



Short Communication

Electrochemical impedimetry of electrodeposited poly(propylene imine) dendrimer monolayer

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ABSTRACT

Voltammetric and electrochemical impedance spectroscopic (EIS) studies of generation one poly(propylene imine) (G1 PPI) dendrimer as an electroactive and catalytic nanomaterials both in solution and as an electrode modifier based on a simple one step electrodeposition method is presented. The G1 PPI exhibited a reversible one electron redox behaviour at E^0 ca 210 mV in phosphate buffer pH 7.2 with diffusion coefficient and Warburg coefficient of $7.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $8.87 \times 10^{-4} \Omega \text{ s}^{-1/2}$ respectively. Cyclic voltammetric electrodeposition of a monolayer of G1 PPI on glassy carbon electrode was carried out between -100 mV and 1100 mV for 10 cycles. The nanoelectrode was electroactive in PBS at E^0 ca 220 mV. Kinetic profiles such as time constant ($4.64 \times 10^{-5} \text{ s rad}^{-1}$), exchange current ($1.55 \times 10^{-4} \text{ A}$) and heterogeneous rate constant ($4.52 \times 10^{-3} \text{ cm s}^{-1}$) obtained from EIS showed that the dendrimer layer catalysed the redox reaction of $\text{Fe}^{2+/3+}$ in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe.

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1. Introduction

Dendrimers are synthetic three-dimensional macromolecules with a well-defined, highly branched and globular shaped molecular structure [1,2]. A notable example among the various types of dendrimers is poly(propylene imine) (PPI). One of the most fascinating uses of dendrimer is in the biomedical environment as gene or drug carriers. In a review by Svenson and Tomalia [3], various applications of dendrimer such as biomimetic proteins, nanoscale containers, gene transfection agent, drug delivery agent, imaging agent, nanoscaffolds and even as nano-drugs were discussed. PPI's nanoscopic size, cationic nature, host guest supramolecular efficiency, biocompatibility, nano-engineering possibilities, multiple attachment sites have been exploited *in vitro* and *in vivo* for biomedical purposes thus demonstrating PPI's DNA friendliness [4–7]. But studies on the electrochemical properties of PPI in solution, on electrodes surface and simple electrode modification methods of this biocompatible nanomaterial (PPI) have not been widely studied at physiological conditions. The application of PPI dendrimer in DNA biosensor design is also at its infancy [8,9] though a few more exists using poly(amidoamine) (PAMAM) [10].

Prior to this work, redox properties of pristine poly(propylene imine) dendrimer have not been reported. Rather, only dendrimer which have been functionalised with redox molecules such as pyridines of transition metal complexes on polyamidoamine (PA-

MAM) [11] and ferrocynyl and cobaltocene on PPI [12,13] are those reported as electroactive and their electroactive nature was ascribed to the functionality. PPI has also been studied at liquid–liquid interface with interesting electrochemistry [14] but it was in fact referred to as nonredox active.

Here, we report the electrochemical characterisation of PPI in (solution and on electrode surface) as an electroactive and catalytic dendrimer in phosphate buffer pH 7.2 and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solutions respectively using voltammetry and electrochemical impedance spectroscopy (EIS). This paper reports a novel method of preparing a redox active PPI modified glassy carbon nanoelectrode by electrodeposition from an aqueous phase.

2. Experimental

2.1. Apparatus and reagents

A three electrode cell with glassy carbon, platinum and Ag/AgCl (3 M NaCl type) as working, auxiliary and reference electrodes respectively was used. All voltammetric experiments were performed on an Epsilon (BASi) electrochemical workstation (LaFayette) with oxidative scan direction except stated otherwise. Square wave voltammetry (SWV) measurements were performed by applying amplitude of 25 mV and frequency of 15 Hz. Electrochemical impedance spectroscopy (EIS) measurements were recorded with Zahner IM6ex Germany, at perturbation amplitude of 10 mV within the frequency range of 100 kHz–100 mHz. SEM images were captured using a scanning electron microscope fitted

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with energy-dispersive X-ray spectroscopy accessory (JEOL-JSM 7500F). 10 mM saline phosphate buffer solution (PBS) pH 7.2 containing Na_2HPO_4 , KH_2PO_4 and 0.3 mM KCl was prepared. For dendrimer solution, 0.1 M phosphate buffer (void of 0.3 M KCl) was used. 5 mM (1:1) solution of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ was prepared in 100 mL of 10 mM PBS pH 7.2. Dendrimer solutions of 10 mM G1 PPI, 10 mM G2, 5 mM G3 PPI and 3 mM G4 PPI (obtained from SyMO-Chem, Eindhoven, Netherlands and Sigma–Aldrich) were prepared in 0.1 M phosphate buffer respectively.

2.2. Electrochemical studies of PPI in solution and electrodeposition

CV and SWV experiments were carried out using clean bare GCE in the presence of blank 0.1 M phosphate buffer (without the dendrimer) and 10 mM G1 PPI in 0.1 M phosphate buffer at different scan rates and frequencies within the potential window of -100 mV and 650 mV. EIS measurements were also made in these two electrolytes (blank and G1 PPI) at different bias potentials from 100 mHz to 100 kHz frequency. The electrode was labelled GCE/G1 PPI_{sol} for studies of PPI in solution. The electrodeposition of G1 PPI onto GCE was carried out using CV from -100 mV to 1100 mV for 10 cycles at 50 mV/s scan rate in 10 mM G1 PPI in 0.1 M phosphate buffer solution and labelled GCE/G1 PPI. G2, G3 and G4 PPI were deposited in a similar manner. EIS of G1 nanoelectrode was carried out in both PBS and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe at different bias potentials. Scanning electron microscopy and energy-dispersive X-ray spectroscopy microanalysis (EDAX) were

carried out using screen printed carbon electrode (SPCE) as the substrate instead of GCE. However the electrodeposition conditions were the same.

3. Results and discussion

3.1. Voltammetric studies of G1 PPI in solution

Fig. 1a shows the cyclic voltammetry (CV) of bare GCE in PBS versus bare GCE in 10 mM G1 PPI respectively. No redox chemistry is observed for GCE in PBS within the potential window chosen. However, in the presence of 10 mM G1 PPI, a redox couple with formal potential $E^0 = 212$ mV is observed. The scan rate dependence results are presented in Fig. 1b (Randles sevcik plot inset). From Fig. 1: E_{pa} and E_{pc} are independent of scan rate (see also supplementary Fig. 1), $\Delta E = 60$ mV, $I_{pa}/I_{pc} \approx 1$, I_p , versus $v^{1/2}$ is linear with correlation coefficient of 0.9994 . These confirm that the electrochemistry of G1 PPI_{sol} is a reversible one electron process and it is diffusion controlled.

The diffusion coefficient, D_e , calculated from CV (Fig. 1b inset) using the Randle Sevcik equation (Eq. (1)) gave $7.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ where $T = 25$ °C, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $F = 96,486 \text{ C mol}^{-1}$, $C = 1 \times 10^{-5} \text{ mol cm}^{-3}$, $n = 1$, $A = 0.071 \text{ cm}^2$ and slope = 5.23×10^{-6} .

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C \quad (1)$$

This value is quite low when compared to other works on dendrimer. For example Abruna [11] reported a D_e value of

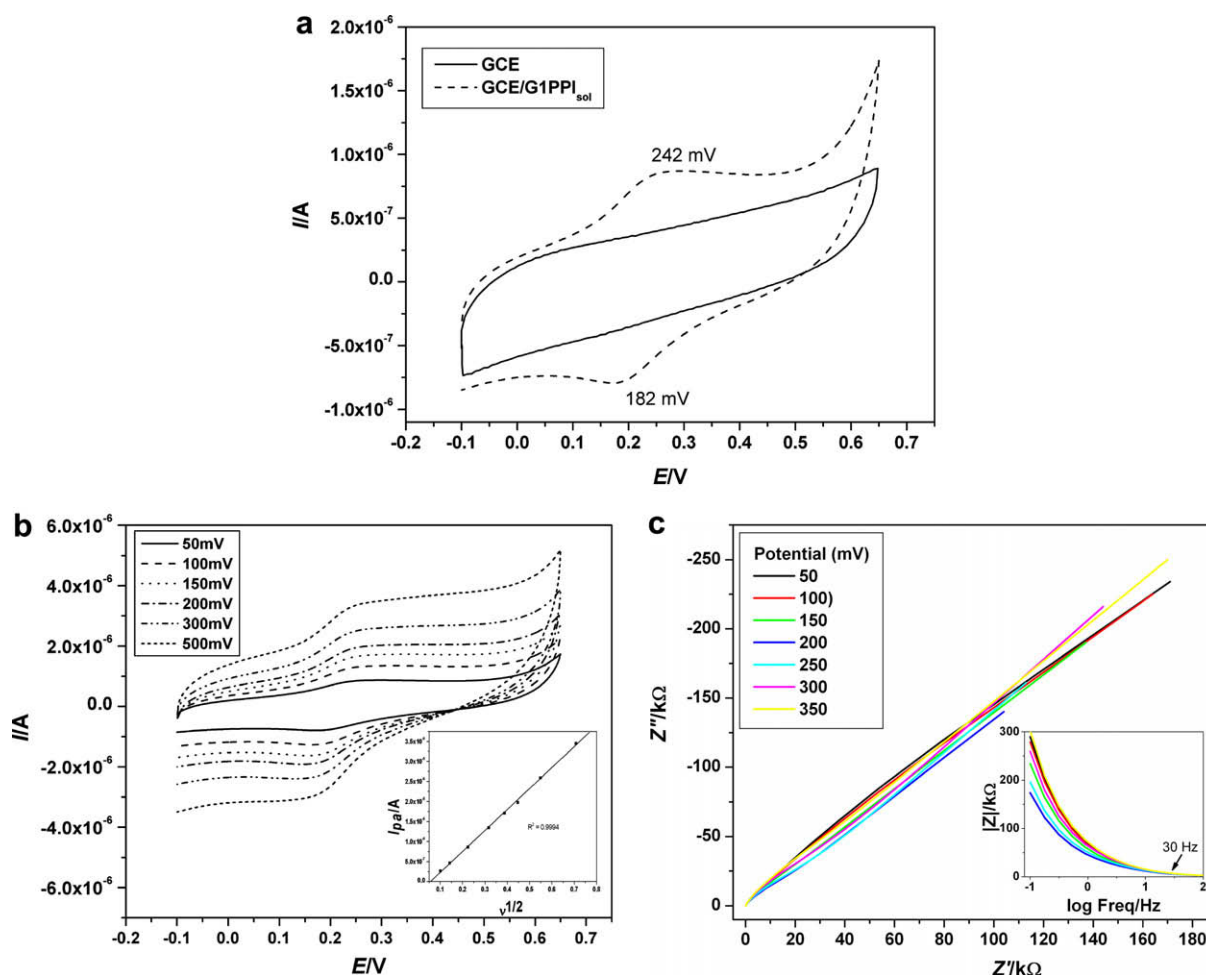


Fig. 1. (a) Cyclic voltammetry of GCE in blank and 10 mM G1 PPI electrolyte. (b) CV at different scan rates of GCE/G1 PPI_{sol}. (c) Nyquist plot of 10 mM G1 PPI in 0.1 M PBS at different potentials (Bode plot inset).

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