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Preparation of Nanostructured/ Microplatinum Surfaces by Application of a Square Wave Potential Regime for Methanol Oxidation

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Abstract: Platinum nanoparticles were electrodeposited on the tantalum electrode by using a square wave potential regime to form a modified electrode. The modified electrode was characterized by scanning electron microscopy (SEM), cyclicvoltammetry and energy-dispersive X-ray spectroscopy (EDX). The size, shape, and uniformity of the distribution of particles are influenced by frequency, lower and upper limits, time application of the square wave potential regime, and the concentration of $[PtCl_6]^{2-}$ in the solution. The optimal deposition time to obtain platinum nanoparticles on the tantalum surface was 2 min. The optimal conditions for preparation of the nanostructured platinum deposits were 100 Hz frequency, -0.4 V to 0.00 V lower and higher limits of the square wave respectively with an amplitude of 0.4 V. The optimal concentration was $1x10^{-4}$ M $[PtCL_6]^{2-}$. The electrocatalytic properties of platinum nanoparticles deposited onto the tantalum substrate were investigated for oxidation of methanol in acidic medium. The modified electrode by nanoparticles showed enhanced electrocatalytic performance compared to the polycrystalline platinum electrode. The sizes of the studied Pt nanoparticles range from 11 to 89 nm, polycrystalline Pt is inferior to nanoparticles Pt for methanol oxidation at above 65.1 mV, and the oxidation current on nanoparticles Pt becomes much higher than that on polycrystalline Pt at above 35μA.The peak current density ratios (j^f/j^b) for the polycrystalline pt and nanoparticles Pt electrodes were 1.01 and 1.87, respectively, indicating that the nanoparticles Pt electrode was much more resistant to catalytic poisoning.

Keywords: Methanol, Oxidation, Nanostructure, Electrocatalysis, Square Wave.

INTRODUCTION

Exploring new electrodes with enhanced electrocatalytic properties or improved electroanalytical selectivity and specificity has been the focus of electrochemists for decades [1,2]. Nanostructures electrodes have been the objective of many publications with a variable degree of success in pursuing the objectives of enhanced reactivity and/or selectivity [3-7].

Increasing attention has been devoted to the use of metal nanoparticles for electroanalysis because of their unique optical, electronic, magnetic and catalytic properties. Because the size and structure of nanoparticles have a significant effect on catalytic reactions, well-controlled nanostructures are essential for achieving excellent performance and in the preparation of catalysts. [8-11]

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To make the best use of the electro catalytic and electron-conducting characteristic of metal nanoparticles, various nanoarchitectures have been developed for modifying metal nanoparticles on electrode surfaces. Chemical and electrochemical approaches to the preparation of nanoparticles have been described in [12]. The electro deposition of nanoparticles provides advantages in terms of simplicity and the control of nucleation and particle growth during preparation if the experimental parameters are well-tuned [13, 15].

Fuel cells powered by small organic molecules (SOMs) for example methanol and formic acid have rapidly progressed due to rising energy demands, depletion of fuel reserves and environmental pollution issues, methanol has increased extraordinary enthusiasm as a fuel, due to good power densities and high performance at low temperature [15–17]. In this manner, Electrochemical sensors are required to identify their level both in the fuel fed in the anodic compartment of the cell and in the cathodic zone, electrochemical sensors are appropriate to this purpose, as they permit simple and rapid detection of compounds even on line with simple and cheap apparatuses [18]. Albeit, under given conditions, these sensors show acceptable performance, their operation suffers from the need of external feeding of oxygen or air to the cathode to allow a complete utilization of the fuel that diffuses to the anode surface. As it is known, platinum-based catalysts are among the most efficient materials and high efficient of electro oxidation for methanol oxidation [19]. On anthoer hand, platinum is susceptible to poisons for example CO, which strongly adsorbs onto the electrode surface active sites resulting in a dramatic decrease in electro catalytic efficiency [17, 20]. Under given conditions, the activity and movement of platinum towards the electro oxidation of methanol can be advanced by either utilizing nano structured platinum electrodes [20,21].The literature surveyed, the square wave potential regime is a train of pulses between two potential limits which approximates in electrochemical terminology a repetitive double potential step waveform. In each pulse one or more of electrochemical events occur and, their inverse, though not necessarily, occur upon reversal [22, 23]. In the previous years, a few intermediates may be created and their fate is affected by the square wave parameters, preparation of copper, gold, and silver nano structured electrodes [24], and electrochemical devastation of some pollutants [25].In this article, fabrication of platinum nanoparticles onto tantalum substrate by application of a square wave potential regime for use in the enhanced catalytic reaction was performed. By determining the optimized parameters of the square wave such as potential values, the concentration of the solution, time of reaction and the frequency, this approach may provide an opportunity to control the particle size, composition, crystallography and distribution of nano structured particles in a surface to prepare highly catalytic surfaces. Characterization is performed by cyclic voltammetry, energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM). Sensing of nanostructure surface towards some ionic species such as silver and catalytic properties toward the electro oxidation of methanol was investigated.

EXPERIMENTAL

Instruments and Materials

A potentiostat (273 A, Princeton Applied Research) interfaced to a laptop through a GPIB interface together with Echem® software system was used for electronic management and information acquisition. The square wave with the planned amplitude and frequency was generated by a function generator (Simpson, A240).The square wave as applied to the electrode was monitored via an oscilloscope (Telequipment S540).

A modified Polarographic 303A cell (Princeton Applied Research) was used for electro deposition of the metallic nanostructures. The cell was modified by passing the electronic circuitry of the 303 Polarographic stands and using the three electrode cell system externally for the deposition process with Ag/AgCl, [Cl^-] = 1.0 M reference electrode. The deposited samples were viewed by scanning electron microscope (Inspect F50, FEI Company, Netherlands). The electron microscope was coupled with an EDX electron micro analyzer which allowed investigation of the elemental composition of deposited structures.

Two cells were used in pursuing the present work; an analytical cell for recording cyclic voltammograms to characterize the starting and prepared surfaces, and a deposition cell for deposition of nanoparticles on tantalum substrates. The analytical cell was a conventional, H-shape cell with two compartments, one for the accommodation of the working electrode while the other for housing the reference and the auxiliary electrodes. The analytical cell was equipped with a multiple inlet/outlet system for admission of supporting electrolyte, purging and blanketing the solution with oxygen-free nitrogen. The working electrode was a 1.0 mm diameter tantalum electrode (99.9% pure, Good fellow).

The immersed part of the wire was curved in order to provide a mark for obtaining a reproducible surface area of the electrode. The reference electrode was an Ag/AgCl/ [Cl^-] = 1.0 M, and all the potentials reported in this paper are referenced to this electrode. The auxiliary electrode was made of platinum (Johnson Matthy, 99.99% minimum purity) wire which was coiled into a spiral to provide a large surface area.

All reagents used were highly pure certified analytical reagent (A.R.) chemicals and were used as received from the suppliers without further purification. Hexachloroplatinate solution (1 mg platinum /ml) dissolved in 10% HCl was purchased from Janssen Chemicals, USA. Methanol (99.95%) was purchased from Sigma-Aldrich. Sulfuric acid (97%) was purchased from Fluka, and nitric acid (69%) was supplied from Sharlu, Spain). The purging nitrogen was G5 grade (99.999% minimum purity) supplied by the National Gas Company and coupled with Oxisorb® cartridge (Supelco) to ensure effective removal of any traces of oxygen. All solutions were made from the above-mentioned reagents dissolved in Millipore water (Merck Millipore) of 18.2 MW and total dissolved solids less than 5 ppb. All experiments were carried out at ambient temperatures (25C°).

Procedures

Initially, the electrode tantalum wire was cleaned by immersion in a freshly prepared 5:2:2(v/v/v) 98% H_2SO_4, 65% HNO_3 and 48% HF solutions for half minutes. The chemically etched tantalum substrate was then extensively rinsed with Millipore water. The electrode was conditioned by cycling the potential between the hydrogen evolution and oxygen evolution limits (-0.20 and 1.20 V) until the regular voltammogram of polycrystalline tantalum was produced to ensure removal of any traces of oxide (Fig.1).

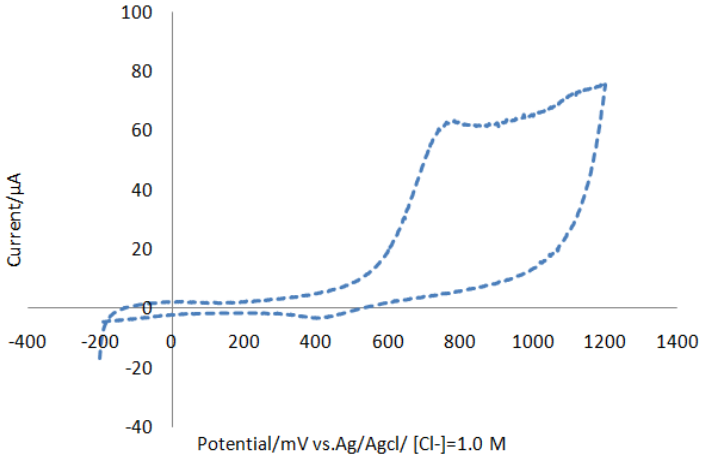

Fig. 1: Cyclic voltammogram of polycrystalline tantalum electrode in 0.5 M H_2SO_4, dE/dt = 100 mV/s.

Electro deposition of platinum nano structured surfaces of tantalum electrodes was carried out in 0.5 M H_2SO_4 + 1.0×10^{-4} M $PtCl^{6-}$ solution. Deposition of platinum nanostructures by application of square wave potential regimes was optimized by variation of the experimental conditions. These included the characteristics of the square wave, the deposition time and the concentration of platinum salt. During deposition the platinum solution was stirred using a magnetic stirrer. The duration of applying the square wave potential regime was varied and the obtained structures were viewed by SEM and cyclic voltammetry to determine the optimal time for deposition in terms of distribution, size, uniformity, and shape of the produced nanostructures. The concentration of the $PtCl^{6-}$ was varied between $1.0x10^{-4}$ M and $1.0x10^{-2}$ M while the deposition time was varied between 90, 120, and 180 s. The characteristics of the square wave involved a variation of the frequency between 25,50 and 100 Hz, the upper and lower limits, and the amplitude of the square wave. Methanol with a concentration of $1.0x10^{-2}$M in 0.5 M H_2SO_4 was used to test the catalytic behavior of the nano structured surfaces.

RESULTS AND DISCUSSION

The Effect of Concentration of the Platinum Solution

The SEM micrographs of platinum nano structures prepared on the tantalum surface (fig.2) were analyzed in terms of the particle size, shape, and distribution homogeneity. The analysis indicated that at $1x10^{-4}$ M $[PtCL6]^{2-}$solution platinum nanostructures have better distribution on the tantalum surface with average diameter 20 nm. Using higher concentrations, $5x10^{-3}$ M and $5x10^{-4}$ M $[PtCL6]^{-2}$solutions, the nanostructures were irregularly scattered and larger in size with an average diameter ranging from 40 to 70 nm respectively.

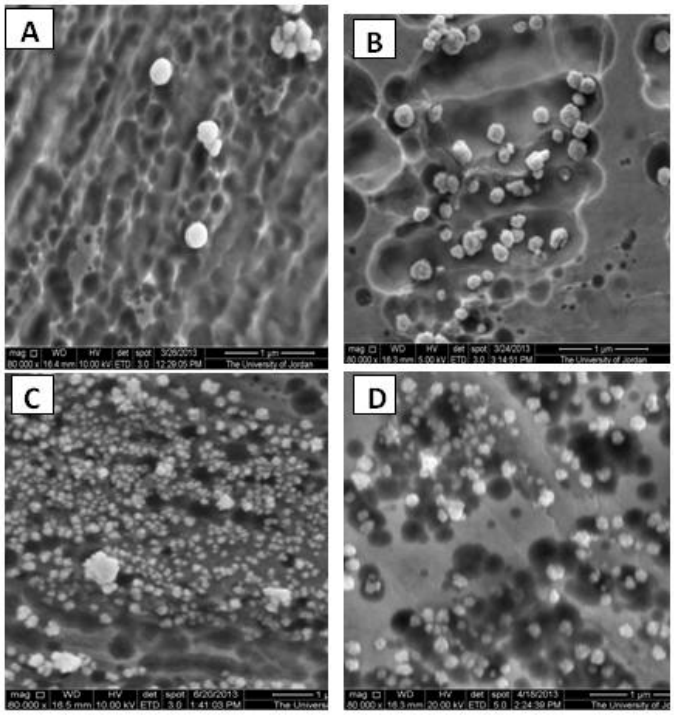

Fig. 2: The SEM micrographs of platinum nanoparticles deposited on the tantalum substrate. Deposition was carried out at different $[PtCL6]^{2-}$Concentrations; A: $1x10^{-3}$M,B: $5x10^{-3}$M,C: $1x10^{-4}$M, D: $1x10^{-5}$by application of the square wave potential regime between the limits, E_l=-0.4and$E$u=0.0V. Deposition time = 2min

The identity of the deposited platinum nanoparticles on tantalum substrate is further confirmed by the EDX spectrum of the deposited particles (Fig. 3). The EDX spectrum shows platinum and tantalum as the major peaks.

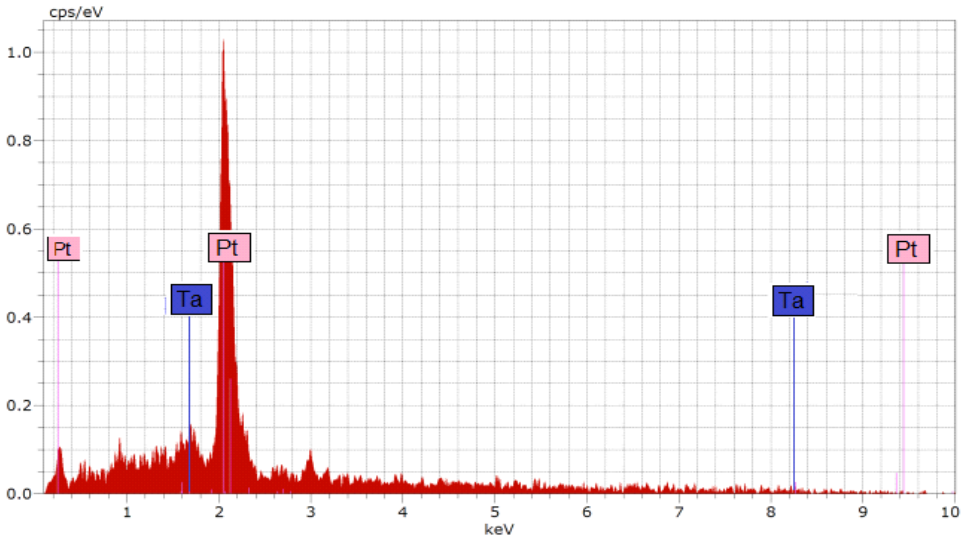

Fig. 3: EDX spectra of deposited platinum nanostructure on tantalum electrode. Experiment parameters: E_L = -0.4, E_H = 0 V, amplitude = 0.4V, frequency =100 Hz, concentration= $1x10^{-4}$M, time = 120 seconds and scan rate = 100mV/s

The voltammogram of the Pt nanoparticles deposited on the tantalum substrate electrode is shown in Fig. 4. The voltammetric features of the well-known polycrystalline platinum electrode, i.e., oxygen adsorption and desorption peaks, are clearly demonstrated on the voltammogram.

The evoltammetric features of tantalum, hydrogen adsorption/desorption and oxygen adsorption/desorption peaksare also obvious on the voltammogram. The voltammogram of the nano structured electrode is a hybrid between the voltammograms of polycrystalline tantalum and those of polycrystalline platinum electrodes. Compared with voltammetric features of the unmodified tantalum

electrode, the modified tantalum electrode exhibits increased hydrogen adsorption and desorption peaks due to the increase in the platinum available surface area available for hydrogen adsorption.

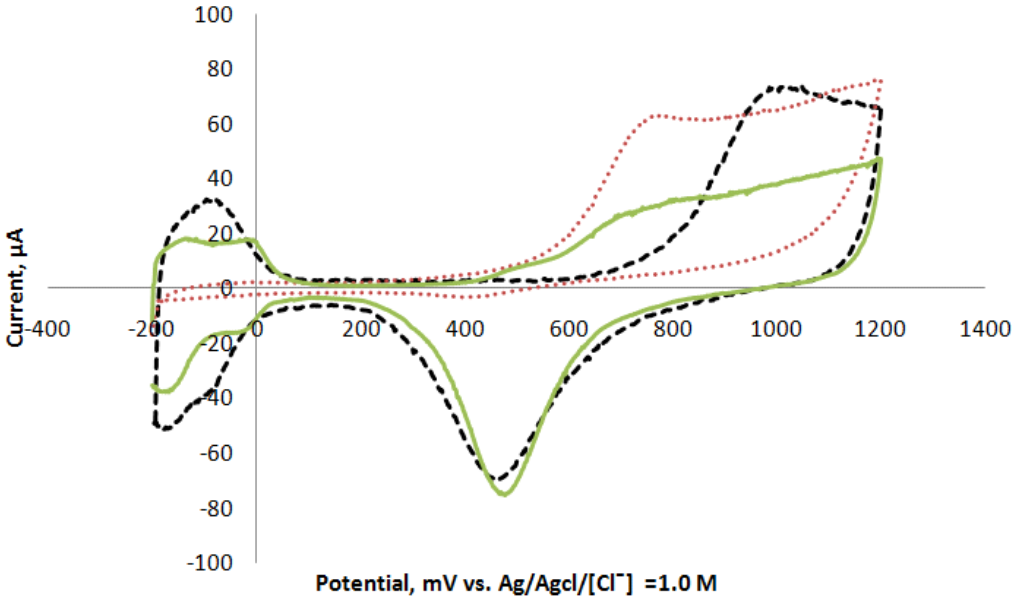

Fig. 4: Cyclic voltammogram of tantalum electrode (……..), polycrystalline platinum electrodes (————) and the voltammogram of the platinum nano structured electrode (--------) recorded in 0.5 M H_2SO_4 at de/dt of 100 mV/s

Surface cover age with platinum nanoparticles was quantified from the degree of suppression of hydrogen adsorption and desorption as referenced to the unmodified tantalum electrode. The coverage with platinum nanoparticles was calculated according to the following equation:

$$\theta = 1- [H_{modified\ electrode} / H_{bare\ electrode}]$$

Where $H_{modified}$ is the charge under neat the hydrogen adsorption or desorption peak for the tantalum electrode modified with platinum nanoparticles and H_{bare} is the charge under neath the hydrogen adsorption or desorption peak for the plain tantalum electrode. The coverage with platinum nanoparticles as a function of the applied square wave frequency is given inTable1.

Table 1: Tantalum surface coverage with platinum nanostructures on tantalum substrate prepared by application of a square wave at different concentration of platinum solution for 2min. Solution: 0.5 M H2SO4 and frequencies 100Hz. Square wave limits; El = -0.40 V and Eh = 0.00 V.

The concentration of the platinum solution	Coverage with platinum
$1x10^{-3}$M	0.52
$5x10^{-3}$M	0.66
$1x10^{-4}$M	0.80
$1x10^{-5}$ M	0.11

The data given in Table 1showthat $1x10^{-4}$M is the optimal concentration of platinum solution for the applied square wave. This in accordance with our conclusions based on the SEM Micrographs.

The Effect of Deposition Time

Application of a square wave regime between -0.4 and 0.0 V with a 100 Hz frequency at different deposition times was found to affect the shape, size, and the uniformity of the deposited particles (Fig. 5). At longer deposition times, 180 seconds, three-dimensional structures tend to form and cover a fraction of the tantalum surface as indicated by the SEM micrographs and i-E traces. At lower deposition times, better distribution of particles with smaller particle size on the surface was formed. The optimal deposition time, which involves the particle size and uniformity of distribution on the surface, was 2 min.

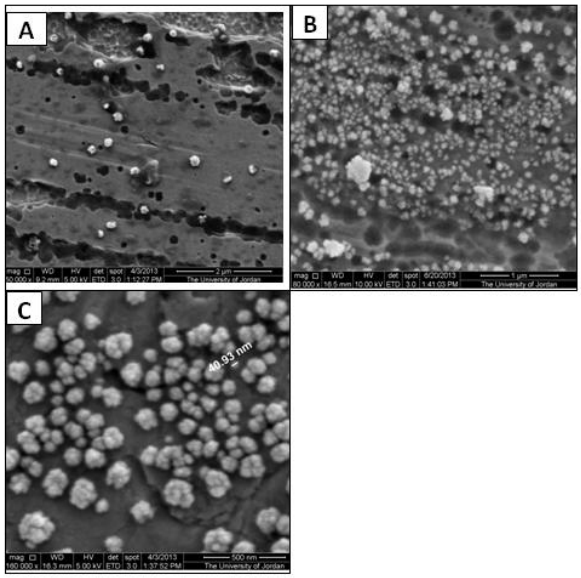

Fig. 5: SEMmicrographs of platinum nano particles deposited on tantalum substrate at different deposition times. Deposition was carried out byapplicationof100 Hzs quare wave potential regimes between the limits, E_l=-0.40V,E_u=0.0Vatdepositiontimesof A=90,B=120andC= 180sec.

The Effect of Frequency

To investigate the effect of optimizing frequency while the other parameters of the deposition process were held constant for the deposition nanoparticle platinum in tantalum surface electrode by square wave potential, a series of experiments were performed at different frequencies (25, 50 and 100Hz), the samples were analyzed by SEM as shown in Fig. 6.

Fig. 6 shows the SEM micrograph of nanostructured platinum electrode deposited from a frequency of 25 and 50 Hz. The SEM denies the existence of a lot of platinum nanoparticles on the tantalum surface, these macrostructure electrodes indicate that fewer numbers of platinum nanoparticles deposited on the tantalum surface.

Accordingly, the particles to a great extent are uniformly distributed on the surface. It is noticed that the maximum surface area was obtained when the frequency applied is 100 Hz. This indicates that the optimal frequency of the square wave for platinum nanoparticle deposition is 100 Hz.

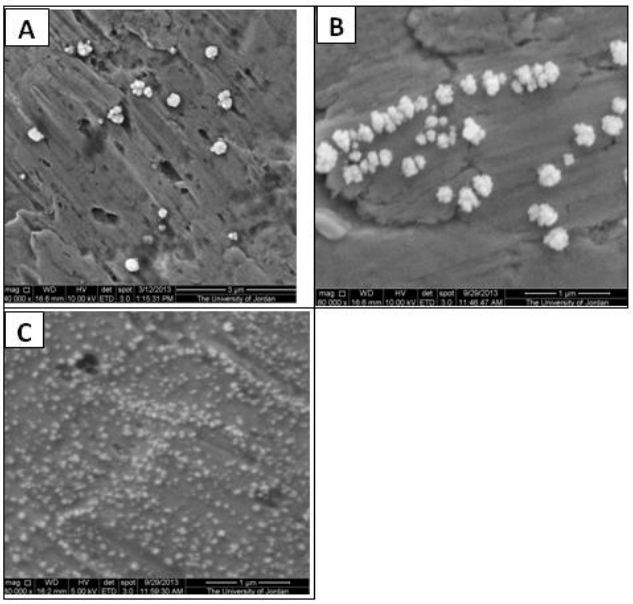

Fig.6: SEMmicrographs of platinum nanoparticles deposited on tantalum substrate at different frequencies. Deposition was carried out by application of the square wave potential regime between the limits, E_l=-0.40V,E_u=0.0V, concentration= $1x10^{-4}$M, time =120 Sec, at frequency A= 25,B= 50andC= 100 Hz.

Characterization of Nanoparticles by Silver Deposition

Fig. 7 shows two voltammograms, one recording of the platinum nanostructured electrode while the second was recorded on the polycrystalline platinum electrode. The voltammograms show different planes of surface nanostructure platinum have two peaks at 0.36 and 0.4 V but polycrystalline platinum has one peak at 0.38V the reason for this is the sensitive surface deposition of silver to platinum nanostructured electrode more than the platinum polycrystalline electrode.

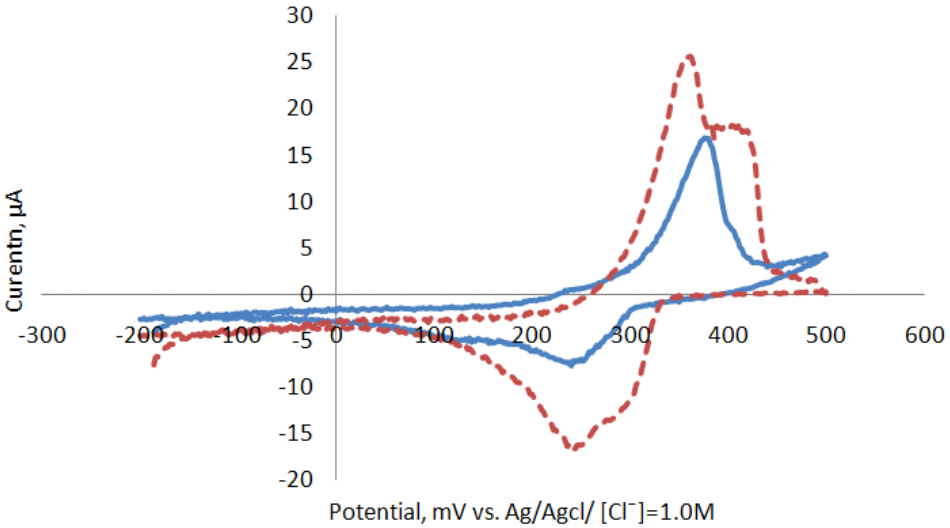

Fig. 7: Cyclic voltammogram (----) nanostructured platinum (——) polycrystalline platinum at a scan rate of 100 mV/s.

Stability of Platinum Nanostructure on Tantalum Electrode

Fig.8 shows seven voltammograms of the same platinum nanostructured electrode recorded in seven days successively. The voltammogram displays great similarity of the nanostructured platinum electrode in seven days. This proves the identity of the deposited nanoparticles very stable on a surface electrode. The voltammogram shows an enhanced characteristic of platinum features. Repetitive cyclization of the electrode potentially adsorbed impurities from the surface and this reduces the charge with the voltammetric features, the similarity in voltammograms refers to reliability and durability of their nanoparticles in surface electrode.

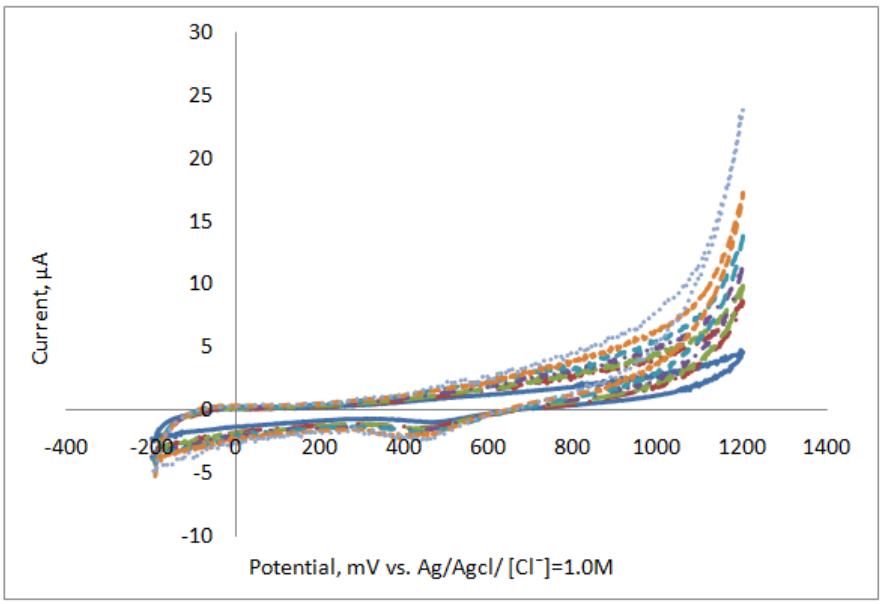

Fig. 8: Cyclic voltammogram nanostructures platinum on tantalum electrodes (——) Run after one day (----) Run after two days (-. -.) Run after three days (-.-.-.) Run after four days, experimental parameters: EL = -0.4, EH = 0 V, amplitude = 0.4V, frequency =100 Hz, concentration= $1x10^{-4}$M, time =120 seconds and scan rate of 100 mV/s

Electro Catalytic Activity of Nano Structured Platinum/Tantalum Electrode

The electro oxidation of Methanol has been studied extensively due to its importance in revealing the mechanism of electro catalysis of small organic molecules that could be considered as models for electro catalysis, as well as its potential application as a fuel in direct methanol fuel cells [26-28]. Fig.9 shows the voltammogram of platinum nanoparticles deposited on a tantalum substrate recorded in a $1.0x10^{-2}$M CH_3OH + 0.5M H_2SO_4 solution.

In the same Figure, the voltammograms recorded under the same experimental conditions, for both platinum polycrystalline and nanoparticles electrodes are displayed. The voltammetric features for oxidation of methanol at the platinum nano structured/tantalum electrode are similar to the voltammetric features of oxidation of methanol at a platinum electrode. Comparing with the polycrystalline platinum electrode, there is a large increase in the charge due to the electro oxidation of methanol at the nano structured tantalum electrode.

The platinum nanostructured tantalum electrode is more active in electro oxidation of methanol than polycrystalline platinum electrodes. The improved anodic performance of the nano structured tantalum electrode mainly attributed to the high surface to volume ratio of platinum nanoparticles compared to the platinum electrode.

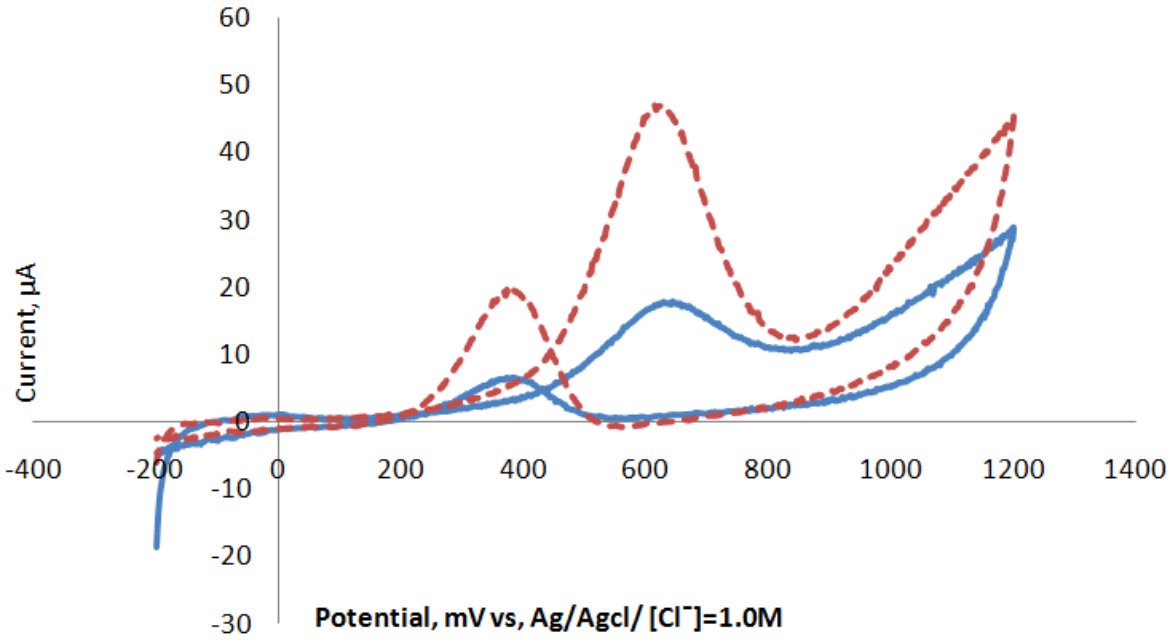

Fig. 9: Cyclic voltammogram of Methanol oxidation on the polycrystalline Platinum electrode (the solid line). (Dashed line is the voltammogram recorded atPt/Taelectrode). Experimental parameters: solution: $1x10^{-2}$M Methanol in 0.5MH_2SO_4,dE/dt= 100 mV/s.

Micro Structured Platinum on Tantalum Electrode

Fig. 10 shows the SEM three-dimensional microstructures Pt on Ta surface by applying a square wave between -0.4 to 0.00 V at longer deposition times of 10 minutes and different frequencies, the SEM micrographs were analyzed in terms of the particle size and shape of the particles. Fig. 10 shows the SEM microstructures of metallic platinum were observed upon application of the square wave potential regime under different frequency, microcrystals were formed on the surface were not of regular shape and were undistributed.

The shape of microcrystals platinum in surface electrode by applying a square wave at different frequencies: (10Hz, like Flower), (50Hz, like Spongy), (75Hz, like Thorn-flower), (100Hz, like Dendritic), (150Hz, like Co-flower) and (200Hz, like Needles). The many microstructures of platinumhave the ability to thevery high specific area along with the latest sites and many sharp edges that could promise in applications in electrochemical systems.

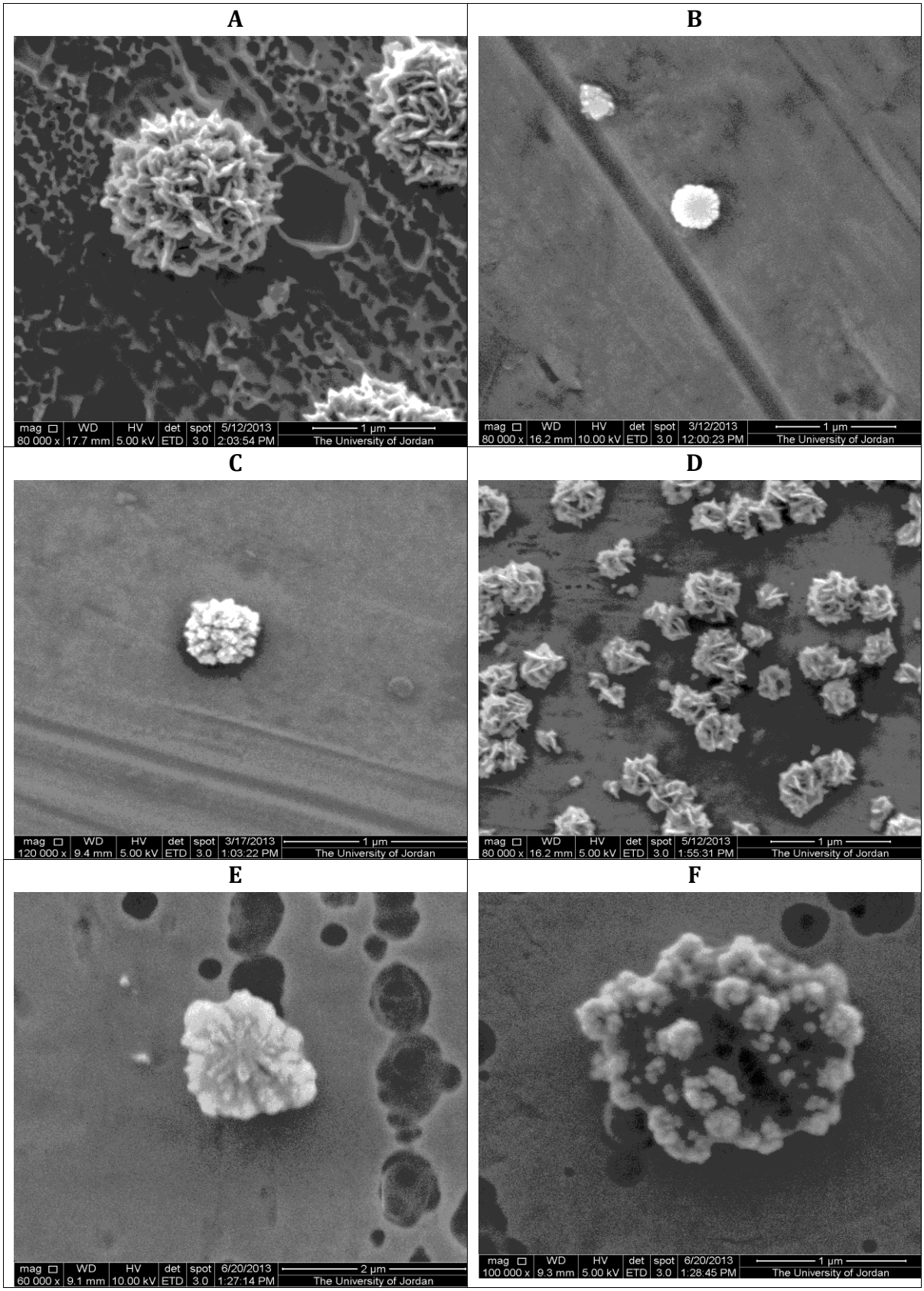

Fig. 10: SEM micrographs of platinum microparticles deposited on tantalum substrate at different frequencies. Deposition was carried out by application of the square wave potential regime between the limits, El = -0.40 V, Eu = 0.0 V, concentration= $1x10^{-4}$M, time =10 min, at frequency A: 10, B: 50, C: 75, D: 100, E: 150 and F: 200 Hz.

CONCLUSIONS

Platinum nanostructures have been developed on the surface of the tantalum electrode by application of the square wave potential regime at a tantalum electrode in a solution containing $[PtCl_6]^{2-}$.The size, shape, distribution, and homogeneity of the platinum nanostructures depend on the amplitude and higher and lower limits of the square wave in addition to the deposition time, the concentration of the ions of metal in the solution and applied frequency. Using a frequency of 100 Hz, the optimal deposition time was found to be 2 min. These parameters have been chosen based on the criteria of homogeneity, distribution, and uniformity of the deposited nanostructures. The electro activity of the nanostructures platinum on tantalum electrode was tested towards the oxidation of methanol. The results indicated that the modified electrode has improved activity compared to that of polycrystalline platinum electrodes.

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