

Article

Magnetic CoFe_2O_4 and NiFe_2O_4 Induced Self-Assembled Graphene Nanoribbon Framework with Excellent Properties for Li-Ion Battery

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Abstract: A magnetically induced self-assembled graphene nanoribbons (GNRs) method is reported to synthesize $\text{MFe}_2\text{O}_4/\text{GNRs}$ ($\text{M} = \text{Co}, \text{Ni}$). It is found that MFe_2O_4 compounds not only locate on the surface of GNRs but anchor on the interlayers of GNRs in the diameter of less than 5 nm as well. The in situ growth of MFe_2O_4 and magnetic aggregation at the joints of GNRs act as crosslinking agents to solder GNRs to build a nest structure. Additionally, combining GNRs with MFe_2O_4 helps to improve the magnetism of the MFe_2O_4 . As an anode material for Li^+ ion batteries, $\text{MFe}_2\text{O}_4/\text{GNRs}$ can provide high reversible capacity and cyclic stability (1432 mAh g^{-1} for $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and 1058 mAh g^{-1} for NiFe_2O_4 at 0.1 A g^{-1} over 80 cycles).

Keywords: CoFe_2O_4 ; NiFe_2O_4 ; graphene nanoribbons; Li battery; magnetism



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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are widely used to meet the ever-increasing demand for fast charging and high-capacity energy storage [1–3]. It is particularly important to search for novel anode materials with both high capacity and outstanding safety for high-performance LIBs. Nowadays, graphite is the most commercial anode material for LIBs owing to its abundant natural resources. However, the relatively low theoretical specific capacity (372 mAh g^{-1}) and the lithium diffusion coefficient ($10^{-7} \sim 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) restrict the further application of high-power LIBs [4–6]. The choice of magnetic transition metal oxides (TMOs) as anodes for LIBs has received considerable attention due to their high energy density and natural abundance. Apart from binary TMOs, ternary TMOs comprising mixed valence in a single crystalline structure have drawn enormous research attention [7,8]. Regarding cobalt ferrite and nickel ferrite (MFe_2O_4 , $\text{M} = \text{Co}, \text{Ni}$), as one of the representative ternary TMOs, better electrical conductivity arises because $\text{Co}^{2+}/\text{Ni}^{2+}$ and 1/2 the Fe^{3+} cation occupy the octahedral sites. In comparison to conventional spinel oxides, MFe_2O_4 with a unique inverse spinel structure has higher Li^+ ion incorporation [9,10]. As a result, MFe_2O_4 is expected to become an appealing anode material for LIBs. Nevertheless, MFe_2O_4 suffers from huge volume expansion and material cracking problems during the periodic charge–discharge process, which results in rapid fading capability [11,12]. Two common approaches have been proposed to address the above issues. One is to prepare variously nanostructured (such as hollow nanospheres, nanowires, nanotubes) [13–16] composite. Nanostructured MFe_2O_4 can shorten the diffusion paths of Li^+ ion, leading to higher electrochemical activity.

The other route is to introduce carbon materials, such as carbon nanotubes (CNTs) and graphene, to fabricate $\text{MFe}_2\text{O}_4/\text{carbon}$ composites [17–19]. Among them, nest structure

MFe₂O₄/carbon composites, due to their porous structure, can increase the efficiency of electron transport and the contact area with electrolytes. Moreover, a network carbon framework can not only effectively accommodate volume change in the MFe₂O₄ and prevent the pulverization, which will enable nest MFe₂O₄/carbon composites to maintain high conductivity and reversible capacity, but also provide nucleation sites that regulate MFe₂O₄ crystal morphology [20–23].

Nest structure MFe₂O₄/carbon composites can be prepared by hydrothermal, chemical vapor deposition, polymer-assisted methods, and so on [24–26]. The 3D framework prepared by the polymer-assisted method is stable in structure and simple in operation. However, the poor-conductivity nature of the polymer would affect the electron transport among the composites. Nest MFe₂O₄/carbon composites with high electron conductivity can be obtained by replacing the polymer with magnetic MFe₂O₄; thus, MFe₂O₄ will not only act as the active material but also as the “binder agent” to stabilize the carbon framework. The common carbon framework is mainly created by graphene or CNTs [26,27]. Compared to them, graphene nanoribbons (GNRs) are more beneficial for improving the electrochemical performance of the composites owing to their high active open edges and specific surface area [28].

Based on our previous work [29], a facile magnetically induced self-assembled graphene nanoribbons (GNRs) method is reported to synthesize MFe₂O₄. The key feature for our synthesis route is taking advantage of the magnetic attraction of MFe₂O₄, which cross-link GNRs in the intersections. By means of this procedure, the self-aggregated phenomenon takes place in magnetic nanomaterials owing to more active sites at the GNRs' junction; MFe₂O₄ particles tend to link to each other and accumulate at the joints. After a following heating treatment, MFe₂O₄/GNRs can be easily achieved. MFe₂O₄/GNRs present excellent cycle performance or LIBs and particularly excellent high reversible capacity and rate capacity, resulting from their unique network structure and the synergy effect of each component. Additionally, research on magnetism indicates that the MFe₂O₄/GNRs are also promising for magnetic devices.

2. Results and Discussion

2.1. SEM and TEM Analysis

Figure 1a illustrates the synthesis route of CoFe₂O₄/GNRs composites by simple refluxing. CNTs were unzipped to obtain GNRs [30]. After that, both GNRs and cobalt organic salt were dispersed in benzyl ether solution under agitation. Thereafter, aqueous solution was refluxed at 220 °C for 0.5 h, during which Co(acac)₃ decomposed to some CoFeO nanoclusters. Then, borders of GNRs filled with dangling C-C bonds were occupied by the CoFeO nanoclusters. Along with the reaction, CoFeO nanoclusters in situ grew and agglomerated as CoFe₂O₄ in the surface, interlayers, and edges of GNRs. After drying, the magnetically induced attraction of CoFe₂O₄ began to focus on the GNRs joints, causing CoFe₂O₄/GNRs composites to self-assemble. The synthesis procedure of NiFe₂O₄/GNRs is similar to CoFe₂O₄/GNRs, except nickel organic is used. The structure of the products was first investigated by SEM. Figure 1b–g represents the SEM images for MFe₂O₄/GNRs composites. The hybrids possessed a porous structure in the low-magnified SEM. From the high-magnification SEM (Figure 1c,f), the surface of the GNRs was anchored by metal oxide nanoparticles, and it can be clearly seen that some aggregates of MFe₂O₄ were in the junctions of GNRs. The aggregates of MFe₂O₄ acted as a “crosslink agent” that fitted together the GNRs to build a 3D porous structure. As presented in Figure 1b,e, the morphology of CoFe₂O₄/GNRs and MFe₂O₄/GNRs seemed very similar, indicating that preparation of porous MFe₂O₄/GNRs was controllable and universal. The SEM images of CoFe₂O₄ and NiFe₂O₄ nanocomposite without GNRs are shown in Figure S1 (Supplementary Materials). CoFe₂O₄ and NiFe₂O₄ are irregular spheres (20–50 nm) and tend to agglomerate together to form large particles without GNRs. The elemental mapping images of MFe₂O₄/GNRs are shown in Figure 1d,g, demonstrating that the C, Ni, Co, Fe, and O are gathered in the junction of GNRs and distributed uniformly along GNRs.

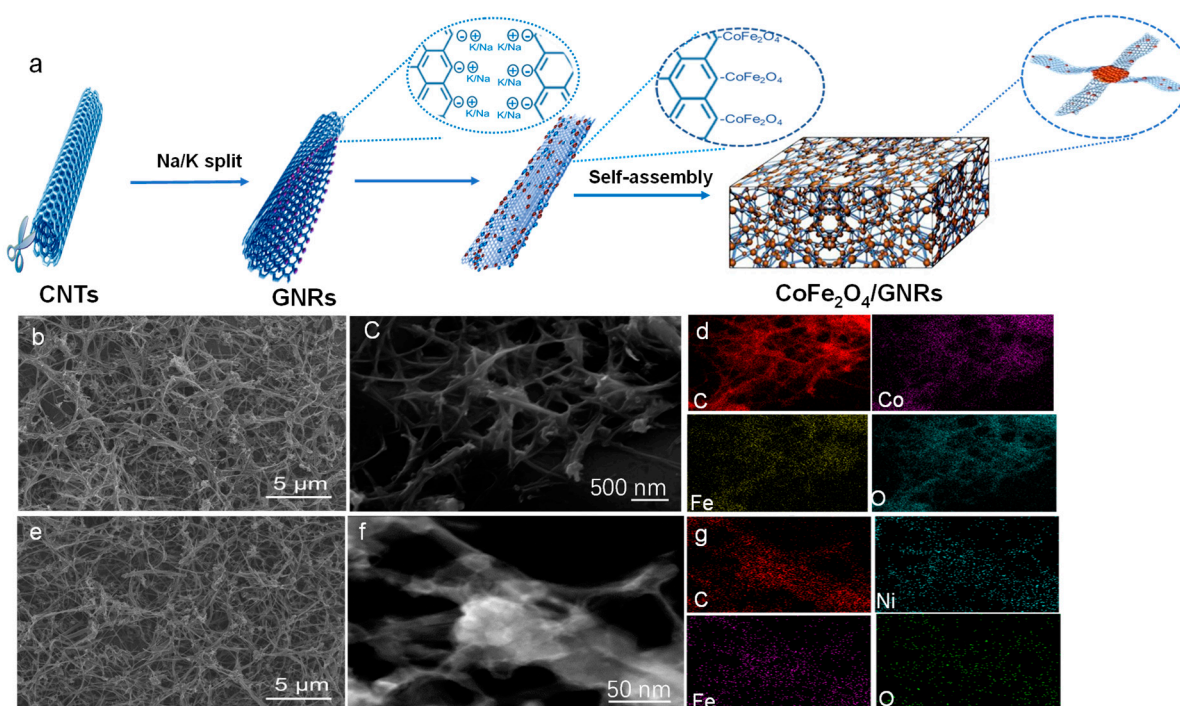


Figure 1. (a) The schematic illustration of the synthesis of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ composites. (b,c) SEM images of as-prepared $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (d) EDS mapping of $\text{CoFe}_2\text{O}_4/\text{GNRs}$. (e,f) SEM images of $\text{NiFe}_2\text{O}_4/\text{GNRs}$ and (g) EDS mapping of $\text{NiFe}_2\text{O}_4/\text{GNRs}$.

The microstructure and composition of the $\text{MFe}_2\text{O}_4/\text{GNRs}$ were confirmed by the TEM. As shown in Figure 2a,d, there are numerous agglomerated metal oxide nanoparticles at the joints of GNRs. With the cross-linking function of these metal oxide nanoparticles, the GNRs self-assembled into a 3D structure. Additionally, it can be observed from Figure 2b,e that the MFe_2O_4 in an average size of 3–8 nm was uniformly distributed on both exteriors and interior layers of the GNRs in the hybrids (Figure S2). It was noted that suspended particles of MFe_2O_4 were found at the borders of GNRs in Figure 2c,f. It was proven that the unsaturated C-C bond at the edge of the GNRs can facilitate the nucleation and growth of MFe_2O_4 . Figure 2c showed the high-resolution lattice images of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ nanoparticles in $\text{CoFe}_2\text{O}_4/\text{GNRs}$ composite. The lattice fringes with a lattice spacing of 0.30 nm and 0.25 nm corresponded to the (220) and (311) planes of CoFe_2O_4 , respectively [31]. Figure 2f showed the high-resolution lattice images of NiFe_2O_4 nanoparticles. The lattice fringes with a lattice spacing of 0.25 nm were assigned to the (311) planes of NiFe_2O_4 [32].

2.2. XRD, Raman, and XPS Analysis

An X-ray diffraction (XRD) analysis was performed to assess the structure, crystallization, and purity of $\text{MFe}_2\text{O}_4/\text{GNRs}$. As shown in Figure 3a, for $\text{CoFe}_2\text{O}_4/\text{GNRs}$ composite, the diffraction peaks at 18.3, 30.2, 35.5, 43.2, 57.1, and 62.7 correspond to the lattice planes (220), (311), (400), (511), and (440), respectively, of cubic spinel structure (JCPDS No. 22-1086 and NiFe_2O_4 with JCPDS card no. 86-2267). In addition, there was also a diffraction peak at 26.5° (star symbol in Figure 3a), which was assigned to the GNRs [31,32]. Raman measurement was performed in Figure 3b,c. D, G, and 2D bands at 1340, 1582, and 2678 cm^{-1} stand for GNRs [32] on account of the strong disorder carbon's in-plane vibrations and graphitic carbon's in-plane vibrations. The three peaks of GNRs in $\text{MFe}_2\text{O}_4/\text{GNRs}$ are basically in the same position as those in GNRs alone, but the strength of all three peaks is significantly reduced since GNRs are combined with MFe_2O_4 . In the enlarged part of the figure, both the composites show three major peaks. CoFe_2O_4 shows at 680, 532, and 320 cm^{-1} . Further, the peaks of NiFe_2O_4 are at 672, 470, and 323 cm^{-1} due to the low Raman-intensity nature

of MFe_2O_4 [33,34], which are all consistent with the XRD results. XPS measurements were performed to further study the surface chemical state of the composites (Figure 3d). For $\text{MFe}_2\text{O}_4/\text{GNRs}$, there were several major peaks, assigned to C, O, Fe, Co, and Ni, respectively. In the high-resolution XPS spectra, C_{1s} of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ had a graphitic C-C/C=C peak at 286.7 eV, together with C=O (287.4 eV), as revealed in Figure 3e [32]. The C-C/C=C and C-O peak of $\text{NiFe}_2\text{O}_4/\text{GNRs}$ are located at 285.4 eV and 287.6 eV, respectively (Figure 3i). The $\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$ peaks of the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ were located at 779.4 and 795.8 eV with a 16.4 eV peak-to-peak separation (Figure 3f), indicating the Co(II) oxidation state [35]. The locations of the Fe_{2p} peaks ($\text{Fe}_{2p_{1/2}}$ at 724.5 eV and $\text{Fe}_{2p_{3/2}}$ at 710.4 eV) in Figure 3g verify the presence of Fe^{3+} cations in CoFe_2O_4 . The O_{1s} spectrum in Figure 3h demonstrates two oxygen attributions. The peaks of 529.7 and 531.2 eV represent a metal-oxygen bond and some surface defect sites, respectively. The deconvolution of the Ni_{2p} spectrum demonstrates four peaks in Figure 3j. At binding energies of 855.7 eV and 876.3 eV are two main peaks followed by two shake-up satellites. Moreover, the signals of $\text{Fe}_{2p_{3/2}}$ and $\text{Fe}_{2p_{1/2}}$ in NiFe_2O_4 peaks were found at 724.7 eV and 711.9 eV, respectively, indicating that the Fe is in the typical trivalent oxidation state (Figure 3k). Peaks of O_{1s} of NiFe_2O_4 are denoted as crystal lattice oxygen and chemisorbed oxygen in Figure 3l [36,37].

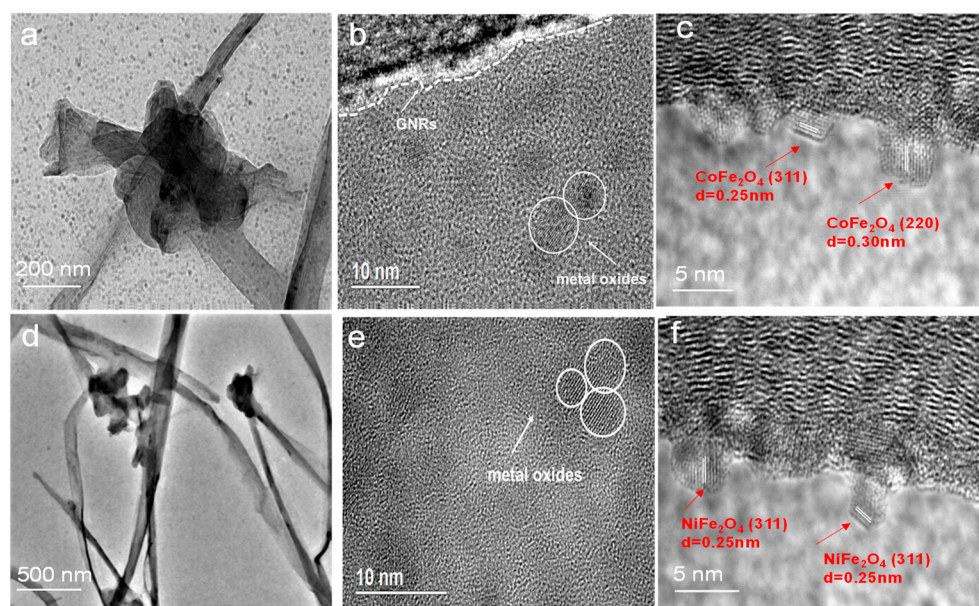


Figure 2. TEM images of as-prepared (a–c) $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (d–f) $\text{NiFe}_2\text{O}_4/\text{GNRs}$.

2.3. BET and TGA Analysis

The nitrogen adsorption-desorption isotherm and pore-size distribution curves are shown in Figure S3a,b. The Brunauer-Emmett-Teller (BET) specific surface areas of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ were measured to be $47.7 \text{ m}^2\text{g}^{-1}$ and $27.5 \text{ m}^2\text{g}^{-1}$, respectively. The sample exhibits a representative type IV curve, indicating a mesoporous structure with distributions ranging from 2 to 10 nm. The foam structure will help the rapid travel of electrolytic ions for accessing the interior MFe_2O_4 in the lithiation-delithiation process.

The TGA curves for $\text{MFe}_2\text{O}_4/\text{GNRs}$ were shown in Figure S4. TGA is performed to analyze the mass ration of MFe_2O_4 and GNRs. There were several stages of weight loss in Figure S4. The drop in weight below 200°C can be ascribed to the evaporation of water. The typical weight loss between 200°C and 550°C can be ascribed to the oxidation of the GNRs. The one after 550°C was mainly due to the oxidation of MFe_2O_4 in air. Based on the weight loss in Figure S4, the weight percentages of CoFe_2O_4 and NiFe_2O_4 in $\text{MFe}_2\text{O}_4/\text{GNRs}$ were estimated to be $\sim 41\%$ and $\sim 23\%$, respectively.

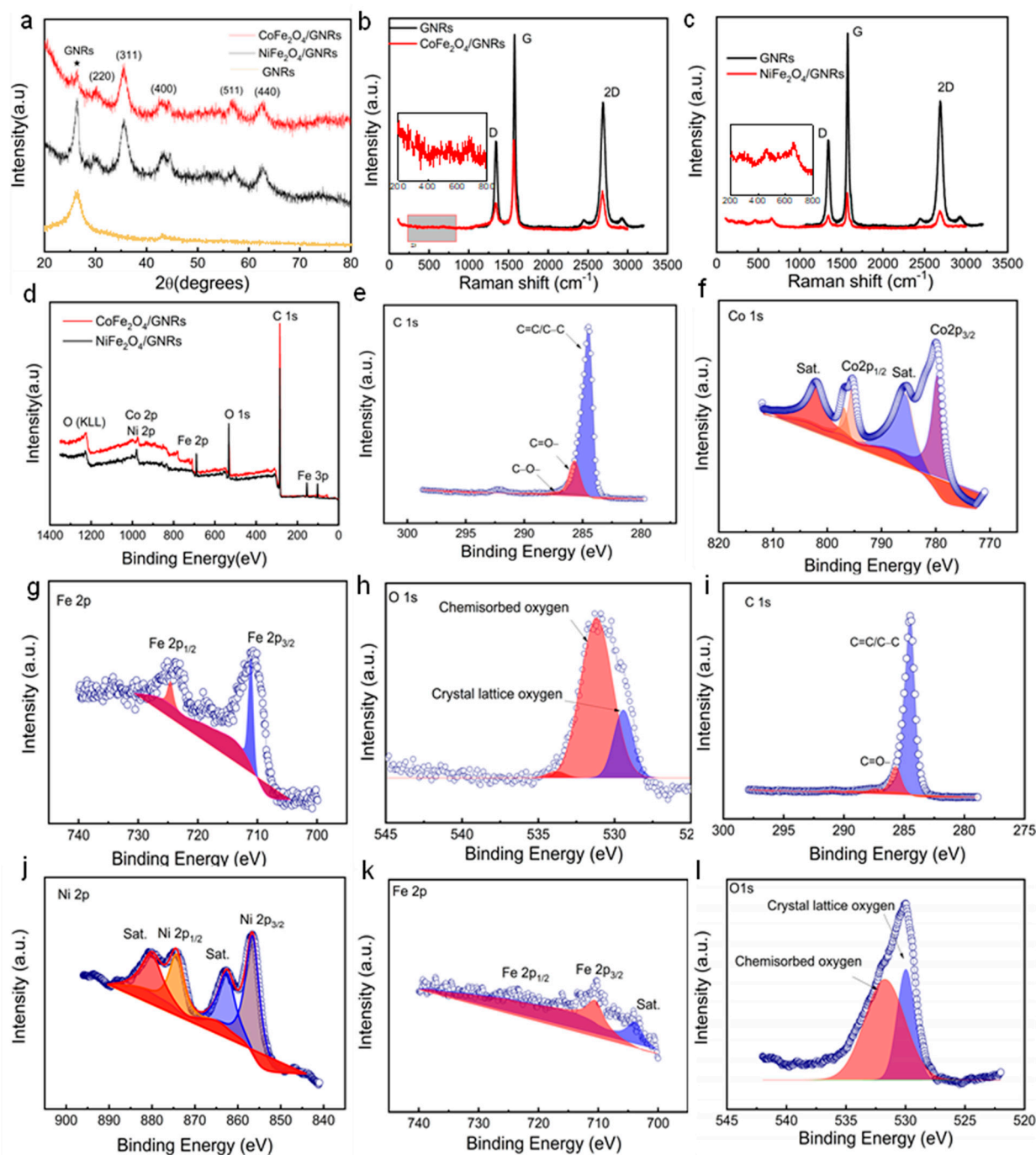


Figure 3. (a) ★ Represents the XRD peaks of graphene nanoribbons (GNRs); XRD patterns and Raman spectra of (b) $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (c) $\text{NiFe}_2\text{O}_4/\text{GNRs}$. (d) Full XPS spectra of as-prepared $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$. XPS survey spectra of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ (e) C 1s. (f) Co 2p. (g) Fe 2p. (h) O 1s and $\text{NiFe}_2\text{O}_4/\text{GNRs}$. (i) C 1s. (j) Ni 2p. (k) Fe 2p. (l) O 1s.

2.4. Electrochemistry Performance

Cyclic voltammetry (CV) tests were investigated in half-cell configurations to assess the Li^+ ion storage properties of the as-prepared $\text{MFe}_2\text{O}_4/\text{GNRs}$. Figure 4a–b showed the CV curves of the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ in the first three cycles. Two cathodic peaks were observed at 0.57 and 0.53 V in the first cycle, corresponding to multistage electrochemical reduction reactions (lithiation) of $\text{MFe}_2\text{O}_4/\text{GNRs}$ with a Li^+ ion and a partially irreversible solid electrolyte interphase (SEI) layer [32]. The main anodic peaks at 1.5–2.0 V for the two composites were ascribed to the oxidation reactions (delithiation) of

MFe₂O₄; in addition, the lithiation and delithiation peaks of GNRs were at 0.13–0.25 V and 0.15–0.24 V, proving that GNRs were helpful for Li⁺ ion storage. The above reactions are as follows [38–41]:

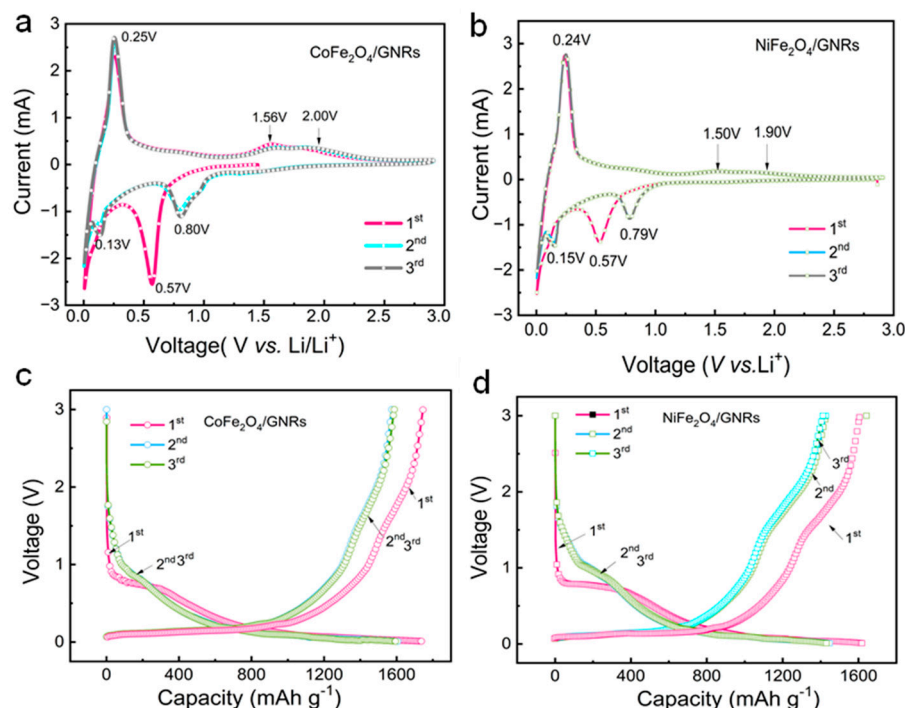


Figure 4. CV curves of (a) CoFe₂O₄/GNRs, (b) NiFe₂O₄/GNRs electrodes, (c) CoFe₂O₄/GNRs, and (d) NiFe₂O₄/GNRs electrodes at a current density of 0.1 A g^{−1} for the 1st, 2nd, and 3rd cycles in the voltage range between 3.00 and 0.01 V.

Figure 4c,d displays the charge-discharge process of MFe₂O₄/GNRs at a current density of 0.1 A g^{−1}. In agreement with the CV curves, the potential platform at ~0.79 V can be found during the first discharge (lithiation) process. CoFe₂O₄/GNRs and NiFe₂O₄/GNRs electrodes delivered initial discharge capacities of 1735 mAh g^{−1} and 1621 mAh g^{−1} and initial charge capacities of 1573 mAh g^{−1} and 1502 mAh g^{−1}, with cycle efficiency of 90% and 92%, respectively. The irreversible capacity losses of the two electrodes in the following cycles were probably associated with the formation of SEI and irreversible lithium loss. It was observed that the second and third cycles of the current curve almost overlapped with each other, proposing that the Li⁺ ion storage of the electrodes was reversible in the following cycles (Figure S5).

To evaluate the rate capability of MFe₂O₄/GNRs, the electrodes were cycled under various current densities from 0.2 to 10 A g^{−1}, and the results were described in Figure 5a and Table S1. With the increase in current density, the specific capacity of the composites decreases. Because of the slow transportation of Li⁺ ions and insufficient lithiation-delithiation process, a number of “dead” Li⁺ ions are generated, leading to a decrease in the capacity of the electrodes. However, when the current density exceeded 5 A g^{−1}, the capacity increased instead. This phenomenon was interpreted by the activation process to facilitate Li⁺ ion pathways between the electrolyte and the electrode under small current density cycling [42]. Meanwhile, the capacity of CoFe₂O₄, NiFe₂O₄, CoFe₂O₄/GNRs, and NiFe₂O₄/GNRs com-

posites can be measured to 937, 867, 1475, and 1235 mAh g⁻¹, respectively, when the current density returned to 0.2 A g⁻¹, indicating high reversible rate capability. Even at the higher current density of 5 A g⁻¹, the discharge capacities of CoFe₂O₄/GNRs and NiFe₂O₄/GNRs composite remain high at stable values of 1330 and 960 mAh g⁻¹, respectively. However, pure CoFe₂O₄ and NiFe₂O₄ cannot maintain capacity in such a high rate due to the lack of GNRs skeleton. In addition, we discovered that the CoFe₂O₄/GNRs electrode shows better rate performance than NiFe₂O₄/GNRs, CoFe₂O₄, and NiFe₂O₄ electrode. The reason might be associated with more stable states and more negative adsorption energy of CoFe₂O₄/GNRs, which could produce extra capacity through the pseudo-capacitive behavior. Moreover, the larger BET surface area and more metal oxides component of CoFe₂O₄/GNRs contribute to better performance in the rate test and the following tests.

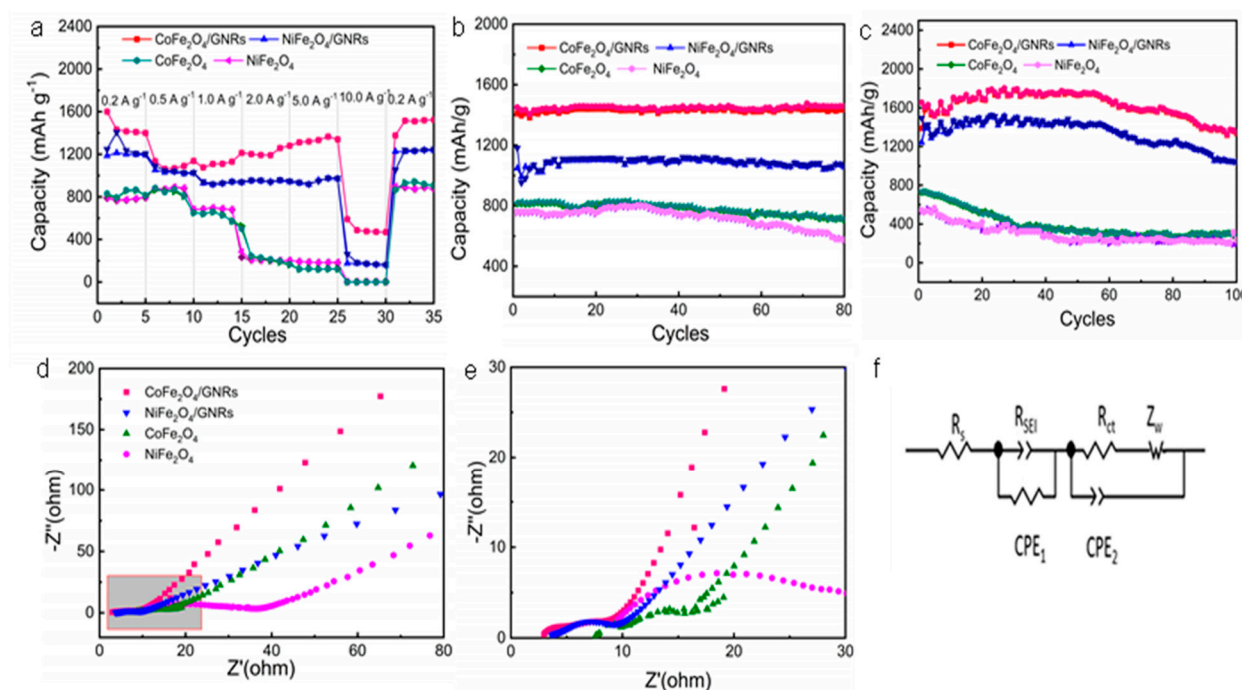


Figure 5. (a) Rate capability of the CoFe₂O₄, NiFe₂O₄, CoFe₂O₄/GNRs, and NiFe₂O₄/GNRs electrodes from 0.2 A g⁻¹ to 10 A g⁻¹. (b) Cycling performance of four electrodes at 0.1 A g⁻¹. (c) Cycling performance of four electrodes at 1.0 A g⁻¹. (d) Nyquist plots of four electrodes in the frequency ranging from 0.01 Hz to 10 kHz. (e) The enlarged part of (d). (f) Equivalent circuit model.

The cycling performance of CoFe₂O₄, NiFe₂O₄, CoFe₂O₄/GNRs, and NiFe₂O₄/GNRs electrodes at the current density of 0.1 A g⁻¹ is presented in Figure 5b. The CoFe₂O₄/GNRs electrode expresses the best cycle performance after 80 discharge/charge cycles with a reversible capacity of 1432 mAh g⁻¹. CoFe₂O₄ (715 mAh g⁻¹), NiFe₂O₄ (569 mAh g⁻¹), and NiFe₂O₄/GNRs (1085 mAh g⁻¹) electrodes with relatively smaller specific capabilities exhibited cycle stability similar to CoFe₂O₄/GNRs. When we increased the current density to 1 A g⁻¹, the results were shown in Figure 5c. After 100 cycles, the discharge capacity of CoFe₂O₄/GNRs and NiFe₂O₄/GNRs was 1720 mAh g⁻¹ and 1414 mAh g⁻¹, respectively, while CoFe₂O₄ and NiFe₂O₄ were 300 mAh g⁻¹ and 201 mAh g⁻¹, respectively. Compared to the previously reported MFe₂O₄ electrodes, the discharge capacity and cycle stability of the electrode materials were superior (Table S2). Furthermore, the capacities that increased gradually in the initial cycles could be the interfacial Li⁺ ion storage or the reversible polymer film produced by Co-, Ni-, and Fe-activated electrolyte degradation [32,42]. In the cycles, network GNRs can be used as the support of MFe₂O₄/GNRs, which can inhibit the volume changes in MFe₂O₄ during the charge-discharge process. In the meantime, the embedded MFe₂O₄ in the interlayers of GNRs would prevent the re-stacking and provide extra Li⁺ ion storage accommodation. Moreover, the transport channels in porous

GNRs can speed up the conduction of electrons/ions. Figure S6 showed the SEM images of $\text{MFe}_2\text{O}_4/\text{GNRs}$ electrodes after 100 cycles at 1 A g^{-1} , illustrating that the network remains intact in the process of cycles, which ensured excellent electrochemical performance. However, the CoFe_2O_4 and NiFe_2O_4 electrodes detached from the substrate and seriously agglomerated.

To obtain better insight into the mechanism of the electrode reactions in the unique $\text{MFe}_2\text{O}_4/\text{GNRs}$ architectures, we performed electrochemical impedance spectroscopy (EIS) for both electrodes, as shown in Figure 5d,e. R_{ct} , R_{SEI} , and R_s correspond to the semicircle in the high-frequency region of typical Nyquist plots; CPE relates to the constant phase element [15] on the basis of equivalent electrical circuit mode. The R_{ct} of the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ electrodes is $9.5\ \Omega$ and $16.8\ \Omega$, respectively, which is smaller than CoFe_2O_4 and NiFe_2O_4 electrodes, showing that GNRs can effectively reduce the resistance of the anode. In the low-frequency region, the sloping line refers to the Warburg impedance (Z_w); the slope of the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ electrode is higher than that of the $\text{NiFe}_2\text{O}_4/\text{GNRs}$, CoFe_2O_4 , and NiFe_2O_4 electrodes, which implies that the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ electrode has lower Li^+ ion diffusion resistance [31] (Table S3).

2.5. DFT Analysis

To further explain the effect of GNRs, we performed DFT calculations focused on the adsorption abilities towards Li^+ ions and charge distribution after intercalation of Li^+ ion [43,44]. CoFe_2O_4 and NiFe_2O_4 are semiconductors with band gaps of about 1.2 and 1.4 eV, respectively (Figure 6a–d). Since VASP is considered as a pseudopotential, the calculated value is relatively small. After the wrapping of GNRs, the hybrid orbitals appear near the Fermi level, leading to better electrical conductivity, which is consistent with the EIS results. According to Bader charge analysis, the number of transferred electrons for CoFe_2O_4 and NiFe_2O_4 is 0.23 and 0.26, respectively, while $\text{CoFe}_2\text{O}_4/\text{GNRs}$ transfer 0.41 e^- and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ transfer 0.33 e^- , indicating the more stable state of $\text{CoFe}_2\text{O}_4/\text{GNRs}$. Moreover, Li atoms adsorption models of MFe_2O_4 and $\text{MFe}_2\text{O}_4/\text{GNRs}$ were constructed to calculate the corresponding adsorption energy (ΔE_{ads}). As can be seen in Figure 6e, the ΔE_{ads} of lithium adsorption in the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ is remarkably higher than that of $\text{NiFe}_2\text{O}_4/\text{GNRs}$, CoFe_2O_4 , and NiFe_2O_4 , exhibiting that the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ can propel the lithium process. Accordingly, the theoretical analysis and experimental results are in a great consistence that the charge/discharge kinetics can be enhanced via GNRs assembling CoFe_2O_4 and NiFe_2O_4 to boost the electric conductivity and the advanced intrinsic Li^+ storage.

The excellent electrochemical performance of $\text{MFe}_2\text{O}_4/\text{GNRs}$ electrodes is probably due to the following reasons [17,45]: (1) as an elastic buffer layer, GNRs in the composites can not only avoid the volume expansion of CoFe_2O_4 and NiFe_2O_4 during lithiation and delithiation but also efficiently prevent the cracking or crumbling of anode materials [46,47]; (2) GNRs have premium electrical conductivity and are regarded as the electron transport path among CoFe_2O_4 and NiFe_2O_4 , reducing the inner resistance of Li^+ ion batteries; (3) the nano-sized active materials act as nanopacers to refrain the re-stacking of GNRs and therefore maintain their high active surface area, which is beneficial for enhancing the capacity of the composites.

2.6. Magnetic Performance Analysis

CoFe_2O_4 and NiFe_2O_4 nanoparticles are typical ferromagnetic nanomaterials. To clarify the effect of magnetism of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$, the magnetic properties were studied by vibrating sample magnetometer system (VSM) at room temperature, as shown in Figure 7. Each CoFe_2O_4 and NiFe_2O_4 exhibited superparamagnetic behavior with little remanence and coercivity, implying that there is no remaining magnetization when the applied magnetic field is removed [48]. However, the saturation magnetization (M_s) values of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ nanocomposites were 11.8 emu/g and 40.4 emu/g , respectively. The saturation magnetization intensity is lower than that of their

bulk material. The main reason for the low saturation magnetization could be the size effect of magnetic nanoparticles; the surface spin coupling of nanoparticles is weaker than that of bulk materials. The saturation magnetization of all MFe_2O_4 /GNRs composites is much higher than that of MFe_2O_4 and GNRs. It is noted that the saturation magnetization of $NiFe_2O_4$ nanoparticles in the $NiFe_2O_4$ /GNRs is improved 10 times as much as that on their own. The improved saturation magnetization of $NiFe_2O_4$ /GNRs is probably due to the increased electron conductivity by the aid of GNRs. In addition, we also calculated the magnetism enhancement after recombination of GNRs; the reason may be the influence of the built-in electromagnetic field on lithium storage (Table S4).

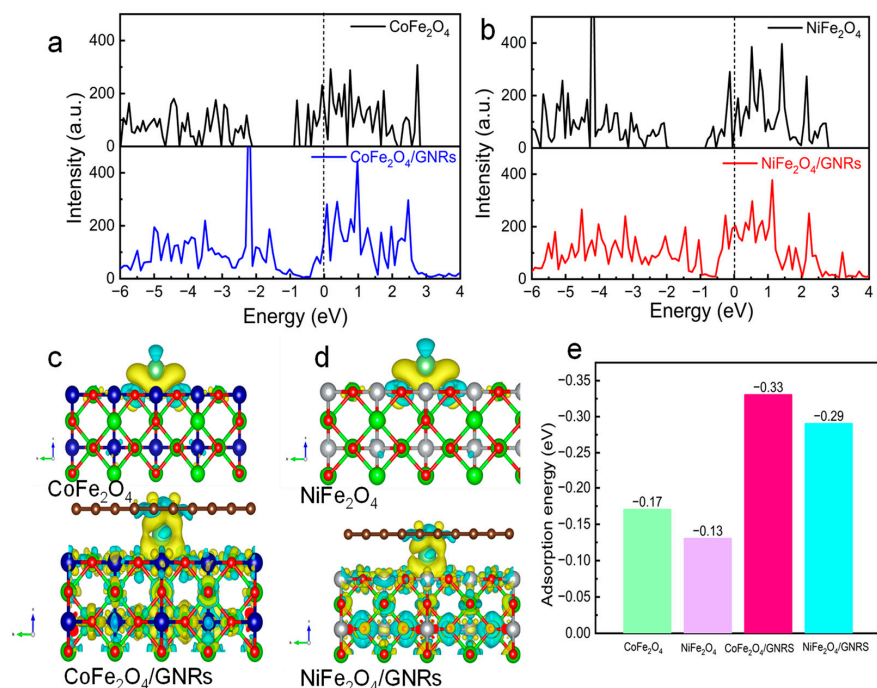


Figure 6. The calculated band gap of (a) $CoFe_2O_4$ and $CoFe_2O_4$ /GNRs. (b) $NiFe_2O_4$ and $NiFe_2O_4$ /GNRs. (c,d) Simulated adsorption configurations and (e) corresponding adsorption energy.

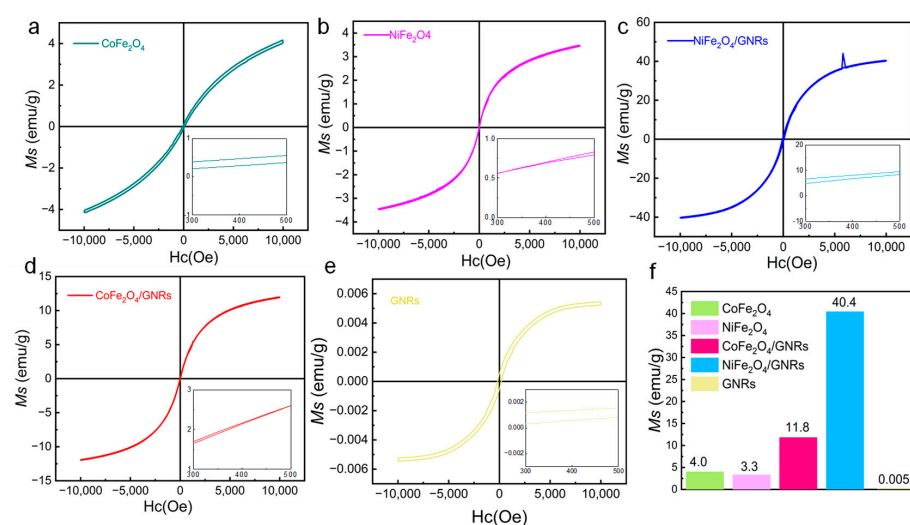


Figure 7. Hysteresis curves of (a) $CoFe_2O_4$, (b) $NiFe_2O_4$, (c) $CoFe_2O_4$ /GNRs, (d) $NiFe_2O_4$ /GNRs, and (e) GNRs (insets are the enlarged part of the samples); (f) saturation magnetization of as-prepared samples.

The $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ have maintained the dispersion and paramagnetism of magnetic nanoparticles, demonstrating their promising applications in magnetic devices.

3. Materials and Methods

3.1. Synthesis

The synthesis processes of GNRs and $\text{MFe}_2\text{O}_4/\text{GNRs}$ were shown in supporting information [30].

3.2. Electrochemical Measurement

Coin cells (CR2430) were used to characterize the electrochemical properties of the sample. The working electrode was prepared by dropping the suspension of composites into a carbon nanofiber paper (CFP, $d \sim 16$ mm, $S \sim 2$ cm²) without any binder, then dried in vacuum. Cyclic voltammetry (CV) was carried out on an electrochemical workstation (Solartron Metrology 1260 + 1287, Bognor Regis, UK) with the scanning rate of 0.1 mV s^{−1} (0.00 – 3.00 V vs. Li/Li^+). Arbin BT (2000, College Station, TX, USA) was used to measure charge–discharge properties of the samples. All the capacities showed in this work have deducted the contribution from the substrate.

3.3. Sample Characterization

X-ray diffraction (XRD, DMAX-2500PC, Tokyo, Japan) was used to record the phase structure of the samples using $\text{Cu}/\text{K}\alpha$ radiation ($k\alpha = 0.15406$ nm). Raman spectra were obtained by a Renishaw Invia Raman Microprobe (Wotton-under-Edge, UK) (100 – 3000 cm^{−1}) using argon ion laser (514 nm). The morphologies of the as-obtained samples were studied using a field emission scanning electronic microscope (FE-SEM, Hitachi S-4800, Tokyo, Japan) and transmission electron microscope (TEM, Zeiss LIBRA 220 FEG, Oberkochen, Germany). X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Thermo Fisher Scientific, Waltham, MA, USA) was carried out to study the surface chemical state of the composites. Brunner–Emmet–Teller (BET) measurements were operated on a Micromeritics ASAP 2020, USA. The content of the sample was analyzed by the thermogravimetric analysis (TGA Perkin ELMER TGA7, Waltham, MA, USA). The measurement of magnetic hysteresis loop was performed using a vibrating sample magnetometer (VSM Lake Shore 7400, Lake Shore Cryotronics, Westerville, OH, USA). All calculations were completed within the framework of the density functional theory (DFT) within the projector's enhanced plane wave method.

4. Conclusions

A general magnetically induced self-assembled graphene nanoribbons method is proposed to prepare network $\text{MFe}_2\text{O}_4/\text{GNRs}$. The formation of these $\text{MFe}_2\text{O}_4/\text{GNRs}$ is due to the surface in situ growth of MFe_2O_4 on GNRs and aggregation at the joints of GNRs, which is mainly driven by their own magnetic interactions. The unique framework of $\text{MFe}_2\text{O}_4/\text{GNRs}$ can effectively prevent the shedding of MFe_2O_4 , inhibiting the re-stacking of GNRs layers and shortening the Li^+ ion transmission path. Consequently, $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$ composites exhibited large reversible capacities (1432 and 1058 mAh g^{−1} at 0.1 A g^{−1}, 1720 mAh g^{−1} and 1414 mAh g^{−1} at 1 A g^{−1}, respectively), excellent cyclic performance, and good rate capabilities. The reason that the $\text{CoFe}_2\text{O}_4/\text{GNRs}$ electrode shows better Li-ion battery performance than $\text{NiFe}_2\text{O}_4/\text{GNRs}$ might be associated with the more stable states and more negative adsorption energy of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ according to DFT results, which could produce extra capacity through pseudo-capacitive behavior. Additionally, combining GNRs with MFe_2O_4 helps to improve the magnetism of the MFe_2O_4 , making $\text{MFe}_2\text{O}_4/\text{GNRs}$ suitable for magnetic applications, such as magnetically mediated targeted drug delivery and magnetic resonance imaging.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28104069/s1>, 1 Synthesis of $\text{MFe}_2\text{O}_4/\text{GNRs}$. 2 Computational Method. Figure S1: (a,b) SEM images of as-prepared CoFe_2O_4 ; (b–d) SEM images of as-prepared NiFe_2O_4 ; Figure S2 (a–e) TEM images of as-prepared $\text{CoFe}_2\text{O}_4/\text{GNRs}$; Figure S3: The nitrogen adsorption/desorption isotherms and porosity distribution of (a,b) $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (c,d) $\text{NiFe}_2\text{O}_4/\text{GNRs}$; Figure S4: TGA curves of $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and $\text{NiFe}_2\text{O}_4/\text{GNRs}$; Figure S5 (a) $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (b) $\text{NiFe}_2\text{O}_4/\text{GNRs}$ electrodes at a current density of 0.1 A g^{-1} for the 1st, 2nd, 3rd, 30th, and 50th cycles in the voltage range between 3.00 and 0.01 V; Figure S6 SEM images of (a,b) $\text{CoFe}_2\text{O}_4/\text{GNRs}$ and (c,d) $\text{NiFe}_2\text{O}_4/\text{GNRs}$ electrode; Figure S7 SEM images of (a) $\text{CoFe}_2\text{O}_4/\text{GNRs}$, (b) $\text{NiFe}_2\text{O}_4/\text{GNRs}$, (c) $\text{CoFe}_2\text{O}_4/\text{GNRs}$, (d,e) CoFe_2O_4 , and (f) NiFe_2O_4 electrode after 100 cycles (1 A g^{-1}). Table S1: Rate capability of the samples; Table S2: Comparison of the electrochemical performance of some Li-ion battery anodes; Table S3: The EIS simulation parameters of as-prepared samples; Table S4: Saturation magnetization of as-prepared samples. References [49–51] are cited in the supplementary materials.

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