Hierarchical assembly of graphene/polyaniline nanostructures to synthesize free-standing supercapacitor electrode

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ABSTRACT

Free-standing composite films based on graphene/polyaniline (PANI) nanostructure were synthesized for supercapacitor application. First, polyaniline nanospheres were prepared by microemulsion polymerization, followed by the incorporation of graphene oxide nanosheets by hierarchical organization. The cationic PANI nanospheres were attached to the anionic GO sheets by electrostatic interaction and hierarchical deposition of GO/PANI nanostructures on a membrane filter via targeted self-assembly. Subsequent *in situ* chemical reduction of GO using hydroiodic acid produced well-defined graphene/PANI nanostructures having interpenetrating network with 3D open structure. The *in situ* GO reduction enabled keeping the hierarchical organization intact. The flexible graphene/PANI film produced was tested as a supercapacitor electrode using voltammograms and Nyquist analysis. The electro-capacitance of the film (448 F/g) was enhanced by 60% through the synergistic combination of graphene and PANI nanostructures. About 81% capacity retention was achieved for the composite compared to 38% for PANI alone after subjecting the samples to 5000 cyclic operations.

1. Introduction

Supercapacitors are emerging alternative power sources for a range of devices and applications, such as, portable electronic items, implantable devices, electric vehicles and renewable energy storage [1,2]. Compared to batteries, they have exceptional cycle life, can be charged/discharged at high rates, possess high power density, require minimal maintenance and are usually safer. A core challenge is scalable fabrication of electrode with high electrochemical performance. Based on their energy storage mechanism, supercapacitors are usually classified into two types: (a) the electrical double layer capacitor (EDLC), where the capacitance comes from electrostatic charge accumulated at the electrode/electrolyte interface, and (b) the pseudo-capacitor (PC), in which fast and reversible faradaic processes take place due to the presence of electro-active species. Polyaniline (PANI), a conjugated polymer, is a promising pseudocapacitive electrode-material because of its high conductivity, redox ability, and thermal and environmental stability.

PANI nanostructures in the form of dispersions, nanowires, nanotubes or nanofibres have shown significant property enhancements in various applications [3]. However, the electrode material

made of pure PANI suffer from poor cycle life and low capacity due to intrinsic capacitance decay on repeated inclusion and exclusion of electrolyte ions. To address these issues, electrically conductive EDLC materials such as porous carbon, carbon spheres, carbon black and other nanomaterials of carbon have been incorporated into polyaniline [4]. However, challenges remain in optimizing the process for scalability and defect minimization, in order to obtain stable hybrid structures with desirable composition and end-use properties.

Apart from its outstanding electrical, mechanical and physicochemical properties, the high surface area of graphene is of significant advantage for synthesizing electrodes [5]. Graphene is able to accommodate ionic charges readily from electrostatic interactions, and can act as a current collector for rapid electron transport from faradaic charge transfer reactions of anchored pseudo-capacitive polymer material. This dual action helps enhance the overall electrochemical performance of a hybrid composite [6]. Graphene/PANI composites have been synthesized using methods such as mixing [7], *in situ* polymerization [8] and electro-polymerization [9]. However, when the composite is mixed with binders or additives to produce electrodes, its structural organization and electrical conductivity are significantly affected [10]. Thus, binder-free electrodes with cyclic stability are desirable to produce supercapacitors suitable for generating complex shapes in applications such as,

foldable devices and electronic items that can be wrapped, worn or shaped into desirable forms [11].

Free-standing electrodes prepared by non covalent deposition of PANI on graphene film via *in situ* [12] and electro-polymerization [9] processes produced structures that were readily worn off on repeated ionic interactions and electrochemical cycling. On the other hand, the graphene/PANI film prepared by simple mixing of GO and PANI is very quick and highly scalable. Though, mixing of GO and PANI has potential to produce 3D interpenetrating structures, post-reduction processes for GO in the polymer composite is complex and pose additional problems of loss in structural consistency and stability. Therefore, a robust design without the detrimental post-reduction effects is desirable. To achieve these, we developed a set of sequential scalable strategies to fabricate 3D composites using hierarchical self-assembly, as highlighted schematically in Fig. 1.

In our process, positively charged PANI nanospheres were attached on negatively charged graphene oxide (GO) sheets via electrostatic forces and were confined to form hierarchical structures via vacuum assisted self assembly (VASA). This was followed by *in situ* chemical reduction to maximize capacitive performance by utilizing the exposed surfaces of both materials. Thus, graphene nanosheets supported by nanospheres were able to avoid wrinkling, restacking and aggregation. The PANI nanospheres sandwiched between the graphene layers help support bonding between the graphene nanosheets and improve mechanical reinforcement, thereby enhancing strength and internal surface access. The composite was characterized for its structural and electrical properties to assess its potential as an electrode in energy storage applications. For our binder-free standalone graphene/PANI composite, the capacitance was 448 F/g (at 1 A/g), which is higher than that of capacitance values of graphene/conducting polymer films reported in the literature prepared using other physical and chemical methods [13,14].

2. Experimental methods

2.1. Preparation of PANI nanospheres by microemulsion polymerization

First, PANI nanospheres were prepared by microemulsion polymerization of aniline. Briefly, 3 g SDS mixed with 30 mL deionized Milli-Q water in a beaker was magnetically stirred, while being heated electrically for 30 min to target 60 °C. 1 g aniline (Sigma–Aldrich) was dissolved in 2.65 mL of 1 M HCl (32%) for 15 min, mixed with 10 mL Milli-Q water and poured into the beaker containing SDS. The mixture was stirred until the heater temperature reached 60 °C. 1.25 g ammonium peroxydisulfate (Sigma–Aldrich) was mixed in 7.35 mL water and the mixture was added dropwise into the reactor. The reactor contents were then stirred for 3 h during the polymerization process.

The PANI suspension, collected from the reactor, was treated with eight successive washes using 100 mL deionized Milli-Q water. After two additional wash with 50 mL acidic water (0.5 M HCl) the mixture was filtered using a 0.2 μm PTFE membrane filter. The wet sample was scraped off the membrane and PANI spheres were resuspended in water, while adjusting the pH and concentration. The sample was subsequently oven dried, weighed and stored.

2.2. Preparation of PANI/GO nanostructure

The GO sample, prepared by Hummer's method; the details of the procedure developed by our group are described elsewhere [15]. The PANI nanospheres were diluted to 0.1 mg/mL and GO to 0.15 mg/mL with deionized water. Both suspensions were sonicated using a Branson 450D ultrasonicator (40 kHz) in Milli-Q water for 15 min, and samples of the mixture having variable pH (2.5–11) were prepared for zeta-potential measurements. The final composition of the composite was set by controlling the volumetric ratio of GO/PANI suspension. We found that about 60 wt% GO with 40 wt% PANI provided desirable morphological and electrochemical properties. Prior to mixing, both GO (pH 3.5) and PANI (pH 2.5) of 150 mL each were kept under sonication for 15 min. Subsequently, PANI dispersion was added drop by drop into the sonicated GO dispersion. The mixture was left in the sonication bath for 30 min to allow coating of PANI nanospheres around the GO nanosheets.

2.3. Preparation of graphene/PANI composite film

The dispersion of PANI nanospheres attached with GO hybrid nanostructure was hierarchically assembled via vacuum assisted
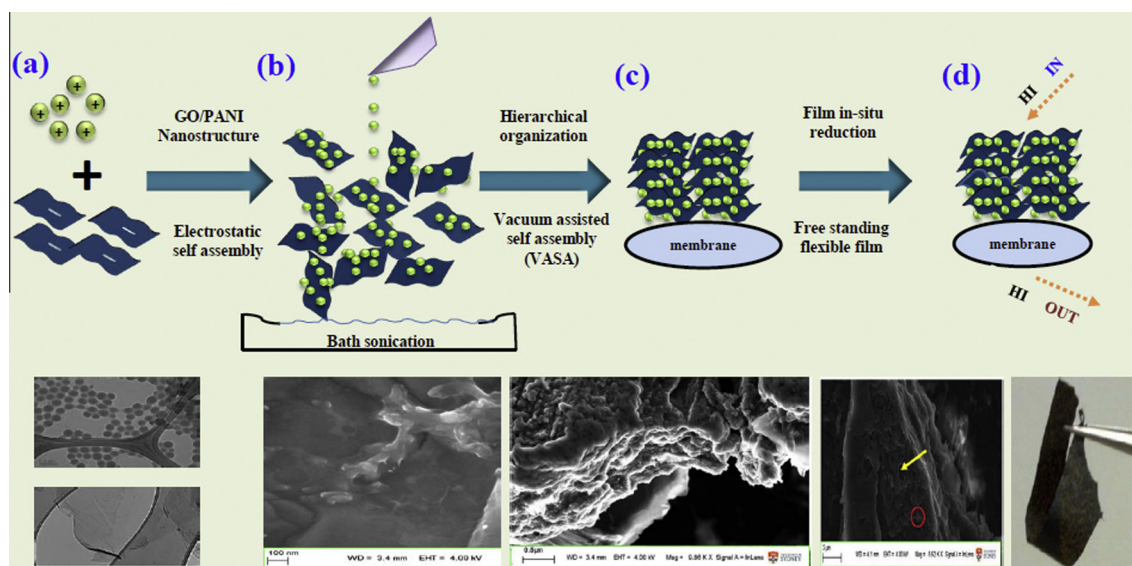

Fig. 1. Schematic diagram of process steps and images of corresponding intermediate products to obtain 3D graphene/PANI composite: (a) Pre-mixing of PANI nanospheres (*green*) and graphene sheets (*blue*) with corresponding TEM images, (b) PANI spheres attached to GO hybrid structure with SEM image, (c) layer by layer assembly of PANI/GO film with SEM image, and (d) graphene/PANI final free-standing film. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)