Electronic Supplementary Information (ESI)

Oxygen-rich nanoflakes-interlaced carbon microspheres for

potassium-ion battery anodes

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Experimental section

Materials

All chemical agents were bought from Sigma-Aldrich, which were utilized without further purification.

Preparation of nanoflakes-interlaced carbon microspheres (NICM)

The fabrication process was modified according to the previous paper¹. 7.5 g formalin (37 wt% formaldehyde solution) and 9.3 g urea were dispersed into 200 mL deionized water, and then 1 g cetyl trimethyl ammonium bromide (CTAB) was added into the solution under stirring until all the solutes are dissolved. Then, 16.5 mL formic acid was mixed with the above solution without stirring during the reaction process, the white precipitation was obtained in 2 hours, nanoflakes-interlaced poly urea-formaldehyde (PUF) resin microspheres were obtained after filtration and drying. To strengthen structure and get better crosslinking, the PUF nanospheres were soaked into 2 M HCl for 48 h, deionized water washing for several times and drying in an oven at 70 °C. 0.6 g as-obtained PUF microspheres was placed into a porcelain boat without a lid, transferred into tubular furnace and preoxidized at air atmosphere. The heating rate was 5 °C min⁻¹, during 20 to 180 °C; 0.5 °C min⁻¹, from 180 to 215 °C and kept 215 °C for 2 h. Then the PUF microspheres with preoxidation was carbonized at argon atmosphere. The heating rate was 5 °C min⁻¹, during 20 to 180 °C; 0.5 °C min⁻¹, from 180 to 400 °C; 5 °C min⁻¹, in the range of 400 to 900 °C, and kept 900 °C for 2 h. After natural cooling to room temperature, nanoflakes-interlaced carbon microspheres (NICM) were successfully fabricated.

Without CTAB, we can obtain condense PUF microspheres with the surface consisting of lamellar nanoflakes, but the inside structure is composed of ultrafine nanoparticles, which was reported in our previous paper.¹ CTAB is a kind of cationic surfactant with a hydrophilic head and a hydrophobic hydrocarbon tail, which can form lamellar micelles as a soft template in aqueous solution, resulting in the vast formation of nanosheets,²⁻⁴ so we can obtain nanoflakes-interlaced structure with adding CTAB during the formation of PUF microspheres, the mechanism is shown in Fig. S1.

Characterizations

The PUF microspheres and NICM were characterized by SEM (Zeiss Merlin model), HRTEM (Tecnai F30), XPS (ESCALAB 250Xi, Thermo Scientific, Al K α X-ray source), Raman spectrometer (RENISHAW GL12 8JR, laser emitting at 532 nm), and XRD (Rigaku SmartLab SE, Cu K α radiation, $\lambda = 0.15406$ nm, step size of 0.02° (20) from 10-80°, scanning rate 5° min⁻¹.), BET adsorption (ASAP 2020, nitrogen adsorption isotherm at 77 K), Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR, PerkinElmer).

Electrochemical performance

Electrochemical performance of NICM was test by coin cells. The electrodes were fabricated by mixing 80 wt% active materials, 10 wt% conducive additive (Super P), and 10 wt% binder (PVDF) in N-Methyl pyrrolidone (NMP). After stirring, the homogeneous slurries were spread onto Cu foils, and then the electrodes were dried in a vacuum oven at 100°C. The electrodes were cut to circles with 16 mm

diameter. The loading mass of active materials on each Cu disk was around 0.8 mg. CR2016 coin cells were assembled in an argon filled glove box (MBRAUN Unilab). Potassium metal foil was the counter electrode. The electrolyte was 0.8 M KPF₆ in the mixture of dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) with volume ratio 1 : 1 : 1. Galvanostatic charge-discharge performance was tested by Neware battery tester. CV and EIS were performed by CHI660 electrochemical workstation.

Computational details

All geometric parameters and electronic properties were implemented in Vienna ab initio simulation package (VASP) using generalized gradient approximation-Perdew, Burke and Ernzerhof (GGA-PBE) method. The structure was fully relaxed with a plane-wave cutoff energy of 500 eV, the convergence energy of 10-6 eV and force less than 0.005 eV/Å. Meanwhile, van der Waals interaction was also considered by using the DFT-D3 approach. The Brillouin zone was sampled with $5\times5\times1$ and $11\times11\times1$ grids for geometry and electronic optimizations, respectively. In addition, the climbing-image nudged elastic band (CI-NEB) method was employed to identify the lowest activated energy and therefore determine preferred pathways for K ions diffusion for pristine, oxygen functional group contained and O-doped graphene monolayer.



Fig. S1 Schematic illustration of the formation mechanism of nanoflakes-interlaced PUF microspheres.



Fig. S2 a, c) Nitrogen adsorption-desorption isotherms of PUF microspheres and NICM; b, d) cumulative pore volume of PUF microspheres and NICM.



Fig. S3 a) TEM image, b) HRTEM image (inset: SAED pattern), c-e) EDS mapping

of NICM.

Fig. S4 XRD pattern of hierarchical carbon microspheres.

Fig. S5 Raman spectrum of NICM.

Fig. S6 XPS spectra of a) PUF microspheres, b) NICM.

Fig. S7 High resolution C1s XPS spectra of a) PUF microspheres and b) NICM. High resolution N1s XPS spectra of c) PUF microspheres and d) NICM.

Fig. S8 ATR-FTIR spectrum of the NICM.

The ATR-FTIR spectrum of the NICM is illustrated in Fig. S8. The strong absorption peak at 3466 cm⁻¹ is corresponding to the hydroxyl (OH) group owing to the unavoidable chemical absorption of H_2O from ambient air in NICM because of its large BET surface area (1021.1 m² g⁻¹). The typical peak at 1637 cm⁻¹ is ascribed to the C=O group, and the peaks located at 1403-1047 cm⁻¹ regions are corresponding to the complex C-O groups, such as carboxy, epoxy, and alkoxy at 1399, 1218 and 1042 cm⁻¹, respectively.⁵⁻⁸

Fig. S9 SEM images of the NICM anode after 900 cycles and then discharged to 0.01

V at different magnifications.

Fig. S10 EDS spectrum of the NICM anode and the corresponding element mapping

images.

Fig. S11 Nyquist diagram of the NICM anode before and after 5 cycles of charge and discharge at 1C over the frequency from 0.01 Hz to 100KHz.

Fig. S12 Contributions of surface capacitive process at different scan rates.

To investigate the potassium storage characteristics in the NICM anode, we analyze the kinetics of the NICM electrodes by conducting CV measurements at different scan rates ranging from 0.2 to 1.2 mV s⁻¹ as shown in Fig. 4a. According to the power-law relationship between the peak current (*i*) and the scan rate (v)^{37, 38}

$$i = av^b \tag{1}$$

Where the *a* and *b* are adjustable constants. By plotting $\log(i)$ against $\log(v)$,

$$\log (i) = \log (a) + b \log (v) \tag{2}$$

we can derive the *b* value from the slope of the plots. If the *b* value is close to 1, indicating a surface charge storage process, while the *b* value is close to 0.5 corresponding to a diffusion controlled process³⁹. Fig. 4b and 4c illustrate the log (*i*) vs log (*v*) plots. The *b* values are 0.50 and 0.89 for cathodic and anodic procedures, respectively, indicating a mixed surface capacitive controlled process and insertion reactions for K⁺ ions storage.⁴⁰ Furthermore, the surface capacitive and diffusion controlled contributions can be quantitated by separating the current responsive *i* at a fixed voltage V based on the following equations^{41, 42}

$$i(V) = k_1 v + k_2 v^{1/2}$$
 (3) or
 $i(V)/v^{1/2} = k_1 v^{1/2} + k_2$ (4)

the $k_2 v^{1/2}$ and $k_1 v$ stand for the diffusion and surface capacitive controlled contributions, respectively^{43, 44}. The results are shown in the Fig. 4d and e.

Fig. S13 Electron localization density distribution maps of K atom adsorbed in the a) pristine carbon structure, b) carbon structure contained oxygen functional groups, c) oxygen doped the carbon structure. K adsorbs at the center of the six-membered graphene ring with isosurface value (0-0.85 e/Å). Brown, purple, yellow and red balls represent C, K, oxygen functional groups (C-O-K), doped oxygen atoms, respectively.

To understand the good performance of the oxygen rich nanoflakes-interlaced carbon anodes, theoretical calculations were performed. The deep color scale of electron localization functions (ELF) value (0.5~0.85) stands for a covalent bond or nucleus, the ionic bond is described by a smaller ELF value (0.0~0.5) with the light color area, and the ELF value of 0.5 presented a metallic bond. As shown in Fig. S13a-S13c, C-C and C-O interactions belong to covalent bond, on the contrary, C-K or C-O-K configuration is ionic bond. In Fig. 6b-6c, electrons transfer from the graphene monolayer to oxygen ions and symmetrically distribute around K ions, indicating a strong interaction between K ions and O-doped graphene monolayer. As the oxygen coverage increases from 0.2 to 1.0 (full coverage), the calculated adsorption energy gradually decreases from -1.28, -1.85, -2.75, to 4.37 eV per K atom, revealing that K is thermodynamically stable in absorbing on the surface of graphene, which further confirms long cycle lifespan.

Fig. S14 Optimized structure of the a) pristine b) oxygen functional group contained c) O-doped carbon structure with an adsorbed K atom. Band structures near the Fermi level for d) pristine, e) oxygen functional group contained, f) O-doped carbon structure with an adsorbed K atom.

The optimized geometric and electronic structure of pristine, oxygen functional groups contained and O-doped graphene monolayer with an adsorbed K atom are shown in Fig. S14a-S14c and Fig. S14d-S14f, respectively. Electronic density of the oxygen functional group contained graphene monolayer redistributes between graphene surface and adsorbed K atoms, introducing the modification of the electronic structure and the increase of the valence bands. The band structure of pure and oxygen-rich graphene shows no gap between lowest unoccupied molecular orbital and the highest occupied molecular orbital near the Fermi level, so they display good electronical conductivity and guarantee good electron transfer (Fig. S15).

Fig. S15 Total density of states (TDOS) and partial density of states (PDOS) of a-d) bare pristine b-e) oxygen functional group contained and c-f) O-doped carbon structures along with the partial density of states (PDOS) of adsorbed K atoms, respectively. The black dotted lines denote the locations of the Fermi level.

The projected density of states (pDOS) of three model systems can be divided into three regions in Fig. S15. Region 1 indicates area less than -2eV and region II represents area ranging from -2 to 2 eV and region III is from 2 to 6 eV, region I in oxygen functional group contained graphene is due to contribution of C2p while region III corresponds to a hybridized O2p with C2p. In the meanwhile, K 4s states are found at a substantially high energy zone between 4 and 6 eV which contribute to the high electronic density in conduction band and therefore further improve the electronic conductivity for battery which reveals a good electronic conductivity. Moreover, the hybridizations between total and K3p orbitals density of state contribution have exhibited an obvious peak overlap, revealing that charge transfer between K ion and O-rich graphene monolayer, which means transferring electrons from surface to K atoms based on absorbability analysis.

Fig. S16 Diffusion barrier profiles for the three paths for K a) pristine, b) oxygen functional group contained c) O-doped graphene monolayer.

To study the K ion diffusion path and energy barriers, climbing-image nudged elastic band (CI-NEB) method was used. In order to further explore the K ions diffusion process, different diffusion pathways are selected along the line between the most favorable adsorption sites on the surface (Fig. S16). The calculated diffusion energy barrier for K ions of pristine graphene monolayer is 0.04 eV. In contrast, the oxygen functional group contained and O-doped graphene exhibit the diffusion barriers of 0.01 and 0.06 eV, respectively which confirm great potential for reversible cells application, especially good rate capability in KIBs. Furthermore, the activation barrier between the nearest neighboring stable active sites were demonstrated. In consideration of the K ion adsorbed on pristine graphene, there are two diffusion pathways shown in Fig. S14a. Path II exhibits a lower barrier of 0.04 eV compared with path I (0.43 eV), which dominates preferred diffusion pathway and promise fast K ion transportation. Similarly, the other two O-containing graphene display low energy barrier and satisfactory rate performance.

Table S1 Comparison of the nanoflakes-interlaced carbon microspheres and the reported carbonaceous anodes for KIBs.

Carbon Materials	Precursors	Performance (mAh g ⁻¹)	Sources
Nanoflakes-interlaced	Poly urea	278.6 at 0.1C, 146.6 at	This work
carbon microspheres	formaldehyde resin	5 C, 192.7 after 900	
		cycles at 1C (1C = 279	
		mA g ⁻¹)	
Carbon nanofibers	Polypyrrole	248 at 25 mA g ⁻¹	Nat.
			Commun. ⁹
Hard carbon	NH2-MIL-101(Al)	130 at 1050 mA g ⁻¹	Adv.
			Mater. ¹⁰
Mesoporous carbon	Sucrose	144.2 at 1 A g ⁻¹	Adv. Energy
			Mater. ¹¹
Activated carbon	Graphite	209 at 0.1 A g ⁻¹ , 30 at	Carbon ¹²
		1 A g ⁻¹	
Expanded graphite	Graphite	175 at 0.2 A g ⁻¹	J. Power
			Sources ¹³
Graphitic carbon	Graphite	100 at 0.2 A g ⁻¹	J. Mater.
			Chem. A ¹⁴
Hard carbon	Sucrose	136 at 5C	Adv. Energy
microspheres			Mater. ¹⁵
Carbon nanofiber	Chitin	123.8 at 1C, 84.7 at 5C	Carbon ¹⁶
Graphite	Graphite	80 at 1C	J. Am.
			Chem.
			Soc. ¹⁷
Carbon nanofiber	Bacterial cellulose	168 at 200 mA g ⁻¹	Nano Lett. ¹⁸
foam	nanofibers		
Carbon nanofiber@	Carbon nanofiber	236 mAh g ⁻¹ at 0.1 C,	ACS Appl.
CNT	and CNT	193 mAh g ⁻¹ at 1 C	Mater.
			Interfaces ¹⁹
rGO aerogel	Reduced graphene	125 at 1.6 C	Energy
	oxide		Storage
			Mater. ²⁰
P-doped hard carbon	Lignin	100 at 1 A g ⁻¹	Chem. Eng.
			J. ²¹

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