

Electrochemical deposition of polyviologen-reduced graphene oxide nanocomposite thin films



Nianxing Wang^{a,b}, Zsófia Lukács^c, Bhushan Gadgil^{a,b}, Pia Damlin^a, Csaba Janáky^c, Carita Kvarnström^{a,*}

^a Turku University Center for Materials and Surfaces, c/o Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, Vatselankatu 2, FI-20014 Turku, Finland

^b University of Turku Graduate School (UTUGS), FI-20014, Turku, Finland

^c MTA-SZTE "Lendület" Photoelectrochemistry Research Group, University of Szeged, H-6720, University of Szeged, Hungary

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ABSTRACT

In previous years, a series of polyviologen films (PVs) have been synthesized through electrochemical polymerization in our group. In order to improve their electrochemical properties, a thin composite film of these redox polymers and reduced graphene oxide were prepared using a one-step technique. In this work, the cyanopyridine based monomer and the graphene oxide flakes were initially dissolved in an ionic liquid (IL), after which the electrochemical reduction was performed. A branched polyviologen film was formed during the electrochemical process, while the graphene oxide flakes were reduced and immobilized in the polyviologens network. The resulting composite film was characterized by electrochemical, spectroscopic, and imaging techniques, such as cyclic voltammetry, electrochemical impedance spectroscopy, UV-vis, FT-IR, Raman spectroscopy, and SEM. The analysis indicated a successful composite film formation: the redox property was enhanced by the presence of graphene in the polyviologen films. Such an easy fabrication process together with inexpensive precursor materials demonstrates a facile way for producing thin composite films for different electrochemical applications, such as electrochromic devices and sensors.

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1. Introduction

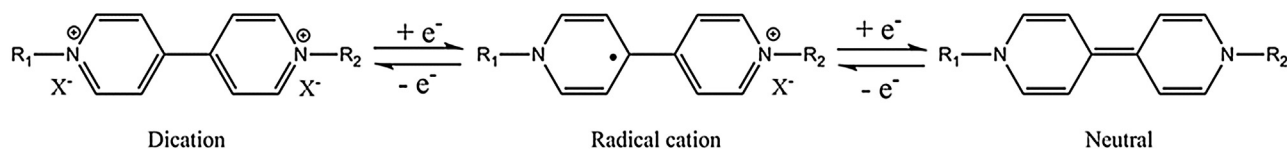
Redox polymers are defined as polymers containing groups that can change their electrochemical properties upon the loss or gain of electrons (oxidation and reduction, respectively). Mainly two types of redox polymers are known: conjugated polymers containing redox active functional groups like ferrocene (the members of this class also have an additional redox activity stemming from the conjugated backbone) or pure redox polymers like polyviologens (PVs). Viologens, which are usually named as 1,1'-disubstituted-4,4'-bipyridinium salts, are one of the most frequently utilized organic functional materials [1]. As a result of their excellent redox properties, viologens are employed in applications, such as electrochromic devices [2–6], sensors [7–9], and fuel cells [10–13]. Generally, the redox transformation of viologens consists of two one-electron steps, resulting in three possible states: the dication state, the radical cation state, and the

neutral state [1]. The different states of the viologens are shown in Scheme 1, each representing unique properties. The dication is the most stable species, where the two pyridine rings are non-parallel to each other at an angle of 40–50° [14,15]. When the viologen is reduced into its radical cation state, however, the two pyridine rings will switch to planar, and will maintain this configuration also in its neutral state. In the reduction process from the dication to radical cation state, the unique color of viologens will appear, which is one of the reasons why viologens are frequently utilized as electrochromic materials. The colors of viologens can be tuned and adjusted by changing the substituent groups (R_1 and R_2), correspondingly, the redox potentials will also change [16,17]. The applications of viologens are mainly based on the first redox process (reduction from dication to radical cation), meaning that the research on the neutral state of viologens is relatively less comprehensive. It shall be mentioned, however that the neutral state of viologens can act as a strong reducing agent, to be utilized in doping of other materials [18,19].

Synthesis of different cyanopyridine based monomers and conjugated monomers functionalized with either cyanopyridinium or viologen moieties have recently been carried out in our

* Corresponding author at: Vatselankatu 2, Turku, 20014, Finland.

E-mail addresses: ckvarnst@abo.fi, carita.kvarnstrom@utu.fi (C. Kvarnström).



Scheme 1. Structure of the three different redox states of viologens.

group. The monomer which has been utilized as the precursor in the electrochemical polymerization is shown in [Scheme 2](#) below [20,21]. An important drawback of these materials is the lack of electrochemical stability. For this reason, composite assemblies were introduced, where the redox active polymers blended with electrically conducting materials, thereby strengthening the electrochemical reversibility of the redox polymer [22,23]. In this work, we use another approach, where reduced graphene oxide (rGO) was employed to prepare the composite film with polyviologens.

Graphene has emerged as a new conductive platform for different electronic devices, due to its exceptional physicochemical, thermal, electronic and mechanical stability [24,25]. One special member of the graphene-related materials family is the graphene oxide (GO), which is usually synthesized by chemical exfoliation of graphite using Hummers method or its modified version [26]. During the oxidation process, oxygen containing functional groups are linked to the graphene backbone leading to a radical decrease in the electrical conductivity of GO [27]. To restore at least some of the graphene structure, electrochemical, chemical or thermal reduction have been introduced. Compared to other methods, electrochemical reduction of GO is preferred, as it is a relatively green approach, with easy integration possibility into flexible electronic devices [28,29].

GO can be dispersed in deionized water, however, when other ions are introduced into the solution, GO usually aggregates. In order to solve this problem, room temperature Ionic Liquids (ILs) were introduced as solvents in the electrochemical synthesis of polyviologen and rGO based composite films. ILs are relatively new solvents which are entirely composed of ion pairs which are in liquid form at room temperature. Due to their unique properties,

such as a broad electrochemical window, high intrinsic electrical conductivity, immiscibility with organic and inorganic solvents, high thermal stability, and no vapor pressure, ILs are widely utilized in various research areas [30–33]. Recently, hydrophilic imidazolium-based ILs have been employed as stabilizers, providing dispersion of graphene nanosheets via π - π and cation- π interactions [34,35]. Because of all these reasons, a commercial IL (BMIMBF₄) was utilized as solvent for the electrochemical synthesis of the composite film.

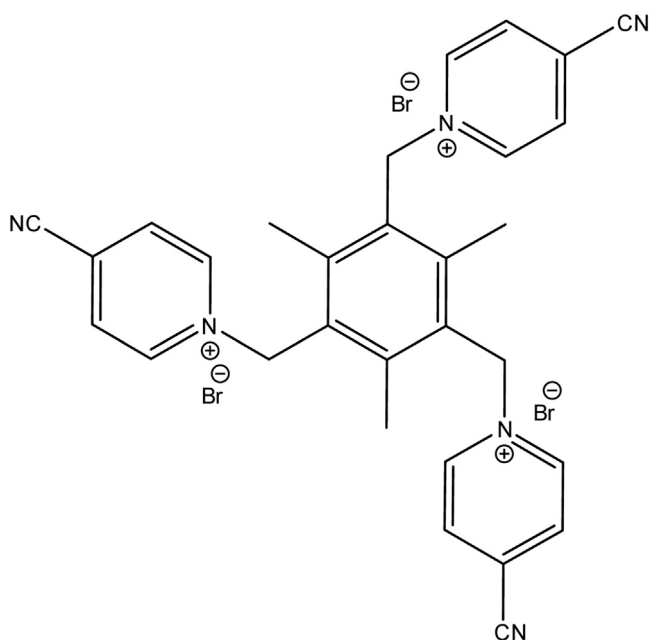
In this work, polyviologen and rGO based composite films were synthesized through a simple one-step method, using an IL as electrolyte. The cyanopyridine based monomer and GO were mixed in IL and electrochemically reduced (polymerized). A branched polyviologen was formed through the coupling of pyridine rings during the reduction process, while GO was reduced into rGO simultaneously. The successful immobilization of rGO in the polyviologen film was driven by π - π stacking and the electrostatic attraction of the negatively charged GO and the positively charged viologens. All the characterization tools indicated a composite film with excellent redox property of the polyviologen that was improved upon the introduction of rGO. The facile fabrication process from functional precursors gives the composite material a remarkable potential to be applied in different electrochemical devices like electrochromic and sensor devices.

2. Experimental

2.1. Chemicals and materials

Potassium chloride (KCl) was purchased from Oy FF-Chemicals Ab, and it was prepared as electrolytes of 0.1 mol/L. The 1,3,5-Tris(4-cyanopyridinium-1-ylmethyl)-2,4,6-trimethylbenzenetribromide (TCP) was prepared according to previous reports [36,37]. All solutions used in the experiments were prepared from deionized water and purged prior to use with N₂. GO was synthesized by a modified Hummers method, and subsequently purified by centrifugation and dialysis. Firstly, a 4g/L aqueous solution of GO was prepared as described in previous work [28] and sonicated for half an hour, followed by centrifugation at 4500 rpm for 20 minutes.

A room temperature IL, BMIMBF₄ was chosen as solvent because the solubility of both the cyanopyridine monomer and GO was high enough to obtain the solutions. The solution was prepared of 5 mmol/L of TCP and 0.2 g/L of GO in BMIMBF₄. GO was dissolved in IL using the following procedure: 4 mg/mL aqueous solution of GO was mixed with the appropriate amount of BMIMBF₄ and stirred overnight. Then the solution was exposed to ultrasound to obtain monodisperse dispersion. After that, the dispersion was dried in vacuum oven at 50 mbar, 45 °C for 8 hours. In a separate batch, 10 mmol/L TCP was dissolved in BMIMBF₄. Finally, the two IL batches were mixed and stirred thoroughly. Finally, the solution was purged with nitrogen for 10 minutes and sonicated for 10 minutes before polymerization.



Scheme 2. Structure of the three branched cyanopyridine monomer (TCP).

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