Large-scale production of holey graphite as high-rate anode for lithium ion batteries

Lithium ion batteries (LIBs) have been widely used in portable and smart devices because of their high energy densities, long cycle life and environmental friendliness. In order to meet the ever-growing demand for human-beings utilizing electronic devices, electric vehicles and energy storage grids, it requires LIBs with much higher power and energy densities [1]. As a core of LIBs, the electrode (including cathode and anode) materials largely determine the development of LIBs. Over the past decades, a large number of anode candidates have been developed to replace graphite, the most commonly used commercial anode, with the limited theoretical capacity (372 mAh g⁻¹) and poor rate capability. Among the candidates, graphene and its analogues (e.g., graphene derivatives and their related composites) have attracted great attention owing to their overwhelming physical properties of large surface areas, high electrical conductivities, excellent mechanical flexibilities, as well as chemical stabilities [2]. Despite the high theoretical capacity and promising electrochemical performances reported, the charge/mass-transfer capability of graphene based materials as anodes for LIBs remains challenges [3]. One of the great challenges is the strong van der Waals interactions between graphene nanosheets leading to the easy restack and agglomeration during the electrode preparation and discharge-charge process.

It is well known that the charge/mass-transfer prefers to reach the edges of graphene and then diffuse along its basal plane (in-plane diffusion) rather than that in through-plane diffusion. On account of this feature, very recently, the holey graphite has attracted a great concern [4–7]. The creation of the through-plane pores within graphene not only enables the electrolyte and charge/mass quickly transporting through holes to reach active sites, but also provides abundant edges along the holes for additional charge/mass loading [8–10] and carbon-edge engineering (e.g., heteroatoms doping [11,12] and molecular adsorption [13]). Benefiting from rich holes as well as the decreased van der Waals interaction, the holey graphite is more prone to forming a thinner and restack film compared to the pristine graphene. As expected, the enlarged accessible surface area and shortened charge/mass diffusion distance endow the holey graphene film with superior power and energy densities, in particular volumetric energy densities [11,14]. So far, many efforts have been devoted to fabricating holey graphene by means of various physical (e.g., template-assisted lithography [15], photodegradation [16], ion irradiation [17], plasma etching [18], chemical vapor deposition [19,20], and hydrothermal methods [14,21]) and chemical approaches (e.g., H₂O₂, HNO₃, H₂SO₄ and KMnO₄) [6,7]. However, the former approaches usually suffer from tedious and complex experimental procedures as well as the low yields. The latter one often requires toxic and environment-harmful reagents or/and involves harsh reaction conditions. Moreover, those synthesis processes could easily damage the carbon basal plane and simultaneously generate many chemical and topological defects in the carbon basal plane [6,7,17]. Although the considerable amounts of structural defects as well as oxygenated groups are favorable for extra charge/mass storage, the conductivities of the fabricated holey graphene are significantly reduced [6,22,23]. In order to improve the conductivity, it often requires additional post-treatment steps such as high-temperature thermal annealing or/and heteroatoms doping reduction reaction. However, such additional steps involve hazardous reducing reagents (e.g., hydrazine, NH₃, NaBH₄) [24–27] and lead to a low reduction conversion.

Despite the significant progress achieved, the reported holey graphene as anode for LIBs still suffers from high average working voltage (e.g., > 0.5 V, Li⁺/Li) and large voltage hysteresis compared to graphite, thus leading to a low energy density when applied in a full LIB. As expected, in combination of the anode advantages of holey graphene and graphite, the study on the holey graphite (namely hG) as high-rate anode for LIBs is highly desirable. Herein, we report a feasible and eco-friendly approach to a large-scale production of hG with well-defined hexagonal-hole structure, armchair edges and high-crystallinity basal plane. As shown in Fig. 1(a), the hG was directly produced by annealing pristine graphite at various temperatures (800–1100 °C) using the low-cost and common H₂O stream as a mild oxidative agent. During the fabrication process, no toxic or/and strong catalysts are used. Benefiting from its unique structural features, the hG as anode for LIBs displays outstanding rate capabilities (e.g., higher average capacities of 225.0 and 95.7 mAh g⁻¹ at 1 and 2 C, respectively, than those of pristine graphite (120.7 and 48.2 mAh g⁻¹)), and excellent cycling stability (e.g., 260.3 mAh g⁻¹ after 500 cycles with an initial capacity retention of 92.9%).

The modification of graphite was carried out in a tube furnace with a fused quartz tube. Commercial graphite powder (99.95%, aladdin) in an alumina crucible was placed at the center of the furnace. After the quartz tube purged with a high purity Ar for several times, the furnace was gradually heated up and kept for 1 h at a temperature range of 800 – 1100 °C under a control flow rate of Ar/H₂O gas mixture. During the cooling process, the flow mixture gas of Ar/H₂O was stopped instead by a flow gas of Ar.

The X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 advance diffractometer (Cu Kα, λ = 0.15406 nm). Raman spectra were obtained at room temperature using a Horiba JobinYvon/LabRAM HR8000 with a laser source at 632.8 nm. The topographic heights of holey graphite were measured by an atomic force microscope (AFM, Asylum Research, MFP-3D). The morphology of holey graphite was characterized by field emission scanning electron microscope (FESEM, Merlin, Zeiss) and high resolution transmission electron microscope.
(TEM, Titan G260-300) images. X-ray photoelectron spectra (XPS) were conducted on a Thermo fisher Scientific K-Alpha+ using C 1 s (B.E. = 284.8 eV) as a reference. The specific surface areas and the mesopore distributions were measured by Brunauer-Emmett-Teller (BET, Micromeritics ASAP 2460). The macropore distribution was analyzed by Mercury porosimetry (Micromeritics AutoPore IV 9500).

The electrochemical measurements were performed using CR 2032 coin-type cells. The electrodes were prepared by blending the active materials with carbon black and polyvinylidenedifluoride (PVDF) binder, in a mass ratio of 9:0.5:0.5, respectively. The N-methyl-2-pyrrolidone (NMP) was used as a blending solvent. The resultant slurry was coated on the Cu foil, dried in a vacuum oven at 90 °C for 24 h. The punched electrode mass was controlled at ~3.5 mg cm⁻². The coin-type cells were assembled in the high-purity Ar-filled glove box. The coin cells were fabricated by using the lithium foil as the counter and reference electrodes, the as-prepared electrode as the working electrode, a porous polypropylene as the separator and 1 M LiPF₆ in a mixture of the EC/DEC (ethylene carbonate/diethyl carbonate, 1/2 (v/v)) as the electrolyte. The fabricated coin-cells were discharged/charged using Land® battery tester system (Wuhan, China). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were measured on CHI 760E electrochemical workstation.

Fig. 1(a) shows a schematic diagram of the synthesis process of hG. Early studies have revealed that carbon can be oxidized by H₂O at high temperatures to produce H₂ and CO [28]. Recent studies have indicated that the point defects/amorphous zone within carbon plane can be transformed to carbon holes (e.g., holey graphene [29]) by using oxidative gas (e.g., H₂O [30,31] and O₂ [29,]) and strong catalysts (e.g., H₃O₂ [6]). In order to better understand the interaction mechanism between H₂O and graphite, a series of hGs were prepared at different temperatures from 800 to 1100 °C under a stream flow of H₂O. Their morphologies were characterized by SEM (Figs. 1(b)–(h) and S1, 2). As shown in Fig. 1(b), at 800 °C, the bulk graphite flakes in the hG-800 keep well their morphologies while the small graphite nanoplatelets in the hG-800 are cut and exfoliated by H₂O molecular into smaller species and few-layered graphene, respectively. This is because the small graphite nanoplatelets have more active edges exposure to H₂O for its intercalation and etching. With the temperature elevated to 900 °C, the bulk graphite is further attacked by H₂O and a number of nanoholes are created on the graphite surface (Fig. 1(c)). This is mainly due to the presence of the weak point defect and amorphous area in the graphite. When the temperatures are further increased to 1000 and 1100 °C, a large number of hexagonal holes are produced in both hG-1000 and hG-1100 (Fig. 1(d,e)). The mass yields of hG-800, hG-900, hG-1000 and hG-1100 reach ~80, ~90, ~86 and ~60 wt%, respectively. The vacancies left in the hG-1000 and hG-1100 are occupied by well-defined hexagonal holes and armchair edges [30–32]. The formation of hexagonal holes and armchair edges is mainly as-
associated with easier cleavage of the C–C bond from the armchair edge than from the zigzag edge of graphene. The different hole sizes, even holes merging and hole depths (Figs. 1(h) and S2) are ascribed to the different distributions of defects and amorphous carbon in the graphite. As shown in Fig. 1(h), some hexagonal holes with more than 600 nm are parallel to each other, indicating their similar crystallographic orientations. These large holes are beneficial for the electrolyte quick penetration and Li⁺ transportation. Nevertheless, the excessively large holes could significantly destroy the structural integrity of hG. Compared to hG-1100, hG-1000 with moderate amounts and sizes of holes and non-fully penetrated depths is expected to maintain a higher conductivity and structural stability. To further examine detailed structures of hG, TEM was performed. As can be seen, characteristic graphitic carbon with a lattice size of 0.34 nm (Fig. 1(f)) and the well-defined hexagonal holes (Fig. 1(g)) of hG-1000 are well confirmed. Besides, the feature of the few-layered graphene exfoliated from the hG is further confirmed both by TEM (Fig. 1(f) and (g)) and AFM (Fig. S3). AFM result (Fig. S3(c)) also supports the presence of holes in the few-layered graphene.

XRD patterns of pristine graphite, hG-800, hG-900, hG-1000, and hG-1100 are shown in Fig. 2(a). As can be seen, all hGs display the similar characteristic peaks to pristine graphite and their (002) peak intensities are significantly reduced with the temperature increase. This is mainly due to the size reduction of graphite flakes and the increased number of holes. The graphitic feature of hG is also revealed by Raman spectra. As shown in Fig. 2(b), all hGs present the distinct G band at ~1584 cm⁻¹ and G' band at ~2726 cm⁻¹ assigned to a graphitic feature and the ambiguous D band at ~1350 cm⁻¹ associated with the disordered/defective carbon. Compared to pristine graphite (0.099), all hGs show the small and close ratios of I_D/I_G (0.16–0.23), indicating the well preservation of graphitic structures for the hG after the oxidation process.

To further identify the chemical composition and their oxidation states, XPS of hG-1000 was performed in Fig. 2(c). According to the analysis, the hG-1000 has 98.4 at% C and 1.6 at% O. The minor oxygen content is attributed to the surface adsorbed oxygen. High resolution XPS C 1s (inset of Fig. 2(c)) and O 1s (Fig. S4) spectra indicate that the C 1s spectrum can be deconvoluted to C–C at 284.3 eV, C = C at 284.7 eV, C–OH at 285.6 eV and C = C–O 287.4 eV while O 1s peak is split into C = O at 532.0 eV and C–O at 533.2 eV. The specific surface areas and mesopore size distributions of hG were separately determined by the BET and Barrett–Joyner–Halenda (BJH) methods. As shown in Fig. 2(d), the hG-1000 has a slightly higher surface area (4.4 m² g⁻¹) than that of pristine graphite (2.6 m² g⁻¹). The minor difference in surface area is mainly due to the similar flake patterns of hG to graphite, indicating structural integrity of hG during the H₂O modification process. Moreover, larger amounts of mesopores (~5 nm, inset of Fig. 1(d)) are observed in hG-1000 than graphite. As for the creation of macro-holes, the hG-1000 analyzed by Mercury porosimetry has an average pore size of ~2 μm (Fig. S5), which is consistent with the SEM results (Fig. 1(d)).

Fig. 3 reproduces electrochemical behaviors of the pristine graphite and hG measured at various C-rates from 0.1 to 5 C (1 C = 372 mAh g⁻¹) in the voltage range of 0.02 – 3 V.
can be seen, the discharge-charge profiles of hG-800, hG-900, hG-1000 and hG-1100 (Figs. 3(a) and S6) at various C-rates are similar to those of pristine graphite (Fig. 3(b)), which are typical electrochemical behavior of commercial graphite [33]. These electrochemical behaviors are also confirmed by their corresponding cyclic voltammetry (CV) at 0.1 mV s⁻¹. As shown in Fig. 3(c) and (d), the CV curves of pristine graphite and hG-1000 display a reduction peak (A1) at ~0.7 V in the first discharge process, and a pair of redox peaks (A2 and C1) at ~0.1 V in each cycle. The existence of the reduction peak at ~0.7 V and its disappearance in the following cycles is mainly correlated to the formation of a strong and irreversible solid state interface (SEI) layer on the electrode surface in the first discharge cycle. The redox peaks at ~0.1 V, corresponding to the discharge/charge plateaus at ~0.1 V (Fig. 3(a) and (b)), are assigned to Li⁺ intercalation into/de-intercalation from graphitic layers. It should be noted that the hG-1000 has larger peak intensity ratios of A2/A1 than those for pristine graphite (Fig. 3(c) and (d)), suggesting its stronger Li⁺ uptake activity. This is mainly attributed to the plenty of holey structures in hG, as well as the close surface area of hG to graphite.

To compare rate capabilities of the pristine graphite and hG, the cells were discharged-charged for 50 cycles at various C-rates from...
0.1 to 5 C between 0.02 and 3.0 V. As shown in Fig. 3(c), initial discharge capacities of pristine graphite, hG-800, hG-900, hG-1000, and hG-1100 are 375.6, 393.8, 425.7, 452.1 and 471.4 mAh g⁻¹, with initial Coulombic efficiencies (CEs) of 89.4%, 89.7%, 87.4%, 83.2% and 87.4%, respectively. The different initial CEs for hG are mainly attributed to the different surface areas and amounts of defects of hG (Fig. 2(d)). Over the 50 cycles, the hG-1000 exhibits a pronounced enhancement in respect to the rate capacity (especially an average capacity of 225.0 mAh g⁻¹ at 1 C and 95.7 mAh g⁻¹ at 2 C). When the C-rate is set back to 0.1 C, all electrodes almost deliver the close capacities to those at the initial cycles, indicating their excellent structural stability during the cycling.

In order to further evaluate long-term cycling stabilities of hG and pristine graphite, the electrodes were measured at 1 C for 500 cycles. As shown in Fig. 4(a), the hG-1000 delivers a much higher initial discharge capacity of 279.2 mAh g⁻¹, followed by hG-900 (166.1 mAh g⁻¹), than those for hG-1100 (119 mAh g⁻¹) and pristine graphite (131.1 mAh g⁻¹). The low capacities of hG-1100 in the initial cycles are probably associated with too rich and holey structure to destroy the structural integrity and thus significantly decrease the electronic conductivity. Nevertheless, the hG-1100 together with hG-1000 present impressive cycling stability, compared to pristine graphite, hG-800 and hG-900. It should be noted that an increasing capacity for hG-1000 over the long cycling stability is most likely due to the electrode-electrolyte activation at a high C-rate. After 500 cycles, the hG-1000 and hG-1100 maintain high discharge capacities of 260.3 and 106.6 mAh g⁻¹, corresponding to initial discharge capacity retentions of 92.9% and 89.6%, respectively, higher than hG-800 (42.4 mAh g⁻¹ and 30.9%), hG-900 (69.8 mAh g⁻¹ and 42.0%) and pristine graphite (34.8 mAh g⁻¹ and 26.5%). The impressive cycling stabilities of hG-1000 and hG-1100 support that the holey structure of hG is favorable for Li⁺ storage and transportation. The stronger kinetics of hG-1000 and hG-1100 are further supported by electrochemical impedance spectroscopy (EIS), which shows the smaller charge transfer resistance (Rct) for hG-1000 and hG-1100 electrodes before cycling than those of other electrodes (Fig. S7). SEM images (Fig. S8) also reveal that the holey structures of hG-1000 and hG-1100 electrodes can be well preserved after 100 cycles.

To better understand lithium intercalation/de-intercalation process of hG-1000, in-situ XRD measurements with a sampling interval of 10 min are carried out for 5 cycles at 0.75 C. The collected full-scale XRD patterns of the electrodes during the cycling are shown in Fig. S9. Detailed analysis of the structural evolutions (C₆ + xLi ↔ LiₓC₆, 0 < x < 1) mainly focuses on the shifts or/and splits of the (002) graphite reflection at 26.5°. As shown in Fig. 4(a), Li⁺ intercalation into graphite during the initial lithiation process (0 < x < 0.5, 26.5° → 26.2°) occurs in an ordered matter. This is evidenced by the clear and sharp (002) peaks with left shifts (26.5° → 26.2°). When x > 0.5, the (002) peaks continue to shift left (26.2° → 25.2°) and become weak and board. The main reason is that Li⁺ (x > 0.5) preferably occupy the outer layers of lithiated graphite particles and then continue to intercalate with an additional driving force of lithium concentration gradient[34]. In the following charge process, the (002) peaks gradually return to the states at previous discharging process until the pristine state before charging. In the subsequent 4 cycles, the hG well maintains the similar change trend to that in the first cycle. Furthermore, the intensity of (002) peaks at the end of charging state at each cycle almost remains unchanged, indicating the highly re-
versatile structures of hG. As shown in Fig. 4(b), the in-situ XRD patterns of pristine graphite also display the similar shift of (002) peak (26.5° → 26.2° → 25.2°) to hG during each discharge–charge process. However, the stronger and more clear (002) peak shifts of hG over the five cycles, once again, support the stronger electrode kinetics for hG-1000 than pristine graphite.

In summary, the holey graphite (hG) with well-defined hexagonal holes was synthesized by a feasible and eco-friendly approach via using a low-cost and common H2O steam as a mild oxidative reagent to directly anneal graphite at high temperatures. When the hG is tested as anode for LIBs, it exhibits remarkable rate capability together with its similar electrochemical behavior to pristine graphite. In particular, the pristine graphite annealed at 1000 °C (hG-1000) shows a much higher average capacities of 225.0 and 95.7 mAh g−1 at 1 and 2 C, respectively, than pristine graphite (120.7 and 48.2 mAh g−1). Apart from its high rate capability, the hG-1000 also displays an excellent long-term cycling stability (e.g., 260.3 mAh g−1 after 500 cycles with an initial capacity retention of 92.9%). Such outstanding lithium ion storage properties are attributed to its unique structural features such as plenty of holey structures and graphic patterns. These features guarantee a high electrode conductivity of hG and are beneficial for the quick penetration of the electrolyte, rapid diffusion of Li+, and extra active sites for Li+ storage. As expected, the approach to synthesis of hG not only is an enormously promising way to develop high-rate graphite as anode for LIBs but also provides the raw materials for the large-scale synthesis of holey graphene.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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