Double Restriction of Bismuth Nanoparticles by Carbon Matrixes for Ultralong−lifespan Sodium Storage

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Abstract. Alloying-type bismuth (Bi) anodes show a high theoretical capacity for sodium-ion batteries (SIB), yet their huge volume expansion and electrode pulverization resulted in poor electrochemical stability. Herein, we proposed a feasible strategy for the preparation of carbon/Bi composite material in which the Bi nanoparticles are uniformly dispersed in the double-layered carbon matrix. Benefiting from the synergistic confinement of the external coating of graphene and the internal layer of MOF-derived carbon, the volumetric expansion and large chemo-mechanical stress of Bi nanoparticles are effectively buffered. Therefore, the GAB@GO-800 anode exhibits a dramatically reversible capacity of 328 mA h g−1 at 0.1 A g−1, exceptional rate capability (299 mA h g−1 at 5 A g−1), and ultrahigh stability of 255 mA h g−1 at 2 A g−1 over 2000 cycles. Such hybrid carbon confinemental strategy via a combination of graphene coating and MOF-derived carbon is expected to be a promising method for the alloying-type anodes of SIBs.

Keywords: sodium-ion batteries; bismuth anode; carbon matrix.

1. Introduction

Sodium-ion batteries (SIBs) are regarded as an effective alternative to lithium-ion batteries in grid-scale energy storage systems due to their naturally abundant sodium resources and low cost.[1, 2] However, graphite, which is commonly used in the anode of lithium-ion batteries, does not apply to SIBs since the radius of sodium ion is ~55% larger than that of lithium ions.[3, 4] Therefore, it is critical to find anode materials with high-rate and long-life to ensure the practical application of SIBs.

Recently, alloying-type anode materials (such as Bi, Sb, Sn, Ge) have received more attention due to their appropriate Na+ insertion potentials and attractive theoretical capacities.[5] Among them, Bi is considered to be a competitive candidate for high performance anode owing to its large interlayer spacing along the c-axis (d (003) = 0.395 nm), flat reaction plateaus (0.6 V vs. Na+/ Na), and high volumetric capacity (3750 mA h cm−3).[6] In previous reports, Bi was directly applied in the anode for SIBs by a two-step alloying reaction mechanism: Bi + Na+ + e− ↔ NaBi and NaBi+ 2Na+ +2e− ↔Na3Bi. However, the fatal drawback is the large volume change (≈244%) from Bi to Na3Bi during the alloying process, which severely disrupts its crystal structure thereby inevitably inducing continuous aggregation and pulverization of active materials.[7] These unwanted consequences will degrade the contact between Bi electrodes and current collectors, which deteriorates the rate performance and cycling stability in practical applications.

Designing nanostructured materials is the most common approach to these problems, which facilitates shortening ion diffusion paths and addresses the volume expansion during the sodium ions insertion or de-insertion process.[8] Despite these advantages for nanostructures, excessive voids greatly reduce the tap density of the active materials, resulting in low energy density of the entire batteries. In addition, it is currently difficult to obtain well-defined nanostructured alloy materials due to their considerable complexity and expensive synthesis. Beyond nanostructure engineering, carbon hybridization is another strategy to improve the sodium storage capacity of Bi anode materials, which not only provides good conductivity to enhance the reaction kinetics but also accommodates the strain of volume change and mechanical stress.[9] Graphene has been widely used as a carbon matrix for incorporating Bi nanomaterials due to its many merits such as light weight, large surface areas, high conductivity, and structural flexibility.[10] However, the

bismuth nanoparticles are easily detached from the graphene sheet due to the large volume change during the alloying process, resulting in poor cycling life.

Herein, a hybrid carbon structured GAB@GO-800 anode was successfully designed, which is derived from Bi-based MOFs (bismuth subgallate) through a thermal treatment. Other than the encapsulated graphene coating process, the development of MOF-based strategies allows a simple route to embed Bi nanoparticles in the double-layered carbon-based frameworks. This configuration of confining the Bi-nanoparticles within an external graphene coating and an internal carbon-based framework is expected to provide multilayered protection against anodic aggregation and volume changes, resulting in a good transport kinetics for electrons and Na+ ions. Accordingly, the GAB@GO-800 anode exhibits superior sodium storage performance for delivering a reversible capacity of 328 mA h g−1 at 0.1 A g−1, exceptional rate capability (299 mA h g−1 at 5 A g−1) and an extraordinary ultrahigh-rate stability of 255 mA h g−1 at 2 A g−1 over 2000 cycles. These results have helped to understand the potential mechanisms of performance enhancement in a wider range of carbon matrixes composites.

2. Experimental Section

2.1 Material Synthesis

2.1.1 *Synthesis of the GAB@GO*

Bismuth nitrate pentahydrate (485 mg) was milled and heated with gallic acid monohydrate (188.12 mg) and graphene oxide dispersion (200 mL, 1 mg mL−1) in a 250 mL borosilicate vial at 80 °C for 6 hours while being stirred with a PTFE-coated stir bar. The resultant black powder of GAB@GO was filtered off, rinsed several times with ethanol and distilled water (DI), then dried in ambient conditions overnight to remove guest molecules.

2.1.2 *Synthesis of the GAB@GO-800*

The corresponding GAB@GO-800 was synthesized by annealing GAB@GO at 800 °C for 1 hour under Ar/H2 atmosphere (92/8 v/v) with a heating rate of 2 °C min−1.

2.2 Material Characterization

Sample microscopic morphologies were analysised using a Hitachi Regulus-8100 field-emission scanning electron microscope (FE−SEM). The crystal structures of the hybrid carbon composites were characterized by TTR−III (XRD, Cu Ka), and the valence states and surface chemical state were observed through XPS (ESCA Lab 220iXL). Bi content and carbon content of materials were tested using TGA (10 °C min−1) in air/N2. Using Raman (Horiba XploRA+)to characterize defects and graphitization on material surfaces.

2.3 Electrochemical Measurement.

The electrode materials and counter electrode of sodium sheets were assembled into a half-cell for electrochemical testing. For assembling the electrodes, the as-prepared GAB@GO-800 powder was mixed with carbon black and polyvinylidene fluoride in NMP (8:1:1) by weight to form a slurry, which was then coated on an aluminum foil (mass loading of 1−1.5 mg cm−2) and dried for 12 h at 80 °C under vacuum. All assembly processes of the battery (CR2032-type coin) are carried out under vacuum in a glove box (MBraun, Germany, <0.1 ppm of O2 and H2O). The components of the battery electrolyte are 1 M NaPF6 in Diglyme. Charge/discharge testing of the prepared half-cells using Land−CT2001A tester (Wuhan, China) at 0.01−1.8 V versus Na/Na+, and EIS and CV tests were conducted on the AMETEK model 1470E.

3. Results and Discussion

GAB@GO precursor was prepared by the simple mixing of Gallic acid (GA) and bismuth nitrate [Bi (NO3)3] in graphene oxide aqueous solution at 80 °C. During this process, Bi3+ was coordinated with the phenolic hydroxyl group (−OH) on GA ligands but not with the carboxyl group. The uncoordinated carboxyl groups are linked two by two by double hydrogen bonds reinforcing the whole framework structure. Then, the GAB@GO was further pyrolyzed at 800 °C under an Ar−H2 atmosphere to form the final product of GAB@GO-800. The morphologies and structural characteristics of the as prepared samples were characterized by a field emission scanning electron microscope (FE−SEM). GAB@GO exhibits the morphology of lamellar MOFs and graphene flakes stacked on top of each other (Fig. 1a). After carbonization, GAB@GO transforms into a hierarchical Bi−carbon hybrid decorated by Bi nanoparticles (Fig. 1d, about 20−100 nm in size).

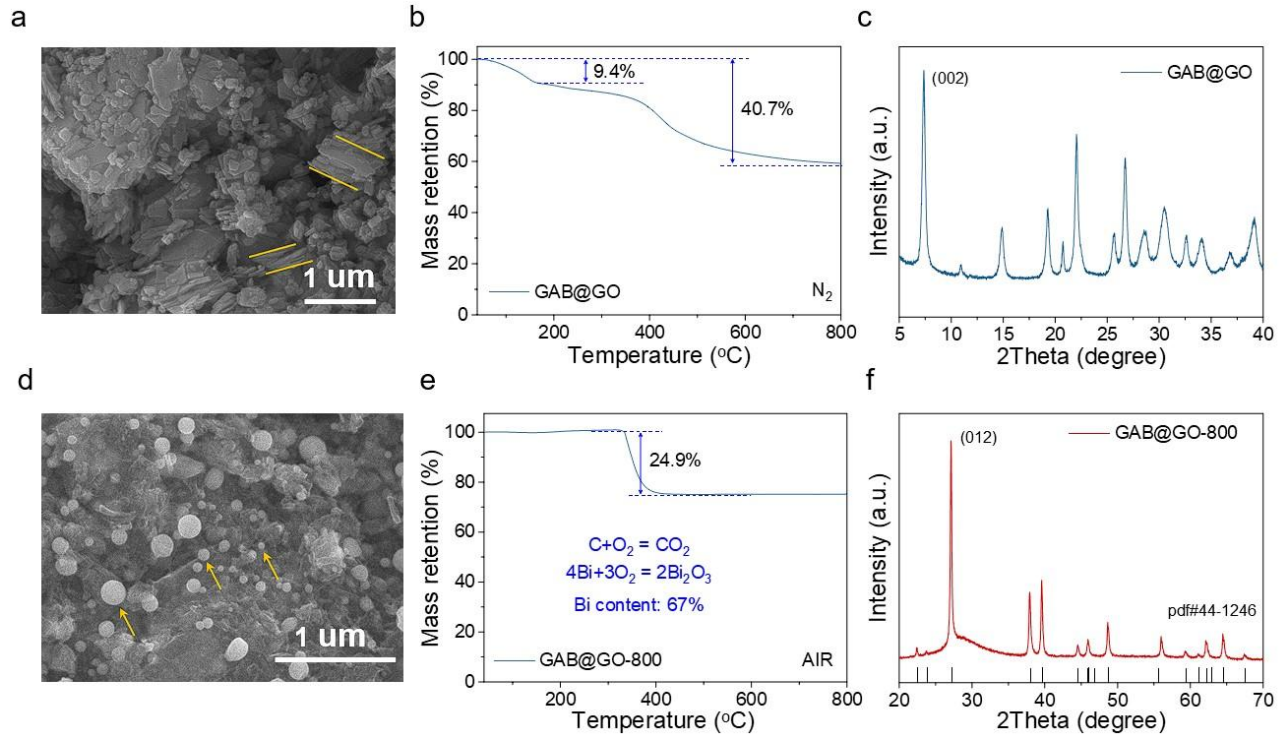

Fig. 1 a) SEM image of GAB@GO. b) TGA curve (in N2) of GAB@GO. c) XRD pattern of GAB@GO. d) SEM image of GAB@GO−800. e) TGA curve (in air) of GAB@GO−800, the calculated weight content of Bi was 67%. f) XRD pattern of GAB@GO−800.

From the thermogravimetric curve (TGA) profile in Fig. 1b, it can be seen that the precursor pyrolysis process is divided into two stages, one at 150 °C to remove the solvent molecules and the other at 350 °C to decompose the organic ligands. In addition, the Bi content in the composites was calculated to be about 67% of the TGA of GAB@GO-800 in air (Fig. 1e). In order to investigate the phase and crystalline characteristics of GAB@GO and GAB@GO−800, X−ray diffraction spectroscopy (XRD) were performed in Figure 1c, f. The XRD profile of GAB@GO is dominated by the coordination structure of GAB. The sharp diffraction peaks in the XRD pattern indicate the presence of the hexagonal Bi phase in GAB@GO−800. A new (012)−oriented phase reflects a two-dimensional (2D) puckered−layer structure of β−Bi. A larger layer spacing of the GAB@GO-800 contributes to improved rate performance.

Fourier−transform infrared spectroscopy (FTIR) experiments were conducted on GAB@GO before and after annealing to study changes in surface chemistry (Fig. 2a). The FTIR profile of GAB@GO exhibits an organic ligands signature with dense sharp peaks, whereas GAB@GO-800 has only a few peaks since most of the functional groups are removed in the carbonization process. Three peaks at 1379.8, 844.6 and 520.7 cm−1 are related to Bi−O and Bi−O−Bi, demonstrating that

there are relatively strong interactions between the Bi nanoparticles and the oxygen−containing functional groups of carbon hybrid rather than a simple mechanical contact between them. In order to further investigate the chemical composition and elemental status of GAB@GO and GAB@GO−800, high-resolution X−ray photoelectron spectroscopy (XPS, Fig. 2b, 2c, 2e, and 2f) was investigated. The C 1s spectra of GAB@GO are divided by four characteristic peaks located at ~ 284.4 eV for C−C, ~ 285.7 eV for C-O, ~ 288.2 eV for C=O, and ~ 290.6 eV for COOH, respectively.[11] As for the GAB@GO−800, it is mainly dominated by sp2- and sp3-hybridized carbon and the peaks of other functional groups are drastically reduced and cleaved after pyrolysis. In the Bi 4f spectra of GAB@GO, there are two peaks located at 164.9 and 159.6 eV, which are assigned to the Bi 4f5/2 and Bi 4f7/2. However, the peaks in GAB@GO-800 shift downward to 164.3 and 159.0 eV, respectively, due to the formation of metallic Bi. Raman spectroscopy (Fig. 2d) of GAB@GO shows a typical D band (~ 1340 cm−1) and G band (~ 1,590 cm−1), with a corresponding ID/IG value of 1.03. After carbonization, the ID/IG value of GAB@GO-800 rose to 1.42, which ascribed to the increase in edge defects. Edge defects in the carbon material help to increase the contact area between the electrode and the electrolyte, thus further shortening the diffusion distance of ions.

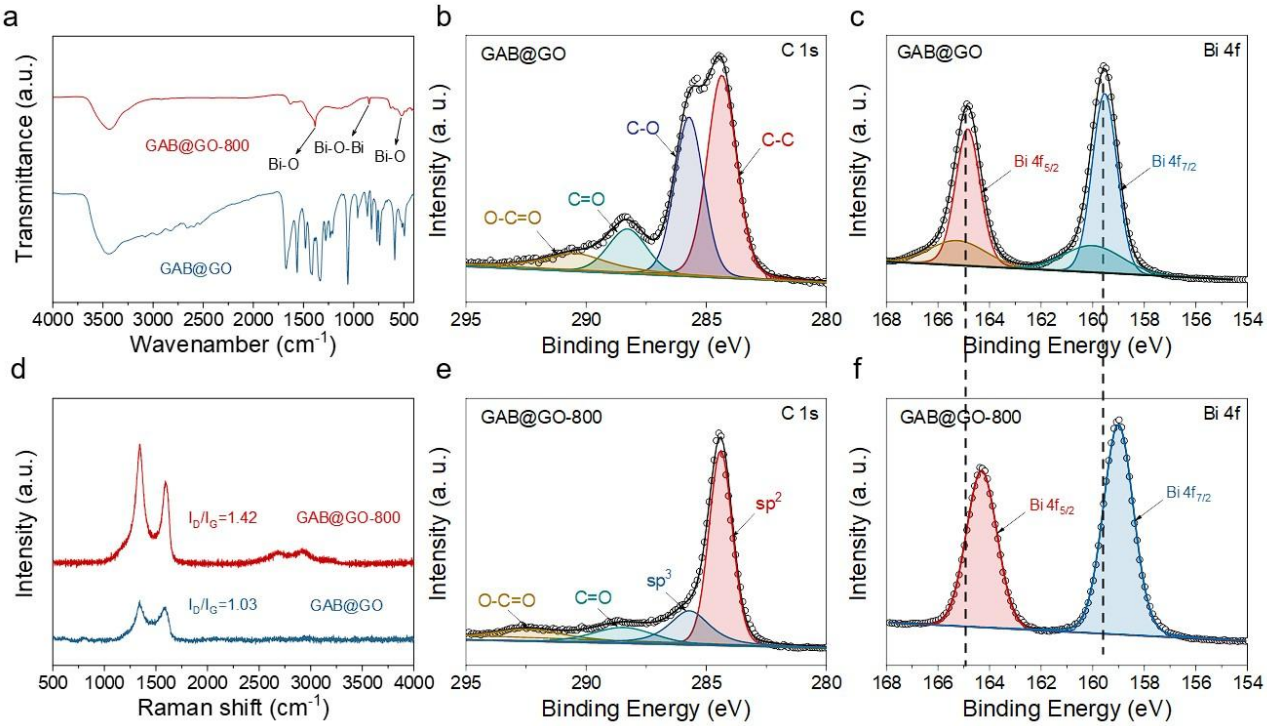

Fig. 2 a) FTIR spectra of GAB@GO and GAB@GO−800. b) XPS spectra of C 1s and c) Bi 4f of GAB@GO. d) Raman pattern of GAB@GO and GAB@GO−800. e) XPS spectra of C 1s and f) Bi 4f of GAB@GO−800.

Cyclic voltammetry (CV) test of the initial five cycles at 0.1 mV s−1 was first conducted to investigate the electrochemical behavior between Na+ and GAB@GO-800 (Fig. 3a). In the first cycle, the broad cathodic peaks located at 0.7 and 0.34 V attributed to the activation process of Bi and the generation of the solid electrolyte interphase (SEI) on its surface. The subsequent cycles show two pairs of highly reversible peaks at −0.63/0.78 and −0.45/0.6 V corresponding to the two-step alloying reaction of Bi + Na+ + e− → NaBi and NaBi+ 2Na+ +2 e− → Na3Bi. The GAB@GO-800 electrode displays reversible capacities of 328, 298, 294, 296, 298, and 299 mA h g−1 at current densities of 0.1, 0.2, 0.5, 1, 2, and 5 A g−1, respectively (Fig. 3b), demonstrating an excellent rate performance. The corresponding galvanostatic charge−discharge (GCD) curves of GAB@GO-800 are presented in Fig. 3d, which exhibit an average voltage close to 0.6 V and low polarization. Its specific capacity can be recovered to 329 mA h g−1 when the current density

returns to 0.1 A g−1, which indicates that the robust interactions between the Bi nanoparticles and the carbon hybrid ensures the overall structure remains stable even at large current densities. Electrochemical impendence spectra (EIS) measurement for the GAB@GO-800 electrode was presented in Fig. 4c. A small semicircle and a large slope straight line are identified in the Nyquist plot, indicating a low charge−transfer resistance (Rct) and a small Warburg impedance, which corresponds to the high conductivity and fast Na+ diffusion inside the electrode bulk.

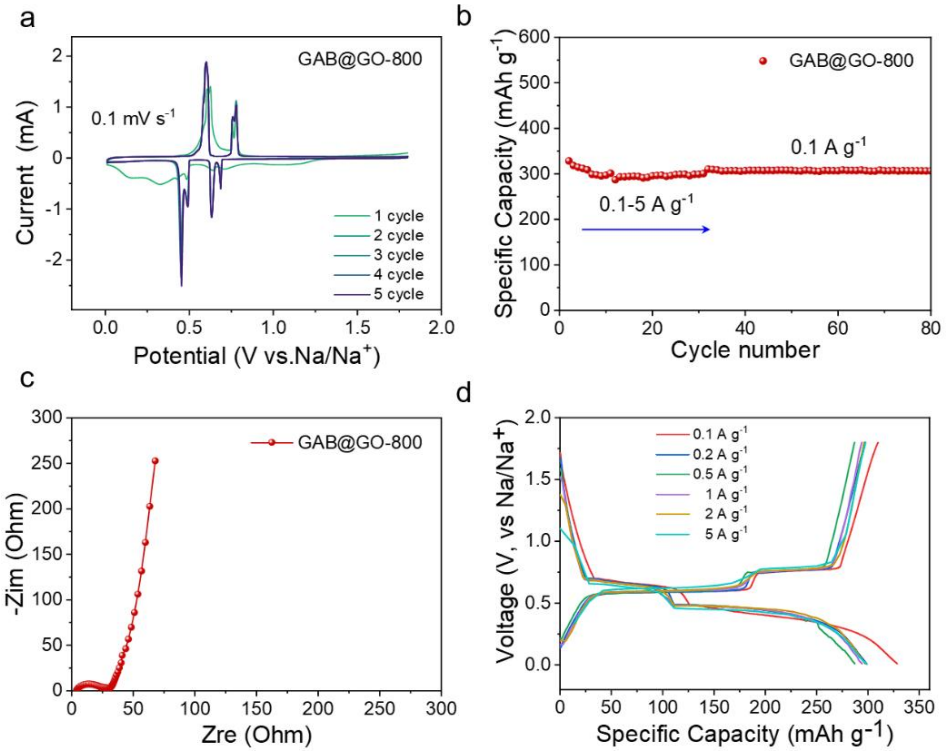

Fig. 3 a) CV curves of GAB@GO-800 at a scan rate of 0.1 mV s−1. b) Rate capability of GAB@GO-800 at 0.1 A g−1-5 A g−1. c) Nyquist plots of GAB@GO-800. d) Charge–discharge curves of GAB@GO-800 at 0.1 A g−1−5 A g−1.

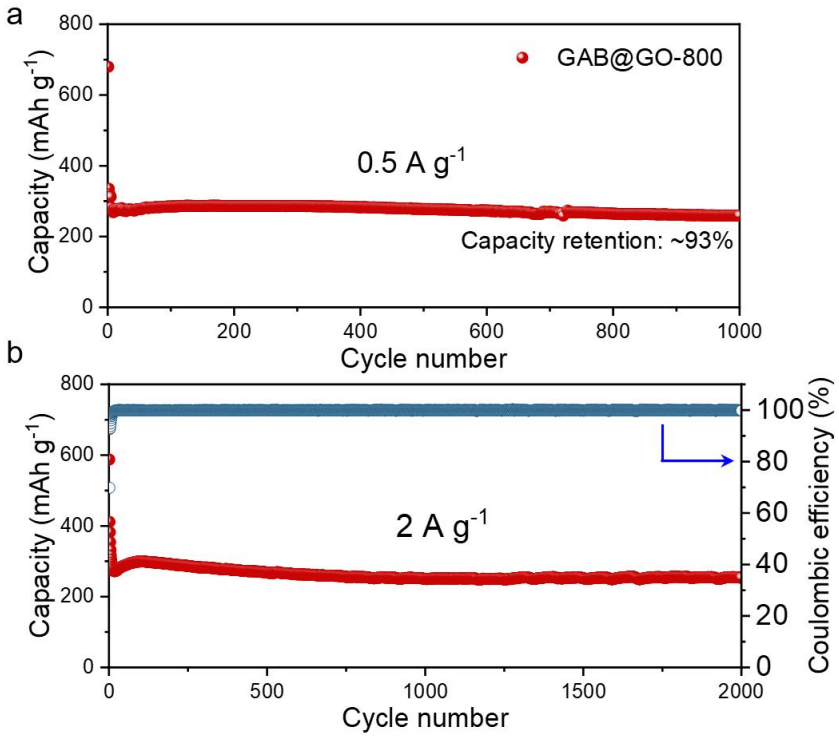

Fig. 4 a) Cycling performances of GAB@GO-800 0.5 A g^{-1} and b) 2 A g^{-1}.

Furthermore, the long-term cycling stability of the GAB@GO-800 electrode was measured at current densities of 0.5 and 2 A g^{-1}. After 1000 cycles at 0.5 A g^{-1}, the GAB@GO-800 electrode maintains a high reversible capacity of 260 mA h g^{-1} with a capacity retention of ~93%. The GAB@GO-800 electrode still delivers a capacity of 255 mA h g^{-1} after 2000 cycles even at a high current density of 2 A g^{-1}, indicating that the inlay structure is effective in mitigating the volumetric change of Bi nanoparticles during the alloying process thereby prolonging the life.

4. Summary

In this study, we demonstrated a hybrid carbon strategy to embed the Bi nanoparticles in MOF-derived carbon and graphene nanosheets for ultralong-lifespan SIB. This structure, which confines Bi nanoparticles within an external graphene coating and an internal carbon−based framework, is expected to provide multilayered protection, limiting the volume expansion of the Bi nanoparticles and thus providing good transport kinetics for high-rate applications. Thus, the GAB@GO-800 anode exhibits superior sodium storage performance for delivering a reversible capacity of 328 m Ah g−1 at 0.1 A g−1, exceptional rate capability (299 mA h g−1 at 5 A g−1) and an extraordinary ultrahigh−rate stability of 255 mA h g−1 at 2 A g−1 over 2000 cycles. Our strategy of hybrid carbon confinement by combination of graphene coating and MOF-derived carbon can shed light on high stability and rate performance alloying-type anodes for SIBs.

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