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Enhanced electron transfer in composite films of reduced graphene oxide and poly(*N*-methylaniline)

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Poly(*N*-methylaniline) (PNMA) has been electropolymerized for the first time from a graphene oxide (GO) dispersion containing 1.0 M HClO₄. Both GO and perchlorate were incorporated in the PNMA matrix during the electropolymerization resulting in the formation of a mixed composite material of PNMA-ClO₄ and PNMA-GO. Under the acidic polymerization conditions, the carboxylic groups of GO are undissociated and GO is therefore mostly mechanically entrapped in the PNMA matrix while perchlorate functions as the primary charge compensating ion. Electrochemical reduction at -0.85 V improved the electron transfer of the composite film due to reduction of GO in the PNMA matrix.

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Polyaniline (PANI) is one of the most studied electrically conducting polymers (ECP) due to its good environmental stability, easy and cost-effective synthesis, and high electrical conductivity at acidic pH [1]. However, PANI is usually deprotonated at slightly acidic and neutral pH resulting in the loss of the conductivity [2]. This property excludes the use of PANI in *in vitro* applications operating at physiological pH. It can be overcome by using poly(*N*-alkylanilines) (PNANI) which maintain their electroactivity even at neutral pH [3]. Despite of their low pH sensitivity [2,4], the PNANIs have been studied to much lesser extent than PANI due to their lower electrical conductivity [5]. The incorporation of graphene or reduced graphene oxide (rGO) into PNANI films is expected to improve their electrical conductivity and mechanical properties. We have recently reported a simple electrochemical method by which 3,4-ethylenedioxythiophene (EDOT) was first electropolymerized in the presence of graphene oxide (GO) as the only dopant [6]. The GO in the composite film of poly(3,4-ethylenedioxythiophene) and GO was then electrochemically reduced to rGO [7]. The successful reduction was confirmed by X-ray photoelectron spectroscopy (XPS). Here we report the electropolymerization of *N*-methylaniline (NMA) from a GO dispersion containing HClO₄. We show that the electrochemical reduction of GO in the poly(*N*-methylaniline) (PNMA) matrix improved the electron transfer in the composite matrix due to the rGO formation.

The electropolymerization of NMA was carried out with cyclic voltammetry between -0.2 V and 0.85 V from a GO dispersion (4.4. mg/l) containing 0.1 M NMA and 1.0 M HClO₄ (Fig. 1a). Before starting the potential cycling, the electropolymerization was initiated by a potential pulse (10 s) at 0.85 V. The synthesis of the GO dispersion has been reported elsewhere [6]. The cyclic voltammograms (CV) recorded during the electropolymerization of 0.1 M NMA in 1.0 M HClO₄, in the absence of GO (not shown), are almost similar to the CVs in Fig. 1a. This indicates that the electrically non-conducting GO does not participate as a charge compensating counter ion to any considerable extent in the PNMA film growth. The PNMA films electropolymerized in the presence and absence of GO were characterized in monomer-

free 1.0 M HClO₄ (Fig. 1b). The CVs of the two PNMA films have almost identical oxidation and reduction behavior suggesting that GO is mostly mechanically entrapped in the PNMA matrix with perchlorate functioning as the primary charge compensating counter ion. Under the acidic polymerization conditions, the carboxylic groups of GO are undissociated (uncharged) further supporting the assumption that GO is mostly mechanically entrapped in the PNMA matrix during the electropolymerization. The scanning electron microscopy (SEM) images in Fig. 2 verify that a mixed composite material was formed consisting of domains of PNMA-GO and PNMA-ClO₄ (Figs 2a and 2c). The incorporation of GO in the PNMA matrix was further confirmed with XPS measurements showing the presence of the peak centered at 286.8 eV originating from C-O groups of GO (epoxy and alkoxy) (Fig. 3b) [8].

The PNMA-ClO₄-GO films were exposed to electrochemical reduction in oxygen-free 0.1 M KCl at -0.85 V (vs. Ag/AgCl/3 M KCl) for 0, 10 and 30 min to reduce GO to rGO in the PNMA matrix. The C 1s XPS spectra of the reduced films in Figs. 3b-3d show that most of the oxygen-containing surface groups of GO (hydroxyl, epoxy, carbonyl and carboxyl) were removed after 30 min reduction (C-C/C=C: 284.7 eV; C-N: 285.7 eV; C-OH/C-O-C: 286.8 eV; C=O: 288.1 eV; O=C-O: 289.4 eV [6,8]). For comparison, the C 1s XPS spectrum of PNMA-ClO₄ is shown in Fig. 3a. The reduction of GO to rGO in PNMA-ClO₄-GO is clearly observed as a considerable decrease of the intensity of the XPS band at 286.8 eV. Simultaneously, the C:O ratio increased from 2.90 (unreduced film) to 4.04 and 4.71 for the films reduced for 10 and 30 min, respectively. Neither FTIR nor Raman spectroscopy could verify the reduction of GO to rGO because the PNMA bands strongly overlap with the GO and rGO bands [6].

The electrical conductivity of thin polymer films prepared on conducting substrates cannot be reliably measured. We therefore chose to investigate possible improvements in the electron transfer of the PNMA-ClO₄-rGO film in the presence of [Ru(NH₃)₆]Cl₂. Another reduction approach was used in these studies to transform GO to rGO. First, the PNMA-ClO₄-

GO film was electrochemically reduced in oxygen-free 0.1 M KNO₃ for 10 min at -0.94 V [8,9]. The CVs of the PNMA-CIO₄-GO film before and after the electrochemical reduction showed that the composite film withstands the reduction without losing its electroactivity (Fig. 4a). After the reduction, CVs of the PNMA-CIO₄, PNMA-CIO₄-GO and PNMA-CIO₄-rGO films, and the glassy carbon (GC) substrate were recorded between -0.6 V and 0.15 V in 0.1 M KNO₃ containing 2 mM [Ru(NH₃)₆]Cl₂ (Fig. 4b). Before starting the potential cycling from -0.6 V, the potential was first held for 2 min at -0.6 V to convert the PNMA matrix to the electrically non-conducting form. Fig. 4b (curve 1) show distinct oxidation and reduction peaks for the Ru(NH₃)₆^{2+/3+} redox couple on GC with the anodic and cathodic peak potentials at E_{p,a}=-0.102 V and E_{p,c}=-0.179 V, respectively, indicating that the redox reaction is nearly reversible ($\Delta E_p=0.077$ V). In contrast to GC, much lower oxidation and reduction currents with higher peak potential separations were observed for the PNMA-CIO₄ and PNMA-CIO₄-GO films. Due to their almost non-conducting nature in the potential interval of Fig. 4b (curves 2 and 3), the electron transfer at the solution-membrane interface and within the PNMA matrix is limited and sluggish resulting in low redox current and high peak separation. It is most likely difficult to fully reduce the PNMA-CIO₄ and PNMA-CIO₄-GO films at -0.6 V which is the reason for their slight redox activity. Moreover, the oxidation of these film matrices starts at ca 0.0 V (Fig. 1b) and consequently, it also slightly contributes to the redox currents observed at E > 0.0 V in Fig. 4b (curves 2-4). However, after electrochemical reduction at -0.94 V, the CV of the PNMA-CIO₄-rGO film in Fig. 4b (curve 4) is very similar to the CV of GC showing almost reversible redox behavior and distinct oxidation and reduction peaks for the Ru(NH₃)₆^{2+/3+} redox couple (E_{p,a}=-0.07 V, E_{p,c}=-0.20 V, $\Delta E_p=0.13$ V). This is in good accordance with the nearly reversible electron transfer kinetics for Ru(NH₃)₆³⁺ on single-layer graphene electrodes in aqueous solutions [10]. We assume that the PNMA-CIO₄-rGO and PNMA-CIO₄-GO films have equal surface areas. Hence, the improved redox behavior of the

PNMA-ClO₄-rGO film indicates that the electrochemical reduction of GO to rGO improves the electron transfer in the composite film.

In conclusion, we have shown that a composite film of rGO and PNMA with enhanced electron transfer can be prepared with a simple electrochemical procedure. It is expected that the composite film can be used, for example, as an ion-to-electron transduction layer in solid-state chemical sensors operating at neutral pH which is usually unsuitable for most PANIs.

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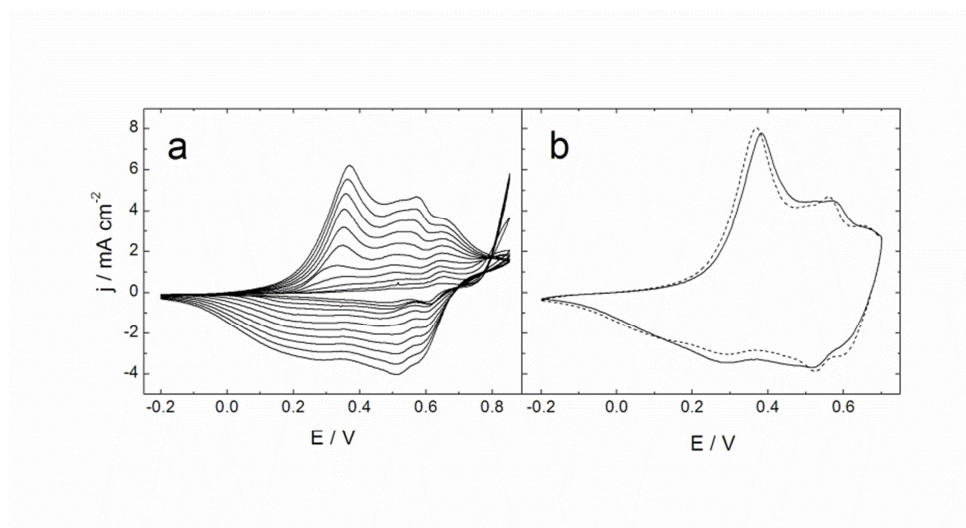


Fig. 1. (a) Electropolymerization of *N*-methylaniline with cyclic voltammetry in an aqueous solution consisting of graphene oxide (4.4 mg/ml) and 1.0 M HClO₄. Every 5th cycle of total 50 cycles is shown in the figure. (b) The characterization of the PNMA-ClO₄-GO (solid line) and the PNMA-ClO₄ (dashed line) films in monomer-free 1.0 M HClO₄. In (a) and (b): RE: Ag/AgCl/3 M KCl, $v=50$ mV/s.

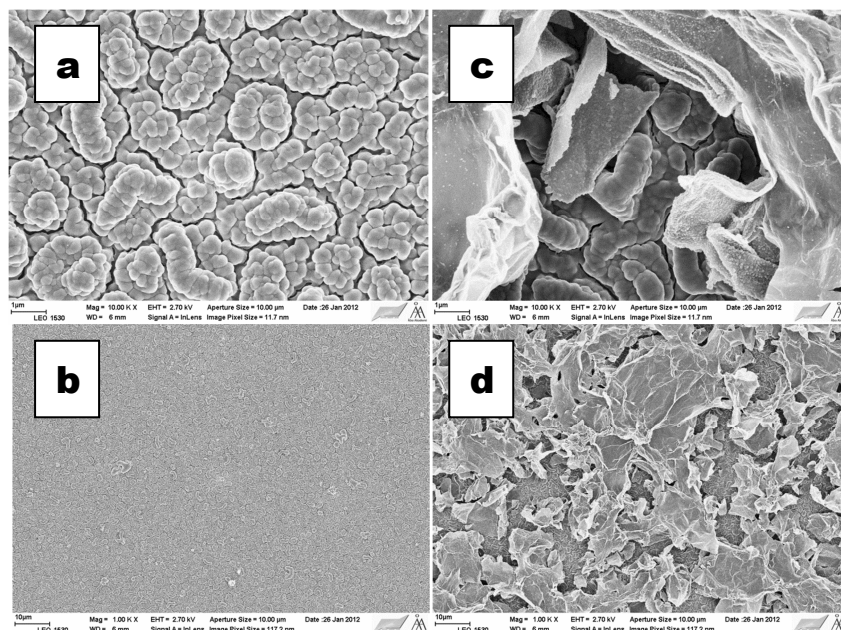


Fig. 2. SEM images of (a, b) the PNMA-CIO₄ and (c, d) the PNMA-CIO₄-GO films. Magnifications: 10000 x (a, c) and 1000 x (b, d).

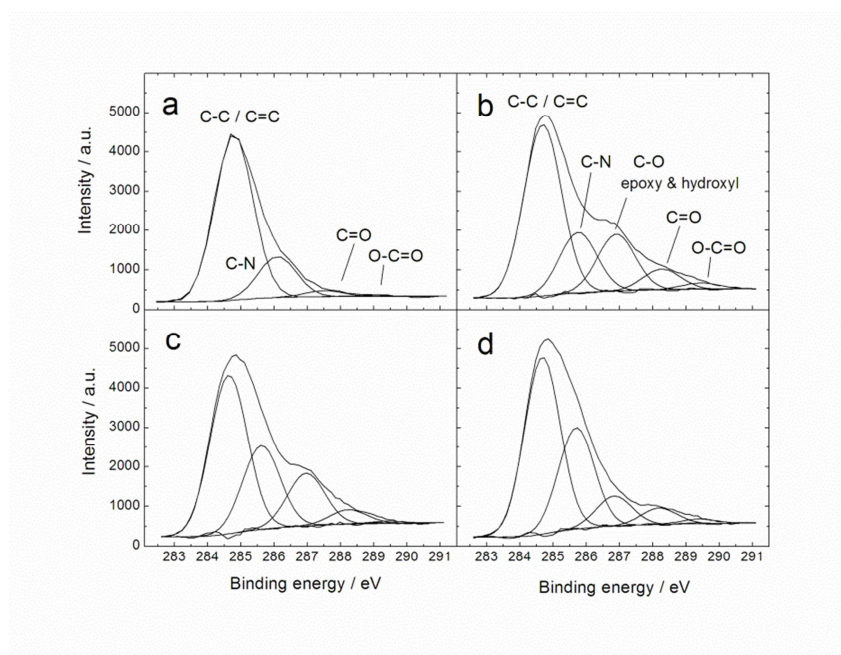


Fig. 3. C 1 s XPS spectra of (a) the PNMA-CIO₄ film ($\chi^2=5.16$) and (b-d) the PNMA-CIO₄-GO films which were electrochemically reduced in 0.1 M KCl at -0.85 V (vs. Ag/AgCl/3 M KCl) for (b) 0 min ($\chi^2=2.48$), (c) 10 min ($\chi^2=4.11$) and (d) 30 min ($\chi^2=3.17$).

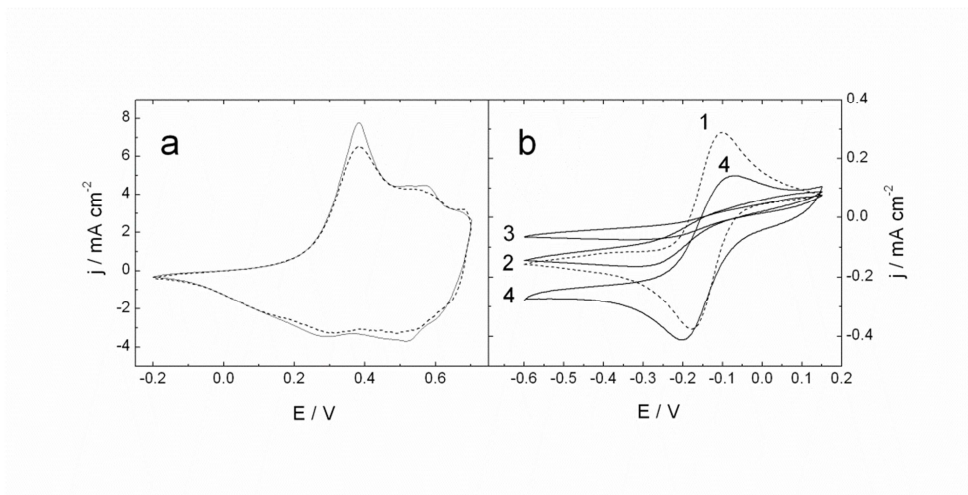


Fig. 4. (a) Characterization of the PNMA-ClO₄-GO film in 1.0 M HClO₄ before (solid line) and after (dashed line) electrochemical reduction for 10 min in 0.1 M KNO₃ at -0.94 V. (b) CVs of the (1) GC substrate, (2) PNMA-ClO₄, (3) PNMA-ClO₄-GO and (4) PNMA-ClO₄-rGO films recorded in 0.1 M KNO₃ containing 2 mM [Ru(NH₃)₆]Cl₂. The PNMA-ClO₄ and the PNMA-ClO₄-rGO films were first electrochemically reduced for 10 min in 0.1 M KNO₃ at -0.94 V prior to the measurements. The films were held at -0.60 V for 2 min before recording the CVs. In (a) and (b): RE: Ag/AgCl/3 M KCl, $v=50$ mV/s.