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All-in-one electrochromic devices with biological tissues used as electronic components

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ABSTRACT

Two novel all-in-one electrochromic devices have been fabricated on the basis of low-cost and environmentally benign marine brown algae laminaria japonica, and jellyfish, which were both utilized as electronic component (gel electrolytes) in combination with electrochromic viologen bis(3-hydroxypropyl) viologen dibromide, and electron mediators 1,1′-ferrocene dicarboxylic acid and 1,1′-ferrocenedimethanol. The electrochromic performance of the as-fabricated devices was tested. The two biological ECDs exhibited driving voltages as low as 1.1 V, which is superior to many traditional viologen-based ECDs. Moreover, following the principles of green chemistry, no waste and organic solvents were introduced during the room-temperature device assembly. Based on abundant content of biological tissues, the device can be presented as a proof-of-concept to find potential applications in the fields of low-cost, green and large-scale ECDs.

1. Introduction

Electrochromic devices can change their optical absorption bands reversibly via electrochemical oxidation and reduction of the electrochromic active molecules [1–3]. The gadget offers various extents of light attentuation, and is used in light control and energy saving such as smart windows and electron displays [4–7]. In general, all electrochromic devices work on the basis of similar working mechanism, whereas the configuration of a particular device is dependent on utility. In order to simplify device configuration, a strategy to combine electrochromic material with electrolyte in one sole layer sandwiching between two ITO electrodes has been pursued. In this kind of device, electrochromic material and suitable electron mediator are dispersed in the electrolyte solution. Such a single-layer “all-in-one” device can reduce the number of deposition steps, avoid electrolyte leakage and can reduce materials waste.

To optimize the all-in-one device, attempts have been made to obtain electrochromic gels. These gels usually include organic polymers, such as poly(methyl methacrylate) (PMMA), polyurethane (PU), polycarbonate (PC), poly(vinylbutyral) (PVB), poly(vinylidenefluorid) (PVDF), as well as polyvinyl alcohol (PVA) [5,8–13]. These organic polymers are basically attained from nonrenewable fossil fuels derivatives and the synthetic process yields harmful chemicals. Moreover, these widely-used polymers are difficult to be biologically degraded, which is a significant threat to environment. In that case, these synthetic polymers are not environmentally benign. By incorporating cellulose based paper matrix into flexible devices based on liquid electrochromic mixtures, researchers finally obtained green electrochromic devices with high performance [14].

Brown algae Laminaria japonica is kind of seaweed and it contains a relatively amount of sodium alginate, which can be seen as natural polymer. Different from Laminaria japonica, jellyfish is a special creature containing 95–98% water, which can also be utilized as ideal natural electrolyte. These two biological tissues are abundant resources in nature and can be available with ease. By simple chemical treatments, laminaria japonica and jellyfish became transparent. Such biological tissues are also green enough that they can be easily degraded under natural environment. Compared with traditional organic polymers, no toxic and hazardous waste come into being during the degradation progress. To the best of our knowledge, no other biologically-based products are functioned as green gel electrolytes in the electrochromic devices.

In this work, we firstly employed biological tissues (seaweeds and jellyfish) to be gel electrolyte. The treated biological materials were immersed in electrochromic mixtures for ten minutes, during which time the electrochromic materials were taken up into the natural products and transported inside the tissues. The spontaneous electroactive species transferring process was controlled by the organism and no

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other auxiliary technique was used in biology tissues [15]. Following the principles of green chemistry, no toxic organic solvents were introduced during the room-temperature device assembly. Besides, the main raw materials are originated from nature. Owing to abundant raw materials and simplified fabrication process, the device could be low-cost and is suitable for mass production. Despite all that, the biological devices exhibited low driving voltages as low as 1.1 V beyond our expectation, which is better than results in the reported literatures [7,14,16,17]. From our point of view, treated biological tissues can be a great impetus to function as green gel electrolytes in terms of low-cost and non-toxic. Environmental-friendly device can also be prospected in our daily life based on these biological tissues.

2. Experimental

2.1. Chemicals

Sodium hydroxide, 1, 1′-Ferrocenedicarboxylic acid and 1, 1′-Ferrocenedimethanol were purchased from Aladdin (99%), hydrogen peroxide from Aladdin (30%) and 4, 4-bipyridine, 3-bromo-1-propanol were purchased from J&K (97%). All the commercial available reagents were of high purity and used without further purification.

The bis(3-hydroxypropyl)viologen dibromide (HPV^{2+}) was prepared according to the previous literature [18]. Firstly, 4, 4′-Bipyridine (620 mg, 4.0 mmol) and 3-bromo-1-propanol (8.3 g, 60 mmol) were dissolved completely in DMF (30 ml) and stirred at 90 °C for 60 h. Secondly, the mixture was poured into acetone (300 ml), and the precipitate was filtered and washed several times with acetone. After that, the resultant product (yellow solid) was then washed with warm ethanol (20 ml) twice, filtered, rinsed with acetone, and dried under vacuum to afford final products (1.59 g, 92%). (^{1}H NMR (400 MHz, D_2O): δ 2.24 (m, 4H, J = 6.3 Hz), 3.63 (t, J= 6.0 Hz), 4.75 (t, 4 H, J = 7.2 Hz), 8.48 (d, 4H), 9.06 (d, 4H); ^{13}C NMR (101 Hz, D_2O): δ 32.7, 57.8, 59.4, 127.1, 145.7, 150.1; MS: 274 (M-2Br) $^+$, 215 (M-C3H6OH-2Br) $^+$, 157 (M-2C3H6-OH-2Br + H) $^+$)

2.1.1. Substrates

The ITO glass substrates were purchased from South China Science and Technology Co.,Ltd, Shenzhen. Before use, the ITO-coated glass substrate (sheet resistance is 15 Ω/□ and average transmittance of the film in visible region is 86%) were cleaned with deionized water, acetone and ethanol for 30 min under sonication, respectively.

2.2. Methods

2.2.1. Treatment of biological products

The seaweeds were purchased from market and handled as follows: firstly, we immersed the seaweeds into water and washed to remove dirt on the surface. After rough handling, these seaweeds were soaked in ethanol for 12 h by soxhlet extractor with the purpose of decolourization. Subsequently, primary products were rinsed with deionized water again. At last, we immersed the seaweeds into dilute hydrogen peroxide (5%) for 2 h for further bleaching. After washed with deionized water twice, we obtained nearly transparent seaweeds. However, treatment of jellyfish was easier than the method above. The jellyfish we purchased was first washed with deionized water for several times to ensure cleanliness. Then we exfoliated cuticular layer of the jellyfish carefully and got transparent jellyfish tissues.

2.2.2. Fabrication of ECDs

About 12 mg 1, 1′-ferrocenedicarboxylic acid or 1, 1′-ferrocenedimethanol was added into the culture dish and then 1.5 ml deionized water was added. After the ferrocene derivatives were completely dissolved, 15 mg viologen was introduced. Then, a little sodium hydroxide (5 mg) was added to adjust PH to dissolve ferrocene derivatives. After the mixture was dissolved completely, dried biological tissues were immersed in the solution for 10 min. Subsequently, the biological tissues were put onto the ITO-coated substrate and another ITO glass substrate was placed onto the top of the biological tissues, giving ITO/biological tissues/ITO configuration of the device. After that, we sealed the ECD with assistance of cure adhesive to ensure airtightness in argon atmosphere.

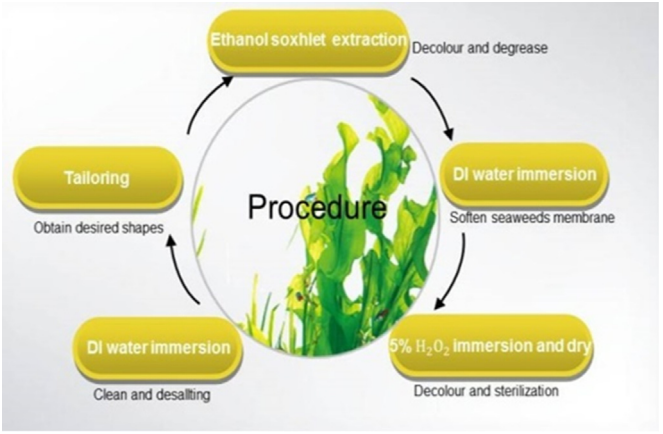

Fig. 1. Procedure of chemical treatments of seaweeds.

2.2.3. Instrumentation and measurements

The micrographs were achieved by Nikon light microscope LV 100ND. All electrochemical measurements were performed on a potentiostat/galvanostat (Chenhua, CHI660E) and a ECDs cyclic testing system. To get electrochemical data, the potentiostat/galvanostat was connected in junction with a spectrophotometer (Aoxi, UV1902PC). All electrochemical measurements of ECDs were obtained under three-electrode system configuration, with reference electrode and counter electrode connection in series.

3. Results and discussion

The specific procedure of chemical treatments of biological tissues is given in Fig. 1. Additionally, schematic diagram of the fabrication process for viologen-based ECDs is illustrated in Fig. 2. Chemical structures of electrochromic compounds and electron mediators are shown in Fig. 3 and bis(3-hydroxypropyl)viologen dibromide abbreviates as HPV^{2+}. Detailed characterization of electrochromic compounds is given in Fig. S1.

In order to investigate performance of biological tissues, electrochemical measurements of two biological ECDs were conducted as depicted in Fig. 4 and Fig. 5. As can be seen clearly from Fig. 4a, natural products-seaweeds showed primary brownness color when purchased from market without additional management. Initial deep color and opaque appearance make the seaweeds unsuitable for transparent gel electrolyte. After different chemical treatments, the seaweeds faded and became nearly transparent under background pictures compared with photographs before treatment as described in Fig. 4b. During chemical

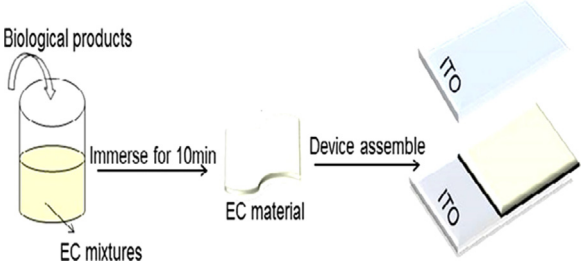

Fig. 2. Schematic diagram of the fabrication Process for viologen-Based ECDs.