Electrochimica Acta 138 (2014) 139–147

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Cost-effective and Scalable Chemical Synthesis of Conductive Cellulose Nanocrystals for High-performance Supercapacitors

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ARTICLE INFO

Article history:
Received 15 March 2014
Received in revised form 3 June 2014
Accepted 13 June 2014
Available online 21 June 2014

Keywords:
Conducting polymers
Polypyrole
Cellulose nanocrystal
Supercapacitors
Sustainable

ABSTRACT

A well-controlled chemical synthetic protocol was developed to prepare a novel conductive, polypyrrole (PPy)/cellulose nanocrystal (CNC) system that is simple, cost-effective and scalable. Carboxylic acid groups were grafted onto CNC via a TEMPO-mediated oxidation providing strong hydrogen bonding to enhance adsorption of pyrrole monomers (Py). *In-situ* chemical polymerization of Py was further performed on a single high aspect ratio CNC. The nanotemplating of CNC controlled the deposition and growth of the polymer layer, which enhanced the electrochemical properties of PPy. Improved processibility of PPy was achieved due to the high mechanical strength and good dispersibility of CNC. By varying the ratio of Py to surface hydroxyl groups of CNCs (Py/OH) systematically, an optimal composition of Py/OH of 16:1 was observed. The mechanism of the electrochemical performance change associated with Py/OH molar feeding ratio was also studied in detail using different spectrometry and SEM methods. PPy/CNC hybrid nanostructures possessed an attractive specific capacitance of 248 F g^{-1}, suitable for supercapacitor applications and exceeding the performance of comparable systems based on carbon nanotubes and graphenes. Compared with other cellulose-polypyrrole systems whose end-products are typically entangled fiber mat, aerogel or cake-form, our CNC nanorods can be readily dispersed and added as fillers into different matrices. The PPy/CNC hybrid nanostructure is extremely light, conductive, cheap, renewable, environmentally friendly, and our solution-phase chemical synthesis is simple to implement and easy to scale up.

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1. Introduction

The energy and environmental challenges facing the world are daunting, thus they call for the development of high-performance devices that can be manufactured with renewable materials at a low processing cost. Supercapacitors (SPs) are recognized as an important element in the overall energy storage system. SP can store far more energy than conventional capacitors, and they also possess a much longer cycle life than batteries [1,2]. Current commercial electrode materials for SPs are active carbon, metal oxides, carbon nantubes (CNTs), and graphenes [3,4]. However, these materials present several challenges, such as high cost, greenhouse effect, metal-depletion, and low-biodegradability. To this end, intrinsically conductive polymers (ICPs), polypyrrole (PPy), polyanaline (PANI) and poly(3,4-ethylene-dioxythiophene) have gained increased attention due to their good conductivity, low cost, and attractive pseudo-capacitive behaviors that combine fast kinetics (i.e. high power) and superior specific capacitance [5]. PPy has been considered to be the most promising ICP for this purpose due to its facile synthesis, long-term stability, outstanding electrochemical properties, and low cost [6,7]. They can be used to replace traditional battery or supercapacitor material to meet the demands for flexible, lightweight or even wearable electronic devices [8]. However, the poor mechanical strength of ICPs limits their processability and results in poor stability due to degradation during charge-discharge cycles [9]. Another drawback is the compactness of the polymer film resulting in a low specific capacitance (F g^{-1}) due to the limited access for dopant ions [10].

In order to strengthen the structure and increase the porosity of ICPs for supercapacitor application, many attempts have been made to produce ICP composite materials over various substrates, such as latex particles [11], CNTs [12–17], graphene oxides [12,18–21], metal compounds [22,23], inorganic oxides and hydroxides [24,25]. An outstanding example of these composite materials is PPy/CNT

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http://dx.doi.org/10.1016/j.electacta.2014.06.089
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which has been proposed for many applications [17,26–29]. The enhanced electrochemical performance of this composite is generally believed to be due to the synergy between highly conductive CNTs and conductive polymers.

Recently, there has been a significant interest in the use of nanotechnology to rejuvenate the forest industry by producing value-added wood-derived nanomaterials with one application being their incorporation into ICPs [30–38]. Various PPy/cellulose hybrid systems have been successfully fabricated via chemical oxidation polymerization in the presence of Pyrrole monomer [34,36,39,40]. Recently, Wang et al. [41] conducted a detailed investigation on the various polymerization parameters to achieve highly conductive composites of bacterial cellulose/PPy for supercapacitor applications. However, due to the length of microfibrillated cellulose system, the end-product can be mostly achieved by forming the entangled films/mat, aerogel, or cake-form that have poor further processibility [24]. Currently, limited studies have focused on individually coated nanofibers, i.e. rods, or whiskers, which can be easily incorporated as conductive fillers into various matrices via mixing [42]. An effective enhancement in electrochemical performance can be obtained by forming individual core-shell structure because it avoids the conductivity loss due to cross-linking network formed during ICP polymerization [43,44].

Only recently extracted from wood fibres at an industrially relevant scale cellulose nanocrystals (CNCs) are regarded as one of the world's latest "wonder materials". In 2012, Canada commissioned the world's first pilot plant to produce CNC using a continuous flow process that is able to produce 1000 kg of CNC per day. This emerging biomaterial is seen as the struggling Canadian forestry industry's next best hope. The high aspect ratio rod-like crystals are produced by removing the amorphous region via acid hydrolysis to produce CNCs with diameters of 5-20 nm and lengths of around 100-400 nm. The prepared CNCs possess sulfate ester groups on their surface that impart stability to the nanoparticle in aqueous solution [45]. Besides the eco-friendliness and cost-competitive of its end-product, other attractive features of CNCs include, but are not limited to having: (i) strength yet lightweight, (ii) high aspect ratio and specific surface area, (iii) enriched surface active groups, (iv) good water-dispersibility (v) low cost and abundance, (vi) biodegradability and biocompatability. All the above makes CNC a promising reinforcing nanomaterial, or a functional nanomaterial for the fabrication of other hybrid nanostructures with enhanced properties [46–49]. In a most relevant work, CNCs derived from cotton has been successfully incorporated into PPy by Soon et al. using electrochemical co-deposition, In their work, the prepared CNC/PPy shows superior electrochemical performance that is comparable to carbon nanotube/PPy synthesized and tested under the similar conditions [30]. The exciting results strongly suggest that the substrate conductivity is not a prerequisite and CNC/PPy is a promising candidate for high performance supercapacitor applications. While electrochemical polymerization yield systems with better performance, the yield of product is limited to the surface area of the electrode not suitable for large-scale production and is generally produced as dense film, which limits its wide application [50].

In this paper, we describe a well-controlled synthesis of conductive CNCs *via* facile *in situ* chemical polymerization. Due to the good dispersibility of CNCs and an ideal dimension that is short enough to prevent entanglement, PPy can be readily polymerized to form a conductive shell on individual CNCs. The one-dimensional structure of CNC not only facilitates the efficient transport of electrons along one controllable direction, but also gives a very low percolation concentration of PPy/CNC to achieve a conductive network [51]. By using well documented chemistry, more negative charges (i.e. carboxylic groups) are introduced to the CNC surface in addition to the existing sulfate ester groups, which provide a stronger interaction (electrostatic attraction, hydrogen bonding) between CNC and PPy thanuntreated-CNC. Compared with polymerization over the cellulose network (i.e. membrane, cake, hydrogel etc.), the polymerization confined to individual CNC fiber is more challenging to achieve. Controlled synthesis has to be designed to enhance the affinity of ICP to the surface of CNC and eliminate the bulk polymerization of PPy or agglormeration. Our optimized synthesis was developed by tuning the feed ratio of Py monomer to hydroxyl group (Py/OH). Zeta-potential measurements were monitored over the polymerization time to ensure an adequate PPy coating was achieved. The effect of electrochemical change associated with different Py/OH ratio was thoughly studied using various characterization techniques, and we were able to elucidate the phenomenon on the observed internal structural changes associated with their electrochemical behavior, which is believed, to the best of our knowledge, the first reported. The electrical conductivity of the prepared PPy/CNC approached 4 S/cm with an outstanding capacitance of 248 F/g. The nanostructure has the added advantage of being a sustainable and cost-effective nanomaterial for the fabrication of light, flexible, high-performance, and cheap energy storage devices. Our solution based synthesis is readily scalable using larger vessels or reactors: from 100 ml to 4 liter vessel, the yield of PPy/CNC from a single batch was increased from 0.2-0.3 g to 10-12 g with the end product being in fine powder form (after freeze drying) that can be readily redispersed in aqueous solution. The rod-shape nanocomposite produced using our approach holds promise for a wide range of applications, such as conductive inks in printable electronics, conductive fillers for various insulating matrix, sensors, conducting and antibacterial films etc. The nanomaterial is also significantly more versatile than that produced using the electrochemical method, where the product is somewhat limited to the deposition of a composite film on an electrode, and such process is less scalable and further processing of the material is somewhat limited.

2. Experimental

2.1. Materials

Cellulose nanocrystal (CNC) was provided by FP Innovations and Celluforce Inc. The chemicals used in this study were analytical grade, purchased from Sigma–Aldrich, and used as received. The chemicals for reaction are: TEMPO reagent, sodium bromide (NaBr), sodium hypochlorite (NaClO), pyrrole monomer and ammonium persulfate (APS).

2.2. Preparation of conductive PPy/CNC hybrid nanostructure

TEMPO-mediated oxidation described elsewhere was first performed on CNC, converting primary hydroxyls to carboxylate functionalities [52]. Freeze-dried TEMPO-CNC was dispersed under sonication in a mixture of $HClO_4$ (1 M) and ethanol (V/V = 1/1) to produce a 0.2%wt suspension. Pyrrole monomers at different molar ratio to surface hydroxyl groups of CNC were then added to the suspension and the mixture was transferred to a double-walled jacketed reaction vessel. The solution was vigorously stirred, and equal molar amounts of ammonium persulfate (APS) to pyrrole monomer was added slowly to initiate the polymerization. The color of the solution gradually turned from transparent to yellow, to dark green and finally to black, which is the color of PPy. The reaction was magnetically stirred below the room temperature overnight for sufficient polymerization. Finally, the reaction was quenched followed by repeated washing with DI water. For comparison, pure PPy was also synthesized under identical conditions in the absence of CNCs.

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