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Recent Progress of Graphene-Polyaniline Complex Electrode Materials for Supercapacitor

Dongyun Su, [1] and Jun Ma [2,3,*]

[1] Departments of Mechanical Engineering, Nantong Vocational University, Jiangsu, China
[2] School of Aviation and Transportation, Jiangsu College of Engineering and Technology, Jiangsu, China
[3] Institute of Materials Engineering, College of Engineering and Applied Sciences, Nanjing University, Jiangsu, China

Abstract. With the increasing energy consumption, it is urgent to find low cost, environmental protection and long-life energy storage equipment. With ultracapacitors, graphene material was attracted wide attention for their advantages about high specific capacitance, excellent rate performance and good electrical conductivity. The preparation methods, electrochemical properties and related mechanisms of graphene materials were summarized, with the purpose of studying the effects of different structures of graphene materials on the performance of supercapacitors, and to find graphene-based materials with excellent performance. Finally, the problems existing in graphene-complex electrode were analysed, and the future research focus was prospected.

1. Introduction

For supercapacitors, many studies have focused on electrode materials with high specific capacitance in electrolyte. The supercapacitor electrode was divided to carbon, metal oxide and conductive polymer [1]. For electric double-layer capacitors, the electrode materials are mainly with high specific surface area, which store energy through electric double-layer [2]. The electrode materials of Faraday quasi capacitor are conductive polymers and metal oxides. The way of energy storage of these electrode materials is through rapid charge and discharge.

The research on carbon electrode has been developed for more than 40 years [3]. The research mainly focuses on the improvement of their performance. At present, the technology has also been gradually industrialized [4]. Carbon based materials that can meet the requirements mainly include graphene, network structured activated carbon and carbonization products of some organic substances. The difference between micro and nano structures, the dimension change from 0 to 3, can reflect the performance of materials through different structures. Among these carbon (carbon) materials, carbon nanotubes and graphene have good research potential [5].

Conductive polymer, also known as conductive polymer material, is a new functional material with excellent performance, which has flexible mechanical properties and processability of polymer [6]. Compared with inorganic electrode materials, conductive polymer electrode materials have high specific energy and large voltage characteristics. The power supply used in aerospace shows its unique performance [7]. The main content of this article is the latest development of graphene based polyaniline composite electrodes.

* E-mail addresses: mjsdy@126.com

2. Graphene Based Capacitors

The energy issue is a global issue and a strategic issue for many countries. In addition to production capacity, it also includes energy storage. In order to meet the growing needs of life, the global demand for energy storage is increasing. With the rapid development of supercapacitors, the application of graphene is becoming increasingly widespread.

The synthesis method of graphene composite electrode and its application in supercapacitors were studied by Minisha and colleagues. Lee and colleagues [8] improved electrode performance by changing the ratio of graphene oxide and activated carbon to prepare their composite materials. In addition, functionalization of reduced graphene oxide using ionic liquids enhances the compatibility and wettability between the electrolyte and the electrode. The electrochemical performance of F-rGO and AC (F-rGO/AC-15) composite supercapacitors was evaluated through electrochemical testing. The energy density of AC supercapacitors is 50.1 Wh kg^{-1}, while the energy density of F-rGO/A-15 composite materials (15:85, w/w%) is as high as 146 Wh kg^{-1}, while the charge transfer resistance is only 0.41 Ω.

The capacitance of graphene composite electrodes depends largely on the pseudo capacitive material, the method of composite, and the morphology of the composite [9].

For modification of graphene sheets, the most common and popular approach is their decoration with zero-dimensional nanoparticles. It may possible that, after combination of these two promising nanomaterials i.e. combination of 2D and 0D/1D/2D structures, a novel nano-hybrid material could be fabricated having both the property of 2D graphene sheets has entirely different property i.e. 3-D nanomaterials (Figure 1). It is also reported that the introduction of metal nanoparticles into dispersed graphene sheets can prevent the aggregation of graphene sheets to give a mechanically graphene with very high surface area, improved mechanical property and electrical conductivity [10-13]. The in situ chemical reduction method is most popularly used strategy for synthesis of graphene-metal nanohybrid. Herein, the metal precursors are directly reduced in the presence of GO or RGO sheets by using reducing agent to give the graphene based nanohybrid [14].

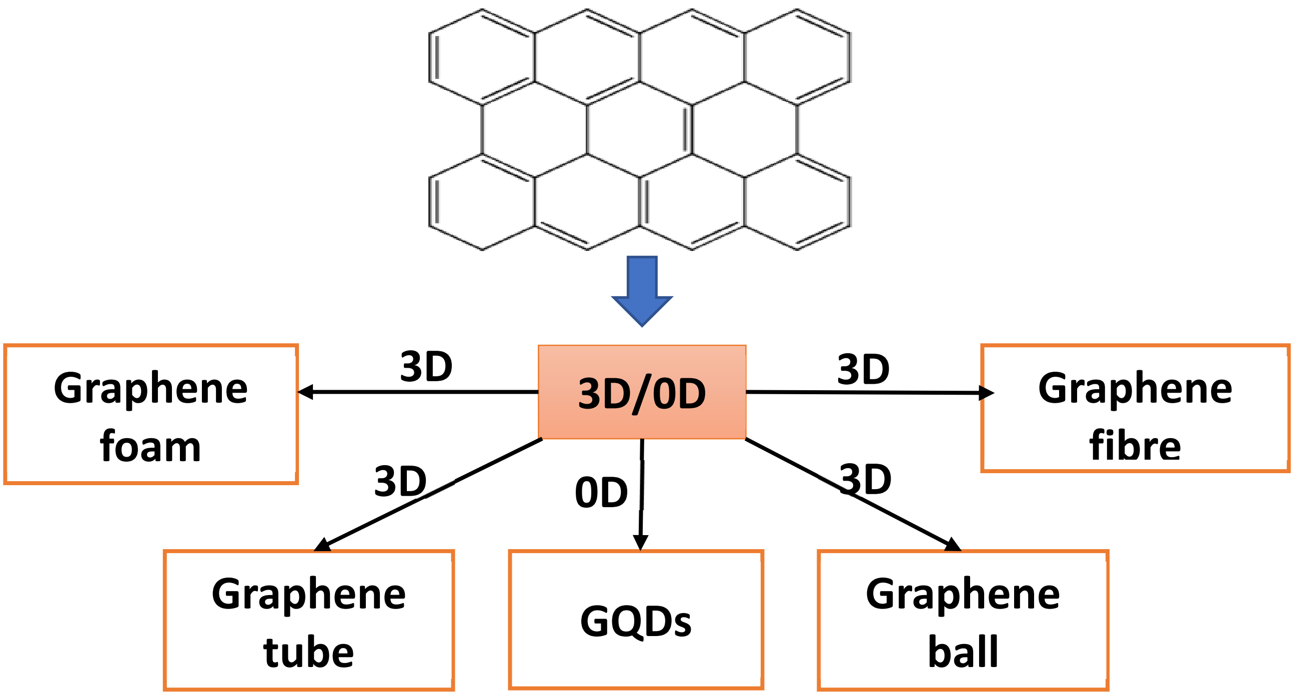

Figure 1 Schematic representation showing the conversion of 2D graphene sheet to 3D dimension nanomaterials.

3. Graphene-Polyaniline Composite Based Capacitors

Polyaniline has high pseudo capacitance as supercapacitors materials. But it was not stable in cycling. To overcome this defect, graphene has been used as a composite material to alter cyclic performance [15-17]. It is compounded with polyaniline, which has a simple synthesis method and high conductivity, as an electrode material. Polyaniline is capable of self-degradation due to its unstable structure [18]. However, the properties of polyaniline are enhanced when it is combined with other materials, especially carbon nanomaterials. In addition, graphene sheets provide active sites for the attachment of polyaniline, PANI co transports high capacitance and admirable electron transfer pathways for the growth of PANI. Due to the brittleness of polyaniline-based composites, the successful preparation of flexible composite films is still a difficult problem. Polyaniline is an excellent organic conductor with good environmental stability and biocompatibility. It has a greater ability to store electric charges. Only pseudopactor materials are limited by their low cycle life, stability, and high resistance values. The main characteristics of polyaniline are good conductivity, low cost, simple manufacturing, and good environmental stability. The synergistic effect of graphene/polyaniline is shown in Figure 2. Graphene was sulfonated to overcome shortcomings such as the tendency of graphene sheets to aggregate and stack. However, the lack of stability of conductive polymer-based supercapacitors has been observed during the long cycle of charge and discharge. Sulfonated graphene reduces structural changes in polyaniline [19]. The nanocomposite material is synthesized by interfacial polymerization, and the minimum distance of ion diffusion forms a low resistance.

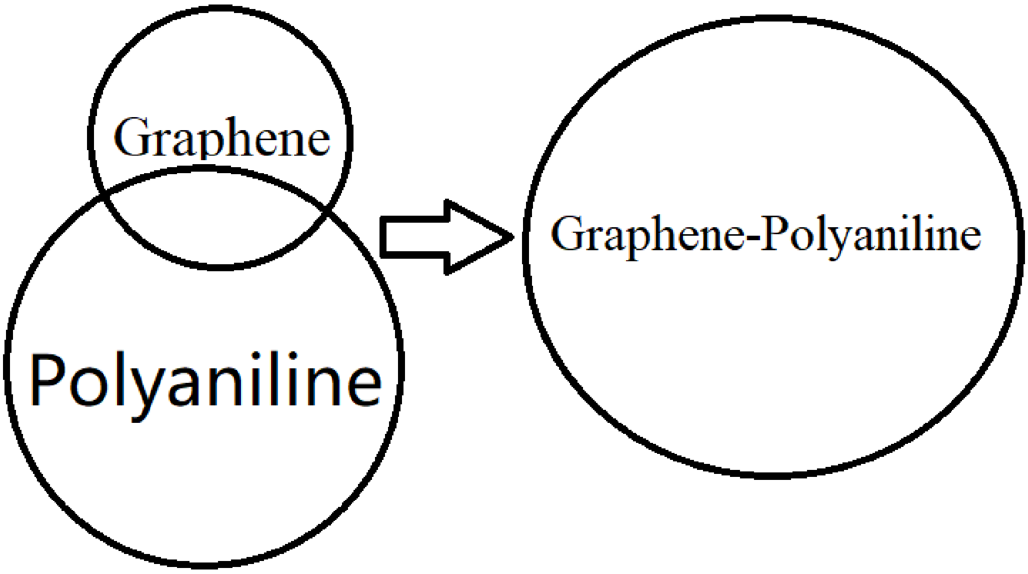

Figure 2 Graphene/polyaniline composites

Nasir A[20] reported conductive nano-hybrid material made by grafting polymerization on γ-radiated graphene oxide (GO). In situ polymerization of aniline was achieved in the presence of graphene oxide. By changing the concentration of monomers, initiators, and surfactants to control the grafting rate, aniline can be polymerized in situ. Under the optimal reaction conditions, the grafting rate of polyaniline (PANI) reached 670%. In addition, polyaniline grafted graphene oxide (GO-g-PANI) nanocompounds were analyzed by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and thermogravimetric techniques. The optimized nanohybrid has 63 S/cm electrical conductivity, which is better than GO substrate. The X-band electromagnetic interference shielding effect of the nano-hybrid material is up to 36.2dB, which is 187.3% better than that. It was due to the high graft rate of polyaniline on GO in grafted nano-hybrids. The developed conductive nanocompound is light in weight and has great potential as an electromagnetic interference [21].

3. Summary

Graphene has attracted great interesting in energy storage (supercapacitor, lithium ion battery, fuel cell, etc.) with its unique porous structure and electronic properties. In addition, more and more researchers found new functional materials related to porous graphene, and have made some good achievements. It is a continuous optimization process to explore new three-dimensional porous graphene based materials with comprehensive electrochemical properties. We firmly believe that these novel hybrid materials based on three-dimensional porous graphene will bring ring interesting results and further promote new applications of supercapacitors.

The following aspects will become the focus of future research:

(1) Functional treatment of GO through physical or chemical methods to improve its structural properties.

(2) Find a better way to synthesize materials and GO, and improve the performance of composites.

(3) Study on electrochemical properties of flexible graphene based integrated device.

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