

Graphene-interconnected Bi@Bi₂O₃CO₃ heterostructures with enhanced electrochemical Kinetics Stability for Supercapacitors

Qiushi Miao¹, Guanwen Wang²(✉), Yufei Zhou¹, Baoyi Mu¹, Zhiyuan Li¹, Pengfei Gao¹, Bin Qi¹, Xinxin Zhao³, Guojun Xu³, Fangna Dai¹(✉), Tong Wei³(✉), Zhuangjun Fan³(✉)

¹ School of Materials Science and Engineering, China University of Petroleum, Qingdao 266580, China

² School of Engineering, Qinghai Institute of Technology, Xining, 810016, China

³ Institute of Energy Hefei Comprehensive National Science Center Hefei 230051, China

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Research Article

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Qiushi Miao¹, Guanwen Wang^{2,*}, Yufei Zhou¹, Baoyi Mu¹, Zhiyuan Li¹, Pengfei Gao¹,
Bin Qi¹, Xinxin Zhao³, Guojun Xu³, Fangna Dai^{1,*}, Tong Wei^{3,*} and Zhuangjun
Fan^{3,*}

¹*School of Materials Science and Engineering, China University of Petroleum, Qingdao
266580, China*

²*School of Engineering, Qinghai Institute of Technology, Xining, 810016, China*

³*Institute of Energy Hefei Comprehensive National Science Center Hefei 230051, China*

*Address correspondence to Tong Wei, weitong666@163.com; Zhuangjun Fan, fanzhj666@163.com; Guanwen
Wang, qhdauidwang@163.com; Fangna Dai, findai@upc.edu.cn

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Abstract: Despite their high theoretical capacity, Bi-based anodes are plagued by sluggish charge-transfer kinetics and severe structural degradation originating from poor electrical conductivity and repeated volume variation during alloying/dealloying. Herein, a graphene nanoribbon-interconnected Bi@Bi₂O₂CO₃ heterostructure (B/BOC-GR_{0.1}) is designed to simultaneously establish a continuous conductive network and reinforce the heterointerface. The Bi₂O₂CO₃ shell effectively accommodates cyclic strain and stabilizes the electrode architecture, while graphene nanoribbons strengthen interfacial electronic coupling and accelerate electron transport, thereby synergistically promoting reaction kinetics and structural

robustness. As a result, B/BOC-GR_{0.1} delivers 1560 C g⁻¹ at 1 A g⁻¹ and retains 795 C g⁻¹ at 50 A g⁻¹, greatly surpassing those of Bi anodes (623 C g⁻¹ at 1 A g⁻¹, 281 C g⁻¹ at 50 A g⁻¹). Moreover, after 5000 cycles at 10 A g⁻¹, B/BOC-GR_{0.1} maintains approximately 90% of its initial capacity. The constructed asymmetric supercapacitor achieves an energy density of 70 Wh kg⁻¹ at a power density of 752 W kg⁻¹, highlighting the potential of the designed heterostructure for advanced electrochemical energy-storage applications.

Keywords: bismuth-based anode, core-shell heterostructure, graphene nanoribbon, supercapacitor, interfacial engineering.

1. Introduction

Supercapacitors are attractive for high-power energy storage, yet their energy density remains limited by the insufficient charge-storage capability of conventional carbonaceous anodes^[1-8]. Despite of high degree of commercialization, carbon materials anodes mainly rely on surface-controlled charge adsorption with limited redox contribution, developing redox-active anodes with both high capacity and fast charge-transfer kinetics is essential for high-energy and high-power supercapacitors.

Bi-based materials, such as Bi anodes, have attracted increasing attention as promising anode candidates due to their high theoretical capacity (3800 mAh cm⁻³) arising from multi-electron redox reactions, together with good reversibility^[9,10]. However, the practical application of metallic Bi is hindered by pronounced volume variation during repeated alloying/dealloying, leading to particle pulverization and loss of electrical contact, while its intrinsically low electrical conductivity further limits electron transport and reaction kinetics. As a result, these issues collectively lead to poor structural stability and unsatisfactory rate performance. Bi₂O₃ has been also explored as an alternative Bi-based anode because of its robust oxide framework and reversible redox chemistry. Nevertheless, its electrochemical response is often

limited by sluggish conversion kinetics and incomplete structural reversibility under high-rate operation, resulting in insufficient capacity delivery. Meanwhile, $\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) featuring a typical layered structure, has been widely investigated due to its favorable ion diffusion pathways and structural stability^[11,12]. However, the electrochemical activation of BOC remains constrained by limited accessible active sites and inefficient interfacial charge transfer, making it difficult to fully exploit its redox capability. Therefore, developing stable Bi-based anodes that simultaneously deliver high specific capacity and excellent rate performance remains a critical challenge.

To address these issues, various strategies have been explored, including heterostructure construction^[11-14], and nanostructure engineering^[15-23] etc. Among them, heterostructure design can modulate interfacial electronic structure and promote charge redistribution. For example, Feng et al. constructed a $\text{Bi}_2\text{O}_3@\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructured electrode on copper foam via a combined strategy of galvanic replacement, thermal calcination, and hydrothermal treatment. The as-prepared electrode delivered a high areal capacity of 16.5 mAh cm^{-2} at 10 mA cm^{-2} ^[11]. Chen et al. constructed a polyaniline-intercalated $\text{Bi}_2\text{O}_2\text{CO}_3/\text{MXene}$ heterostructure via a self-assembly strategy. When evaluated as a potassium-ion battery anode, the material delivered a capacity of 375.4 mAh g^{-1} after 100 cycles at 50 mA g^{-1} ^[14].

Integrating nano carbon materials have been widely recognized to improve the electronic conductivity and integrity of electrodes^[15,16]. However, conventional carbon additives, such as carbon nanotubes, mainly improve macroscopic conductivity but often fail to construct robust and continuous electron-percolation networks at the individual-particle level^[17-20]. Graphene sheets, while offering high intrinsic conductivity and large surface area, tend to restack and form dense agglomerates, which significantly reduces accessible active interfaces and limits effective charge transport pathways. Apart from them, graphene nanoribbons (GR) with extended one-dimensional ribbon-like geometry and high conductivity, can effectively bridge adjacent particles to construct continuous conductive pathways, thereby enabling long-range electron transport and alleviating interfacial polarization^[21-23].

Nevertheless, despite the remarkable potential of GR for constructing highly conductive architectures and regulating interfacial electron transport, their application in Bi-based anode materials remains largely unexplored.

Herein, we report a GR-interconnected B/BOC core-shell heterostructure as a high-rate and stable anode material. BOC effectively mitigates the severe volume fluctuation of Bi during alloying/dealloying processes and suppresses particle pulverization, thereby maintaining structural integrity and enhancing cycling stability, while the Bi/BOC heterointerface regulates local electronic distribution and facilitates reversible structural evolution. With the integration of conductive GR networks, the B/BOC-GR_{0.1} composite not only establishes continuous electron transport pathways to accelerate charge-transfer kinetics, but also further alleviate the volume expansion, and promotes the electrochemical activity of the BOC component, thereby synergistically enhancing reaction reversibility and long-term cycling durability. This strategy establishes a heterointerface-coupled conductive-network strategy for activating alloy-type anodes toward high-rate and durable electrochemical energy storage.

2. Experimental section

2.1 Chemicals

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AR), bismuth pentantrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR) and ethyl alcohol were purchased from Aladdin Industrial Co., Ltd. Potassium hydroxide (KOH, AR) was supported by Beijing Chemical Corp. Ltd. Deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was purified through Arium Pro of Sartorius Corp. Nickel foam was purchased from Canrd Technology Co. Ltd. To completely remove the oil and oxide layer, the nickel foam was ultrasonically pre-treated in 0.5 M HCl, ethanol and deionized water for 20 minutes, respectively.

2.2 Preparation of Bi, B/BOC and B/BOC-GR_{0.1}

Graphene nanoribbons were prepared according to the former literature^[24]. Firstly, graphene nanoribbons (10 wt.% based on the theoretical mass of the inorganic

product) were dispersed in 5 mL of ethanol via ultrasonication for 2 h to ensure a uniform dispersion. Subsequently, 0.5 mmol of bismuth nitrate pentahydrate was introduced into the suspension, followed by further ultrasonication for 30 min to achieve complete dissolution and homogeneous mixing. The resulting mixture was then magnetically stirred at room temperature for 30 min to form a stable and uniform precursor solution. For comparison, the BOC precursor (without graphene nanoribbons) was synthesized under identical conditions by following the same procedure in the absence of graphene nanoribbons. Then, the obtained suspension was transferred into a Teflon-lined stainless-steel autoclave, sealed, and maintained at 200 °C for 48 h to facilitate the solvothermal reaction. After the reaction, the autoclave was naturally cooled to room temperature. The resulting precipitate was collected and washed several times with deionized water and ethanol to remove residual impurities and unreacted species. Finally, the product was dried in a vacuum oven at 80 °C for 12 h and ground into fine powder, yielding the final composite material, denoted as B/BOC-GR_{0.1}. (Here, the subscript (x) in B/BOC-GR(x) denotes the nominal amount of GR added during synthesis and does not represent the actual GR content in the final composite.) Subsequently, the obtained BOC was subjected to thermal reduction in a tubular furnace under a H₂/Ar atmosphere at 350 °C for 2 h to generate metallic Bi nanoparticles.

3. Results and discussion

Figure 1 presents the design concept of the GR-interconnected B/BOC heterostructure. Bare Bi suffers from poor conductivity, sluggish kinetics, and severe volume-induced pulverization during cycling. The conformal BOC shell is introduced to buffer volume variation and stabilize the Bi interface, while GR interconnects B/BOC units into a continuous conductive network. This integrated architecture combines structural protection with fast electron/ion transport, thereby promoting high-rate capability and long-term cycling stability.

As shown in Figure 2a, GR exhibits a typical ribbon-like and interconnected morphology, forming an open three-dimensional conductive network. Compared with

conventional stacked graphene sheets, the nanoribbon structure provides more exposed surface and continuous electron-transport pathways, which is beneficial for improving the electrical conductivity and facilitating electrolyte penetration. The morphology and microstructure of the samples were investigated by SEM (Figure 2b, c, Figure S1a). Pristine Bi exhibits a microspherical morphology with an average diameter of $\sim 20\ \mu\text{m}$, accompanied by severe aggregation, which can lead to excessive grain growth, limited contact with the electrolyte, and potential particle fracture (Figure S1a). The B/BOC composite retains a similar spherical morphology with a significantly reduced particle size of $\sim 600\ \text{nm}$ (Figure 2b), suggesting that the formation of the BOC shell inhibits excessive particle growth and improves structural uniformity. Further the incorporation of GR, the average size of composite particles is further refined to $\sim 100\ \text{nm}$. B/BOC particles are further dispersed and anchored onto the GR framework, forming a highly interconnected architecture (Figure 2c). The layered nanosheet structure observed in this sample was primarily derived from the BOC phase, while GR acts as a conductive scaffold that interconnects these nanosheets. This hierarchical architecture improves particle uniformity and dispersion, increases the accessible surface area, establishing continuous mass transport pathways and enhancing electrochemical utilization. Moreover, an appropriate amount of GR effectively constrains the B/BOC particles, thereby enhancing their structural integrity and electrochemical stability. In Figure 2d, TEM image of B/BOC particle exhibits a typical core-shell architecture, confirming that BOC forms a well-defined coating layer on the surface of Bi. HRTEM image of B/BOC-GR_{0.1} displays, lattice fringes with interplanar spacings of 0.3321, 0.2655, and 0.2314 nm, which are assigned to the (002) plane of GR and the (110) planes of BOC and Bi, respectively (Figure 2e). These observations indicate intimate nanoscale contact among the different components. The SAED pattern of B/BOC-G displays well-defined diffraction rings, confirming its polycrystalline nature (Figure 2f). The red rings are assigned to the (003) and (012) planes of metallic Bi, while the yellow rings correspond to the (017) and (020) planes of BOC. In contrast, pristine Bi shows discrete diffraction spots, indicative of a single-crystalline structure (Figure S1c). The transition from

single-crystalline Bi to polycrystalline B/BOC-G demonstrates the successful in situ growth of BOC nanosheets on Bi and the formation of a coupled Bi/BOC heterointerface, which can enrich interfacial active sites and facilitate charge-transfer kinetics. Elemental mapping results further reveal that Bi is mainly concentrated in the core region, while C and O are predominantly distributed in the shell. These results collectively confirm the formation of a well-defined Bi/BOC core-shell heterostructure in B/BOC-GR_{0.1} (Figure 2g-i). Additional SEM, HRTEM, and EDS mapping results (Figure S1) further support the uniformity of the structure and the formation of the core-shell configuration.

To investigate the detailed phase composition, XRD patterns of Bi, B/BOC, and B/BOC-GR_{0.1} were employed (Figure 3a). The diffraction peaks of B/BOC can be indexed to metallic Bi and BOC, confirming the coexistence of both phases within the composite system. A comparative analysis reveals that B/BOC-GR_{0.1} exhibits weakened Bi peaks and enhanced BOC peaks while maintaining consistent diffraction features without detectable impurity phases, indicating that GR does not alter the original crystal structure. Meanwhile, a slight broadening and attenuation of diffraction peaks can be observed, which is mainly associated with the reduced crystallite size and the introduction of lattice distortion. This behavior can be attributed to the modulation of nucleation and growth processes induced by the formation of the BOC shell and the incorporation of GR, leading to the suppression of excessive crystal growth. In addition, the coexistence of Bi and BOC phases, together with the peak variation, suggests the formation of heterogeneous interfaces and structural coupling between different components. The N₂ adsorption-desorption isotherms of B/BOC and B/BOC-GR_{0.1} exhibit typical type IV characteristics, indicating a mesoporous-dominated structure. Compared with Bi (15 m² g⁻¹) and B/BOC (17 m² g⁻¹), B/BOC-GR_{0.1} shows a much higher specific surface area of 61 m² g⁻¹ and exposes more accessible active sites (Figure 3b, c, Figure S2). More importantly, the refined structure promotes the formation of abundant Bi/BOC heterointerfaces, facilitating interfacial electron transfer and enhancing redox activity. Further analysis of the pore size distribution reveals that the increased pore population

at ~ 3 nm contributes to the enhanced specific surface area. Notably, after the formation of the BOC phase, the pore size distribution remains nearly unchanged, indicating that the introduction of BOC does not disrupt the original porous framework but preserves its structural integrity during the composite formation process. In addition to the emergence of multi-scale mesopores, B/BOC-GR_{0.1} exhibits a significantly higher pore volume, as evidenced by the increased intensity of the pore size distribution curve. With the incorporation of GR, the pore distribution at ~ 3 nm becomes more pronounced, suggesting a higher density of small mesopores. Meanwhile, a broader and more continuous pore size distribution is observed, extending to larger mesopores (~ 5 nm). The hierarchical pore structure reflects the structural evolution induced by GR incorporation and indicates the formation of the interconnected porous network.

Thermogravimetric (TG) analysis conducted in air further elucidates the role of GR (Figure 3d, e and Figure S3). For pristine Bi, a distinct weight gain is observed in the temperature range of 200-300°C, which can be attributed to the oxidation of metallic Bi to Bi₂O₃, accompanied by oxygen uptake. A less pronounced weight increase (~ 1.96 wt.%) is also observed for B/BOC, indicating that partial oxidation still occurs in the composite. In contrast, B/BOC-GR_{0.1} exhibits only a marginal weight increase (0.34 wt.%) in this temperature range, indicating that GR incorporation alters the thermal oxidation behavior of the composite and suppresses the oxidation-related weight gain in this temperature range. At higher temperatures, the continuous weight loss is mainly associated with the decomposition of the BOC phase and the consumption of carbon species. The additional weight loss observed for B/BOC-GR_{0.1} relative to pristine B/BOC is attributable in part to GR, giving an estimated GR content of approximately 3.1 wt.%. The relatively high residual mass at 800 °C suggests the formation of thermally stable inorganic residues, further confirming the structural stability of the composite.

The bonding characteristics were further investigated by FTIR spectroscopy (Figure 3f). Relative to metallic Bi, B/BOC and B/BOC-GR_{0.1} display a series of characteristic CO₃²⁻ vibrational bands in the ranges of 1391, 846, and 668 cm⁻¹, which

are assigned to ν_3 (asymmetric stretching), ν_2 (out-of-plane bending), and ν_4 (in-plane bending), respectively, confirming the formation of structural carbonate species and thus the successful generation of the BOC phase^[27-29]. Notably, the CO_3^{2-} bands in B/BOC-GR_{0.1} show increased intensity along with slight peak broadening, suggesting a modification of the local coordination environment of carbonate groups. Meanwhile, subtle variations in the Bi-O vibration region (559 cm^{-1}) are also observed after GR incorporation, indicating changes in the local bonding configuration of Bi-O units. These results suggest that GR incorporation induces adjustments in both carbonate coordination and Bi-O bonding environments within the composite. X-ray photoelectron spectroscopy (XPS) was employed to investigate the interfacial electronic structure evolution of Bi, B/BOC, and B/BOC-GR_{0.1} (Figure 3g-i and Table S1). Compared with pristine Bi, the introduction of the BOC phase leads to a significant increase in the Bi^{3+} component (from 9.75% to 90.25%), accompanied by a shift of the carbonate-related O 1s peak from 532.3 eV to 532.6 eV^[28-30]. This positive shift indicates a decrease in electron density of the carbonate species, suggesting electron transfer from Bi to the BOC framework during heterostructure formation. Upon further incorporation of GR, a distinct electronic reconstruction is observed. The carbonate-related O 1s peak shifts back to lower binding energy (532.3 eV), while the Bi-O component simultaneously shifts from 530.3 eV to 530.1 eV, indicating an overall increase in electron density within the BOC framework^[28-30]. In addition, the relative proportion of Bi^{3+} decreases from 90.25% to 78.28%, accompanied by a corresponding increase in metallic Bi^0 (from 9.75% to 21.72%), confirming that GR induces electron donation to the Bi/BOC system and partially reduces Bi species. Interestingly, despite the reduction in Bi^{3+} content, the Bi 4f peaks exhibit a slight positive shift ($\sim 0.2\text{ eV}$), which can be attributed to interfacial electronic coupling and charge redistribution. This behavior reflects the formation of a strongly coupled Bi/BOC/GR heterointerface with modified electronic structure.

To further investigate the surface oxidation state, the XPS spectra of B/BOC and B/BOC-GR_{0.1} before and after Ar ion etching were compared (Figure S4). After etching, the B/BOC sample shows an increased relative intensity of metallic Bi,

accompanied by a corresponding decrease in the Bi^{3+} component, indicating that the oxide-related species are predominantly distributed in the surface region (Table S2). A similar evolution trend is observed for B/BOC-GR_{0.1}, suggesting a consistent structural configuration with a BOC-enriched surface layer and a Bi-dominated interior. This spatial distribution further supports the formation of a core-shell heterostructure, which is essential for establishing effective interfacial electronic interaction and facilitating the coupled electrochemical process. To clarify the surface carbon bonding states, the high-resolution C 1s spectra were further deconvoluted into sp^2 C=C and sp^3 C-C/C-H contributions (Figure S5). Bi and B/BOC exhibit both sp^2 C=C (~ 284.7 eV) and sp^3 C-C/C-H (~ 285.2 eV) components, with the latter possibly associated with trace disordered carbonaceous species remaining after the H_2/Ar thermal treatment. In contrast, B/BOC-GR_{0.1} is dominated by the sp^2 C=C component (~ 284.8 eV), consistent with the conjugated carbon framework of GR.

To optimize the GR content, the electrochemical performances of B/BOC-GR_x composites with different GR addition amounts were systematically compared (Figure S6). Among the investigated compositions, B/BOC-GR_{0.1} exhibits the best overall electrochemical performance, suggesting an optimal balance between the construction of an effective conductive network and the preservation of accessible Bi/BOC active sites. Therefore, B/BOC-GR_{0.1} was selected as the optimized composition for further comparison with Bi and B/BOC.

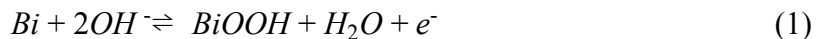
The electrochemical behaviors of Bi, B/BOC, and B/BOC-GR_{0.1} were subsequently evaluated by cyclic voltammetry (CV) (Figure 4a,b). The Bi electrode exhibits well-defined oxidation and reduction peaks at -0.44 V and -0.83 V, reflecting the reversible redox process of Bi in alkaline media. Notably, a weak response -0.63 V can still be detected, which is attributed to residual Bi species, suggesting that the transformation of Bi is not fully completed within this potential window^[31]. Compared with pure Bi, B/BOC shows an enhanced current response, suggesting improved interfacial redox activity after the introduction of BOC. More importantly, B/BOC-GR_{0.1} presents the largest integral area of the CV curve among the three samples, reflecting stronger charge-storage behavior. At the scan rate of 20 mV s^{-1} , Bi

undergoes obvious peak distortion and potential shift, whereas B/BOC-GR_{0.1} retains a relatively high current response and more stable redox features. This result indicates that B/BOC-GR_{0.1} possesses superior rate capability and faster interfacial kinetics, owing to the synergistic contribution of the Bi/BOC heterointerface and the GR conductive network.

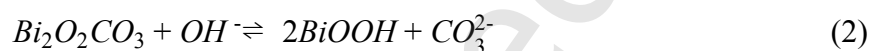
Figure 4c and 4d present the galvanostatic charge-discharge (GCD) curves of Bi, B/BOC, and B/BOC-GR_{0.1} at different current densities. At 1 A g⁻¹, the pristine Bi electrode exhibits the shortest discharge time and an obvious voltage hump during the charging process, indicating limited charge-storage capability and severe polarization due to sluggish reaction kinetics. Upon incorporation of the BOC phase, the discharge duration is extended and the voltage hump is significantly attenuated, suggesting that the BOC shell provides a more regulated reaction pathway by moderating Bi oxidation and stabilizing the electrode/electrolyte interface. With the addition of GR, the B/BOC-GR_{0.1} electrode delivers the longest discharge time, and the voltage profile becomes smooth and monotonic, reflecting markedly reduced polarization and more uniform reaction kinetics. When the current density increased to 10 A g⁻¹, both Bi and B/BOC electrodes display pronounced potential dips at the early stage of charging, corresponding to local Bi dissolution-redeposition processes under strong cathodic polarization in alkaline electrolyte. For B/BOC, the initial reduction of the BOC shell further amplifies this effect, leading to a more prominent voltage dip. Finally, the B/BOC-GR_{0.1} electrode maintains a smooth charging profile without apparent dips, demonstrating that the profitable interfacial electronic structure, suppressing localized Bi dissolution and activating BOC phase as a dynamically participating component in redox process. Collectively, the BOC shell stabilizes Bi and regulates the reaction pathway, while GR enhances electron transport and interfacial kinetics, resulting in enhanced charge-storage capability, reduced polarization, and improved high rate performance.

The charge storage behavior revealed by CV curves is dominated by a single pair of redox peaks, corresponding to the Bi/BiOOH redox couple (Figure S9). This discrepancy indicates that the transformation between BiOOH and the BOC phase is

not an independent electrochemical step, but rather a fast chemical process coupled with the electrochemical reaction. The reversible redox reactions of Bi in alkaline electrolyte dominate the charge storage behavior of this system:



The potential-dependent attenuation and recovery of the Bi-O and carbonate-related bands indicate that the BOC phase is not electrochemically inert but actively participates in reversible surface transformation during cycling. Meanwhile, BOC can undergo the following reversible reaction under alkaline conditions:



Therefore, the overall process can be described by an EC (electrochemical-chemical) mechanism, where the Bi/BiOOH conversion represents the electrochemically controlled step, while the reversible reconstruction of the BOC framework proceeds through a chemically coupled pathway. In this mechanism, Bi serves as the primary redox-active center, while the BOC phase acts as a structurally dynamic component that participates in the reaction via interfacial coupling.

EIS analysis reveals negligible differences in the high-frequency intercept among the samples, suggesting similar solution resistance (R_Ω). In contrast, B/BOC-GR_{0.1} exhibits a smaller semicircle in the mid-frequency region and a more vertical response in the low-frequency region. These features indicate that GR incorporation reduces interfacial charge-transfer resistance (R_{ct}) while simultaneously alleviating ion diffusion limitations (Table S3).

As illustrated in Figure 4e, B/BOC-GR_{0.1} achieves a high specific capacity of 1560 C g⁻¹ at 1 A g⁻¹. Even when the current density increases to 50 A g⁻¹, it still retains 795 C g⁻¹ with a capacity retention of 51%, which is significantly superior to those of the electrodes with other GR contents. Notably, in the high-rate region above 20 A g⁻¹, both B/BOC and B/BOC-GR_{0.1} exhibit relatively stable capacity retention, whereas pristine Bi continues to show a gradual decay in capacity. These results highlight that the synergistic interplay between the Bi/BOC heterointerface and the GR network enhances charge-storage activity at low rates and stabilizes the

electrochemical process under high-rate conditions. The conductive network constructed by GR and the synergistic regulation of the Bi/BOC interface on electron transport and structural evolution collectively contribute to the enhanced rate capability. Meanwhile, solvothermal temperature, reaction time, solvent composition, and different carbon materials were systematically optimized (Figure S10-S17).

To further elucidate the reaction kinetics, the relationship between peak current and scan rate was analyzed using a power-law fitting approach:

$$i = av^b \quad (3)$$

$$\log i = \log a + b \log v \quad (4)$$

The oxidation peak currents were analyzed according to the power-law relationship ($i_{pa}=av^b$) (Figure S18, Table S4), giving b values of 0.59, 0.69, and 0.73 for Bi, B/BOC, and B/BOC-GR_{0.1}, respectively, suggesting that the charge storage involves both diffusion-controlled and surface capacitive contributions. Relative to Bi, the progressively increased b values for B/BOC and B/BOC-GR_{0.1} reflect a higher contribution from surface-controlled processes, indicating improved reaction kinetics. Moreover, B/BOC-GR_{0.1} delivers higher peak currents at identical scan rates, indicating improved electrochemical responsiveness and superior rate capability. As the scan rate increases, the capacitive-controlled contribution rises from 56% to 91%, exhibiting a capacitive-controlled behavior for fast redox kinetics (Figure S19). After 5000 cycles at 10 A g⁻¹, B/BOC-GR_{0.1} maintains approximately 90% of its initial capacity, significantly outperforming B/BOC, which retains only ~60% (Figure 4g). To elucidate the structural origin of the superior cycling stability, post-cycling SEM observations were conducted (Figures 4h and 4i). After long-term cycling, the pristine Bi electrode undergoes severe internal cracking and structural fragmentation, indicative of accumulated mechanical stress arising from the repeated volume expansion/contraction during alloying/dealloying. Such crack formation inevitably disrupts the electronic transport pathways, exposes fresh surfaces to continuous side reactions, and accelerates electrode pulverization, ultimately leading to rapid capacity decay. In contrast, B/BOC-GR_{0.1} maintains an intact hierarchical architecture after

prolonged cycling, indicating that the BOC scaffold and graphene network effectively accommodate the repeated strain associated with alloying/dealloying. More importantly, maintaining structural continuity preserves electrical percolation and stable electrode/electrolyte interfaces, effectively suppressing polarization growth and irreversible active-material loss during prolonged cycling. To further evaluate the reversibility during repeated alloying/dealloying, the last five charge-discharge curves were compared (Figure S20). B/BOC-GR_{0.1} exhibits nearly identical charge-discharge profiles with negligible variation in discharge time, indicating highly reversible reaction kinetics and suppressed electrochemical polarization throughout long-term cycling. In contrast, the Bi electrode displays progressively enlarged deviations among the final cycles, suggesting the irreversible structural degradation and polarization. These results collectively demonstrate that the robust BOC/graphene framework effectively mitigates structural degradation while maintaining highly reversible electrochemical reactions, thereby accounting for the exceptional long-term cycling stability and capacity retention of B/BOC-GR_{0.1}.

To explore the structural evolution of B/BOC and B/BOC-GR_{0.1} during electrochemical cycling, in situ Raman spectroscopy was employed (Figure 5a-d). At 0 V, several characteristic bands associated with metallic Bi phases appear: peaks at ~ 73 and 97 cm^{-1} are assigned to the E_g and A_{1g} vibrational modes of metallic Bi^[26,27]. The E_g and A_{1g} of B/BOC-GR_{0.1} appear relatively weaker, which is due to the partial coverage of GR. In charging process, both samples exhibit the pronounced intensification of E_g and A_{1g} peaks. Upon discharging, these Bi-related peaks gradually diminish, indicating a reversible structural response of the Bi phase. BOC-related band at $\sim 156\text{ cm}^{-1}$ corresponds to the lattice vibration of Bi-O bonds within the positively charged $[\text{BiO}]^+$ slabs of the BOC structure^[26-29]. The peaks at 1068 and 1400 cm^{-1} are assigned to the symmetric (ν_1) and asymmetric stretching (ν_3) vibrations of CO_3^{2-} groups in BOC, respectively^[29,30]. When applying negative potentials, both samples show a progressive attenuation of the Bi-O band and the carbonate-related bands progressively weaken. When the potential is back to 0 V, the attenuation and recovery of the Bi-O band, which originates from the $[\text{BiO}]^+$ slabs of

BOC, together with the synchronous variation of CO_3^{2-} bands, demonstrate that the BOC framework undergoes a dynamic and reversible reconstruction during reaction. Compared with B/BOC, B/BOC-GR_{0.1} exhibits significantly stronger Bi-O and CO_3^{2-} bands, as well as more pronounced and reversible spectral evolution, elucidating the activation of the BOC framework. As a result, the $[\text{BiO}]^+$ slabs and carbonate units in BOC become more responsive to electrochemical perturbation and participate more actively in the coupled reaction process. In addition, B/BOC-GR_{0.1} exhibits distinct D and G bands at ~ 1350 and 1580 cm^{-1} , characteristic of graphitic carbon^[32-34]. Importantly, the nearly unchanged G band confirms that GR does not directly participate in the redox reaction, but act as a conductive and electronically interactive framework that promotes uniform charge transfer and strengthens the coupling between the Bi redox process and BOC structural evolution.

To verify the interfacial electronic modulation, charge density difference and density of states (DOS) calculations were performed^[30,35](Figure S21). The charge density difference maps reveal that, upon introducing the BOC phase, electrons are transferred from Bi to the BOC framework, leading to electron depletion around Bi and electron accumulation on the oxygen-rich regions of BOC. After further incorporation of GR, the charge redistribution becomes more pronounced and extends across the GR/BOC and GR/BOC/Bi interface. Electrons are partially transferred from GR toward the Bi/BOC system, resulting in increased electron density within the BOC framework and enhanced interfacial coupling. This suggests that GR not only serves as a conductive bridge but also participates in electronic regulation at the interface (Figure 6a, c and e). The results further support these findings. Compared with pristine Bi, the DOS of Bi/BOC leads to enhanced overlap between Bi-derived and O-derived states below the Fermi level, indicating strengthened orbital hybridization and interfacial interaction. With the addition of GR, the electronic states near the Fermi level are significantly intensified, indicating an enhanced intrinsic electronic conductivity. The enhanced overlap among Bi, O, and C states suggests stronger electronic coupling and more continuous electron transport pathways (Figure 6b, d and f). Overall, the results reveal a synergistic electronic regulation mechanism,

in which BOC induces electron transfer from Bi to form a heterointerface, while GR further promotes electron delocalization and interfacial coupling (Figure 6g). This local-to-global electronic coupling converts isolated interfacial modulation into continuous charge transport, thereby accelerating redox kinetics and sustaining stable structural evolution during cycling.

To assess the practical energy storage performance of B/BOC-GR_{0.1}, an aqueous asymmetric supercapacitor (ASC) was constructed with B/BOC-GR_{0.1} as the anode and Ni(OH)Cl as the cathode^[36]. According to the charge balance principle and the stable potential windows of both electrodes, the optimal mass ratio of B/BOC-GR_{0.1} to Ni(OH)Cl was set at 1:1.2 (Figure S22). The CV profiles of the individual electrodes were recorded within their respective potential windows of -1.0-0 V (B/BOC-GR_{0.1}) and 0-0.6 V (Ni(OH)Cl) (Figure S23a). The results demonstrate that both electrodes exhibit stable electrochemical behavior within their respective potential ranges, providing the basis for constructing an ASC with an extended voltage window. Although the combined potential windows suggest a theoretical voltage limit of ~1.6 V, pronounced polarization at higher voltages is observed; therefore, 1.5 V is selected as the stable operating voltage based on CV analysis under different voltage windows (Figure S24). As illustrated in Figure 7a, the CV curves at 1.5 V display pronounced redox features accompanied by a capacitive background response. With increasing scan rate, no significant distortion of the CV curves is observed, indicating stable electrochemical performance at high rates. The GCD profiles further illustrate the charge storage characteristics of the device (Figure 7b). Even at high current densities, the GCD curves maintain good symmetry with a small *iR* drop, indicating effectively suppressed polarization. Based on the GCD curves, the device achieves a specific capacity of 335 C g⁻¹ at 1 A g⁻¹ and retains 176 C g⁻¹ at 20 A g⁻¹ (Figure S23b). Cycling tests show that 90.2% of the initial capacity is retained after 4000 cycles (Figure 7c). To demonstrate practical applicability, two ASC devices connected in series successfully power a red LED (3.0 V) for over 180 s (Figure 7c inset). The Ragone plot further illustrates the relationship between energy density and power density (Figure 7d). The ASC delivers an energy density of 70 Wh kg⁻¹ at a power

density of 752 W kg⁻¹ and maintains 30 Wh kg⁻¹ even at 15 kW kg⁻¹. Compared with reported Bi-based aqueous supercapacitors, this device exhibits competitive energy and power density, demonstrating great potential for practical applications.

Conclusion

In summary, a GR-interconnected Bi@Bi₂O₂CO₃ (B/BOC-GR_{0.1}) core-shell heterostructure is constructed to overcome the intrinsic kinetic limitations of Bi-based anodes. The BOC shell stabilizes the structure by suppressing grain growth and mitigating volume variation, while GR establishes efficient conductive pathways and induces interfacial electron redistribution. This synergistic regulation activates the BOC phase and enhances charge-transfer kinetics. As a result, the electrode exhibits improved rate capability and cycling stability. More importantly, this work demonstrates that interfacial electronic regulation, beyond simple conductivity enhancement, is an effective strategy for activating coupled phases and improving electrochemical performance, providing new insights for the design of advanced energy storage materials.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of Interest Statement

All the contributing authors report no conflict of interests in this work.

Author contributions statement

Q. Miao, G. Wang, T. Wei, F. Dai and Z. Fan conceived and supervised the research. Q. Miao designed, performed the main research experiments and wrote the manuscript. G. Wang carried out the theoretical computations and the revision of the manuscript. Y. Zhou, B. Mu, Z. Li, P. Gao, B. Qi, X. Zhao, G. Xu discussed the results and participated in the preparation of this paper.

Use of AI statement

None.

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FIGURES

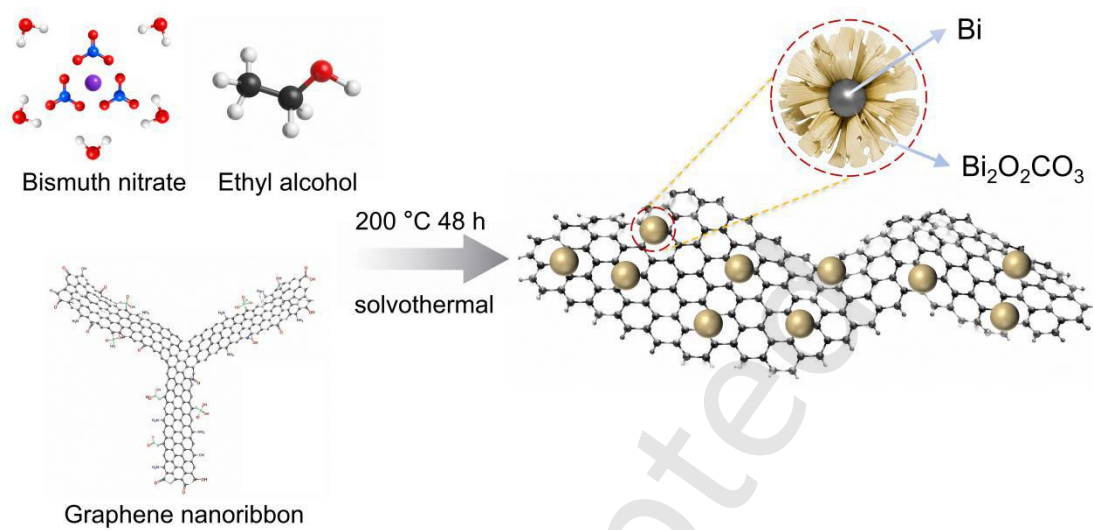


Figure 1. Schematic illustration of the formation mechanism of B/BOC-GR.

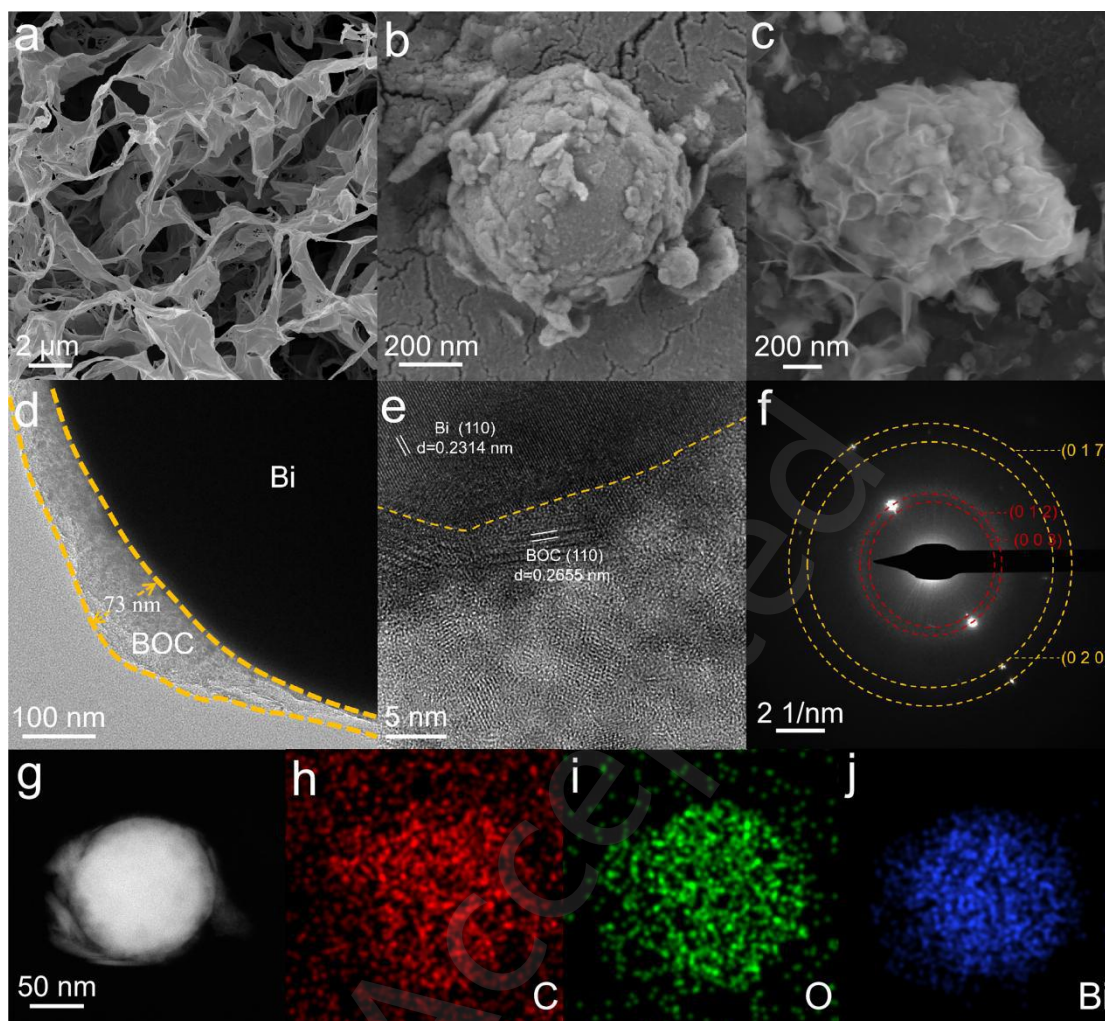


Figure 2. SEM image of a) GR, b) B/BOC, and c) B/BOC-GR_{0.1}; d) TEM image highlighting the nanosheet structure; e) HRTEM image of B/BOC-GR_{0.1}; f) SAED patterns of B/BOC-GR_{0.1}; g-j) Elemental mapping images of B/BOC-GR_{0.1} for h) C, i) O and j) Bi elements.

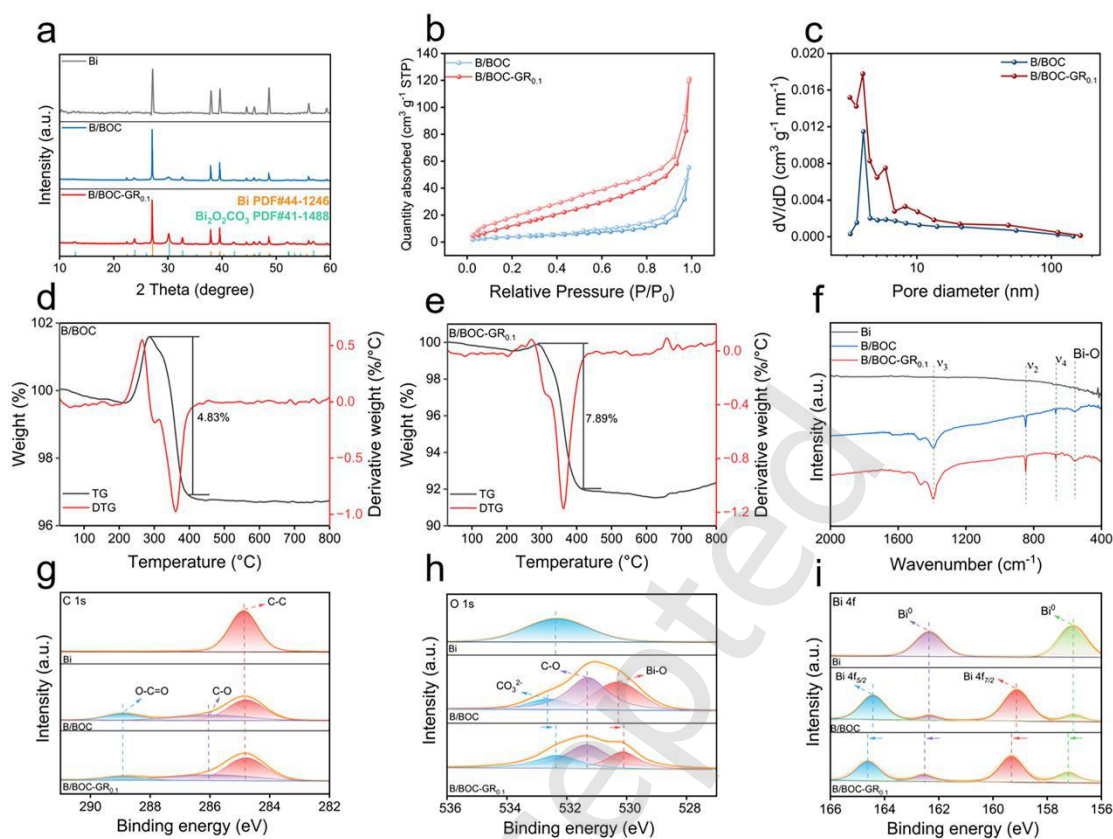


Figure 3. a) XRD patterns of Bi, B/BOC and B/BOC-GR_{0.1}; b) N₂ adsorption-desorption isotherms of B/BOC and B/BOC-GR_{0.1}; c) Pore size distributions of B/BOC and B/BOC-GR_{0.1}; d, e) TG curves of B/BOC and B/BOC-GR_{0.1}; f) FT-IR spectra of Bi, B/BOC and B/BOC-GR_{0.1}; High-resolution XPS spectra of g) C 1s, h) O 1s, i) Bi 4f for Bi, B/BOC and B/BOC-GR_{0.1}.

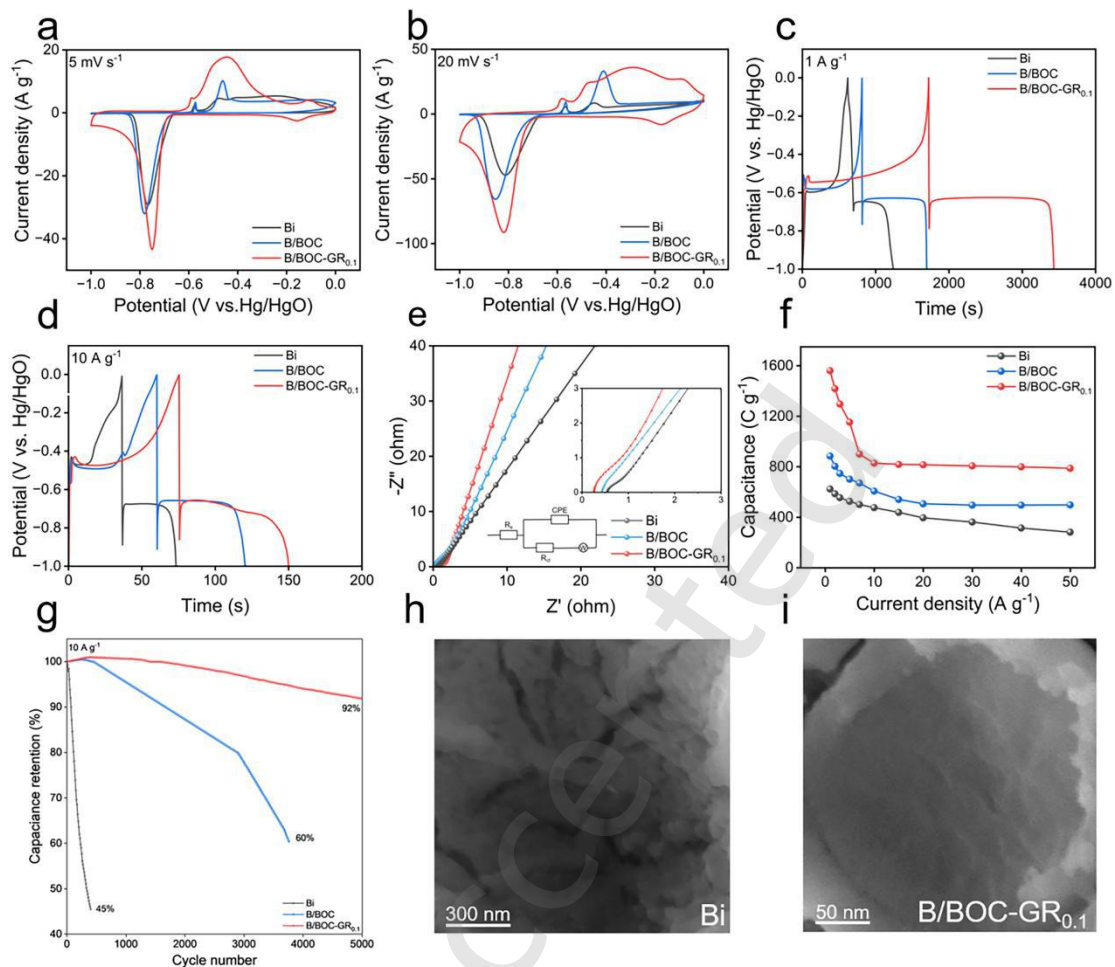


Figure 4. CV curves of Bi, B/BOC and B/BOC-GR_{0.1} at the scan rate of a) 5 mV s⁻¹; b) 20 mV s⁻¹; GCD curves of Bi, B/BOC and B/BOC-GR_{0.1} at the current density of c) 1 A g⁻¹; d) 10 A g⁻¹; e) Nyquist plots of Bi, B/BOC and B/BOC-GR_{0.1}; f) Rate performance of Bi, B/BOC and B/BOC-GR_{0.1}; g) Cyclic performance of Bi, B/BOC and B/BOC-GR_{0.1}; SEM images obtained after cycling: h) Bi, i) B/BOC-GR_{0.1}.

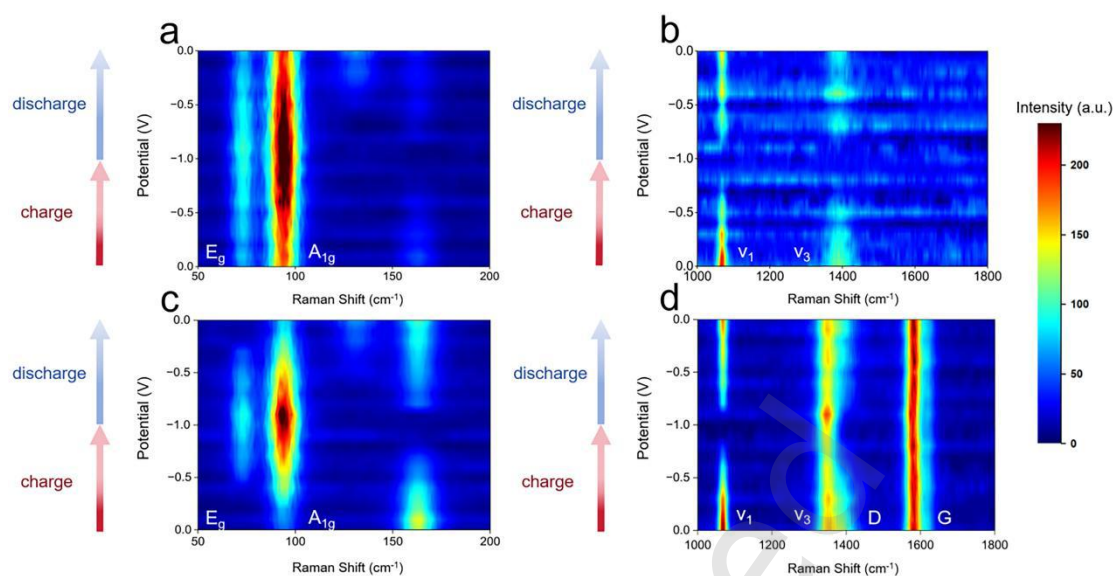


Figure 5. In situ Raman spectra of B/BOC at a) 50-100 cm⁻¹; b) 1000-1800 cm⁻¹; and of B/BOC-GR_{0.1} at c) 50-200 cm⁻¹ and d) 1000-1800 cm⁻¹; collected from open circuit potential (OCP) to -1.0 V, and then returned to OCP.

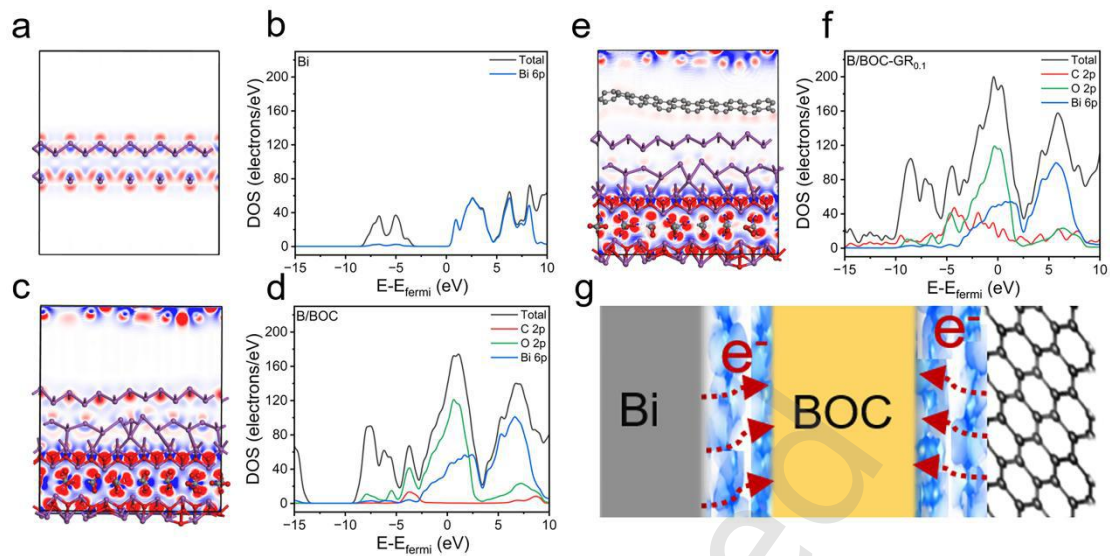


Figure 6. DFT calculations and proposed synergistic mechanism of B/BOC-GR heterostructure. Electron density difference maps of a) Bi, c) B/BOC and e) B/BOC-GR_{0.1}; PDOS curves of b) Bi, d) B/BOC and f) B/BOC-GR_{0.1}; g) Schematic illustration of the synergistic mechanism.

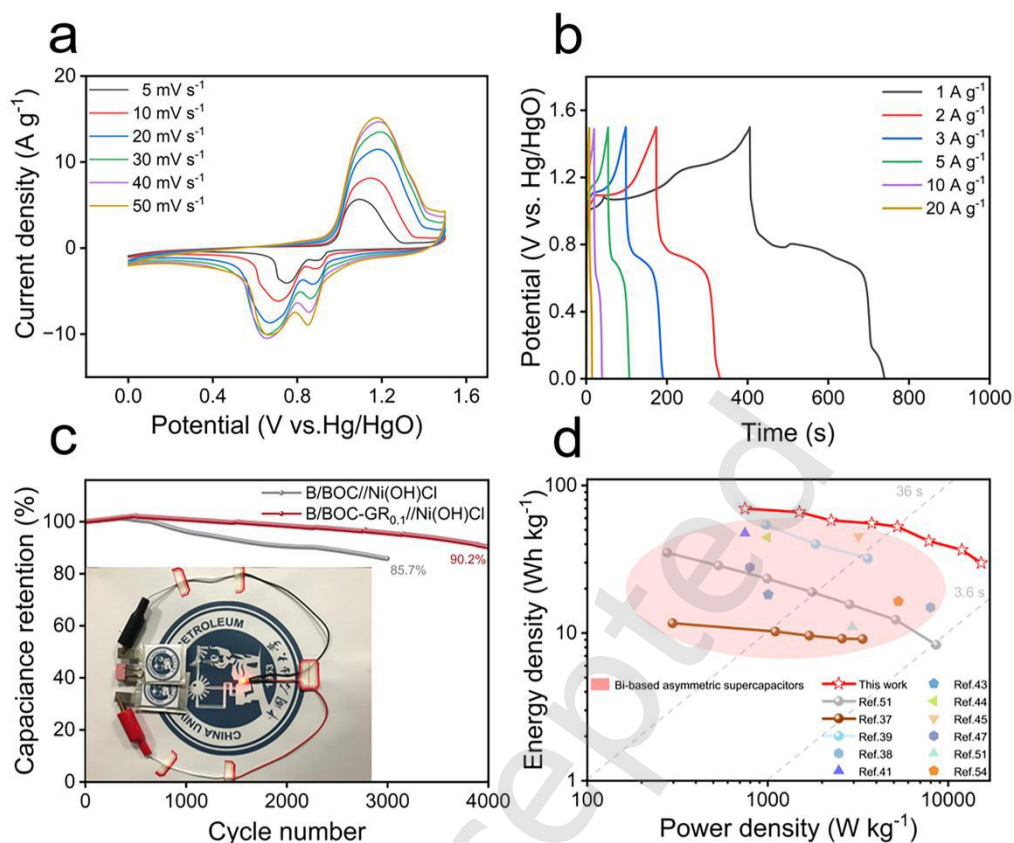


Figure 7. Electrochemical performance of B/BOC-GR_{0.1}//Ni(OH)Cl ASC. a) CV curves of B/BOC-GR_{0.1}//Ni(OH)Cl ASC; b) GCD curves of B/BOC-GR_{0.1}//Ni(OH)Cl ASC from 1 to 20 A g⁻¹; c) Cyclic performance of B/BOC-GR_{0.1}//Ni(OH)Cl ASC at scan rate of 10 A g⁻¹, along with a schematic illustration of the soft-pack device.; d) Ragone plots compared with reported bismuth-based ASCs.

Electronic Supplementary Material

Graphene-interconnected Bi@Bi₂O₂CO₃ heterostructures with enhanced electrochemical Kinetics Stability for Supercapacitors

Qiushi Miao¹, Guanwen Wang^{2,*}, Yufei Zhou¹, Baoyi Mu¹, Zhiyuan Li¹, Pengfei Gao¹,

Bin Qi¹, Xinxin Zhao³, Guojun Xu³, Fangna Dai^{1,*}, Tong Wei^{3,*} and Zhuangjun Fan^{3,*}

¹*School of Materials Science and Engineering, China University of Petroleum, Qingdao 266580, China*

²*School of Engineering, Qinghai Institute of Technology, Xining, 810016, China*

³*Institute of Energy Hefei Comprehensive National Science Center Hefei 230051, China*

*Address correspondence to Tong Wei, weitong666@163.com; Zhuangjun Fan, fanzhj666@163.com; Guanwen Wang, qhdavidwang@163.com; Fangna Dai, findai@upc.edu.cn

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1 Experimental Section

1.1 Material characterization

The morphology of the samples was systematically examined using scanning electron microscopy (SEM, Hitachi Regulus 8200) and transmission electron microscopy (TEM, JEOL, JEM-2100Plus). The crystalline structures were characterized by X-ray diffraction (XRD, Bruker D2 PHASER). The chemical composition and surface chemical states were analyzed via Fourier transform infrared spectroscopy (FTIR, Shimadzu IRTracer-100) and X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI-5700 ESCA system). The pore size distribution and specific surface area were determined from N₂ adsorption–desorption isotherms at 77 K

(Quantachrome IQ2) using the Brunauer-Emmett-Teller (BET) and non-local density functional theory (NLDFT) models. Thermal stability was evaluated by thermogravimetric analysis (TGA, Netzsch TG-209F3) from room temperature to 800 °C under a air atmosphere with a heating rate of 5 °C min⁻¹.

1.2 In-situ Raman characterization

Raman spectrometer (Horiba, Labram HR evolution) was utilized to test the in-situ Raman spectra. The wavelength of excitation laser was 532 nm from a He-Ne laser. Si wafer was used for the calibration of Raman frequencies. B/BOC-GR_{0.1} was dispersed in ethanol to prepare slurry without acetylene black and PTFE. Then, the slurry was dropped uniformly onto the nickel foam and dried at 80 °C in vacuum for 12 hours. The measurements of in-situ Raman spectra were carried out in CV test at the potential range of -1-0 V. 6 M KOH as the electrolyte solution and cellulose paper as the separator. The Raman spectra were collected per 100 s for one spectrum curve one time, accumulation four times.

1.3 Electrochemical Measurements

Electrochemical measurements were conducted by a CHI660E electrochemical workstation. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were carried out in a three-electrode configuration with a Hg/HgO reference electrode, a platinum counter electrode, and 6 M KOH electrolyte. EIS measurements were conducted over a frequency range from 0.01 Hz to 100 kHz. The working electrode was prepared by uniformly mixing 80 wt.% B/BOC-GR as the active material, 10 wt.% conductive carbon black, and 10 wt.% polytetrafluoroethylene (PTFE). The loading mass of the electrode is 2.0 mg. The asymmetric supercapacitors (ASCs) were assembled using Ni(OH)Cl electrode as positive electrode and B/BOC-GR_{0.1} as negative electrode with 6M KOH solution electrolyte. The gravimetric specific capacitance (C_s , C g⁻¹), power density (P , W kg⁻¹) and energy density (E , Wh kg⁻¹) of B/BOC-GR_{0.1}/Ni(OH)Cl were calculated based on the equation:

$$C_s = \frac{it}{m\Delta V} \quad (1)$$

$$E = \frac{1}{2} C_s (\Delta V)^2 = \frac{i \int V dt}{M * 3.6} \quad (2)$$

$$P = \frac{E}{t} * 3600 \quad (3)$$

Where i and t are the discharge current and discharge time, m means the loading mass of cathode active material. The ΔV represents the charging-discharging potential window. M represents the total active material loading mass of the positive electrode and negative electrode.

1.4 DFT calculations

Density functional theory (DFT) calculations were conducted within the generalized gradient approximation using the Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional. Spin-polarized calculations were performed with the DMol3 package to determine the ionization energy, while the CASTEP package was employed to calculate the electron density difference and partial density of states (PDOS). A Monkhorst-Pack k-point mesh of $1 \times 1 \times 1$ was used for Brillouin zone sampling. The convergence thresholds were set to 1.0×10^{-5} Ha for the self-consistent field energy, 0.002 Ha $\text{\AA}^{-1}$ for the maximum force, and 0.005 $\text{\AA}^{-1}$ for the maximum displacement.

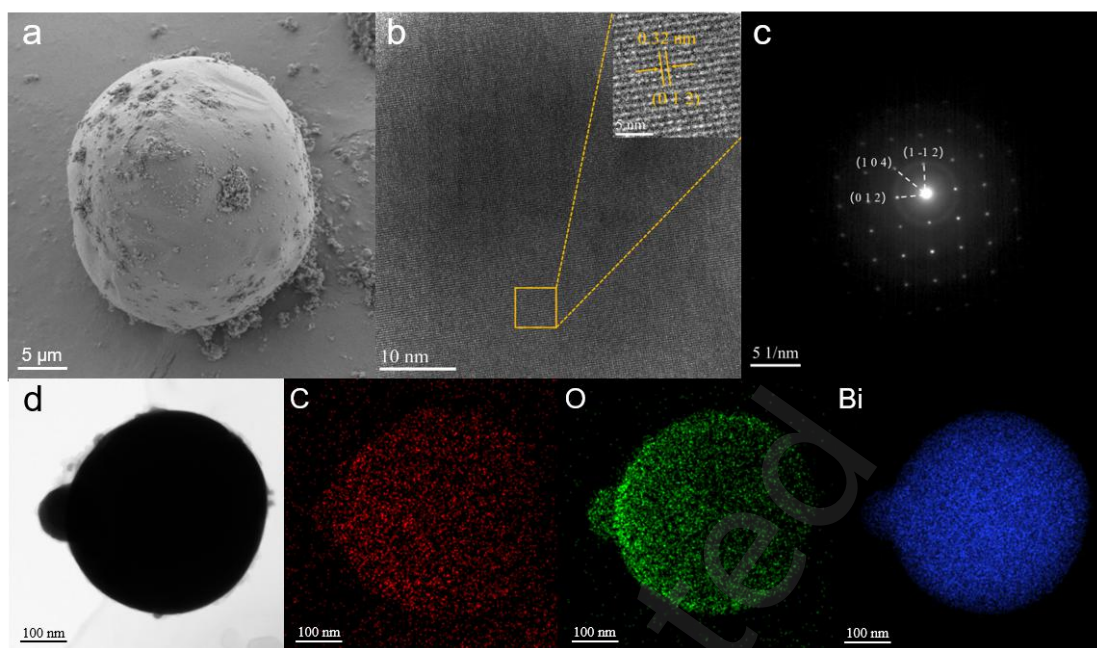


Figure S1. a) SEM images of Bi; b) HRTEM image of Bi; c) SAED patterns of Bi; d) EDS mapping images of Bi for C, O and Bi elements.

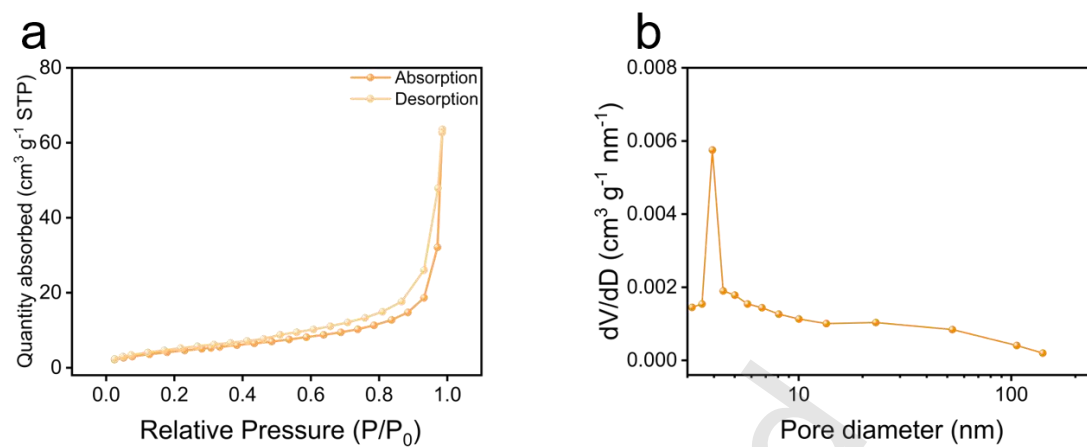


Figure S2. a) N_2 adsorption-desorption isotherms of Bi; b) Pore size distributions of Bi.

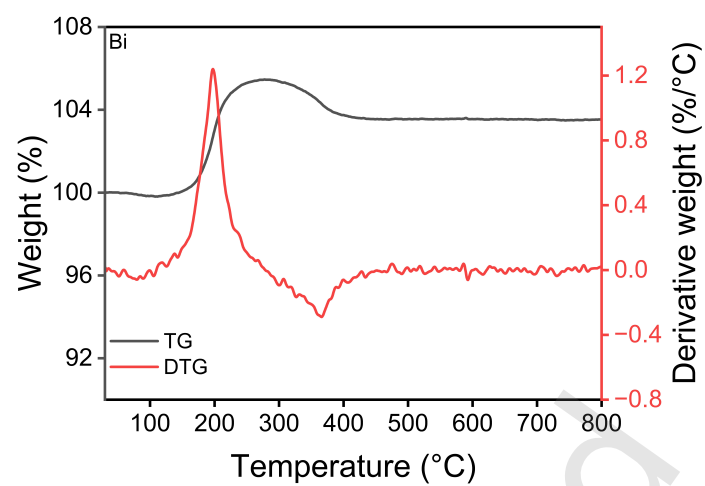


Figure S3. TG curves of Bi.

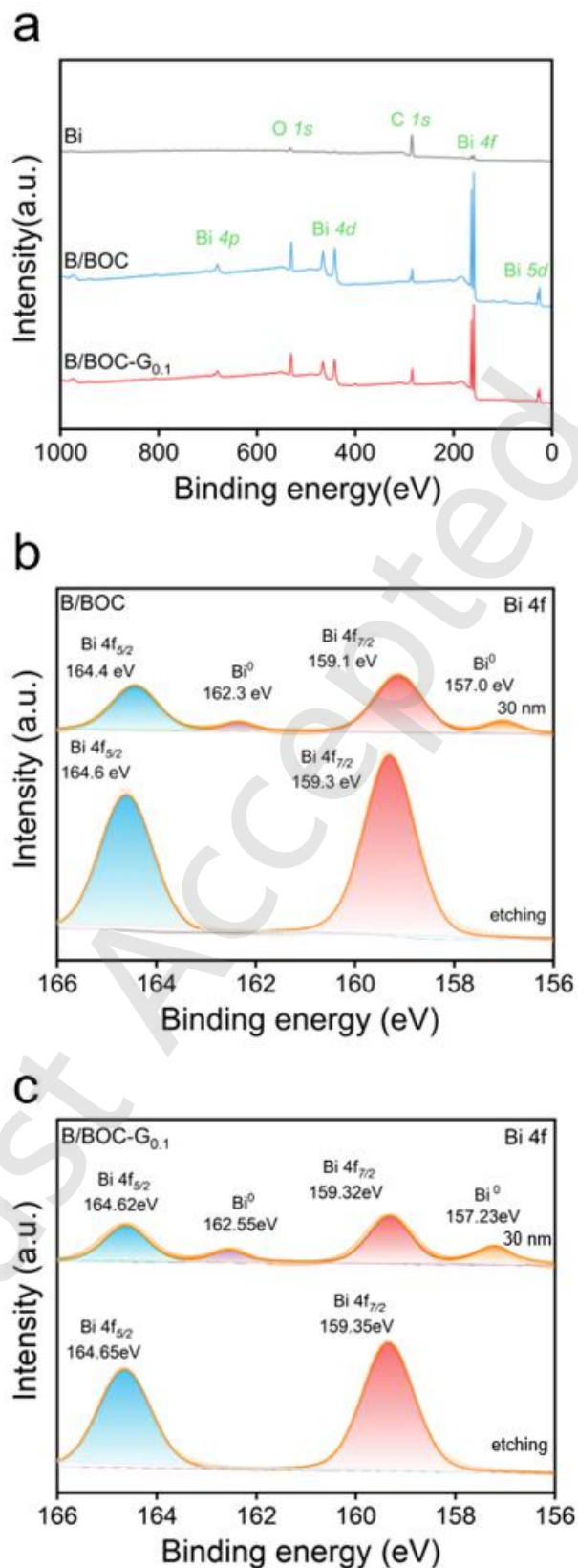


Figure S4. XPS analysis of B/BOC and B/BOC-Gr_{0.1}: a) survey spectra; b) Bi 4f spectra of B/BOC collected before and after Ar etching; and c) Bi 4f spectra of B/BOC-Gr_{0.1} collected before and after Ar etching.

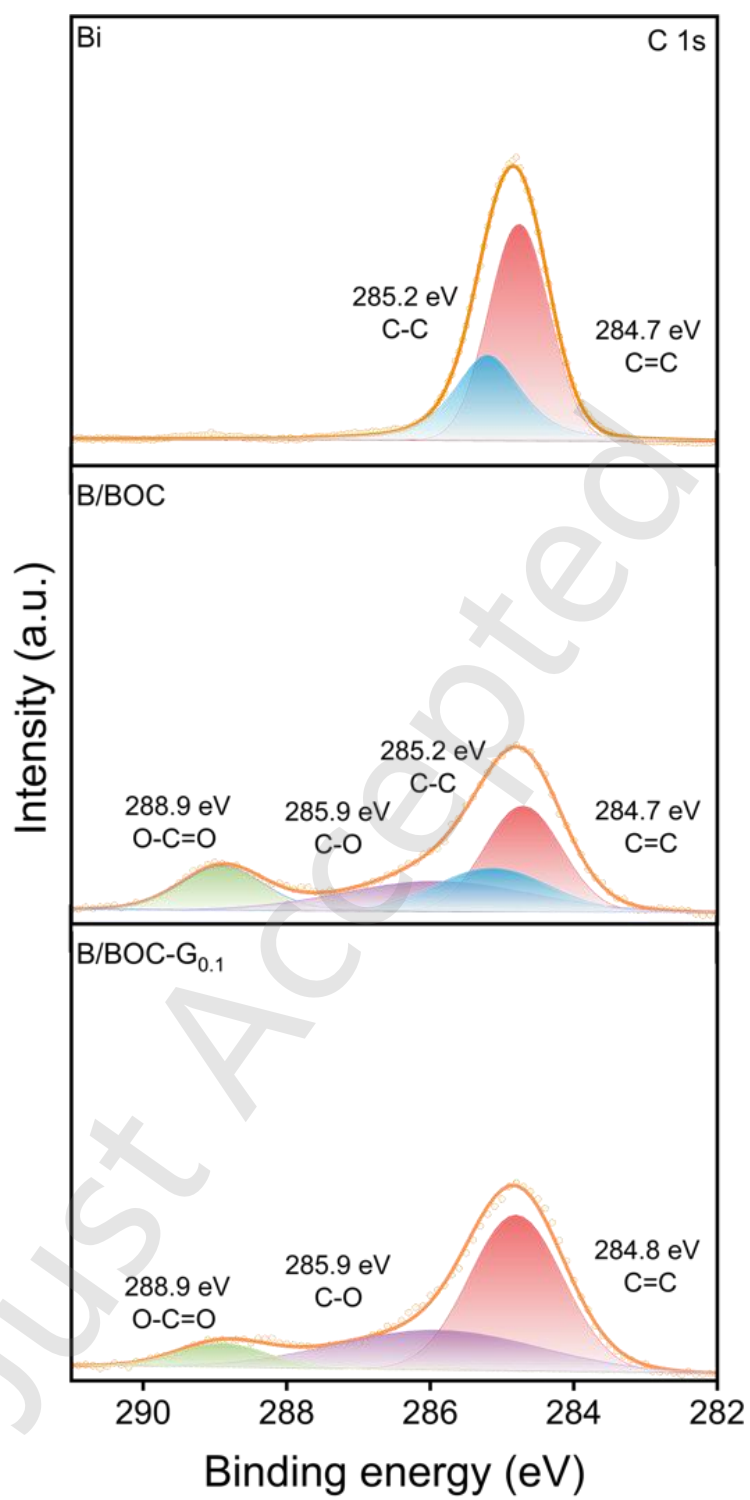


Figure S5. High-resolution C 1s XPS spectra and corresponding peak deconvolution of Bi, B/BOC, and B/BOC-GR_{0.1}.

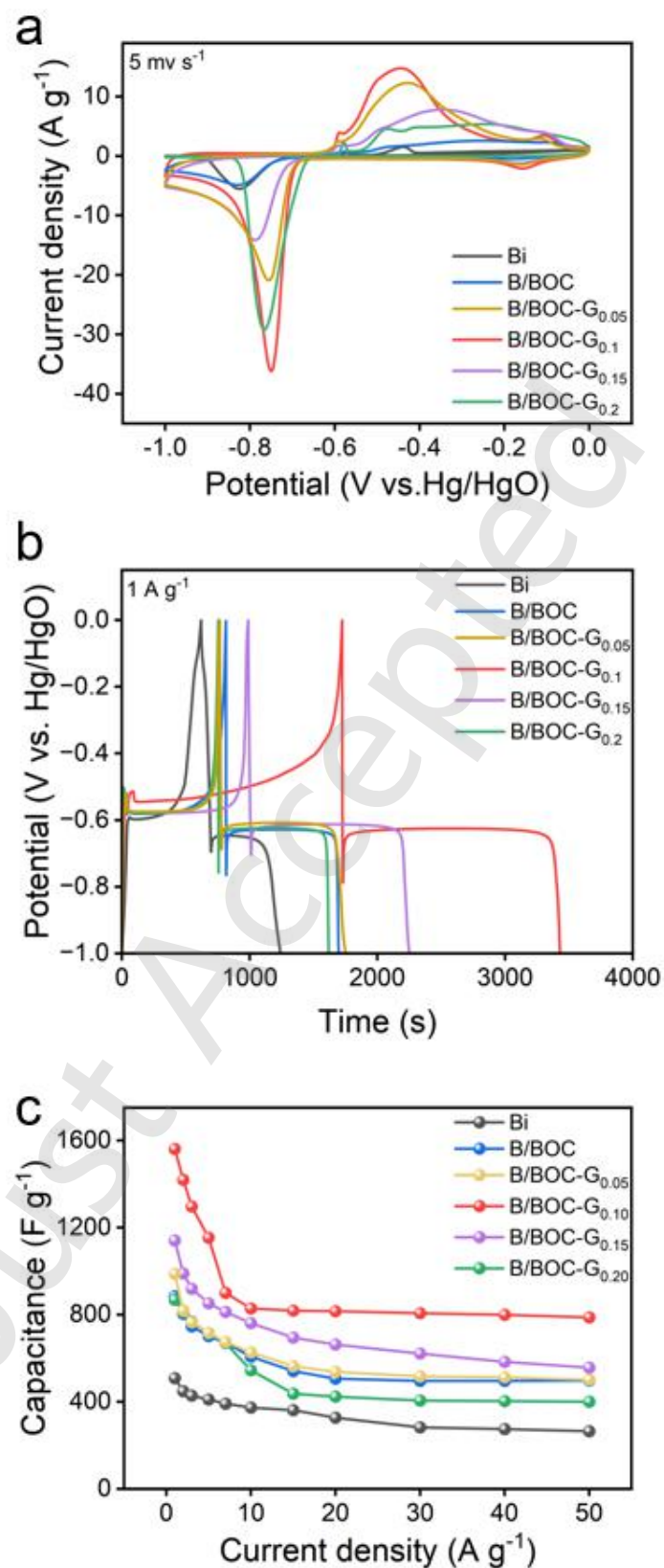


Figure S6. a) Comparison of CV curves at 5 mV s⁻¹, b) discharging curves at 1 A g⁻¹, c) Rate performance of B/BOC-GR(x) composites with different GR addition amounts.

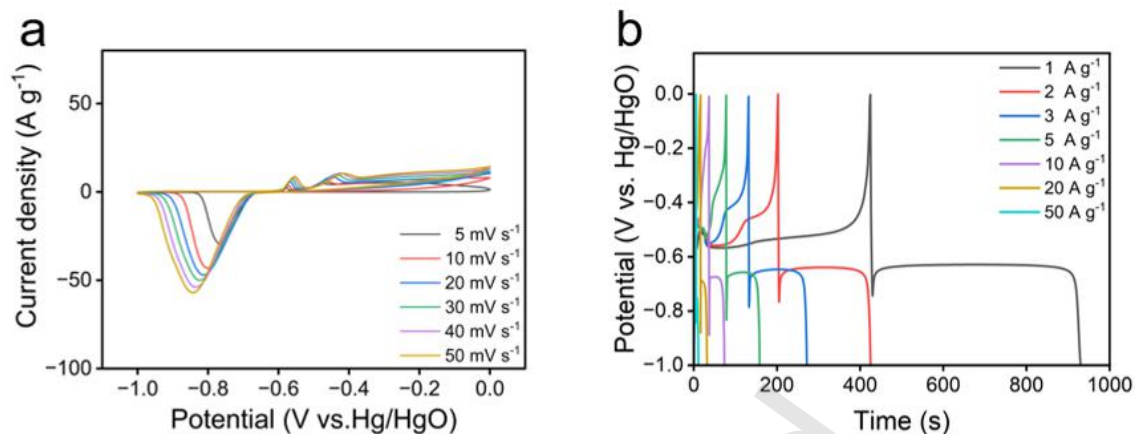


Figure S7. a) CV curves and b) GCD profiles of Bi.

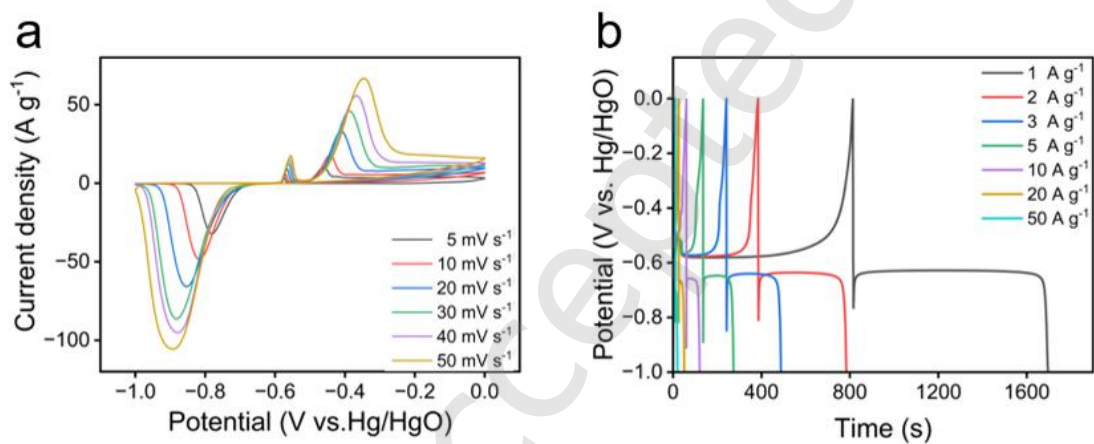


Figure S8. a) CV curves and b) GCD profiles of B/BOC.

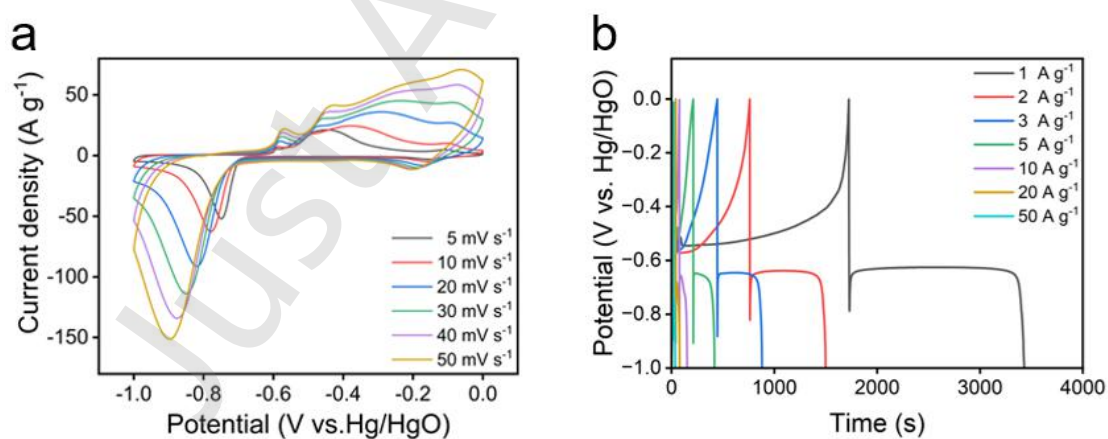


Figure S9. a) CV curves and b) GCD profiles of B/BOC-GR_{0.1}.

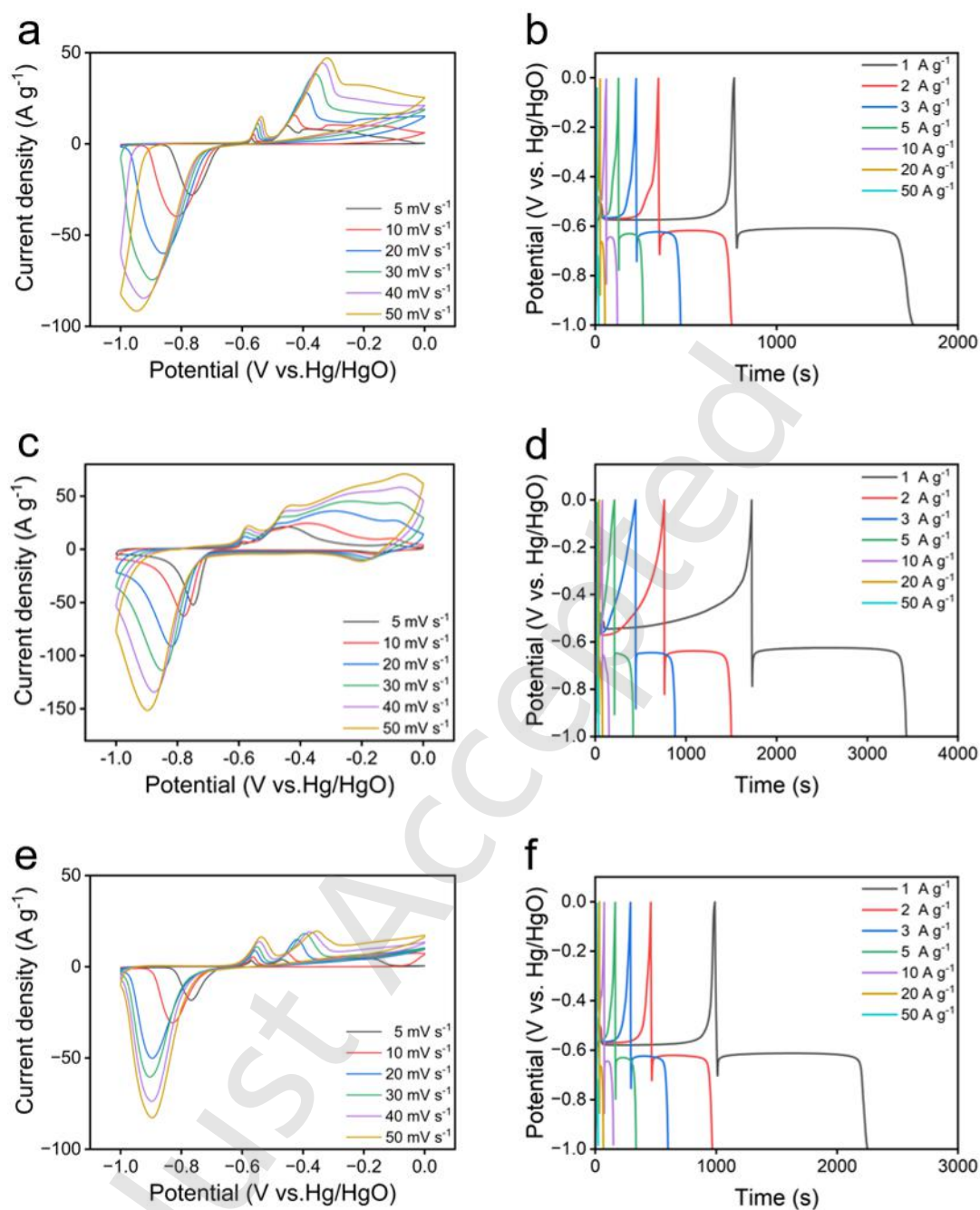


Figure S10. CV curves and GCD profiles of B/BOC-GR_{0.1} with the different solvothermal temperature a, b) 180 °C c, d) 200 °C, e f) 220 °C.

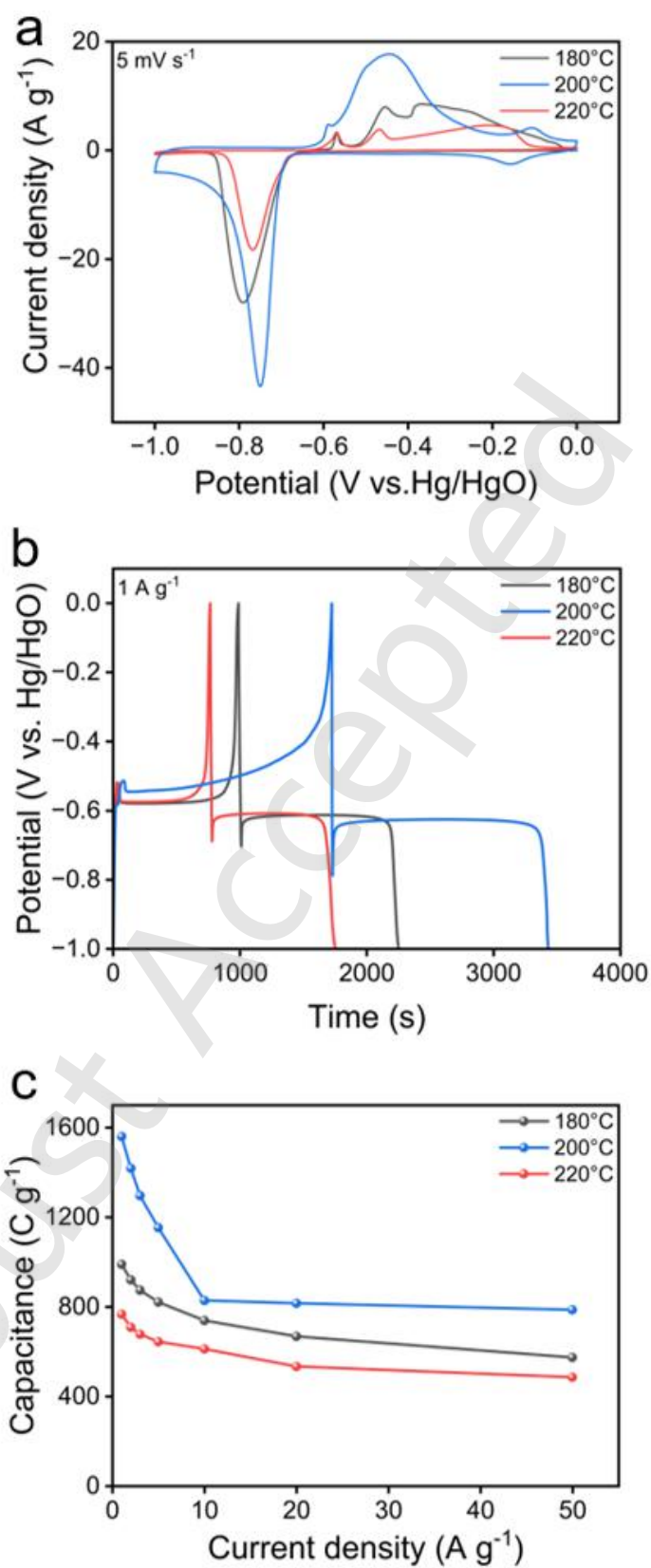


Figure S11. a) Comparison of CV curves at 5 mV s⁻¹, b) discharging curves at 1 A g⁻¹, c) Rate performance of B/BOC-GR_{0.1} with the different solvothermal temperature.

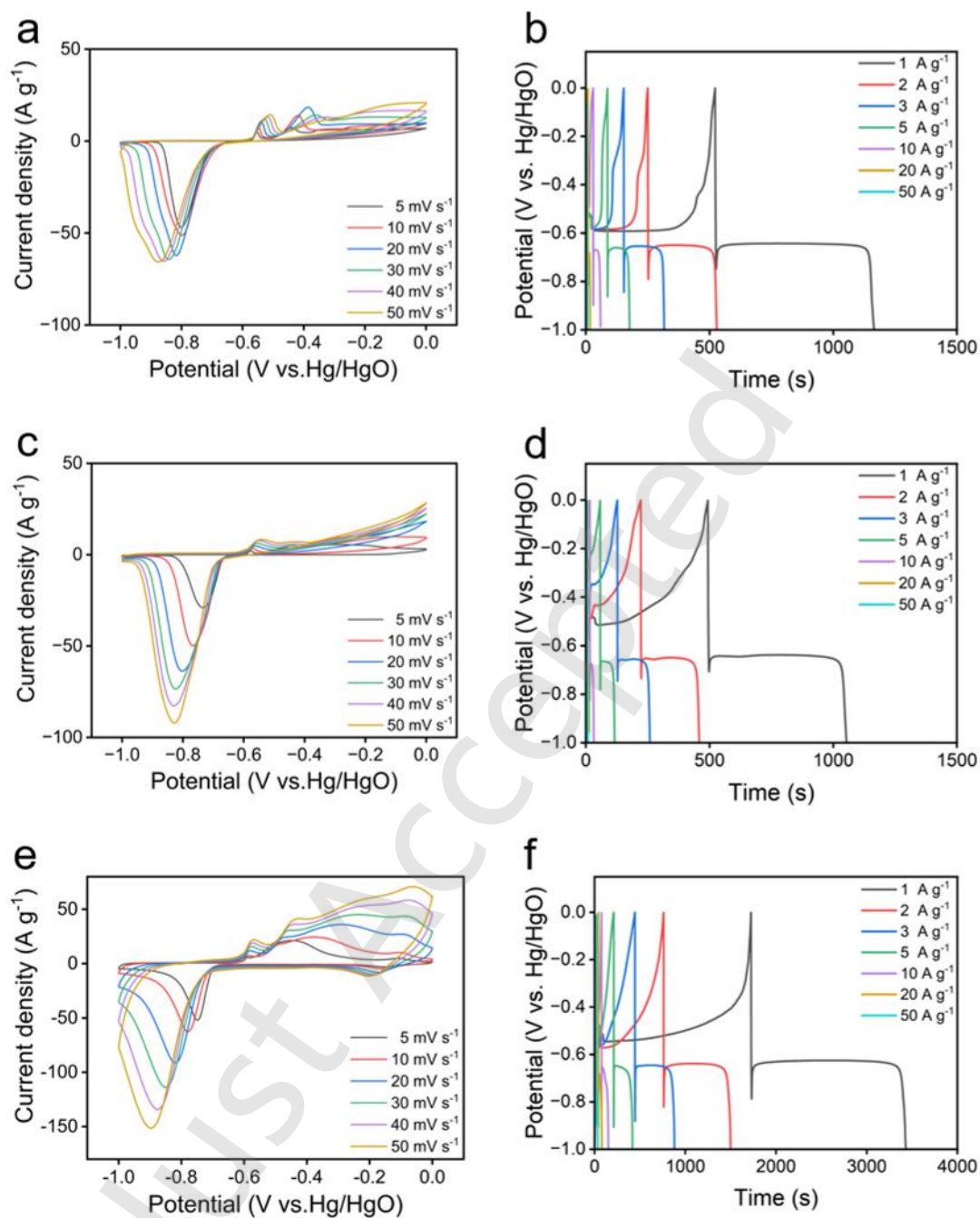


Figure S12. CV curves and GCD profiles of B/BOC-GR_{0.1} with the different solvothermal time a, b) 12 h c, d) 24 h e, f) 48 h.

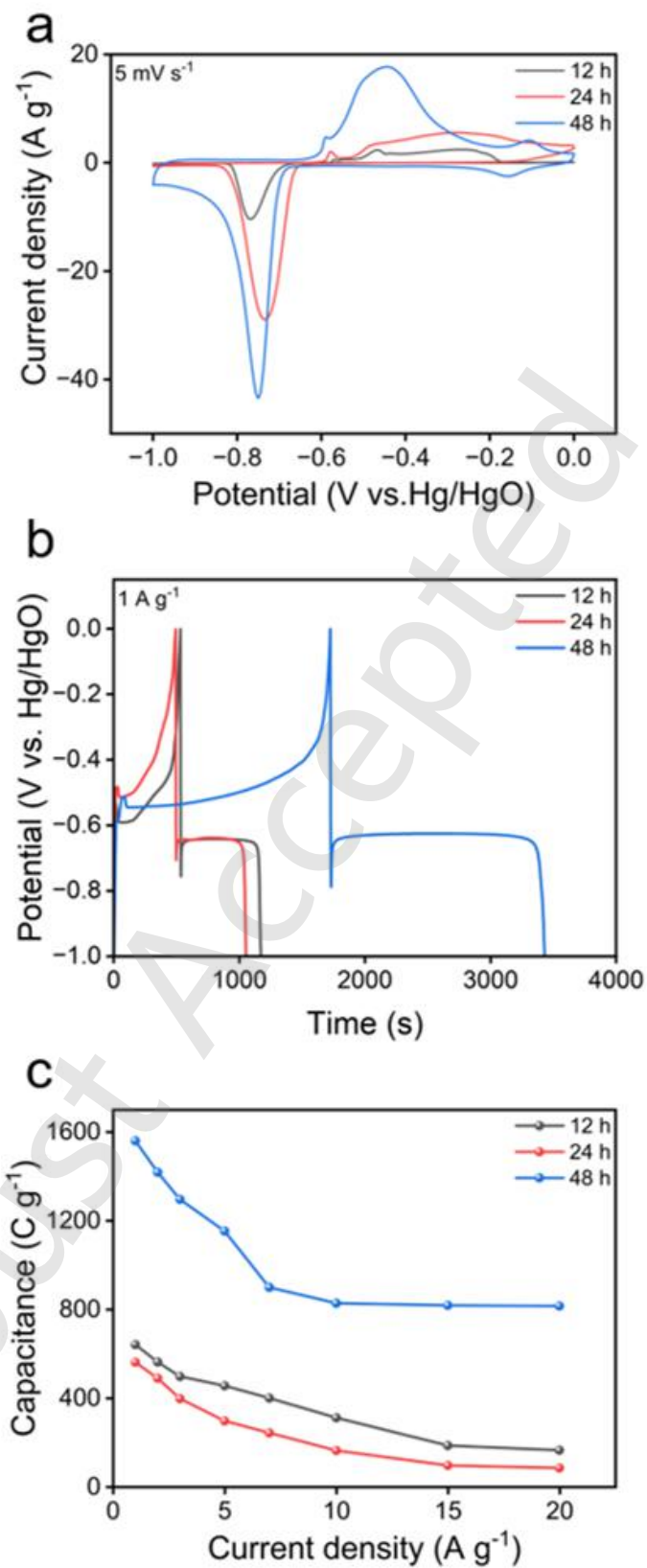


Figure S13. a) Comparison of CV curves at 5 mV s^{-1} , b) discharging curves at 1 A g^{-1} , c) Rate performance of B/BOC-GR_{0.1} with the different solvothermal time.

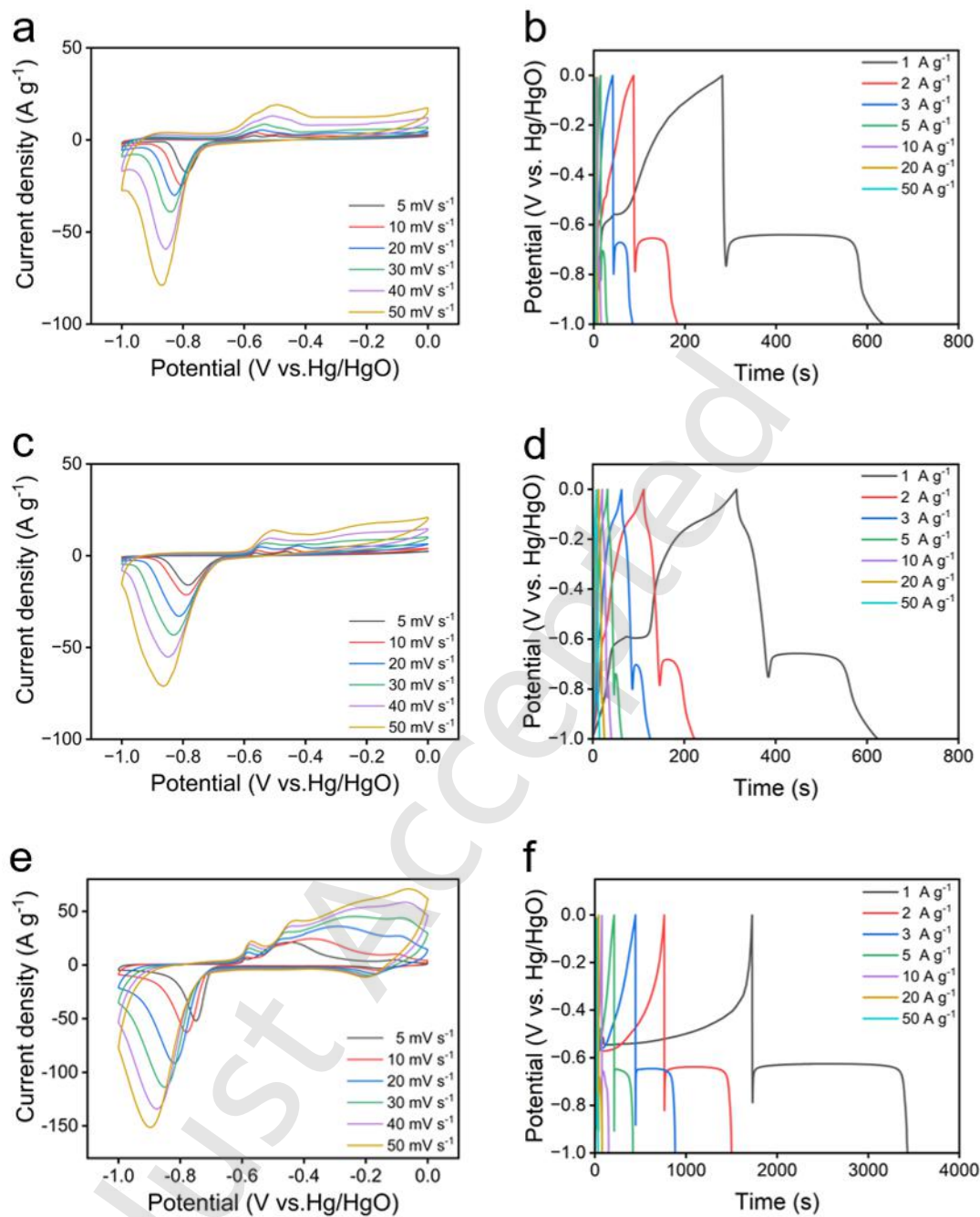


Figure S14. CV curves and GCD profiles of B/BOC-GR_{0.1} with the different ethanol/water solvent ratios a, b) 3:2, c, d) 4:1 e, f) 5:0.

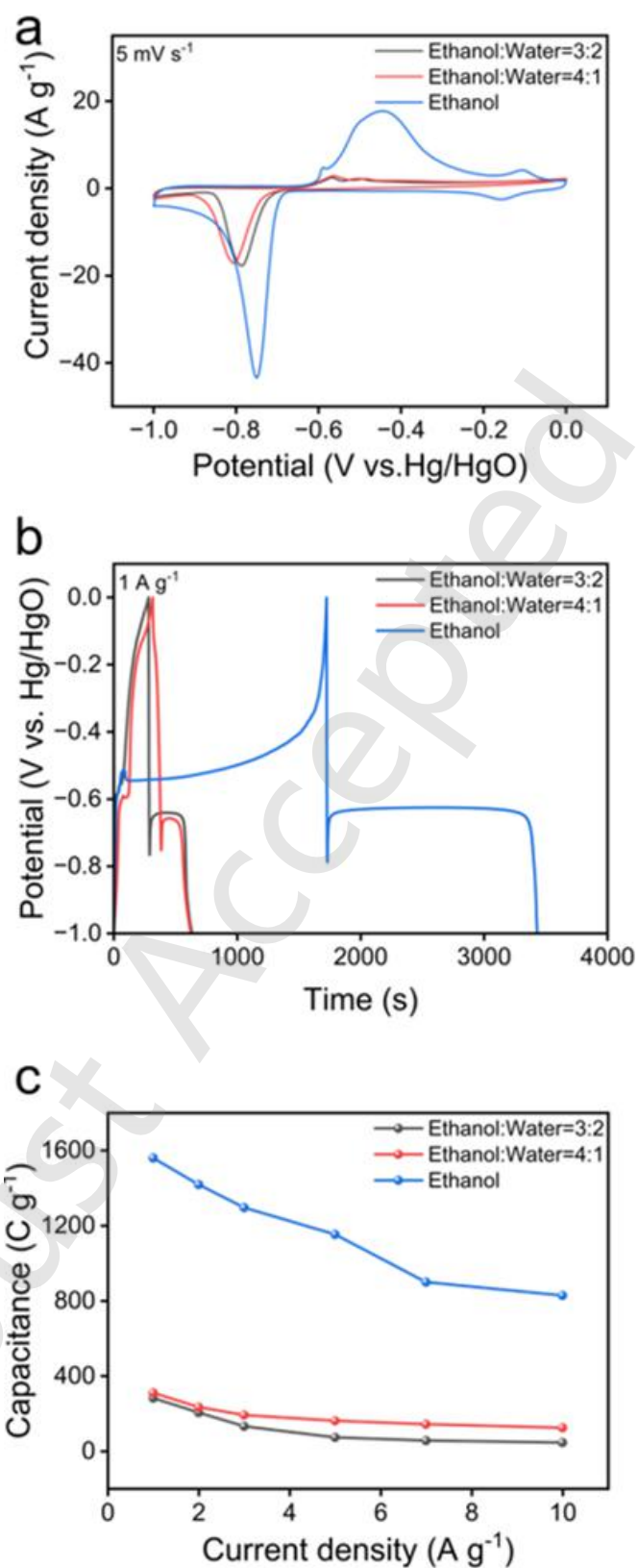
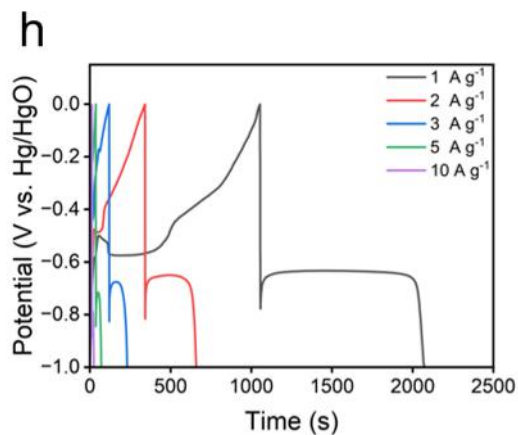
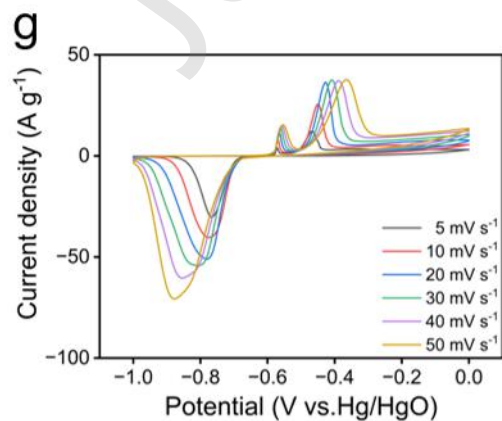
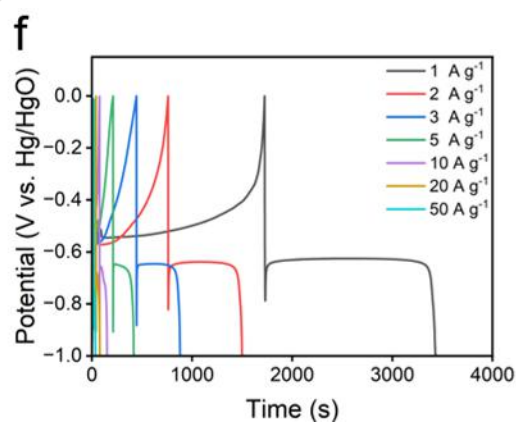
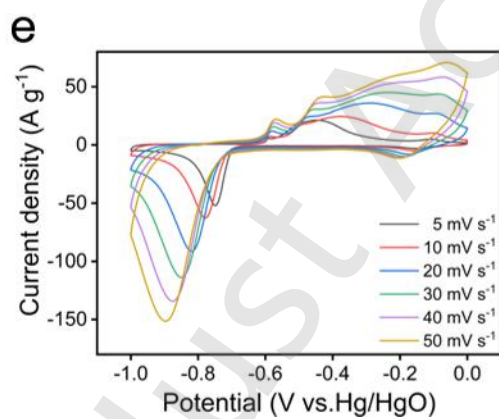
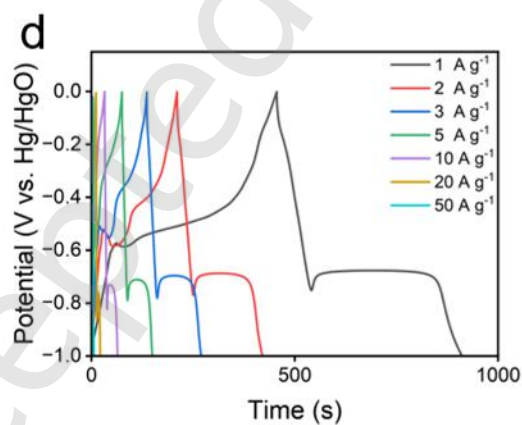
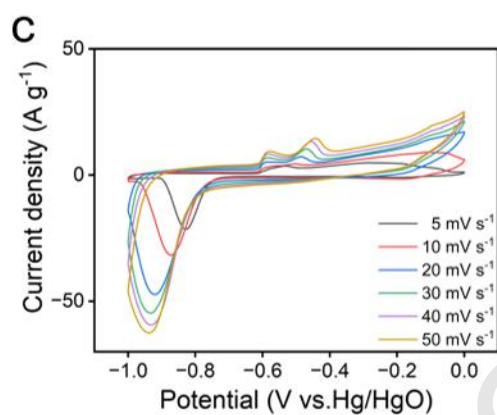
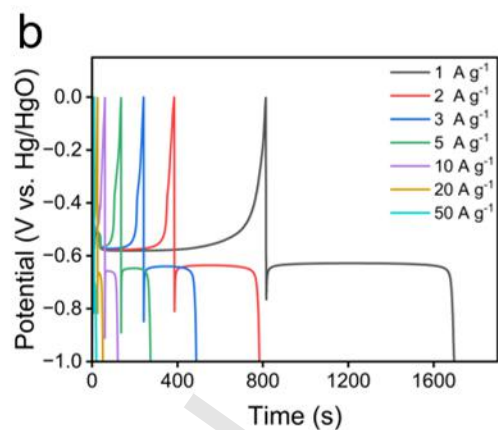
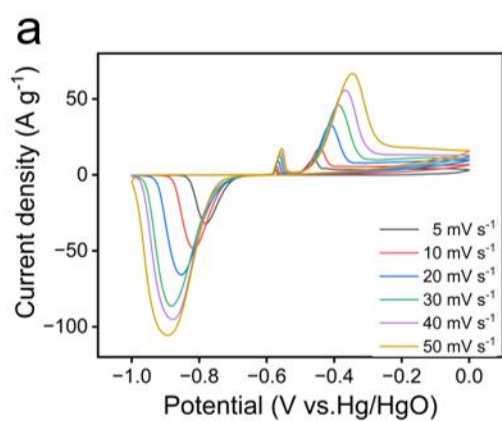


Figure S15. a) Comparison of CV curves at 5 mV s⁻¹, b) discharging curves at 1 A g⁻¹, c) Rate performance of B/BOC-GR_{0.1} with the different ethanol/water solvent ratios.



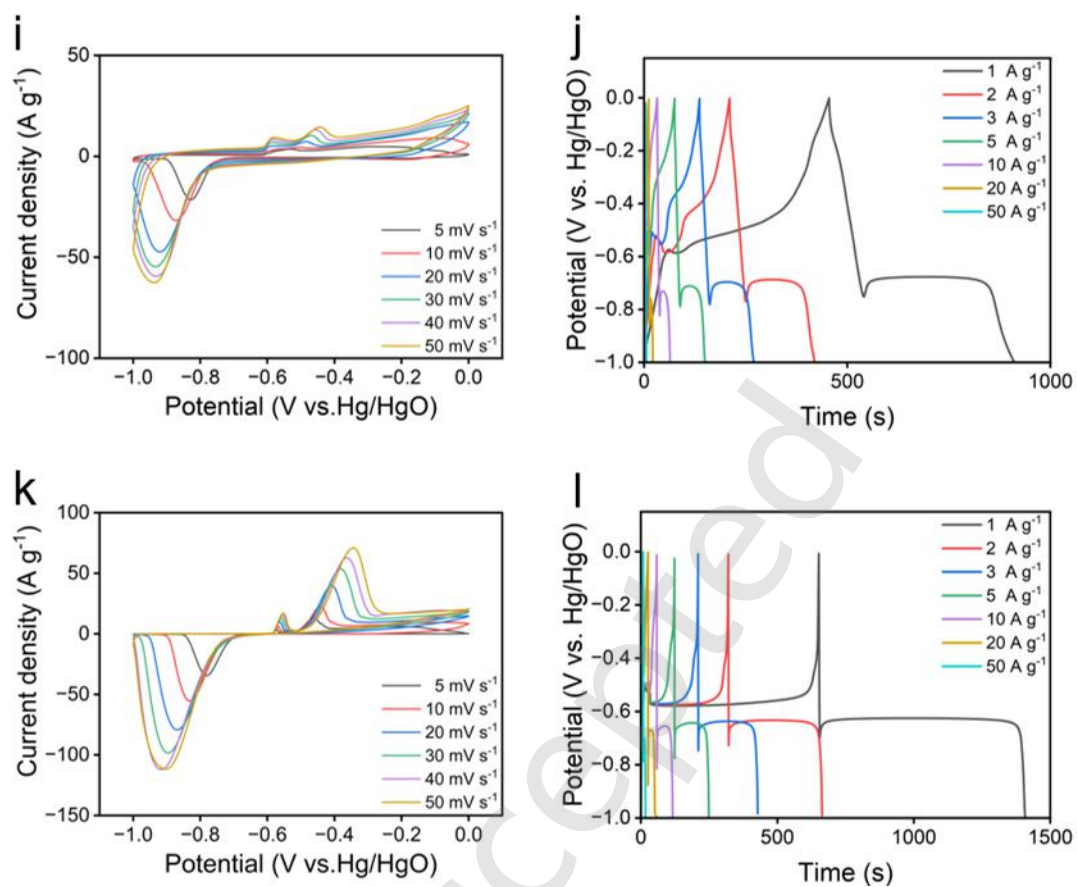


Figure S16. CV and GCD curves of B/BOC samples incorporating different carbon materials a, b) B/BOC without carbon materials, c, d) GR, e, f) GQD, g, h) GO, i, j) rGO, k, l) rGR.

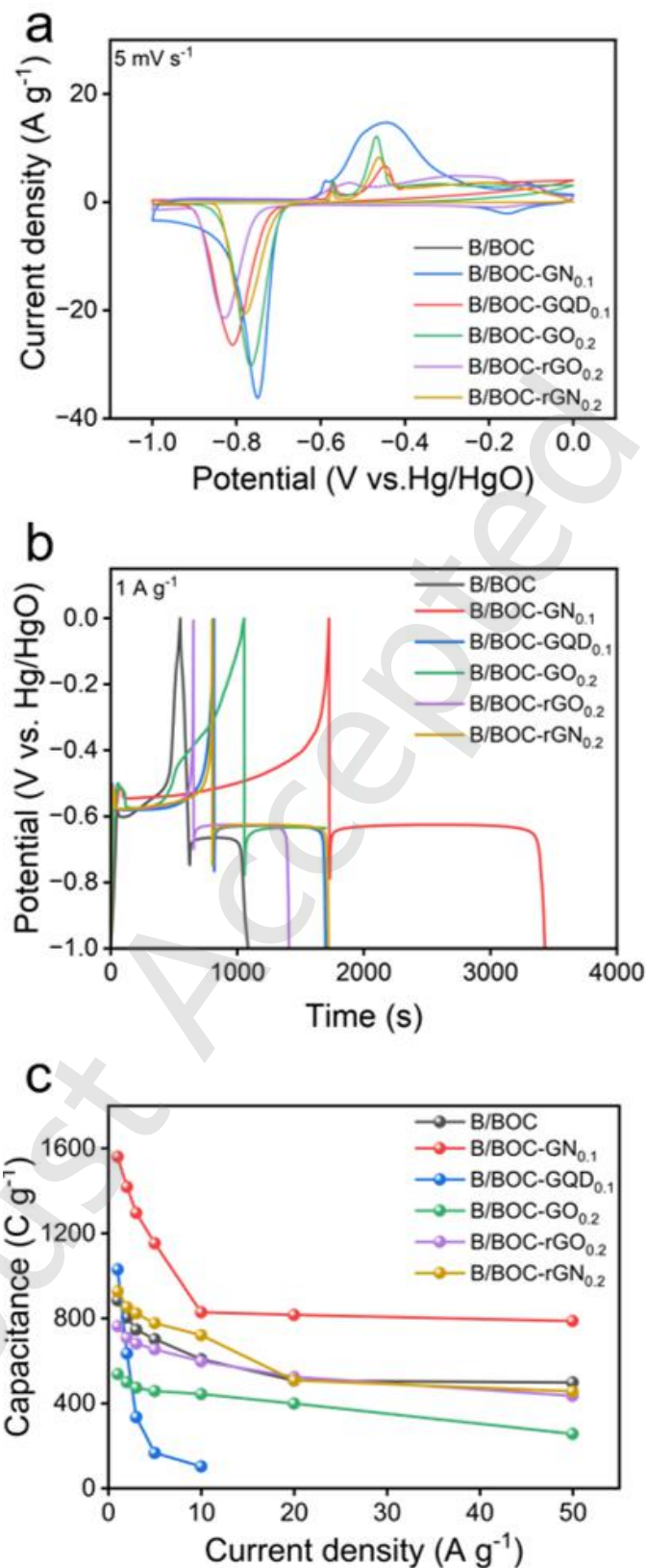


Figure S17. a) Comparison of CV curves at 5 mV s⁻¹, b) discharging curves at 1 A g⁻¹, c) Rate performance of B/BOC samples incorporating different carbon materials.

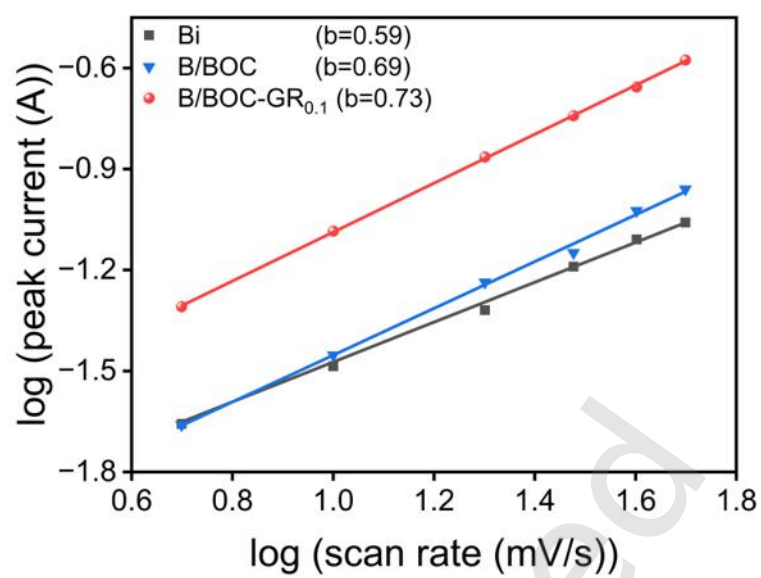


Figure S18. Linear fitting of $\log(i)$ versus $\log(v)$ for Bi, B/BOC and B/BOC-GR_{0.1}.

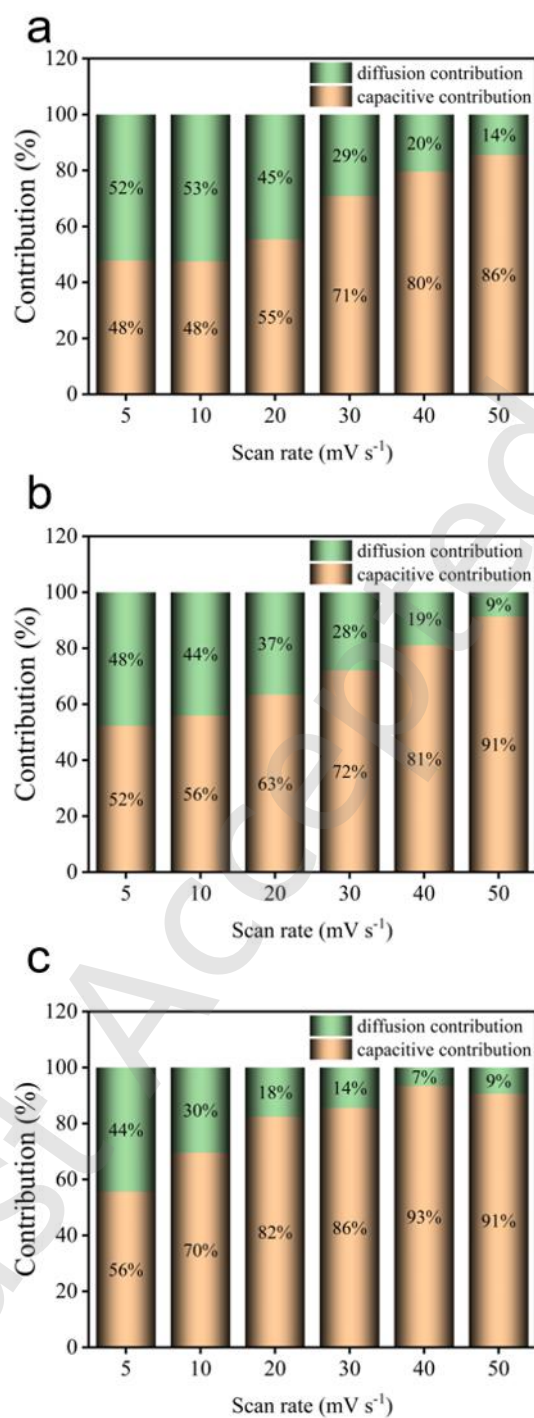


Figure S19. Diffusion-controlled and capacitive contributions of Bi, B/BOC and B/BOC-GR_{0.1} at diverse scan rates.

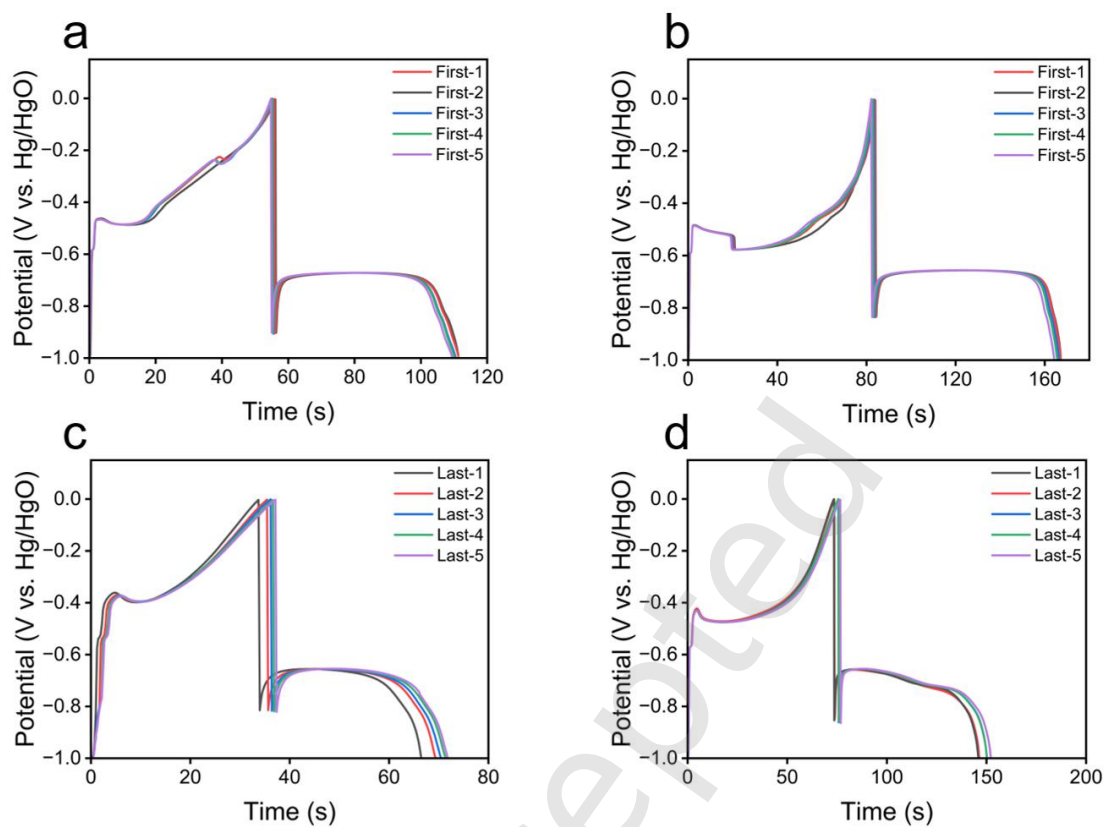


Figure S20. Comparison of the last five charge-discharge cycles of B/BOC and B/BOC-GR_{0.1} electrodes (a,b) first five cycles; (c,d) last five cycles.

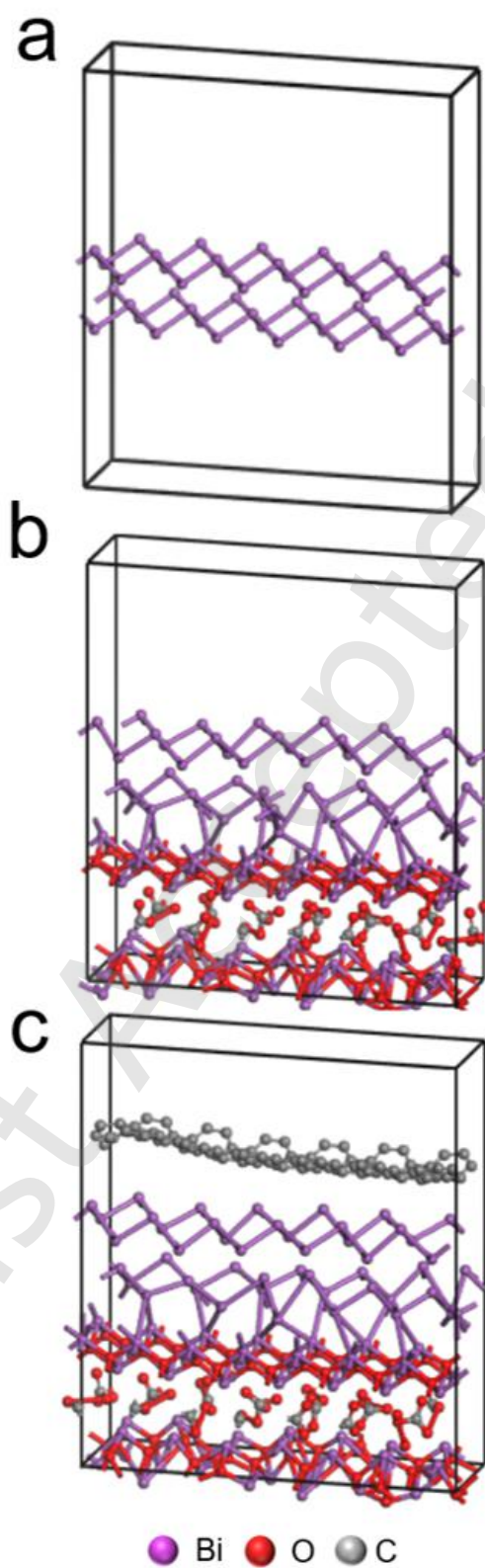


Figure S21. Layered structure models of a) Bi, b) B/BOC and c) B/BOC-GR_{0.1} along (001) plane.

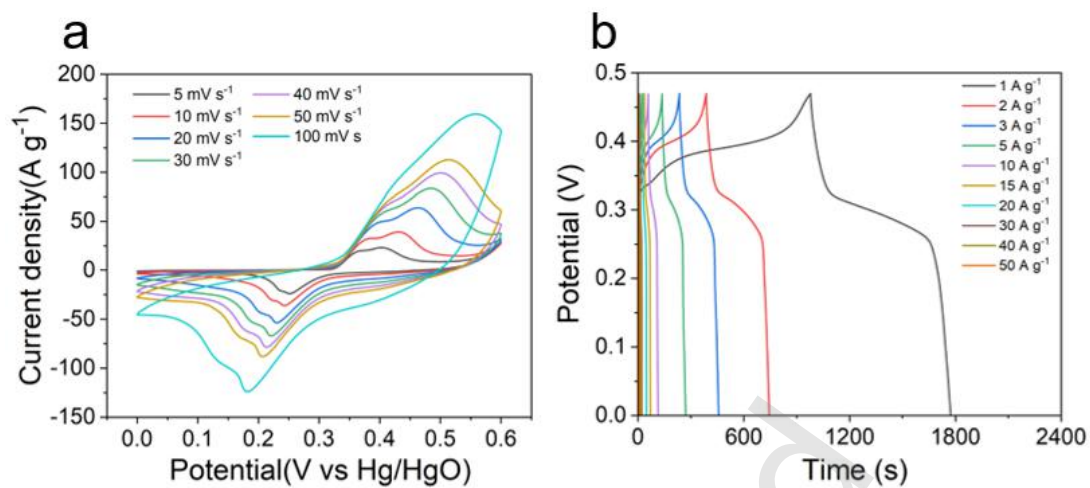


Figure S22. a) CV curves and b) GCD profiles of Ni(OH)Cl.

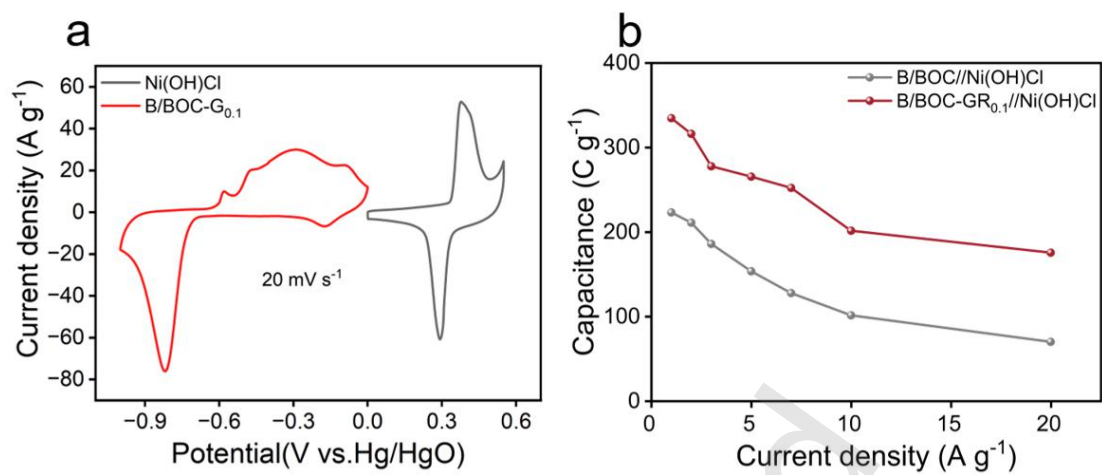


Figure S23. a) CV curves of Ni(OH)Cl and B/BOC-GR_{0.1} at 20 mV s⁻¹; b) Rate performance of B/BOC-GR_{0.1}/Ni(OH)Cl ASC.

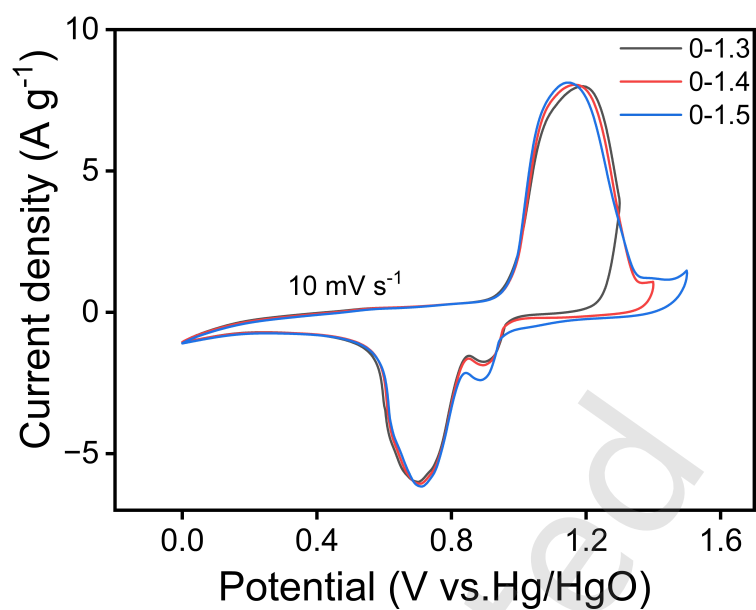


Figure S24. CV curves of B/BOC-GR_{0.1}/Ni(OH)Cl ASC at different potential windows.

Table S1. Quantitative fitting results of C 1s, O 1s, and Bi 4f XPS spectra for Bi, B/BOC, and B/BOC-GR_{0.1}, including binding energies and relative area percentages.

Sample	Component	Binding Energy (eV)	Area (%)
Bi	C-C	284.8	100
B/BOC	C-C	284.8	55.28
	C-C	285.9	28.26
	O-C=O	288.9	16.46
B/BOC-GR _{0.1}	C-C	284.8	59.22
	C-C	285.9	31.93
	O-C=O	288.9	8.86

Sample	Component	Binding Energy (eV)	Area (%)
Bi	CO ₃ ²⁻	532.3	100
B/BOC	CO ₃ ²⁻	532.6	13.56
	C-O	531.3	46.54
	Bi-O	530.3	39.89
B/BOC-GR _{0.1}	CO ₃ ²⁻	532.3	26.03
	C-O	531.3	47.38
	Bi-O	530.1	26.6

Sample	Peak	Binding Energy (eV)	Area (%)
Bi	Bi ⁰	157	100
	Bi ⁰	162.3	
B/BOC	Bi 4f 7/2	159.1	90.25
	Bi 4f 5/2	164.4	
	Bi ⁰	157	9.75
	Bi ⁰	162.3	
B/BOC-GR _{0.1}	Bi 4f 7/2	159.3	78.28
	Bi 4f 5/2	164.6	
	Bi ⁰	157.2	21.72
	Bi ⁰	162.5	

Table S2. Relative elements ratio of Bi⁰/Bi³⁺ and for B/BOC, B/BOC-GR_{0.1}

B/BOC:

element valence	Bi 4f 7/2	Bi 4f 5/2
0	4.3%	5.4%
+3	53.2%	37.1%

B/BOC-GR_{0.1}:

element valence	Bi 4f 7/2	Bi 4f 5/2
0	10.4%	11.4%
+3	45.2%	33%

Table S3. Internal resistance and contact resistance of Bi, B/BOC, and B/BOC-GR_{0.1}.

	Internal resistance (R_{Ω} , Ω)	Contact resistance (R_{ct} , Ω)
Bi	0.32	1.272
B/BOC	0.49	0.42
B/BOC-GR _{0.1}	0.26	0.4

Table S4. Linear fitting results of $\log(i)$ versus $\log(v)$ for the oxidation peak currents of Bi, B/BOC, and B/BOC-GR_{0.1} electrodes, including the calculated b values and corresponding correlation coefficients (R^2).

Sample	b	R^2
Bi	0.59	0.9868
B/BOC	0.69	0.9972
B/BOC-GR _{0.1}	0.73	0.9997

Table S5. Comparison of specific capacity and cyclic performance of B/BOC-GR_{0.1} and other reported Bismuth-based materials.

Sample	Specific capacity	Rate performance	Cyclic performance	Reference
B/BOC-GR _{0.1}	1560 F g ⁻¹ at 1 A g ⁻¹	890 F g ⁻¹ at 50 A g ⁻¹	92% after 5000 cycles (10 A g ⁻¹)	This work
Bi ₂ O ₃ @C	120 mAh g ⁻¹ at 0.8 A g ⁻¹	48 mAh g ⁻¹ at 26.7 A g ⁻¹	87.0% after 1200 cycles	Ref. 51
Bi-Bi ₂ O ₃ /CNT	850 F g ⁻¹ at 1 A g ⁻¹	714 F g ⁻¹ at 30 A g ⁻¹	—	Ref. 38
Bi ₂ O ₂ S@rGO-2	250.5 mAh g ⁻¹ at 1 A g ⁻¹	197.9 mAh g ⁻¹ at 10 A g ⁻¹	110% after 5000 cycles (6 A g ⁻¹)	Ref. 39
Bi ₂ O ₃ -Ni-F	557 F g ⁻¹ at 1 mA cm ⁻²	436 F g ⁻¹ at 10 mA cm ⁻²	85% after 2000 cycles (1 mA cm ⁻²)	Ref. 40
ESCNF@Bi ₂ O ₃ -1	530 mF cm ⁻² at 1 mA cm ⁻²	320 mF cm ⁻² at 10 mA cm ⁻²	87% after 2000 cycles (1 mA cm ⁻²)	Ref. 52
Bi ₂ O ₃	332.6 F g ⁻¹ at 1 A g ⁻¹	—	—	Ref. 55
α-Bi ₂ Mo ₃ O ₁₂	714 F g ⁻¹ at 1 A g ⁻¹	150 F g ⁻¹ at 5 A g ⁻¹	86.6% after 5000 cycles (5 A g ⁻¹)	Ref. 41
La-Bi ₂ O ₃	1418 F g ⁻¹ at 2 A g ⁻¹	960 F g ⁻¹ at 6 A g ⁻¹	78% after 10000 cycles	Ref. 42
Bi ₂ O ₃ /FSSM	421.8 F g ⁻¹ at 10 mA cm ⁻²	120 F g ⁻¹ at 40 A g ⁻¹	60% after 1000 cycles	Ref. 43
Bi ₂ S ₃	245.5 mAh g ⁻¹ at 0.5 A g ⁻¹	400 mAh g ⁻¹ at 4 A g ⁻¹	—	Ref. 45

Sample	Specific capacity	Rate performance	Cyclic performance	Reference
$\text{Bi}_2\text{S}_3/\text{g-C}_3\text{N}_4$	631 F g^{-1} at 1 A g^{-1}	188 F g^{-1} at 10 A g^{-1}	94% after 5000 cycles (1 A g^{-1})	<i>Ref. 44</i>
$\text{Bi}_2\text{S}_3\text{-3}$	233 F g^{-1} at 1 A g^{-1}	155 F g^{-1} at 10 A g^{-1}	67.4% after 10000 cycles (10 A g^{-1})	<i>Ref. 47</i>
$\delta\text{-Bi}_2\text{S}_3$	565 F g^{-1} at 1 A g^{-1}	393 F g^{-1} at 16 A g^{-1}	98% after 2000 cycles (2 A g^{-1})	<i>Ref. 48</i>
dr- $\text{Bi}_2\text{S}_3/\text{S-NCNF}$	466 F g^{-1} at 1 A g^{-1}	299 F g^{-1} at 8 A g^{-1}	81.5% after 1000 cycles (8 A g^{-1})	<i>Ref. 55</i>
BiOCl	1242 F g^{-1} at 1 A g^{-1}	582 F g^{-1} at 5 A g^{-1}	90.3% after 3000 cycles (5 A g^{-1})	<i>Ref. 53</i>
BiOCl/rGO	256 F g^{-1} at 5 mV s^{-1}	48 F g^{-1} at 100 mV s^{-1}	—	<i>Ref. 46</i>
$\text{BiOCl/Bi}_{24}\text{O}_{31}\text{Cl}_{10}$	411 C g^{-1} at 1 A g^{-1}	250 C g^{-1} at 10 A g^{-1}	99.5% after 10000 cycles (10 A g^{-1})	<i>Ref. 55</i>
BS-C15	1116 F g^{-1} at 2 A g^{-1}	207 F g^{-1} at 30 A g^{-1}	98% after 15000 cycles (2 A g^{-1})	<i>Ref. 56</i>
$\text{Cu}_9\text{S}_5/\text{Bi}_2\text{S}_3/\text{Bi}$	928 C g^{-1} at 2 A g^{-1}	229 F g^{-1} at 20 A g^{-1}	95.8% after 5000 cycles (20 A g^{-1})	<i>Ref. 57</i>
VCBO	850 F g^{-1} at 1 A g^{-1}	370 F g^{-1} at 10 A g^{-1}	—	<i>Ref. 58</i>
M/p-CNTs	558 F g^{-1} at 0.5 A g^{-1}	800 F g^{-1} at 10 A g^{-1}	—	<i>Ref. 59</i>
$\text{NiCo}_2\text{O}_4\text{-Bi}_2\text{O}_3/\text{CNTs}$	2762 F g^{-1} at 1 A g^{-1}	2500 F g^{-1} at 10 A g^{-1}	90.5% after 15000 cycles (10 A g^{-1})	<i>Ref. 60</i>

Sample	Specific capacity	Rate performance	Cyclic performance	Reference
CNF@Ag/Mn/Bi/Fe	156 F g ⁻¹ at 2 mV s ⁻¹	61.1 F g ⁻¹ at 500 mV s ⁻¹	96.4% after 1400 cycles (5 A g ⁻¹)	<i>Ref. 61</i>
Bi ₂ O ₂ Se/PANI	630 mAh g ⁻¹ at 1 A g ⁻¹	333.8 mAh g ⁻¹ at 6 A g ⁻¹	73% after 5000 cycles (20 A g ⁻¹)	<i>Ref. 62</i>
Bi-Ni ₃ Se ₂ /rGO	1194 F g ⁻¹ at 1 A g ⁻¹	913 F g ⁻¹ at 3 A g ⁻¹	93.2% after 5000 cycles (1 A g ⁻¹)	<i>Ref. 63</i>
NiO-Bi ₂ O ₃	1218 F g ⁻¹ at 1 A g ⁻¹	849 F g ⁻¹ at 50 A g ⁻¹	98.3% after 5000 cycles (10 A g ⁻¹)	<i>Ref. 64</i>

Table S6. Comparison of maximal energy densities and corresponding power densities between B/BOC-GR_{0.1}/Ni(OH)Cl ASCs with other reported ASCs.

Sample	Power density (P)	Maximal energy density (E _{max})	Reference
Ni(OH)Cl/B/BOC-GR _{0.1}	752 kW kg ⁻¹	70 Wh kg ⁻¹	This work
NiO/Bi ₂ O ₃ @C	12.2 kW kg ⁻¹	6.8 Wh kg ⁻¹	<i>Ref. 51</i>
MnO ₂ /Bi ₂ O ₃	3370 W kg ⁻¹	9.1 Wh kg ⁻¹	<i>Ref. 37</i>
Ni(OH) ₂ /CNT//Bi-Bi ₂ O ₃ /CNT	8000 W kg ⁻¹	19 Wh kg ⁻¹	<i>Ref. 38</i>
(NiCo) ₉ S ₈ //Bi ₂ O ₂ S@rGO	980 W kg ⁻¹	54 Wh kg ⁻¹	<i>Ref. 39</i>
Bi ₂ O ₃ -Ni-F//AC	1.1 kW kg ⁻¹	11.4 Wh kg ⁻¹	<i>Ref. 40</i>
ESCNF@Bi ₂ O ₃ //CF@NiCo ₂ O ₄	2949 W kg ⁻¹	11 Wh kg ⁻¹	<i>Ref. 52</i>
Bi ₂ O ₃ /N-GNTs@CoNi ₂ S ₄ NPs	1.4 kW kg ⁻¹	152 Wh kg ⁻¹	<i>Ref. 49</i>
Bi ₂ O ₃ @TiO ₂ //Bi ₂ O ₃ @TiO ₂	750 W kg ⁻¹	316.9 Wh kg ⁻¹	<i>Ref. 50</i>
Bi ₂ O ₃ //MnO ₂	102.6 W kg ⁻¹	9.5 Wh kg ⁻¹	<i>Ref. 54</i>
Bi ₂ Mo ₃ O ₁₂ //AC	750 W kg ⁻¹	47.5 Wh kg ⁻¹	<i>Ref. 41</i>
NiO/NiCo-LDH/CC//La-Bi ₂ O ₃	10 kW kg ⁻¹	112.8 Wh kg ⁻¹	<i>Ref. 42</i>

Sample	Power density (P)	Maximal energy density (E _{max})	Reference
Bi ₂ O ₃ //AC	1008.7 W kg ⁻¹	18.2 Wh kg ⁻¹	<i>Ref. 43</i>
Bi ₂ S ₃ /g-C ₃ N ₄ //AC	999 W kg ⁻¹	44.4 Wh kg ⁻¹	<i>Ref. 44</i>
Bi ₂ S ₃ /Ni//AC	3202 W kg ⁻¹	45.1 Wh kg ⁻¹	<i>Ref. 45</i>
BRG ₇₅	1.4 kW kg ⁻¹	21.2 Wh kg ⁻¹	<i>Ref. 46</i>
Bi ₂ S ₃ -3//AC	798.5 W kg ⁻¹	27.8 Wh kg ⁻¹	<i>Ref. 47</i>
dr-Bi ₂ S ₃ /S-NCNF//S-NCNF	5317 W kg ⁻¹	16.4 Wh kg ⁻¹	<i>Ref. 55</i>
BiOCl//AC	4.9 kW kg ⁻¹	6.2 Wh kg ⁻¹	<i>Ref. 53</i>
BiOCl/Bi ₂₄ O ₃₁ Cl ₁₀	923.8 W kg ⁻¹	35.7 Wh kg ⁻¹	<i>Ref. 55</i>
BS-C15	498.9 W kg ⁻¹	2.4 Wh kg ⁻¹	<i>Ref. 56</i>
Cu ₉ S ₅ /Bi ₂ S ₃ /Bi	2744 W kg ⁻¹	73 Wh kg ⁻¹	<i>Ref. 57</i>
VCBO	4250 W kg ⁻¹	41.3 Wh kg ⁻¹	<i>Ref. 58</i>
M/p-CNTs	745 W kg ⁻¹	18.8 Wh kg ⁻¹	<i>Ref. 59</i>
NiCo ₂ O ₄ -Bi ₂ O ₃ /CNTs	450 W kg ⁻¹	109.7 Wh kg ⁻¹	<i>Ref. 60</i>

Sample	Power density (P)	Maximal energy density (E _{max})	Reference
CNF@Ag/Mn/Bi/Fe	8753 W kg ⁻¹	25.9 Wh kg ⁻¹	<i>Ref. 61</i>
Bi-Ni ₃ Se ₂ /rGO	1140 W kg ⁻¹	15 Wh kg ⁻¹	<i>Ref. 63</i>
NiO-Bi ₂ O ₃	750 W kg ⁻¹	114.6 Wh kg ⁻¹	<i>Ref. 64</i>