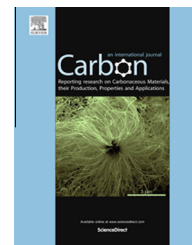


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A facile one step electrostatically driven electrocodeposition of polyviologen–reduced graphene oxide nanocomposite films for enhanced electrochromic performance

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ABSTRACT

Polyviologen (PV)–reduced graphene oxide (rGO) nanocomposite films were fabricated by simple, one-step reductive electropolymerization of cyanopyridinium based precursor monomer (CNP) in an aqueous dispersion of graphene oxide (GO). Since the polymer formation and reduction of graphene oxide occurs within the same potential window, electrocodeposition method was preferred for obtaining nanostructured PV–rGO films. Cyclic voltammetry experiments of PV–rGO displayed two well resolved, reversible one-electron redox processes typical of viologen. Being a redox polymer, incorporation of rGO further enhances the electroactivity of the PV in the composite films. Vibrational spectral analysis with surface characterization revealed structural changes after composite formation along with subsequent reduction of GO within the polymer matrix. The PV–rGO nanostructured film exhibits a high-contrast electrochromism with low driving voltage induced striking color changes from transparent (0 V) to purple (–0.6 V), high coloration efficiency, fast response times and better cycling stability compared to a pristine PV film. This improved performance can be attributed to the high stability of the electrochrome in the composite assembly induced by electrostatically driven non-covalent interactions between redox PV²⁺ and negatively charged rGO, improved electrical conductivity and enlarged surface area accessed through reinforced nanostructured graphene sheets for tethering PV molecules.

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1. Introduction

Upon oxidation–reduction or electron transfer reactions, certain electroactive materials undergo voltage induced

reversible color changes observed in the visible or near IR region of the spectrum. This phenomenon is known as electrochromism [1]. The electrochromic (EC) materials can be broadly divided into three categories: (i) inorganic metal

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oxides; e.g. NiO, WO₃, ZnO etc, (ii) transition metal complexes; e.g. Prussian blue, Ru (II)–Ru (III) complexes etc, and (iii) organic materials; e.g. conjugated polymers like PEDOT or PANI, viologen etc [2]. As can be expected from the rapidly growing field of synthetic organic chemistry, the main focus has always been on organic EC materials due to that a vast number of organic compounds exhibit electrochromism [3]. Such EC materials have already been applied for diverse purposes, e.g. in display devices, solar control windows, mirrors etc. [4,5]. In particular, EC windows and mirrors used in automobiles and airplanes have been commercially available for a while [6]. The main parameters for ideal EC materials is the color diversity, memory effect, low cost, easy processibility, low driving voltage and fast response time. In addition, another factor for enhancing the EC performance is the stability of the electrochrome which must undergo many repeatable color changes between colored and bleached states, thus remain operable over long scanning periods. Therefore, inexpensive, durable and easily processible organic electrochromes is a need of future optoelectronic industry.

Among the EC materials, viologen have certain advantages in comparison to the conjugated polymers. The advantages include highly stable redox activity, intensely colored radical cation formation, low driving voltages for visual changes and high optical contrast [7–9]. In last few years, researchers have developed different derivatives of polymers bearing viologen side groups by playing with synthesis methods [10]. Polyviologen materials possess viologen as repeating unit in its backbone which might be helpful in exploring wide-ranging applications related to viologen materials [11,12]. Researchers have also synthesized viologen precursors which have been functionalized with conjugated groups in order to provide some conducting properties to the resulting structure [13,14]. Yet, the electrical conductivity was very low compared with intrinsically conjugated polymers. Moreover, despite of low material cost and good processibility, viologen materials are lacking good cyclic reversibility and fast response times. For this reason, scientists have tried to combine viologen with large area semiconductors like TiO₂ or ZnO, where the good electron transfer properties combined with well-ordered host structure facilitates the electrochrome anchoring systematically into the pores and improves the overall EC properties [15,16]. However, comparably insignificant surface area, intermediate coloration speed and inadequate long term stability were the downsides in such hybrid systems.

In recent years, graphene has emerged as promising 2D material owing to its exceptional chemical, thermal and mechanical stability, excellent electronic and electrochemical properties, large surface area and high carrier mobility [17–19]. Due to its ease in processibility and low cost, large amount of graphene has been prepared as graphene oxide (GO) and its subsequent reduction thereof [20–22]. Since the oxidation of graphite to GO diminishes its excellent conducting properties, reduction of GO is desired to partially restore its sp² network. Due to the harsh reaction conditions involved in chemical, mechanical or thermal reduction methods, electrochemical reduction of GO is considered as green strategy which offers mild reduction conditions [23,24]. Such electrochemical reduction dramatically reduces oxygen containing groups

from GO, although not 100%, therefore called reduced graphene oxide (rGO). Such an electrochemically rGO has shown to possess relatively strong conducting properties [25]. Recently there have been many reports on the development of rGO based composites for electrochemical applications [26,27]. However, there are very few studies devoted to the EC applications using GO, rGO or graphene. Recently, Son et al. [28] demonstrated that Prussian blue nanoparticles on high quality, CVD grown graphene possess slow response times during EC switching. This might be due to the slow electron transfer behavior in high quality graphene reported by Banks et al. [29]. On the other hand, rGO based NiO hybrid films has shown to possess faster switching times and better cycling performance owing to the better electrochemical stability and porosity of rGO which facilitates the electrolyte access [30]. Very recently, E. Hwang et al. developed a flexible EC system comprising methyl viologen and graphene quantum dots that showed excellent EC switching and operational stability [31]. Consequently, the low cost and fast electron transfer kinetics made rGO a prominent electrode material for future ECDs.

Our research group has been widely exploring new electrochromic systems based on viologen derivatives [32,33]. We employ simple electroreduction of cyanopyridine based monomers in order to obtain highly stable and strongly adhered viologen/polyviologen films on the electrode substrates. Considering the high mobility and optical transparency of graphene materials, we anticipated that the electrochrome (PV) stability would significantly enhance in presence of rGO, owing to its non-covalent attachment with polymer chains. In this paper, we report for the first time the enhanced electrochromic performance of the PV–rGO nanocomposite films. Especially considering better conductivities and large accessible surface area in rGO sheets, the EC response times as well as the reversible potential cycling stability of nanostructured PV–rGO composite films were compared with those of the pure homopolymeric PV films. Given that monomer precursor of PV being soluble in aqueous medium, a one-step reductive electrocodeposition of monomer-GO dispersion was favored for obtaining composite material, where the GO deposit in the nanocomposite films gets simultaneously reduced during cathodic scanning.

2. Experimental section

2.1. Preparation of GO

Preparation of GO was carried out using a modified Hummers method [34]. In brief, natural graphite flakes (2 g) were dispersed in a mixture of conc. H₂SO₄ (68 ml) and NaNO₃ (1.5 g). KMnO₄ (9 g) was then added slowly into the above mixture for ca. 1/2 h and the reaction mixture was continuously stirred in an ice bath for approximately 2 h. The reaction mixture is then kept at room temperature and was allowed to react for 5 days. Afterwards, the oxidation reaction was terminated by dropwise addition of 5 wt.% H₂SO₄ in an ice bath and the remaining KMnO₄ was consumed by adding 30% H₂O₂ at room temperature. The brown colored mixture was

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