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Review

High-performance supercapacitors based on polyaniline–graphene nanocomposites: Some approaches, challenges and opportunities

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ABSTRACT

A simple electrochemical reduction procedure can be applied to nanostructured composite films of polyaniline (PANI) and graphene oxide (GO), which results conversion of GO into reduced GO (rGO) with improved electroactivity of the PANI composite films. These also suffer from certain drawbacks like cyclic stability and lesser electrochemical properties. Three-dimensional hollow balls of graphene/polyaniline (3D-HBGP) hybrid and poly(methyl methacrylate) (PMMA)/polyaniline, sulfonated graphene/polyaniline (SG/PANI) and colloidal graphene oxide/polyaniline (PANI CGO) with high energy density 24.3 W h kg^{-1} and power density 28.1 kW kg^{-1} are good candidates for this purpose. This review summarizes developmental stage of different nanocomposites based on graphene and polyaniline.

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Introduction

Electronic technology has rapidly progressed during the past few decades. There is more emphasis on making better, faster and smaller electronic devices for different applications to keep pace with fast developing modern life. Presently, almost all electronic devices are made-up from semiconductor silicon. Advanced silicon chip can store 16 million bits of information within an area less than 1 cm^2, but there is a practical limit to the density of stored information in a chip. If the size of chip is decreased further, then there is a possibility of overheating between electronic components, which can affect their performance adversely. The best possible way to overcome this limitation is to use organic materials such as proteins, pigments, conducting polymers (CP) *etc.* in place of conventional semiconductors to carry out the same functions that are at presently being performed. This approach led to the evolution of an interdisciplinary field, called molecular electronics (ME). This is so named because it uses molecules to function as switches and wires. ME is a term that refers to both; the use of molecular materials in electronics and electronics at molecular level. Among organic materials, conjugated polymers (CPs) have attracted much attention for their possible applications in ME devices because of their unique properties and versatility [1,2]. The first conjugated polymer, polythiazyl $(SN)_x$, was discovered in 1975, which possesses metallic conductivity and becomes superconductor at 0.29 K. However, the idea of using polymers for their electrical conducting properties actually emerged in 1977 with the findings of Shirakawa et al. that the iodine doped trans-polyacetylene, $(CH)_x$, exhibits conductivity of 10^3 S cm^{-1}. Since then, a momentum was gained by this field and an active interest in preparing other organic polymers possessing this property was initiated [2]. As a consequence, other CPs having π–electron conjugated structure (conjugated polymers), such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), polyfuran (PFu), poly(*p*-phenylene) and polycarbazole have been synthesized to explore this possibility in electronic devices. CPs and their applications offer the advantages of lightweight, flexibility, corrosion-resistivity, high chemical inertness, electrical insulation and the ease of processing.

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. The compound was discovered over 150 years ago. Since then, polyaniline has captured the intense attention of the scientific community; however, this interest is mainly due to the discovery of high electrical conductivity of PANI. Amongst the family of conducting polymers and organic semiconductors, polyaniline possesses attractive processing properties. Due to its rich chemistry, polyaniline is one of the most studied conducting polymers in last few decades. Aniline is the monomer of polyaniline, which was obtained first time in 1826, from the pyrolytic distillation of indigo and was called “Krystallin” because it produced well formed crystalline salts with sulfuric and phosphoric acid [3]. Letheby (1862) also obtained colorless oil from indigo, called it aniline from the Spanish word anil (indigo), and oxidized it to polyaniline (PANI) [4].

PANI is a well studied material for supercapacitor due to its low cost, high conductivity and easy synthesis [5,6]. Ordered nanostructures of PANI show a great potential for good cycling stability, high specific capacitance and excellent rate capability because they shorten the diffusion path for ions, enlarge the specific surface area and accommodate the strain caused by the charge–discharge process [7].

Graphene is pure carbon in the form of a very thin and nearly transparent sheet, which is one atom thick. It is remarkably strong in spite of its very low weight (about 100 times stronger than steel) and it conducts heat and electricity with great efficiency. Technically, graphene is a crystalline allotrope of carbon with 2-dimensional properties. Carbon atoms are densely packed in a regular sp^2-bonded atomic-scale chicken wire (hexagonal) pattern in graphene. Graphene and chemically modified graphene have attracted attention of the researchers due to their high surface area, extraordinary mechanical properties and excellent conductivity [8]. Supercapacitors are also called ultracapacitors and electric double layer capacitors (EDLC) capacitors. These have capacitance values greater than any other capacitor type available today (Fig. 1). The advantage of using graphene as a part of electrode material, for supercapacitors, is their higher specific capacitance value (10–135 F g^{-1}) [7]. Supercapacitors have been proposed as the most promising energy storage device of this century. These can be used in digital cameras, flashlights, portable media players, automated meter reading, particularly where extremely fast charging is desirable.

Wang et al. [9] reported an *in situ* anodic electrochemical polymerization of aniline on graphene paper and achieved 233 F g^{-1} electrochemical capacitance for the composite. Zhang et al. [10] achieved specific capacitance as high as 480 F g^{-1} at a current density of 0.1 A g^{-1} for polyaniline doped graphene composite. Chemical modification of graphene has been carried out to achieve homogeneous aqueous suspension as well as to improve electrical and mechanical properties. Park et al. [11] reported a route to produce homogeneous aqueous suspension of chemically modified graphene, which shows good electrical conductivity, when fabricated as a paper material.

Graphene oxide based nanocomposites were prepared through *in situ* polymerization of aniline and pyrrole to study the interaction of graphene oxide with polyaniline (PANI) and polypyrrole (PPy) [12]. Moreover, the binding energy of polypyrrole–graphene oxide was found to be higher than polyaniline–graphene oxide because of the absence of oxygen containing functional groups.

Electrochemical reduction procedure

A variety of chemical methods are available to fabricate ordered nanostructures of PANI including template preparation [13], self-assembly [14], wet chemical process [15] and electrochemical polymerization [16]. The electrochemical polymerization enables active materials to be directly deposited on electrodes, resulting in uniformity, good adhesion and a compact interface compared with other three methods relying on the removal of templates or using binder materials. Composite materials of electrically conducting polymers (ECP) and graphene [17], graphene oxide [18] and reduced graphene oxide (rGO) [19] have gained a lot of interest due to the synergistic effect of these materials. Their composite with electrically conducting polyaniline (PANI) has been extensively