

A Simple and Rapid Method for Preparing Carbon Nanopore Electrode Ensemble by Coating A Glassy Carbon Electrode with Chromate

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ABSTRACT

A simple preparation method for carbon nanopore electrode ensemble (CNEE) was reported. The CNEE consists of a number of pinholes which remain after coating a carbon surface with chromate. The transformation from transient to steady-state voltammetric behavior of carbon surface was presented. The effect of electrochemical technique to structure of chromate film was investigated. The optimum deposition time and optimum concentration of chromate solution for coating carbon surface substantially were determined for bulk electrolysis (BE) technique. On the other hand for cyclic voltammetry (CV), the effects of scan rate, number of cycle and coating solution concentration on forming uniform partly-insulating layer have been examined. The CNEE prepared by BE technique showed larger hysteresis which means more resistivity than the one prepared by CV. Under the optimum coating conditions the thinner and more useful CNEE with lower resistivity can be prepared by CV.

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Carbon nanopore electrode ensemble (CNEE), chromate, steady-state current, radial diffusion, microelectrode.

INTRODUCTION

Since the early 1980s, a number of voltammetric studies have been carried out with microelectrodes that have dimensions that are smaller than an order of magnitude. The electrochemical behavior of these tiny electrodes is significantly different from classical electrodes, whose diameters are generally in between 1.5 mm and 3 mm, and appears to offer advantages in certain analytical applications [1-4]. Such electrodes have been called microscopic electrodes, or ultramicroelectrodes, to distinguish them from classical voltammetric electrodes. Nanoelectrodes may be defined as electrodes with a critical dimension in the nanometer range, here critical dimension is the dimension that controls the electrochemical response. On the other hand, a microelectrode or ultramicroelectrode may be viewed as any electrode in which the electrode is smaller in magnitude than the diffusion layer which can be achieved in an experiment, yielding an electrode with a critical dimension of the order of 25 μm . When the electrode's critical dimension is decreased to the

order of the thickness of the electrical double layer or the molecular size, the experimental behavior starts to deviate from that of the larger electrodes [5].

The primary reason for the use of ultramicroelectrodes and smaller electrodes is the benefit obtained from the enhanced mass transport [6-11]. As electrodes decrease in size, 3-dimensional (radial) diffusion becomes dominant and results in faster mass transport. This high rate of diffusion at small electrodes enables measurement of kinetics by steady-state experiments rather than by transient techniques. Analytical measurement systems can potentially exploit the increased mass transport characteristics of microelectrodes in achieving shorter response times to freely-diffusing species in solution. Another analytical benefit should be the increased faradaic to charging current ratio obtained, due to the enhanced mass transport for diffusion-controlled faradaic currents.

Microelectrodes take several forms. The most

common one is a planar electrode formed by sealing a carbon fiber with a radius of 5 μm or a gold or platinum wire having dimensions from 0.3 to 20.0 μm into a fine capillary tube; the fiber or wires are then cut flush with the ends of the tubes. Cylindrical electrodes are also used, in which a small portion of the wire extends from the end of the tube. There are several other forms of these electrodes.

Besides above mentioned benefits of nanoelectrodes, there are some difficulties in their fabrication, and handling as well as the sensitivity of the instrumentation available with which to make reliable electrochemical measurements. Fortunately, several commercial sources of microelectrodes now exist with higher prices than that of bigger ones. In order to solve the sensitivity of instrumentation problems, the microelectrode arrays or ensembles have been fabricated. The individual electrodes in the array operate in parallel thus amplifying the signal while retaining the beneficial characteristics of the microelectrodes. However, it is generally required a complicated and expensive equipment to prepare these arrays or ensembles [12].

Clark and McCreery examined the oxygen reduction reaction on copper, platinum, and glassy carbon electrodes, with regard to its inhibition by exposure of the electrode to chromate ion, Cr (VI), in NaCl solution [13]. They reported that all three electrode materials exhibit a mass transport limited current for the oxygen reduction reaction at sufficiently negative potentials, but this current was strongly inhibited in the presence of Cr (VI).

In this study a simple and fast method has been proposed for fabricating an electrode which exhibit microelectrode behavior while being a classical GC voltammetric electrode. Despite the microelectrodes are commercially available, this method may represent an economically viable alternative to the do-it-yourself approach. In addition, since most of the commercial carbon fiber microelectrodes contain Epoxy resins [14, 15] it is difficult to modify these electrodes. The electrode prepared with this method has a potential usage in modification studies.

For coating the normal size commercial glassy carbon electrode, $\text{K}_2\text{Cr}_2\text{O}_7$ solution in NaCl was used. Both cyclic voltammetry (CV) and constant potential coulometry (bulk electrolysis, BE) were used to reduce Cr (VI) and form Cr (III) film on the glassy carbon surface. The conductivity of this coated surface has been studied with ferrocene electrooxidation, which is known as outer sphere redox system that does not require adsorption to the electrode surface.

It is not the purpose of the present study to provide a detailed mechanism for Cr (VI) reduction, yet we agree on

the mechanism proposed by Hurley et al. [16]. Mainly, we aimed to use the pin holes retained on the surface while forming the Cr (III) monolayer as individual microelectrodes. The effects of voltammetric technique used for coating, scan rate and number of cycle for CV, coating time and $\text{K}_2\text{Cr}_2\text{O}_7$ concentration for BE were investigated.

2. MATERIALS AND METHOD

2.1. Reagents

Acetonitrile (ACN), ferrocene (FC), silver nitrate (AgNO_3) and tetrabutylammonium tetrafluoroborate (TBATFB) were purchased from Sigma-Aldrich Chemical. All other chemical compounds used in this study ($\text{K}_2\text{Cr}_2\text{O}_7$, NaCl etc.) were reagent grade commercial products. Milipore Water Purification System was used to obtain deionized water with resistivity of 18.3 $\text{M}\Omega\cdot\text{cm}$. Unless otherwise noted, 0.1 M NaCl served as the supporting electrolyte for aqueous solutions and 0.1 M TBATFB for acetonitrile. The stock coating solution was 0.005 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.1 M NaCl and the other coating solutions were prepared from this stock solution by diluting. The testing solution for the coated electrodes was prepared as 0.001 M FC in 0.1 M TBATFB.

2.2. Carbon nanopore electrode ensemble (CNEE)

The production of carbon nanopore electrode ensemble (CNEE) by coating GC electrode with Cr (VI) was executed in two electrochemical techniques which were BE and CV, respectively. Firstly, the electrolysis potential was determined from CV experiment of 0.005 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 0.1 M NaCl depending on the reduction peak potential of chromate. Thus the suitable electrolysis potential was chosen as -1 V vs Ag/AgCl which is 0.2 V beyond the end of reduction peak. The produced CNEE from both techniques was controlled by CV and LSV of 0.001 M FC solution in 0.1 M TBATFB in ACN. The GC electrode was coating for 10 min in 0.005 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 0.1 M NaCl by applying the electrolysis potential to cover most of its conductive area. Following the coating step, the electrode was rinsed with water and ACN, respectively, and then placed in 0.001 M FC solution in ACN.

2.3. Instrumentation and electrochemical techniques

The electrochemical studies were carried out with CH Instruments (CHI) Model 660C Electrochemical Analyzer equipped with an ENTEK C4 Cell Stand and CHI 200 Picoamp Booster and Faraday Cage. The experimental solutions were purged with argon (99.99% purity) for at least 15 min just before the voltammetric experiments and throughout the hydrodynamic experiments like

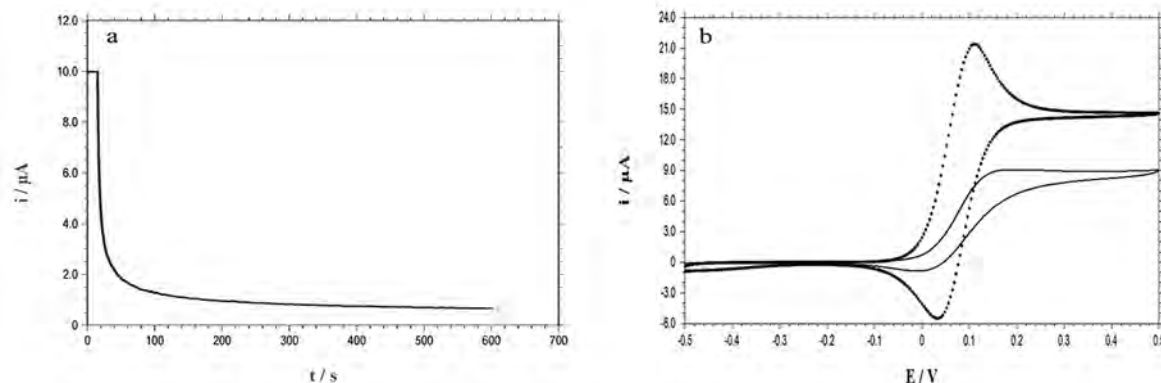


Figure 1. (a) Amperometric result for 0.05 M $K_2Cr_2O_7$ in 0.1 M NaCl in water at GC electrode, deposition potential is -1 V, deposition time is 10 min. (b) Cyclic voltammograms of 1 mM FC in 0.1 M TBATFB in ACN at Bare-GC (---) and Cr-GC (—) electrodes, scan rate is 0.01 V/s

Bulk Electrolysis. The working electrode was Glassy Carbon electrode (CHI 104 Model, 3 mm diameter, GC) and the counter electrode was a Pt wire. The reference electrode employed in non-aqueous experiments was $Ag|Ag^+$ containing 0.01 M $AgNO_3$ and 0.1 M TBATFB in ACN medium. Experiments in water utilized $Ag/AgCl$ as the reference electrode and all potentials quoted with respect to this reference. The electrochemical coatings were made with the use of cyclic voltammetry (CV), and bulk electrolysis (BE) techniques. The coated surface was inspected by CV and linear scan voltammetry (LSV) for determining the electrochemical behavior.

Commercial GC electrode (CHI 104, 0.071 cm^2 area) were polished successively in 1-, 0.3-, and $0.05\ \mu\text{m}$ alumina slurries made from dry Buehler alumina and deionized water on Buehler polishing microcloth. Polished GC electrodes were sonicated in water and then in a mixture of 50:50 (v/v) 2-propanol/acetonitrile in both cases for 10 min. After sonication, the electrode was rinsed with ACN and then with the water, dried with an argon gas stream.

The Cr(III) oxyhydroxide coated surface of GC obtained from both optimization studies for electrolysis time and electrolysis solution concentration was characterized by using 0.001 M FC solution in 0.1 M TBATFB in ACN. The effect of electrolysis time on the number and dimensions of

members of the ensemble was investigated for four different potential application period, $t=2, 5, 10$ and 20 min.

3. RESULTS AND DISCUSSION

A typical $i-t$ curve acquired from BE experiment is given in Figure 1a for $0.005\text{ M } K_2Cr_2O_7$ solution in 0.1 M NaCl in aqueous medium. Figure 1b shows the voltammetric responses (0.01 V/s) of bare GC (dashed) and chromate coated GC (strait line) in the 0.001 M FC solution. The voltammetric response of GC electrode has changed after coating step. In agreement with the theory and previous results of voltammetry at classical disc shaped electrodes, the voltammetric response for bare GC displays peak-shaped voltammogram. On the other hand, the voltammogram for chromate coated GC has a sigmoidal shape, characteristic of the radial diffusion. The magnitude of the steady-state current ($\sim 9\ \mu\text{A}$) was much more than that of the current for a single micro/nano scale electrode (in nano ampere scale) at the same time retained steady-state behavior as expected from the nano electrode ensemble (NEE) at intermediate sweep rate [17-20]. These results were demonstrated that GC surface was coated partly with chromate blocking the electron transfer.

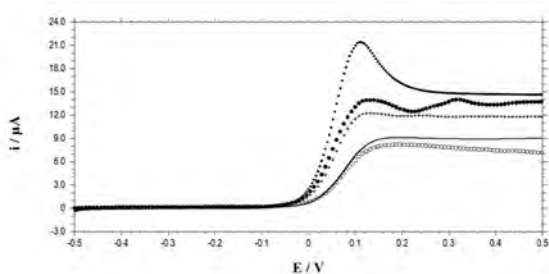


Figure 2. The effect of deposition time on the coating of GC surface with chromate, (♦) Bare-GC, (●) 2 min, (*) 5 min, (-) 10 min and (◊) 20 min deposition times, scan rate is 0.01 V/s for all voltammograms.

The linear sweep voltammetric responses of the electrodes coated for different periods were shown in Figure 2. According to Figure 2 the oxidation peak or steady-state current for FC decreased with increasing electrolysis time while the peak or half wave potential was almost stable. The steady-state behavior started after 5 min deposition and further the active electrode area became smaller. Even though the 10 min coating had an ideal steady-state behavior the 20 min coating could also be used in order to get smaller CNEE. In the studies of concentration effect on coating, 0.0001, 0.0005, 0.001 and 0.005 M $K_2Cr_2O_7$ solutions prepared in 0.1 NaCl were used. It was found that the oxidation peak or steady-state current of FC decreased with increasing the concentration of coating solution. It

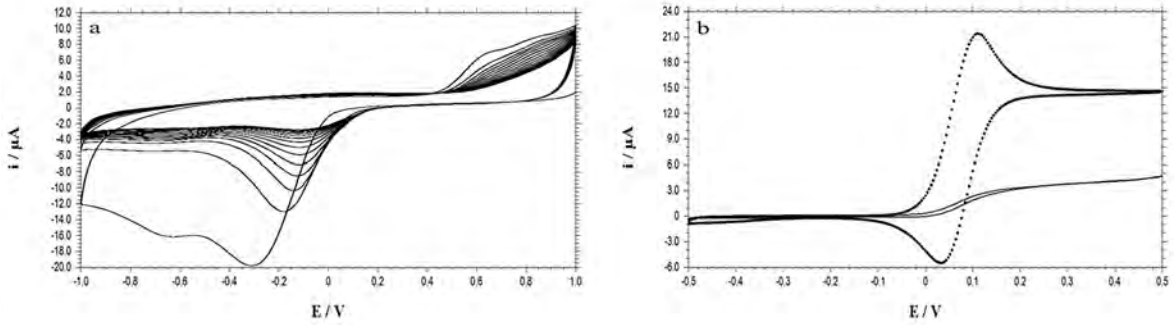


Figure 3. (a) The successive cyclic voltammogram for 0.05 M $K_2Cr_2O_7$ in 0.1 M NaCl in water at GC electrode, scan rate is 0.1 V/s, number of cycle is 15. (b) Cyclic voltammograms of 0.001 M FC in 0.1 M TBATFB in ACN at Bare-GC (---) and Cr-GC (—) electrodes, scan rate is 0.01 V/s

means that the higher concentration for coating solution the wider coated area on the GC surface. Otherwise the longer deposition process like 20 min in more concentrate solution caused the chromate film to be thicker and the voltammetric response started to turn into a peak shape voltammogram. These results proved that all pin holes among the coating behaves as a nanopore electrode, individually [21].

Alternatively, another voltammetric technique, CV, was investigated for coating method. The successive cyclic voltammogram of 0.005 M $K_2Cr_2O_7$ in 0.1 M NaCl for 15 cycles at 0.1 V/s scan rate is given in Figure 3a. The chromate reduction peak is seen in the first cycle at 0.31 V and shifts to the more positive potentials together with decreasing peak current at the further scans. The shifted in peak potential and the decrease in peak current result from both changing the electrode surface feature and degrowth of the active surface area, respectively. The voltammetric response after coating the GC electrode using CV technique supported these results. The shape of cyclic voltammogram turned from a peak to a sigmoidal form and the resulting steady-state current is also smaller than the peak current obtained at the bare GC surface (Figure 3b). The effect of scan rate on CV coating of GC surface was illustrated in Figure 4. The electrode coated with chromate by CV at 0.01, 0.1, 1 and 10 V/s scan rates, respectively. The number of cycle and the potential scan interval were adjusted to five and “-1 V – 1 V”, respectively, for all the experiments in order to be sure that

all the parameters were same except scan rate.

Figure 4a shows the transformation of the voltammetric response from a peak-shaped form to the sigmoid forms. The coating at high scan rate (10 V/s) with CV was not sufficient to get small enough pin holes needed for a steady-state response. Smaller pin holes (e.g. individual nano electrode) could be obtained by slowdown the scan rate in CV coating. When the scan rate is 1 V/s for coating experiment it is possible to have the sigmoidal steady-state voltammogram for oxidation of FC. The steady-state current decreased with decreasing scan rate on the coating stage. Furthermore, the coating at 0.01 V/s has almost totally inhibited the electron transfer from and to the GC electrode. Detailed inspection of the coatings done at 1 V/s and 0.1 V/s scan rates shows that the more useful CNEE can be prepared by 0.1 V/s scan rate (Figure 4b). The voltammograms for two of them have a sigmoidal shapes but the one belonging to 1 V/s scan rate coating displays more hysteresis than the other. The faster scan causes to form thicker chromate film, more and bigger pin holes because of enhanced electrolysis speed. On the other hand, more homogenous CNEE with thinner chromate film could be generated with the scan rate of 0.1 V/s as seen from the cyclic voltammetric response with very small hysteresis.

The thickness of chromate film is also affected by the number of cycles applied in the coating method. In this part

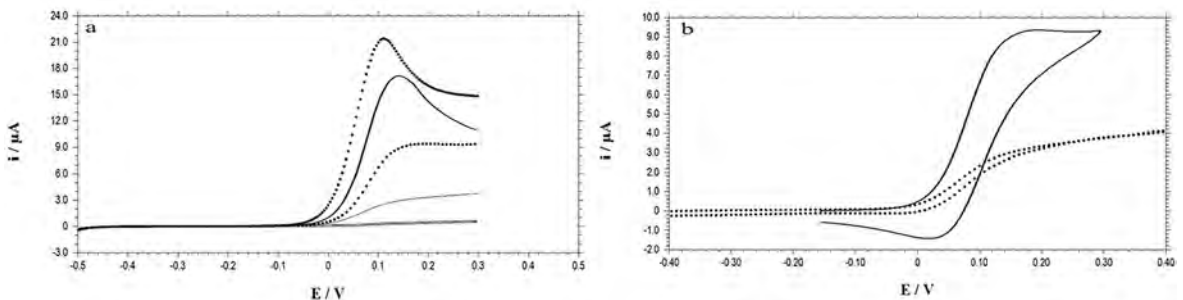


Figure 4. (a) The effect of scan rate on the CV coating of GC surface. The linear scan voltammograms of 0.001 M FC in 0.1 M TBATFB at (◆) Bare-GC, after coating at (-) 10 V/s, (●) 1 V/s, (○) 0.1 V/s and (◐) 0.01 V/s scan rates. (b) The cyclic voltammograms of 0.001 M FC in 0.1 M TBATFB at chromate coated-GC at scan rates of (-) 1 V/s and (●) 0.01 V/s. Scan rate for all voltammetric responses is 0.01 V/s.

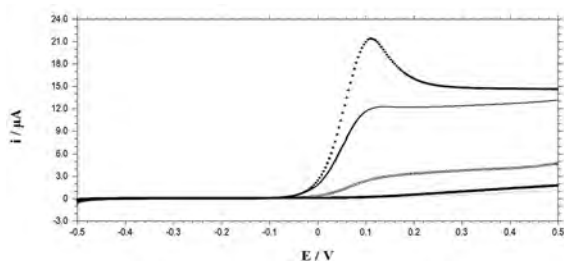


Figure 5. The effect of number of cycle on the CV coating of GC surface with chromate. The linear scan voltammograms of 0.001 M FC in 0.1 M TBATFB at (♦) Bare-GC, after coating with (---) 1 cycle, (⋯) 5 cycles, (—) 10 cycles and (-·-) 15 cycles, scan rate is 0.01 V/s for all voltammograms.

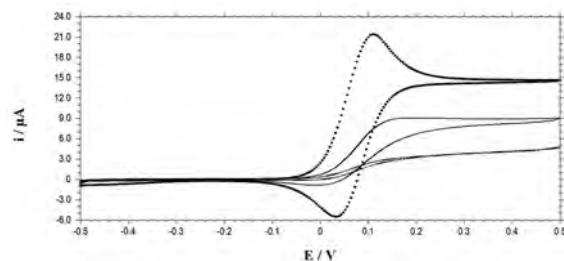


Figure 6. The comparison of electrochemical coating techniques. The cyclic voltammograms of 0.001 M FC in 0.1 M TBATFB at (♦) Bare-GC, (-) the chromate coated-GC prepared by BE coating for 10 min deposition and (⋯) the chromate coated-GC prepared by CV coating at 0.1 V/s scan rate for 15 cycles, scan rate is 0.01 V/s for all voltammograms.

of study four different electrodes were prepared with 1, 5, 10 and 15 cycles at 0.1 V/s scan rate and compared with each other and bare GC as well. When the optimum scan rate (0.1 V/s) was used the steady-state response was reached even with only one cycle coating (Figure 5). The active electrode area and thus the steady-state current decrease as the number of cycle increase. Moreover, if the number of cycle is equal to or more than 15 one can obtain almost totally insulating surface which is called as “dead electrode”. From the results acquired so far, the optimum experimental conditions for preparing the better designed, readily made CNEE by CV technique have determined as the scan rate of 0.1 V/s, the cycle number of 10 and the coating solution

concentration of 0.005 M.

The comparison of the two methods used for coating GC surface is shown in Figure 6. The electrolysis time for BE method is 10 min and the total experiment time for deposition step by CV is 3.33 min (for 5 cycle potential scan between 1 V and -1 V at 0.1 V/s scan rate). As seen from the experiment times the CV method is 3 times faster than BE method. In addition the limiting current of FC on CNEE prepared by BE is about 3 times higher than the other. It means that despite the shorter experiment time for CV method the coating ratio of bare GC is higher compared with BE method. On the other hand, when we inspect the voltammograms generated by two different NEEs closely, both of them have a sigmoidal shape but the one belonging to BE method displays much more hysteresis. The CV technique causes not only smaller nanopores on the chromate coated surface but also thinner coating with lower resistivity.

The prepared surface by using optimum conditions has been inspected under an optical microscope (Figure 7). It is seen from the figure that the polished GC electrode surface is very smooth (Figure 7a and 7b). After electrodeposition of chromium on the GC, a new inhomogeneous surface forms (Figure 7c and 7d). It is also seen that there are too many round pin holes and different shape holes and cracks behaving conductive area.

In addition to optical zoom the optical micrograph of chromium coated surface (Figure 8a) has been also magnified by the software program 5 times digitally (Figure 8b). Thus the micron and submicron pin holes could be seen closely. From the 3D form (Figure 8c) of the new micrograph the roughness of the surface is also realized.

A summary of CNEE formation is presented Figure 9a. At the chromate deposition step in either BE or CV,

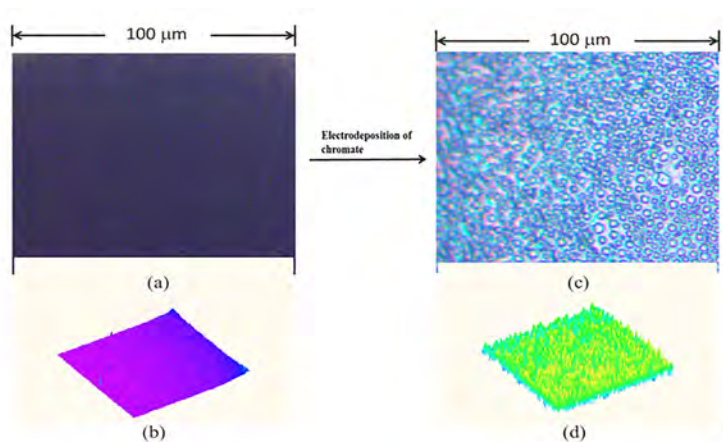


Figure 7. (a) Optical micrograph of polished GC surface, (b) 3D image of polished GC surface, (c) optical micrograph of chromium coated GC surface, (d) 3D image of the coated GC surface.

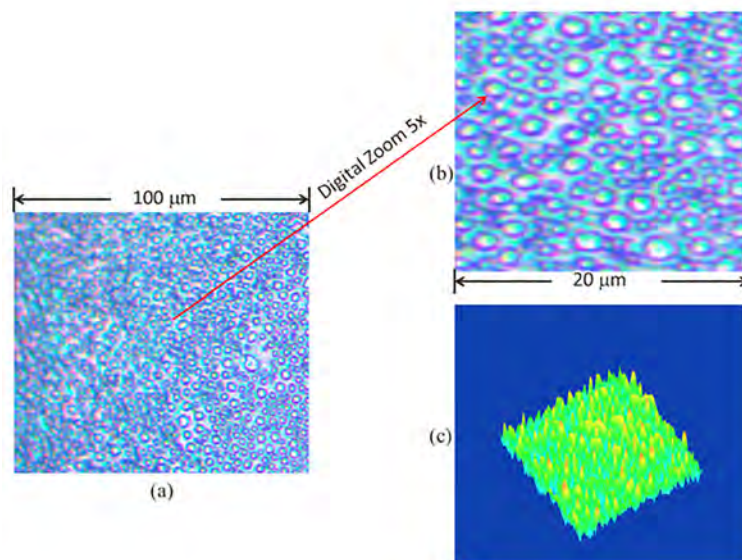


Figure 8. (a) Optical micrograph of chromium coated GC surface, (b) 5X digitally magnified image of the micrograph, (c) 3D image of the magnified micrograph.

the GC surface partially coated with chromate which blocks the electron transfer from or to CG surface. After deposition, some parts of the GC surface remain uncoated and let electrons pass. The voltammetric behaviors of the two surfaces are different (Figure 9b). As seen from Figure 9b, the partially coated GC surface shows steady-state voltammetric behavior corresponding to the radial diffusion regime while the voltammetric response is dominating by planar diffusion regime at bare GC surface. This steady-state response of chromate coated GC surface is similar to that of a single nanopore electrode [22].

4. CONCLUSION

The preparation and electrochemical characterization of carbon nanopore electrode ensemble was described. It was concluded that the chromate solution could be used as partly insulating agent for carbon surface and thus to prepare a carbon nanopore electrode ensemble. The electrochemical coating technique was also affective on the thickness of coating and number of holes act as nanopore electrode. Two different electrochemical techniques were examined as coating method and

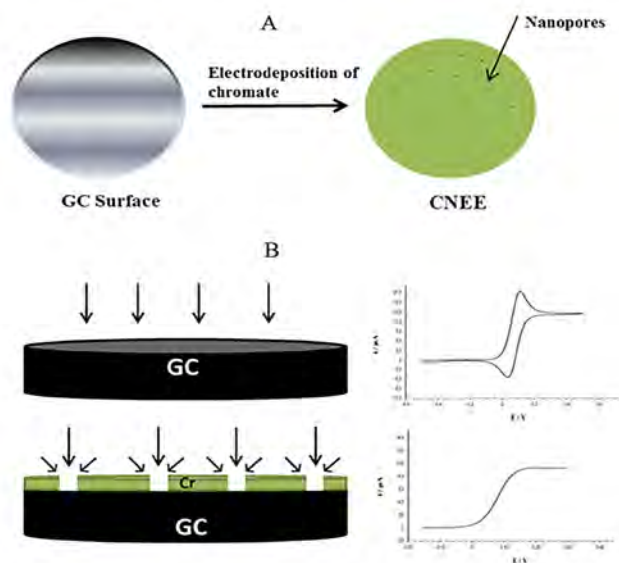


Figure 9. Scheme of a CNEE prepared by electrochemical chromate deposition of GC electrode. (A) preparation of the CNEE, (B) two different diffusion regimes and corresponding voltammetric responses at bare-GC and chromate coated GC. Note: Some dimensions are only indicative and not in scale.

compared for determining optimum preparation conditions. The CV technique was found useful to form a thinner and more homogenous partly insulating film on GC surface in shorter experiment time. On the other hand the BE method could also be used at coating step for different purposes.

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