Synthetic Metals 204 (2015) 39–47

Contents lists available at ScienceDirect

Synthetic Metals

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

Conducting poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) film electrode with superior long-term electrode stability in water and synergistically enhanced electrocatalytic ability for application in electrochemical sensors

Hui Zhang [a,b], Jingkun Xu [a,*], Yangping Wen [b,*], Zifei Wang [a,b], Jie Zhang [a,b], Wanchuan Ding [a,b]

[a] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China
[b] Key Laboratory of Applied Chemistry, Jiangxi Agricultural University, Nanchang 330045, PR China

ARTICLE INFO

Article history:
Received 3 January 2015
Received in revised form 26 February 2015
Accepted 11 March 2015
Available online 19 March 2015

Keywords:
Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate)
Carboxymethyl cellulose
Stability
Adhesion
Electrocatalytic ability

ABSTRACT

A novel poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) composite film with superior stability in water, adhesion and flexibility, which is very critical for maintaining the long-term stability in water of the PEDOT:PSS film electrode, was easily prepared by introducing a water-soluble, anionic, non-toxic and biocompatible biopolymer (sodium carboxymethyl cellulose, Na-CMC) into a commercially available aqueous dispersion of the conducting polymer (PEDOT:PSS dispersion). The high conducting PEDOT:PSS-CMC film exhibited good flexibility and long-term stability in water after being soaked in water for 35 days. The high performance film electrode with excellent adhesion, long-term electrode stability in water (retaining almost 99.4% of its original activity for 105 days), and electrochemical properties was prepared facilely by drop-coating, and displayed good synergistically enhanced electrocatalytic ability towards the anodic oxidation of harmful substances and nutritional ingredients in edible agro-products, which were employed for its application in electrochemical sensors. The simultaneous or individual detection of maleic hydrazide, salicylic acid, nitrite, sunset yellow, and tryptophan was successfully realized using PEDOT:PSS-CMC/GCE, and exhibited superior sensing stability. All satisfactory results indicated that the introduction of CMC into PEDOT:PSS could improve the flexibility, adhesion, long-term electrode stability in water and electrocatalytic ability, which would provide a promising platform for the application in electrochemical fields of the high performance film electrode, especially the application in electrochemical sensors.

1. Introduction

The commercially available aqueous dispersion of poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) is today the most successful electronically conducing polymers with processibility produced on a large-scale and sold for different application such as antistatic coatings, conducting coatings, hole injection layers, electrochromic windows, photovoltaic devices, electroluminescent devices, organic thermoelectric devices, organic light-emitting diodes, printed wiring board manufacturing owing to its superior physicochemical properties [1–7]. In this commercial aqueous dispersion of PEDOT:PSS, PEDOT is charge transporting species and carries positive charges, and PSS acts as a charge-compensating counter polyanion and charge-balancing dopant to stabilize PEDOT and form a processable water-borne dispersion of negatively charged swollen colloidal particles consisting of both conducting PEDOT and excess insulating PSS. In addition, PEDOT:PSS has also been employed as excellent electrode material for biological sensors and chemical sensors [8], pressure sensors [9], strain sensors [10,11], electrocatalysts [12], capacitors [13,14], solar cells [7,15,16] and transistors [17,18] due to its exceptional advantages of high electrical conductivity (σ), excellent electrochemical and environmental stability, unique processibility, good biocompatibility, superior film-forming properties, and fine tuning of their physicochemical properties

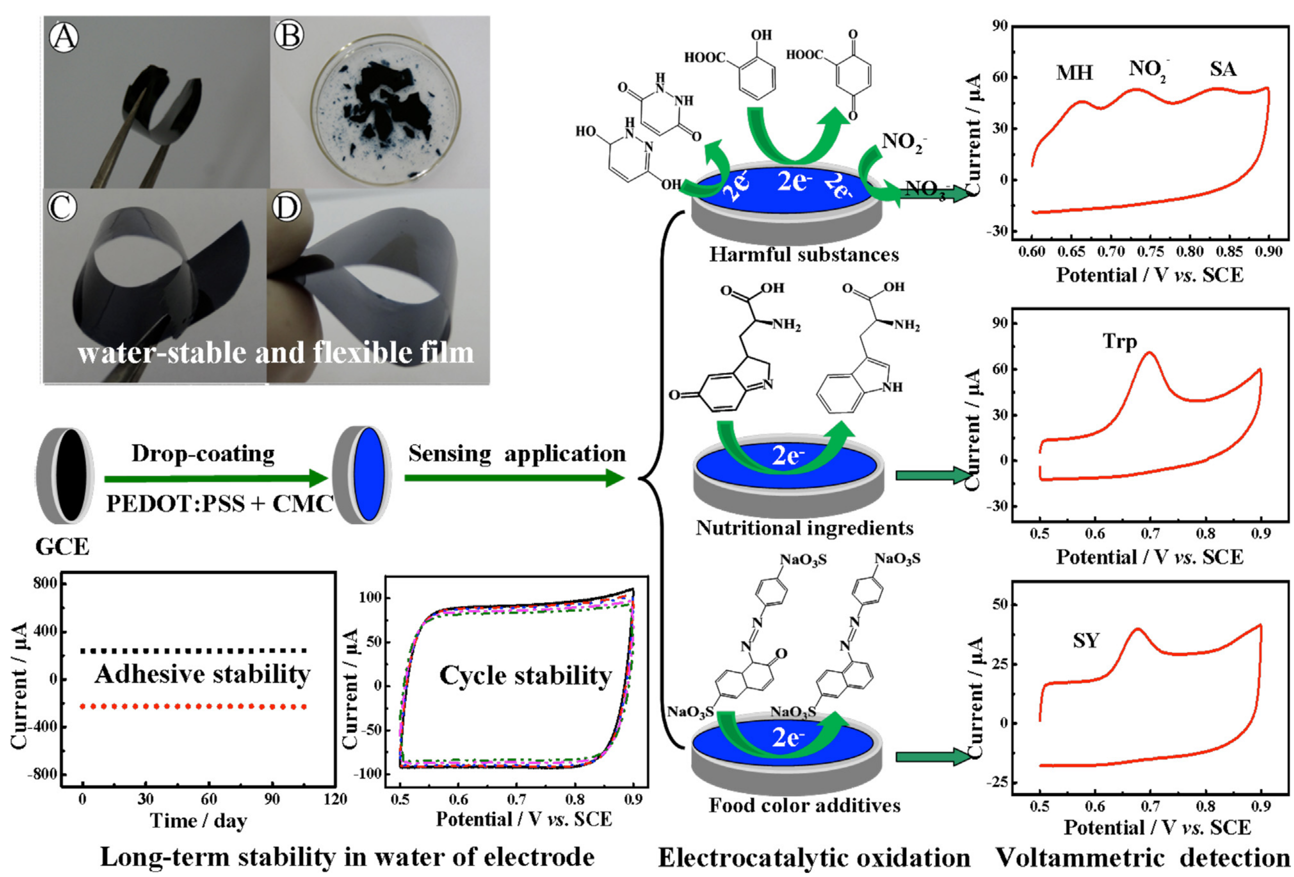
* Corresponding authors. Tel.: +86 791 88537967; fax: +86 791 83823320.
E-mail addresses: xujingkun@tsinghua.org.cn (J. Xu), wenyangping1980@gmail.com (Y. Wen).

http://dx.doi.org/10.1016/j.synthmet.2015.03.010
0379-6779/

by precise synthesis [1–3], However, the pristine PEDOT:PSS film is extremely hydrophilic because of the existence of the water-soluble PSS chain in the dispersion [19], which tend to swell or disintegrate significantly in aqueous media [20], and become much more easily crack or peel off from the surface of substrate electrode after soaking in water [21]. Moreover, the σ of PEDOT:PSS film would decrease rapidly with time, especially under high relative humidity conditions [22,23]. Therefore, the bad water resistance and weather stability of PEDOT:PSS film would limit the widespread application in electrochemical fields of high performance film electrode. It is very necessary and important to explore a highly water-stable, flexible, adhesive and conducting PEDOT:PSS composite film to overcome these existing shortcomings.

Many researchers have been committed to obtaining water-stable, flexible, adhesive and conducting PEDOT:PSS composite films. A variety of strategies were proposed to specifically address these issues, for instance, ionic liquids [24], ionic cross-linking [25], multivalent cations [26], and bis(fluorinated phenyl azide) [27], have been selected to improve the aforementioned problems with PEDOT:PSS. Although these efforts have enhanced the water-resistance and weather stability of PEDOT:PSS films, and lowered the swelling and disintegration of PEDOT:PSS films to a large extent [28–30], The long-term stability in water of the PEDOT:PSS film still needed to be addressed in the practical application. In our previous work, we reported a highly soaking stable and adhesive PEDOT:PSS composite film which was prepared firstly using a mixed solution with the proper volume ratio of Nafion and PEDOT:PSS, then doped secondarily by voltammetric method in common ionic liquid [31], this work was employed for the electrochemical application in bio/chemo sensors [32–34], but the long-term stability in water of PEDOT:PSS film electrode still needed to be further improved. Moreover, the introduction of Nafion resulted in the sharp decline of the σ of the PEDOT:PSS film. Subsequently, poly(vinyl alcohol) (PVA) was also selected to enhance the adhesion and binding force between PEDOT:PSS film and substrate electrode interface, and improve the swelling and cracking of PEDOT:PSS film in water, but the very poor electrocatalytic ability of this PEDOT:PSS composite film was enhanced by electrocatalysts such as grapheme, carbon nanotube [35]. In addition, different biomacromolecules such as enzymes, DNA/RNA [36], proteins, [37] and electrocatalysts like carbon nanomaterial [38,39], metals and metal oxide nanoparticles [40–42], were also incorporated into a commercially available aqueous dispersion of PEDOT:PSS, which could improve the poor electrocatalytic ability, molecular recognition capability, and electrode stability in water of PEDOT:PSS.

In this paper, sodium carboxymethylcellulose (Na-CMC), a good water-soluble binder, food additive, thickener with desirable properties such as nontoxicity, biocompatibility, biodegradability, hydrophilicity, and good film forming ability [43–45], was selected for enhancing the stability in water, adhesion, and flexibility of PEDOT:PSS film. The PEDOT:PSS-CMC film electrode was obtained by drop-coating the PEDOT:PSS-CMC mixed aqueous solution onto the surface of glassy carbon electrode (GCE), and displayed superior flexibility, adhesion, long-term electrode stability in water and synergistically enhanced electrocatalytic ability, which was employed for the voltammetric determination of harmful substances and nutritional ingredients in edible agro-products and their foodstuffs using linear sweep voltammetry (LSV), and its sensing performance of PEDOT:PSS composite modified electrode was also assessed (Scheme 1).



Scheme 1. The facile design and electrochemical sensing application of the highly water-stable, flexible, adhesive and conducting PEDOT:PSS composite film with superior synergistically enhanced electrocatalytic ability and long-term electrode stability in water.