



Reversible Switched Detection of Dihydroxybenzenes Using a Temperature-sensitive Electrochemical Sensing Film



Yuanqing Zhou^{a,1}, Chao Chen^{a,1}, Jia Zhao^b, Junjie Fei^{a,*}, Yonglan Ding^a, Yuanli Cai^{a,c}

^a Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, PR China

^b College of Resource and Environment, Hunan Agricultural University, Changsha 410128, PR China

^c Department of Polymer Science and Engineering, Soochow University, Suzhou 215123, PR China

ARTICLE INFO

Article history:

Received 6 November 2015
Received in revised form 21 January 2016
Accepted 25 January 2016
Available online 28 January 2016

Keywords:

graphene oxide
multi-walled carbon nanotube
electrochemical sensor
temperature-responsive polymer
electrochemical “on/off” detection

ABSTRACT

A composite sensing film (PGS), consisting of poly(N-isopropylacrylamide)₁₀₁-b-poly(2-acrylamidoethyl benzoate)₃₇ (PNIPAM₁₀₁-b-PAAEB₃₇), graphene oxides (GO) and short multi-walled carbon nanotubes (SMWCNs), was fabricated and modified onto a working electrode. The sensing film served as a reversible switch for electrochemical detection, with the switching behaviour responding to thermal stimuli. Cyclic voltammetry of hydroquinone (HQ) and catechol (CC) at the PGS film-modified electrode displayed large peak currents when the temperature was above the lower critical solution temperature (LCST) of PNIPAM₁₀₁-b-PAAEB₃₇. These large currents disappeared at low temperature. Interestingly, the composite film showed reversed electrochemical “on/off” behaviour as compared to previously reported switchable electrodes, which were modified only with temperature-responsive polymers. This behaviour can be attributed to the temperature-dependent phase transition of PNIPAM₁₀₁-b-PAAEB₃₇ and cooperative effects of the other two functional components (SMWCNs and GO). The repeatable “on/off” switching of the voltammetric responses of HQ/CC on the PGS-modified electrode were achieved via regulating the solution temperature. This research provides a new type of temperature-controlled switchable electrode with potential applications in the design of novel sensors, fuel cells and electronics.

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1. Introduction

Chemically modified electrodes with reversible “on/off” switching or tunable interfacial properties toward external physicochemical signals are intriguing systems for fundamental research, and offer great promise in such fields as switchable biosensors for biomedical applications [1,2], switchable fuel cells [3], electrochemical information processing systems [4], and other electrochemical devices [5]. One approach to switchable electrode construction involves applying metallic or magnetic species in electrochemical devices. The electrode interfacial properties (e.g., conductivity) can be significantly tuned by variable potentials or an external magnetic field [6–11]. For instance, Cu²⁺ ions in a poly(acrylic acid)/CdS matrix immobilized on an Au electrode surface were reduced to metallic clusters and then oxidized back to the cationic state by altering the potentials, which caused dramatic changes in the conductivity of the polymer layer [7].

Stimuli-responsive polymers, which exhibit changes in conformation or structure due to external stimuli [12–17], provide another approach to switchable electrode construction. Electrode surfaces coated with responsive polymers can significantly change their interfacial properties (e.g., charged state, permeability, and pH [18–20]) in response to external signals such as light, temperature or chemical/biochemical input, and show tunable or switchable electrochemical behaviours [21–27]. Tam [19] reported that indium tin oxide (ITO) electrodes modified with poly(4-vinyl pyridine) (P4VP) brushes showed switchable interfacial activity toward redox species. This was due to the high permeability for redox species of the protonated, swollen P4VP brush state (electrochemical “on” state) and the impermeability of the deprotonated, hydrophobic, shrunken P4VP brush state (electrochemical “off” state). Temperature-sensitive polymers can undergo swelling–shrinking phase transitions in response to thermal stimuli [28,29], and have attracted interest as temperature-controlled electrochemical switch devices [30,31]. Poly(N-isopropylacrylamide) (PNIPAM) has been extensively studied as a temperature-sensitive polymer in the sensor field. Its LCST is approximately 32 °C [32,33], just within the manageable temperature range for conventional electrochemical experiments.

* Corresponding author. Tel.: +86 731 58298876; fax: +86 731 58292251.
E-mail address: fei_junjie@xtu.edu.cn (J. Fei).

¹ These authors contributed equally to this work.

PNIPAM films fabricated on electrode surfaces show a reversible, temperature-controlled “on-off” property toward redox probes. Specifically, electrochemical responses of redox probes appeared when the PNIPAM brush was in the swollen state (below 32 °C) but disappeared when the PNIPAM brush was in the shrunken state (above 32 °C) [24].

Carbon nanomaterials such as fullerenes, carbon nanotubes, and graphene exhibit unique optical, electronic, and catalytic properties. In the sensor field, carbon nanomaterials used in electrode modification can accelerate signal transduction through catalytic activity, conductivity, and biocompatibility [34–37]. Graphene oxide (GO), a carbon nanomaterial, possesses a two-dimensional, graphene-like structure with oxygen-containing functional groups such as epoxide, —OH, and —COOH. Due to this structure, GO exhibits good hydrophobicity, moderate conductivity, high chemical stability and excellent electrochemical properties, and can act as a support for the deposition of inorganic nanocatalysts or polymers. GO is widely used in the sensing field to facilitate or mediate the charge/electron transfer between the electroactive species and the electrode surface [38,39]. The integration of stimuli-responsive polymers and carbon nanomaterials generates hybrid systems that combine the properties of the nanomaterials with stimuli-responsive functions, to obtain switchable or tunable electronic, photonic and catalytic properties [40–45]. To date, hybrid materials have attracted substantial attention and have extensive applications in the sensor field [46,47]. A major goal of such studies is linked to achieving synergistic efforts to bring advanced properties to the hybrid materials, which can improve upon their individual properties [48].

In this paper, a hybrid material consisting of the temperature-sensitive copolymer PNIPAM₁₀₁-*b*-PAAEB₃₇, GO and SMWCNs was utilized to develop a temperature-controlled switch electrode. PNIPAM₁₀₁-*b*-PAAEB₃₇ contains benzene rings, which can be noncovalently attached to GO surfaces through π - π stacking interactions, which can improve the stability of the hybrid film [49]. The electrochemical responses of hydroquinone (HQ)/catechol (CC)

at the PGS-modified electrode were switched off when PNIPAM₁₀₁-*b*-PAAEB₃₇ was swollen, but switched on while PNIPAM₁₀₁-*b*-PAAEB₃₇ was shrunken (shown in Scheme 1). This switchable behaviour was reversed from that of previously reported switchable electrodes (modified only by stimuli-responsive polymers), which were switched off in their hydrophobic shrunken state and switched on in their swollen state [19,24]. The opposite “on/off” behaviour of the composite PGS electrode can be attributed to the cooperative, synergistic effect of PNIPAM₁₀₁-*b*-PAAEB₃₇, GO and SMWCNs in response to temperature stimuli. The PGS electrode also showed reversible and repeatable electrochemical “on-off” properties through controlling the solution temperature.

2. Experimental section

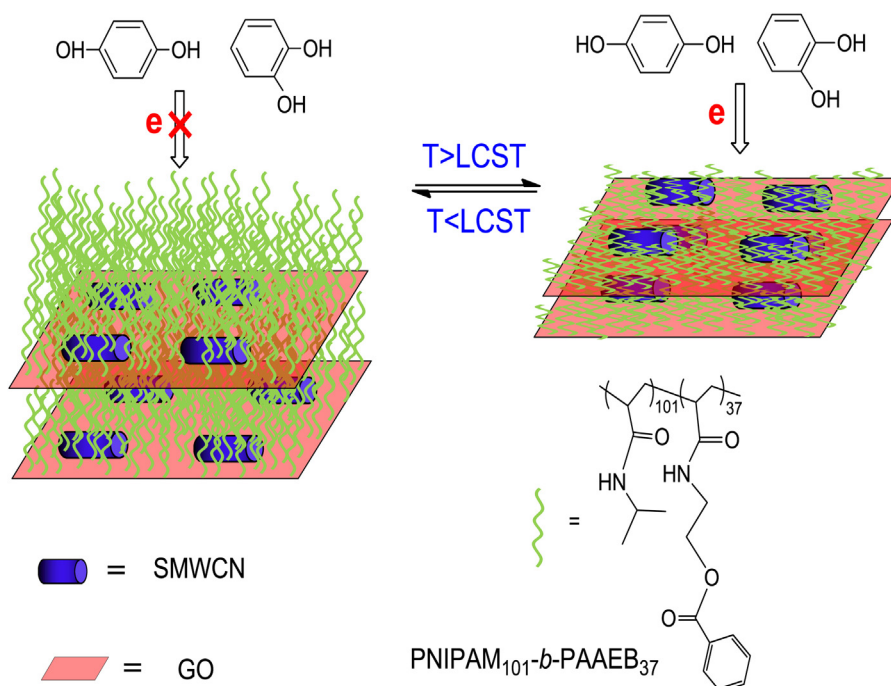
2.1. Reagents and Materials

SMWCNs (OD <8 nm, Length: 0.5–2 μ m, Purity >95 wt%) were obtained from the Chinese Academy of Sciences, Chengdu Organic Chemistry Company. Hydroquinone (HQ) and catechol (CC) were purchased from Shunyi Chemical Company of China and used without further purification. GO was prepared according to previous procedures [50]. PNIPAM₁₀₁-*b*-PAAEB₃₇ was prepared according to previous procedures [51]. Synthesis details of PNIPAM₁₀₁-*b*-PAAEB₃₇ and its ¹H NMR and GPC data are presented in the Supplementary Material, Fig. S1 and Fig. S2. All other chemical reagents were of analytical grade. Water was purified twice by distillation.

2.2. Fabrication of the Modified Electrodes

Glassy carbon electrodes (GCE) were carefully polished with 0.5- μ m alumina on a polish cloth, followed by sequential cleaning for 5 min with ethanol and double-distilled water in an ultrasonic bath, then dried in air before use.

The GO solution (45 μ L, 2 mg mL⁻¹) was added to a PNIPAM₁₀₁-*b*-PAAEB₃₇ aqueous solution (75 μ L, 10 mg mL⁻¹), and the mixture was



Scheme 1. Reversible, temperature-controlled “on/off” electrochemical response of HQ/CC at the PGS interface.

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