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Novel in situ electrochemical deposition of platinum nanoparticles by sinusoidal voltages on conducting polymer films

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Abstract

Platinum (Pt) nanoparticles were successfully electrodeposited in situ on an organic conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), using for the first time sinusoidal voltages of various frequencies in a chloroplatinic acid solution. The organic PEDOT matrix was electrodeposited on Pt electrode chips. The Pt electrode chips consist of a 150 nm Pt layer deposited on 100-oriented standard 3'' silicon wafers. The cyclic voltammograms of the PEDOT-Pt-nanoparticles composite material recorded in 0.5 M H₂SO₄ aqueous solution demonstrated that Pt nanoparticles are electrochemically active. Values of the roughness of the composite materials, measured by optical non-contact 3D profilometry, ranging from 880 nm to 1.6 μm were obtained

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depending on the time of deposition of the nanoparticles. The PEDOT-Pt-nanoparticles composite deposited by a sinusoidal voltage with a frequency range of 0.1 Hz – 100 kHz, 50 frequencies, has the largest active surface area (5.16 cm²) compared with other composite coatings prepared in this work and those previously reported. Atomic force microscopic (AFM) images revealed the presence of numerous deposited Pt nanoparticles on the organic PEDOT polymer film.

Keywords: Atomic force microscopy, Sinusoidal voltage, Poly(3,4-ethylenedioxythiophene), Platinum metal nanoparticles

1. Introduction

The preparation of nanoparticles based composite materials has attracted considerable interest due to their applications in electrochemical sensors and biosensors [1-6]. Noble metal nanoparticles (NP) have been incorporated in conducting polymers (CPs) using various preparation procedures [7-10]. Usually the NPs are prepared via a chemical route [11-13] and are then incorporated into CP layers by electrochemical polymerization of the appropriate monomer [7] or using the layer-by-layer deposition technique [14, 15]. Recently, a great deal of interest has been devoted to innovative synthesis route of Pt nanoparticles, for example by the help of ultrasound [16]. Another possibility might lie in the in situ preparation of Pt nanoparticles achieved via electrochemical methods [17-26]. In situ preparation of Pt nanoparticles has been achieved via electrochemical methods, and in particular potentiostatic deposition at a fixed potential value which is sufficiently negative to assure reduction of the appropriate precursors to metallic states. The reduction of the precursors to metallic states was

carried out in strong acidic solutions by applying a constant potential for a fixed period of time or by potential cycling in appropriate potential ranges.

The aim of this paper is to demonstrate the suitability of a new in situ electrodeposition preparation procedure based on electrochemical impedance spectroscopy (EIS) technique for Pt nanoparticles deposition on PEDOT coatings. To this purpose, in situ electrochemical preparation of Pt nanoparticles on PEDOT films using sinusoidal voltages of various frequencies is reported here. Use of sinusoidal signals for in situ preparation of Pt nanoparticles is first reported here and is in fact an innovative aspect of this paper in the field of in situ nanoparticles electrodeposition. It is worth to note that the proposed approach is similar to the EIS technique, which makes use of the same materials and method. The use of large amplitude sinusoidal voltages eliminated the possible reduction of proton during the Pt nanoparticles deposition and this resulted in a finer control of the nanoparticles size and roughness of the composite coatings. The resulting composite modified electrodes were investigated in 0.5 M H₂SO₄ aqueous solution by cyclic voltammetry (CV), which revealed that Pt nanoparticles are electrochemically active. The PEDOT-Pt-nanoparticles composite coatings were further characterized by the AFM technique.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. 3,4-ethylenedioxythiophene (EDOT, Aldrich) was used for electrochemical preparation of the corresponding polymer. Deionised water Millipore (18 MΩ cm) was used to prepare

aqueous solutions. Freshly prepared solutions were used for electrochemical measurements.

2.2. Electrochemical measurements

The electrochemical experiments were carried out with an Autolab potentiostat/galvanostat 30 (Ecochemie, The Netherlands). A conventional three-electrode system was used, including a Pt electrode chip as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. All electrochemical measurements were carried out at room temperature, under a high purity nitrogen atmosphere. The platinum electrode chips (0.64 cm^2) were fabricated according to a procedure previously reported [27]. Before each electrochemical measurement, the surface of the working electrode was checked by cyclic voltammetry in aqueous solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl. The impedance spectra were recorded through FRA2 soft of the Autolab potentiostat in the frequency range 0.1 Hz – 100 kHz using a sinusoidal excitation signal (single sine) with excitation amplitude (ΔE_{ac}) of 50 mV. A variety of frequency domains ranging from 100 kHz to 0.1 Hz were used for in situ preparation of Pt nanoparticles.

2.3. Surface analysis of PEDOT-Pt-nanoparticles composite coatings

Polymer morphology examinations were performed using a commercial Atomic Force Microscope (stand-alone SMENA scanning probe microscope NT-MDT, Russia) in the contact mode. The experiments were conducted in a controlled environment with a laminar flow (humidity 30 % and 25°C). Adhesion of the polymer films was estimated through pull-off measurements. The Si rectangular AFM cantilever, with a stiffness of

0.3 N/m, was fixed, and the substrate moved vertically. Pull-off measurements were taken with a cantilever to which a borosilicate sphere ($r = 5 \mu\text{m}$ radius) was glued on the free extremity and beneath it (Novascan Technologies, Ames, USA). Consequently, pull-off force represents in this case the adhesion between the borosilicate sphere on the tip AFM cantilever and the substrate. Ten measurements were taken at different points on the same sample with a driving speed of $1 \mu\text{m/s}$. Roughness of the polymer films was also determined by AFM.

2.4. In situ electrodeposition of Pt nanoparticles on PEDOT

The composite PEDOT-Pt-nanoparticles films were prepared by a two-step method. Firstly, the PEDOT layer was electrodeposited from an aqueous solution containing 0.01 M EDOT, and 0.1 M LiClO_4 as a supporting electrolyte by potential cycling in the potential range from open-circuit potential, OCP, to $+1.0 \text{ V} / \text{SCE}$ and reversed back to $-0.6 \text{ V} / \text{SCE}$, at a scan rate of 0.05 V s^{-1} for 5 or 10 consecutive scans, respectively. In the second step, in situ deposition of Pt nanoparticles was carried out in 0.001 M K_2PtCl_6 , 0.1 M HClO_4 aqueous solution by applying the following procedure: sinusoidal voltages of various frequency ranges, i.e. $100 \text{ kHz} - 0.1 \text{ Hz}$, $100 - 10 \text{ kHz}$, with an excitation amplitude (ΔE_{ac}) of 50 mV were applied at a fixed dc potential value of $-0.20 \text{ V} / \text{SCE}$. The resulting composite modified electrode is referred to as Pt/PEDOT-Pt-nanoparticles.

3. Results and discussion

3.1. Electrodeposition of PEDOT onto Pt electrode chip

Figures 1A and 1B show the CVs recorded during electrochemical deposition of PEDOT coating performed on a naked electrode. Polymerization of the EDOT monomer takes place in the potential range from 0.85 to 1.00 V / SCE, as can be seen from the increase in anodic current. Growth of the organic PEDOT layer was controlled by the potential cycle number applied in the electrochemical polymerization process, namely 5 (see Fig. 1A) or 10 (see Fig. 1B) consecutive scans.

Figure 1 near here

3.2. Optimisation of the PEDOT-Pt-nanoparticles composite coatings preparation procedure

The potentiostatic deposition of Pt nanoparticles onto PEDOT films is usually performed in strong acidic solutions, at negative potential values, i.e. -0.2 to -0.3 V. Due to high proton concentration it may be possible that at such negative potential values required for the reduction of platinum precursors to metallic states, the proton reduction can occur simultaneously with the Pt nanoparticles deposition. To this purpose, we investigated the electrochemical behaviour of naked Pt electrode chips in 0.1 M HClO₄ aqueous solution. Figure 2A reports the cyclic voltammograms recorded at Pt electrode in acidic solution. From this figure one can observe that the proton reduction starts at a potential value of ca. -0.3 V / SCE. Furthermore, the Pt/PEDOT modified electrode was also investigated by cyclic voltammetry in 0.1 M HClO₄ aqueous solution. From Fig. 2B it can be seen that there is no proton reduction until a potential value of -0.3 V / SCE. Therefore, the deposition potential value used for the in situ electrodeposition of Pt nanoparticles was chosen as -0.2 V/SCE. Once the PEDOT layer was deposited onto

Pt electrode, the modified electrode was immersed in chloroplatinic acid solution and the preparation procedure, described in Section 2.4, was applied for in situ Pt nanoparticles electrodeposition on PEDOT films.

Figure 2 near here

3.3. Preparation of PEDOT-Pt-nanoparticles composite coatings by sinusoidal voltages

Various sinusoidal voltages were applied for in situ deposition of Pt nanoparticles on PEDOT layer. The duration of the measurements depends on the frequency range used, which resulted in different Pt nanoparticles sizes, that is from 120 s up to 480 s. Moreover, the amplitude (ΔE_{ac}) of 50 mV of the sinusoidal excitation signal (single sine) was chosen to allow for the fact that this large amplitude can contribute to fine control of nanoparticles size. Figure 3A reports the impedance spectrum recorded at the Pt/PEDOT modified electrode in chloroplatinic acid solution in the frequency range 100 kHz – 0.1 Hz. Appearance of a capacitive loop can be observed in the high frequency range of 100 – 18 kHz. This loop is magnified in the inset of Fig. 3A, and should be attributed to the interfacial behaviour between the Pt/PEDOT modified electrode and the solution. Two other loops can be observed in the medium frequency range of 18 kHz – 3 kHz and 3 kHz – 100 Hz. These loops can be associated with Faradaic reactions. These reactions should be the reduction of the precursor Pt^{4+} complex ions to Pt^{2+} , and then to Pt^0 with the formation of Pt nanoparticles. Finally, at low frequencies, the impedance spectrum is dominated by the Warburg impedance. This impedance spectrum is depicted as Bode plot in Fig. 3B. From the Bode plot one can observe that at low frequencies a slope of -0.8 for $\log Z$ vs. $\log f$ was obtained, which is closed to the

theoretical value of -1, while for high frequencies a slope close to $\sqrt{3}$, indicative for diffusion-reaction reduced impedance, is obtained. Furthermore, the phase vs. $\log f$ plot depicted in Fig. 3B shows that at low frequencies a phase of ca. 80 degrees is obtained, while for high frequencies the phase tends to zero, which is indicative of capacitive behaviour. A value of ca. 78 Ohms for the charge transfer resistance (R_{ct}) can be obtained from the Z' vs. $1/\omega^2$ plot, which is depicted in Fig. 3C. From this value, the exchange current density (i_0) was determined as $1.29 \times 10^{-4} \text{ A cm}^{-2}$, according to the equation (1):

$$R_{ct} = RT/(nFi_0) \quad (1)$$

where $n=4$, and the other symbols have their usual significance [28].

Therefore, it is worth to note that the new preparation procedure allows for the electrochemical parameters, such as charge transfer resistance and exchange current density, to be also determined. This feature is brought by the EIS powerful technique used in the Pt nanoparticles electrodeposition and can be considered as an advantageous tool compared with the classical potentiostatic methods applied for nanoparticles deposition.

Figure 3 near here

3.4. Electrochemical characterization of PEDOT-Pt-nanoparticles composite materials

After deposition of Pt nanoparticles onto the PEDOT layer, the modified electrodes were characterized in 0.5 M H_2SO_4 aqueous solution using cyclic voltammetry. Figure 4 reports the cyclic voltammograms recorded for various types of PEDOT-Pt-nanoparticles coatings prepared on different experimental parameters, i.e. the frequency

range, the number of measured frequencies, and the number of deposition scans applied in the preparation procedure of the PEDOT coatings. Two well-separated pairs of peaks can be observed between -0.25 and 0.0 V / SCE, which are due to adsorption and desorption of hydrogen atoms on Pt nanoparticles surfaces. Pt oxide formation occurred in the potential range from 0.8 V to 1.0 V / SCE, and the corresponding reduction peak of Pt oxide is located at 0.6 V / SCE. The features of the voltammograms were similar to the polycrystalline Pt electrode, with typical peaks at -0.13 V and -0.05 V / SCE, whereas the pure PEDOT the current is low and only influence by its capacitance. The peak currents for the reduction waves located in the potential range -0.25 – 0.0 V / SCE increased with deposition time corresponding to different frequency ranges and the number of measured frequencies used in the preparation procedure.

It is important to notice the drastic increase in the anodic peaks, which rose from 2.6 μA at -0.05 V for naked Pt up to 126 μA at -0.05 V /SCE, maximum met for nanoparticles deposited by a sinusoidal voltage (100 kHz-0.1 Hz, 50 frequencies, on PEDOT deposited by 5 scans). These results demonstrate that Pt nanoparticles deposited on PEDOT coating by a sinusoidal voltage were electrochemically active. By comparison, nanoparticles prepared by classical potentiostatic methods, deposition time 1200 s [22], give electrodes with a similar behaviour.

The electrochemically active surface area can be estimated by using the characteristic value of the charge density for a monolayer of hydrogen adsorbed on polycrystalline platinum electrode, i.e. 0.21 mC cm^{-2} [23, 29-31]. The cyclic voltammograms presented in Fig. 4 indicate that the PEDOT-Pt-nanoparticles composite, deposited by a sinusoidal voltage with a frequency range of 0.1 Hz – 100 kHz, 50 frequencies, has the largest active surface area (5.16 cm^2) compared with other

composite coatings prepared in this work and those previously reported [23]. The values of the estimated electroactive surface area for the Pt nanoparticles composite coatings are presented in Table 1.

Figure 4 near here

Table 1 near here

The thickness of the PEDOT layer influences the electrodeposition of Pt nanoparticles as can be seen from Fig. 4 on the CV trace for a PEDOT coating obtained by applying 10 consecutive deposition scans. In this case the increased thickness of the PEDOT layer hindered the formation of Pt nanoparticles and as a result the hydrogen adsorption-desorption peaks are not well defined. Therefore, an extended frequency range and/or a larger number of measured frequencies should be used for the Pt nanoparticles electrodeposition by sinusoidal voltages when thicker PEDOT coatings are involved. The increased numbers of deposition scans used in the electropolymerization of the EDOT monomer resulted in an enhanced surface area of the electrode, as can be seen from Table 1, but the adsorption/desorption hydrogen peaks are not well defined. Furthermore, the Pt electrode modified with a pure PEDOT coating shows no peaks in the potential range from -0.25 to 0.0 V / SCE and this result supports the above findings concerning the electrochemical activity of the Pt nanoparticles.

3.5. Surface analysis of the PEDOT-Pt-nanoparticles composite coatings

2D and 3D AFM images were performed on PEDOT-LiClO₄ films (Figures 5A and 5B) and on PEDOT-Pt-nanoparticles composite films obtained by a sinusoidal voltage in chloroplatinic acid solution at a fixed potential value of -0.20 V / SCE for the frequency range 100 kHz – 0.1 Hz (Figures 6A and 6B). The AFM of the PEDOT-LiClO₄ films exhibited a granular, regular and homogeneous structure. Grain size is less than 200 nm and height can be estimated at 80-90 nm.

Figure 5 near here

On the contrary, the PEDOT-Pt-nanoparticles films have a slightly different structure since the surface showed a rougher relief, with a strong increase in heterogeneities. This change of topography is due to the nanoparticles inserted in the polymer film. The nanoparticles thus led to an increase in film roughness, and the height of the grains growing on the nanoparticles can be estimated at 270 nm. Therefore, one can assume that the nanoparticles size is approximately 170-180 nm.

Figure 6 near here

The adhesion force, known as the “pull-off force”, was measured for all polymer coatings versus their electrodeposition conditions (with or without deposition of nanoparticles). The pull-off values are presented in Table 2.

Table 2 near here

The results presented in this table show marked differences in the adhesion forces between PEDOT-LiClO₄ and PEDOT-Pt-nanoparticles samples. Indeed, PEDOT-LiClO₄ exhibited an attractive pull-off force of -40.4 nN. On the contrary, the pull-off force was only included in the range between -5 and -15 nN, indicating a marked modification in surface properties and proving once again the presence of Pt nanoparticles. Moreover, the less negative pull-off values (- 3.79 and -5.13 nN) were obtained with the thickest films (obtained through 50 frequencies instead of 5 or 10 for the two other samples), confirming that the presence of Pt nanoparticles influences the adhesion properties of the films.

3.6. Advantages of the novel reported preparation procedure

The presented results clearly show that the in situ electrodeposition of Pt nanoparticles by using sinusoidal voltages offer some advantages compared with the potentiostatic method. First of all, the novel procedure provides a finer control of the nanoparticles size and especially of the surface roughness of the composite coatings. Values of the roughness ranging from 880 nm to 1.6 μ m were obtained depending on the time of deposition of the nanoparticles. Moreover, by applying a sinusoidal voltage over the dc fixed voltage of -0.2 V / SCE in acidic media the proton reduction was totally hindered thanks to the large amplitude of the sinusoidal voltage of 50 mV, even if it is shown that under these experimental conditions the proton reduction starts at ca. -0.3 V / SCE (see Fig. 2A). The large amplitude of the sinusoidal voltage used in this work prevented the agglomeration of Pt nanoparticles and the proton reduction, resulting in a smaller size of Pt nanoparticles and roughness values. The use of various frequencies pointed out that the optimum range is 0.1 Hz – 100 kHz. When the same number of frequencies was

employed, the peak currents were higher for the 0.1 Hz – 100 kHz range in comparison with 10 – 100 kHz range, noting that the duration of the measurement was almost the same. Furthermore, the peak currents of the adsorption / desorption of hydrogen are comparable with those reported in Ref. 22, where the Pt nanoparticles were deposited by potentiostatic method at -0.2 V in 1.1 mM H_2PtCl_6 , 0.5 M H_2SO_4 solution for a deposition time of 1200 s, which is 2.5 times higher in respect to the time used for the Pt nanoparticles deposition by a sinusoidal voltage with a frequency range of 0.1 Hz – 100 kHz. Therefore, it can be concluded that the use of sinusoidal voltages in Pt nanoparticles in situ electrodeposition provides a better control of the nanoparticles size and surface roughness. Finally, it is worth to note that this new in situ preparation procedure allows the estimation of the electrochemical parameters, such as charge transfer resistance and exchange current density. This feature is brought by the EIS powerful technique used in the Pt nanoparticles in situ electrodeposition and can be considered as an appealing advantage compared with the classical potentiostatic methods applied for metal nanoparticles deposition.

4. Conclusions

Pt nanoparticles were successfully electrodeposited in situ, for the first time, on PEDOT organic conductive polymers using sinusoidal voltages of various frequencies in a chloroplatinic acid solution. The cyclic voltammograms recorded in 0.5 M H_2SO_4 aqueous solution demonstrated that Pt nanoparticles deposited via this novel preparation procedure are electrochemically active. Values of the roughness ranging from 880 nm to 1.6 μm were obtained depending on the time of deposition of the nanoparticles. This

novel in situ preparation procedure provides PEDOT-Pt-nanoparticles composite electrode with a large active surface area (5.16 cm²) compared with other composite coatings previously reported. The AFM measurements revealed the presence of numerous deposited Pt nanoparticles on the organic PEDOT polymer film. The novel reported method for Pt nanoparticles in situ electrodeposition on conducting polymer films provides a better control of the nanoparticles size and surface roughness. This work thus proposes a novel and efficient strategy for in situ electrochemical deposition of Pt nanoparticles on an organic conductive polymer matrix.

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Captions to figures

Fig. 1. Cyclic voltammograms recorded during electrochemical polymerization of EDOT at the Pt electrode chip in an aqueous solution containing 0.01 M EDOT and 0.1 M LiClO₄ as a supporting electrolyte. Potential scan rate: 0.05 V s⁻¹. The first 5 (A) and 10 (B) consecutive scans are depicted, respectively.

Fig. 2. Cyclic voltammograms recorded at (A) Pt naked electrode chip and (B) Pt/PEDOT modified electrode in 0.1 M HClO₄ aqueous solution at a potential scan rate of 0.05 V s⁻¹.

Fig. 3. (A) Impedance spectrum recorded on Pt/PEDOT modified electrode at a fixed dc potential value of -0.2 V for frequency range from 100 kHz to 0.1 Hz in an aqueous solution containing 0.001 M K₂PtCl₆ and 0.1 M HClO₄. (B) The Bode plot and (C) the Z', Z'' vs. 1/ω² plot of the impedance spectrum obtained as described in Fig. 3A.

Fig. 4. Cyclic voltammograms recorded at Pt/PEDOT-Pt-nanoparticles composite modified electrodes and naked Pt electrode in 0.5 M H₂SO₄ aqueous solution at a scan rate of 0.05 V s⁻¹.

Fig. 5. (A) 2D and (B) 3D AFM images (contact mode) of PEDOT films obtained through 5 cycles.

Fig. 6. (A) 2D and (B) 3D AFM images (contact mode) of Pt-nanoparticles prepared in situ on PEDOT film at a fixed potential value of -0.20 V for frequency range from 100 kHz to 0.1 Hz (5 deposition cycles for PEDOT matrix, 50 frequencies).

Table 1

The estimation of the electrochemically active surface areas of the polymer composite modified electrodes.

Table 2

Estimation of the pull-off values, using AFM, of the polymer films in the presence or absence of nanoparticles.

Table 1. The estimation of the electrochemically active surface areas of the polymer composite modified electrodes.

Composite electrode	Electrochemically active surface area (cm²)
PEDOT - LiClO ₄ (5 scans) -Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 0.1 \text{ Hz}$, 50 frequencies	5.16
PEDOT - LiClO ₄ (5 scans) – Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 50 frequencies	4.64
PEDOT - LiClO ₄ (5 scans) – Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 10 frequencies	1.64
PEDOT - LiClO ₄ (10 scans) - Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 10 frequencies.	2.28

Table 2. Estimation of the pull-off values, using AFM, of the polymer films in the presence or absence of nanoparticles.

Sample	Pull-off (nN)
PEDOT - LiClO ₄ 5 scans	- 40.4
PEDOT - LiClO ₄ (5 scans) -Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 0.1 \text{ Hz}$, 50 frequencies	- 5.13
PEDOT - LiClO ₄ (5 scans) – Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 50 frequencies	- 3.79
PEDOT - LiClO ₄ (5 scans) – Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 10 frequencies	- 9.45
PEDOT - LiClO ₄ (10 scans) - Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 10 frequencies.	- 91.3
PEDOT-LiClO ₄ (10 scans) - Pt nanoparticles deposited by a sinusoidal voltage, $\Delta F = 100 \text{ kHz} - 10 \text{ kHz}$, 5 frequencies.	- 14.2

Figure-1A

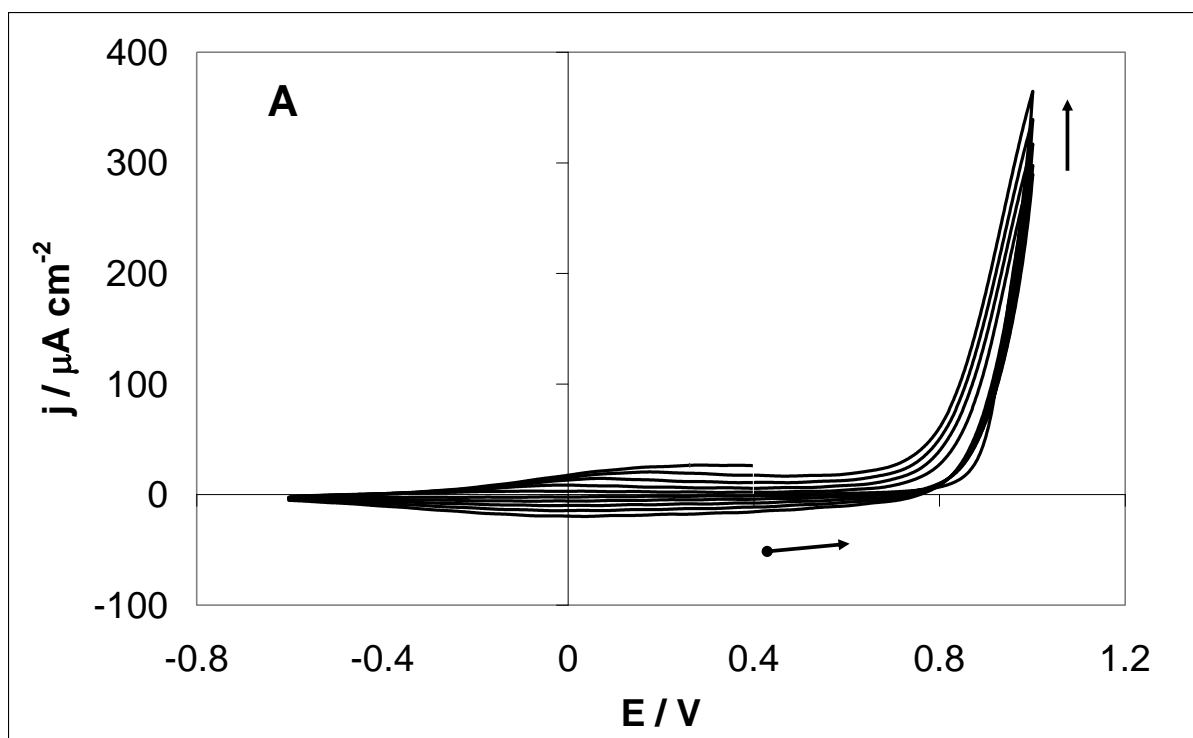


Figure 1A.

Figure-1B

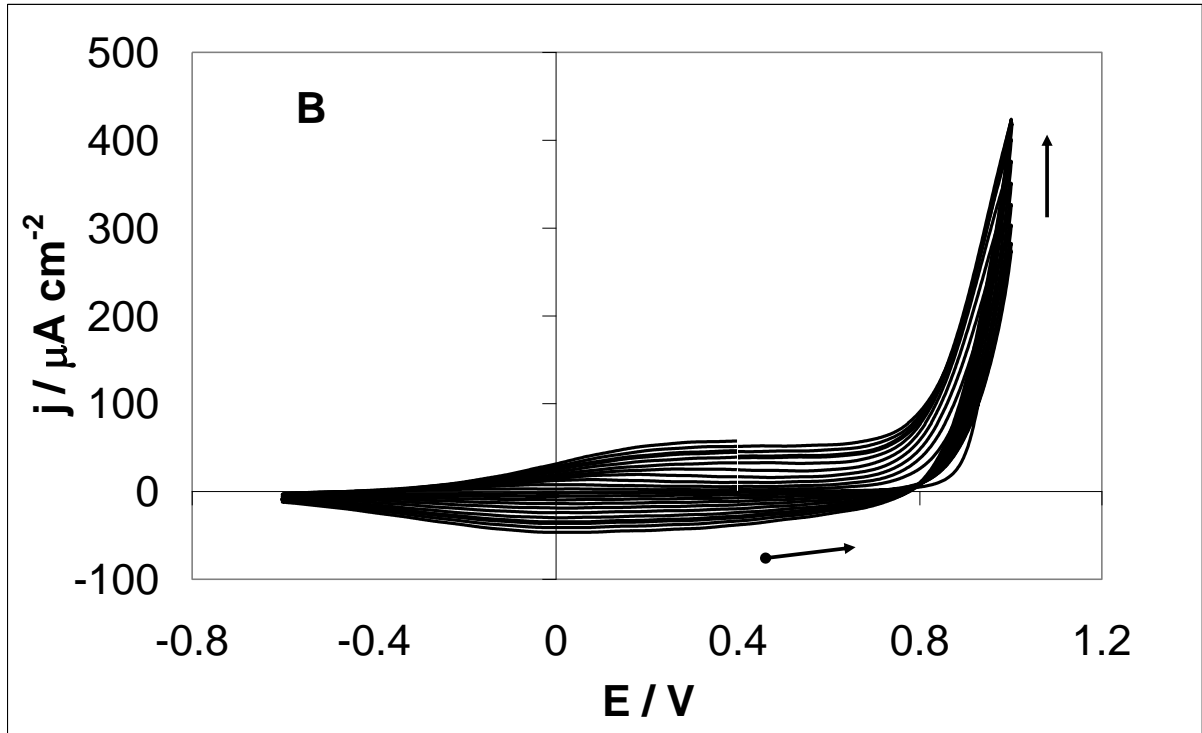


Figure 1B.

Figure-2A

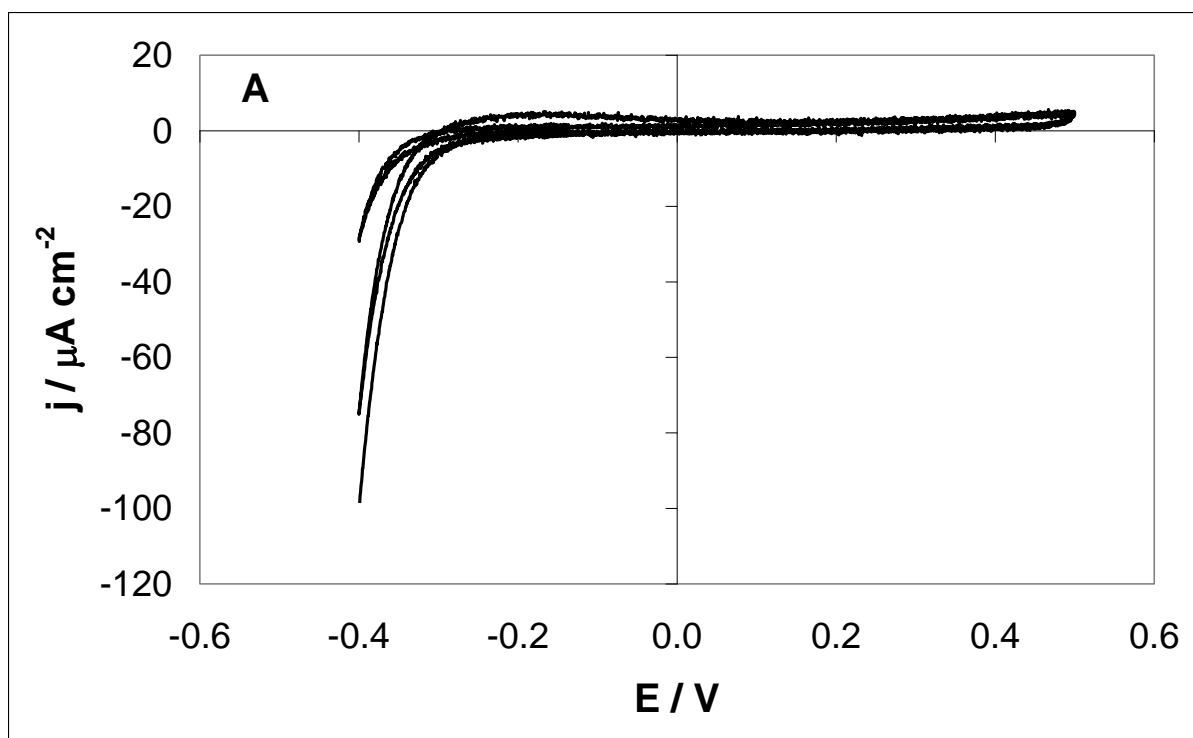


Figure 2A.

Figure-2B

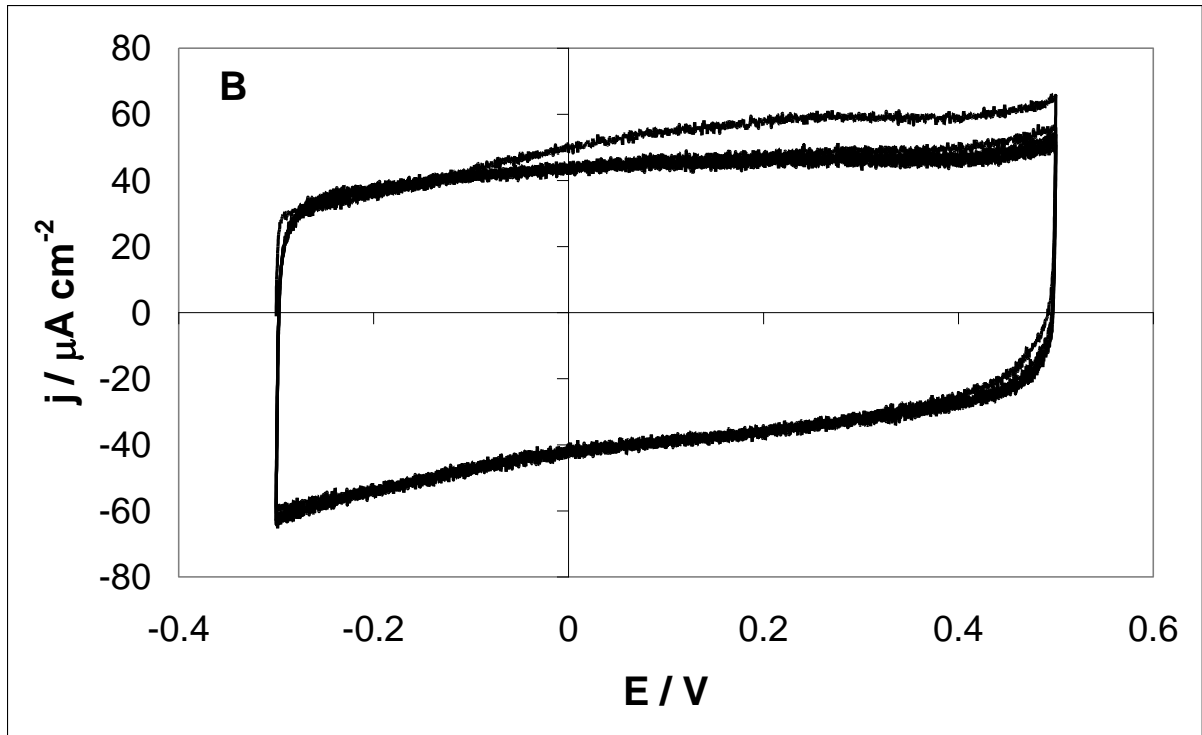


Figure 2B.

Figure-3A

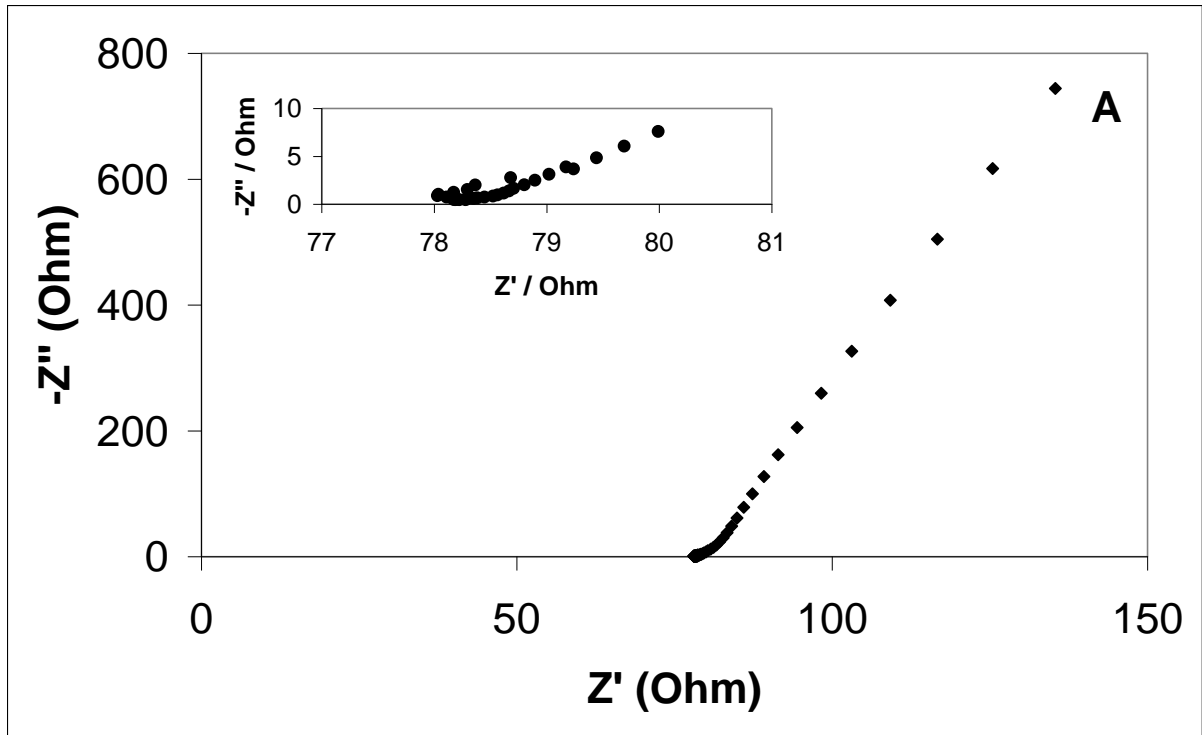


Figure 3A.

Figure-3B

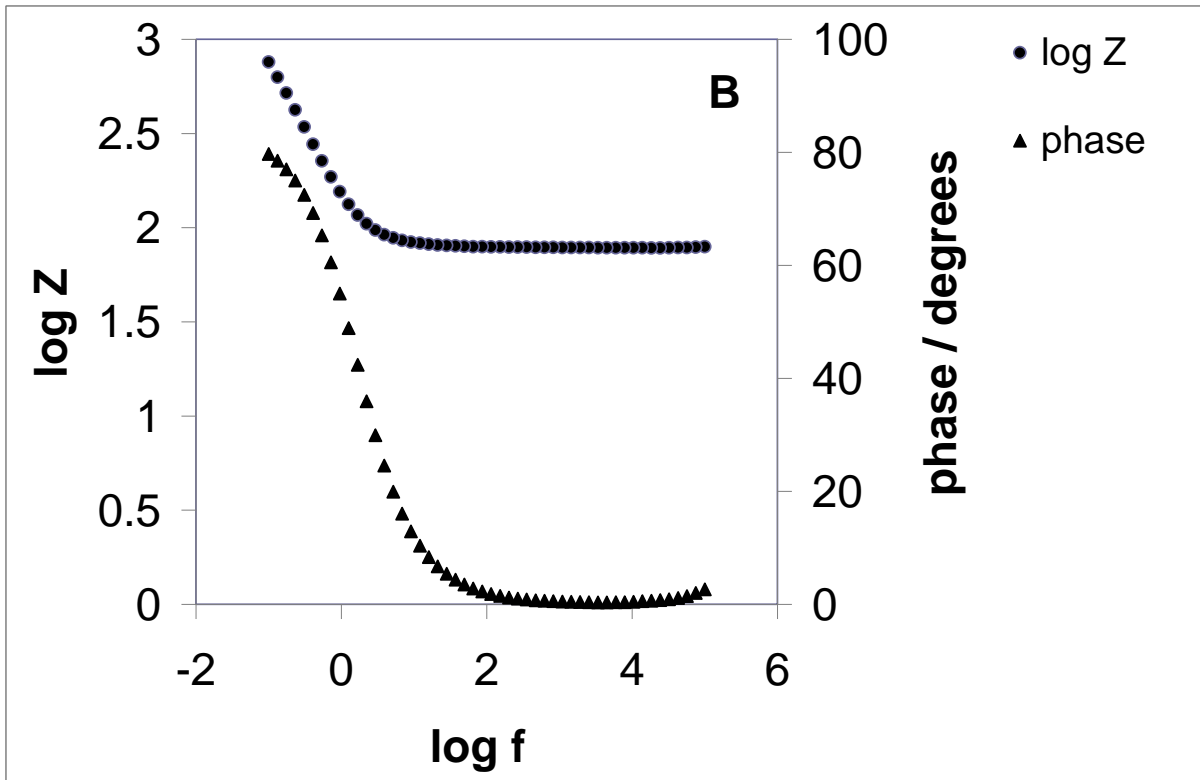


Figure 3B.

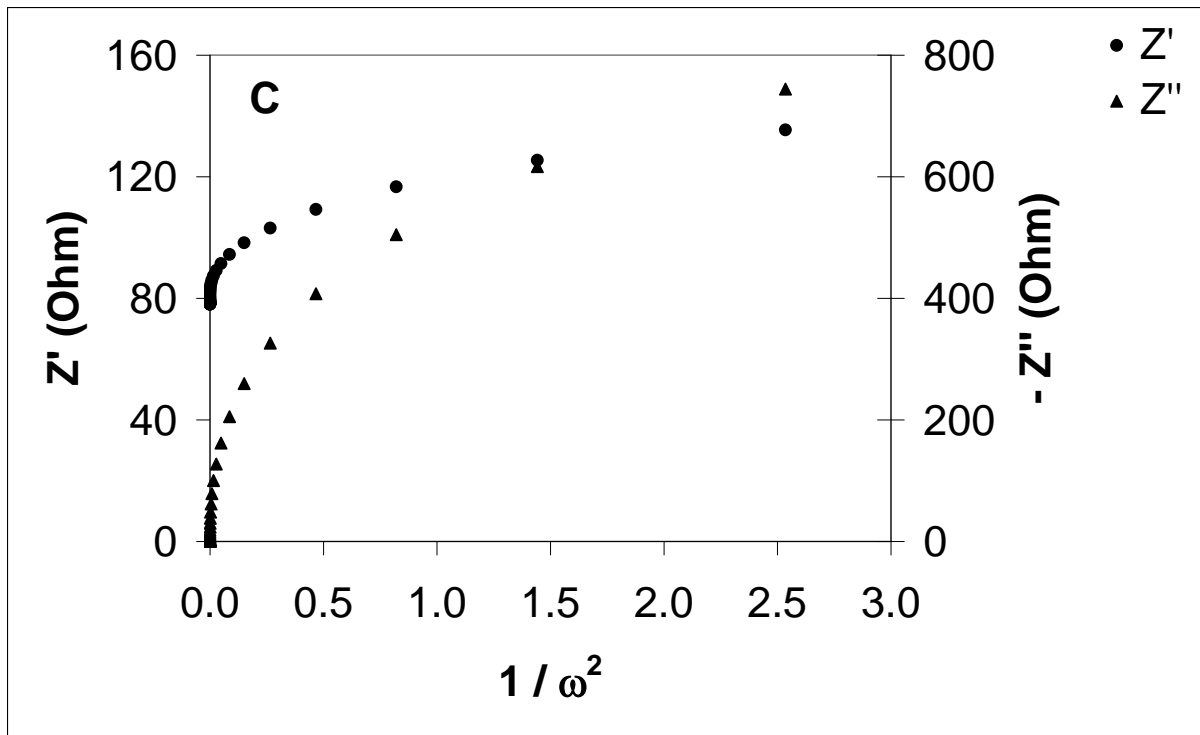


Figure 3C.

Figure-4

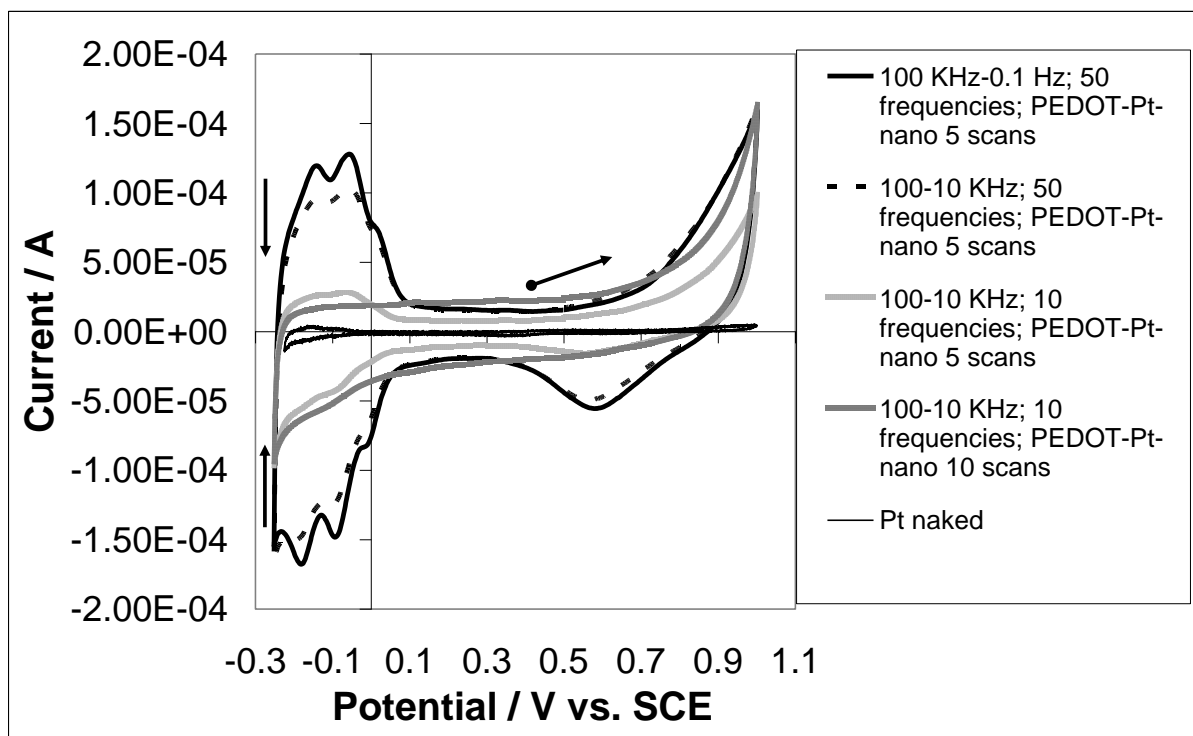


Figure 4.

Figure-5A

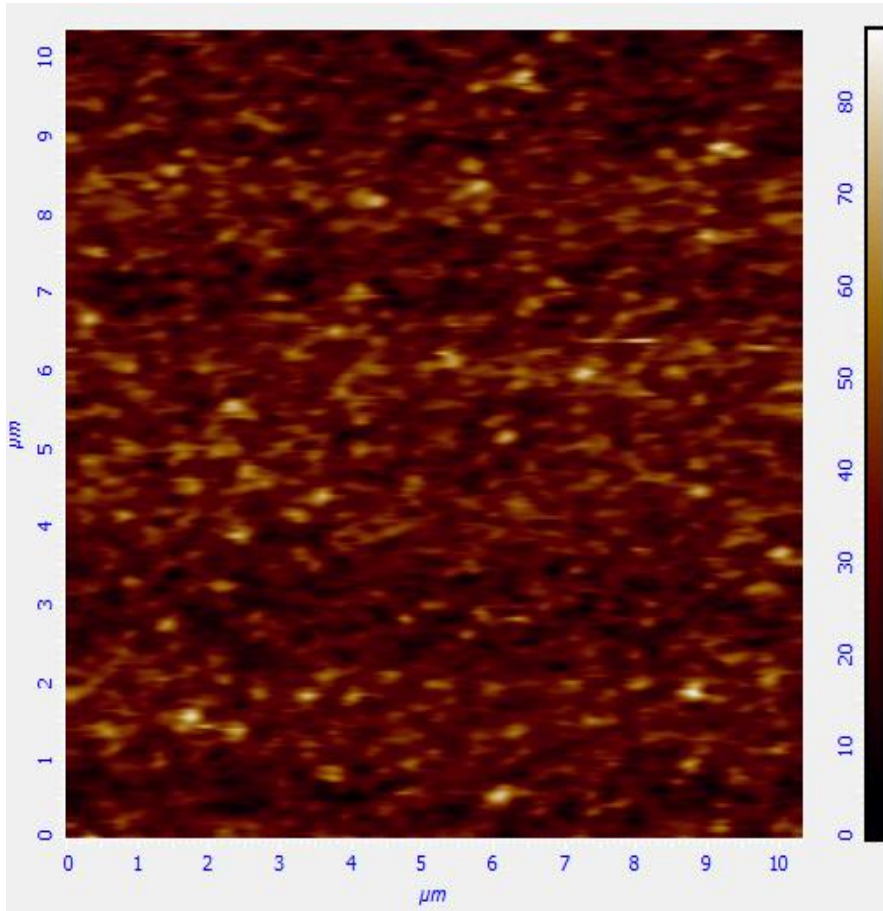


Figure 5A.

Figure-5B

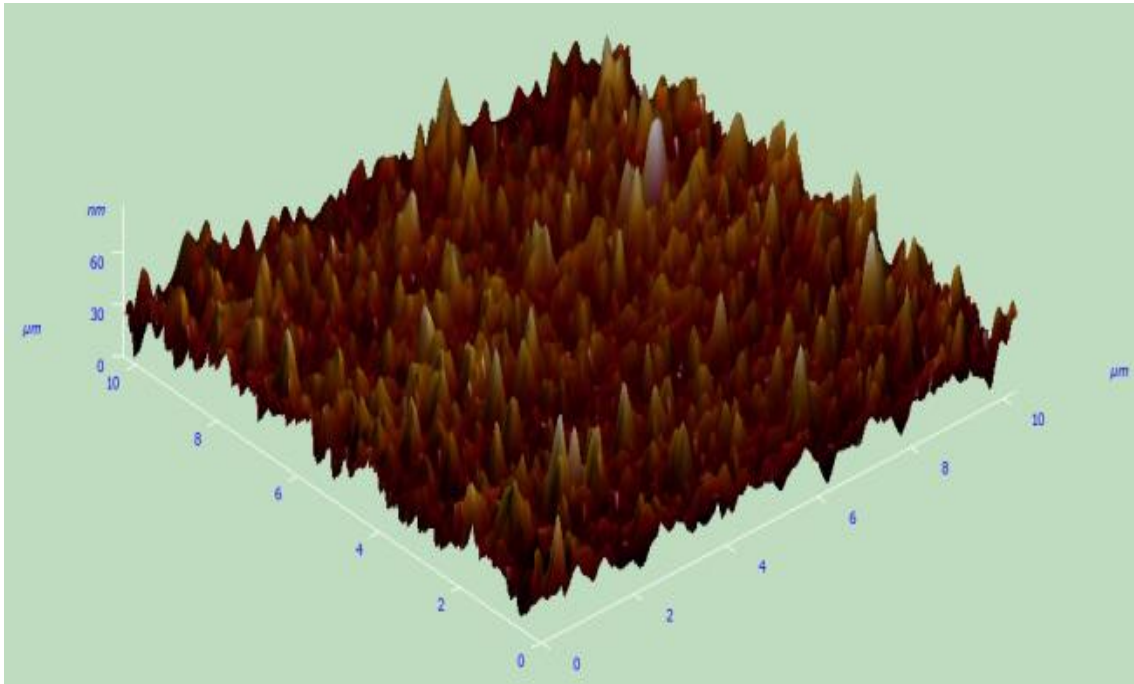


Figure 5B.

Figure-6A

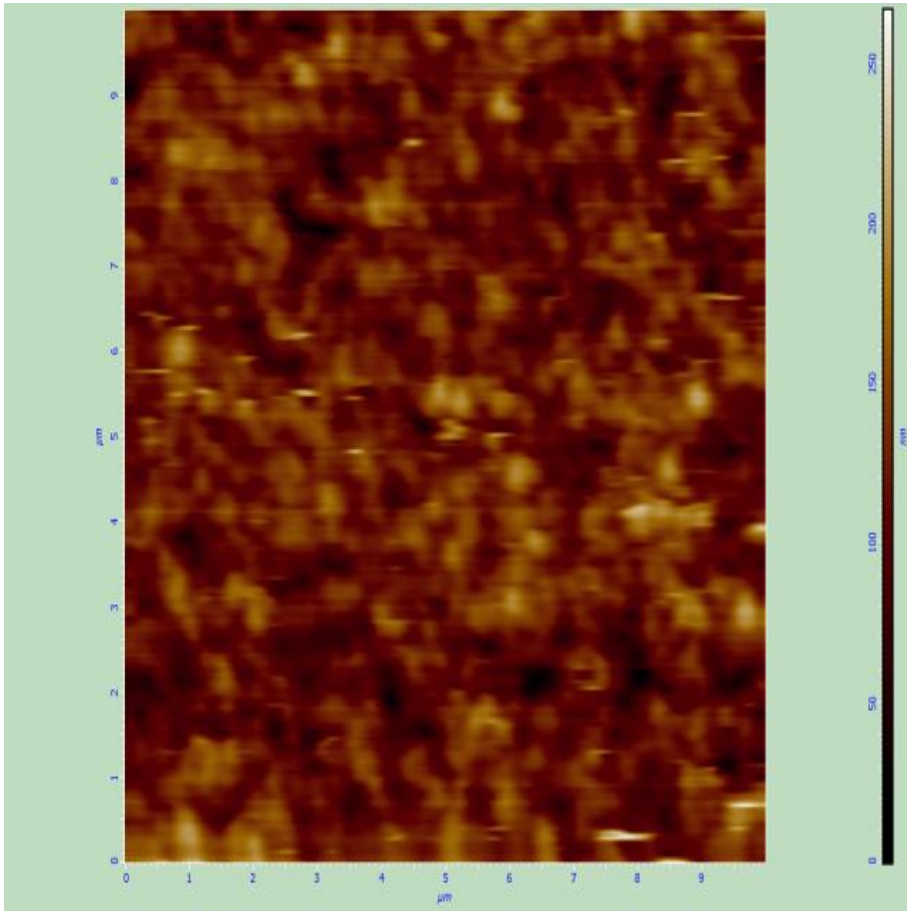


Figure 6A.

Figure-6B

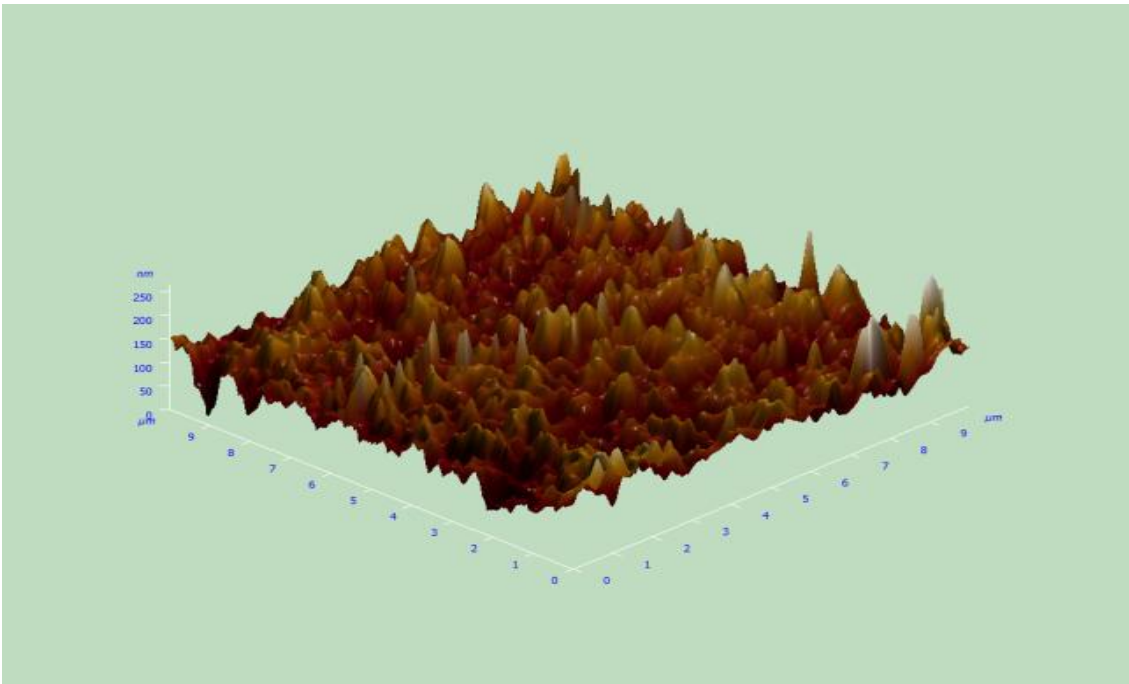


Figure 6B.