



Nanostructure and Electrochemical Performance of SiGe/Nitrogen-doped Graphene Nanocomposite for Use as Anode Materials for Lithium-ion Batteries

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ABSTRACT

Electrochemical batteries are ideal systems to meet the energy storage demand. Lithium-ion batteries (LIBs) are the most essential energy storage and have attracted a plentiful attentiveness in many research and commercial applications. Most researchers have widely investigated on the enhancement of anode materials because of the safety risk issues. Therefore, this research aims to develop the electrochemical performances of nanocomposite anode materials, especially, silicon-germanium/nitrogen-doped graphene (SiGe/NrGO). This nanocomposite was prepared via facile solution route method. Phase analysis of the preparative products showed the composite patterns. The electron microscope images revealed that the Si and Ge nanoparticles were uniformly distributed on NrGO surface. The Si-Ge/NrGO composition delivered the initial capacity of ~650 mAh g⁻¹ and also provided good stability and conductivity after 100 cycles. The experimental results suggested that the NrGO can act as a stabilizer to buffer volume expansion. Consequently, these nanocomposites have the potential to exhibit high capacity and can be substituted for commercial graphite. They could be used as an anode material for the next generation of LIBs.

INTRODUCTION

Lithium-ion batteries (LIBs) are the innovative technology among electrochemical energy storage devices with regards to being the most attractive type of rechargeable batteries for the future. It has become the energy storages for portable electronic devices which respond to use in daily life, such as mobile phone, laptop computer, smartwatch, electronic tablet, and electric vehicle [1,2]. Currently, The LIBs are dependent on the use of graphitic carbon anode that provides low theoretical capacity and safety concerns [3,4]. Hence, the emerging anode materials include silicon (Si), germanium (Ge), and tin (Sn) are the most attractive materials in the present. These elements have high theoretical capacity and energy density which are attractive in several fields. Nonetheless, the elements using bulk electrodes have high volume expansion. It leads to electrode cracking during the cycle. Therefore, this problem needs to be solved in order to extend the LIBs' life cycle [5].

Nitrogen-doped graphene (NrGO) has been widely investigated by recent research because its high surface area benefits as an excellent supporter and obstruct of the volumetric change. Besides, the character of the NrGO is promising anode material for high-power LIBs since the lone electron pairs of nitrogen, located on the disordered surface. The doped nitrogen performs a delocalized conjugated system with an sp²-hybridization carbon framework, presenting a great conductivity

[6,7]. Moreover, the high nitrogen-doping level enhances the rate capacity and reversible capability. Therefore, NrGO is expected to improve anode performance [8,9].

Especially, the alternative anode materials, the group IV elements, including silicon (Si) and germanium (Ge) have been developed to replace the commercial graphite because of their high theoretical capacity of 4200 mAh g⁻¹ (Si) and 1600 mAh g⁻¹, which are more than 10 times of graphite [10]. The great characteristic of LIBs includes; a high energy/power density, good cycling stability, high operating voltage, environmentally friendly, and low cost for practical applications [11]. However, the challenge of practical application as anode materials of these metals is, they have large structural and volumetric change (more than 400%) during the charge and discharge process of LIBs. These faults result in the cracking of the electrode surface and losing of electrical contact between the active materials and current collector, leading to poor reversibility and rapid capacity fading.

To counter the volume expansion, the most effective approach is to disperse nano-sized Si and Sn particles into the carbon matrix. Also, the increasing of lithiation process (alloying and intercalation). It could be due to the large surface originated in the nanostructure of active materials [12]. In many current reports, several types of carbon allotropes including amorphous carbon, mesoporous carbon, graphite, carbon

nanotube, and graphene have been studied to use as the anodes and supporter in Si and Ge based composite [13,14]. Interestingly, the flexibility of graphene acts as a buffer material to reduce the extreme strains from the large volumetric expansion of Si and Ge during lithiation and delithiation processes [15,16]. Moreover, the Ge ductile nature in nanostructure facilitates the volume expansion and also has been employed for lithium insertion, increasing the charge transfer across the electrolyte/active material interface [17].

The solution method is commonly used in composited synthesis because of its low cost, safety, simplicity, high yield, and convenience. For instance, the solution method allows adding other chemicals into the reaction system, in the term of convenience [18,19]. The condition of the composite ratio will shade light on the particle size, agglomeration behavior, morphology, and distribution on the NrGO sheet. This research proposes the preparation of Ge nanocomposites with modified carbon in the form of NrGO by using the solution dispersion method [10,20]. This facile method has the potential to obtain the SiGe/NrGO nanocomposite materials which have a competitive advantage in LIBs industry. Besides, this research focused on the distribution of the as-prepared nanocomposite, which can also indicate the electrochemical properties of this nanocomposite.

METHODOLOGY

NrGO preparation

Graphite powder (Aldrich, $\leq 20 \mu\text{m}$) was milled by zirconia ball to reduce the size and applied the modified hummers method to prepare graphene oxide (GO). After that, the thermal reduction at under the nitrogen atmosphere was employed to eliminate the oxide on the surface to obtain reduced graphene oxide (rGO). The rGO powder was then homogeneously mixed with melamine (Aldrich, $\geq 99.9\%$). The mixed powder was annealed under a nitrogen atmosphere to obtain the NrGO. The NrGO preparation process and characterization had already been reported in our previous work [16,21].

SiGe/NrGO nanocomposite synthesis

SiGe/NrGO nanocomposite was synthesized by the solution dispersion method. The ratio of Si:Ge:NrGO was shown in Table 1. Si nanopowder (Aldrich, $\leq 100 \text{ nm}$) and GeO_2 (Aldrich, $\geq 99.99\%$) were used as precursors. Sodium borohydride (NaBH_4) (Aldrich, $\geq 98\%$) was used as a reducing agent. Firstly, Ge nanoparticles (GeNPs) were prepared via chemical reduction. GeO_2 was dissolved in NH_4OH solution under constant stirring to receive the aqueous germanate ion. Then, cold and fresh NaBH_4 was added dropwise and stirred continuously. Afterward, the GeNPs were collected and washed using DI water. Secondly, GeNPs were dispersed in Ethylene Glycol which was previously bubbled by N_2 . After that, Si nanopowder, and NrGO were added into the GeNPs dispersed solution. The mixed solution was homogeneously dispersed by ultra-sonication. Then, the precipitations were collected by centrifugation and washed with ethanol. Finally, the as-prepared powder product was dried at under an inert atmosphere to obtain SiGe/NrGO nanocomposite.

Material characterization

The phase compositions of the synthesized products were characterized by X-ray diffractometer (XRD, Rigaku Miniflex II

desktop). The morphology of the as-prepared products were investigated by scanning electron microscope (SEM, JEOL JSM- 7800F-Prime) and transmission electron microscope (TEM, JEOL JEM-2010).

Electrochemical measurements

Electrochemical experiments were carried out using coin-type cells (CR2032). The electrodes were prepared by mixing the active materials, carbon black (Sup-P), and styrene-butadiene rubber and carboxymethylcellulose (SBR/CMC) binder until the homogeneous slurry was obtained. The electrode composition was represented in Table 2. The as-prepared slurry was then coated on Cu collector by the doctor blade technique. The lithium chip was used as the counter electrode. The electrolyte used in this investigation was lithium hexafluorophosphate (LiPF_6) in ethylene carbonate/dimethyl carbonate 1:1 (V/V). To measure the electrochemical performance, the preparative electrodes were performed by the battery test station at a current density of 100 mA g^{-1} in the voltage range of 0.01–3.00 V.

RESULTS AND DISCUSSION

SiGe/NrGO characterization

To investigate the crystallinity and phase formation of the prepared SiGe/NrGO product, XRD technique was conducted as shown in Figure 1, in which the reference patterns were inserted inset. It is clearly

Table 2. the ratio of composition in SiGe/NrGO electrode.

Electrode	Composition (wt.%)		
	Active material	Sup-P	SBR/CMC
SiGe/NrGO	10	10	80

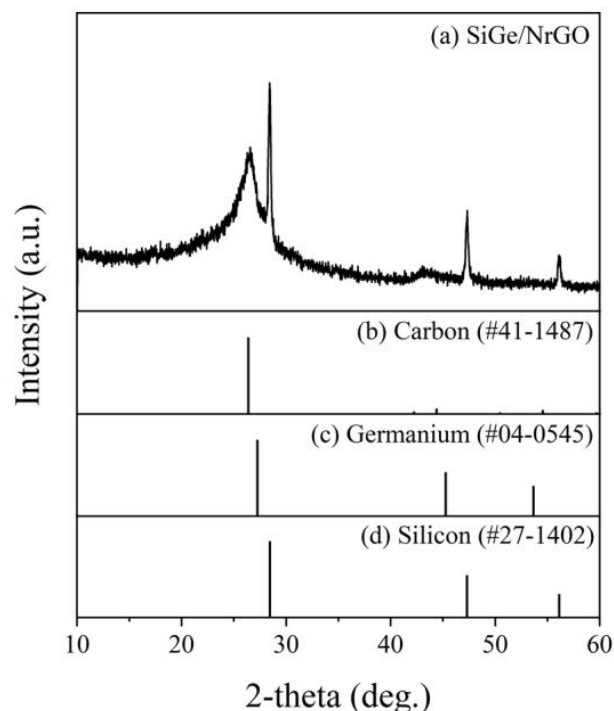


Figure 1. (a) XRD pattern of as-prepared SiGe/NrGO. The labels of diffraction patterns for references: (b) Carbon, (c) Germanium, and (d) Silicon are shown in set.

Table 1. The ratio composition of as-prepared SiGe/NrGO.

Sample	Composition (wt.%)		
	Si	Ge	NrGO
SiGe/NrGO	10	10	80

seen that three sharp peaks can be indexed as characteristic patterns of silicon. For the broadening peaks, these patterns agreed with the standard value for carbon (JCPDs no.41-1487) in the form of graphene. However, the pattern of the germanium was not observed in this composite pattern because its composition had low crystallinity. This could be due to the overlapping patterns of germanium and carbon patterns, which were observed in a similar 2-theta location. Corresponded to the previous report[22], Ge nanoparticles (GeNPs) exhibited generally two broadening peaks, indicating that the GeNPs had small crystallite size and low crystallinity. This also could be indexed as the cubic structure of germanium. Therefore, the germanium composition was distinguished and confirmed by TEM technique.

The morphology and topography of the synthesized 10SiGe/NrGO product were observed by SEM. The SEM images of 10SiGe/NrGO nanocomposite are shown in Figure 2, which represented the SEM in the magnification of 10000x (Figure 2(a)) and 20000x (Figure 2(b)). It can be seen that the structure of NrGO is the multilayer of thin wrinkled paper-like graphene. This was the result of deformation upon the exfoliation and restacking processes. Besides, there were some agglomerated particles of silicon and germanium. Considering all areas of product, the small particle has appeared good distribution of NrGO. Because of the limitation of SEM techniques, the SEM images of SiGe/NrGO cannot be indicated the location of each element (silicon and germanium) on NrGO sheets.

For the high magnification view of SiGe/NrGO nanocomposite, TEM technique is useful for observation. The TEM images with selected area electron diffraction (SAED) patterns of preparative nanocomposite was provided in Figure 3. The as-prepared samples showed some

clusters of silicon, (111) (220) (311) and germanium, (111) (220), decorated on the NrGO sheets. Interestingly, these germanium clusters were self-agglomeration of individual nanoparticles. This suggested that they were formed by hydrogenated germanium formation. Spectacularly, the cluster size of the germanium in this nanocomposite appears as a larger cluster than that of silicon. In the reduction reaction of germanium preparation, the high reaction of hydrogenate germanium was taken and could induce agglomeration behavior. This could be due to the structural connections between small germanium particles were continuously promoted, leading to the large agglomerations [23]. The distribution of silicon and germanium on the NrGO sheet was primarily due to the large surface area of the NrGO sheet. This resulted in the good dispersion ability of nanoparticles because it obstructed the agglomerated matrix of nanoparticles. To confirm the phase formation as investigated by XRD technique, the SAED patterns were taken from the prepared nanocomposites. The SAED patterns were very well matched with the patterns of silicon and germanium. It should be noted that the SAED patterns of germanium were found and indexed. Therefore, this result can confirm the existence of germanium in this sample. Although, it was no observed in the XRD results.

Electrochemical performances

To understand the battery performance of anode material, the synthesized SiGe/NrGO nanocomposites were also fabricated as the electrode in the coin cell and then measured the electrochemical properties as shown in Figure 4. To observe the specific capacity and cycling stability of SiGe/NrGO electrode, the electrochemical performances were performed in the term of galvanostatic charge-discharge profiles, and cycle stability. Both electrochemical performances were measured and represented in Figure 4(a) and Figure 4(b), respectively. The galvanostatic charge-discharge profiles were preliminarily investigated at a current density of 100 mA g^{-1} between 0.01 and 3.00 V to indicate the chemical reaction inside the prepared electrode during lithiation-delithiation processes.

To reveal the correlation of Li-ion insertion/extraction reaction mechanism into the anode structure, the charge-discharge curves demonstrated that the prepared electrode was initially observed potential plateaus below $\sim 0.5 \text{ V}$ (vs. Li^+/Li) corresponding to Li-ion intercalation

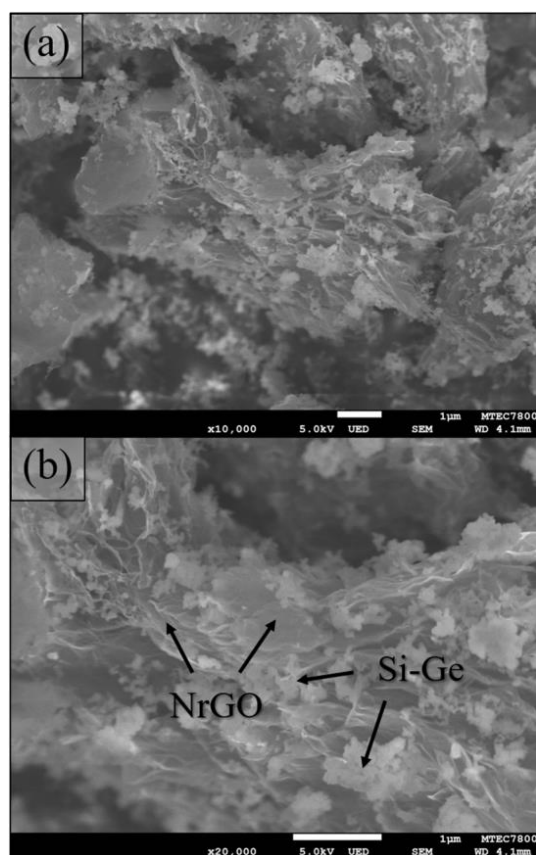


Figure 2. SEM images of SiGe/NrGO nanocomposite at the magnification of (a) 10000x and (b) 20000x.

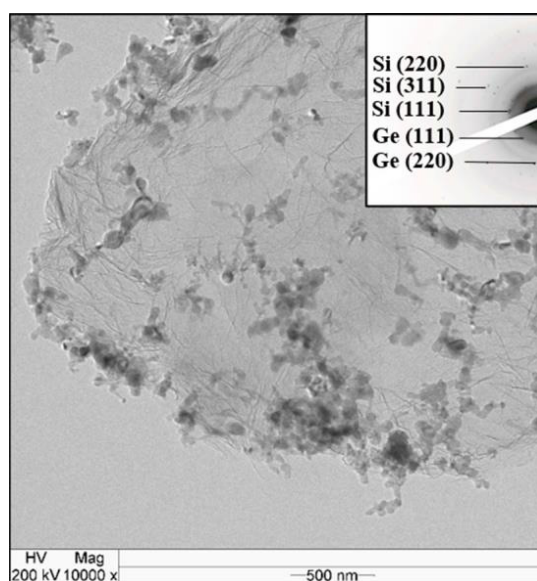


Figure 3. SEM images of all ceramics sintered at 1,400 °C.

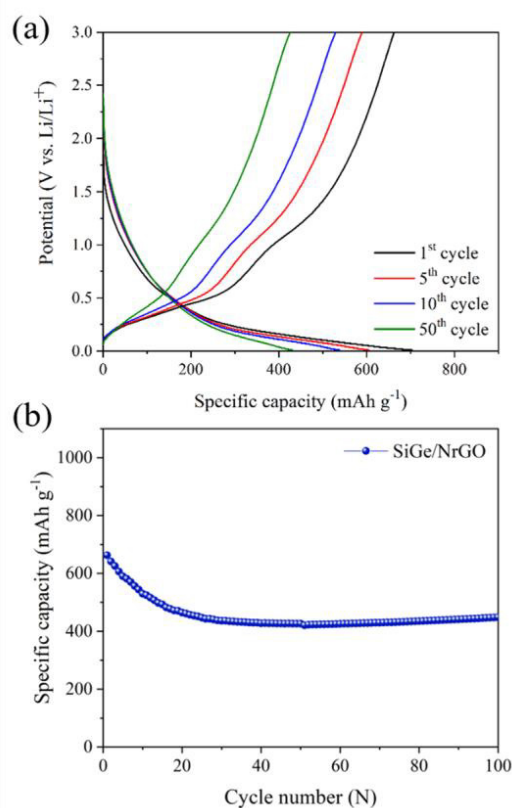
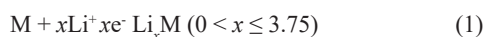


Figure 4. (a) Galvanostatic charge-discharge profiles and (b) Cycle performance of prepared SiGe/NrGO electrode for 100 cycles at a current density of 100 mA g^{-1} in the voltage cut of 0.01–3.00 V.

into the graphene. It could be due to Li^+ intercalation into the graphene layers [24]. Also, the threshold potentials were approximately displayed at 1.0 V. Once the threshold potential was reached, a charge transfer will take place, possibly by the Li-ion intercalation and alloying of silicon and germanium [25]. When Si and Ge used as anodes, they behave similarly Li-alloying mechanism to form a series of Li–M alloys ($\text{M} = \text{Si}$ or Ge) according to the following mechanism [26] as shown in equation (1):



It was worth noting that the capacity at the beginning of the discharge first cycle of this electrode (650 mAh g^{-1}) was higher than those in the subsequent cycles. The specific capacity of electrodes rapidly dropped from the first cycle to the second cycle. The initial capacity loss can be attributed to the formation of the solid electrolyte interface (SEI) film in the reversible reaction of the lithiation-delithiation process [27,28]. The SEI formation is caused by electrolyte decomposition and the irreversible lithium oxide (Li_2O) [29,30]. The Li_2O can be formed by the reaction of oxide on the surface of nanoparticles and NrGO sheet. After the 2nd cycle, the characteristic cycle performances of electrodes trended to gradually decrease. This phenomenon was possibly caused by the volume change of metals. In the lithiation process, the volume of Ge elements is generally expanded due to the alloying process. This leads to the expansion-contraction behavior via the charge-discharge processes, causing electrode cracking after several cycles. Hence, the small fading capacity was observed. To evaluate the

stability of the anode material for the LIBs, the product samples were also studied for the cycle-life and charge/discharge profiles as shown in the Figure 4(b). After long term cycling, The good stability and high specific capacity (500 mAh g^{-1}) were found in this electrode. The silicon and germanium promoted the high lithium alloying owing to capacity increasing. More importantly, the NrGO could also effectively overcome the electrode stability because its capacity retention remained over 70%. For this reason, it is one of the promising materials for supporting the volume expansion problem that could cause the electrode cracking in LIBs [31]. Especially, SiGe/NrGO can be a good candidate for anode electrode material in the LIBs.

CONCLUSION

In this work, the SiGe/NrGO nanocomposites were successfully synthesized via a chemical reduction method followed by a solution dispersion method. The NrGO has presented a wrinkled sheet structure decorated with the silicon and germanium nanoparticles to form the nanocomposite materials. Obviously, the SiGe/NrGO represented the good electrochemical properties. Its capacity at the current density of 100 mAh g^{-1} is approximately 650 mAh g^{-1} at the 1st cycle and 500 mAh g^{-1} after the 100th cycle. The cycle performance and charge/discharge profiles illustrated that the fabricated electrodes remain with good stability during 100 cycles. As consequence, this nanocomposite has the possibility to exhibit high capacity and the NrGO can be the innovative stabilizer to solve the volume change problem of the high-capacity materials for using as an anode material for the high-performance LIBs in the future.

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REFERENCES

- [1] Sun Y.-K., Myung S.-T., Park B.-C., Prakash J., Belharouak I. and Amine K., High-energy cathode material for long-life and safe lithium batteries. *Nat. Mater.*, 8: 2009, 320.
- [2] Liu W., Song M.S., Kong B. and Cui Y., Flexible and Stretchable Energy Storage: Recent Advances and Future Perspectives. *Adv. Mater.*, 2017, 29
- [3] Tobishima S.I. and Yamaki J.I., A consideration of lithium cell safety. *J. Power Sources*, 81: 1999, 882–886.
- [4] Bieker G., Winter M. and Bieker P., Electrochemical in situ investigations of SEI and dendrite formation on the lithium metal anode. *Phys. Chem. Chem. Phys.*, 17: 2015, 8670–8679.
- [5] Goriparti S., Miele E., De Angelis F., Di Fabrizio E., Zaccaria P.R. and Capiglia C., Review on recent progress of nanostructured anode materials for Li-ion batteries. *J. Power Sources*, 257: 2014, 421–443.

- [6] Wu Z.-S., Ren W., Xu L., Li F. and Cheng H.-M., Doped Graphene Sheets As Anode Materials with Superhigh Rate and Large Capacity for Lithium Ion Batteries. *ACS Nano*, 5: **2011**, 5463–5471.
- [7] Wang H., Zhang C., Liu Z., Wang L., Han P., Xu H., Zhang K., Dong S., Yao J. and Cui G., Nitrogen-doped graphene nanosheets with excellent lithium storage properties. *J. Mater. Chem.*, 21, 2011, 5430–5434.
- [8] Wang H., Maiyalagan T. and Wang X., Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications. *ACS Catal.*, 2, 2012, 781–794.
- [9] Xu H., Ma L. and Jin Z., Nitrogen-doped graphene: Synthesis, characterizations and energy applications. *J. Energy Chem.*, 27: 2018, 146–160.
- [10] Wu X.L., Guo Y.G. and Wan L.J., Rational design of anode materials based on group IVA elements (Si, Ge, and Sn) for lithium-ion batteries. *Chem. - An Asian J.*, 8: 2013, 1948–1958.
- [11] Tian H., Xin F., Wang X., He W. and Han W., High capacity group-IV elements (Si, Ge, Sn) based anodes for lithium-ion batteries. *J. Mater.*, 1, 2015, 153–169.
- [12] Nitta N., Wu F., Lee J.T. and Yushin G., Li-ion battery materials: Present and future. *Mater. Today*, 18, 2015, 252–264.
- [13] Qin J. and Cao M., Multidimensional Germanium-Based Materials as Anodes for Lithium-Ion Batteries. *Chem. - An Asian J.*, 11: 2016, 1169–1181.
- [14] Liang B., Liu Y. and Xu Y., Silicon-based materials as high capacity anodes for next generation lithium ion batteries. *J. Power Sources*, 267: 2014, 469–490.
- [15] Du Y., Zhu G., Wang K., Wang Y., Wang C. and Xia Y., Si/graphene composite prepared by magnesium thermal reduction of SiO_2 as anode material for lithium-ion batteries. *Electrochem. commun.*, 36: 2013, 107–110.
- [16] Autthawong T., Chayasombat B., Laokawee V., Jarulertwathana N., Masuda T. and Sarakonsri T., Nanostructural Study of Silicon-Cobalt/Nitrogen-Doped Reduced Graphene Oxide Composites by Electron Microscopy for Using as Anode Material in Lithium-Ion Batteries. *Solid State Phenom.*, 283: 2018, 37–45.
- [17] Hu Z., Zhang S., Zhang C. and Cui G., High performance germanium-based anode materials. *Coord. Chem. Rev.*, 326: 2016, 34–85.
- [18] Zhao Y., Zhang Z. and Dang H., Preparation of tin nanoparticles by solution dispersion. *Mater. Sci. Eng. A*, 359: 2003, 405–407.
- [19] Laokawee V., Autthawong T., Chayasombat B., Yu A. and Sarakonsri T., Electron Microscopy Investigation of Rice Husk-Derived Silicon-Tin/Nitrogen-Doped Graphene Composites Nanostructure. *Solid State Phenom.*, 302: 2020, 51–61.
- [20] Yodying W., Autthawong T., Chimupala Y. and Sarakonsri T., Nanostructural Characterization of Nitrogen-Doped Graphene/Titanium Dioxide (B)/Silicon Composite Prepared by Dispersion Method. *Solid State Phenom.*, 302: 2020, 27–35.
- [21] Namsar O., Autthawong T., Laokawee V., Boonprachai R., Haruta M., Kurata H., Yu A., Chairuangsi T. and Sarakonsri T., Improved electrochemical performance of anode materials for high energy density lithium-ion batteries through $\text{Sn}(\text{SnO}_2)\text{-SiO}_2/\text{graphene}$ -based nanocomposites prepared by a facile and low-cost approach. *Sustain. Energy Fuels*, 4, 2020, 4625–4636.
- [22] Wu J., Sun Y., Zou R., Song G., Chen Z., Wang C. and Hu, J. One-step aqueous solution synthesis of Ge nanocrystals from GeO_2 powders. *CrystEngComm.*, 13(11): 2011, 3674–3677.
- [23] Jing C., Zang X., Bai W., Chu J. and Liu A., Aqueous germanate ion solution promoted synthesis of worm-like crystallized Ge nanostructures under ambient conditions. *Nanotechnology*, 20, 2009, 20, 505607.
- [24] Tian L., Zhuang Q., Li J., Shi Y., Chen J., Lu F. and Sun S., Mechanism of intercalation and deintercalation of lithium ions in graphene nanosheets. *Chinese Sci. Bull.*, 56: 2011, 3204.
- [25] Battery L., Li X., Yang Z., Fu Y., Qiao L., Li D., Yue H. and He D., Germanium Anode with Excellent Lithium Storage Performance in a Germanium / Lithium Å Cobalt Oxide. *ACS Nano*, 9, 2015, 1858–1867.
- [26] Kennedy T., Brandon M. and Ryan K.M., Advances in the Application of Silicon and Germanium Nanowires for High-Performance Lithium-Ion Batteries. *Adv. Mater.*, 28: 2016, 5696–5704.
- [27] Lu M., Cheng H. and Yang Y., A comparison of solid electrolyte interphase (SEI) on the artificial graphite anode of the aged and cycled commercial lithium ion cells. *Electrochim. Acta*, 53: 2008, 3539–3546.
- [28] Jin Y., Li S., Kushima A., Zheng X., Sun Y., Xie J., Sun J., Xue W., Zhou G., Wu J., Shi F., Zhang R., Zhu Z., So K., Cui Y. and Li J., Self-healing SEI enables full-cell cycling of a silicon-majority anode with a coulombic efficiency exceeding 99.9%. *Energy Environ. Sci.*, 10, 2017, 580–592.
- [29] Yao Y., Zhang J., Xue L., Huang T. and Yu A., Carbon-coated SiO_2 nanoparticles as anode material for lithium ion batteries. *J. Power Sources*, 196: 2011, 10240–10243.
- [30] Feng J., Zhang Z., Ci L., Zhai W., Ai Q. and Xiong S., Chemical dealloying synthesis of porous silicon anchored by in situ generated graphene sheets as anode material for lithium-ion batteries. *J. Power Sources*, 287: 2015, 177–183.
- [31] Li X., Geng D., Zhang Y., Meng X., Li R. and Sun X., Superior cycle stability of nitrogen-doped graphene nanosheets as anodes for lithium ion batteries. *Electrochem. commun.*, 13, 2011, 822–825.