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Synthesis and characterization of polypyrrole by cyclic voltammetry at different scan rate and its use in electrochemical reduction of the simulant of nerve agents

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ABSTRACT

In this study, polypyrrole (pPy) was *in-situ* electrosynthesized on gold electrode surface using four different scan rate variations such as 5, 10, 25 and 50 mV/s with the help of cyclic voltammetry. Scanning electron microscopy (SEM) characterization revealed a scan rate dependent surface morphology for the pPy modified electrodes. The surface functional groups and elemental composition of the modified electrodes were deduced using Raman spectroscopy and energy dispersive X-ray spectroscopy (EDS), respectively. These pPy modified electrodes were utilized to study the electrochemical behavior of the nerve agents' simulant dimethyl methyl phosphonate (DMMP) in aqueous medium. These modified electrodes exhibited electrochemical parameters with DMMP depending on the scan rate used for the *in-situ* synthesis of pPy conducting polymer.

1. Introduction

Conducting polymers are materials and were extensively studied for the last 40 years. Although they are of organic materials by nature, their conductivity can achieve a value that is comparable to semiconductors and metals because as the conducting polymers (CPs) are having π-conjugated chain structures [1–3]. The examples of CPs are polyacetylene, polypyrrole (pPy), polythiophene (pTh), polyaniline (PANI) and their derivatives. Moreover, CPs are also called as conjugated polymers and in their neutral state they are insulators. Neutral conjugated polymers with a small conductivity, typically in the range from 10^{-10} to 10^{-5} S cm^{-1} can be converted into semiconductive or conductive states with conductivities from 1 to 10^{4} S cm^{-1} through chemical or electrochemical redox reactions [2] and this process is called as doping. After doping, the backbone of CPs carries positive (p-doping) or negative charge carriers (n-doping).

Polypyrrole conductive polymer films can be *in-situ* generated on electrode surfaces by using less oxidation potential (0.8 V) when compared to other heterocyclic monomers and this is also lower than the oxidation potential of water. Consequently, pPy is readily synthesized from a range of aqueous and non aqueous solvents [4]. In fact, pPy is one of the few electronically conducting polymers that can be prepared in aqueous solution [4]. Polyaniline can be synthesized from acidic aqueous media, while polythiophene must be grown from organic solvent in which the monomer is soluble [5].

Electroactive polymeric films have acquired wide popularity, since they are easier to *in-situ* generate on the electrode surface than monolayer [6]. Moreover, the increased number of active sites in the polymer film rendered enhanced electrochemical processes at its surface than at the monolayer-modified electrode. Earlier studies with polymer modified electrodes showed an enhanced response for the determination of various environmentally important species [7–11]. In addition, conducting polymer modified electrodes also imparted excellent electrochemical activity with different species [12–18].

Dimethyl methyl phosphate (DMMP) is primarily used as a flame retardant (Fyrol DMMP), in epoxy resins, acrylic latexes, unsaturated polyesters, vinyl copolymers, urethane coatings and urethane rigid foam. DMMP is also used as a pre ignition additive in gasoline, antifoam agent, plasticizer and stabilizer, textile conditioner and anti static agent as well as a solvent for low-temperature hydraulic fluids [19]. DMMP is a physical and spectroscopic simulant for anticholinesterase agents (nerve gases) tabun (GA), sarin (GB) and soman (GD). Conversely, DMMP does not share the dangerous biological properties of nerve agents, which makes it a desirable surrogate for testing G-agent protective clothing, detection equipment and developing analytical methods.

In this study, we have synthesized conducting pPy film on gold electrode using different scan rate variations such as 5, 10, 25 and 50 mV/s in order to get different thickness of pPy film. The surface morphology, elemental composition and functional groups of

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pPy on the electrode surface were obtained from scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy, respectively. Finally, these modified electrodes were characterized electrochemically and utilized to study the electrochemical reduction of dimethyl methyl phosphonate (DMMP) so as to know its electrochemical properties because of the vital nature of this compound in Chemical Weapons Convention (CWC) [20].

2. Experimental

2.1. Chemicals and reagents

AR grade of sodium perchlorate (Aldrich) was used as received. Pyrrole (Aldrich) was purified under a reduced pressure and stored in a refrigerator. Simulant of nerve agents (DMMP 97%) AR grade (Aldrich) and all other chemicals and reagents used were of AR grade. The phosphate buffer solution of pH 6.0 was used in this study for the electrochemical characterization purposes.

2.2. Instruments and electrodes

Electrochemical studies were performed using a potentiostat/galvanostat with frequency response analyzer (Autolab-302 with FRA-II, The Netherlands). ESEM-EDX (Quanta400-ESEM with EDAX-FEI, The Netherlands), Renishaw Invia Raman Microscope (Gloucestershire, U.K.) and Eutech instruments pH meter (pH-1500, Singapore) were utilized in this study. All electrochemical experiments were performed at a temperature of $25 \pm 2\,^{\circ}C$ by using a three-electrode cell system. The gold working, Ag/AgCl (3 M KCl) reference and the auxiliary platinum electrodes used in this study were supplied by Metrohm Switzerland.

2.3. Characterization of the pPy modified electrodes

The pPy modified electrodes are extensively characterized by cyclic voltammetry to know the electrochemical activity, electrochemical impedance spectroscopy in order to know the interfacial properties, Raman spectroscopy to know the functional groups present on the electrode surface, SEM to have an idea about surface morphology and EDS to deduce the elemental composition of the modified electrode surface.

2.4. Electrode modification and handling of chemical warfare agent simulant

The gold electrode was mechanically polished with alumina (Al_2O_3) slurry on micropads and washed ultrasonically with Milli-Q water (18.2 MΩ.cm) to remove any traces of alumina present on the electrode surface. The electrode was cleaned by electrochemical etching in 0.05 M H_2SO_4 by potential scanning between −0.3 V and +1.5 V until a reproducible cyclic voltammogram was obtained. Then, the gold electrode was rinsed with copious amount of Milli-Q water and used for the modification with pyrrole monomer. pPy film was prepared by electropolymerization from a aqueous solution containing of freshly prepared 0.1 M pyrrole and 0.1 M sodium perchlorate. The electropolymerization was carried out at room temperature on the gold electrode surface by cycling the potential in the potential range between −0.1 V and +1.1 V for 2 cycles with different scan rate such as 5, 10, 25 and 50 mV/s. The resultant black film was extremely stable and exhibited different thickness at different scan rate i.e. electrode (scan rate 5 mV/s) had very thick film because scan rate was very slow so that more time for nucleation, owing to this reason more polymerization occurred. The pPy was also found to be adhered very strongly to the electrode surface. Next the polymerized electrode surface was washed with water to remove the un-reacted monomer. Finally, the electrode was dried and then used for further characterization and also to know the electrochemical reduction properties of DMMP. The electrochemical characterization and other studies were performed with DMMP with required protective measures in a fume hood (*Caution: DMMP is a Chemical Warfare Agent (CWA) simulant and care should be taken while using*).

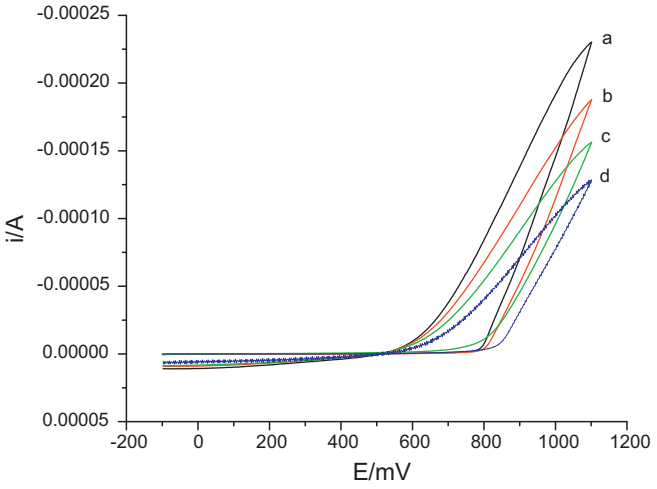

Fig. 1. Overlay of cyclic voltammograms for the polymerization of pPy at different scan rate with (a) 5 mV/s, (b) 10 mV/s, (c) 25 mV/s and (d) 50 mV/s.

3. Results and discussion

3.1. Electrochemical polymerization of pyrrole with sodium perchlorate

Fig. 1 shows the cyclic voltammograms scanned between −0.1 V and +1.1 V for the oxidation of pyrrole on the Au electrode in order to get polypyrrole modified electrode at different scan rate. It is observed from Fig. 1 that the pyrrole oxidation starting potential is dependent on the scan rate used for the polymerization such as 0.482 V, 0.564 V, 0.571 V and 0.603 V, respectively for 5, 10, 25 and 50 mV/s scan rate. It clearly explicates that the Au electrode exhibited different electroxidation pathway that is the increase in scan rate increased the oxidation potential required for the pyrrole monomer oxidation. Especially, at 5 mV/s scan rate the Au electrode surface oxidized pyrrole monomer at 0.482 V. Therefore, at 5 mV/s scan rate higher polymerization takes the advantage of a higher oxidation level with high conductivity of pPy is obtained. On the other hand, the higher oxidation level also results from the electron transfer from pPy to Au $(ClO_4)_4^-$ or $AuCl_4^-$ [21]. Appearance of a current loop at the potential 0.482 V, 0.564 V, 0.571 V, and 0.603 V and 0.75 V, 0.78 V, 0.81 V and 0.85 V, respectively for 5, 10, 25 and 50 mV/s scan rate at the forward and reverse scan indicates the new phase formation on the electrode surface [21] or nucleation over the potential range.

Moreover, it is observed that the thickness of the film is different with different scan rate and the film thickness was calculated according to an earlier report [22] and was found to be 27.40 nm, 11.58 nm, 4.01 nm and 1.63 nm, respectively for 5, 10, 25 and 50 mV/s scan rates. A black color pPy film was observed with all scan rates used for the preparation of pPy.

3.2. Morphological characterization by SEM

The gold electrode and pPy modified gold electrodes at different scan rate are characterized by SEM to know their surface morphologies. The SEM images are depicted as Fig. 2A for bare gold electrode and Fig. 2B–2E for pPy electro-polymerized gold electrodes at dif-