

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF POLY *O*-AMINOPHENOL – SiO₂ NANOCOMPOSITE

ELEKTROKEMIJSKA SINTEZA IN KARAKTERIZACIJA NANOKOMPOZITA POLI *O*-AMINOFENOL – SiO₂

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We report on the influence of SiO₂ on the electropolymerization of *O*-aminophenol (OAP). A poly *O*-aminophenol (POAP) nanocomposite with different particle sizes was deposited on a glassy carbon (GC) electrode in a solution having OAP 0.01 M and sulfuric acid 0.5 M using cyclic voltammetry (CV). The surface morphologies of the POAP films were studied using scanning electron microscopy (SEM). The results indicated that a modified surface, having a high surface coverage and an improved specific capacitance with semiconducting properties, was obtained. The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) studies confirmed that the nanocomposite films have a higher capacitance than the pure POAP films. The presence of SiO₂ led to an obvious improvement in the overall electrochemical performance of the GC surface covered by POAP films.

Keywords: poly (*O*-aminophenol), glassy carbon electrode, electropolymerization

Poročilo obravnava vpliv SiO₂ na elektropolimerizacijo *O*-aminofenola (OAP). Nanokompozit poli *O*-aminofenol (POAP) z različno velikostjo delcev je bil nanosen na elektrodo iz svetlečega ogljika (GC) s ciklično voltametrijjo (CV) v raztopini z OAP 0,01 M in žvepleno kislino 0,5 M. Morfologija površine POAP-nanosa je bila pregledana z vrstičnim elektronskim mikroskopom (SEM). Rezultati so pokazali, da ima spremenjena površina visoko pokritost površine, izboljšano specifično kapacitivnost in izkazuje polprevodniške lastnosti. Študije ciklične voltametrije in elektrokemijske impedančne spektroskopije (EIS) so potrdile, da ima nanokompozitni nanos višjo kapacitivnost kot čisti POAP-nanos. Prisotnost SiO₂ je pokazala občutno izboljšanje splošnih elektrokemijskih zmogljivosti površine GC, pokrite s POAP-nanosom.

Ključne besede: poli (*O*-aminofenol), elektroda iz svetlečega ogljika, elektropolimerizacija

1 INTRODUCTION

Nanotechnology is a rapidly growing area of nanostructured material science because of its huge number of applications in various fields, such as catalysis,^{1,2} sensors,^{3,4} electronics,⁵ optics,^{6,7} and medical sciences.^{8–10} Nanometer silicon dioxide (nano-SiO₂) is one of the most popular nanomaterials that are being employed in different areas, like industrial manufacturing, packaging, composite materials, disease labeling, drug delivery, cancer therapy, and biosensors. The modified silica is low-price, esuriently oxide with a high chemical and thermal stability.¹¹ The development of chemically modified electrodes (CMEs) is an area of great interest. CMEs can be broadly divided into two main categories: as (a) surface-modified and (b) bulk-modified electrodes. Methods of surface modification include adsorption, covalent bonding, attachment of polymer films, etc.¹² Polymer-coated electrodes can be differentiated using other modification methods, like adsorption and covalent grafting on the surface. Depending on the surface properties and the experimental conditions, films with a different morphology, such as multilayer or monolayer, will be deposited. A conducting polymer provides an excellent opportunity for the preparation of composites

having desirable mechanical properties. These include their applications in storage batteries,¹³ electrochemical devices,^{14,15} light-emitting diodes,¹⁶ corrosion inhibitors,¹⁷ and sensors.^{18,19} Understanding the nature of these polymers is of great importance for developing electrochemical devices. Among the conducting polymers, polyaniline (PANI) and its derivatives have been studied extensively due to the commercial availability of the monomer, an easy protocol for synthesis, a well-behaved electrochemical response, a high environmental stability, and a high conductivity. In recent years, various composites of PANI and inorganic compounds have been fabricated with improved characteristics.^{20,21} Although silica is an insulating material, some of its composites showed conductivity at the level of conducting PANI.²² However, some of silica composites displayed enhanced conductivity, which may be due to the change in morphology of the conductive films in the hybrid materials.²³ Electrochemical polymerization offers the advantage of a reproducible deposition in terms of film thickness and loading level, making the immobilization procedure of a metal-based electrocatalyst very simple and reliable. By considering this point that the nature of the working-electrode surface is a key factor in observing the electrochemical response of a deposited polymeric film,

the electropolymerization of an OAP monomer in a suspension of silica nanoparticles is investigated in the present research for the first time. The silica nanoparticle is selected because of its good stability in common aqueous acidic solutions such as H_2SO_4 , HCl and HClO_4 . Accordingly, a poly (*O*-aminophenol)/ SiO_2 nanocomposite as a novel organic matrix was fabricated and characterized.

2 EXPERIMENTAL

2.1 Materials

The solvent used in this work was bi-distilled water. Sulfuric acid (purity 99 % from Merck) was used as a supporting electrolyte. The OAP (purity 98 % from Merck) was utilized as the monomer and distilled prior to be used. Silica nanoparticles (purity 99 % with average size of 10 nm and a surface area of $600 \text{ m}^2 \text{ g}^{-1}$) were purchased from Aldrich and used as an additive. Buffer solutions with various pHs between 5 and 12 were prepared using *O*-phosphoric acid and its salts (purity 99 % from Fluka).

2.2 Instruments

Cyclic voltammetry experiments were carried out using a Potentiostat/Galvanostat EG&G Model 263 (USA) that was well controlled and operated using M 270 software. Impedance spectroscopy measurements were performed using a potentiostat/galvanostat (model Autolab, PGSTAT30, Eco Chemie, Netherlands) with FRA software. All the measurements were conducted using a three-electrode cell configuration system. The utilized three-electrode system was composed of $\text{Ag}/\text{AgCl} \cdot \text{KCl}$ (saturated) as the reference electrode, a platinum wire as the auxiliary electrode and GCE as the working electrode substrate. The surface morphology of the deposited films was characterized by scanning electron microscopy (model VEGA-TESCAN). A pH meter (model 3030, JENWAY) was used to read the pH of the buffer solutions. The pH values for the solution of phosphate were adjusted by either a solution of sulfuric acid or sodium hydroxide depending on the pH needed.

2.3 Electrode modification

Prior to the modification of the GCE, it was polished with alumina slurries on a polishing cloth to a mirror finish and then ultrasonically cleaned for 2.0 min in ethanol. Then, the electrode was rinsed thoroughly with distilled water.

3 RESULTS AND DISCUSSION

3.1 Electrochemical polymerization

The POAP film and POAP/ SiO_2 nanocomposite were prepared at the surface of the GCE in the absence and

presence of nanoparticles SiO_2 ($w = 2 \%$) in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.1 \text{ M OAP}$ using the potentiostatic method at $E = 0.6 \text{ V}$.

3.2 Surface morphology

The morphology of POAP film and its blend with SiO_2 nanoparticles was characterized using scanning electron microscopy (**Figure 1**). The SEM image of the pristine POAP film on the GCE (**Figure 1a**) shows a composed morphology of elongated globules (densely smooth film). **Figure 1b** shows the structure of the nanocomposite (POAP/ SiO_2) surface. The surface of the POAP film prepared in the presence of SiO_2 nanoparticles exhibited discretely shaped agglomerates due to the influence of the SiO_2 nanoparticles. The clusters of small SiO_2 nanoparticles are not uniformly adhered on the surface of POAP globules. This structure allows the electrolyte constituent better access to the interior of the nanocomposite. Certainly, the high dispersion of SiO_2 nanoparticles on the surface of the POAP spheres might have improved the surface area and the stability of the

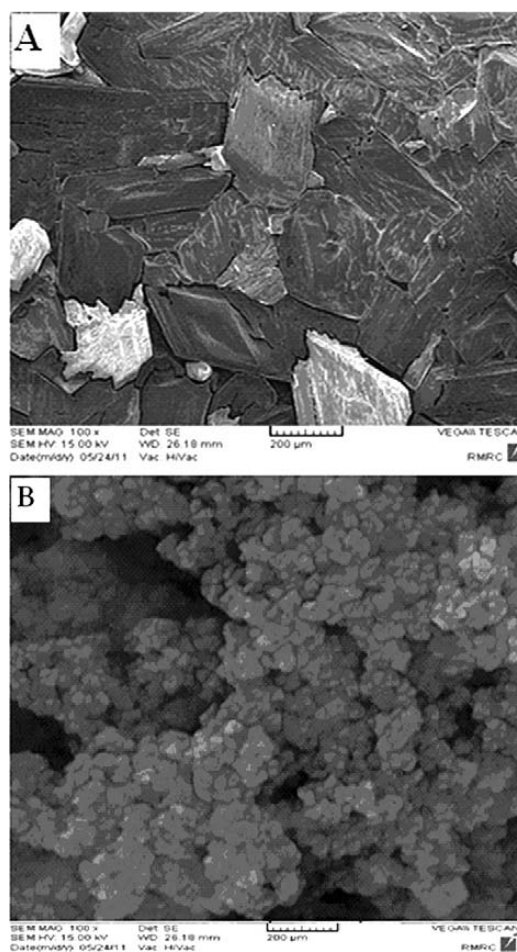


Figure 1: SEM images of: a) POAP film and b) POAP/ SiO_2 synthesized in H_2SO_4 solution 0.5 mol L^{-1}

Slika 1: SEM-posnetka: a) POAP-nanosa in b) POAP/ SiO_2 , sintetiziran v raztopini H_2SO_4 $0,5 \text{ mol L}^{-1}$

nanocomposite. This may be attributed to possible interactions via the hydrogen bonding between the imine (-NH) group of POAP and the hydroxyl (-OH) group on the surface of the nano-silica.

3.3 Cyclic voltammetry of POAP/SiO₂ and POAP films

Figure 2 shows 15 consecutive voltammograms, from 0 V to 1.3 V, to deposit the POAP/SiO₂ film in a phosphate solution at pH = 3 at a scan speed of 0.2 V/s. By the 5th cycle the anodic peak could not be observed. When the number of scans increased over 5, an anodic peak current (*I_a*) was observed clearly at +0.65 V.

The charge measured by the integration of the anodic peak area was found to be 12.02 mC cm⁻² for the 15th cycle, and oxidation of the POAP film occurred at 0.65 V. The voltammetric behavior of the POAP film in the same electrolyte solution and in the same potential range is shown in **Figure 3**.

Although a similar polymerization charge was used to synthesize both of the films (POAP/SiO₂ and POAP), the voltammetric behavior of the POAP film was significantly different. During the 1st to the 5th cycle, the cyclic voltammogram did not show any change. The shift of the anodic peak potential to higher currents was continued until the 10th cycle. The reached anodic peak charge for the POAP/SiO₂ film after the 15th cycle was not similar to the charge measured for the pure POAP film until the same cycle. It seems that a transition from the so-called POAP(II) structure to the POAP(I) structure occurred. The changes in the POAP(II) structure during the voltammetry traces could be related to the nature of the transporting species like counter ions and/or nanoparticles.²⁴ The increase in the anodic peak current of the POAP/SiO₂ film can be attributed to the re-structuring of the POAP during cycling, where the polymer forms a more incompact structure, which required the lower overall potential to be flattened.

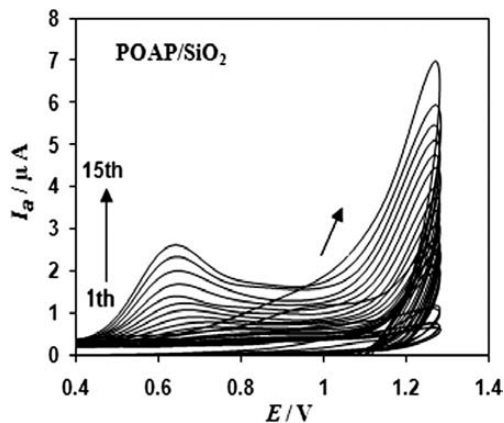


Figure 2: Cyclic voltammograms of the POAP/SiO₂ nanocomposite in a phosphate solution at pH = 3, scan rate: $v = 0.2 \text{ V s}^{-1}$. The 15 cycles are shown ($E_i = 0$ to $E_f = +1.5 \text{ V}$).

Slika 2: Ciklični voltamogrami nanokompozita POAP/SiO₂ v fosfatni raztopini pri pH = 3, hitrost skeniranja $v = 0,2 \text{ V s}^{-1}$. Prikazanih je 15 ciklov ($E_i = 0$ do $E_f = +1,5 \text{ V}$).

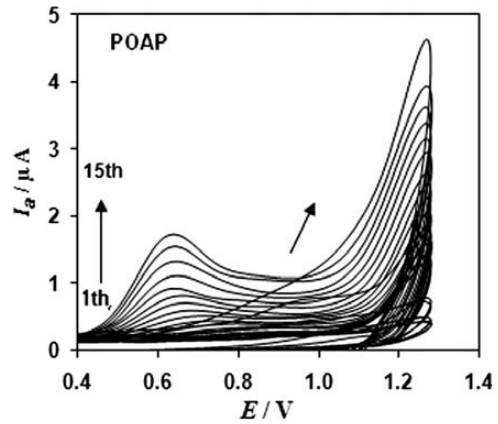


Figure 3: Cyclic voltammograms of the POAP in a phosphate solution at pH = 3, scan rate: $v = 0.2 \text{ V s}^{-1}$. The 15 cycles are shown ($E_i = 0$ to $E_f = +1.5 \text{ V}$).

Slika 3: Ciklični voltamogrami POAP v fosfatni raztopini pri pH = 3, hitrost skeniranja $v = 0,2 \text{ V s}^{-1}$. Prikazanih je 15 ciklov ($E_i = 0$ do $E_f = +1,5 \text{ V}$).

The silanol groups of SiO₂ could be adsorbed onto the GC surface. This changes the interfacial structure and the property of the GC/electrolyte solution, which benefits the electropolymerization process. However, the organic-inorganic interactions between the POAP and SiO₂ involved in the electropolymerization process pushed the polymer chains and so facilitated the growth of the polymer chains. The anodic peak current increased by increasing the number of cycles for both of the systems, but its values were higher for the nanocomposite than for the pure POAP system.

3.4 Effect of the scan rate

The effect of the scan rate (v) was investigated in a phosphate solution at pH = 3 in order to compare the electrochemical behavior of the deposited polymeric films. The results of this investigation are shown in **Figure 4**.

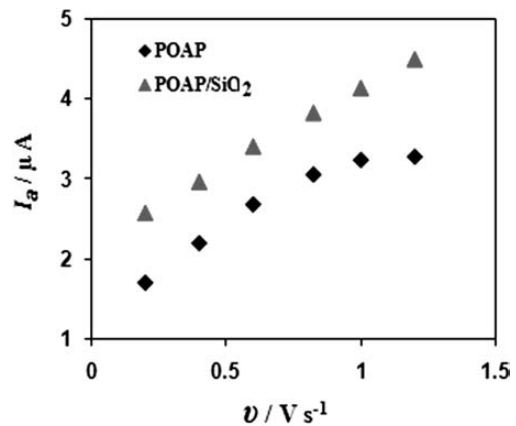


Figure 4: The anodic peak current (*I_a*) of POAP/SiO₂ and POAP films at various scan rates $v = 0.2-1.2 \text{ V s}^{-1}$

Slika 4: Vrh anodnega toka (*I_a*) pri POAP/SiO₂- in POAP-nanosu pri različnih hitrostih skeniranja $v = 0,2-1,2 \text{ V s}^{-1}$

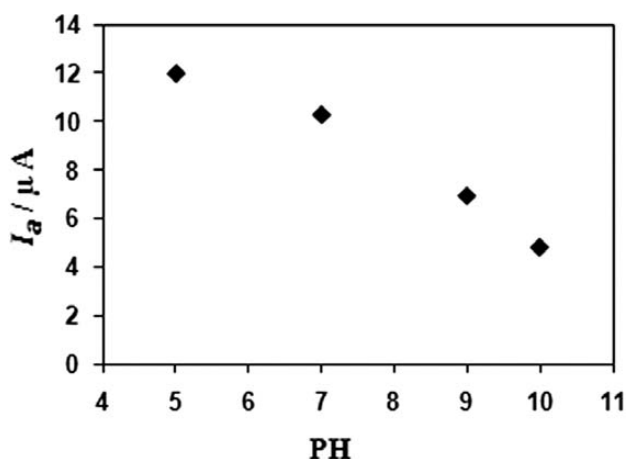


Figure 5: The anodic current (I_a) of POAP in different buffer solutions of *O*-phosphoric acid at pH = (5, 7, 9 and 10)

Slika 5: Anodni tok (I_a) POAP v različnih puferških raztopinah *O*-fosforne kisline pri pH = (5, 7, 9 in 10)

The oxidation current clearly increased as the scan rate increased. An increase in the scan rate is likely due to an enhancement of the electron flow. It appears that the increased collision of electrons resulted in a reduction in the velocity of the electrons leading to a saturation of the current. The oxidation current for the POAP/SiO₂ system increases linearly with the square of the scan rate. The above result indicated that the redox process was confined to the surface of the GCE, confirming the immobilized state of the POAP/SiO₂. The differences in the redox currents reflect the effective active surface areas that are accessible to the electrolytes for the POAP/SiO₂. It seems that the porous POAP/SiO₂ film has a higher effective surface area. This improvement of the doping/undoping rate is a result of the increase in the surface area and the porous structure, which are of benefit to the ion diffusion and migration.

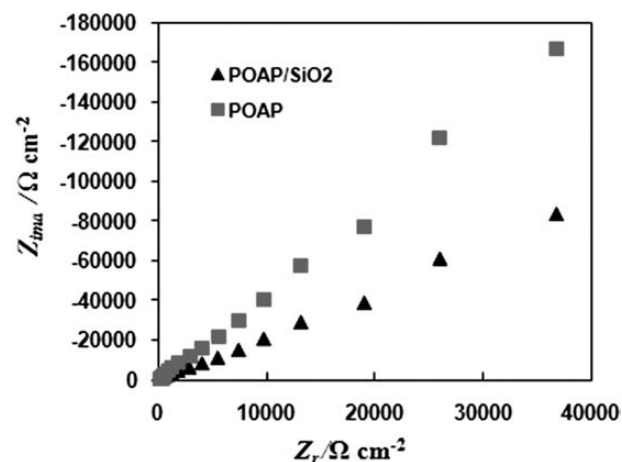


Figure 6: Impedance profiles of the produced films in phosphate electrolyte solution 0.1 M for: a) the POAP and b) the POAP/SiO₂ nanocomposite

Slika 6: Profil impedance nanosov v raztopini fosfata 0,1 M za: a) POAP- in b) POAP/SiO₂-nanokompozit

3.5 The influence of pH on the electropolymerization of POAP

It is well known that the electrochemical process involving aniline-type polymers requires the exchange of electrons and protons.²⁵ Accordingly, the solution pH has a significant effect on the electrochemical behavior of the polymeric films. **Figure 5** shows the cyclic voltammograms of POAP films deposited at various pH values. The results indicated that the current intensity increased as the pH of the electrolyte solution became more acidic. From this it can be implied that the doping/undoping rates in acidic media are more facilitated. In the other situation the POAP film becomes more electro-inactive in basic media.

3.6 EIS measurements

EIS experiments were conducted to provide some insights into the electrode/polymeric film/electrolyte interface. **Figure 6** displays typical impedance spectra of the POAP/SiO₂ and pure POAP in a phosphate solution 0.1 M recorded at a dc potential of 0.65 V for the frequency range 40 mHz to 60 kHz. The semicircle obtained from the high-frequency region was ascribed to the blocking properties of a single electrode, which can be related to the faradic process of an ion exchange that is extremely slow at the polymer/electrolyte interface.

The charge-transfer resistance (R_{ct}) for the POAP/SiO₂ was determined to be $2 \times 10^2 \text{ k}\Omega \text{ cm}^{-2}$, which is smaller than the value found for the pure POAP ($2.52 \times 10^3 \text{ k}\Omega \text{ cm}^{-2}$). In other words, the pure POAP film presents a higher electrochemical charge-transfer resistance than the nanocomposite film. This could be assigned to the compact structure of the chains in POAP film and its less active sites for faradic reactions. These results were also confirmed by the cyclic voltammetry observations, where the peak current values increased in the presence of silica nanoparticles.

4 CONCLUSIONS

In this work, a new nanocomposite based on OAP was prepared by the electropolymerization of OAP at the surface of GCE, as a low-cost substrate, in the presence of SiO₂ nanoparticles. Apart from the higher electropolymerization rate, the POAP/SiO₂ nanocomposite showed good electrochemical behavior, which can be due to the different morphology of the POAP in the presence silica nanoparticles. A discrete agglomerated morphology of the prepared composite was observed owing to the influence of the SiO₂ nanoparticles. The nanoparticles can reduce the possible interactions between the POAP chains and, hence, have an important role in the dynamics of the polymeric chain. Impedance spectroscopy results confirmed that the POAP film is more resistive toward charge transfer than the POAP/SiO₂ nanocomposite. Therefore, the presence of SiO₂ nano-

particles results in the improved conductivity of the POAP films.

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