



Electrochemical properties, optical modeling and electrocatalytic activity of pulse-electropolymerized ternary nanocomposite of poly (methylene blue) in aqueous solution



Narges Ajami ^{a,*}, Ali Ehsani ^b, Ferydon Babaei ^c, Reza Safari ^b

^a Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697, Tehran, Iran

^b Department of Chemistry, Faculty of Science, University of Qom, Qom, Iran

^c Department of Physic, Faculty of Science, University of Qom, Qom, Iran

ARTICLE INFO

Article history:

Received 23 August 2015

Accepted 7 December 2015

Available online xxxx

Keywords:

Poly (methylene blue)

Indium tin oxide

Pulse galvanostatic method

Nanoparticle

Nanostructure

ABSTRACT

This paper aims to investigate the relationship between surface morphology of poly (methylene blue) (PMB) films and pulse synthesis conditions. A simple and general strategy, namely in situ electropolymerization has been used for electrosynthesis of PMB on the Indium Tin Oxide (ITO) substrates by pulse galvanostatic method. The obtained surface analysis results revealed that the morphology and particle sizes of PMB strongly depended on the synthetic conditions. PMB nanoparticles with good electrochemical stability were obtained by optimization of synthetic conditions. Then, Ni (II) and Mn (II) ions were incorporated to electrode by immersion of the polymerically modified electrode in a stirred solution containing Ni and Mn ions to form Ni–Mn/PMB films. Furthermore, the experimental absorbance spectra of nanocomposite were compared with the results from the Maxwell-Garnett theory (MGT) and the value of energy, E_g , of composite obtained. Modified electrodes (Ni–Mn/poly methylene blue) were examined for their redox and electrocatalytic activities in the oxidation of methanol in alkaline solutions. The electrochemical results reveal that Ni–Mn/poly methylene blue modified electrode shows a significantly higher response for methanol oxidation in alkaline solution.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Recently, conducting polymer nanostructures have attracted considerable interest because of their importance in different fields [1–10]. Especially, pulsed electrodeposition is a novel process to synthesize polymers with interesting morphology such as nanowires and nanofibers [11–13]. Pulsed polymerization is a novel process, which is known for micro- and nano-structuring of the metals and semiconductors [13]. Exercising the pulse variables of polymerization, a drastic improvement in conducting polymer capacitance, operating potential and stability for long cycle life is realized. During the time when the current pulse is ON, charges allow polymer chain to nucleate over the substrate surface only for a very short period followed by the off time pulses that do not start fresh nucleation but terminate the growing chains. Relatively longer off time helps the already grown chains to oxidize completely and orient over the surface with the fullest conjugation before the next pulse charges and another polymer chain nucleates over it. During the off pulse growth on the initial sites of the electrode is

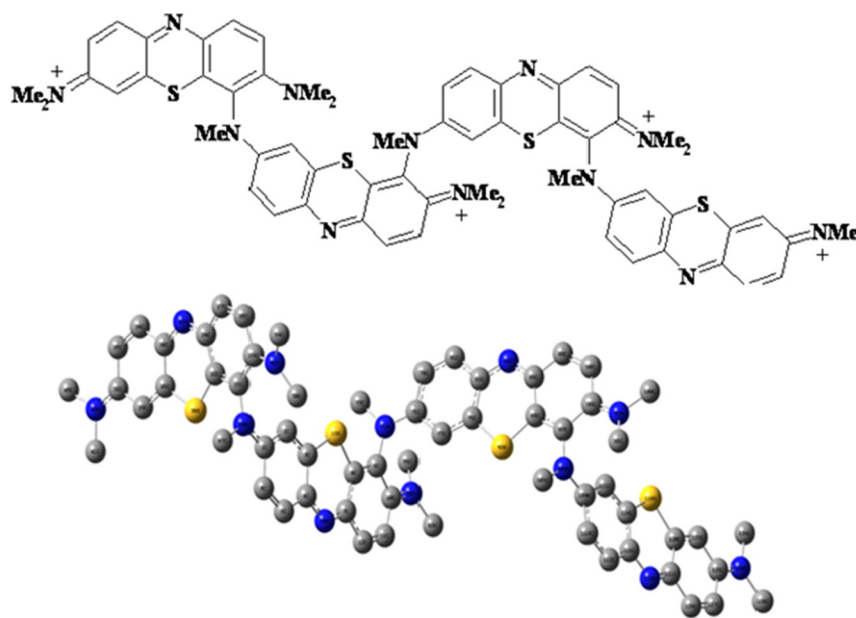
frustrated and hence the growth on the fresh sites of the electrode is more probable leading to a large number of equivalent nucleation and growth sites. Pulse galvanostatic electrosynthesis is a reliable method in controlling the morphology of the samples [13–18].

Some organic dyes, such as methylene blue (MB), have highly conjugated ring shaped structures and own excellent electroactivity [19]. MB has been used in modified different electrode surfaces and as effective electron redox mediator [20]. Electron transfer processes have been shown to occur very fast at the interface in the presence of MB [21–23]. Optimized structures for tetramers of PMB have been presented in Scheme 1. It has been shown that dye-polymer modified electrodes have a high conductivity, high stability [19], high redox reversibility, and swift change in film color with potential. Surprisingly application of pulse galvanostatic method for electrosynthesis of PMB has not been reported in the literature.

The aim of this work is to investigate the influence of pulse method on electrosynthesis of the high electroactive PMB. The effects of synthetic conditions on the morphology and the size of the PMB particles were investigated. Ni and Mn doping into the polymeric films was achieved chemically followed by enrichment through cycling the potential. The electro-oxidation of methanol on Ni–Mn/poly methylene blue was investigated.

* Corresponding author.

E-mail address: n_ajami@pnu.ac.ir (N. Ajami).



Scheme 1. Molecular structure and optimized structure of tetramer of PMB have been obtained from DFT calculation.

2. Experimental

The chemicals used in this work were obtained from Merck Chemical Co. and used without further purification. All the electrochemical experiments were carried out by Autolab (PG STAT-12/30/302) into double-electrode of ITO used as the working and reference electrodes, respectively. PMB film was electrodeposited on ITO substrate of 1 cm^2 surfaces. PMB nanostructures were synthesized at constant current density (1 mA cm^{-2}) and pulses for a very short period of time. Pulse on time was varied from 0.1 to 1.25 and pulse off time was chosen as 0.1 s. No current was applied during off period. Polymerization charge was constant in all experiments by keeping the total growth time as 1000 s with applying a current density of 1 mA cm^{-2} . PMB was deposited onto the cleaned ITO electrode by pulse electrosynthesis and cyclic voltammetry (DC) from an aqueous solution containing 0.8 mM MB, 0.05 M Borax and 0.5 M KCl. The potential was swept from -0.4 to a final potential of 1.1 V (vs. saturated Ag/AgCl), at a scanning rate of 50 mV s^{-1} . The morphologies of the electrosynthesized conductive polymer obtained were analyzed using field emission scanning electron microanalyzer model KYKY-EM3200.

3. Result and discussion

Fig. 1 a and b shows the SEM of the surface of synthesized PMB by pulse electrosynthesis and CV, respectively. As observed, the film morphology in both cases was porous whereas the pulse polymerized film displayed different structure from the CV polymerized film.

To investigate the effects of relaxation time on the morphology of the synthesized PMB, the value of t_{off} was varied from 0.1 to 1.5 s while the values of the t_{on} were 0.1 s. Fig. 2 displays the SEM images of PMB samples synthesized at different relaxation times. Pulse on time is the main factor in controlling chain size and defects [24]. The relaxation time plays an important role in the mechanism of the particle growth in pulse electropolymerization. At low relaxation times, a nanotype structure with an average size of 5–40 nm and more ordered growth of PMB is formed. The application of low relaxation time for polymerization has a major effect on the polymer structure and chain length. The short polymer chains are the ideal structures.

In order to evaluate the electrochemical properties of electro-synthesized film in DC and pulse methods, the PMB film was immersed in 0.5 M KCl and 0.5 M H_3BO_3 solutions after the nanostructures were

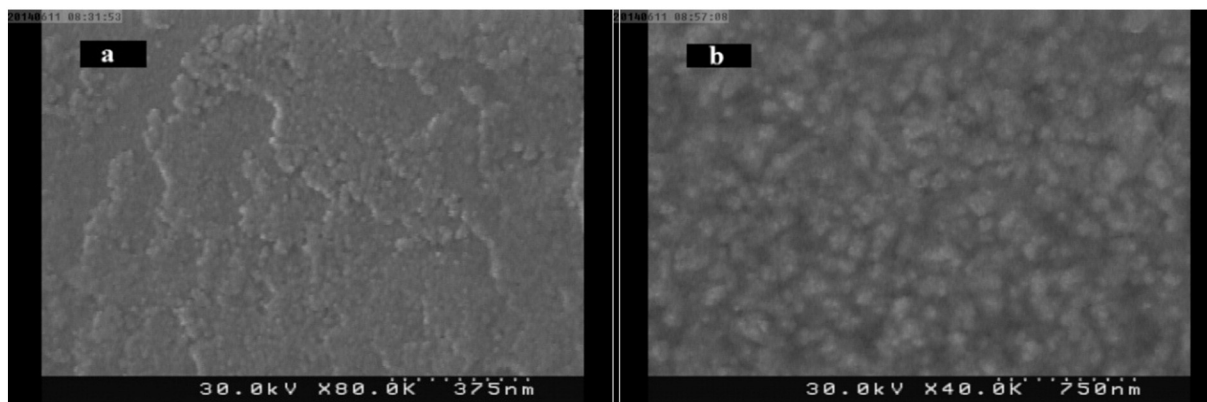


Fig. 1. The surface morphology of a); pulse electrosynthesized PMB nanostructures, b); cyclic voltammetry polymerized PMB film.

Download English Version:

<https://daneshyari.com/en/article/5410274>

Download Persian Version:

<https://daneshyari.com/article/5410274>

[Daneshyari.com](https://daneshyari.com)