Double-Holey-Heterostructure Frameworks Enable Fast, Stable, and Simultaneous Ultrahigh Gravimetric, Areal, and Volumetric Lithium Storage

Zhonghui Chen,†¶ Jiadong Chen,†¶ Fanxing Bu,†¶ Phillips O. Agboola,‡ Imran Shakir,*§ and Yuxi Xu*†

†State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
‡Mechanical Engineering Department, College of Applied Engineering, King Saud University (Al Muzahimiyah Branch), Riyadh 11421, Saudi Arabia
§Sustainable Energy Technologies Center, College of Engineering, King Saud University, Riyadh 11421, Kingdom of Saudi Arabia

Supporting Information

ABSTRACT: Deliberate design of advantageous nanostructures holds great promise for developing high-performance electrode materials for electrochemical energy storage. However, it remains a tremendous challenge to simultaneously gain high gravimetric, areal, and volumetric capacities as well as high rate performance and cyclability to meet practical requirements mainly due to the intractable insufficient ion diffusion and limited active sites for dense electrodes with high areal mass loadings. Herein we report a double-holey-heterostructure framework, in which holey Fe$_2$O$_3$ nanosheets (H-Fe$_2$O$_3$) are tightly and conformably grown on the holey reduced graphene oxide (H-RGO). This hierarchical nanostructure allows for rapid ion and electron transport and sufficient utilization of active sites throughout a highly compact and thick electrode. Therefore, the free-standing flexible H-Fe$_2$O$_3$/H-RGO heterostructure anode can simultaneously deliver ultrahigh gravimetric, areal, and volumetric capacities of 1524 mAh g$^{-1}$, 4.72 mAh cm$^{-2}$, and 2621 mAh cm$^{-3}$, respectively, at 0.2 A g$^{-1}$ after 120 cycles, and extraordinary rate performance with a capacity of 487 mAh g$^{-1}$ (1.51 mAh cm$^{-2}$) at a high current density of 30 A g$^{-1}$ (93 mA cm$^{-2}$) as well as excellent cycling stability with a capacity retention of 96.3% after 1600 cycles, which has rarely been achieved before.

KEYWORDS: double-holey heterostructure, 3D framework, lithium storage, areal and volumetric capacity, electrochemical energy storage

Electrochemical energy-storage devices including batteries and supercapacitors have played vital role in our current society.\cite{1-3} The electrode materials are the central components of these devices and largely dictate their ultimate performance. With the rapid development of portable electronic products and newly emerging large-scale applications such as electric vehicles and the electricity grid, the state-of-the-art commercial devices cannot meet the increasing requirements for the energy devices such as larger energy density, higher charge-discharge rates, and longer cycling life.\cite{4-5} For example, the commercial anodes for lithium-ion batteries (LIBs) are mainly graphite, which severely suffers from low capacity (372 mAh g$^{-1}$) and poor rate performance.\cite{6,7} Therefore, considerable efforts have been devoted to the exploitation of other anode materials with higher theoretical capacity, such as metal/silicon, metal oxides, and organic polymers.\cite{8-10} In this regard, deliberate synthesis of advantageous nanostructures has achieved great success in efficiently improving the electrochemical performance of these promising anode materials.\cite{11-16} However, most previous studies focus on the enhancement of gravimetric capacity, and these excellent results are usually achieved in relatively thin and highly porous electrodes with low areal mass loading (<1 mg cm$^{-2}$) and low packing density (<1 mg cm$^{-3}$), which result in negligible low areal and volumetric capacities.\cite{17-19} Although the gravimetric capacity is traditionally used as the figure-of-merit to evaluate an electrode material in basic studies, the areal and volumetric performances have become critical parameters for assessing its practical potential for applica-
It is generally recognized that the excellent performance of such thin and loosely packed electrodes cannot be readily translated into a thick and dense electrode due to the significantly increased ion- or electron-transport resistance and lower utilization of active sites. To develop a practical high-performance energy-storage device, simultaneously gaining high gravimetric, areal, and volumetric capacities while retaining excellent rate capability and cyclability is urgently desired but presents a tremendous challenge to the design of electrode materials.

Herein we report a double-holey-heterostructure framework consisting of holey Fe$_2$O$_3$ nanosheets (H-Fe$_2$O$_3$) conformably grown on the holey reduced graphene oxide (H-RGO) by using GO/metal–organic framework composite aerogels as the precursor via a facile calcination route. Compared with previous various nanostructures, this double-holey-heterostructure framework possesses many significant advantages: (i) In situ and conformable growth of ultrathin H-Fe$_2$O$_3$ layers on H-RGO can facilitate interfacial electron transfer between graphene and Fe$_2$O$_3$ for sufficient electrochemical reaction. (ii) The H-Fe$_2$O$_3$ nanosheet assembled by chemically interconnected ultrasmall Fe$_2$O$_3$ nanoparticles provides shortened ion diffusion paths and increased active sites as well as abundant voids to effectively buffer the volume expansion/contraction effect. (iii) Both H-Fe$_2$O$_3$ and H-RGO have uniformly distributed in-plane nanopores and are well integrated into a...
highly continuous 3D network with open channels, which can significantly promote ion- and electron-transport across the entire dense and thick electrode. Therefore, when used as binder-free anodes for LIBs, the H-Fe$_2$O$_3$/H-RGO heterostructure framework can simultaneously deliver ultrahigh gravimetric, areal, and volumetric capacities of 1524 mAh g$^{-1}$, 4.72 mAh cm$^{-2}$, and 2621 mAh cm$^{-3}$, respectively, at 0.2 A g$^{-1}$ after 120 cycles. Furthermore, it also displays excellent cycling stability with a capacity retention of 96.3% after 1600 cycles and extraordinary rate performance with a capacity of 487 mAh g$^{-1}$ (1.51 mAh cm$^{-2}$) at a high current density of 30 A g$^{-1}$ (93 mA cm$^{-2}$).

RESULTS AND DISCUSSION

The synthesis process of the H-Fe$_2$O$_3$/H-RGO is shown in Figure 1. Prussian blue (PB, Fe$_4$[Fe(CN)$_6$]$_3$), a typical resource abundant, low-cost, and environmentally benign metal organic framework, was chosen as the precursor of Fe$_2$O$_3$. It can be easily prepared by coprecipitation of an Fe$^{III}$ salt and [Fe$^{II}$(CN)$_6$]$^{4-}$ in water and shows a face-centered cubic crystal structure where alternating Fe$^{III}$ and Fe$^{II}$ are bridged by the cyanide ligands. Therefore, the composition and structure of the PB derivatives could be well designed and controlled. The Prussian blue/graphene oxide (PB/GO) composite with homogeneous and dense growth of PB nanoparticles on GO was synthesized using a modified excessive metal-ion-induced self-assembly route developed by our group.23,26,27 After freeze-drying of the aqueous dispersion of PB/GO, the obtained PB/GO aerogel was directly used as the precursor to fabricate the H-Fe$_2$O$_3$/H-RGO heterostructure framework by annealing in air. During the annealing process, the organic ligands in PB framework were decomposed, accompanied by oxidization of the iron element into Fe$_2$O$_3$, which resulted in the collapse and contraction of the 3D skeleton in PB.25,28 Meanwhile, because of the uniform and dense distribution of PB nanoparticles on GO, the as-formed Fe$_2$O$_3$ nanoparticles were interconnected and fused to some extent to form a continuous holey nanosheet with abundant nanovoids. Simultaneously, GO was thermally reduced, and many of the defective domains on GO were simultaneously thermally degraded into uniformly distributed nanopores,29,30 all of which result in a double-holey heterostructure framework. By selectively removing each layer of this double-holey heterostructure, we can obtain individual pure holey nanosheets, that is, H-Fe$_2$O$_3$ or H-RGO, for further characterization.

Figure 2 shows the morphologies and microstructures of the PB/GO precursor and the H-Fe$_2$O$_3$/H-RGO heterostructure framework. The PB/GO aerogel has an interconnected 3D porous network with hierarchical sub-micro- and microsized pores, which is assembled by ultrathin PB/GO composite nanosheets shown in Figure 2a,b. High-resolution transmission electron microscopy (HRTEM) (Figure 2c) and elemental mappings (Figure S1) images of the PB/GO composite reveal that the PB nanoparticles with average diameter of $\sim$5 nm are uniformly and densely grown on GO surface. The growth of PB nanoparticles on GO has also been confirmed by the result of Fourier transform infrared spectroscopy (FTIR) (Figure S2), as a new and strong peak at 2083 cm$^{-1}$ appears in the spectrum of PB/GO, which can be ascribed to the C=N bond of PB. The XRD pattern of PB/GO shows weak and broad peaks (Figure S3), which suggests that the ultrasmall PB nanoparticles are poorly crystallized. Besides, on the basis of the Scherrer formula, the calculated average size of PB
nanoparticles on GO is ∼5.6 nm, which is very close to TEM results (Figure 2b,c). After calcination in air, the interconnected 3D porous network structure of the aerogel can remain intact, as shown in Figure 2d. TEM images of the H-Fe2O3/H-RGO (Figure 2e) show ultrathin nanosheets with uniform surface nanoporosity. The diffuse diffraction rings in the selected-area electron diffraction (SAED) pattern (the inset of Figure 2e) suggest the amorphous or weak crystallized nature of the H-Fe2O3, which is consistent with the result of XRD (Figure 2f). Raman spectra indicate the complete conversion of PB nanosheets due to the thermal degradation of the defective nanometers. Meanwhile, many nanopores (about a few nanometers) are also uniformly distributed on H-RGO nanosheets (Figure 3a) and the H-Fe2O3 has a strong binding interaction with RGO. The FESEM images confirm that PB nanosheets were separated and characterized, as shown in Figure 3 and Figure S7. H-RGO could be easily obtained by dispersing the H-Fe2O3/H-RGO composite in 2 M HCl solution and hydrothermal treatment. Furthermore, the H-Fe2O3/H-RGO composite shows a significantly larger intensity ratio of the D band to G band (Figure S3), which indicates that the H-Fe2O3/H-RGO composite is a double-holey-heterostructure structure, as shown in Figure 2h. Ultrasmall Fe2O3 nanoparticles with an average diameter of ∼5 nm are chemically interconnected to form continuous holey nanosheets with abundant voids. Meanwhile, many nanopores (about a few nanometers) are also uniformly distributed on H-RGO nanosheets due to the thermal degradation of the defective domains on GO. This double-holey-heterostructure framework imparts the H-Fe2O3/H-RGO not only a high weight content of Fe2O3 up to 72.3% (Figure S4) but also a high specific surface area of 280 m2/g determined by N2 adsorption test (Figure S5). The pore-size analysis reveals that the pores are mainly located between 1 and 5 nm (Figure S5b), which can be ascribed to the nanopores from both H-Fe2O3 and H-RGO. Raman spectra indicate the complete conversion of PB into metal oxide. The Fe 2p XPS spectrum (Figure S5b) indicates only Fe, O, and C elements in the H-Fe2O3/H-RGO composite, which is consistent with the XPS spectra of H-Fe2O3. Together, the above results can clearly demonstrate a double-holey-heterostructure structure consisting of strongly coupled self-supportable H-Fe2O3 and H-RGO nanosheets.

Because of the robust interlock of the graphene sheets in the H-Fe2O3/H-RGO aerogel, the monolithic H-Fe2O3/H-RGO aerogel can be compressed to a highly compact flexible film with a packing density up to 1.72 g cm−3 without obvious restacking of graphene sheets (Figure 4a–c). Such double-holey heterostructure framework can be expected to show great advantage for unimpeded and sufficient ion diffusion through a compact and thick electrode architecture over previous nanostructures (Figure S1). To further study the advantage of double-holey-heterostructure framework structure on the electrochemical performance, we used a thick H-Fe2O3/H-RGO film with a high areal mass loading of 3.1 mg cm−2 as binder-free LIBs anode to assemble the cells. For comparison, we synthesized and tested two control anodes, namely, H-Fe2O3/H-RGO aerogel, 3,23 the monolithic H-Fe2O3/H-RGO film. (c) XR patterns of the H-Fe2O3/H-RGO aerogel before compression and film after compression. (d) Schematic illustration of the sufficient and unimpeded ion diffusion within the H-Fe2O3/H-RGO heterostructure.
Fe$_2$O$_3$/RGO and Fe$_2$O$_3$/H-RGO (Figures S8 and S9), all of which have single-holey structure, to understand the structure–property relationship. The H-Fe$_2$O$_3$/RGO was obtained by annealing the PB/GO precursor at a relatively low temperature of 300 °C, which is enough for the conversion of PB into H-Fe$_2$O$_3$ but cannot create nanopores in RGO (Figure S10). The Fe$_2$O$_3$/H-RGO was obtained by directly annealing the H-Fe$_2$O$_3$/H-RGO at a high temperature of 600 °C in a N$_2$ atmosphere, which can destroy the holey structure of H-Fe$_2$O$_3$ due to the induced crystallization (Figure S9) and strong aggregation of Fe$_2$O$_3$ nanoparticles but maintain the structure of H-RGO (Figure S11). The BET-specific surface areas of H-Fe$_2$O$_3$/RGO (152 m$^2$/g) and Fe$_2$O$_3$/H-RGO (104 m$^2$/g) are much lower than those of H-Fe$_2$O$_3$/H-RGO (280 m$^2$/g), further demonstrating the highly porous feature of the double-holey structure (Figure S12). Furthermore, the electrical conductivity of the H-Fe$_2$O$_3$/H-RGO measured by a four-point probe method is 662 S/m, which is close to that of the H-Fe$_2$O$_3$/RGO (697 S/m) but higher than that of Fe$_2$O$_3$/H-RGO (416 S/m).

Figure 5a shows the typical galvanostatic charge/discharge curves of the H-Fe$_2$O$_3$/H-RGO anode at 0.2 A g$^{-1}$ between 0.01 and 3 V (versus Li/Li$^+$/). There are two voltage plateaus at 1.5 and 0.9 V in the first charge curve and one voltage plateau at 1.25 V in the first charge curve, which can be ascribed to the multistep electrochemical reactions between the Fe$_2$O$_3$ and Li$^+$. The similar voltage plateaus can also be observed in the galvanostatic charge/discharge curves H-Fe$_2$O$_3$/RGO and Fe$_2$O$_3$/H-RGO anodes, as shown in Figure S13. The H-Fe$_2$O$_3$/H-RGO anode delivered a high initial discharge capacity of 2318 mAh g$^{-1}$ and an initial charge capacity of 1582 mAh g$^{-1}$ with a limited initial coulomb efficiency of 68.2%, which could be ascribed to the degradation of electrolyte and the formation of solid electrolyte interface (SEI). Meanwhile, the discharge–charge curves almost overlapped for the 2nd, 5th, 10th and 100th cycles, with the coulomb efficiency rapidly increasing to 99% in a few cycles, demonstrating its excellent cycling stability. After 120 cycles, the capacity of H-Fe$_2$O$_3$/H-RGO anode could still retain as high as 1524 mAh g$^{-1}$, which was much higher than that of H-Fe$_2$O$_3$/RGO anode (902 mAh g$^{-1}$) and Fe$_2$O$_3$/H-RGO anode (795 mAh g$^{-1}$) (Figure 5b). The capacity of H-Fe$_2$O$_3$/H-RGO is also higher than the theoretical capacity of Fe$_2$O$_3$ (1007 mAh g$^{-1}$), similar to many recently reported nanostructured Fe$_2$O$_3$-based anodes presented in Table S1, which could be ascribed to extra Li$^+$ storage via interfacial reaction due to the charge separation at the metal/Li$_2$O phase boundary or the formation of polymeric gel-type layer. The rate performance of these anodes was evaluated at current densities from 0.2 to 30 A g$^{-1}$. Figure 5c showed the galvanostatic discharge–charge curves of the H-Fe$_2$O$_3$/H-RGO anode at different current densities, and the corresponding reversible capacities are 1524, 1410, 1298, 1203, 1044, 876, and 668 mAh g$^{-1}$ at 0.2, 0.5, 1, 2, 5, 10, and 20 A g$^{-1}$, respectively, far surpassing those of H-Fe$_2$O$_3$/RGO and Fe$_2$O$_3$/H-RGO anodes (Figure 5d). Even at a superhigh current density of 30 A g$^{-1}$ (93 mA cm$^{-2}$), the H-Fe$_2$O$_3$/H-RGO anode could still achieve an impressive capacity of 489 mAh g$^{-1}$, whereas the corresponding capacities of H-Fe$_2$O$_3$/RGO and Fe$_2$O$_3$/H-RGO anodes were merely 183 and 69 mAh g$^{-1}$, respectively, demonstrating the extraordinary rate performance of the H-Fe$_2$O$_3$/H-RGO anode. Moreover, the reversible capacity of the H-Fe$_2$O$_3$/H-RGO anode recovered to 1473 mAh g$^{-1}$ when the current density returned to 0.2 A g$^{-1}$, indicating its excellent structural stability. In addition, we have also tested the control sample (H-RGO) without H-Fe$_2$O$_3$ (Figure S14) and confirmed that the excellent electrochemical performance of H-Fe$_2$O$_3$/H-RGO was mainly due to the synergistic effect of H-RGO and H-Fe$_2$O$_3$. We observed that H-RGO anode showed obvious capacity fading during the first 10 cycles, which could be ascribed to its holey structure, resulting in the large specific surface area (608 m$^2$/g, Figure S14c) and more active sites. Thus it needed longer time to fully form stable SEI films. Because of the relatively low specific surface area compared with H-RGO, H-Fe$_2$O$_3$/H-RGO anode showed stable cycling performance during the initial charge/discharge stage. H-RGO could largely improve the electrical conductivity of H-Fe$_2$O$_3$ and showed almost no negative impact on ion transport, which synergistically promoted the release of electrochemical properties of H-Fe$_2$O$_3$. Thus a stable cycling performance could be gained. Note that the capacity and rate performance of the H-Fe$_2$O$_3$/H-RGO anode are higher than most Fe$_2$O$_3$-based and other metal-oxide-based anodes for LIBS reported thus far.
(Figure 5e, Tables S1 and S2). The electrochemical processes of these electrodes were further investigated and compared by electrochemical impedance spectroscopy (EIS). As shown in Figure 5f, the Fe$_2$O$_3$/H-RGO anode showed a smaller charge-transfer resistance (the depressed semicircle in the high- to medium-frequency region) and a lower Warburg impedance (the nearly straight line in the low-frequency region) than those of H-Fe$_2$O$_3$/H-RGO and Fe$_2$O$_3$/H-RGO anodes, which indicated that the double-holey-heterostructure framework could greatly promote electrolyte diffusion and ion/electron transport within the H-Fe$_2$O$_3$/H-RGO anode, thus speeding up and maximizing the electrochemical reaction and leading to the distinct enhancement of the electrochemical performance of H-Fe$_2$O$_3$/H-RGO. In particular, the common graphene composites such as H-Fe$_2$O$_3$/RGO could not achieve sufficient electrolyte diffusion throughout a compact and thick electrode architecture due to the blocking effect of large 2D graphene sheets in the vertical direction. However, this blocking effect could be effectively alleviated by the double-holey-heterostructure structure because there were abundant nanopores existing in each layer of the H-Fe$_2$O$_3$/H-RGO, which resulted in higher capacity even at a low current density of 0.2 A g$^{-1}$. In addition, the capacities of H-Fe$_2$O$_3$/H-RGO anode at low current densities were obviously higher than those of the Fe$_2$O$_3$/H-RGO anode, which could be ascribed to the lack of holey Fe$_2$O$_3$ nanolayers, lower specific surface area, and fewer accessible active sites of the Fe$_2$O$_3$/H-RGO anode caused by the serious agglomeration and fusion of Fe$_2$O$_3$ nanoparticles in Fe$_2$O$_3$/H-RGO. The long-term cycling performance of the H-Fe$_2$O$_3$/H-RGO anode at a high current density of 5 A/g was further studied (Figure 5g). After 1600 cycles, the H-Fe$_2$O$_3$/H-RGO anode still achieved a high reversible capacity of 990 mAh g$^{-1}$ with a high capacity retention of 96.3%, demonstrating its superior structural stability. The EIS analysis of H-Fe$_2$O$_3$/H-RGO, H-Fe$_2$O$_3$/RGO, and Fe$_2$O$_3$/H-RGO anodes obtained after long-term cycles has been conducted, as shown in Figure S15. Compared with EIS plots of these anodes before cycling (Figure 5f), the semicircles in the high-frequency region became slightly larger, and the slope of straight lines in the low-frequency region reduced, indicating the slightly increasing charge-transfer resistance and Warburg impedance of these anodes due to long cycle tests. Besides, the Warburg impedance of the H-Fe$_2$O$_3$/H-RGO anode after long-term cycles was smaller than those of H-Fe$_2$O$_3$/RGO and Fe$_2$O$_3$/H-RGO anodes, which could demonstrate the robust structure stability of the double-holey-heterostructure framework.

To better understand the excellent electrochemical performance, we have performed sweep voltammetry experiments to analyze the reaction kinetics of the H-Fe$_2$O$_3$/H-RGO, H-Fe$_2$O$_3$/RGO, and Fe$_2$O$_3$/H-RGO anodes (Figure 6 and Figure S16). With a 50-fold increment in scan rate from 0.2 to 10 mV s$^{-1}$, the peaks were retained and not significantly altered in the CV curves of H-Fe$_2$O$_3$/H-RGO and H-Fe$_2$O$_3$/RGO anodes. However, the peaks of the Fe$_2$O$_3$/H-RGO anode at a high scan rate show obvious shift and distortion. The sweep rate dependence on peak current ($i = \alpha \nu^b$) is used to distinguish between diffusion-controlled and surface-controlled currents. Here $i$ is the peak current, $\nu$ is the sweep rate, $\alpha$ is a constant, and $b$ is an adjustable parameter. The calculated $b$ values of the H-Fe$_2$O$_3$/H-RGO anode (0.87 and 0.76) are obviously larger than those of H-Fe$_2$O$_3$/RGO (0.81 and 0.74) and Fe$_2$O$_3$/H-RGO (0.71 and 0.54) anodes, as shown in Figure S16b,d. It suggests more dominant surface-controlled kinetics for the H-Fe$_2$O$_3$/H-RGO anode, which is consistent with the extraordinary rate performance of the H-Fe$_2$O$_3$/H-RGO anode because a surface-controlled reaction is favorable to obtain high rate performance. Furthermore, we have also performed TEM characterization of the H-Fe$_2$O$_3$/H-RGO anodes after long cycling tests (Figure 6c,d), and their overall double-holey-heterostructure framework was not destroyed and remained intact. In addition, the Fe 2p XPS spectrum of the H-Fe$_2$O$_3$/H-RGO anode at fully charged states (3 V) after long cycling tests (Figure S17) indicated that the material on H-RGO was primarily composed of Fe$_2$O$_3$ due to its reversible electrochemical reactions with Li$^+$. These results further explicate the remarkable electrochemical performance of our designed double-holey-heterostructure framework structure.

To evaluate the practical potential of this double-holey-heterostructure framework for electrochemical energy storage, we have also compared the H-Fe$_2$O$_3$/H-RGO anode with various representative anodes with regard to the areal capacity versus areal current density ($i=\alpha\nu^b$) when matching with suitable cathodes. Moreover, the H-Fe$_2$O$_3$/H-RGO anode exhibits a more gradual change in areal capacity with increasing current density and thus can still provide a notable areal capacity at such high current density. Meanwhile, the H-Fe$_2$O$_3$/H-RGO anode has a superior volumetric capacity of 2621 mAh cm$^{-3}$ due to its high packing density of 1.72 g cm$^{-3}$, which is larger than many reported anode materials, as shown in Figure 7b and Table S3. Such excellent volumetric lithium-storage performance of H-Fe$_2$O$_3$/H-RGO anode can be ascribed to the compact H-Fe$_2$O$_3$/H-RGO film with high packing density showing no obvious restacking of graphene sheets and retaining its abundant and penetrating nanopores. As a result, there are limited electron- or ion-transport barriers.
within the compact H-Fe₂O₃/H-RGO anode during charge–discharge process. In a comprehensive comparison with previous anodes, our H-Fe₂O₃/H-RGO anode has a significant advantage, as it can simultaneously achieve high gravimetric, areal, and volumetric capacities (Figure 7c). Such superiority of our composite anode can be attributed to its double-hole-heterostructure framework, which provides substantial and unimpeded pathways for ion/electron transport and sufficient electrochemical reaction even under a compact and thick electrode condition.

CONCLUSIONS

A double-hole-heterostructure framework has been successfully synthesized. This deliberately designed nanostructure composed of 3D interconnected H-Fe₂O₃/H-RGO heterostructure nanosheets with abundant nanopores in each layer allows for rapid ion and electron transport and sufficient utilization of active sites throughout a highly compact and thick electrode. When used as binder-free anodes for LIBs, the entire H-Fe₂O₃/H-RGO anode simultaneously delivers ultra-high gravimetric, areal, and volumetric capacities of 1524 mAh g⁻¹, 4.72 mAh cm⁻², and 2621 mAh cm⁻³, respectively, at 0.2 A g⁻¹ after 120 cycles and also displays excellent cycling stability with a capacity retention of 96.3% after 1600 cycles as well as an extraordinary rate performance with a capacity of 487 mAh g⁻¹ (1.51 mAh cm⁻²) at a high current density of 30 A g⁻¹ (93 mA cm⁻²), thus holding great potential for lithium storage. This study not only suggests a promising electrode architecture for practical high-performance LIBs but also will inspire the design and development of other efficient energy storage and conversion systems.

EXPERIMENTAL SECTION

Synthesis of GO. GO was prepared from natural graphite powder (325 mesh) according to a modified Hummers’ method. In brief, 1.5 g of graphite powder was first immersed into 35 mL of concentrated H₂SO₄ under ice bath. Then, 0.75 g of NaNO₃ and 4.5 g of KMnO₄ were slowly added to keep the temperature of the suspension lower than 20 °C. The reaction system was kept at 40 °C for 30 min under magnetic stirring. Subsequently, 250 mL of deionized water and 20 mL of H₂O₂ (30%) were slowly added. The mixed solution finally turned bright yellow. Then, a purification process was carried out. The mixed solution was allowed to stand for 5 h; then, the supernatant liquid was removed. 200 mL of 10% HCl solution was added to remove metal ions. After centrifugal separation, plenty of deionized water was used to wash the obtained solid product until pH 7 by a high-speed centrifugation of 12 000 r/min. Finally, a low-speed centrifugation (4000 r/min) was used to remove the remaining natural graphite. The obtained solution was dispersed under ultrasonication for 1 h to obtain a homogeneous GO dispersion for the following experiments.

Synthesis of H-Fe₂O₃/H-RGO. The H-Fe₂O₃/H-RGO was prepared by a facile thermal treatment method. Typically, 100 mL of GO aqueous solution (0.4 mg/mL) was prepared and dispersed by ultrasonic treatment for 30 min. Then, 0.2 mL of NaFe(CN)₆ solution (0.5 M) was added to it under stirring. After 1.5 min, 2 mL of FeCl₃ solution (0.5 M) was rapidly added to the mixed solution, and it immediately turned blue. After stirring for 1.5 h, the mixed solution was centrifuged, washed, and freeze-dried to obtain PB/GO aerogel. The H-Fe₂O₃/H-RGO composite was prepared by directly annealing PB/GO aerogel in air. Suitable annealing temperature and time is crucial to gain the H-Fe₂O₃/H-RGO composite. First, the PB/GO aerogel was heated to 300 °C in air and maintained for 3 h. Then, the product was annealed at an increased temperature of 370 °C for another 1 h. The obtained H-Fe₂O₃/H-RGO monolithic aerogel could be directly used as binder-free electrodes for LIBs.

As a control, we have elaborately designed and fabricated two anodes, namely, H-Fe₂O₃/RGO and Fe₂O₃/H-RGO. The H-Fe₂O₃/RGO without holey RGO was prepared by annealing the PB/GO aerogel at 300 °C for 3 h in air. Another control sample, Fe₂O₃/H-RGO without holey Fe₂O₃, was prepared by thermal treatment of the prepared H-Fe₂O₃/H-RGO composite at 600 °C for 3 h in N₂ during which the holey Fe₂O₃ layer in H-Fe₂O₃/H-RGO composite were destroyed, whereas its holey RGO substrate was retained.

Synthesis of H-Fe₂O₃ Nanosheets. H-Fe₂O₃ nanosheets were obtained by calcining the H-Fe₂O₃/H-RGO aerogel at 430 °C for 4 h in air. In the annealing process, the H-RGO substance was burnt out, whereas H-Fe₂O₃ still maintained its original morphology. Finally, the black H-Fe₂O₃/H-RGO aerogel turned into yellow-brown H-Fe₂O₃.

Characterizations. The morphology and microstructure of the as-prepared materials were performed by field-emission scanning electron microscope (FE-SEM, Zeiss Ultra-55) and high-resolution transmission electron microscopy (HRTEM, Nova NanoSem 450). Raman measurements were conducted on an Invia/Reflex Lasser micro-Raman spectroscope (Horiba Jобin Yvon, France) with excitation laser beam wavelength of 532 nm. XRD analysis was performed on a D/Max 2500 X-ray diffractometer with Cu-Kα radiation (k = 1.54 Å) with a scanning speed of 5° min⁻¹ from 10 to 70°. The BET test was carried out under an Autosorb IQ Gas Sorption System at 77 K. X-ray photoelectron spectroscopy (XPS) was conducted by the PHI 5000C ESCA system. Thermo-gravimetric analysis (TGA) was conducted with a Mettler Toledo TGA instrument with a heating rate of 20 °C/min under 50 mL/min of flowing air.
Electrochemical Characterization. The prepared composite aerogels including H-Fe$_2$O$_3$/H-RGO, H-Fe$_2$O$_3$/RGO, and Fe$_2$O$_3$/H-RGO were directly used as anodes upon mechanical compression at a pressure of 10 MPa for LIBs. The areal mass loadings of our electrode materials were ~3.1 mg cm$^{-2}$. LIBs were assembled in an argon-filled glovebox with metallic lithium and Celgard 2400 as counter electrode and separator, respectively. LiPF$_6$ (1 M) in EC/DMC (1:1 by volume ratio) was used as the electrolyte. The galvanostatic experiments were conducted on a battery-testing system (LAND, Wuhan China) in the voltage window from 0.01 to 3 V. The EIS and CV curves were measured on a CHI 760D electrochemical workstation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b08071.

Supplementary figures and tables (PDF)

AUTHOR INFORMATION

Corresponding Authors
*Y.X.: E-mail: xuyuxi@fudan.edu.cn.
*I.S.: E-mail: imranskku@gmail.com.

ORCID

Yuxi Xu: 0000-0003-0318-8515

Author Contributions

∥Z.C., J.C., and F.B. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the support by the National Natural Science Foundation of China (51673042, 51873039), the Young Elite Scientist Sponsorship Program by CAST (2017QNRC001), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (TP2015002). We extend our sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the Research Group Project no RGP-VPP-312.

REFERENCES

(8) Zhang, Z. L.; Wang, Z. L.; Li, X. M. Multishelled Si@Cu Microparicles Supported on 3D Cu Current Collectors for Stable and Binder-Free Anodes of Lithium-Ion Batteries. ACS Nano 2018, 12, 3587–3599.
(14) Zhang, J. N.; Wang, K. X.; Xu, Q.; Zhou, Y. C.; Cheng, F. Y.; Guo, S. J. Beyond Yolk-Shell Nanoparticles: Fe$_2$O$_3$@Fe$_3$O$_4$@Core@Shell Nanoparticles as Yolks and Carbon Nanospindles as Shells for Efficient Lithium-Ion Storage. ACS Nano 2015, 9, 3369–3376.


