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Novel actuators based on polypyrrole/carbide-derived carbon hybrid materials

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ABSTRACT

Polypyrrole (PPy) hybrid films incorporated with porous carbide-derived carbon (CDC) particles are synthesized through a novel one-step electrochemical synthesis process that provides a simple and efficient alternative for current tape-casting and inkjet printing technologies to make conducting polymer–CDC-based electroactive composites. The resulting porous, robust and electrically conductive hybrid layer was used to fabricate electroactive polymer actuators both as perpendicularly expanding actuators and as bending trilayer actuators. Raman and FTIR spectroscopy confirm successful incorporation of CDC in the PPy matrix. Cyclic voltammograms confirm slightly higher charging/discharging currents of the PPyCDC hybrid. This indicates the successful coupling of CDC in order to increase electric double-layer capacitance in the hybrid films. The maximum steady state electromechanical diametrical strain is 13% for hybrid material which is in the same order of magnitude as for PPy and 10× more than previously reported CDC films made with non-conducting polymer binders. Furthermore, the expanding actuators made from hybrid material are more efficient than non-modified PPy actuators, having doubled the amount of swelling per injected charge. This improvement is very important since the low energy efficiency is a major shortcoming for ionic electroactive polymers. The high pseudocapacitance makes these new hybrid materials also interesting for energy storage applications.

1. Introduction

Materials that can transform electrical energy into a mechanical force are extremely useful as actuators for a wide span of applications ranging from robotics to manipulation of single cells [1–4]. So called ionic electroactive polymers (EAPs), comprising conducting polymers (CPs), ionic polymer–metal composites (IPMCs), responsive gels, and carbonaceous materials such as carbon nanotubes, are specifically interesting due to their low driving potentials, but their low energy efficiency is still a major shortcoming. CPs such as polyaniline, polypyrrole, and poly(3,4-ethylene-dioxythiophene) have been widely studied as active material for actuators especially for use in biomedical applications [5–8]. The volume change of CPs is caused by insertion and extraction of ions and solvent from the electrolyte the when material is electrochemically switched between the oxidized and reduced states [5,9].

The volume change of EAPs based on porous carbons such as CDC on the other hand is caused by the intercalation of ions due to the electric double layer charging of the electrodes

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[10,11]. Generally it is understood that high electric double-layer capacitance of porous carbon is related to high surface area and precise pore size distribution according to electrolyte used [12,13]. CDC synthesis allows formation of highly porous carbon materials with good mechanical properties. Microstructure, pore size, pore shape, and surface termination of nanoporous CDC can be precisely controlled by changing the synthesis parameters and the composition and structure of the initial carbide precursor [13]. As such, the process allows optimization of nanoporous CDC for various applications [11,14].

Charging of electrical double-layers in polymer-supported carbon matrixes made of highly porous CDC is highly efficient and could potentially be used to boost the CP charge injection. Here we describe hybrid materials combined with highly porous carbon and CPs as the actuating material to acquire stable and efficient actuation and to enhance the performance of ionic EAPs. We expect the addition of CDC nanoparticles having a large specific surface area in the CP matrix to lead to an increased charge injection as well as to an enhanced overall stability and energy efficiency of CP actuators.

CPs have been combined with different carbon materials prior to, but either synthesized onto or into the carbon electrodes or *vice versa* as CP electrodes with carbonaceous coatings, and not as a single hybrid material. They have been characterized for electromechanical actuator applications, [15–18] as well as electrode materials for electrochemical capacitors specially due to the high electrical conductivity, high pseudocapacitance, and relatively low cost [19,20]. However, the considerable volume change of the electrode films caused by the intercalation and depletion of ions during the reversible charge and discharge process resulted in a poor mechanical stability in advanced battery and supercapacitor applications [18,21,22]. Aforementioned works do not describe an *in situ* co-polymerization methodology of conducting polymer and highly porous CDC. Here, we present for the first time a hybrid PPyCDC material, where the CDC particles are embedded in the conducting polymer matrix. We describe a novel direct co-electropolymerization method of polypyrrole and carbide-derived carbon composite materials in presence of dodecylbenzenesulfonate dopant on plain gold films and onto Au wire working electrodes in order to develop energy efficient and electromechanically active hybrid layers. The hybrid composite films are expected to bridge highly porous carbide-derived carbon materials and polypyrrole. CDC store electric energy physically and efficiently by ion adsorption, while PPy has attracted intense interest due to significantly higher electromechanical strain and higher specific capacitance (pseudocapacitance) than carbon materials.

2. Experimental section and methods

2.1. *Preparation of PPy(DBS)CDC hybrid films*

Pyrrole was acquired from Sigma Aldrich and vacuum-distilled prior to use. Sodium dodecylbenzenesulfonate (NaDBS) was received from TCI Europe (Purity > 95%), and CDC was received from Skeleton Technologies Ltd. [23]. PPyCDC hybrid films were prepared from a CDC/Pyrrole precursor suspension using electrochemical synthesis routes. Gold coated silicon wafers were used as working electrodes and Au coated Si wafers or Pt wire were selected as counter electrode. For the diametrical strain measurements a Au wire working electrode (AuWE) was made using high purity gold wire (0.5 mm diameter) obtained from Goodfellow (Fig. 1A and B).

Electrochemical synthesis of electroactive PPy(DBS) and PPy(DBS)CDC composite films were carried out in the three

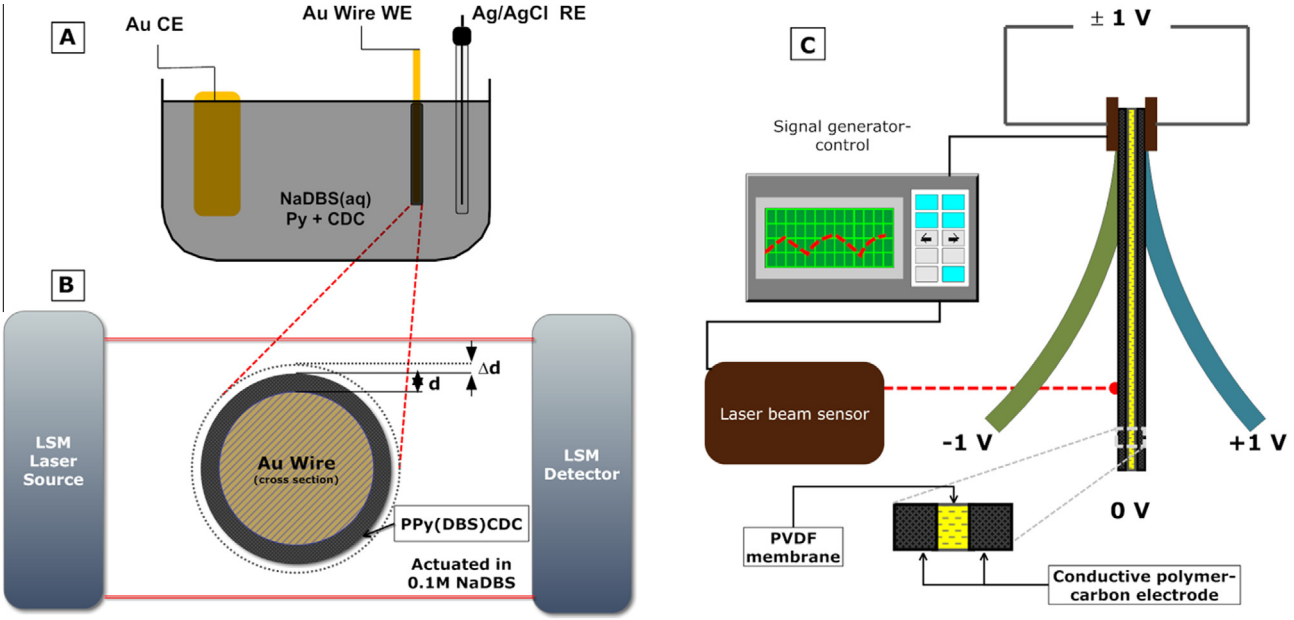

Fig. 1 – Illustration of experimental set-up for hybrid material synthesis (A), diametrical strain measurement with a laser scanning micrometer (LSM) (B), and strain measurement of triple layer actuator device in the bending mode (C). (A color version of this figure can be viewed online.)