

Article

Facile Synthesis Sandwich-Structured Ge/NrGO Nanocomposite as Anodes for High-Performance Lithium-Ion Batteries

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Abstract: This work aimed to design a facile preparation of sandwich-liked Ge nanoparticles/nitrogen-doped reduced graphene oxide (Ge/NrGO) nanocomposites used as anode in lithium-ion batteries through the chemical solution route. The advanced electron microscopy, STEM-HAADF and STEM-EDS mapping, evidenced that the individual Ge particles with sizes ranging from 5 to 20 nm were distributed and wrapped as sandwiches within the multi-layered NrGO sheets, which were mainly composed of the pyridinic-N form (4.8%wt.). The battery performances of the 20Ge/NrGO nanocomposite anode exhibit a high reversible capacity (700 mAh g⁻¹) and retained its outstanding stability during long-term cycling. The internal resistance (28.0 Ω) was also decreased after cycling, according to EIS measurement. The sandwiched structure of Ge-based nanocomposite with the interconnected NrGO layers discussed in this article possessed the high-performance LIBs with great potential application in energy storage technologies.

Keywords: germanium; nitrogen-doped reduced graphene oxide; nanocomposite design; sandwiched structure; anode material; lithium-ion battery

1. Introduction

Exploration of renewable and environmentally friendly alternative energy sources has become an important goal to replace energy from fossil. To accommodate this requirement, electrochemical batteries, as ideal systems, need to be used to store energy. Lithium-ion batteries (LIBs) are the most essential energy storage and have attracted great attention in research and commercial applications. It has become energy storage for portable electronic devices for daily use, such as mobile phones, laptop computers, smartwatches, electronic tablets, and electric vehicles [1,2]. Currently, the LIBs are dependent on using a graphitic carbon anode that provides a low theoretical capacity and has safety concerns [3–5]. Hence, the emerging anode materials including silicon (Si), germanium (Ge), and tin (Sn), in particular, Ge-based materials with exceptionally high theoretical energy capacities have

recently attracted much attention as prospective lithium-ion battery anodes. The theoretical specific capacity for $\text{Li}_{15}\text{Ge}_4$ (1384 mAh g^{-1}) [6] is much higher than commercial graphite (372 mAh g^{-1}). Moreover, germanium-based materials have many other apparent advantages, including high lithium-ion diffusivity ($6.51 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), high electronic conductivity (2.1 S m^{-1}), high energy/power density, high operating voltage, environmentally friendly, and low cost for practical applications [7,8]. These materials may indeed enhance Li insertion/extraction kinetics and cycle performance, making them a promising anode candidate to address the growing need for better energy and power densities in batteries. However, similar to other alloying anode materials, Ge also experiences massive lithium-induced volume expansion. Crystalline Ge will undergo a volume expansion up to 370%. The volume expansion will lead to the generation of deep cracks [9], consequently resulting in the formation of unstable solid-electrolyte interphase (SEI) layers and electrode pulverization [10]. Extensive research has been conducted to solve the aforementioned problems.

For the last decade, most of the research has widely investigated the electrochemical enhancement of anode materials. Several strategies have been proposed to alleviate the issues mentioned above. Especially, nanocomposites have been utilized in many applications including food, biomedical, electroanalysis, energy storage, wastewater treatment, automotive, etc. [11,12]. For anode materials, the nanocomposites design with electronic conductive substrates, such as graphene and other carbon materials, have become the most attractive approach. The flexibility of graphene acts as a buffer layer to reduce the extreme strains from the large volumetric expansion of Ge during lithiation and delithiation processes [13]. For instance, Ge on seamless graphene carbon nanotube (GCNT) hybrids were prepared by the chemical vapor deposition (CVD) method. This GCNT delivered a high specific capacity of 1315 mAh g^{-1} after 200 cycles at 0.5 A g^{-1} [14]. I. Sultana and co-workers also reported that nano Ge incorporated thin graphite nanoplatelets (GeNPs) synthesized through a magneto ball-mill under high pressure demonstrated promising electrochemical performance with a charge capacity of 822 mAh g^{-1} after 200 cycles at 0.1 C [15]. J-H. Koo et al. have prepared Ge/ GeO_2 -reduced graphene via a modified Hummer's method and microwave-assisted treatment. For the prolonged cycles, this electrode showed stable cyclability over 150 cycles with a discharge capacity of 1080 mAh g^{-1} at 100 mA g^{-1} . Nitrogen-doped reduced graphene oxide (NrGO) has also been widely investigated because of its high surface area benefits as an excellent supporter and because it obstructs volumetric change [16,17]. The lone electron pairs of nitrogen located on the disordered surface perform a delocalized conjugated system with a sp^2 -hybridization carbon framework, presenting an outstanding conductivity [18,19]. Moreover, the high nitrogen-doping level enhances the rated current capacity and reversible capability [20]. NrGO can function as a stabilizer to buffer volume expansion of Ge and it is expected to improve alloying anode performance, especially for Ge-based materials [21]. Besides, decreasing the dimension of Ge to nano-size is an effective route to resolve pulverization and capacity fading during charging and discharging [9]. Thus, whereas these Ge/NrGO nanocomposites outperformed pure Ge nanoparticles and bare graphene, they nevertheless displayed low Ge consumption and high irreversible capacity loss during the first cycle. Evidently, Ge nanoparticles that form randomized agglomerates damage the electrode during the volume expansion reaction induced by the lithium insertion-extraction processes. Thus, a more efficient method to synthesize Ge/NrGO nanocomposite materials is needed. Excellent cycling stability with high capacity of Ge/NrGO nanocomposite anodes are anticipated if a substantially dispersed distribution of Ge nanoparticles on NrGO sheets can indeed be achieved. Therefore, this research focuses on strategies for minimizing substantial volume changes in Ge structure during cycling and enhancing their electrochemical characteristics through the use of Ge nanoparticles composited uniformly on NrGO.

Thus far, many efforts have been made to synthesize Ge nanostructures, including thermal decomposition of organogermane [22], reduction of germanium halides [23], ther-

mal reduction with zintl salts [24], sol-gel process [25], and nonthermal plasma [26]. This work proposes an efficient single-step Ge synthesis in an aqueous solution at ambient temperature and pressure. It is a green chemical strategy for the synthesis of Ge nanoparticles that is high-yielding, simple, and low in raw material requirements [27,28]. Importantly, germanium oxide (GeO_2) was used as a Ge precursor instead of the other hazardous Ge forms.

Herein, the solution route method is commonly used for nanocomposite synthesis because of its low cost, safety, simplicity, high yield, and convenience [29,30]. This facile method has the potential to produce Ge/NrGO nanocomposites in a variety of compositions. The particle size, agglomeration behavior, morphology, and distribution of Ge on the NrGO sheets will be controlled by the condition of the composite ratio.

2. Materials and Methods

2.1. Preparation of Ge/NrGO Nanocomposites

Graphite powder (Sigma-Aldrich, $\leq 20\ \mu\text{m}$, technical grade, MO, USA) was ball milled for 20 h to decrease the size before preparing graphene oxide (GO) using the modified hummer's method. Following that, a 5 h thermal reduction at $800\ ^\circ\text{C}$ in a nitrogen atmosphere was also used to eliminate the oxide and functional groups on the surface, producing reduced graphene oxide (rGO). The rGO was then homogeneously mixed with melamine (Aldrich, 99.9% analytical standard, MO, USA), which served as a nitrogen source. To produce the NrGO, the combined powder was annealed at $800\ ^\circ\text{C}$ for 1 h in a nitrogen environment [31,32].

After that, GeNPs were prepared as followed [33]. The Ge precursors in this process were GeO_2 (Sigma-Aldrich, $\geq 99.99\%$ MO, USA). In addition, sodium borohydride (NaBH_4 , Sigma-Aldrich, $\geq 98\%$, MO, USA) was used as a reducing agent. Deionized (DI) water was applied as a solvent. Ge nanoparticles (GeNPs) were firstly prepared by facile chemical reduction. Firstly, GeO_2 was dissolved in a 5 vol.% NH_4OH solution (QR eC , 25%, AR grade, Selangor, Malaysia) to form the aqueous germanate-ion. Subsequently, to obtain the brown GeNPs suspensions, cold and fresh NaBH_4 solution was slowly added and continuously stirred for 12 h to obtain the GeNPs suspension.

In the nanocomposite preparation, Ge/NrGO was synthesized by the solution route method. The NrGO powder was dispersed in DI water, and the GeNP suspension was added. Then, the mixture was transferred to ultrasonication for 1 h to form a homogeneous mixture. Finally, the synthesized precipitations were collected by centrifugation and washed with DI water until neutral to remove the excess NH_4OH . All final products were dried overnight at 120°C in a nitrogen atmosphere to obtain Ge/NrGO nanocomposites. For comparison, the synthesized ratio of GeNPs to NrGO was varied to 10 and 20 wt.%. The nomenclature used for the final products was xGe/NrGO, where x was the weight percent of GeNPs.

2.2. Materials Characterization

An X-ray diffractometer (XRD, Rigaku Miniflex II desktop, Tokyo, Japan) characterized the phase compositions and crystallinity of the synthesized products. Raman spectroscopy (Raman, Jobin Yvon Horiba, model T64000, Palaiseau, France) was used to observe a structural fingerprint. The Barrett-Emmett-Teller specific surface areas of the modified carbon were investigated by the gas adsorption technique (BET, Quantachrome Instruments, model Autosorb-1C, FL, USA). X-ray Photoelectron Spectroscopy was used to determine the nitrogen content and chemical state (XPS, Kratos analytical-AXIS ultra DLD, Manchester, UK). The morphology and composition of the as-prepared products were investigated by field emission-scanning electron microscope (FE-SEM, JEOL JSM-7800F-Prime, Tokyo, Japan) and transmission electron microscope (TEM, JEOL JEM-2010, Tokyo, Japan) for obtaining selected area electron diffraction (SAED). The high-angle annular dark-field (HAADF) and energy dispersive spectroscopy (EDS) mapping images were taken by scanning transmission electron microscopy equipped with an EDS spectrometer (STEM-

HAADF and STEM-EDS, JEOL JEM-ARM200F, Tokyo, Japan). The thermal decomposition of the samples has been examined employing thermogravimetric analysis (TGA, Rigaku, Thermo plus EVO2, Tokyo, Japan) at a heating rate of 5 °C/min throughout the heat treatment up to 1000 °C.

2.3. Electrochemical Measurements

Electrochemical experiments were carried out using coin-type cells (CR2016). In the electrode preparation, active materials, conductive Super-P (conductive carbon black, NCM HERSBIT Chemical Co. Ltd., Beijing, China), styrene-butadiene rubber (SBR), and carboxymethylcellulose (CMC) binder (Sigma Aldrich, Oakville, ON, Canada) in aqueous solution were homogeneously mixed with a weight ratio of 80:5:5:10. The homogeneous slurry was then coated onto a copper foil using a doctor blade technique. In the coin-cell fabrication, the lithium chip was used as the counter electrode, whereas the Celgard 2400 is employed as the separator. The electrolyte used in this investigation was 1 M lithium hexafluorophosphate (LiPF_6) solution in ethylene carbonate/dimethyl carbonate (EC)/(DMC) (1:1 by vol.%). To measure the electrochemical performance, the fabricated coin-cells were performed on the battery test station (Espec, Osaka, Japan), and the electrochemical impedance spectroscopy (EIS) was also recorded on potentiostat/galvanostat equipment (VSP-300, BioLogic Science Instruments, Seyssinet-Pariset, France) in the frequency range of 100 kHz to 100 mHz.

3. Results and Discussion

3.1. Graphene-Based Material Characterization

Figure 1a depicts XRD patterns of graphite (GP), GO, rGO, and NrGO (a). The peak located at 26.3° (JCPDs no.41-1487) belonged to graphite's (002) plane and was comparable to the d-spacing of 0.348 nm. The introduction of a number of oxygen-containing groups on the edge of each layer increased the distance between the layers when the graphite was oxidized to produce the GO [34]. The GO pattern showed the highest peak at 10.6° , which matched the (001) plane of GO (JCPDs no.75-2078) [35,36]. The rGO and NrGO displayed broad peaks of the (002) plane after heat treatment, with a slight shift to lower angles compared to graphite patterns. The interlayer spacing of rGO (0.362 nm) contributed to the exfoliation of GP after the thermal reduction process. When compared to the rGO pattern, the pattern of NrGO appeared to have a slight peak shift to higher angles at 25.8° , corresponding to a slight decrease in interlayer spacing (0.346 nm). This implied that the oxygen functional groups and a few carbon sides of the rGO were substantially replaced by nitrogen atoms [37]. XRD analysis revealed that the structural characteristics of graphite differed significantly from graphene-based sheets, implying that graphene-based materials could well be successfully formed.

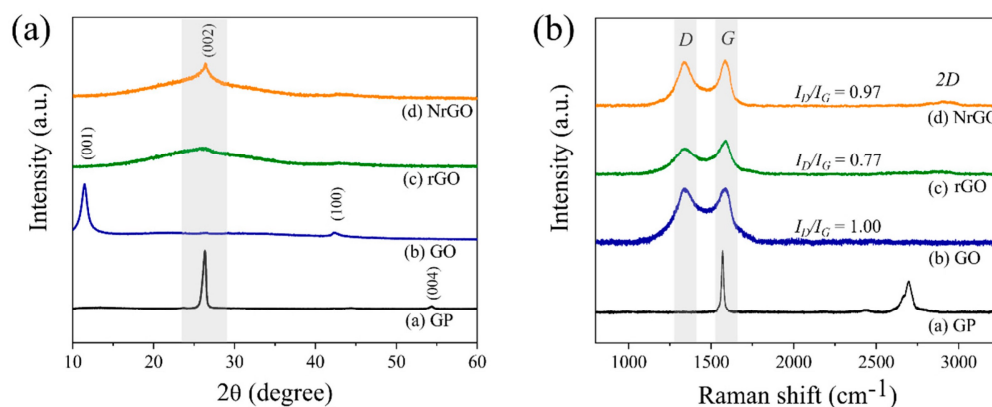


Figure 1. (a) XRD patterns and (b) Raman spectra of prepared modified graphene; GP, GO, rGO, and NrGO.

Raman spectra were used to determine the defects of the modified carbon and the findings are presented in Figure 1b. The Raman spectrum of GP revealed the characteristic G band at $\sim 1588\text{ cm}^{-1}$ and the 2D band at $\sim 2675\text{ cm}^{-1}$. In GO, rGO, and NrGO samples, the G band was detected at $\sim 1580\text{ cm}^{-1}$ and the D band was detected at $\sim 1333\text{ cm}^{-1}$. These D bands are implied as defects in the graphitic layer, i.e., in-plane substitution heteroatoms, vacancies, or grain boundaries/edges [38]. Significantly, the intensity ratio of the D and G band I_D/I_G of rGO was 0.77, which was lower than that of GO ($I_D/I_G = 1.00$) suggesting that the GO had a lower degree of disordered structures [34]. While rGO had a slight amount of the diminished in the size of the plane sp^2 domain and increased the edge of planes as well as the expansion of the disorder [39]. The I_D/I_G of the NrGO was 0.97, implying that the nitrogen-doping process had modified the graphene surface with a high degree of defect [40]. Additionally, the G and 2D bands of the NrGO spectrum had shifted significantly higher in frequency, which could be attributed to strain and the nitrogen-carbon heteroatom's electron-donating and graphene delocalizing capabilities. The broad 2D bands in the range of $2500\text{--}2800\text{ cm}^{-1}$ indicated that the rGO and NrGO had a low degree of multi-layer structures [41].

The morphology and elemental distribution of the rGO and NrGO were investigated using SEM techniques (Figure 2a,b), in which both materials appeared as multi-layered exfoliated graphene sheets and some small-isolated sheets. The NrGO preserved the two-dimensional thin structure of the rGO after the nitrogen-doped process. The EDS mapping images, which were taken from the high-kV SEM image in Figure 2c, show the elemental distribution of nitrogen (Figure 2d), carbon (Figure 2e), and oxygen (Figure 2f) in NrGO. The results could well be utilized to validate the nitrogen distribution on the 2D-sheet surface as well as to reveal the residual oxide functional group in the graphene structure, which correlates to the XPS results mentioned in the next section. =

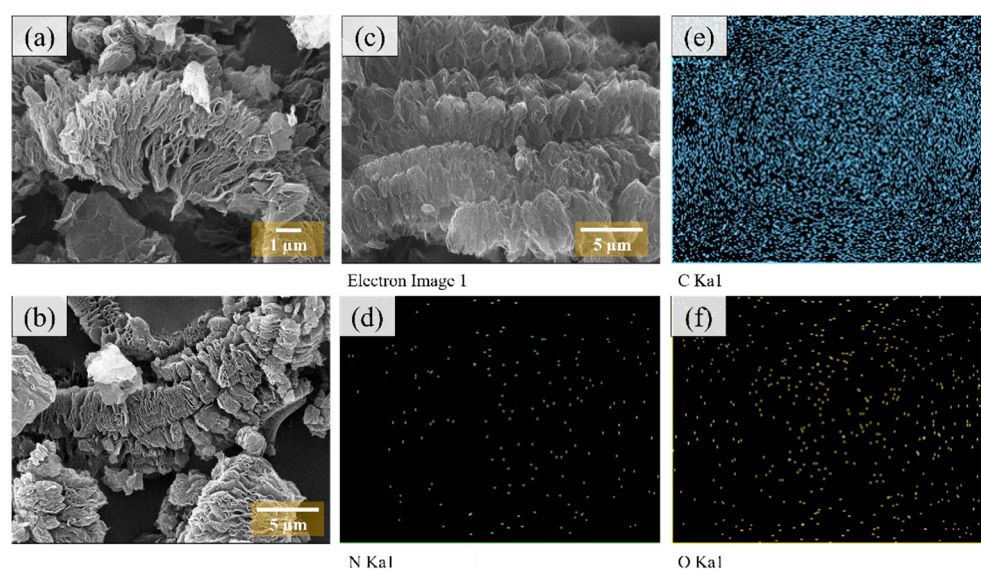


Figure 2. SEM images of (a) rGO and (b) NrGO, and (c) high-kinetic energy SEM image of NrGO equipped with element mapping, corresponding to (d) N, (e) C, and (f) O signals.

As the EDS observation implied that nitrogen was observed in the graphene structure, it was necessary to further confirm the result by the XPS technique. Figure 3 depicts the XPS spectra of NrGO powder. Figure 3a showed that the survey spectrum revealed the principal $C1s$, $N1s$, and $O1s$ core levels and the percentage of the elements. The occurrence of $N1s$ peak at 398.4 eV suggested that the nitrogen had been effectively doped on the rGO sheets with a mass percentage of 6.61%. The high-resolution $C1s$ and $N1s$ spectra were exhibited in Figure 3b,c, respectively. The $C1s$ spectra revealed the highest intensity peak at 284.9 eV , which corresponded to sp^2C - sp^2C hybridization. The formation of the C-N and C = N bonds, on the other side, indicated the existence of doped nitrogen. Furthermore,

the high-resolution N1s peak represented three components at 398.6 eV, 400.2 eV, and 401.9 eV, which correlated to the pyridinic-N, pyrrolic-N, and graphitic-N characteristics, respectively [42]. The pyridinic-N structure was discovered as the predominant structure in high-resolution N1s spectra. Not only would the lithium-ion be intensely crowded at the nitrogen location during the lithiation process, but also because its lone pair electron can thoroughly delocalize on a 2D-sheet. Therefore, nitrogen doping could assist to enhance the specific capacity and conductivity of anodes. It is reasonable to state that NrGO was effectively synthesized based on the characterization.

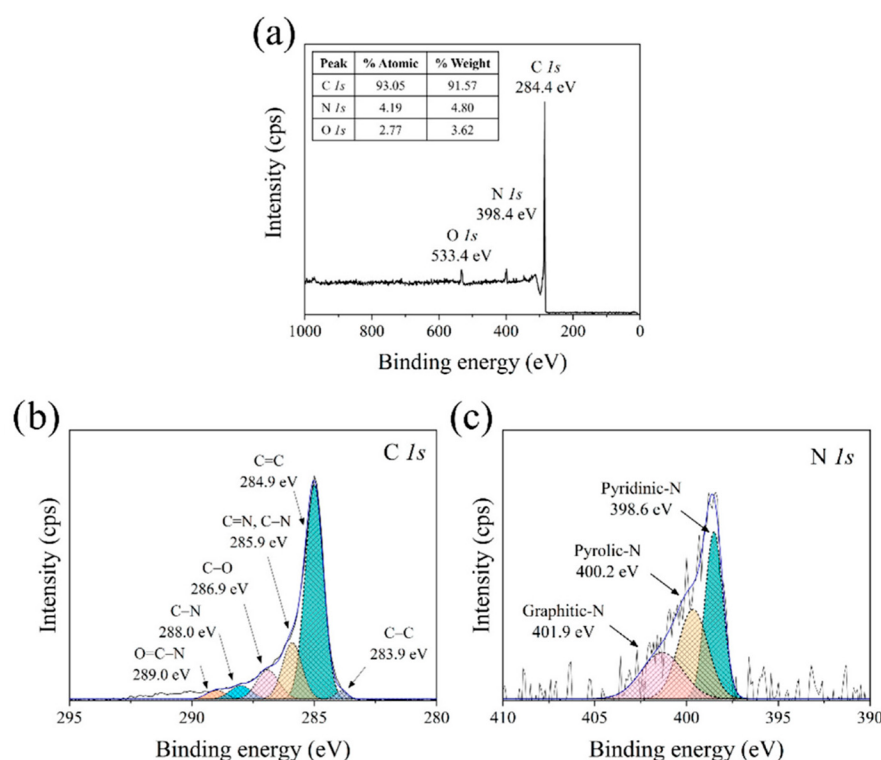


Figure 3. (a) XPS survey spectra equipped with element percent inset, and the high magnified XPS curve fitting of (b) C 1s and (c) N 1s spectra of prepared NrGO.

3.2. Ge/NrGO Nanocomposite Characterization

To investigate the crystallinity and phase formation of the preparative products, XRD was conducted, as shown in Figure 4a. The XRD pattern of the GeNPs exhibited two broadening peaks, which could be attributed to germanium's cubic structure (JCPDs no.04-0545), corresponding to the previous report [27]. These broadening peaks suggested that the GeNPs had a small crystallite size and low crystallinity. All other NrGO, 10Ge/NrGO, and 20Ge/NrGO peaks agreed with the standard carbon (JCPDs no.41-1487). However, there were no diffraction peaks of germanium observed clearly in composites samples due to its low contents or very tiny particle size.

FE-SEM images of all products, including GeNPs, NrGO, 10Ge/NrGO, and 20Ge/NrGO, are shown in Figure 5. The GeNPs (Figure 5a) particles were aggregated to form large agglomerations. This could be due to the reaction time having a substantial impact on the shape and size of the Ge product. In this experiment, a reaction duration of 12 h produced a micro-structured sample comprised of small and large particles. This could be because the worm-like structures were generated by connecting particles with diameters ranging from 50 to 100 nm. In particular, the interaction of hydrogenated Ge particles in a liquid medium is consistent with the Ostwald ripening mechanism, which is facilitated in the growth process. That is, because of different particle sizes, small particles prefer to connect particles to one another [43]. The topography of both 10Ge/NrGO (Figure 5b) and 20Ge/NrGO (Figure 5b) exhibits GeNPs clusters uniformly dispersed on graphene

sheets as well as some clusters that were enveloped by graphene sheets. The high surface area ($714.03 \text{ m}^2 \text{ g}^{-1}$) and physical defects on NrGO could operate as active sites for GeNPs deposition, resulting in a homogenous distribution of GeNPs on the surface of graphene sheets. The integrated graphene nanosheets are demonstrated to suppress the agglomeration of GeNPs in composites.

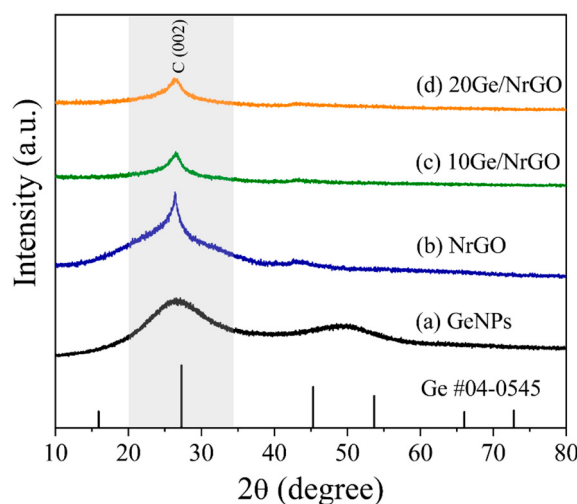


Figure 4. (a) XRD patterns of prepared products with Ge database reference inset; (a) GeNPs, (b) NrGO, (c) 10Ge/NrGO, and (d) 20Ge/NrGO.

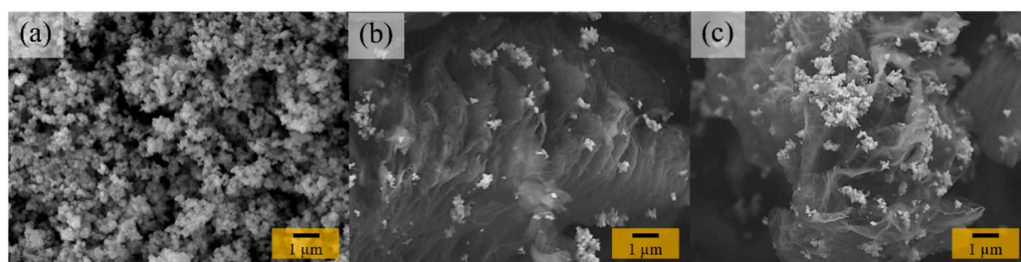


Figure 5. FE-SEM images of preparative materials; (a) GeNPs, (b) 10Ge/NrGO, and (c) 20Ge/NrGO.

TEM images with SAED patterns of NrGO and Ge/NrGO nanocomposites were provided in Figure 6. The TEM image of NrGO in Figure 6a displays a sheet-like morphology with micro wrinkles. Significantly, all prepared nanocomposites showed comparable microstructural characteristics, which consisted of GeNPs dispersed well over NrGO sheets, as can be observed in Figure 6b,c. However, some agglomeration of nanoparticles on the NrGO was observed for 10Ge/NrGO and 20Ge/NrGO products, as was observed in SEM images. The cluster size of GeNPs in the 20Ge/NrGO composition appeared to be larger than that of the 10Ge/NrGO composition. This could be owing to the presence of a high proportion of germanium intermediate phase in the hydrogen reduction process. In the high magnification TEM image displayed in Figure 6d, it is possible to identify not only some agglomeration induced by a high proportion of germanium but also individual GeNPs on NrGO sheets, which were clearly unseen in the low-magnification views (Figure 6b,c). In addition, the individual Ge particle sizes were in the range 5–20 nm. It was noticed that the good dispersion of Ge particles was observed on the NrGO sheet because NrGO obstructed the agglomerated matrix of nanoparticles, resulting in an increased dispersion ability of nanoparticles. Overall, the TEM investigation concluded that both the separated nanostructure and cluster morphology of GeNPs were presented in the prepared composites. Moreover, the SAED patterns in Figure 6b,c matched very well with the patterns of Ge, confirming the existence of Ge, which was unobservable in the XRD patterns.

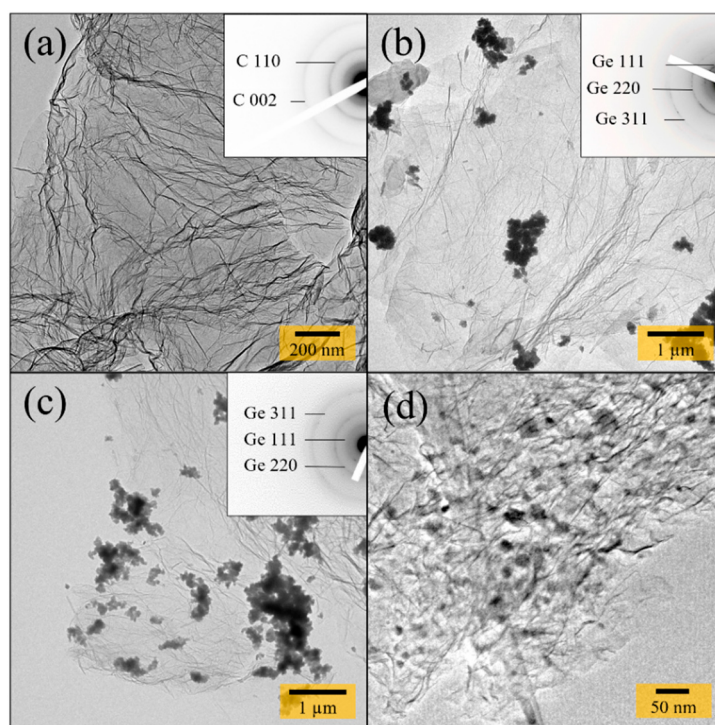


Figure 6. TEM images of as-prepared (a) NrGO, (b) 10Ge/NrGO, (c) 20Ge/NrGO products, and (d) high magnification TEM image of 20Ge/NrGO nanocomposite.

The HAADF-STEM image of C, N, Ge, and O in the 20Ge/NrGO nanocomposite in Figure 7a demonstrated that the GeNPs were uniformly well dispersed on NrGO sheets and clearly observed a sandwich-like composite structure. STEM-EDS mapping images in Figure 7b–e revealed C and N signals from the NrGO sheet, Ge from GeNPs, and N and Ge elements were obviously dispersed consistently across the entire NrGO nanosheet surface. These EDS data can confirm the existence of Ge in the nanocomposite products and corresponded to SAED results. Whereas the O signals were collected from the partial oxidation of highly reactive nanometer GeNPs to GeO_2 and the incomplete reduction of graphene oxide by the thermal reduction process.

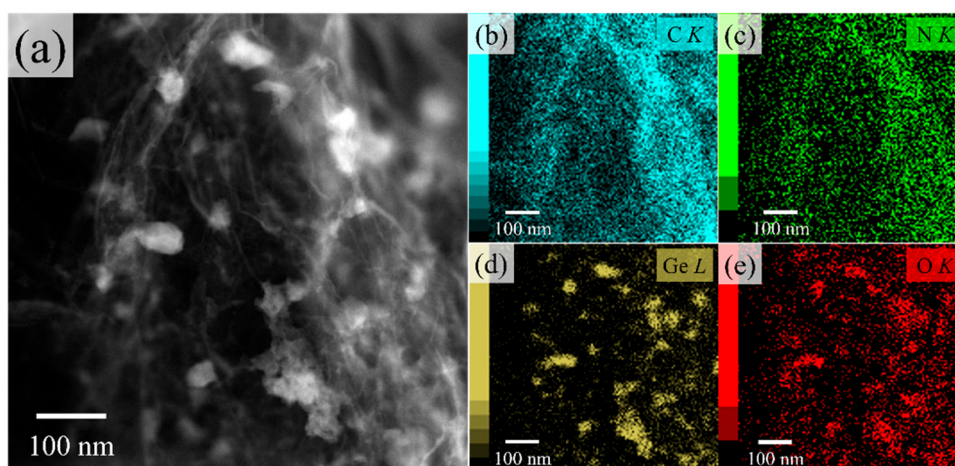


Figure 7. (a) HAADF-STEM image and EDS mapping images of element distribution corresponded to (b) C, (c) N, (d) Ge, and (e) O signals.

The weight ratio of the GeNPs and NrGO presented in the nanocomposite products was successfully determined utilizing thermogravimetric analysis (TGA), as shown in

Figure 8. The prepared products were heated to temperatures ranging between RT–1000 °C in an ambient atmosphere at a heating rate of 10 °C min^{−1}. The TGA curves of prepared products, as observed in all products, obviously demonstrate two stages of weight loss procedures. In the initial stage of TGA curves, the weight loss below 150 °C was attributed to the evaporation of absorbed moisture contained on the surface of the NrGO sheet. Following that, the gradual weight loss over temperatures ranging from 150 °C to 300 °C indicated that the residual oxygen functions in NrGO had been decomposed. The samples lost some weight at temperatures ranging from 300 to 500 °C, which was attributed to the elimination of more permanent nitrogen-doped units in NrGO [31]. The substantial weight loss recorded over 500 °C appears to be particularly related to pyrolysis and carbonization of the carbon backbone chain, resulting in the emission of CO₂. The GeNPs in nanocomposite products, on the other hand, could well be completely oxidized to generate GeO₂ throughout the ambient air at almost the same temperature range of carbonization [44,45]. The TGA curves showed that the NrGO sample was completely decomposed, whereas the weight loss of Ge/NrGO nanocomposite products remained relatively stable beyond 750 °C. This implies that the residual product of Ge/NrGO nanocomposite after high-temperature analysis was GeO₂, correlating to its higher thermal durability. The quantity of GeO₂ in the 10Ge/NrGO and 20Ge/NrGO was calculated to be 14.98 and 21.38 wt%, respectively. Therefore, the GeNPs content in the 10Ge/NrGO and 20Ge/NrGO were calculated to be 10.73 and 15.40 wt%, while the NrGO contents were 89.27 and 84.60%, respectively. The summarized TGA data and its corresponding calculated theoretical specific capacity are reported in Table 1.

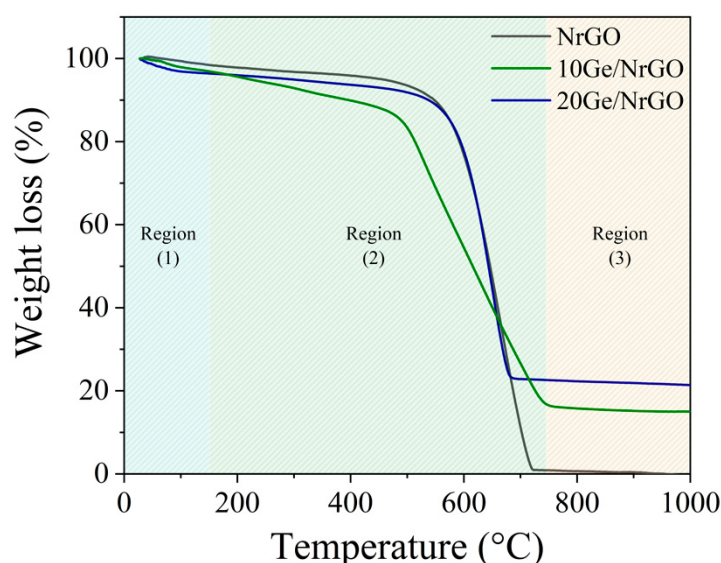


Figure 8. The TGA analysis curves of as-synthesized products.

Table 1. The results of TGA data analysis for content determination and theoretical specific capacity calculation.

TGA Data Analysis Results	As-Synthesized Products		
	NrGO	10Ge/NrGO	20Ge/NrGO
Region (1), RT–150 °C (wt% loss)	1.56	3.09	3.61
Region (2), 150–750 °C (wt% loss)	97.57	73.83	73.83
Region (3), 750–1000 °C (wt% loss)	0.87	1.52	1.18
Solid weight after 1000 °C, GeO ₂ (wt%)	0.00	14.98	21.38
GeNPs (wt%)	0.00	10.73	15.40
NrGO (wt%)	100.00	89.27	84.60
Theoretical specific capacity (mAh g ^{−1})	744.00	812.70	842.57

3.3. Electrochemical Performances

To know the effectiveness and performance of the prepared anode materials in LIB devices, three prepared nanocomposites, i.e., NrGO, 10Ge/NrGO, and 20Ge/NrGO, were used as the working electrodes in lithium-ion half coin cells and their electrochemical properties in terms of charge-discharge profiles, cycle stability, and EIS were investigated as shown in Figure 9.

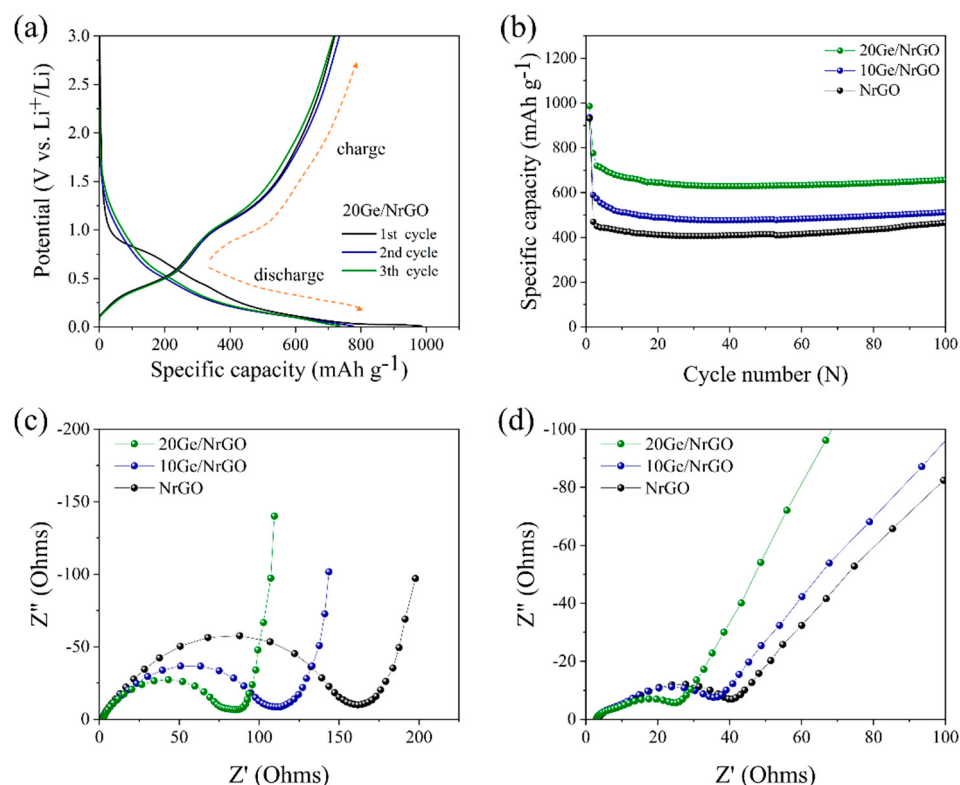
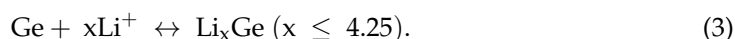
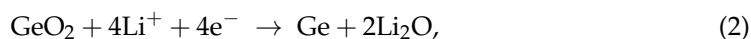
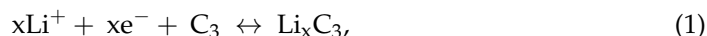


Figure 9. Electrochemical measurements; (a) Galvanostatic charge-discharge profiles of 20Ge/NrGO electrode for initial three cycles between 0.01 and 3.00 V vs. Li/Li^+ under the current density of 100 mA g^{-1} , (b) Cycle performances at a current density of 100 mA g^{-1} . Nyquist plots of prepared electrodes (c) before cycling and (d) 100th cycle over the frequency range from 100 kHz to 0.01 Hz.

Figure 9a shows the galvanostatic charge-discharge phenomena curves of 20Ge/NrGO nanocomposite anodes, which were carried out for three cycles at a constant current density of 100 mA g^{-1} and at a potential range between 0.01 and 3.00V (vs Li/Li^+). The initial discharge/charge capacity of $986/776 \text{ mAh g}^{-1}$ was obtained, which means the initial discharge was higher than the theoretical specific capacity ($842.57 \text{ mAh g}^{-1}$). The high initial releasing capacity can originate from the formation of the SEI layer [46,47] and the irreversible Li_2O formation from GeO_2 . Another aspect would be that NrGO had many more active binding sites than bare graphene, which could bind with more Li ions and raise the capacity to be more than that of bare graphene (744 mAh g^{-1}) [48]. Interestingly, it is able to determine the related small charging potential plateaus below 0.5 V. These reveal a minor polarization effect of NrGO, equivalent to the Li-ion intercalation in the graphene layers during the charge-discharge process [49,50]. The basic reaction mechanism of lithium-ion intercalation in the graphene electrode can be expressed in Equation (1) [51]. Furthermore, an initial conversion process, as demonstrated by Equation (2), describes the irreversible lithium mechanism of GeO_2 . From the second cycle onward, the formation of the Li_xGe alloy can be attributed to the apparent plateaus of the discharge curve located at 0.31 and 0.48 V [46,52]. The plateaus located at 0.41, 0.53, and 0.92 V upon charge profiles are attributed to the dealloying reaction of Li_xGe [53]. Equation (3) depicts the mechanism of the Li-Ge alloying processes. It is conceivable that a charge transfer will occur in the

Ge/NrGO nanocomposite electrode, potentially by Li-ion intercalation and alloying [54]. After the first cycle, all charge-discharge profiles of the composite electrode remain stable, suggesting the reversibility of the electrochemical reactions of the Ge/NrGO electrode and indicating GeNPs were well distributed encapsulated in the NrGO matrix [55].



Herein, Figure 9b presents the cycling performance of NrGO, 10Ge/NrGO, and 20Ge/NrGO between 0.01 and 3.00 V at a current density of 100 mAh g^{-1} for 100 cycles. The cycle stability results throughout all prepared electrodes demonstrated excellent stability for the long-term cycle. Notably, 20Ge/NrGO achieved better discharge capacity and cycle performance than 10Ge/NrGO because of the higher Ge content in 20Ge/NrGO, as confirmed in TGA results. Because of the irreversible reaction of Li_2O , the Ge/NrGO electrode resulted in poor stability, where the capacity progressively drops during the initial cycles. However, in the following cycles, reversible capacity was observed to slightly drop and then gradually rise for all tested composite electrodes because of the GeNPs cluster pulverization and NrGO buffering effects. The repeated discharge-charge cycles induced a volume change in GeNPs during the initial discharge-charge cycles. Because of the frequent volume changes, these particle clusters were subjected to a significant degree of mechanical stress. As a result of this pulverization, the particle clusters were degraded to individual nanoparticles. This enhanced not only the active surface for the lithiation process but also the progressive capacity increase in the long-term period. The electrical connection of GeNPs with the NrGO, as framework current collector, significantly rises when pulverized particles encourage contact with one of those certain and with the NrGO sheet. However, when the breakdown of the Ge particle cluster within the sandwiched structure occurred, it induced greater electrical conductivity across all-composite electrodes. Therefore, the Ge/NrGO nanocomposite has a stable structure and can better tolerate volume change during repeated lithium insertion and extraction, resulting in great cycling performance. Especially, the 20Ge/NrGO exhibits the highest capacity retention of over 90% with a relatively large reversible capacity of 700 mAh g^{-1} at the 100th cycle. For this reason, it is one of the most promising materials to solve the volume expansion problem that could cause electrode cracking in LIBs. Surprisingly, following a long-term cycle test of the NrGO electrode, the specific capacity clearly climbed gradually to be close to 10Ge/NrGO electrode's capacity. After the fifth cycle, the NrGO specific capacity performs stably and then increases from $414.17 \text{ mAh g}^{-1}$ at the 50th cycle to $465.46 \text{ mAh g}^{-1}$ at the 100th cycle. This suggests that the capacity increase in NrGO electrodes was driven by the exfoliation of multi-layered NrGO as well as the change in thickness of graphene [56]. These were induced by the Li-ion insertion and extraction processes during cycling to break up the multilayered structure. These results indicate that the exfoliated layer of NrGO can not only provide more active sites but also efficiently store the Li-ions, resulting in a significant increase in capacity during long-term cycling.

To further investigate the structural and interfacial behavior of prepared nanocomposite electrodes, electrical impedance spectroscopy (EIS) was carried out before and after 100 cycles at a current density of 100 mAh g^{-1} and over a frequency range of 100 kHz to 0.1 Hz at room temperature. Figure 9c,d show the Nyquist plots of the NrGO, 10Ge/NrGO, and 20Ge/NrGO electrodes before and after cycling, respectively. The semicircle at high-to-medium frequency corresponds to the charge-transfer resistance (R_{ct}) and double-layer capacitance through the electrode-electrolyte interface, whereas the inclined line at low-frequency corresponds to the Warburg diffusion impedance (Z_w) and also corresponds to the diffusion resistance of lithium-ions through solid-state electrodes as described in the literature [57,58]. Noticeably, the smaller semicircle at a high-to-medium frequency of prepared electrodes corresponded to the decreasing of the interfacial impedance, which

came from the higher conductive Ge content [59]. Considering the interfacial impedance of the pre-cycle electrode, as shown in Figure 9c, it was found that the R_{ct} of the 20Ge/NrGO ($\sim 75.0 \Omega$) shows the smallest resistance corresponding to the increment of lithium-ion diffusion, whereas the R_{ct} of the 10Ge/NrGO is around $\sim 110 \Omega$. It means the Ge composited materials have better effects in reducing interfacial impedance than the bare NrGO ($\sim 162.0 \Omega$). This is attributed to the high electronic conductivity of Ge and the higher ionic conductivity of NrGO compared with Ge [60,61]. According to the surface defects of NrGO, which thoroughly consist of doped nitrogen, especially pyridinic-nitrogen atoms, could enhance the high capacity of graphene by the faster Li-ion diffusion possesses and enhanced electronic conductivity [62,63]. Figure 9d represents the Nyquist plots of the electrodes after 100 cycles. When compared to the pre-cycle electrode, all cycled-electrodes exhibited a lower interfacial impedance, which might be due to Ge cluster fragmentation in the sandwiched NrGO layers via volumetric expansion during the alloying-dealloying process. This characteristic could enhance the electrical contraction, promoting a reduced internal resistance and facilitation of Li-ion transport in the composited electrode. However, the 20Ge/NrGO electrode still exhibited the smallest charge transfer resistance of $\sim 28.0 \Omega$ after 100 cycles, whereas 10Ge/NrGO and NrGO exhibited relatively slight increments of $\sim 42.0 \Omega$ and $\sim 49.0 \Omega$, respectively. These results suggest that the combination of GeNPs and NrGO improves electric conductivity and decreases overall cell resistance, resulting in the high performance of 20Ge/NrGO nanocomposite electrodes.

The 20Ge/NrGO nanocomposite with a high surface area NrGO sheet and the abundant GeNPs function well together to enhance lithiation/de-lithiation kinetics during battery cycling and exhibits considerably enhanced capacity with excellent cycle stability. Impressively, the lithium storage performance of as synthesized 20Ge/NrGO is superior than that of most previous studies. The electrochemical performance comparison of the present work with reported Ge-based materials were represented in Table 2.

Table 2. The electrochemical performance comparison of the present work with reported Ge-based materials.

Samples	Current Density (mA g ⁻¹)	Cycle Number	Specific Capacity (mAh g ⁻¹)	Ref.
Ge@C	50	50	490	[64]
	100	10	520	
Ge@CNF@C Ge@C@CNF	50	50	553	[65]
		50	200	
Ge GeNPs/GR	200	15	116	[66]
		15	532	
Ge/C Ge/graphene	640	100	44.5	[67]
		160	644	
Ge/NC (RPF) Ge/C (RF)	200	200	337	[68]
		200	278	
NrGO	100	100	466	This work
10Ge/NrGO			520	
20Ge/NrGO			700	

According to the results, the Ge nanoparticles in Ge/NrGO in this study were low in crystallinity. There is substantial discussion over the relevance of crystallinity to the electrochemical performance of Ge-based electrodes. The crystalline and amorphous nature of anode materials has been shown to have an effect on the electrochemical performance of Ge-based electrodes. Crystallized Ge possesses different stoichiometry, density, porosity, stress, defect density, and resistivity than amorphous Ge. Despite the fact that well-crystallized materials are expected to exhibit higher cyclability, the majority of research on Ge-based anode materials has focused on poorly crystallized and amorphous Ge materials.

Because of their amorphous structure, they provide the short structural coherence length that circumvents the electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation-delithiation process [69]. Rahmat Agung Susantyoko et al. have concluded and reported on the research results among many evaluations of the literature that are consistent with the majority of amorphous and crystalline Ge-based anodes [70]. The significant proportion of amorphous Ge-based anodes has a higher specific capacity than most crystalline Ge-based anodes. However, when the emphasis was on operating at high current densities above 1000 mA g^{-1} , there have only been a few reports employing amorphous Ge-based materials. This could be because amorphous Ge-based materials have a higher electrical resistance across grain boundaries when there are substantial amorphous areas [71]. A slightly increased capacity over charge-discharge cycles suggests that a crystalline Ge-based anode could be appropriate for the fast-charge stage. As a result, a Ge-based anode with both a nanostructure and a balance between amorphous and crystallized-Ge, which were observed in this Ge/NrGO nanocomposite, would be an effective solution to achieve a high-performance Ge-based anode material in LIBs.

In considerations of electrochemical performance, they revealed that Ge/NrGO has good electronic conductivity because the NrGO matrix can afford sufficient electron transport for active materials. According to these studies, the unique sandwich-like structure of Ge/NrGO, as illustrated schematically in Figure 10, can offer substantial void space to accommodate the volume change of Ge without cracking throughout lithiation and delithiation processes. Importantly, the outer NrGO layer creates a continuous, mechanically strong, and flexible framework for accelerated electron and lithium-ion transport, ensuring the electrode's high structural stability and good electrochemical performance. Additionally, during cycling, the outer NrGO nanosheets can increase electrical conductivity and create a stable SEI layer, corresponding to the reduction of internal resistance after long-term cycling. Because of the higher proportion of GeNPs sandwiched in the NrGO layer, the 20Ge/NrGO composite electrode has the best stability. This sandwiched structure can accommodate the volume change problem, affecting the structural damage of the electrode, and providing excellent stability.

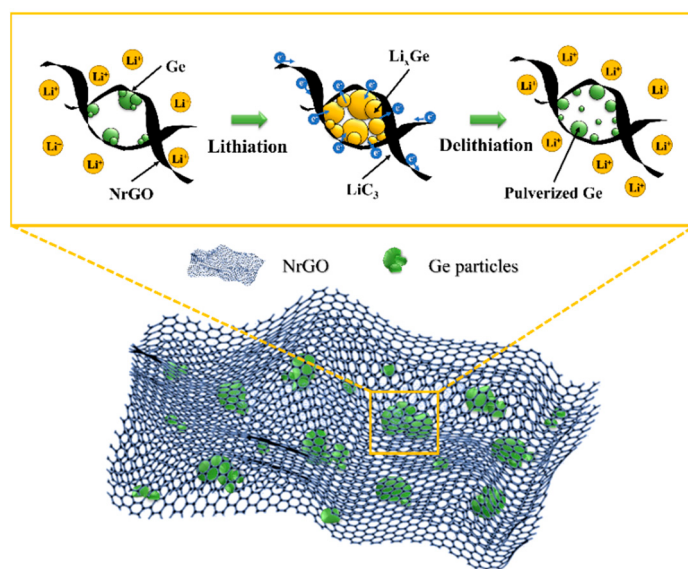


Figure 10. Schematic illustration of Ge/NrGO transformation between an expanded state and a contracted state during lithiation and delithiation processes.

4. Conclusions

In summary, the Ge/NrGO nanocomposites were successfully synthesized using a solution route method. As a result, the GeNPs were decorated on the surface of the wrinkled NrGO structure and wrapped as sandwiches within the multi-layered NrGO. The

best electrochemical characteristics were obtained from the 20Ge/NrGO nanocomposite. When utilized with a current density of 100 mAh g^{−1}, this electrode delivered a capacity of 700 mAh g^{−1} after 100 cycles, with a superior capacity retention of ≥90%. The cycle capability and EIS revealed that the fabricated electrodes maintained excellent stability and performed with lower internal resistance during long-term cycling. Therefore, these Ge/NrGO nanocomposites have the possibility to exhibit high energy density, whereas the NrGO can be an innovative stabilizer to tackle the volume change problem of the alloying materials. These Ge/NrGO nanocomposites have the potential to be efficient anode materials, offering a promising anode candidate to satisfy the rising need for batteries with better energy and power densities.

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