Chapter

Graphene-Based Heterogeneous Electrodes for Energy Storage

Ning Wang, Haixu Wang, Guang Yang, Rong Sun and Ching-Ping Wong

Abstract

As an intriguing two dimensional material, graphene has attracted intense interest due to its high stability, large carrier mobility as well as the excellent conductivity. The addition of graphene into the heterogeneous electrodes has been proved to be an effective method to improve the energy storage performance. In this chapter, the latest graphene based heterogeneous electrodes will be fully reviewed and discussed for energy storage. In detail, the assembly methods, including the ball-milling, hydrothermal, electrospinning, and microwave-assisted approaches will be illustrated. The characterization techniques, including the x-ray diffraction, scanning electron microscopy, transmission electron microscopy, electrochemical impedance spectroscopy, atomic force microscopy, and x-ray photoelectron spectroscopy will also be presented. The mechanisms behind the improved performance will also be fully reviewed and demonstrated. A conclusion and an outlook will be given in the end of this chapter to summarize the recent advances and the future opportunities, respectively.

Keywords: graphene, heterogeneous electrode, energy storage, hydrothermal, EIS, XPS

1. Introduction

In order to overcome the exhaustion of fossil fuels and to address the ever-growing demands for clean, sustainable and high efficient energy supply [1–3], the advanced energy storage techniques, including the supercapacitors, rechargeable batteries (Li-ion battery (LIB), Na-ion battery (SIB)), fuel cells as well as the solar cells have been widely investigated for the commercial use [4–6]. In the advanced energy storage devices, especially for the rechargeable batteries, the electrode materials should have the following features: high energy density, high working voltage, high power density, long cycling stability, high rate capacity as well as the environmental friendly [7–10].

In the rechargeable batteries, e.g. LIBs, the commercial anode material is graphite, whose theoretical-specific capacity is only 372 mA h/g [10], which cannot meet the requirement of the advanced energy storage techniques as described above. In order to overcome the low specific capacity of the graphite anode, amounts of substitute anode materials, e.g. Si (4200 mAh/g) [11], SnO (790 mAh/g) [12, 13], SnSb (825 mAh/g) [14, 15], Sn (993 mAh/g) [16], SbS_3 (947 mAh/g) [17], have been developed for high-capacity rechargeable batteries (**Figure 1**). However, the cycling stability became the most challenging issue for the high-capacity anode materials

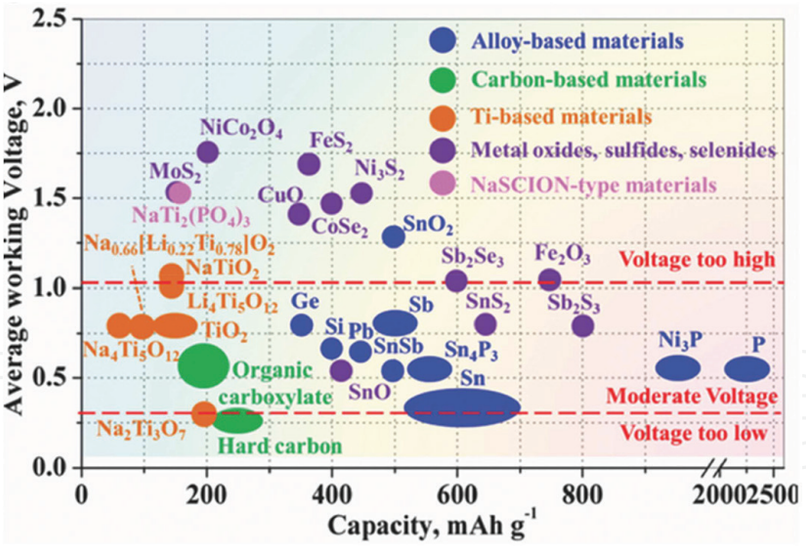

Figure 1.
Performance data of anode materials for SIB, reproduced with permission [19].

due to the volume expansion along with the charge–discharge process [18], e.g. 320% expansion for Si anode. Therefore, the gradient and/or the heterostructured anode materials could be the alternative approaches for the long cycling-stability, high specific capacity rechargeable batteries.

As a promising two dimensional (2D) material, graphene has attracted intense interest in the field of transparent electrode [20–24], field emission transistors (FET) [25–27], flexible devices [28–31], corrosion protection [32–34], catalysis [35–37] and energy storage [38–40], due to its large electrical conductivity, high thermal/chemical stability as well as the flexibility. With respect to the electrode materials, the graphene based heterogeneous electrodes were expected to occupy the excellent electrical conductivity, the long cycling stability and the high rate capability.

In this chapter, the assembly strategies for the graphene based heterogeneous electrodes, including the ball-milling, hydrothermal, electrospinning, microwave-assisted approaches, and the characterization methods will be fully reviewed. The mechanism behind the enhanced performance with graphene will be discussed, and an outlook on the challenges that should be addressed in the future will also be illustrated in the end.

2. Strategies for the assembly

2.1 Ball-milling

As a low-temperature alloying method, ball-milling is highly efficient in preparing the alloys and composites [41–46]. As for the graphene based heterogeneous electrode materials, ball milling exhibited the advantages in the size/layer reduction [47], interface-contact enhancement [48, 49] as well as the low cost and time saving [50].

As illustrated by Tie et al. [47], in the ball milling preparation of Si@SiO_x/graphene heterogeneous anode material (**Figure 2**), the graphene nanosheets (GNS) could be exfoliated from the expanded graphite (EG) due to the accumulated mechanical shearing force of the agate balls, and the particle size of silicon could be reduced to 50–100 nm, which contributed to the uniform dispersion of Si nanoparticles on the GNS, and finally gave rise to the Si@SiO_x/graphene composite. Owing to the reduced Si nanoparticle size, the SiO_x adhesion layer as well as the synergistic

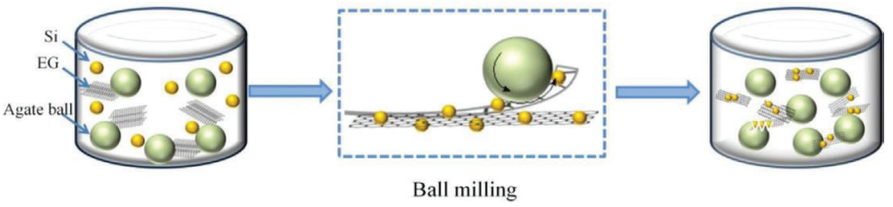

Figure 2.
Schematic illustration for ball milling synthesis of Si@SiO_x/grapheme anode material [47].

effect of GNS, the Si@SiO_x/graphene heterogeneous anode material exhibited the enhanced cycling stability, high reversible capacity, and rate capability.

Besides, the ball milling method could also be used to prepare other graphene based anode materials. Sun et al. [48] reported the ball milling synthesis of MoS_2/graphene anode materials used for high rate SIBs, where the bulky MoS_2 and graphite were firstly expanded by the intercalation of Na^+ and K^+ between the layers, and then the several-layer MoS_2 nanosheets and the graphene sheets could be exfoliated from the loose counterparts, which finally resulted in the formation of the restacked MoS_2/graphene heterostructures owing to the high surface energy and the interlayer Van der Waals attractions. Chen et al. [51] prepared the center-iodized graphene (CIG) and edge-iodized graphene (EIG) through the ball milling method, and the CIG were found to be an advanced anode material to boost the performance of the LIBs. In the other cases, Xia et al. [52] assembled the layer-by-layered SnS_2/graphene anode materials for the LIBs via ball-milling, where the volume change of SnS_2 could be buffered by the graphene, and the shuttle effect in the cycling could also be suppressed, both of which gave rise to an excellent rate capability and the negligible capacity fading over 180 cycles; Ma et al. [49] prepared the $MoTe_2$/FLG (few-layer graphene) anode material for the LIBs through the ball milling of $MoTe_2$ and graphite, which exhibited a high reversible capacity and an ultrahigh cycling stability.

2.2 Hydrothermal assembly

Hydrothermal method is an efficient and cost-effective approach for the assembly of metastable crystalline structures [53–57], especially for the heterogeneous structure with solid interface contact [58–61]. As for the graphene based heterogeneous electrode materials, the use of hydrothermal assembly could effectively reduce the cost, improve the crystallinity, and consolidate the interface contact, and therefore improve the energy storage performance.

Pang et al. [62] reported the hydrothermal assembly of VS_4@GS (graphene sheets) nanocomposites used as the anode material for the SIBs. As shown in **Figure 3**, the CTA^+ (hexadecyl trimethyl ammonium ion) cations were firstly absorbed on the negatively charged GO (graphene oxide) sheets, and then the TAA (thioacetamide) and VO_4^{3-} were attached onto the CTA^+ to form the TAA-VO_4^{3-}-CTA^+-GO complex, which was then transferred into the VS_4/GS composite under the hydrothermal conditions. As an anode material, this composite exhibited a large specific capacity, good rate capability, and remarkable long cycling stability, which should be ascribed to the porous structure together with the synergistic interaction between the highly conductive graphene network and the VS_4 nanoparticles.

In other cases, hydrothermal assembly could also be used to fabricate the polyaniline (PANI)/graphene [58, 63], TiO_2/graphene [64], Mn_3O_4/CeO_2/graphene [65], α-Fe_2O_3/graphene [59], and Mn_3O_4/graphene electrode materials [66]. As illustrated in the literatures, the hydrothermal assembly of graphene based heterogeneous electrode materials is usually starting with the graphite oxide (GO), the active electrode materials and/or surfactants, which should be

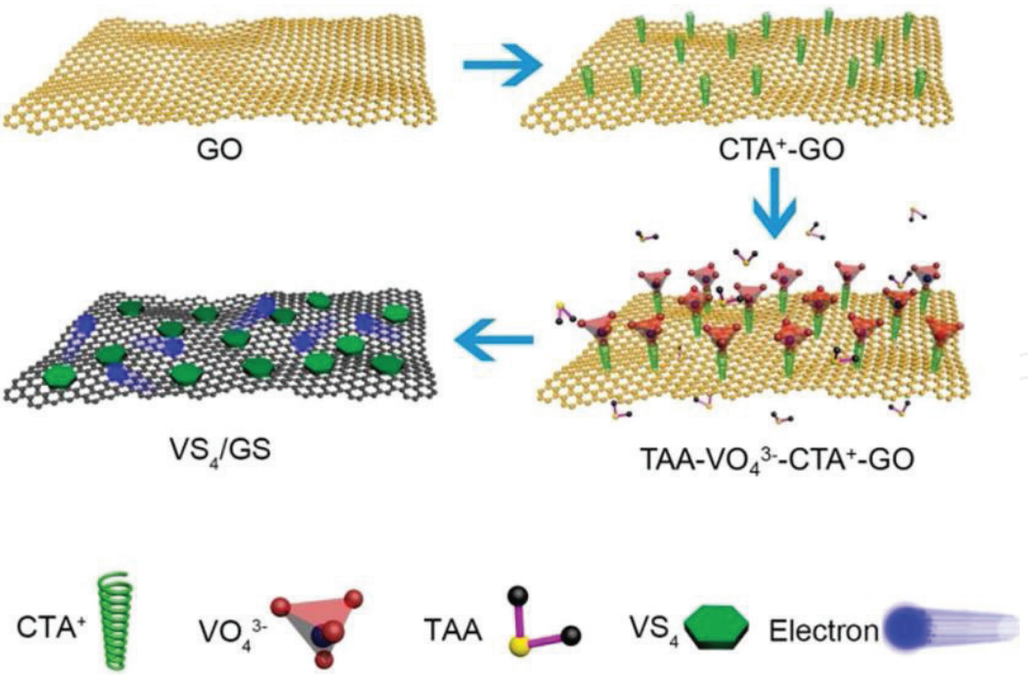

Figure 3.
Hydrothermal synthesis route for the VS_4@GS nanocomposites [62].

mainly due to the intrinsic negatively charged surface of the GO that could be easily attached to the positively charged surfactants, and facilitate the nucleation and the growth of active materials on the reduced graphite oxide (rGO, graphene) sheets under the hydrothermal conditions. The strong interface adhesion and the high crystallinity of the hydrothermal assembled composite should benefit the electrode with improved energy storage performance.

2.3 Electrospinning

As an efficient fabrication method for nanofibers [67–73], the electrospinning method has also been developed for producing nanofiber/graphene heterogeneous electrode materials for the energy storage applications [74–78].

As an example, Wei et al. [78] demonstrated an electrospinning fabrication of GO-PAN/PVDF (GPP) membrane electrode for fuel cell applications. In the preparation of GPP membrane electrode material (**Figure 4**), the uniform GPP precursor was prepared by dispersing the PAN, PVDF, and GO in DMF solvent, and then the GPP nanofibers were coated onto the carbon paper sheet attached on a collector drum via the electrospinning. Finally, the electrode was assembled by loading the Pt/C catalysts on the GPP nanofiber membranes.

As a promising procedure, the electrospinning method was also reported to prepare the carbon nanofibers [74], carbonized gold (Au)/graphene (G) hybrid nanowires [75], GO/PVA composite nanofibers [76], and graphene/carbon nanofibers [77] electrode materials for the supercapacitor, biosensor applications.
It should be noticed that the uniformity and the viscosity of the precursor should be carefully controlled, since both of which are critical for the mechanical strength and the electrochemical performance of the ultimate products.

2.4 Microwave-assisted assembly

As a quick and even heating method throughout the sample, the microwave assisted heating method has been widely used in the preparation of nanomaterials [79, 80].

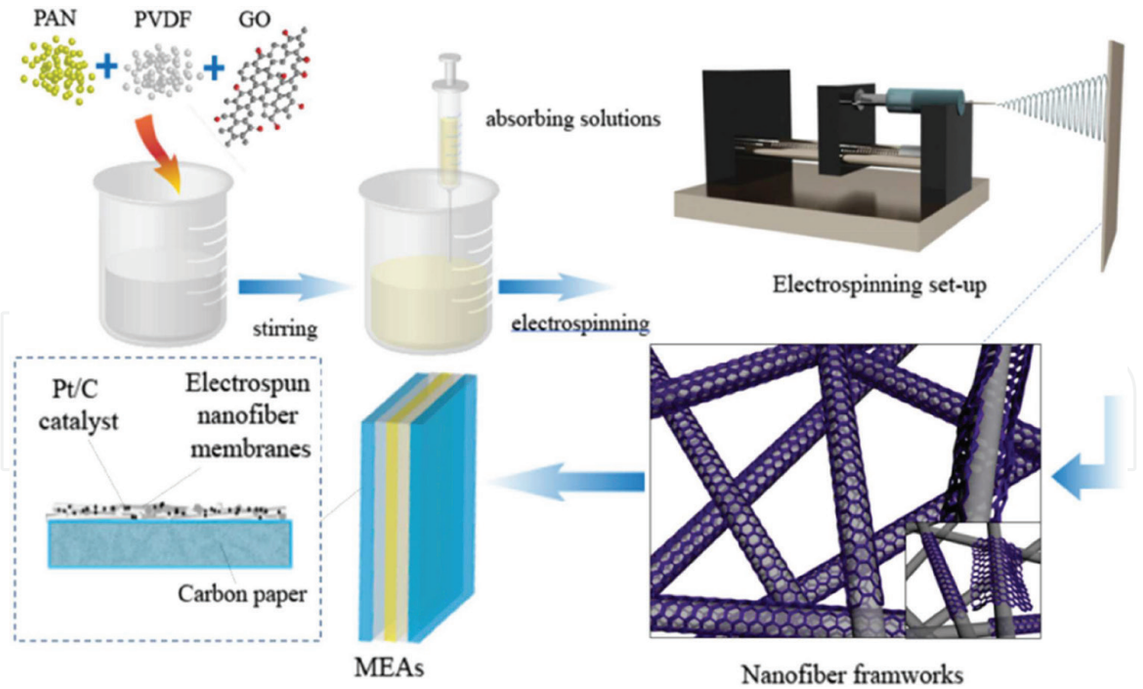

Figure 4.
A synthetic route to GO-PAN/PVDF (GPP) nanofibers [78]. PAN is polyacrylonitrile, and PVDF is polyvinylidene fluoride.

In the preparation of graphene based electrode materials, the microwave assisted method has shown the advantages in the reduction and exfoliation of GO, the time efficiency, and the energy saving [9, 81–83].

As shown in **Figure 5**, Kumar et al. [81] reported the microwave assisted synthesis of palladium (Pd) nanoparticle intercalated nitrogen doped rGO (NrGO) and the application as anode material for the fuel cells. In this synthesis, the GO nanosheets could be reduced and exfoliated under the microwave irradiation with pyridine treatment, and the nitrogen doping could also be achieved via the further

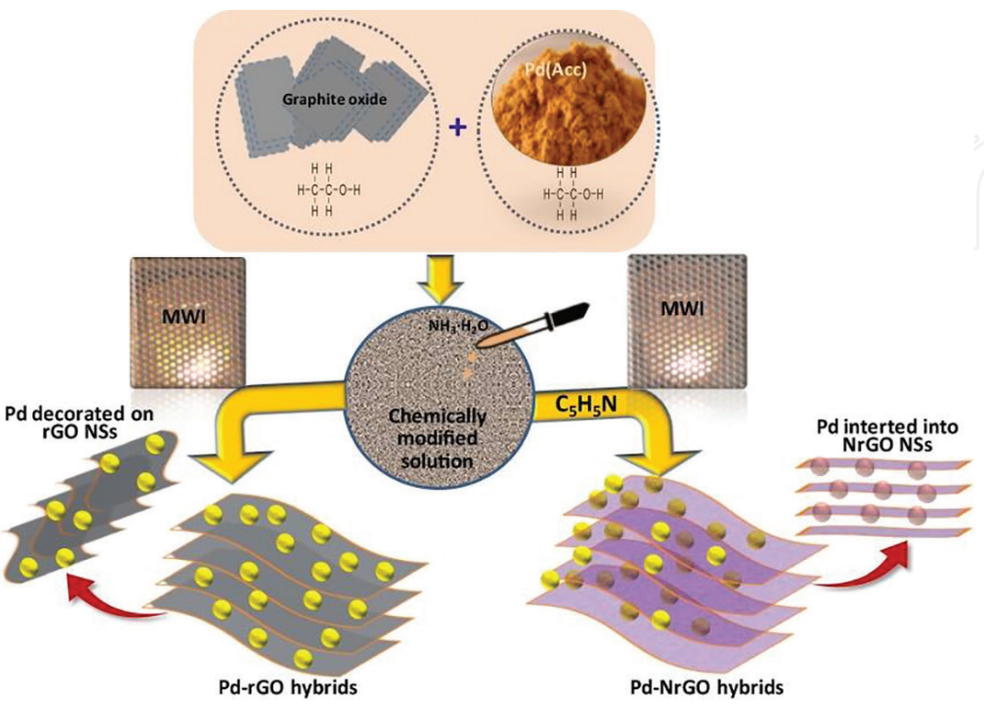

Figure 5.
Schematic illustration of the microwave assisted synthesis of Pd-rGO and Pd-NrGO hybrids [81].

modification with pyridine. The obtained porous rGO and NrGO could be decorated with Pd nanoparticles, which gave rise to a high electroactive surface, and therefore resulted in a high catalytic activity.

For the energy storage electrode materials, the microwave assisted method has been used to ultrafast assembly of the $Mn_{0.8}Co_{0.2}CO_3$/graphene composite [9], SnO_2/graphene composite for LIBs [82], and SnO_2@graphene/N-doped carbons for SIBs [83]. The ultrafast and uniform heating effect of the microwave method should be due to the dielectric heating principle, under which the polar molecules in the microwave radiation could rotate in a high frequency, and thus generate thermal energies evenly across the samples, which benefits the synthesis with environmental friendship, low cost, low energy consumption as well as the porous structures that especially provide the quick transfer channels of the Li^+/Na^+ cations in the rechargeable batteries.

3. Characterization methods

3.1 Scanning electron microscopy (SEM)

In the morphology analysis of the graphene based heterogeneous electrode materials, the top-view and cross-section SEM (**Figure 6**) could be used to determine the distribution of the active materials wrapped or attached by the layered graphene substrates based on the high resolution detector for the secondary electrons emitted on the sample surface. Combined with the EDS (energy dispersive X-ray spectroscopy) technique, the interface of the heterogeneous electrode could also be figured out clearly via the elemental mapping for the active materials and the graphene substrates [48, 51, 82].

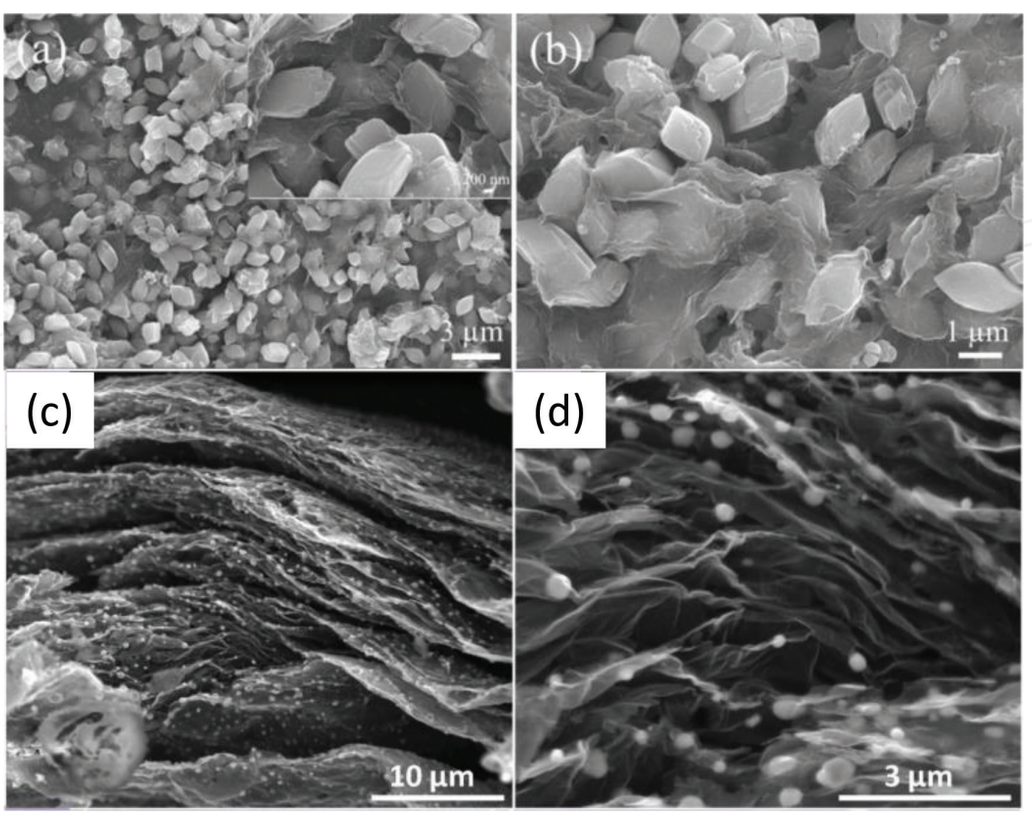

Figure 6.
SEM images for the $Mn_{0.8}Co_{0.2}CO_3$/graphene oxide (a, b) [9] and Pd-NrGO hybrides (c, d) [81].

3.2 Transmission electron microscopy (TEM)

As a powerful characterization method, TEM has been widely used to determine the morphology, crystal structure as well as the interface adhesion of the heterogeneous structures due to its atomic level resolution and the sensitivity to the contrast changes along with the elemental differences on the interface [84, 85]. With respect to the graphene based heterogeneous electrode materials, as shown in **Figure 7**, the uniform dispersion of SnO_2 on the graphene layers could be determined in the low magnification TEM image (**Figure 7b, c**), and the well crystallized SnO_2 nanoparticles could be clearly indexed in the HRTEM (high resolution transmission electron microscopy) and the corresponding FFT (Fast Fourier Transform) patterns (**Figure 7d–i**). The morphology and the crystal structure determined by TEM should be consistent with the result of SEM and XRD, respectively.

3.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a promising technique for determining the stoichiometry, the valence states, and the bonding conditions of the elements in the compounds, which has been widely used to characterize the functional materials [86–90]. Regarding to the graphene based heterogeneous electrode materials, as shown in **Figure 8** for the high resolution XPS scan of Pd-NrGO hybrids [81], the C 1s XPS peak could be split into the peaks for C=C (284.6 eV), C—O (286.4 eV), C—N

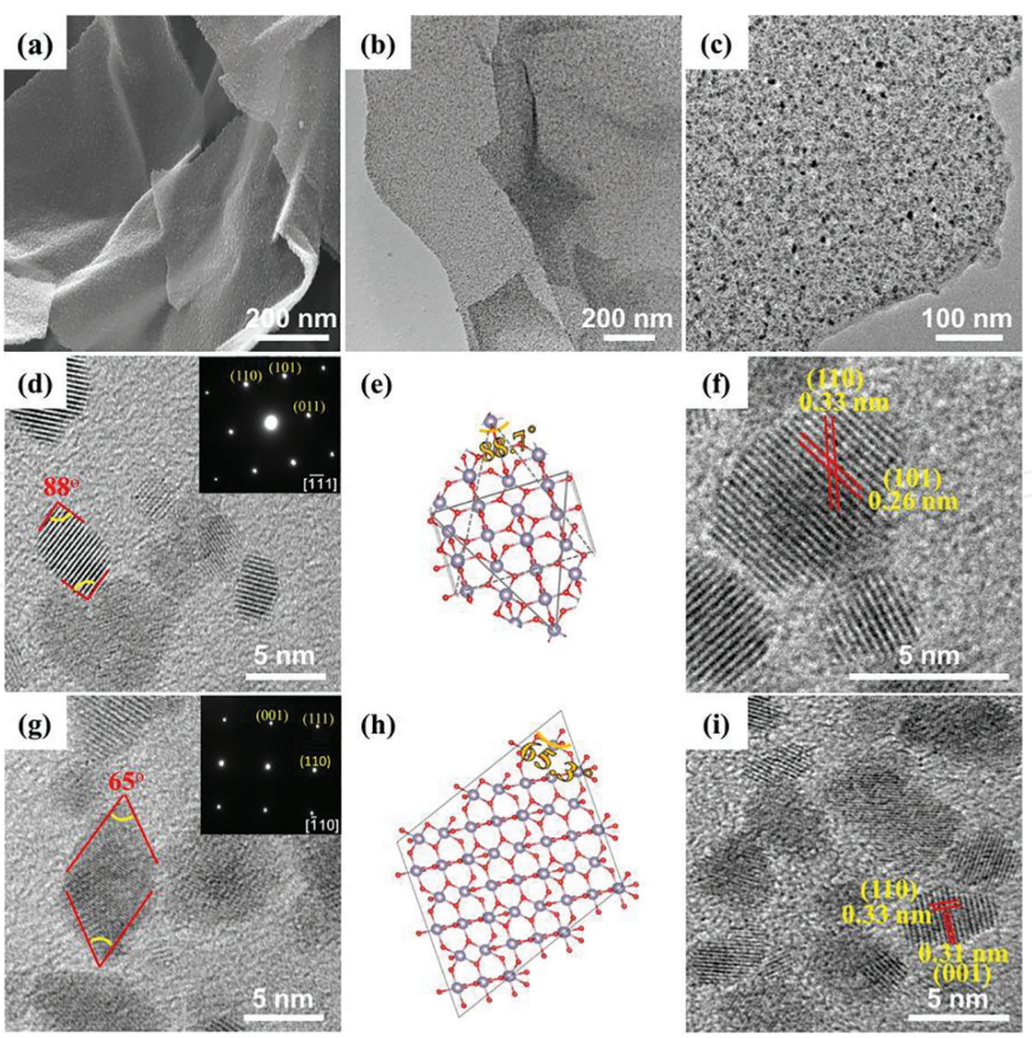

Figure 7.
(a) SEM image. (b, c) Low-magnification TEM images for the SnO_2/graphene hybrids. HRTEM images showing the octahedral SnO_2 model enclosed by {221} facets with (d–f) [$\bar{1}$ $\bar{1}$ 1] and (g–i) [$\bar{1}$ 0 1] zone axes [7].

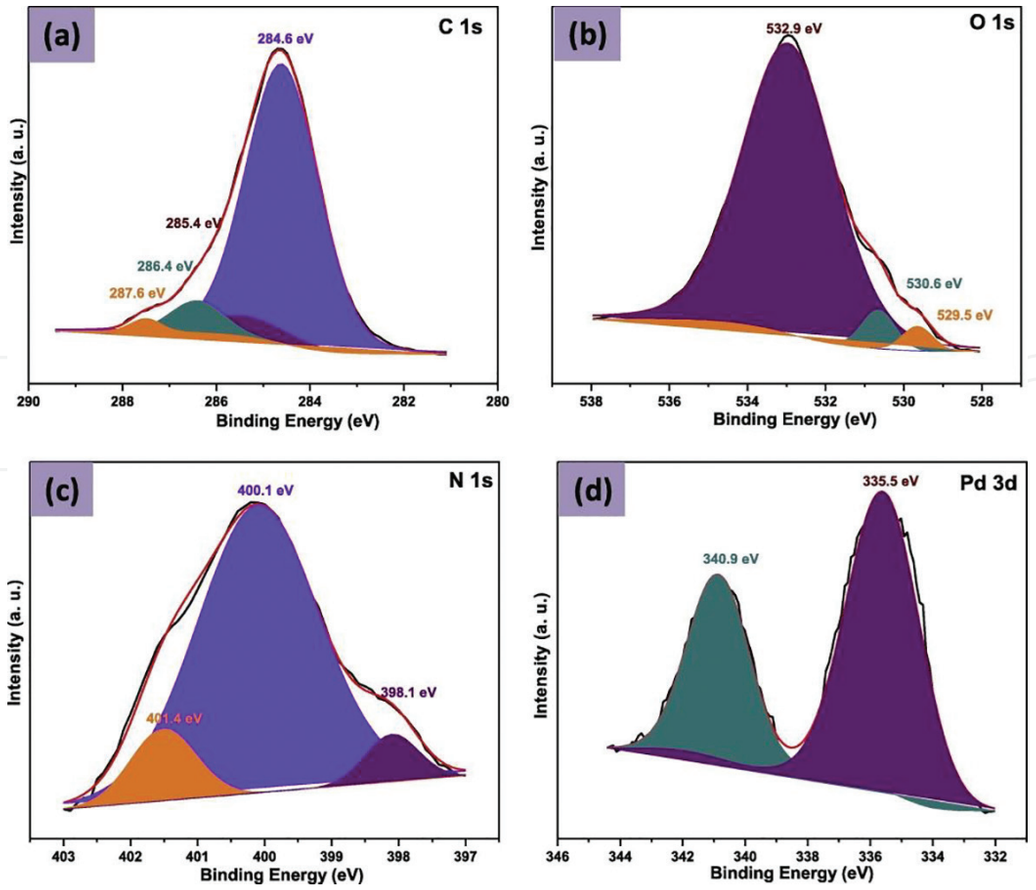

Figure 8.
High resolution XPS spectra for (a) C 1s, (b) O 1s, (c) N 1s and (d) Pd 3d of Pd-NrGO hybrids [81].

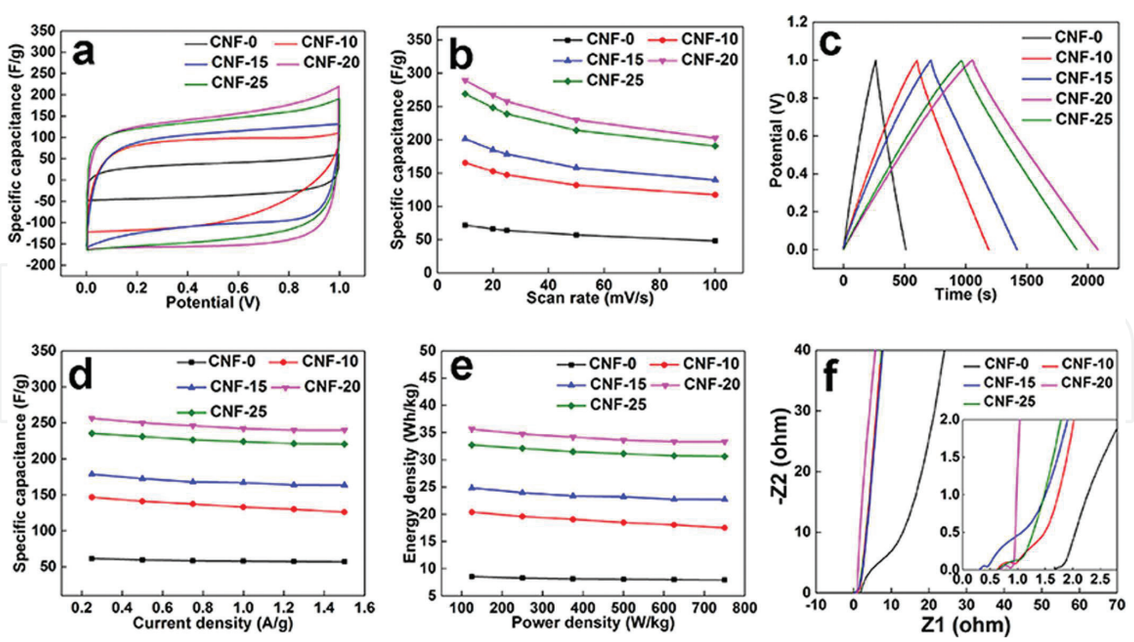

Figure 9.
(a) Cyclic voltammetry (CV) curves of carbon nanofiber samples, (b) rate capability curves of carbon nanofiber from 10 to 100 mV/s, (c) GCD curves of carbon nanofiber samples, (d) rate capability curves of carbon nanofiber from 0.25 to 1.5 a/g, (e) Ragone plots of the supercapacitor devices, and (f) Nyquist plots of carbon nanofiber samples [74].

(285.4 eV), and C=N (287.6 eV), the N 1S peak could be split into the graphitic-N (401.4 eV), pyrollic-N (400.1 eV) and pyridinic-N (398.1 eV) peaks, and the O 1S could be split into the Pd—O (529.5 eV), C—O (530.6 eV), and C=O (532.9 eV) peaks, which fully revealed the bonding information within the Pd-NrGO hybrids.

Apart from the SEM, TEM, and XPS, X-ray diffraction (XRD), Raman, FTIR, and thermal analysis methods (TGA, DSC) were also used to determine the crystal structure, morphology, thermal stability, and other physical/chemical characteristics of the graphene based heterogeneous electrode materials. The electrochemical performance for the energy storage was usually evaluated by the tests, including the cyclic voltammetry (CV), rate capability, galvanostatic charge/discharge (GCD), cycling specific capacity, and the electrochemical impedance spectra (EIS, e.g. Nyquist plots) (**Figure 9**).

4. Mechanisms

As for the active materials in the anode for the energy storage devices (e.g. supercapacitor, LIBs, and SIBs), the modification via bonding or attaching with the graphene or rGO always results in the improvement of the electrochemical performance with respect to the cycling stability, rate capability as well as the high specific capacity.

Behind the enhancement of the performance, there exist several possible mechanisms for the property promotion as illustrated in the following:

a. The growth of nanoparticles for the active materials could be effectively restricted by the graphene, giving rise to the uniform dispersion of the nanoparticles that facilitates the increase of specific area and the active sites for K^+/Na^+ storage [7].

b. The non-faradaic capacitance could be contributed by the graphene due to the electrical double layer-effect [7].

c. The fragmentation of the active materials due to the volume expansion and contraction during the charge–discharge cycles could be depressed by the flexible graphene, which benefits the devices with excellent cycling stability and rate capability [7, 52].

d. The conductivity of the active materials could be enhanced by the graphene, which gives rise to the increase of reversible capacity [52].

e. The graphene in the composite could supply a physical barrier between the active materials and the electrolyte, which effectively suppresses the shuttle effect of the byproducts in the de-charge process that could fade capacity of the batteries [52].

5. Conclusions and outlook

In summary, the synthesis and the characterization of the graphene based heterogeneous electrode materials for the energy storage applications (e.g. SIBs, LIBs, and supercapacitor) have been fully reviewed and discussed in this chapter. In the synthesis of the title materials, ball milling and hydrothermal methods show the cost-effective advantages. Comparatively, the electrospinning method exhibits the benefits in the nanowire composite assembly, and the microwave assisted approach occupies the superiority in the ultrafast fabrication. With respect to the characterization, the morphology could be determined by the SEM and TEM, and the electrochemical performance could be evaluated by the cyclic voltammetry (CV), rate capability, galvanostatic charge/ discharge (GCD), cycling specific capacity, and the EIS tests. In the composite, the graphene could restrict the growth of the nanosized active materials, contribute the non-faradaic capacitance, improve the conductivity, suppress the fragmentation, and supply a physical barrier between the active materials and the electrolyte, which benefit the devices with excellent cycling stability, large rate capability as well as the high specific capacity.

In the future, the most interesting and challenging applications of the graphene in the nanocomposite for the energy storage devices should be the ultrafast rechargeable batteries, the large-energy-density supercapacitors, and the all-solid-state LIBs.

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Conflict of interest

The authors declare no conflict of interest.

Acronyms and abbreviations

LIBs	lithium ion batteries
SIBs	sodium ion batteries
SEM	scanning electron microscopy
TEM	transmission electron microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier-transform infrared spectroscopy
TGA	thermal gravimetric analysis
DSC	differential scanning calorimetry

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