Microwave-assisted Synthesis of Semiconductor Nanomaterials for Energy Storage

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Abstract: Semiconductor nanostructure has attracted tremendous attention due to its potential in electrochemical energy storage systems. The energy capacity is related to the properties of electrode materials. In this treatise, we will survey the recent advancement of the semiconductor nanostructures synthesized by microwave assisted method for electrode materials in electrochemical energy storage, and these nanostructures are found to show the improved electrochemical performance compared with the traditional synthesized methods.

Keywords: LIBs, microwave-assisted method, semiconductor, SIBs.

1. INTRODUCTION

Global warming and ever-growing energy consumption have become the focus of global concern. Development of electrochemical energy storage systems such as rechargeable batteries (lithium/sodium ion batteries, LIBs/SIBs) is considered as a promising choice to solve the energy crisis owing to their high capacity, long cycle life, and environmental friendliness [1-3]. Currently, most of the commercial cells use carbonaceous materials such as electrode materials. However, using carbonaceous material electrode limits the possibility of extracting higher energy density from the battery, which cannot satisfy the requirements of practical application [4]. Therefore, exploring other electrode materials with high specific capacity and excellent cycling stability for SIBs and LIBs remains a great challenge.

Recently, semiconductor nanostructures have attracted much attention due to their wide applications such as energy storage devices. Investigations have been carried out to prepare the semiconductor nanostructures via the conventional methods such as hydrothermal/solvothermal, sol-gel, coprecipitation, and surfactant-assisted methods for energy storage. However, they have several disadvantages such as high temperature, long reaction time, high energy consumption, nonuniform reaction conditions or requirement of special conditions [5]. Recently, microwave-assisted synthesis

has attracted great interest due to its rapid heating means [6]. Microwave irradiation as an inexpensive, quick, clean, and versatile technique can facilitate mass production in a short time with little energy consumption and form an intimate contact between the components [7-10]. Many semiconductor nanomaterials with different morphologies such as nanorods, nanowires, nanofibers, nanotubes, nanosheets and nanoparticles have been synthesized by the microwave-assisted method [11-23].

In this work, we highlight the recent progress in exploring various semiconductor nanomaterials via a microwave-assisted method. Application of these semiconductor nanomaterials in the energy storage for LIBs and SIBs is also demonstrated.

2. PRINCIPLES OF MICROWAVE-ASSISTED SYNTHESIS

Microwave irradiation is electromagnetic radiation with the frequency range of 0.3~300 GHz, corresponding to wavelengths of 1 mm~1 m. The industrial and domestic microwave apparatus for heating operates at a wavelength of 12.2 cm, corresponding to a frequency of 2.45 GHz to avoid the interference with telecommunication and microwave radar equipment. Microwave heating technology has been used for the synthesis of ceramic materials in 1975. The heating mechanism involves dipolar polarization and ionic conduction processes. The dipoles in the reaction mixture are involved in the dipolar polarization effect, and the charged particles in a sample contribute to ionic conduction [21, 24]. Microwave irradiation induces interaction of the dipole moment of polar molecules or molecular ionic aggregates with alternating electronic and magnetic fields, causing molecu-

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lar-level heating which leads to homogeneous and quick thermal reactions with low thermal gradient [25, 26]. In microwave irradiation process, the factors such as solvent type, concentration, and geometry of reaction vessel can influence the uniform and reproducible heating. The different solvents have different abilities to generate heat under microwave irradiation [27]. The ability of a given solvent to convert microwave energy into heat can be described by the loss tangent ($\tan \delta = \epsilon''/\epsilon'$), where ϵ'' is the loss factor, indicative of the efficiency with which the electromagnetic radiation is converted into heat, and ϵ' is the dielectric constant describing the ability of a dielectric material to store electrical potential energy in the electric field. Solvents can be divided into high ($\tan \delta > 0.5$), medium ($\tan \delta 0.1-0.5$), and low microwave absorbing ($\tan \delta < 0.1$) ones [28]. A reaction medium with high loss factor is required for efficient absorption and rapid heating [29]. For example, ethanol has a higher loss tangent, thus shows better the microwave absorption, leading to a more rapid heating [27]. Compared with other conventional heating methods, microwave synthesis has been considered as an efficient method for higher heating rate and selectivity, improved reproducibility, lower reaction temperature, less reaction time, and automatization and high throughput synthesis [30-32].

3. MICROWAVE-ASSISTED SYNTHESIS OF SEMICONDUCTOR NANOMATERIALS FOR LIBs/SIBs

LIBs are composed of three major components: cathode, anode, and electrolyte (Fig. 1). The energy capacity is related to the properties of electrode materials. Currently, the graphite is frequently used in the anode materials for LIBs owing to its long cycle life, low cost and abundant material supply. Li ions are extracted from cathode and simultaneously inserted into the graphite anode, coupling with negatively charged electrons to keep overall charge neutrality [32] during the charging process. During the discharging process, Li ions are reversibly extracted from the anode and simultaneously inserted into the cathode [32]. However, the use of graphite anode electrode limits the possibility of extracting higher energy density from the battery, which cannot satisfy

the requirements of practical application. Furthermore, the high cost and possible supply risk of Li terrestrial reserves have gained more attention. As a potential alternative, SIBs have recently attracted much attention due to the abundance of sodium resources, lower cost, relatively low toxicity of sodium, and the similar chemistry between sodium and lithium. Unfortunately, the diameter of sodium ion is about 55% larger than that of the Li ion, and only a few host materials for LIBs are suitable to allow the sodium ion intercalation and deintercalation. Therefore, exploring electrode materials with high specific capacity and good cycling stability for LIBs/SIBs remains a great challenge.

Intensive efforts have been made to explore new electrode materials involving alloy [33] and semiconductor materials [34] with enhanced charge capacity, high energy density, long cycle life and environmental stability for LIBs/SIBs. Semiconductor materials prepared by microwave assisted method such as TiO_2 , SnO_2 , Fe_2O_3 *et al.*, have been envisaged as anode materials owing to their high surface area, porosity, etc. In contrast to graphite materials, lithium storage in semiconductor materials such as Fe_2O_3 is mainly achieved via a reversible conversion reaction, by forming Fe nanoparticles dispersed in Li_2O matrix [35]. Unfortunately, they suffer from poor cycling performance due to the large volume changes and serious aggregation of particles during repeated Li insertion and extraction reactions [36]. Reducing the size and constructing open channels in the electrode materials have been suggested to overcome the aforementioned problems [37, 38]. Recently, nanostructured materials have attracted much interest because of their novel physical and chemical properties compared to those of their bulk counterparts. Nanostructured semiconductor can accommodate the strain during cycling, and reduce the diffusion pathway for electronic/ionic transport, leading to the excellent power density. Another attractive strategy is to design and develop hybrid electrode materials based on carbon matrix such as carbon nanotubes, carbon fiber and graphene, which not only maintain the structural integrity of the composite electrode by preventing large volume changes and particle agglomeration but also increase the conductivity [39]. In this section, we summarize various semiconductor nanomaterials via a microwave assisted synthesis for LIBs/SIBs. They show the improved electrochemical performance compared with the ones synthesized via conventional methods.

3.1. Semiconductor Oxide

TiO_2

TiO_2 with a theoretical capacity of 335 mAh/g is considered as the most promising candidate for LIBs due to its high operating voltage (~ 1.5 V vs Li/Li^+), excellent safety characteristics, abundance, and nontoxicity [40, 41]. Many research groups have carried out to study the TiO_2 nano/microstructures such as nanosheets, hollow nanostructures, nanowires, nanotubes, nanospindles, and quantum dot for LIBs [40].

Single-crystal-like TiO_2 with honey-like pores shows the large surface area and excellent structural durability, which is favorable for shortening the diffusion length of ion transport and reducing volumetric change. Zhang et al. [3] fabricated the single-crystal like anatase TiO_2 with “honeycomb”

Fig. (1). Schematic representation of the most commonly used LIBs based on anodes and cathodes.

porous structure via a microwave assisted approach using a microwave digestion system (Ethos TC, Milestone) at 150 °C for 90 min. Field emission scanning electron microscopy (FESEM) images (Fig. 2a, b) show that the prepared TiO₂ shows the honeycomb-like nanosphere with open porous structure. The average diameter of prepared TiO₂ is 700 nm. Transmission electron microscopy (TEM) images (Fig. 2c,d) show a core-corona architecture, and the core is much denser than the corona, indicating the formation of dense core and porous surface. Such single crystal-like porous anatase TiO₂ shows high surface area, large internal voids, and robust structure, which grants more lithium insertion sites, larger space to buffer the volume change, and reduced effective lithium ion diffusion distance during the charge-discharge process. The as-prepared TiO₂ exhibited a charge capacity of 155.8 mAh/g at a current density of 200 mA/g, and a high coulombic efficiency of 99.8% in the first cycle. A capacity of 100 mAh/g can still be delivered after 100 cycles at a current density of 1000 mA/g. Therefore, the porous anatase TiO₂ single crystal architectures showed stable cyclability at high current density, better reversibility, and high Coulombic efficiency for lithium storage.

Fig. (2). FESEM images (a,b) and TEM images (c,d) of porous TiO₂ single crystals obtained after 90 min microwave irradiation [3]. (Reprinted with permission from ref. [3]. Copyright (2012) American Chemical Society).

Yoon *et al.* [4] further prepared the anatase, rutile, and brookite of TiO₂ via a facile microwave assisted solvothermal process without surfactants in an Anton Paar microwave synthesis (Synthos-3000) with a power of 600 W at 190 °C for 30 min, employing TiCl₄ or TiCl₃ as precursors in various alcohol. The morphology, crystal structure, and crystallite size of TiO₂ are related to the Ti/Cl ion concentration, reaction pH, and size of the alcohol molecule. The rutile TiO₂ spheres synthesized using TiCl₄ in octanol exhibited the best electrochemical performance with a capacity of > 200 mAh/g at a current density of 30 mA/g after 100 cycles and high rate capability due to the nanorod-building morphology and mesoporosity of TiO₂ spheres, which can provide the good electrical contact, accommodates the strain smoothly, and facilitates facile lithium ion diffusion.

SnO₂

Owing to the high theoretical specific capacity of 782 mAh/g of SnO₂, it has attracted much interest as a promising anode material for LIBs. Wang *et al.* [6] synthesized the porous SnO₂ nanotubes by a rapid microwave-assisted hydrothermal method in a microwave system (CEM Discover S-Glass) at 150 °C for 30 min followed by annealing at 500 °C for 1 h in air. As shown in Fig. (3a and b), the SnO₂ shows the short tubes morphology with length, diameter, and wall thickness ranging from 0.5 to 1.5 μm, 200 to 400 nm, and 50 to 100 nm, respectively. The SnO₂ nanotubes comprise interconnected nanocrystals of ~8 nm in diameter along with abundant mesopores formed among adjacent nanocrystals (Fig. (3e and f)). The SnO₂ nanotubes showed the charge capacity of 1258 mAh/g at 0.1C owing to their unique geometry and porous structure.

Fig. (3). (a, b) SEM images, (c) TEM image, (d) SAED pattern, (e) magnified TEM image, and (f) HRTEM image of the as-synthesized SnO₂ product [6]. (Reproduced with permission from ref. [6]).

Yoshinaga *et al.* [42] synthesized the ultrafine SnO₂ nanoparticles via a microwave-assisted synthesis in a household microwave oven (Shikoku Instrumentation Co., Ltd.) at 100 °C for 5 min. Nanosized SnO₂ particles with the diameter of 5 nm exhibited ellipsoid shapes. SnO₂ nanoparticles exhibited the initial lithium insertion capacity of 1670 mAh/g, which was significantly larger than that of a speci-

men synthesized via the conventional method. The capacity retention of the SnO₂ nanoparticles was about 60% from the 2nd to the 50th cycle.

Co₃O₄

Recently, Co₃O₄ with special textural characteristics, such as porous Co₃O₄ nanotubes, nanowires, nanoneedles, and nanorods, has been explored as a promising anode material for LIBs due to its high capacity (890 mAh/g) [43]. Wang *et al.* [44] prepared the Co₃O₄ via a rapid microwave-assisted method in a microwave accelerated reaction system (MARS-5, CEM Corporation, USA) followed by thermal treatment. The porous Co₃O₄ nanowire exhibited excellent capacity retention and rate capability at high current density. The reversible capacity of 600 mAh/g could be maintained after 100 cycles at the high current density of 400 mA/g.

Fe₂O₃

Many research demonstrated that nanosized Fe₂O₃ exhibits higher capacity for LIBs, whereas it is difficult for conventional large particles to use as an active material due to an irreversible phase transition at the first discharge process [45]. Kijima *et al.* [46] synthesized the ultrafine α -Fe₂O₃ nanoparticles via a microwave heating in a household microwave oven (Shikoku Instrumentation Co., Ltd.). The α -Fe₂O₃ nanoparticles were used as anode in LIBs and showed good rechargeable capacity of 150 mAh/g. Hematite porous α -Fe₂O₃ nanostructures has a higher specific capacity of 264 mAh/g at a higher current density of 5 C. Furthermore, in SIBs, it exhibited a reversible capacity of 300 mAh/g with excellent cycle ability and Coulombic efficiency at 0.1 C up to 100 cycles [47].

NiO

NiO has been widely used in fuel cells, solar cells, LIBs and supercapacitors owing to the high theoretical capacity (718 mAh/g), higher density (6.81 g/cm³) than that of graphite (2.268 g/cm³), nontoxicity and low cost [48]. Rai *et al.* [10] prepared the NiO nanoparticles by a rapid microwave-assisted method in a conventional microwave oven (MM-M 301, LG-Korea) with a power of 1000 W for 10 min, followed by annealing at 600 °C in air. The NiO nanoparticles, which showed the irregular shaped morphology with the sizes of 50–60 nm, had a large initial discharge capacity of 1111.08 mAh/g at 0.03 C and retained 80% of initial capacity (884.30 mAh/g) after 20 cycles with 98% of Coulombic efficiency. More than 32% of the capacity (253.1 mAh/g) was retained even at a high current rate of 3.7 C. The enhanced electrochemical performance was due to the high specific surface area, good electric contact among the particles and easier lithium ion diffusion. The NiO nanorod cluster also showed a high reversible capacity of 725 mAh/g at a constant current density (100 mA/g). The reversible capacity still maintained 584 mAh/g after 16 cycles [49].

3.2. Semiconductor Sulfides

Sb₂S₃

Sb₂S₃ is a kind of semiconductor with high photosensitivity and thermoelectric power for the application of solar en-

ergy conversion and LIBs [50]. Yang *et al.* [51] successfully synthesized Sb₂S₃ via microwave irradiation by the reaction of SbCl₃ and CS(NH₂)₂ with PVP as the surfactant in a domestic microwave oven for 15 min. The as-prepared Sb₂S₃ sample showed the rod-like structure with the diameter of 30–50 nm, and showed a large first discharge capacity of 677.89 mAh/g.

Cu₂ZnSnS₄

Cu₂ZnSnS₄ (CZTS) consists of Cu, Zn, and Sn elements that are electrochemically active toward lithium, and thus is regarded as a promising anode material for LIBs. Yang *et al.* [52] reported a simple microwave-assisted method to synthesize the CZTS nanocrystals in a CEM Discover microwave reactor with a power of 220 W at 260 °C. Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, SnCl₄·5H₂O, and sulfur powder were used as starting materials. The as-prepared CZTS nanoparticles with mono-dispersed size of about 10–15 nm was applied as anode material for LIBs. The CZTS nanocrystals anode showed a reversible capacity of 288 mAh/g at 0.1 A/g current density, and still maintained capacity retention of 81 % after 30 cycles. The CZTS anode had a good reversibility and the structure of the electrode was stable even under high rates cycling.

3.3. Semiconductor Composites

Pure semiconductor suffers from poor cycling performance resulting from the huge volume changes during Li insertion and extraction processes, which lead to pulverization of the electrode and electrical disconnection of the active materials. Recently, an attractive option is to design and develop composite materials base on pure semiconductor to solve the problem. Many studies have been reported that embedding semiconductor in the graphene nanosheet matrix can enhance the electrochemical performance of semiconductor in LIBs/SIBs [53, 54]. The enhanced electrochemical performance of graphene or CNTs-based composites can be attributed to the synergistic effect from the semiconductor and graphene or CNTs, which is similar to those reported results [55, 56]. Firstly, the conductive network structure in the graphene or CNTs-based composites can ensure efficient and continuous electron transport [57, 58]. Secondly, the graphene or CNTs can act as the buffer layer to accommodate the volume expansion and prevent pulverization of pure semiconductor during charge and discharge process [57, 59]. Finally, the large surface area of the graphene or CNTs-based composites can provide a sufficient electrode-electrolyte interface to adsorb lithium/sodium ion and facilitate the rapid charge-transfer reaction. However, excessive graphene will stick together and significantly block the channels for sodium ion diffusion, leading to the decreased electrochemical performance of graphene-based composites [60].

Qin *et al.* [60] reported a simple microwave-assisted method to synthesize the MoS₂-graphene composites by reduction of graphene oxide in MoS₂ precursor solution with maximum microwave irradiation power of 100 W for 10 min at 150 °C using a microwave system (Explorer48, CEM Co.), followed by annealing in N₂/H₂ atmosphere at 800 °C for 2 h. As shown in Fig. (4), the MoS₂ and RGO are interconnected tightly, forming a three dimensional hierarchical nanostruc-

Fig. (4). (a) HRTEM image and (b) SAED pattern of MoS₂-graphene composites [60]. (Reproduced with permission from ref. [60]).

tures. This is favorable for the fast collection and conduction of electrons and diffusion of sodium ions during the charge-discharge process. At the optimum RGO loading, the MoS₂-graphene composites exhibited a stable discharge capacity of about 305 mAh/g at current density of 100 mA/g after 50 cycles.

The same group [61] also fabricated the Fe₂O₃-graphene composites via a facile microwave-assisted method using a microwave system with maximum microwave irradiation power of 100 W for 10 min at 150 °C using a microwave system (Explorer 48, CEM Co.), and investigated as anode material for SIBs. The Fe₂O₃ nanoparticles with diameters of 4–8 nm are uniformly anchored on RGO sheets in the Fe₂O₃-graphene composite to form a conductive network structure (Fig. 5). As shown in Fig. (6), Fe₂O₃-graphene composite with 30 wt.% graphene exhibits a maximum reversible capacity of 289 mA h/g at a current density of 50 mA/g after 50 cycles and excellent rate performance due to the synergistic effect between Fe₂O₃ and graphene. A higher capacity of ~310 mA h/g at a current density of 100 mA/g after 150 cycles was achieved for the Fe₂O₃-graphene composites prepared by Zhang *et al.* [62].

Fig. (5). HRTEM images of (a-b) Fe₂O₃ and (c) Fe₂O₃-graphene composites; (d) SAED pattern of Fe₂O₃-graphene composites [61]. (Reproduced with permission from ref. [61]).

Fig. (6). Cycle performances of RGO, and Fe₂O₃-graphene composites electrodes at a current density of 50 mA/g [61]. (Reproduced with permission from ref. [61]).

Unfortunately, the graphene has poor electrical conductivity, which is because that incomplete chemical reduction is frequently observed in chemically reduced graphene oxide process. Attempts to combine highly conductive carbon nanotubes (CNTs) and graphene have been reported in efforts to obtain a hybrid with superior electrochemical, electrical or catalytic properties. Therefore, the incorporation of CNTs into SnO₂-graphene composites to form ternary hybrid materials should be a promising method to design advanced anode materials for LIBs. Chen *et al.* [63] developed a facile one-step microwave assisted method to fabricate the SnO₂-graphene-CNTs composites using a microwave synthesis system (Explorer-48, CEM, USA) at 150 °C with a microwave irradiation power of 100 W for 10 min. As shown in Fig. (7), graphene sheets show the two-dimensional sheet structure with wrinkles, and SnO₂ nanoparticles with diameters of 3–5 nm are densely attached to the RGO sheets. The CNT weaves between RGO and SnO₂ nanoparticles to build a network structure, which favors electron transfer between them. SnO₂-graphene-CNTs composites with 60 wt.% SnO₂ showed a maximum capacity of 502 mA h/g at 100 mA/g after 50 cycles. A capacity of 344 mA h/g was maintained even at a high current density of 1000 mA/g. The enhanced electrochemical performance is due to the synergistic effect of SnO₂, RGO and CNTs, in which RGO sheets support SnO₂ nanoparticles and CNTs act as wires conductively connecting the large RGO sheets together.

Fig. (7). TEM images of SnO₂-graphene-CNTs composites [63]. (Reproduced with permission from ref. [63]).

4. SUMMARY AND OUTLOOK

Semiconductor materials synthesized by microwave assisted method have been reviewed for LIBs/SIBs. Compared

with other conventional heating, microwave synthesis offers several advantages such as rapid heating, higher reaction rate and selectivity, lower reaction temperature, shorter reaction time, homogeneous thermal transmission, and phase purity with better yields due to the thermal and non-thermal effects of microwave, i.e. superheating, polarization, dielectric properties, hot spot formation, nuclear spin rotation and spin alignment [64]. However, there are several challenges remaining. One of the major drawbacks is the equipment cost. With the technique development, less expensive equipment should become available [28]. In addition, the short penetration depth of microwave irradiation into the medium limits the size of the reactor, which will limit the application of microwave in the synthesis of semiconductor nanomaterials for energy storage. Another crucial challenge is to understand the effect of microwave heating on nucleation and growth of semiconductor nanomaterials [31]. All in all, as a promising synthesis technique, microwave-assisted synthesis has been becoming more and more popular method for the preparation of semiconductor nanomaterials for the wide application of energy storage field.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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