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Aramid fibre-based wearable electrochemical capacitors with high energy density and mechanical properties through chemical synergistic combination of multi-coatings

Hao Fang [a, b, c], Li Yuan [a, b, c], Guozheng Liang [a, b, c, **], Aijuan Gu [a, b, c, *]

[a] State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, China
[b] Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, China
[c] Department of Materials Science and Engineering, College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, China

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ABSTRACT

Fibrous electrochemical capacitors (FECs) with outstanding wearability, mechanical properties and satisfactorily high energy density are greatly required for developing wearable smart devices and sustainable energy sources. Herein, new high performance FECs based on flexible but insulating aramid fibres (KFs) were developed through chemically grafting composite coatings of Ag nanoparticles, carbon nanotubes (CNTs) and capacitive polypyrrole (PPy), successively. Their structures and integrated performances were intensively studied. The PPy loading plays an important role on the capacitive properties of new KFs, and there is an optimum content of PPy for getting the best integrated performances. It is interesting to find that the capacitive property of KF/Ag/CNT/PPy is not the simple combination but much higher than those of KF/Ag/PPy and KF/CNT/PPy, proving that there is a synergistic effect between Ag and CNT coatings. This synergistic effect endows KF/Ag/CNT/PPy fibres with high specific capacitance and large energy density. For example, the specific capacitance and energy density of the novel aramid fibre capacitor with the optimum content of PPy (KF/Ag/CNT/PPy0.2) are as high as 84.3 F cm^{-3} (or 24.8 F g^{-1}) and 7.49 mW h cm^{-3} (or 2.21 mW h g^{-1}), respectively. In addition, KF/Ag/CNT/PPy0.2 exhibits enhanced cyclability and wearability (its capacitance retains 94.0% after 1000 cycles and 93.2% after bending for 500 times) because of the special design of strong interactions between different components. Note that KF/Ag/CNT/PPy0.2 also has high tensile strength, modulus and break extension. These attractive integrated performances demonstrate that KF/Ag/CNT/PPy0.2 makes obvious breakthrough on developing FECs based on polymer fibres, and thus have great prospect in fabricating wearable electronic devices and sustainable energy sources.

1. Introduction

Flexible and wearable smart devices are one of the hottest and most expected products in present electronic industry [1,2]. To obtain fully flexible and wearable electronic devices, developing light-weight, miniaturized, flexible and wearable energy-storage units has become the greatest challenge [3,4]. With combined advantages of small volume, light weight, flexibility, high efficiency and ease to be integrated, fibrous electrochemical capacitors (FECs) have great application prospect in fabricating wearable energy-storage units [5–7].

FECs are composed of fibre electrodes and electrolyte in parallel [8–10], twisted [11–13] or coaxial [14–16] configurations, so their properties are greatly dependent on those of electrode materials [17]. To promote FECs from concept to application, high performance fibre electrodes are needed to be developed, which should

* Corresponding author. State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, China.
** Corresponding author. State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, China.
E-mail addresses: lgzheng@suda.edu.cn (G. Liang), ajgu@suda.edu.cn (A. Gu).

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not only have outstanding electrochemical properties, but also own good flexibility and wearability simultaneously [5,17].

Up to date, a variety of fibres have been reported to prepare fibre electrodes. Carbon fibres are brittle and thus cannot be bent frequently [18]. Metal fibres, such as stainless steel fibres, nickel fibres, *etc*., are ductile but with inherent rigidity and plasticity [19]. Graphene and carbon nanotube (CNT) fibres are still not applicable in large scale due to their high price [18]. Consequently, highly flexible polymeric fibres are regarded to be right candidate for preparing fibre electrodes at present.

However, FECs reported based on polymeric fibres have three bottlenecks. One is poor conductivity of fibre electrodes and low capacitance of FECs. To endow polymeric fibres with capacitive properties, the general strategy is producing a coating on the surfaces of polymeric fibres, and the coating materials include carbonaceous materials (CNT, graphene, *etc*.) [20], conductive polymers (polypyrrole, polyaniline, *etc*.) [21] or transition metal oxides (MnO_2, ZnO, $NiCo_2O_4$, *etc*.) [22,23]. However, even though these materials were formed on polymeric fibres, polymeric fibres belong to insulators and make no contribution to capacitive properties, so the capacitance of polymeric fibre-based FECs is also relatively low.

Secondly, inorganic coatings have poor interaction with polymeric fibres, and thus tend to detach from fibre substrate during frequent deformation or electrochemical cycling, leading to unsatisfactory wearability. Actually, few existing studies involve the interaction between multi-components.

The third issue needed to be solved is the undesirable mechanical properties. Till now, conventional polymeric fibres such as polyester fibres [22], polyamide fibres [24], polyurethane fibres [25], cotton yarns [21], *etc*., were used to prepare FECs, however, they usually have low tensile properties [26,27] and mainly satisfy the applications in daily life rather than in conditions that have harsh requirement on high mechanical properties such as bullet-proof products.

Therefore, developing polymeric fibre-based FECs with outstanding electrochemical and mechanical properties as well as good flexibility and wearability is still a challenge. Among polymeric fibres, aramid fibres have been attracting great attentions worldwide since their birth owing to their outstanding mechanical, thermal and chemical properties [28,29]. In fact, aramid fibres have been widely used in many cutting-edge fields including aerospace, automobile, military, sports products, electronic information, *etc*. [30,31], so FECs based on aramid fibres will have high mechanical properties, and overcome the problems in present FECs. Recently, the pioneer work on preparing capacitors by forming Pt and V_2O_5 coatings on surfaces of poly(*p*-phenylene terephthalamide) yarns was reported [32]; however, similar as other polymeric fibre-based FECs, the capacitive performance and adhesion between poly(*p*-phenylene terephthalamide) yarns and inorganic coatings need to be improved. Unfortunately, to the best of our knowledge, except this work, no more FEC based on aramid fibre has been reported.

This paper gives the first report on developing high performance wearable FECs through producing multi-coatings of Ag, CNT and PPy on aramid fibres with chemical hybridization and composite technology. The influence and mechanism of compositions on structure and properties were systematically investigated, and an interesting synergistic effect between multi-coatings on the capacitive property of KFs was found and explained.

2. Experimental section

2.1. Materials

Aramid fibres used herein were Kevlar-49 fibres (KF, DuPont Company, USA), which were immersed and refluxed for 3 h in acetone, petroleum ether and deionized water, successively. The obtained fibres were dried in a vacuum oven at 40 °C for 6 h to get clean ones, denoted as KF.

CNTs used herein were multi-walled CNTs (MWNT-10, its purity was more than 97%, outer diameter in the range of 7–15 nm, and length in the range of 5–15 μm) obtained from Shenzhen Nanotech Port Co. Ltd. China. Activating treatment was carried out prior to usage. Typically, CNTs were treated in 3 mol L^{-1} HNO_3 at 60 °C for 8 h, followed by refluxing in 5 mol L^{-1} HCl at 120 °C for 6 h, successively, to get CNTs with active groups.

Dopamine hydrochloride and tris(hydroxymethyl)aminomethane hydrochloride were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. China. Sodium hydroxide, silver nitrate, ammonium hydroxide, polyvinyl pyrrolidone, glucose, pyrrole, ethanol, polyvinyl alcohol (PVA, polymerization degree of 1750 ± 50) and phosphoric acid were obtained from Sinopharm Chemical Reagent Co. Ltd. China. γ-(2,3-Epoxypropoxy)propytrimethoxysilane (KH560) was bought from Shanghai Yuanye Biological Technology Co. Ltd. China.

2.2. Preparation of KF electrode with composite coatings

KF electrode was prepared through four steps, as shown in Fig. 1.

Typically, 100 mL mixed solution consisting of 2 g L^{-1} dopamine hydrochloride and 10 mmol L^{-1} tris(hydroxymethyl)aminomethane hydrochloride was prepared, of which the pH value was adjusted to 8.50 by adding 0.5 mol L^{-1} NaOH solution. 0.5 g KF fibres were immersed in the above solution, and then oscillated at 25 °C for 24 h. After that the fibres were rinsed with water and dried in a vacuum oven at 40 °C, successively, the obtained fibre is denoted as KF/PDA.

Ammonium hydroxide was added dropwise into 50 mL $AgNO_3$ solution (30 g L^{-1}) until the solution became transparent again; thereafter, 0.5 wt% polyvinyl pyrrolidone was added to get a solution A, into which 0.5 g KF/PDA fibres were soaked, and oscillated at 25 °C for 15 min. After that, 50 mL glucose solution (60 g L^{-1}) was added dropwise into the above mixture, and oscillated at 25 °C for 30 min. The resultant fibres were washed with water and vacuum dried at 40 °C, successively, designed as KF/Ag.

2.5 wt% KH560 was added into 100 mL deionized water. Then 0.5 g KF/Ag fibres were immersed in the mixture, and oscillated at 65 °C for 5 h. After that, fibres were rinsed with water and vacuum dried at 40 °C, successively. The obtained fibres were denoted as KF/Ag/KH560.

1.0 wt% CNT was added into 100 mL ethanol, and then 0.5 g KF/Ag/KH560 fibres were immersed in the mixture, and oscillated at 70 °C for 12 h. After that, fibres were rinsed with water and vacuum dried at 40 °C. The obtained fibres were coded as KF/Ag/CNT.

Similarly, KF/CNT fibres were also prepared using the above procedure for KF/Ag/CNT, except that KF/Ag fibres were replaced by KF/PDA.

0.5 g KF/Ag/CNT fibres were immersed in 50 mL pyrrole solution with different concentration (0.1, 0.2 or 0.3 mol L^{-1}), and oscillated at 25 °C for 15 min, into which 50 mL $AgNO_3$ solution with half the concentration of pyrrole (0.05, 0.1 or 0.15 mol L^{-1}) was added and oscillated at 25 °C for 24 h. The resultant fibres were washed with water and vacuum dried at 40 °C, successively, denoted as KF/Ag/CNT/PPy0.1, KF/Ag/CNT/PPy0.2 or KF/Ag/CNT/PPy0.3.

Similarly, KF/PPy0.2, KF/Ag/PPy0.2 or KF/CNT/PPy0.2 was prepared using above-mentioned procedure, except that KF/Ag/CNT fibres were replaced by KF, KF/Ag or KF/CNT, and the concentration of pyrrole solution was 0.2 mol L^{-1}.