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# Laser Reactivation of Gold and Glassy Carbon Electrodes

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In the present work, we have studied an in-situ electrochemical and laser reactivation for pretreatment of gold and glassy carbon electrodes surface used as a working electrode in electrochemical determination of cefazolin antibiotic. The activation processes were studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The activated electrodes were used for electro oxidation of cefazolin antibiotic. Also, the $N_2$ laser and dye laser were applied for activation of polluted glassy carbon (GC) and gold electrodes. The results show that cathodic electrochemical activation had more efficient that anodic activation, variables of pulse duration, power density, energy and wavelength have been investigated.

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**Keywords:** Laser Reactivation, Electrochemical Reactivation, Glassy Carbon Electrode, Gold Electrode

## 1. INTRODUCTION

Electrochemical determination methods have been considered as one of the fastest and cheapest techniques in analytical quantitative determination of different analytical species [1]. Also the maintenance of a clean, reproducible electrode surface is of critical importance in making meaningful electro analytical measurements [2], but in most cases the electrode behavior degrades with time due to adsorption of impurities from the solution or chemical changes to the electrode surface [3]. Classically, potential passivation problems were alleviated through the use of a dropping mercury electrode [DME] but this device is less suitable than those based on solid electrodes for many [such as on-time] analytical purposes, and entirely inapplicable if significant oxidizing potentials are required. In addition, mercury is environmentally compromising. Accordingly, the development of methods to facilitate the wider and more general use of solid electrodes would be timely [2]. Although one of the specific problems which occur during the electrochemical measurements by solid electrode is the contamination or passivation of the electrodes during and after the measurements, therefore solid electrode becomes unsuitable for quantitative measurements [3, 4].

Nowadays, electrode surface cleaning has been achieved most simply through different ways including ex-situ mechanical polishing[5-7], plasma treatment [8], heat treatment[9,10], flaming[11,12], various chemical reactions[11,13] ,electrochemical treatment [14,15],and laser activation [2,3,16-17]. Recently, the use of lasers to keep electrode surface clean and activation has attracted considerable interest. Hinoue and co-workers [18] used an infrared laser source of relatively high power to maintain fresh platinum and gold electrode surface via the phenomenon of laser ablation, this followed the work by McCreery and co-workers [19-23] who used high intensity in-situ infrared laser pulses to activate the surface and to increase the rate of the heterogeneous electron-transfer kinetics at glassy carbon and platinum electrodes. Oltra et.al [24] additionally used laser pulses to depassivate an iron electrode under hydrodynamic conditions in a channel flow cell. Hinoue, et al. [25] used an argon-ion laser to examine the effect of heating on the electrochemistry of the Fe (II/III) redox couple in flow system. Hinoue and co-workers [26] used pulses from Q-switch Nd: YAG laser (1064nm, 360mW/cm$^2$) to study the oxidation of L-ascorbic acid.

Laser activation is based on the laser irradiation on the electrode surface, when two different interactions may be occurring during the process: one type of interaction is cleaning of electrode surface, and another is the ablation process. When the pulse lasers were used in addition to cleaning of electrode surface, an enhancement of the roughness of the electrode surface is observed because of the ablation phenomenon and as a result, this process might active the electrode more strongly to response to the electro active species [1, 4, and 27]. The variables which control the surface alterations of the laser irradiated electrode can be classified into three groups:

(a) The electrode materials.
(b) The laser type.
(c) The medium in which irradiation occurs.

Electrode material variables include the refraction index, the heat capacity, density, thermal conductivity and the melting point.

Laser variables are wavelength, FWHM duration, power density, angle of incident and spatial beam uniformity. Indeed, laser activation allows electrochemical processes associated with depassivate processes to be monitored with in-situ electrode cleaning. By variations in the intensity and pulse width of laser beam, surface layer may be removed from the electrode surface and even ablation of the electrode material can be observed.

In this work, the reactivation of glassy carbon electrode and gold electrode was investigated in the electrochemical determination of cefazolin antibiotic. The activation processes were studied using cyclic voltammetry, differential pulse voltammetry and laser irradiation.

## 2. EXPERIMENTAL PART

### *2.1. Sample Preparation*

Cefazoline was used as an electro active compound. Also, sodium carbonate was used in this work as supporting electro active with analysis grade of Merck origin and without any further purification. All solutions were prepared by double distilled water. We used of Pyrex cell as an electrochemical cell, and in this cell glassy carbon and gold electrode as working electrodes, platinum as an auxiliary electrode and saturated calomel as a references electrode were used.

The laser beam was focused by lens into a quartz window which was specially made for this cell. The distance between quartz window and electrode surface was decreased to the least amount (about 0.5 mm) in order to decrease the laser irradiation adsorbed by solution.

### *2.2. Apparatus*

Electrochemical measurements or cyclic voltammograms were preformed, using an analytical system under the name of Potentiostate/Galvanostate and a computer unit.

The electrode samples were irradiated using $N_2$ laser and dye laser.

$N_2$ laser was operated at the power density of 2.3-9.5 MW/cm$^2$ and repetition rate of 10 Hz at 337 nm with pulse width of 5 ns.

A dye laser (pumped by Nd: YAG at 532 nm) was also used to treat the electrode samples at wavelength of 585, 575, 565 and 555 nm. It was operated at 10 Hz with typical pulse energy of 1.8 mJ and pulse duration of 20 ns.

The laser beam is assumed to be spatially homogeneous across the irradiated electrodes and its temporal profile is assumed Gaussian.

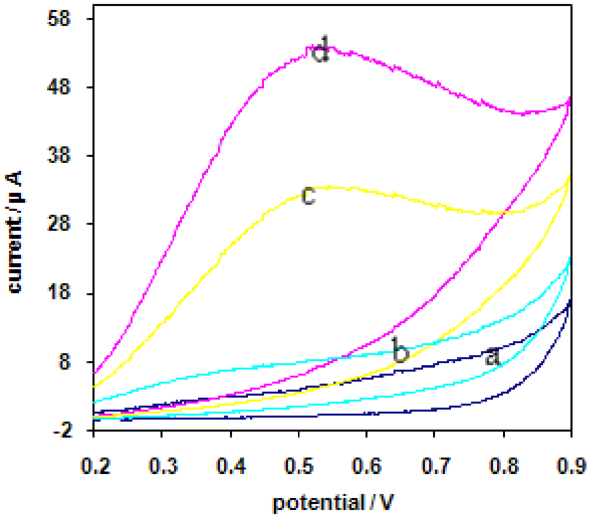

**Figure 1.** Cyclic voltammograms at the fresh glassy carbon electrode in $Na_2CO_3$ solution 0.1M in the presence of different concentration of Cefazolin, the potential sweep rate is 50mVs$^{-1}$. a) $Na_2CO_3$ supporting without analyte. b) $10^{-4}$ M Cefazolin solution c) $5.00\times10^{-4}$M Cefazolin solution d) $10^{-3}$ M cefazolin solution.

## 3. RESULTS AND DISCUSSION

### *3.1. Voltammetric analysis*

In this work, we chose sodium carbonate 0.1M as supporting electrolyte in electrochemical measurements of cefazolin by solid electrodes; meanwhile we investigated by using voltammetery techniques(CV and DPV). Also, to choose suitable concentration of cefazolin for reactivation experiments, cyclic voltammograms of different concentrations of cefazolin was studied. Fig (1) shows that proper concentration for matter is $5.00\times10^{-4}$M of cefazolin.

### *3.2. Electrochemical reactivation*

*Glassy carbon:*

In order to investigate the pretreatment of glassy carbon electrode the following steps have been taken:

first, 10 cyclic voltammograms of related samples ($5.00\times10^{-4}$M cefazolin and supporting electrolyte without cefazolin) have been taken successively in potential range of 0.2 to 0.9V, the current reduction during the successive CV show that electrode surface became inactive to contaminate by absorbed substances. Then for electrochemical reactivation polluted electrode a fixed potential in the range of 0.2V to -0.9V (cathodic reactivation) was applied to the contaminated electrode in the same solutions for one minute, and after each fixed potential pretreatment a CV has been taken in similar manner Fig(2,3).

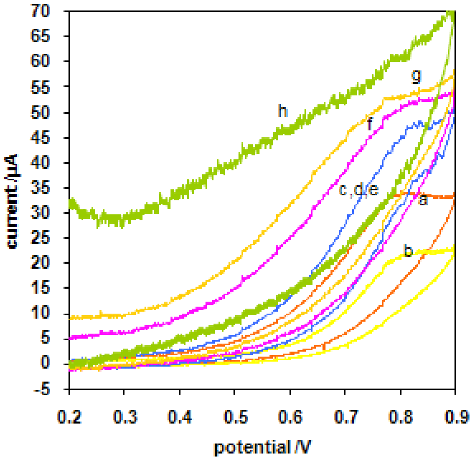

**Figure 2.** Electrochemical reactivated cyclic voltammograms for oxidation process of $5.00\times10^{-4}$M cefazolin in the0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$.

a) fresh electrode(alumina powder:1,0.3.0.05 micron)

b) after 10 successively scan

c to h ) voltammograms after activating electrode surface by fix potential in the range of 0.1V, 0V, -0.1V, -0.2 V, -0.3V, -0.5V.

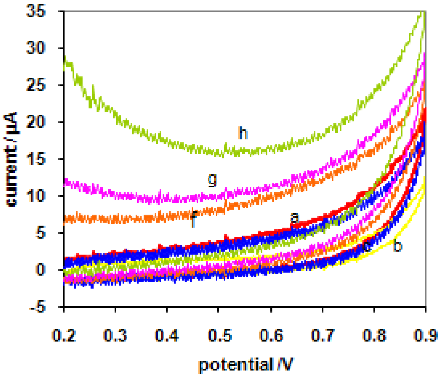

**Figure 3.** Electrochemical reactivated cyclic voltammograms for supporting electrolyte 0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate 50.0mVs$^-$

a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)

b) After 10 successively scan

c to h) voltammograms after activating electrode surface by fix potential in the range of 0.1V, 0V, -0.1V, -0.2V , -0.3V, -0.5V.

*Gold electrode:*

At this electrode, electrochemical reactivation in 5.00×10$^{-4}$M cefazolin solution was studied by differential pulse voltammetry and cyclic voltammeters techniques. In both cases, first 10 cyclic voltammograms of related sample have been taken successively in potential range of 0.6 to 1.1V and 0.7 to 1.2V, and after current reduction voltammograms for cleaning of electrode surface a fixed potential in the range of 0.5V to -0.3V (cathodic electrochemical reactivation) was applied, and the related voltammograms at various pretreatment potential are shown in Fig (4, 5). For both working electrodes (glassy carbon and gold), anodic electrochemical reactivation was studied which result shows that cathodic reactivation was more efficient. Fig (6) shows anodic electrochemical reactivation for gold electrode.

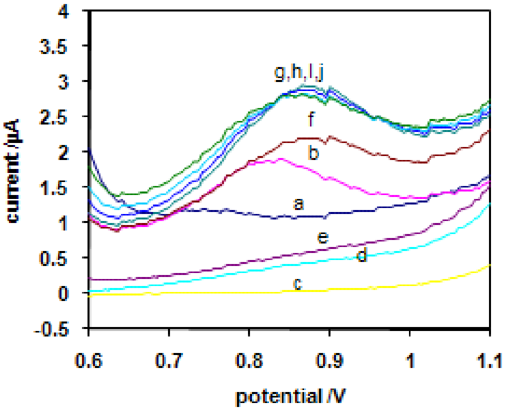

**Figure 4.** Cathodic Electrochemical reactivated differential pulse voltammograms for oxidation process of 5.00×10$^{-4}$M cefazolin in the 0.1M $Na_2CO_3$ solution (PH=9.2) at the gold electrode and scan rate 10.0mVs$^{-1}$.

a)supporting electrolyte(without Cefazolin)

b) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)

c) After 10 successively scan

d to j ) voltammograms after activating electrode surface by fix potential in the range of 0.5V, 0.4V, 0.3V, 0.2 V, 0.1V, 0V, -0.1V.

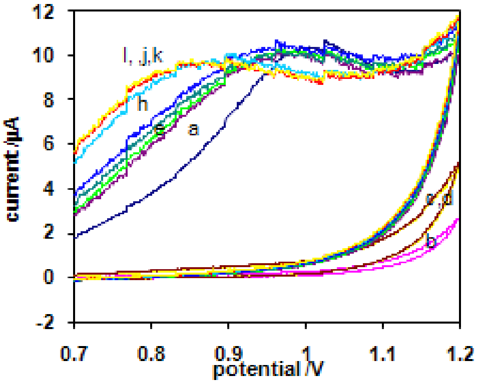

**Figure 5.** Cathodic electrochemical reactivated Cyclic voltammograms for oxidation process of $5.00\times10^{-4}$M cefazolin in the $Na_2CO_3$ solution 0.1M (PH=9.2) at the gold electrode and scan rate $50.0mVs^{-1}$.
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to j ) voltammograms after activating electrode surface by fix potential in the range of 0.5V, 0.4V, 0.3V, 0.2 V, 0.1V, 0V, -0.1V,-0.2,-0.3

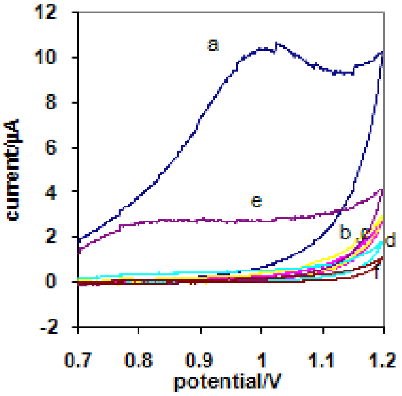

**Figure 6.** Anodic electrochemical reactivated Cyclic voltammograms for oxidation process of $5.00\times10^{-4}$M cefazolin in the 0.1M Na2CO3 solution (PH=9.2) at the gold electrode and scan rate $50.0mVs^{-1}$.
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to g ) voltammograms after activating electrode surface by fix potential in the range of 1.5V, 1.7V, 1.9V, 2.1 V, 2.3V.

### *3.3. Laser reactivation of working electrodes by $N_2$ laser*

In this investigation, similarly electrochemical reactivations of glassy carbon and gold electrode, which are mentioned for inactivating of electrodes surface by cyclic voltammetry and differential pulse voltammetry, have been studied. To reactivate surface of glassy carbon and gold electrodes, the $N_2$ laser was applied and also the effects of different laser power density was studied in two ways. One was applying simultaneous irradiation of laser pulses with electrochemical measurement, and the other was non-simultaneous irradiation of laser pulses with electrochemical measurement, where the appropriate result had not obtained from simultaneous irradiation. Figs (7, 8) show simultaneous laser reactivation of glassy carbon surface with cyclic voltammetry measurement for cefazolin $5.00\times10^{-4}$M and supporting electrolyte (without cefazolin). The existence of the noise in the voltammograms (see Figs 14 and 15) is attributed to the disturbance effect in the solution. Figs (9, 10) show the results of non-simultaneous laser reactivation of this electrode surface with cyclic voltammetry measurement of cefazolin $5.00\times10^{-4}$M and supporting electrolyte without it (cefazoline). Also we investigated non –simultaneous laser activation for this electrode in the fixed power density with different activated times in $5.00\times10^{-4}$ M cefazolin solution Fig (11).

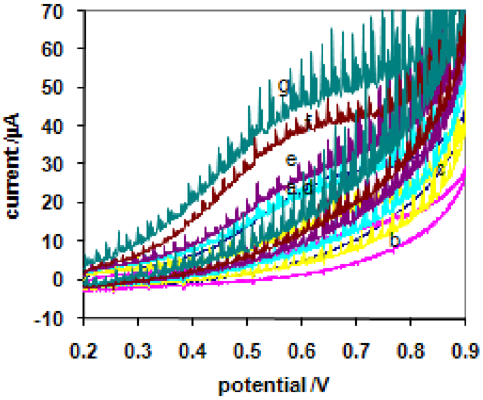

**Figure 7.** Laser reactivated cyclic voltammograms by $N_2$ laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the0.1M $Na_2CO_3$solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was simultaneous with electrochemical determination)

a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)

b) After 10 successively scan

c to g ) voltammograms after activating electrode surface by laser irradiation with power density, respectively: 2.9 MW/cm$^2$, 3.45 MW/cm$^2$ , 3.86 MW/cm$^2$ , 6.5 MW/cm$^2$ , 7.22 MW/cm$^2$

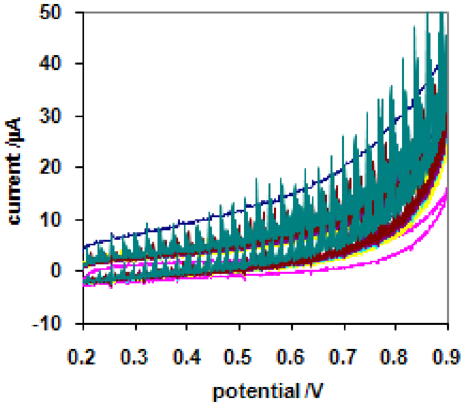

**Figure 8.** Laser reactivated cyclic voltammograms by $N_2$ laser for supporting electrolyte 0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was simultaneous with electrochemical determination)

a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)

b) after 10 successively scan

c to g ) voltammograms after activating electrode surface by laser irradiation with power density, respectively: 2.9 MW/cm$^2$, 3.45 MW/cm$^2$ , 3.86 MW/cm$^2$ , 6.5 MW/cm$^2$ , 7.22 MW/cm$^2$.

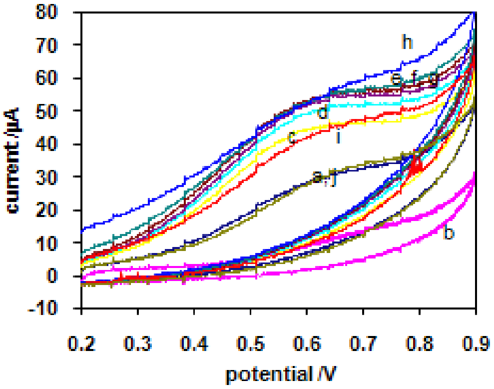

**Figure 9.** Laser reactivated cyclic voltammograms by $N_2$ laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to g ) voltammograms after activating electrode surface by laser irradiation with power density, respectively: 2.9 MW/cm$^2$, 3.45 MW/cm$^2$ , 3.86 MW/cm$^2$ , 6.5 MW/cm$^2$ , 7.22 MW/cm$^2$. (Irradiation time: 60s)

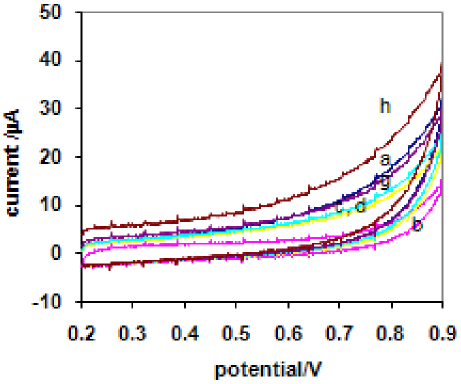

**Figure 10.** Laser reactivated cyclic voltammograms by $N_2$ laser for supporting electrolyte 0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon and scan rate $50.0mVs^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to g ) voltammograms after activating electrode surface by laser irradiation with power density, respectively: 2.9 MW/cm$^2$, 3.45 MW/cm$^2$ , 3.86 MW/cm$^2$ , 6.5 MW/cm$^2$, 7.22 MW/cm$^2$. (Irradiation time: 60s)

Figs (12, 13) are related to non–simultaneous laser reactivation of gold electrode surface with differential pulse voltammetry and cyclic voltammetry measurements by $N_2$ laser in $5.00\times10^{-4}$M cefazolin. Exposed glassy carbon (GC) and gold spots size were determined by the distance between the focusing lens and the electrode, when power density varied with this distance. The laser can produce large activated spots on the electrode, if such spots are of the same size as electrode diameter.

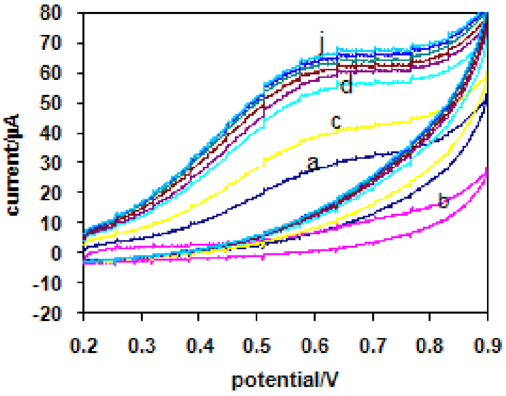

**Figure 11.** Laser reactivated cyclic voltammograms by $N_2$ laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the 0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate 50.0mVs$^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to j ) voltammograms after activating electrode surface by laser irradiation with power density 3.86 MW/cm$^2$ in different irradiation times , respectively:1,2,3,5,7,10,13,15 minute

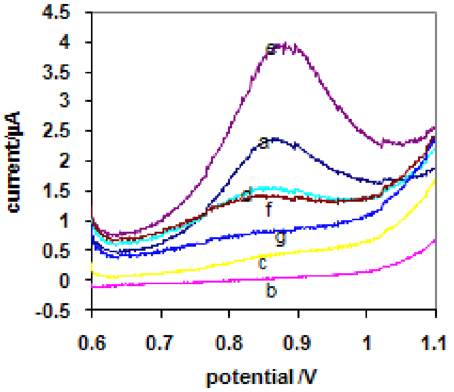

**Figure 12.** Laser reactivated differential pulse voltammograms by $N_2$ laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the 0.1M $Na_2CO_3$ solution (PH=9.2) at the gold electrode and scan rate 10.0mVs$^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to e) voltammograms after reactivating electrode surface by laser irradiation with power density, respectively: 2.39 MW/cm$^2$, 4.84 MW/cm$^2$ , 9.56 MW/cm$^2$.
F, g) two successively run after laser off

### *3.4. Laser reactivation of glassy carbon surface by Dye Laser*

In this study, the effect of different wavelengths of laser irradiation was examined. The selected wavelength was: 585nm, 575nm, 565nm, 555nm, and other laser beam parameters such as energy, repetition rate of irradiation were fixed at 1.8mJ and 10 Hz, respectively. Fig. 14 shows the dependence of reactivation on laser wavelength, with shorter wavelengths activating at low energy. The effect of energy was also examined at the laser wavelength of 565 nm and repetition rate of 10 Hz. As can be seen in Fig. 15, the optimized reactivation efficiency can be achieved using 32.6 mJ laser energy . It was observed that the required energy for reactivation depended on the laser wavelength.

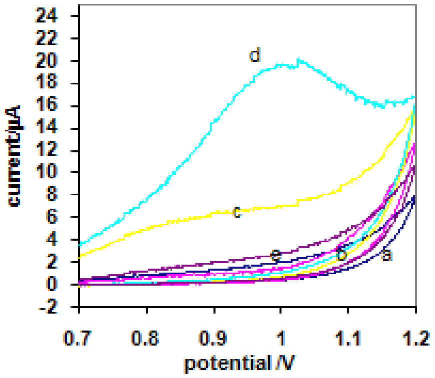

**Figure 13.** Laser reactivated cyclic voltammograms by $N_2$ laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the 0.1M $Na_2CO_3$ solution (PH=9.2) at the gold electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)

a) polluted electrode after several successively scan

b to d) voltammograms after activating electrode surface by laser irradiation with power density, respectively: 2.39 MW/cm$^2$, 4.84 MW/cm$^2$ , 9.56 MW/cm$^2$.

e) laser off

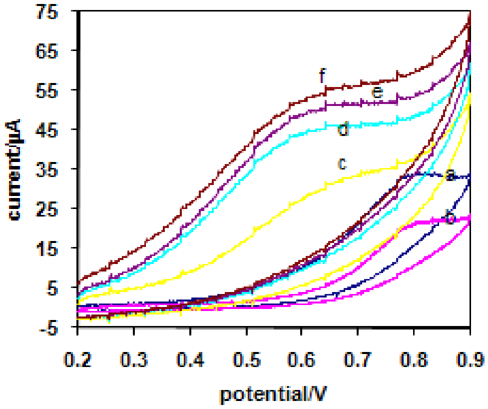

**Figure 14.** Laser reactivated cyclic voltammograms by Dye laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)

a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)

b) After 10 successively scan

c to f ) voltammograms after activating electrode surface by laser irradiation with different wavelength of laser beam respectively: 585nm,575nm,565nm,555nm. Another laser beam parameters were constant (laser pulse energy: 1.80mJ, and repetition rate: 10Hz)

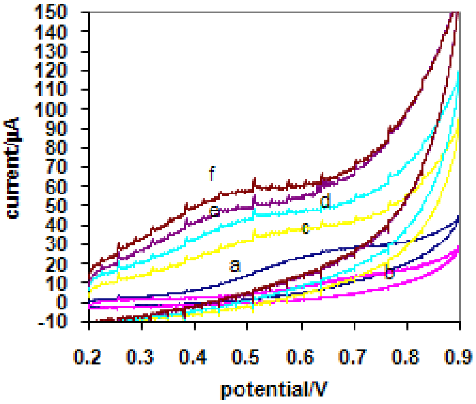

**Figure 15.** Laser reactivated cyclic voltammograms by Dye laser for oxidation process of $5.00\times10^{-4}$M cefazolin in the 0.1M $Na_2CO_3$ solution (PH=11.7) at the glassy carbon electrode and scan rate $50.0mVs^{-1}$. (Laser irradiation was non-simultaneous with electrochemical determination)
a) Fresh electrode (alumina powder: 1, 0.3, 0.05 micron)
b) After 10 successively scan
c to f ) voltammograms after activating electrode surface by laser irradiation at 565 nm with different energy of laser beam respectively: 12.1mJ, 14.6mJ, 24.4mJ, 32.6mJ.

## 4. CONCLUSIONS

In this paper, we have compared laser reactivation with electrochemical process to provide useful insight into factors affecting the reactivation process such as wavelength, pulse duration and laser energy.

The experiment results are as follows:

1) In low energy (power density) the laser pulse removes the layer of chemical or physisorbal impurities, micro particles and polishing debris present on electrode surface (surface cleaning ).
2) In high energy (power density) the laser pulse generates an active site at which electron transfer occurs (laser ablation).
3) The laser energy (power density) required for reactivation of the gold is higher than that for glassy carbon.
4) The laser reactivation and electrochemical process exhibit similar behavior on gold and GC for the simple matrix.
5) The laser wavelength dependence on reactivation, with shorter wavelengths reactivating at lower energy is shown.
6) The electrochemical cathodic and anodic activation are investigated; the results indicate that the cathodic activation of both electrodes has positive response, while the anodic activation has no observable response.

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