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Review

Progress on the Microwave-Assisted Recycling of Spent Lithium Battery Graphite

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Abstract: The robust development of electric vehicles has driven a surging decommission stream of lithium-ion batteries (LIBs) owing to their limited service life. The recycling of spent LIBs has become an urgent and essential task for the sustainable development of the LIB industry. However, the prevailing recycling methods focus only on recycling valuable metal, whilst the graphite anode materials are usually discarded or burned as fuels, leading to great waste of valuable carbon material. A facile strategy to obtain value-added products in an efficient manner is of great significance for the recycling of spent graphite. As graphite has excellent microwave absorption capability and electrical conductivity, microwave radiation on spent graphite can induce a Joule heat–discharge–plasma coupled effect, leading to a rapid heating process, especially when discharge occurs, exhibiting a thermal shock effect with the generation of a large number of high-energy electrons and active materials. This special feature facilitates microwave heating that is tailored for assisting the removal of impurities, structure repair, and graphite intercalation and exfoliation in an efficient manner. Therefore, different from the conventional graphite recycling route that is associated with energy/solution-intensive processes, this paper reviews the progress on microwave-assisted removal of impurities, repair of damaged graphite structure, and innovatively discusses the breakthroughs in microwave-assisted preparation of graphite intercalation compounds, expanded graphite, graphene and graphene-based materials, and porous graphene, with an aim to provide a scientific reference for the value-added resource utilization of spent graphite and preparation of new energy storage materials.

Keywords: microwave; spent graphite; regeneration; expanded graphite; graphene

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1. Introduction

In order to meet its pledge to peak carbon dioxide emissions by 2030 and target carbon neutrality by 2060, China is taking great actions in developing green and low-carbon transportation. As a result, electric vehicles (EVs) have been robustly developed in the past three years. According to the China Association of Automobile Manufacturers, the number of EVs sold annually has grown from 1.3 million in 2020 to a whopping 6.8 million in 2022, and it is expected to reach 9 million in 2023 [1]. Along with the robust development of EVs, the demand and upgradation of lithium-ion batteries (LIBs) as the main power source are greatly promoted, leading to a surging decommission stream in the next 3–5 years due to the limitation of service life [2–4]. Considering the limited resources and environmental sustainability, the sustainable recycling of spent LIBs is of great significance. However, the recycling of spent graphite is far behind the development of LIBs. Currently, the industrial-scale reclamation of spent LIBs is mainly based on pyrometallurgy and hydrometallurgy, with the focus on recovering valuable metal elements only [5]. In contrast, the resource utilization of anode materials that account for 12–21 wt% [6] of the total mass of spent

LIBs (about 11 times that of lithium) is still immature, resulting in most anode materials being directly discarded or incinerated as fuel. At present, the commercial anode materials mainly include graphite, hard carbon, soft carbon, etc. Among them, graphite is the main one, accounting for about 98% of the LIB anode material market [7]. As an important strategic resource, graphite is known as "black gold". Directly discarding or incinerating spent graphite will not only cause significant waste in terms of resources but also lead to environmental problems, such as carbon emissions. Therefore, the resource recovery and utilization of spent graphite is a process of great urgency and significance. According to the working principle of LIB and structural composition of the anode (Figure 1), spent graphite usually contains electrolytes (composed of lithium salts (e.g., $LiPF_6$ or $LiClO_4$) dissolved in organic solvents (e.g., ethylene carbonate, dimethyl carbonate)), adhesives (e.g., polyvinylidene fluoride, sodium carboxymethyl cellulose, styrene–butadiene rubber), a solid electrolyte interfacial (SEI) layer, copper foil, and other pollutants [8,9]. Owing to these impurities, spent graphite presents great differences compared to fresh graphite in terms of structure and surface morphology, making it unable to be reused directly. Impurity removal is essential in order to reuse the spent graphite. Furthermore, due to electrochemical oxidation, there are oxygen-containing functional groups attached to the layer surface of spent graphite, resulting in the conductive sp2 hybrid structure being changed into the nonconductive sp3 hybrid structure. Accordingly, structure repair is required for the reuse of spent graphite, which usually adopts high-temperature annealing treatment [10]. However, compared with natural flake graphite, the interlayer distance of spent graphite is greatly enlarged due to the repeated intercalation/deintercalation of lithium ions during battery charge and discharge [11], leading to the interlayer van der Waals force being remarkably weakened, and thereby it is much easier to be intercalated to form graphite intercalation compounds (GICs) or exfoliated to obtain graphene and its derivatives. On basis of the abovementioned characteristics of spent graphite, its recycling can be classified into three main technical routes, including impurity removal and regeneration, high-temperature repair, preparation of GIC, expanded graphite (EG), graphene and its composite nanomaterials, etc.

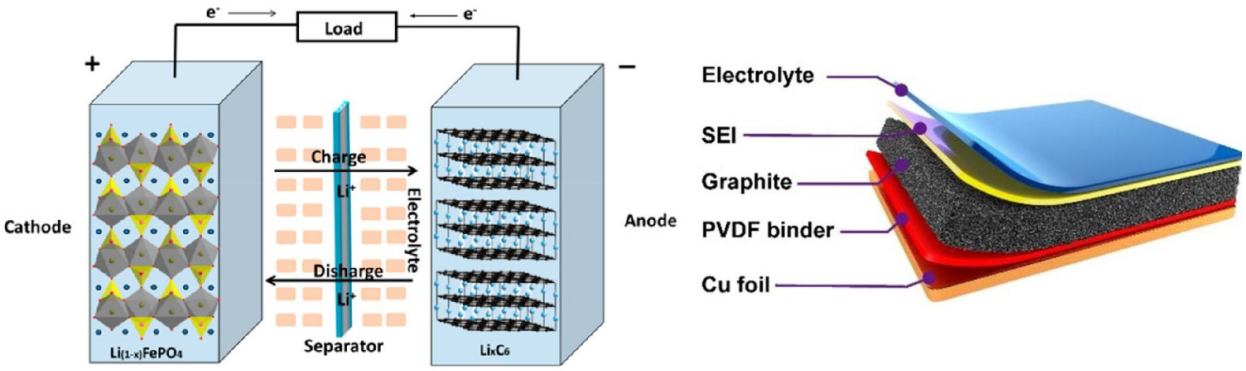

Figure 1. Working principle of LIBs [12] and structural composition of the anode [13].

Despite the availability of certain chemical treatment processes, thermal treatment is essential for the recycling of spent graphite. Microwave heating is different from traditional heating methods that rely on thermal conduction, convection, and radiation. It operates by causing frictional collisions between polar molecules and free ions/electrons. The specific mechanisms are dipolar polarization and ionic polarization/Joule heating, correspondingly, leading to an excellent heating effect that mainly manifests in rapidity, selectivity, uniformity, and easy control. In spite of Joule heating, a discharge phenomenon can be induced when a conducting material (e.g., metal strip/wire/fiber, graphite, carbonaceous material) is implanted in a microwave field, leading to instantaneous release of significant heat and generation of active species and plasmas [14,15]. For example, microwave treatment facilitates the recovery of metals from spent LIBs as an alternative to

traditional pyrometallurgy, where the anode graphite acts as a microwave absorber and reductant [16]. Notably, due to the excellent microwave absorbing property and conductivity of graphite, microwave–graphite interaction can induce Joule heat–discharge–plasma coupled effect, leading to the rapid heating process. Especially when discharge occurs, there is a thermal shock effect (heating rate can amount to 10^5~10^6 K/s), with the generation of a large number of high-energy electrons and active materials, which can remarkably strengthen the gas–solid reactivity and trigger reactions that cannot be completed or are difficult to complete under conventional conditions (e.g., etching, controllable doping, stripping, and reduction) [17]. Therefore, based on the unique microwave–graphite interaction, microwave heating can be tailored to assist the impurity removal, structure repair, and graphite-derived materials preparation.

This paper reviews the latest progress in microwave-assisted impurity removal, high-temperature repair, and preparation of GIC, EG, graphene and graphene-related materials, and porous graphene in order to provide a reference for the integration and application of the spent graphite recycling technology.

2. Microwave-Assisted Regeneration of Spent Graphite by Inducing Flash Evaporation

The current reuse and/or regeneration of spent graphite mainly includes acid leaching for impurity removal [6] and high-temperature repair [18]. Acid leaching can remove impurities, such as metals and electrolytes, in the spent graphite. However, due to the strong oxidation of graphite during the acid leaching process, the graphite layer spacing expands, and the sp2 hybrid structure with good conductivity transforms into the non-conductive sp3 structure [19,20]. In addition, the organic electrolyte and binder partially remain on the material surface after acid leaching, resulting in a poor removal rate of organic impurities, and the quality of the recovered graphite cannot meet the standards of commercial graphite. Moreover, acid leaching consumes a large amount of reagent (e.g., HCl, H_2SO_4, H_2O_2) and discharges waste liquid and exhaust gas, greatly increasing the risk of secondary contamination. The above issues severely restrict the application of this technology.

High-temperature repair is usually to expose the spent graphite in a high-temperature furnace at 2600 to 3300 °C, which can repair its ordered structure through graphitization, as well as remove binders, electrolytes, metals, and their oxides through gasification [21]. Yu et al. [22] investigated the effects of temperature, duration, and atmosphere on graphite crystal lattice restoration and found that the highest degree of graphitization was achieved by calcination at 3000 °C for 6 h under the N_2 atmosphere. Although the graphite obtained by ultra-high-temperature treatment is of good quality, the process requires significant energy consumption, a strict atmosphere, and a long duration, which leads to high repair costs [23]. Therefore, finding an energy-efficient method to overcome the existing issues is necessary to regenerate the spent graphite sustainably.

The outstanding advantages of microwave heating reveal an efficient pathway for the regeneration of spent graphite. Microwave radiation on spent graphite can not only induce a rapid heating process (more than 1000 °C in seconds) [24–26] but also induce local hot spots and superheating effects in the form of arc plasma, which can be tailored to remove impurities and reconstruct the structure of graphite. Yuwen et al. [27] showed that microwave radiation on the LIB anode for 20–30 s (800 W) in a nitrogen atmosphere can effectively remove the binder and electrolyte as well as separate copper foil from spent graphite. Similarly, Ma et al. [11] utilized the microwave-assisted exfoliation process to prepare reconstructed graphite with sp2 + sp3 carbon surfaces from spent graphite. In this process, ethylene glycol, as the expansive agent and the dispersion medium, continuously hits the graphite layer while absorbing microwave energy, which causes the edge-unstable graphite nanofragments and impurities (e.g., conductive agents, binders) to be exfoliated from the spent graphite. It is demonstrated that impurities in spent graphite can be effectively removed by microwave radiation, and the regenerated graphite can be reused in LIB.

In addition to the impurity removal, the microwave-induced rapid heating process facilitates the reconstruction of ordered graphite structure to restore its electrochemical properties. Fan et al. [28] regenerated spent graphite using fast and effective microwave heating, repairing the damaged structure of the graphite while reducing energy consumption and costs. The regenerated graphite has a regular surface, and the electrochemical properties are significantly enhanced. For the specific effects of microwave-treated graphite as an anode material for LIBs regarding electrochemical performance enhancement, Hou et al. [29] found that the microwave-assisted reconstruction process created additional open sites and channels for the storage, rapid transfer, and diffusion of lithium ions during charging and discharging processes to achieve efficient lithium storage performance. As illustrated in (Figure 2), the microwave-modified spent graphite (MW-G) obtained by processing for 15 s at a microwave power of 800 W adopts a clear layered structure and possesses some small holes on the flake, thus displaying a higher reversible capacity and better rate performance than the fresh commercial graphite (~300 mAh g^{-1}).

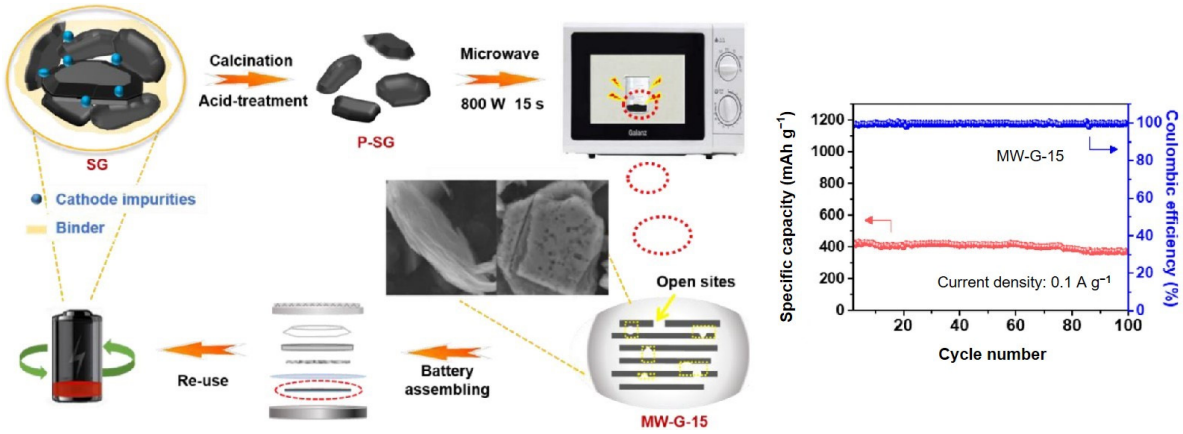

Figure 2. Schematic diagram of the microwave-assisted process during the reconstruction and utilization of spent graphite (SG) and electrochemical performance of MW-G-15 [29].

Furthermore, microwave-assisted regeneration can be tailored to enlarge the graphite layer spacing to expand the application of regenerated graphite in potassium-ion batteries [30]. When the graphite is retired, many impurities are trapped between the layers, including lithium embedded in the graphite [31,32], electrolyte, copper foil, and oxygen-containing functional groups, which can be regarded as the graphite intercalated by the above impurities. The microwave-induced rapid heating effect can promote the gasification and removal of intercalated impurities in spent graphite. During this process, the instant release of gasification products increases the interlayer pressure and widens the interlayer spacing, facilitating the transport of ions with larger sizes. Therefore, the obtained regenerated graphite after microwave treatment can be used in potassium-ion batteries.

To conclude, as an efficient means of rapid heating, microwave treatment can not only effectively remove impurities and restore the ordered structure of graphite but also plays an important role in reducing processing time, chemical reagent usage, and energy consumption compared with the conventional approach. The regenerated graphite can exhibit an equivalent and even enhanced electrochemical performance when compared with commercial graphite. On this basis, by adjusting the microwave treatment process, the recycling of spent graphite can be greatly simplified, remarkably promoting the reuse of recycled graphite in the field of batteries, supercapacitors, and other energy storage devices.

3. Microwave-Assisted Preparation of Graphite Intercalation Compounds

Due to the unique interlayer structure of graphite, different guest species can be inserted into the graphite flakes to form chemical bonds, which is called intercalation, and the products obtained are GICs [33]. The physical and chemical properties of GICs are

dependent on the quality of graphite and the properties of the intercalant species (e.g., alkali metals, metal chlorides and oxides, oxyhalides, Lewis acids) [34]. For example, the GICs obtained after the intercalation of substances that easily vaporized at high temperature have excellent expandability and can be used as precursors for preparing EG. In addition, substances such as metal chlorides enable GICs with outstanding electrical conductivity to be available as electrode materials for LIBs. Thus, various possibilities promote the development of GICs in different fields, such as energy storage and electrocatalysis. It is of great importance to search for an efficient and convenient preparation method.

In general, the common methods for the preparation of GICs include chemical oxidation, electrochemical oxidation, the vapor diffusion method, and ultrasonic oxidation [35–38]. Among these methods, chemical oxidation is the most prevailing, but it consumes many chemical reagents and may cause serious environmental pollution. Unlike natural graphite, which requires strong oxidants ($KMnO_4$, concentrated sulfuric acid, etc.) to open the edge layers for the intercalant insertion, spent graphite with significantly widened layer spacing can reduce the dependence on strong oxidants, resulting in decreased consumption of oxidants. For example, Zhang et al. [19] found that, compared with natural graphite, the consumptions of $KMnO_4$ and concentrated H_2SO_4 were, respectively, reduced by 28.6% and 40% when performing the oxidative intercalation of spent graphite due to the enlarged layer spacing and structural defects. Therefore, the special structure characteristics of spent graphite are congenital advantages for the intercalated reaction to prepare GICs, providing an attractive direction for spent graphite reuse.

Notably, the microwave-induced plasma effect can effectively promote the process of graphite intercalation, leading to more efficient preparation of GICs with excellent properties than the time-consuming conventional oxidative intercalation method. Wang et al. [17] demonstrated that microwave-induced arc plasma can enhance the internal energy of the gaseous reactant molecules around the graphite surface and strengthen intercalation reaction kinetics. In this process, the π electrons driven by high-frequency microwaves are able to jump out of the graphite conjugate network and produce high-energy-density arc plasmas, converting the electron kinetic energy into the internal energy of the surrounding molecules and accelerating the intercalation during the preparation of GICs. Wei et al. [39] utilized microwave-assisted oxidative intercalation with H_2SO_4 and $K_2S_2O_8$ as the intercalant and oxidant, respectively, to synthesize GICs efficiently, and they were subsequently used as precursors for the preparation of EG. Furthermore, $FeCl_3$–graphite intercalation compounds ($FeCl_3$–GICs) prepared by the microwave-plasmas-accelerated approach can be used as LIBs anodes to replace normal commercial graphite, exhibiting high capacity (1650 mAh cm^{-3}) [17]. However, practical applications of $FeCl_3$–GICs are limited by rapid capacity decay as a result of chloride dissolution. Li et al. [40] achieved effective chloride immobilization in $FeCl_3$–GICs by oxidizing a fraction of $FeCl_3$ to Fe_2O_3 through microwave radiation. Due to the polar interaction mechanism, the suitable Fe_2O_3 content guarantees abundant polar active sites for chemically bonding the $FeCl_3$ and LiCl while retaining the intact graphite-like structure. The amount of Fe_2O_3 can be appropriately adjusted by tuning the microwave radiation time. Therefore, the microwave treatment has a surprisingly assisted function regarding the modification of GICs.

Conclusively, the microwave-assisted preparation of GICs from spent graphite is efficient since the unique structure of spent graphite reduces oxidant consumption and intercalation reaction time, while the microwave-induced arc plasma can enhance the intercalation reaction kinetics. This method provides not only a solution for waste graphite treatment but also a significant reference for the development of GICs in the field of energy storage, such as electrode materials for LIBs.

4. Microwave-Assisted Preparation of Expanded Graphite

EG is generally obtained by subjecting GIC to a rapid high-temperature treatment (e.g., flame heating [41], inductively coupled plasma [42], laser irradiation [43], microwave irradiation), in which the compound intercalated in graphite layers decomposes with gas

products released instantly to expand the graphite layer spacing. The unique thermal shock effect of microwave–graphite interaction can instantly reach the high temperature that causes the precursor to expand. Thus, the obtained EG with a large expansion volume and high thermal and electrical conductivity can be used as an effective electrode material for supercapacitors [44] or to improve the thermal storage properties and thermal stability of phase change materials [45]. In addition, the enlarged specific surface and pore volume ender EG with a high adsorption capacity can be applied in the adsorption separation process, such as removing toxic organic dyes, chemical reagents, and other pollutants from waste water [46,47]. Not only is the EG prepared by microwave radiation comparable to that prepared by rapid direct heating in the furnace at 1000 °C [47,48] but this method has the outstanding advantages of effectively reducing time and energy consumption and increasing production efficiency.

GIC prepared by chemical/electrochemical intercalation can be used as the precursor of EG, and then the EG can be readily fabricated by microwave radiation [49]. Hua et al. [50] prepared a GIC with acetic anhydride as the inserting agent and potassium dichromate as the oxidizing agent and then utilized microwave radiation on the GIC for 60 s to obtain EG at a microwave power of 1000 W. Sykam et al. [47] utilized microwave heating (800 W, 50–60 s) to induce the rapid evaporation of the $HClO_4$ intercalated in the GIC, in which smoke and sparking phenomena were observed. As a result, they obtained a highly porous EG with a worm-like structure (Figure 3) that exhibited remarkable adsorption performance in the effective removal of various organic pollutants, chemical solvents, and oils from aqueous solutions.

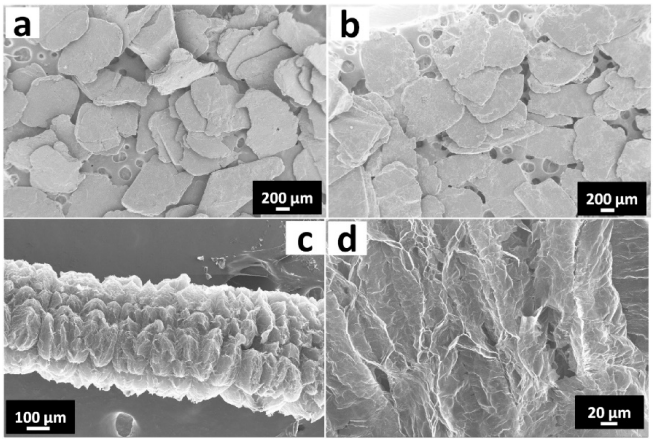

Figure 3. FESEM images of (**a**) NFG, (**b**) GIC, and EG at (**c**) lower and (**d**) higher magnification [47].

Based on the feasibility of microwave-assisted intercalation to form GICs and microwave-induced thermal shock on GICs to produce EG, the potential exists for synergy between these two processes. Wei et al. [51] simply mixed natural graphite, nitric acid, and potassium permanganate in the weight ratio of 1:2:1. After 1 min of microwave irradiation at 700 W, the maximum expansion volume of the prepared EG can reach 312 mL/g, which significantly reduces the preparation time and energy consumption. Conclusively, the featured microwave–graphite interaction enables the integration of the intercalation and expansion processes in one step to enhance the EG synthesis efficiency and simplify the preparation process.

Similar to GICs, graphite oxide can be used as the precursor for the preparation of EG. Deng et al. [52] synthesized EG from anthracite coal by microwave radiation after high-temperature graphitization and oxidation treatment (Figure 4) and used it as anode material for LIBs. The prepared EG exhibits an ordered microcrystalline structure, a unique morphology of porous layered nanosheets, and desirable electrochemical properties, such as cycling performance (up to 278.0 mAh g^{-1} after 300 cycles at 0.2 C) and coulombic efficiency (up to 99.17%). Liu et al. [53] utilized a modified Hummers method to convert

natural flake graphite into graphite oxide. After microwave radiation (1000 W) of the treated graphite oxide for 2 min, slight-expanded graphite (SEG) with about four times expansion was obtained. The laminar structure of SEG is distinct from that of natural graphite, curling inward in an upward manner and plicating. Obviously, both microwave parameters and precursor types can significantly impact the preparation of EG, and the expansion multiplier varies from less than ten to several hundreds. Notably, the interlayer distance of spent graphite is enlarged after repeated charging and discharging of LIBs, and there are certain oxygen-containing functional groups attached to the spent graphite in the electrochemical oxidation environment, which results in the properties of the spent graphite being quite similar to the EG precursors. Liu et al. [54] utilized the structural characteristics of spent graphite to synthesize micro-expanded graphite (MEG) by using $HClO_4$ as an intercalant and oxidant in a one-step process. The synthesized MEG exhibits excellent rate capability (up to 340.32 mAh g^{-1} at 0.1 C) and cycling stability (up to 81.73% after 100 cycles at 1 C) as anode materials for LIBs.

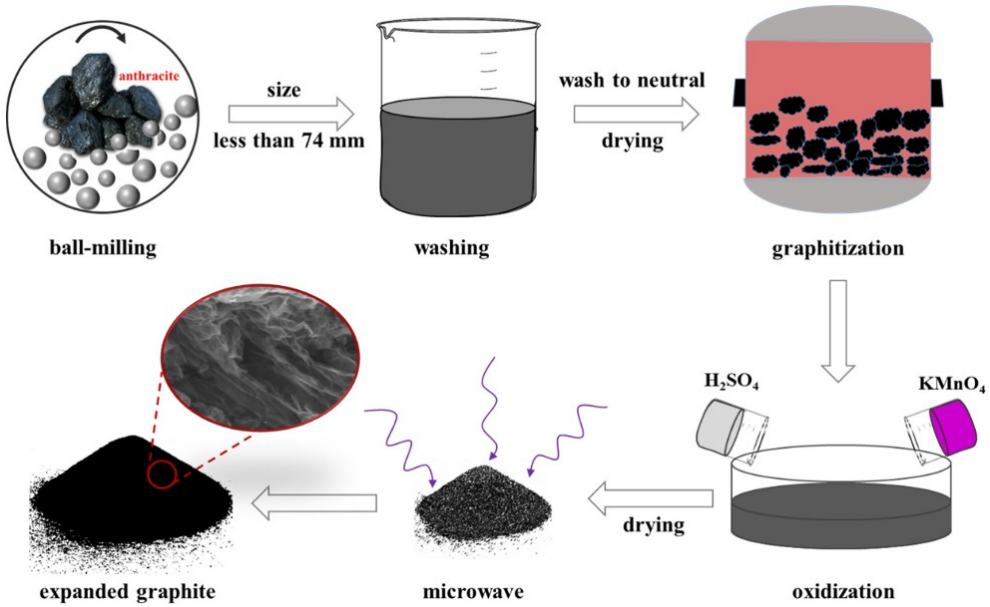

Figure 4. Schematic illustration for the preparation of EG [52].

In summary, the featured microwave heating mechanism can be tailored to prepare EG in an efficient, energy-saving, and process-simplified way. On the one hand, the generation of arc plasma under microwave treatment enhances the kinetics of the intercalation reaction. On the other hand, the thermal shock effect can rapidly expand the precursor at a high temperature. Considering that spent graphite has larger layer spacing and a higher degree of oxidation than natural graphite, using spent graphite as a raw material can further improve the preparation efficiency of EG.

5. Microwave-Assisted Preparation of Graphene and Graphene-Derivative Functional Material

5.1. Graphene

The graphene preparation methods include mechanical stripping [55], chemical vapor deposition [56], liquid stripping [57], epitaxial growth [58], chemical oxidation–reduction [59], electrochemical [60], organic synthesis [61], and so on. Among them, the oxidation–reduction method has been the most widely used method for production. The process can be approximately divided into three parts: graphite oxidation, exfoliation of oxidized graphite to obtain graphene oxides (GO), and reduction of GO to produce reduced graphene oxides (rGO). As mentioned in the preparation of GICs, the unique structure of spent graphite can effectively decrease the intercalation difficulty and reduce the consumption of oxidants.

In addition, Chen et al. [62] found that the exfoliation efficiency of spent graphite was 3–11 times higher than that of natural graphite in a study on the preparation of graphene by sonication-assisted liquid-phase exfoliation. Furthermore, due to the lithium-ion intercalation and deintercalation in the graphite during charge/discharge, the spent graphite exhibits an irregular expansion and the pre-expansion process enabled four times enhancement in graphene productivity compared with the pristine graphite [63]. Therefore, spent graphite as a raw material for graphene preparation can reduce oxidant consumption and improve exfoliation efficiency, which has inherent advantages.

In addition, a large amount of oxygen functional groups can be removed from the few-layer graphene by microwave irradiation [64]. Voriy et al. [65] reported in *Science* that the rapid high temperature generated by microwave-induced discharging can almost wholly remove oxygen functional groups and rearrange the carbon atoms in the graphene basal plane to obtain microwave-reduced graphene oxide (MWrGO), which provides a new technological route for the efficient preparation of high-quality graphene from spent graphite. The MwrGO can be prepared by 1 to 2 s pulses of microwave radiation, presenting a highly ordered structure compared to rGO obtained by general thermal reduction. Jiang et al. [66] conducted research based on the effect of graphite as it pertains to inducing microwave discharge plasma to assist the reduction of GO to prepare MwrGO. By adding 5 wt% of prepared MwrGO into the cathode material of LIBs, the layered structure of MwrGO increases the contact area between lithium ions and electrolytes, which promotes the rapid transfer of lithium ions and electrons, thereby enhancing the electrochemical performance. Yan et al. [67] utilized a microwave-assisted solvothermal treatment to reduce graphene oxide by glucose to prepare rGO, presenting shortened reaction time and improved reaction efficiency compared to the conventional oxidation–reduction method. The obtained rGO possesses good electrochemical properties (a specific capacitance of 179 F g^{-1} at a scan rate of 2 mV s^{-1}).

Furthermore, ultrasonic–microwave synergistic assisted preparation of graphene by liquid phase exfoliation has also been extensively studied. Sreedhar et al. [68] exposed graphite to domestic microwave radiation to obtain EG, which was sonicated in an ethanol environment to obtain graphene. Song et al. [69] obtained an rGO suspension by heating up to 110 °C under microwave radiation at 300 W and discontinuous sonication for 30 min, which shortened the reduction time of GO and enhanced the firmness of the rGO anchored onto the modified material. Therefore, the ultrasonic–microwave synergistic method is remarkably effective in terms of improving exfoliation and reduction efficiency, which is a novel and efficient approach for preparing high-quality graphite in bulk.

Conclusively, compared with most conventional graphene preparation methods that feature complicated steps, high reagent input, high energy costs, and are time-consuming, the adoption of spent graphite as a raw material integrated with a microwave-assisted exfoliation/reduction process can achieve efficient preparation of high-quality graphene, promoting the batch production of graphene and value-added utilization of spent graphite.

5.2. Graphene-Derivative Functional Material

As mentioned above, GO is rich in oxygen-containing functional groups (e.g., epoxide, carbonyl, carboxyl, hydroxyl groups) compared to pristine graphene, and microwave radiation can efficiently remove oxygen-containing groups, which provides opportunities for doping modification of graphene and compounding with functional materials. Dai et al. [70] utilized a microwave process to carry out deep reduction and nitrogen doping in GO, using ethylenediamine (EDA) as the nitrogen source. Functional graphene sheets (FGS) were synthesized by the ring-opening reaction of EDA with the epoxy group of GO. After microwave radiation treatment for 1 min, the polar oxygen-containing functional groups showed obvious decomposition, and nitrogen long-pair electrons were conjugated to the graphene π system to obtain nitrogen-doped graphene sheets (NGS). Fei et al. [71] used amine-functionalized GO (AGO) as a nitrogen source and accomplished the reduction and N-doping of the AGO simultaneously through the high-energy environment

created by short-time microwave radiation. The amino groups were easily released and formed chemical bonds, such as C–N bonds, under microwave thermal reduction, resulting in nitrogen-doped graphene with a high doping rate. Through microwave-assisted heteroatom (e.g., nitrogen, boron) doping, graphene exhibits superior structural characteristics and enhanced physicochemical properties, showing great potential in energy storage, catalysis, sensors, and so on.

The microwave thermal shock effect can facilitate the effective integration of diverse functional materials with graphene to prepare graphene-derivative nanocomposites. These nanocomposites can be divided into two categories: graphene/inorganic nanocomposites and graphene/polymer nanocomposites, which may be obtained by adding graphene to materials with special functional properties or vice versa. In the case of graphene/inorganic nanocomposites, the inorganic class can be divided into metals (e.g., Cu [72,73], Mg [74]), metal oxides (e.g., MnO_2 [75], SnO_2 [76]), and nonmetals (e.g., Si [77], ceramic [78]). The addition of graphene nanosheets (GNs) significantly improved the mechanical, tribological [72], and energy storage [75] properties of the nanocomposites, broadening their application areas.

Fei et al. [71] further embedded atomic metals into graphene while achieving nitrogen doping and found the microwave-assisted thermal reduction of GO created defects or vacancies during the removal of oxygen-containing functional groups, which could serve as anchoring sites for metal atoms and effectively prevent the aggregation of mass atomic metals. The graphene-supported single atomic metals synthesized by the microwave heating process have special catalytic, magnetic, and electronic properties that are difficult to achieve via other methods. Kim et al. [76] proposed a method for the synthesis of graphene/SnO_2 nanocomposites based on the ability of microwave-generated plasma to perform rapid surface chemical reactions. The composite material obtained by microwave treatment has extremely high and selective sensitivity to NO_2 gas, which makes it useful in gas sensor applications. Kumar et al. [79] prepared ZnO/rGO nanocomposites by chemical oxidation and microwave radiation (Figure 5). During the preparation process, the high temperature generated by microwave radiation promoted the exfoliation and reduction of GO (500 W, 90 s) and the formation of ZnO nanoparticles (900 W, 45 s). The ZnO/rGO nanocomposites obtained can serve as excellent electrode materials for supercapacitors, with outstanding cyclic stability (82.5% for 3000 cycles at high scan rate 100 mV/s). Zhang et al. [80] utilized a one-step ultra-fast microwave approach to prepare nickel–cobalt sulfide (NCS)/graphene composite in 1 min. The prepared NCS/graphene composite can be used as a promising electrode material for supercapacitors with high specific capacitance and prominent cycling stability.

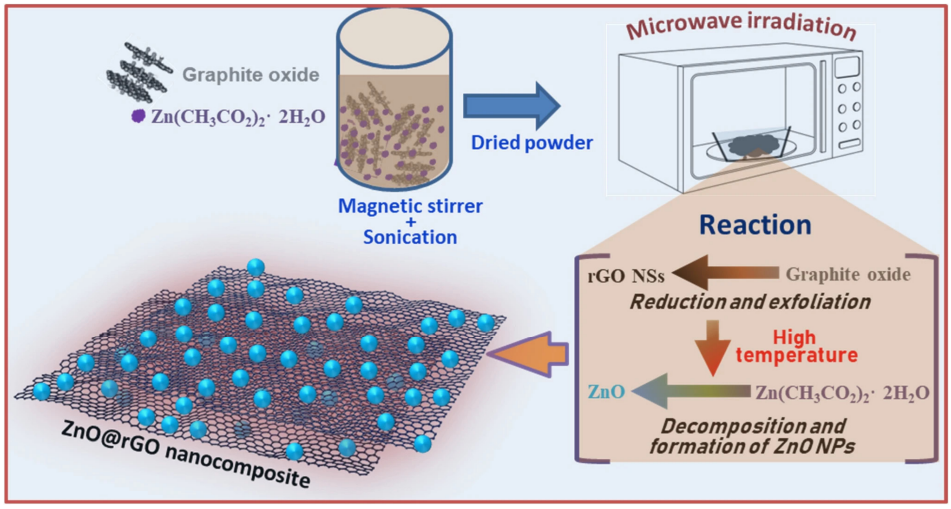

Figure 5. Schematic illustration for synthesis and formation of ZnO@rGO nanocomposites [79].

In addition to the graphene/inorganic nanocomposites, the microwave aspect also plays an important role in assisting the fabrication of graphene/polymer nanocomposites. Hou et al. [81] synthesized reduced graphene oxide/polystyrene (rGO/PS) nanocomposites by using microwave treatment to achieve the reduction of GO and the polymerization of styrene simultaneously. The accelerated monomer polymerization by microwave radiation facilitates the production of polymer-based dielectric nanocomposites with tunable dielectric constants, expanding their applications in energy storage. Aldosari et al. [82] conducted microwave-assisted preparation of polymethylmethacrylate–graphene (PMMA/RGO) nanocomposites and found that the composites obtained by microwave radiation had better morphology, superior dispersion, and higher thermal stability than those obtained by natural polymerization or the direct polymerization of free radical initiators. Based on the excellent properties of graphene, PMMA/RGO composite materials have significantly enhanced electrical, thermal, and optical properties, exhibiting promising applications as it pertains to energy storage materials, catalyst carriers, lightweight fillers, etc.

As a new material in the 21st century, graphene has fascinating properties in many aspects. However, its batch production is still challenged by complex processes, harsh reaction conditions, an inefficient exfoliation rate, and secondary pollution caused by the major wastewater discharge. Therefore, developing an efficient, simple, and controllable technology for graphene preparation is of great significance. The microwave-featured technology provides a novel, efficient, and simplified route for the preparation of graphene and graphene-derivative functional nanomaterials. Firstly, microwave-induced impurity gasification significantly enlarges the graphite layer space, which provides a favorable basis for the exfoliation process. Secondly, microwave-induced Joule heat and thermal shock effect can accelerate the intercalation and expansion steps, resulting in effective high-quality exfoliation and reduction of graphene. Lastly, the featured high-temperature environment and plasma effect facilitate surface chemical reactions to fabricate graphene-derivative functional materials. As an efficient technical route, microwave-assisted fabrication of graphene and graphene-derivative material has significant meaning for the value-added recycling of spent graphite.

6. Microwave-Assisted Preparation of Porous Graphene

Although graphene has outstanding properties, it has some inherent defects in practical applications. On the one hand, due to van der Waals forces and π–π stacking, graphene nanosheets are prone to restacking and agglomeration, greatly reducing the specific surface area and active sites. On the other hand, large-sized molecules or ions are unable to penetrate the well-structured graphene but transport and diffuse along the edges or junctions of the graphene nanosheets, resulting in long transport/diffusion paths and poor transport kinetics. In contrast, porous graphene with in-plane pores can not only effectively reduce agglomeration and increase contactable area but also expose abundant edges/active sites for ion storage, catalysis, and/or atomic doping/composite functionalization, as well as generate more channels for electrolyte penetration and ion transport, resulting in shorter diffusion paths and effective enhancement in ion transport performance, as illustrated in Figure 6. Therefore, to enhance the properties of graphene further and broaden its application areas, many studies focus on the preparation of porous graphene structures. It is worth noting that, similar to GO, spent graphite has oxygen-containing functional groups and structural defects, so it can be bonded to other atoms through sp, sp2, and sp3 hybridization orbitals, which makes it easier to build porous structures [83]. Developing effective and controllable synthetic methodologies of porous graphene is vital for expanding its potential applications.

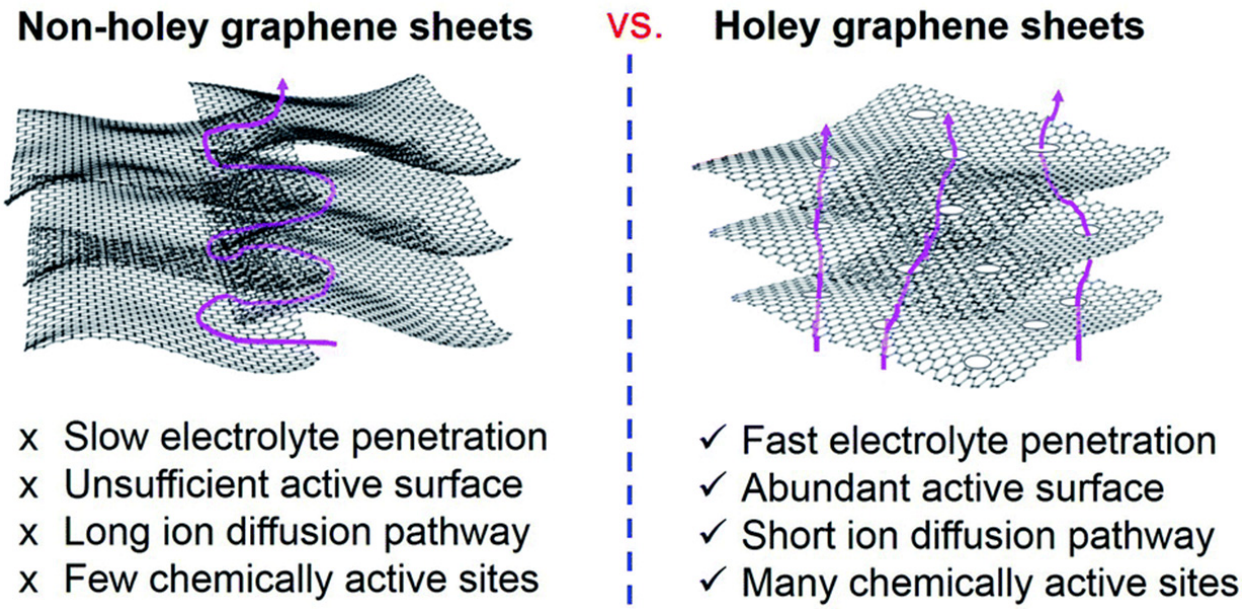

Figure 6. Schematic of the advantageous features of holey graphene sheets as compared with non-holey graphene sheets [84].

Currently, the methods for preparation of porous graphene include the template method [85], etching method [86], and chemical vapor deposition method [87]. Etching is the most accessible approach for large-scale preparation, but conventional chemical etching tends to destroy the graphene–carbon-based structure, resulting in poor conductivity of the obtained porous graphene. Notably, due to the absorbing coupled discharge effect caused by microwave action on carbon materials, which can produce a thermal shock effect with a large number of high-energy electrons and active species [88], microwave treatment has a significantly higher heating rate and enhanced/catalytic chemical reaction capabilities compared to traditional heating methods. Therefore, the potential exists to tailor microwave radiation to enhance the expansion of spent graphite as well as induce active etching to prepare porous graphene, proposing a solution to simultaneously realize efficient graphene stripping and controllable generation of in-plane pore structure to guarantee the quality of porous graphene. Wan et al. [89] utilized rapid microwave heating and the catalysis of active metal nanoparticles to prepare pore-size-controllable porous graphene (Figure 7). Based on the reduction capacity of graphite under microwave radiation, various metallic compounds (e.g., silver acetate, cobalt nitrate, ammonium molybdate, and copper nitrate) were reduced to active metallic nanoparticles, which can form the holey structure on the graphene layer by the etching reaction through the microwave heating process. Due to the fact that graphite can effectively absorb microwave energy to be heated rapidly, Zhao and He [90] synthesized hierarchically porous reduced graphene oxide (HPRGO) through catalytic oxidation by microwave combustion, utilizing graphite to ignite the reduction process (Figure 7). Notably, it was discovered that the porous structure and reduction degree of HPRGO are strongly influenced by the duration and power of microwave radiation. The prepared porous graphene can play a significant part in applications regarding energy storage, electrocatalysts, and photoelectron devices. For example, due to its good stability and high specific surface area, porous graphene can be used as electrode material for LIBs. The pores of porous graphene provide transport channels for lithium ions, and the edge structure is beneficial to improve the adsorption and diffusion efficiency of lithium ions [91].

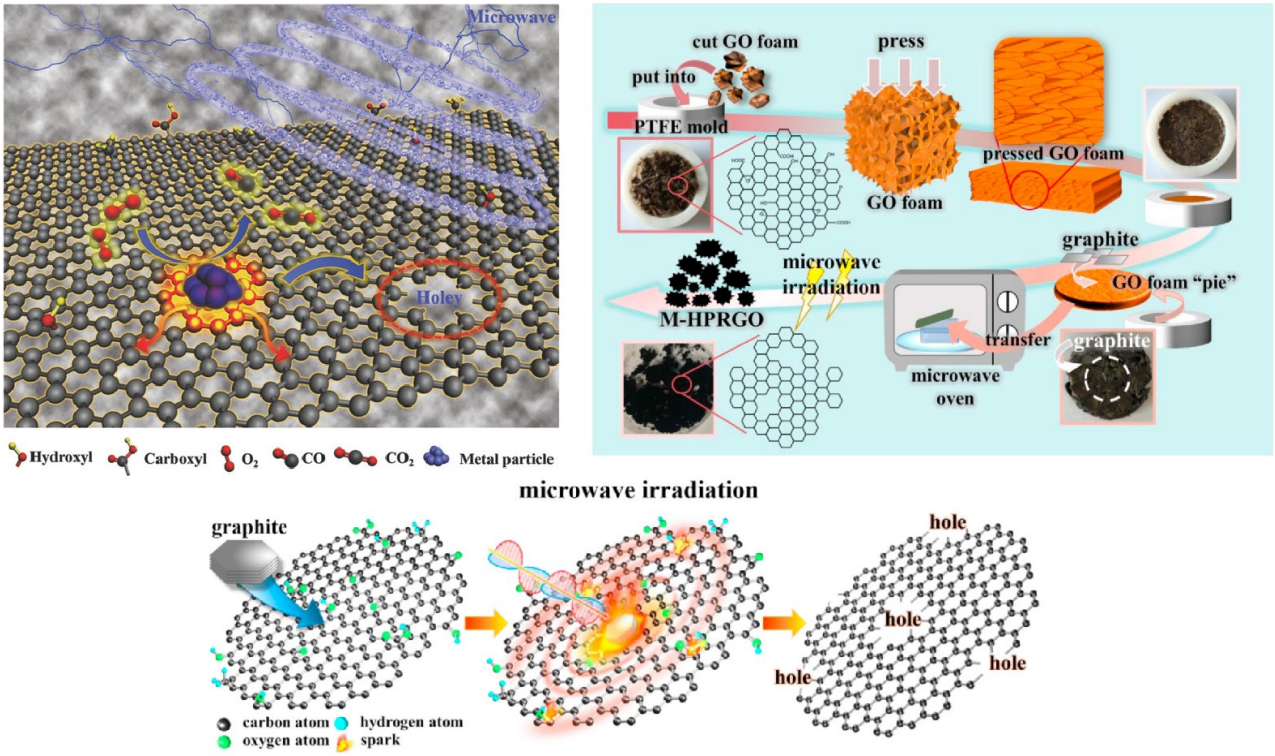

Figure 7. Mechanism schematic of the fabrication process for porous graphene [89], schematic synthesis procedure of hierarchically porous reduced graphene oxide (HPRGO), and mechanism schematic of microwave synthesis of HPRGO by graphite-ignited reduction propagation [90].

In summary, microwave radiation is instantaneous and easy to control, which is particularly significant for the synergy of conductivity and pore structure of porous graphene. As a result, microwave-assisted etching for the preparation of porous graphene is more efficient and controllable than other conventional methods. Furthermore, the obtained porous graphene has great application potential regarding energy storage, catalysis, chemical sensors, gas separation/storage, and other applications [91–93]. Microwave-assisted preparation of porous graphene is a more advanced and efficient method for the resource utilization of spent graphite.

7. Conclusions

In the background of green growth and sustainable development, the resource utilization of spent graphite is an urgent concern. Recycling spent graphite using microwave assistance is a promising strategy that can offer a novel, efficient, controllable, and energy-saving approach for the value-added utilization of spent graphite. Firstly, the rapid heating process and thermal shock effect of microwave–graphite interaction can lead to efficient removal of impurities, structure repair, and expansion of graphite layer spacing. Secondly, microwave thermal shock can provide an innovative method for efficient intercalation, expansion, exfoliation, and reduction of graphite. Finally, the synergy of the microwave thermal shock and the etching of active species can develop a facile method for the controllable preparation of porous graphene. To conclude, microwave-assisted treatment of spent graphite can achieve efficient preparation of GIC, EG, graphene and graphene-derivative materials, and porous graphene. These obtained materials can be applied in energy storage, catalysis, sensors, and other fields, which is of great significance to the resource utilization of graphite and the development of emerging industries.

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