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Full Length Article

Sunlight-charged electrochromic battery based on hybrid film of tungsten oxide and polyaniline

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ABSTRACT

Electrochromic (EC) energy storage devices that could realize the multifunctional integration of energy storage and electrochromism have gained much recent attention. Herein, an EC battery based on the hybrid film of $W_{18}O_{49}$ and polyaniline (PANI) is developed and assembled, which integrates energy storage and EC functions in one device. The $W_{18}O_{49}$/PANI-EC battery delivers a discharging capacity of 52.96 mA h g^{-1}, which is about two times higher than that of the $W_{18}O_{49}$-EC battery. Sunlight irradiation could greatly promote the oxidation reactions of both $W_{18}O_{49}$ and PANI during the charging process of the $W_{18}O_{49}$/PANI-EC battery, thus effectively accelerating the charging rate. This work provides a green, convenient, environmentally friendly, and cost-free charging strategy for the EC energy systems and could further advance the development of the multifunctional EC devices based on the organic/inorganic composites.

1. Introduction

Electrochromic (EC) devices, which demonstrate color alteration when subjected to a low external electrical potential, have found a wide range of applications in energy-saving smart windows, automobiles, military camouflage, displays, and so on [1–6]. Meanwhile, electrochemical energy storage devices such as batteries and supercapacitors have also gained tremendous attention for their applications ranging from portable electronics to electric vehicles [7–11]. Since EC devices and electrochemical energy storage devices share very similar features in device configuration (both contain two electrodes and electrolyte) and reaction kinetics (both are replied on reversible electrochemical reactions), their combination can bring in highly desired advantages over the individual devices [12–16]. Fox example, the bi-functional PB/Al device with PB and Al as electrodes combined the energy storage ability with EC behavior in one device, which can function as both self-powered EC window and self-rechargeable battery [13]. The $W_{18}O_{49}$/Al EC battery could not only exhibit a very high discharging capacity when charged by H_2O_2 but also present integrated color-changing behavior during the charge/discharging process [14]. The WO_3-based pseudocapacitive glass windows exhibited excellent bi-functionalities of energy storage and EC, with a high specific capacitance of 639.8 F g^{-1} and a broad optical modulation of 76.2% [15]. The complementary EC energy storage systems with organic and inorganic EC materials as separate electrodes have gained much recent research interests. Mai et al. reported an EC asymmetric supercapacitor window by introducing WO_3 and polyaniline (PANI) as the negative and positive electrodes, respectively, showing a high energy density of 7.7×10^{-3} mW h cm^{-2} [17]. Notably, the energy status of the EC supercapacitor could be determined by simply observing its color change with the naked eye. Li et al. developed a large-scale EC energy storage device by constructing $WO_3 \cdot H_2O$ and Prussian white film as electrodes, which could be integrated with solar cells to realize the adjustment of indoor sunlight intensity via solar energy [18].

Both the tungsten oxides ($WO_{x\leq3}$) and PNAI are suitable electrode materials for constructing EC-energy storage devices because the two commonly-used EC materials have also been proven to possess promising pseudocapacitive performance [19–21]. Since $WO_{x\leq3}$ and PNAI own different redox potentials, their combination could generate multicolor EC composites with enhanced EC or electrochemical properties or both, which could provide novel ideal candidate for the development of high-performance multifunctional EC devices. For example, Wei et al. prepared the WO_3/PANI nanocomposite films by electropolymerization of aniline onto

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WO_3, which displayed dual EC behaviors at both positive and negative potentials and exhibited much higher coloration efficiency (CE) than that of pure WO_3 and PANI [22]. Geng et al. prepared $WO_{x\leq3}$/PANI composite films through concurrent electropolymerization of aniline and electrochemical deposition of $WO_{x\leq3}$ on partial exfoliated graphite [23]. Compared to the $WO_{x\leq3}$ and PANI-based supercapacitors, the $WO_{x\leq3}$/PANI-based supercapacitor exhibited highly enhanced energy storage behaviors (*i.e.* higher specific capacitance and energy density). Zhang et al. synthesized the WO_3 nanorods/PANI composite thin films using a surface-initiated-polymerization method, and this composite film exhibited fast switching speed, high EC contrast, and ideal durability [24]. Tian et al. designed a smart supercapactior "sign" with pattern and background composed of $W_{18}O_{49}$ nanowires and PANI, respectively, which could display color variations with the varied level of energy storage [25]. Obviously, most of previous works have been focused on the $WO_{x\leq3}$/PANI hybrids-based EC devices or supercapacitors, only a few works so far on the related multifunctional EC devices have been reported. Additionally, in-depth research on the working mechanisms of the $WO_{x\leq3}$/PANI hybrids-based multifunctional EC devices is still lacking and needs to be further studied.

Charging approach is crucial to the EC energy storage devices because it determines the size, structure, cost, and application range of the final devices. To date, the EC batteries/supercapacitors have been mainly charged by three methods: applying external power (method 1), exposure to air (*i.e.* self-charging process) (method 2), addition of H_2O_2 (method 3), as schematically illustrated in Fig. 1a. The charging route by applying external power needs power supply or special equipment like electrochemical workstation, while the self-charged process involves very long charging time (>12 h). Despite that the H_2O_2-charged EC battery can deliver very high capacity, reaction between the metal electrode like Al and H_2O_2 is unavoidable, which would deteriorate the cyclic stability of the battery. Therefore, it is of great importance to develop a green, convenient, environmentally friendly, and low-cost charging strategy for the EC energy storage devices. In this work, an EC battery using the $W_{18}O_{49}$/PANI hybrid film and Al as electrodes and $AlCl_3$ as electrolyte was assembled and its capacitive behaviors were investigated. Interestingly, we found that sunlight irradiation could obviously accelerate the charging rate of the $W_{18}O_{49}$/PANI-EC battery, which could reduce the charging time by six times in comparison with the self-charging process (method 2). The operating mechanisms of the $W_{18}O_{49}$/PANI-EC battery and the relation between the EC process and the charging/discharging process have also been discussed.

2. Experimental details

2.1. Chemicals

Tungsten hexachloride (99.5%, WCl_6), sulphuric acid (H_2SO_4), aniline, ethanol, and deionized water was purchased from Sinopharm Chemical Reagent Co., Ltd. Indium tin oxide (ITO) coated transparent conductive glass (<7 Ω/sq) was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.

2.2. Preparation and electrochemical measurement of $W_{18}O_{49}$/PANI hybrid film

2.2.1. Synthesis of $W_{18}O_{49}$ NFs

The $W_{18}O_{49}$ NFs were synthesized by a solvothermal method, as widely described in previous reports [26–29]. Typically, 50 mg of WCl_6 was dissolved in 30 ml of ethanol to form a yellowish solution, which was then added into a 50 ml PTFE-lined autoclave. The autoclave was heated at 180 °C in a furnace for 5 h and then cooled down naturally to room temperature. Finally, the as-synthesized $W_{18}O_{49}$ NFs were washed with deionized water twice and centrifuged with ethanol for collection.

2.2.2. Preparation of $W_{18}O_{49}$/PANI hybrid film

The $W_{18}O_{49}$ NFs were firstly dispersed in ethanol to form a homogenous solution with a concentration of 3.5 M. Subsequently, the $W_{18}O_{49}$ NFs film was deposited onto the ITO glass using a spin-coating method on a spin coater at a rotating speed of 350 r/s for 5 s and then 450 r/s for 20 s. The $W_{18}O_{49}$/PANI hybrid film was prepared using an electrochemical polymerization process on an Autolab electrochemical workstation in a three-electrode system. The ITO glass coated with the $W_{18}O_{49}$ NFs, Ag/AgCl, and Pt foil were used as the working electrode, reference electrode, and counter electrode, respectively. 0.2 M H_2SO_4 and 1 M aniline in deionized water were used as the electrolyte. A typical polymerization was carried out for 6 cycles with potential in the range of 0.2–1.3 V at a scanning rate of 50 mV/s.

2.2.3. Characterization

Scanning electron microscopy (SEM) was carried out with a JSM 7500F electron microscope operated at 20 kV. Localized electrochemical impedance spectroscopy (LEIS) was carried out using a three-electrode system on a M470 scanning electrochemical workstation (Bio-logic, France), with current amplitude of 10 μA and single frequency of 10 Hz. The $W_{18}O_{49}$/PANI hybrid film, a carbon

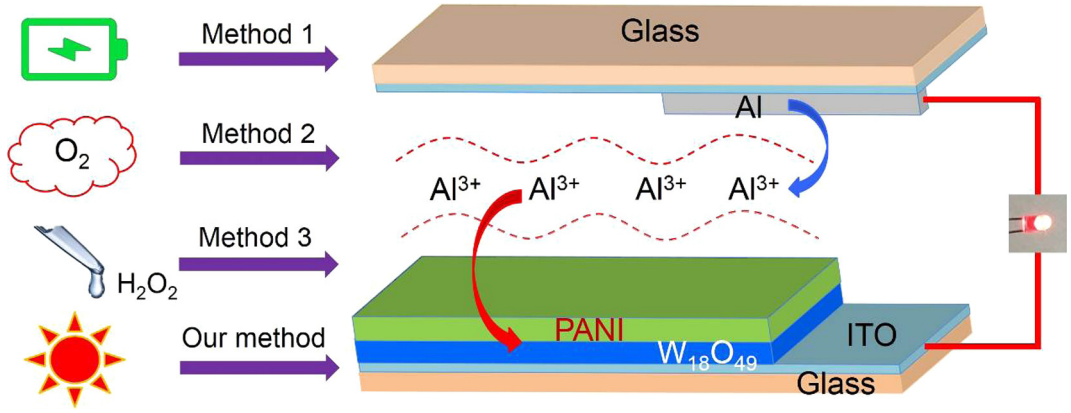

Fig. 1. Schematic of charging routes for $W_{18}O_{49}$/PANI-EC battery. The battery can be charged by four methods: applying external current (method 1), exposure to air (method 2), addition of H_2O_2 (method 3), and sunlight irradiation (method in this work).