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Electro-chemical preparation and characterization of poly(1-amino-9,10-anthraquinone) films in a micelle solution of sodium dodecyl sulfate

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ABSTRACT

In this work, the poly(1-amino-9,10-anthraquinone) (PAAQ) films are synthesized electro-chemically by the direct anodic oxidation of 1-amino-9,10-anthraquinone (AAQ) on a platinum substrate in an ionic micelle solution containing the environmental friendly surfactant sodium dodecyl sulfate (SDS). The PAAQ–SDS films prepared are characterized by cyclic voltammetry (CV) and scanning electron microscopy (SEM), and a comparative study is carried out on the PAAQ films prepared under the identical conditions but in the absence of SDS. The results obtained show that the AAQ polymerization rate increases initially with an increase in the concentration of SDS, passed through a maximum around 0.4 mM, and then decreased towards lower values, with a further increase in the SDS concentration. The PAAQ films deposited onto the electrode surface using the CV technique were adhesive and homogeneous. A distribution of the small particles and an extended surface area were observed in the SEM images for the porous PAAQ–SDS films. The preliminary results obtained show that the reliability and stability of the PAAQ–SDS modified electrode provide a good possibility for the electro-analytical determination of catechol.

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1. Introduction

Over the past two decades, there have been a number of excellent reviews on the conducting polymers [1–6]. These polymers have been extensively investigated in all the emerging fields because of their numerous applications in batteries [7–9], electronic devices [10], sensors and capacitors [11], catalysts [12], electromagnetic radiation shielding, anti-static coatings, gas separation membranes, non-linear optics, and electro-chromic devices [13]. The chemical and electro-chemical synthesis of the conducting polymers continues to receive great attentions in the fundamental as well as the applied studies. In particular, the micro- and nano-structures of the conducting polymers are under active investigation because of the many existing and new possibilities for their applications in the optical, electrical, and sensing devices [14–21]. The formation of these structures in the presence of active surface materials in aqueous media has received less attention in spite of their obvious economical advantages.

The ionic as well as non-ionic surfactants have been used to make micellar solutions in the synthesis of conducting polymers. The presence of a surfactant or polyelectrolyte significantly modifies both the microscopic and macroscopic properties of the final polymer [22–30]. Sodium dodecyl sulfate (SDS) is an anionic surfactant, having a bulky hydrocarbon tail and a sulfonate group in its polar head. SDS has been used extensively as a surfactant for the micellar/emulsion polymerization of aniline using both the chemical and electro-chemical polymerization routes [24–30]. It has been postulated that the aniline monomer is solubilized in the micellar assembly formed on the substrate leading to a highly concentrated monomer. An enhancement in the rate of polymerization has been observed in the presence of SDS, and this has been attributed to the high local concentration of the aniline monomer in the micellar reaction medium. However, de Albuquerque Maranhaoand and Torresi [28] have observed a decrease in the rate of polymerization of the aniline derivatives in the presence of SDS when their concentrations are either below or around the critical micellar concentration (CMC).

Poly(1-amino-9,10-anthraquinone) (PAAQ) is regarded as one of the most versatile conducting polymers due to its excellent properties such as the environmental stability, good electro-activity, high electrical conductivity, powerful specific electro-capacity, fast reversible redox ability, and its uses as electrode materials for biosensors [31]. It is also used in the lithium batteries

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[32] and electro-chemical capacitors [33]. The electro-polymerization of AAQ has been carried out in aqueous [34] and non-aqueous [35] media. PAAQ, having the 1,4-benzoquinone groups and polyaniline-like main chains, has a higher electro-activity than polyaniline [36]. There are considerable interests in the preparation of the PAAQ film-coated electrodes in the presence of additive materials as a modified electrode for catalytic purposes. Recently, we have reported a detailed study on the characterization of the PAAQ nano-composite films, prepared in the presence of multi-walled carbon nanotubes (MWCNTs) on a glassy carbon electrode in a non-aqueous medium [37]. To the best of our knowledge, there is no report on the electro-polymerization of AAQ in the presence of ionic surfactants. In the present work, investigation of the electro-polymerization of AAQ was extended in a micelle solution of SDS. The effects of the presence of SDS on the electro-polymerization of AAQ, and the electro-chemical behavior and structural morphology of the PAAQ–SDS films were studied, and a comparison was made with the PAAQ films prepared under identical conditions but in the absence of SDS. Furthermore, the ability of the PAAQ–SDS modified electrode as an electro-chemical sensor was investigated.

2. Experimental

2.1. Materials

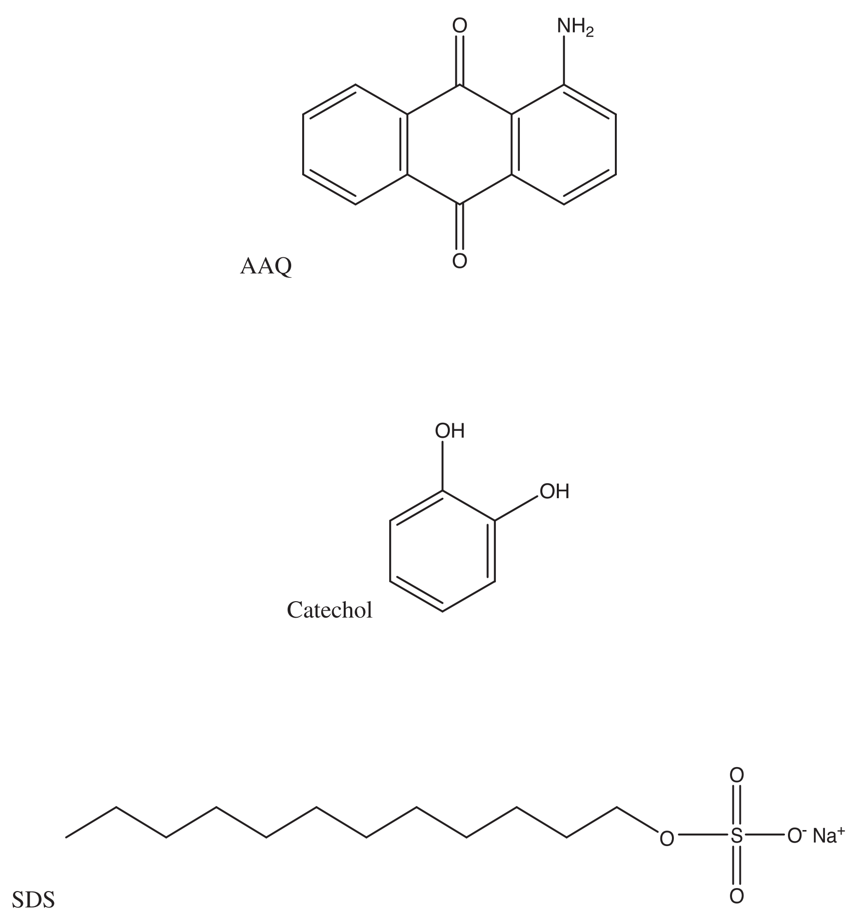
All the chemicals used were of analytical grade, including 1-amino-9,10-anthraquinone (AAQ) (Merck), sodium dodecyl sulfate (SDS) (Sigma–Aldrich), sulfuric acid (Merck), catechol (Merck), and phosphate-buffered saline (Sigma–Aldrich), and were used as received without further purification. The solutions were prepared using triply distilled water. The structural formulas of the materials used are depicted in Scheme 1.

2.2. Instrumentation

A standard three-electrode cell was used with a platinum disk (Pt) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter-electrode. The working electrode had a surface area of 0.07 cm^2. Before each experiment, the working electrode was polished mechanically with alumina powder of 1.0 mm diameter, washed, and then rubbed against a smooth cloth. All the electro-chemical measurements were carried out using the electro-chemical system Behpajuh Electric (Iran), equipped with a PC and an electro-chemical setup that was controlled with a software. Except otherwise stated, all the experiments were carried out at room temperature ($25 \pm 0.1\,°C$), and all the potentials were referred to SCE. The scanning electron microscopy (SEM) images were taken using a Hitachi instrument (S-4160) at various magnifications.

2.3. Preparation of PAAQ–SDS composite films

The conventional PAAQ and PAAQ–SDS films were synthesized on the Pt working electrode (unless otherwise stated) by both the potentio-dynamic and potentio-static electro-chemical techniques in an aqueous solution containing the AAQ monomer (4 mM) and H_2SO_4 (6.0 M). Normalization of the modified electrodes was investigated by cyclic voltammetry (CV) according to the Randles–Sevcik equation [38] using ferricyanide as a redox probe in order to estimate the electro-active areas.



Scheme 1. Structural formulas for 1-amino-9,10-anthraquinone (AAQ), catechol, and sodium dodecyl sulfate (SDS).

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