the samples were degassed at 95 °C for 6 h. The specific surface areas were calculated by the BET method. Pore size distribution curves were computed from the desorption branches of the isotherms using the Barrett, Joyner, and Halenda (BJH) method.

Electrochemical measurements. The Li-/Na-iodine batteries (half-cell) were assembled in an argon-filled glove box. 1 M LiTFSI in DOL/DME (1:1 by volume) with 1 wt% LiNO₃ and 1 M NaClO₄ in EC/DEC (1:1 by volume) were used as the electrolytes, respectively, for Li- and Na-iodine battery test. Cyclic voltammetry (CV) was performed on a CHI 760e electrochemical workstation. The charge and discharge curves were recorded on a Land CT2001A battery test system. Prior to full-battery fabrication, the anode and cathode were electrochemically activated in a half cell, this step is critical to circumvent the large irreversible capacity and the low Coulombic efficiency (CE).

Computational methods. Density functional theory (DFT) and molecular dynamics (MD) calculations were performed using the Vienna ab initio simulation package⁵¹. The core-valence interaction was described by the projector augmented-wave (PAW) method⁵². The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE)⁵³ was used to account for the exchange-correlation functional. The plane-wave energy cutoff was set to 400 eV. The Monkhorst-Pack scheme⁵⁴ 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 (I₂/LiI₃) adsorption for the systems of pure graphene and 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 reasonable 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.

Additional information

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