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ORIGINAL PAPER

An innovative approach to electro-oxidation of dopamine on titanium dioxide nanotubes electrode modified by gold particles

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Abstract Au/TiO_2/Ti electrodes were prepared by galvanic deposition of gold particles from an acidic bath containing $KAu(CN)_2$ in the presence of a citrate buffer onto TiO_2 nanotubes layer on titanium substrates. Titanium oxide nanotubes were fabricated by anodizing titanium foil in a DMSO fluoride-containing electrolyte. The morphology and surface characteristics of Au/TiO_2/Ti electrodes were investigated using scanning electron microscopy and energy-dispersive X-ray, respectively. The results indicated that gold particles were homogeneously deposited on the surface of TiO_2 nanotubes. The nanotubular TiO_2 layers consist of individual tubes of about 40–80 nm diameters. The electro-catalytic behavior of Au/TiO_2/Ti electrodes for the dopamine electro-oxidation was studied by cyclic voltammetry and differential pulse voltammetry. The results showed that Au/TiO_2/Ti electrodes exhibit a considerably higher electro-catalytic activity toward the oxidation of dopamine. The catalytic oxidation peak current showed a linear dependence on dopamine concentration and a linear calibration curve was obtained in the concentration range of 0.5–2.5 mM of dopamine.

Keywords Au/TiO_2/Ti electrode · Cyclic voltammetry · Electro-catalytic · Dopamine

1 Introduction

Dopamine (DA) is an important neurotransmitter. Extreme abnormalities of dopamine concentration levels may lead to several health problems, e.g., Parkinson's disease. Many researchers have thus attracted to work on the determination of dopamine. Dopamine can be investigated and determined by electrochemical methods due to its intrinsic redox nature [1, 2]. The electrochemical oxidation of dopamine in aqueous solutions occurs as a two-electron process leading to the formation of principally, *O*-dopaminoquinone. In the second step, this molecule may be converted to leucodopaminochrome. This species undergoes further oxidation (a two electron process) to form dopaminochrome. However, polymerization of the oxidation product of dopamine leads to deposition of polymer on the electrode surface, thus promoting a gradual loss of activity (electrode poisoning or fouling) [3–5]. Various methods, mainly based on the chemical modification of traditional electrode materials, have been developed to resolve this problem [6–9]. The poor reproducibility of direct electrochemical oxidation of dopamine has led to interest in the use of mediators and modified electrodes to catalyze the electrochemical oxidation of dopamine. For example, electrode surfaces modified with immobilized organic monolayers [10], polymers films [11–14] and carbon nanotubes [15] have been studied. Immobilization of the noble metal particles in an active matrix may enhance the overall reactivity of the catalytic metal centers. For example, our recent studies have shown that large surface area uniform TiO_2 nanotubes can fabricated by the anodic oxidation of titanium substrates. These TiO_2 nanotubes are very promising for the immobilization of noble metal particles. Study of electro-catalytic activity of TiO_2 nanotubes modified with platinum and gold nanoparticles has shown that the modification of electrode surface by anodizing of titanium improves the electro-catalytic activity to a great extent [16, 17]. Anodizing of titanium in different solutions and synthesis of TiO_2 nanotubes with high quality

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nano-structures, high surface-to-volume ratios and immobilization of the metal nanoparticles and nanocylinders on these TiO_2 nanotubes has reported by some authors [18–25]. In this research, we report the preparation and application of Au/TiO_2/Ti electrodes formed by anodizing of the titanium substrate to produce TiO_2 nanotubes with subsequent coverage of the nanotubular TiO_2 surface by cathodic deposition of gold. Self-organized TiO_2 films were formed in a DSMO electrolyte containing 2% (v/v) HF. Then deposition of gold takes place under galvanostatic conditions from an acidic bath containing $KAu(CN)_2$ in presence of a citrate buffer. The electrochemical catalytic activity of Au/TiO_2/Ti electrodes on the dopamine electrochemical response using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were investigated. The surface morphology and element analysis of gold coating on TiO_2 nanotubes were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX), respectively.

2 Experimental

2.1 Solutions and chemicals

All chemicals used were of analytical grade. All electrochemical experiments were carried out at room temperature. Double distilled water was used throughout.

2.2 Electrochemical cells, electrodes and instrumentation

The electrochemical experiments were performed in a three-electrode cell arrangement. A platinum sheet of the geometric area of about 20 cm^2 was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel reference electrode (SCE). Electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical System run by PowerSuite software.

2.3 Anodizing of titanium and synthesis of highly ordered TiO_2 nanotube arrays on titanium electrode

Titania nanotube samples were prepared by anodizing of titanium in a nonaqueous fluoride-containing electrolyte. Titanium samples, as working electrodes (1 × 1 cm) were cut from titanium sheet (purity %99.99) and mounted using polyester resin. Titanium samples were degreased by sonicating in acetone and ethanol followed by rinsing with distilled water. Electrochemical anodizing of titanium was carried out using a DC power supply. All anodizing experiments were carried out at room temperature using a two-electrode system (2 cm separation between anode and cathode). Anodic films were grown from titanium by potentiostatic anodizing in a DSMO electrolyte containing 2% by vol. HF (standard 38–40% aqueous HF) at a constant voltage of 40 V for 12 h at room temperature using a platinum sheet electrode as cathode.

2.4 The electrodeposition of gold on TiO_2 nanotube arrays

After anodizing of titanium, the samples were ultrasonically cleaned in distilled water for 10–20 min to remove surface contaminants. Then the TiO_2/Ti electrodes were immerged into the bath for electrolytic deposition; the distance of the two electrodes was 2 cm. Deposition of gold on TiO_2/Ti electrodes was performed under galvanostatic conditions. The deposition conditions were a current density of 10 mA cm^{-2} for 10 min, in an acidic bath containing $KAu(CN)_2$ in presence of a citrate buffered with pH 4. The temperature is maintained at 45 °C.

2.5 Determination of Au/TiO_2/Ti surface area

In order to compare prepared electrodes with pure gold electrode and to electrochemically characterize the real surface of the Au/TiO_2/Ti electrode, the surface area of the electrode was determined using 1 mM $K_4Fe(CN)_6$ in 0.1 M KNO_3 by recording the cyclic voltamograms. From the cyclic voltammetric peak current and the diffusion coefficient of hexacyanoferrate, the surface area of the electrode was calculated by using the following equation [26, 27]:

$$i_{pa} = \left(2.69 \times 10^5\right) n^{3/2} A D_o^{1/2} v^{1/2} C_o^* \qquad (1)$$

where n = number of electrons transferred, i.e. 1, A = surface area of the electrode, D_o = diffusion coefficient (9.382×10^{-6} cm^2 s^{-1}), v = scan rate (100 mV s^{-1}), C_o^* = concentration of electro-active species (1 mM). The surface area of Au/TiO_2/Ti electrode was estimated to be about 10 times of bare gold electrode.

2.6 Physical characterization

Morphology, alignment, and composition of the TiO_2 nanotube array and gold coating on nanotubular TiO_2 films were characterized with a scanning electron microscope (Philips, Model XL30) and energy-dispersive X-ray spectroscopy (EDAX).

3 Results and discussion

3.1 Characterization of the electrodes morphology

Figure 1 shows SEM micrographs of the titanium dioxide nanotubes prepared by anodic oxidation. The average tube diameter was about 50–80 nm, which can be used as good carrier of particle catalyst. Figure 2 shows the SEM micrographs of gold particles electrodeposited on titanium dioxide nanotubes. It can be seen that the gold particles with diameters around 30–40 nm are distributed almost homogeneously on the surface of the titanium dioxide nanotubes. Figure 3 shows the energy dispersive X-ray (EDAX) spectrum of Au/TiO_2/Ti after 10 min electroplating of gold on anodized titanium. Energy dispersive spectroscopy (EDS) results confirm the presence of gold particle in the surface film.

3.2 Electro-oxidation of dopamine

In order to compare Au/TiO_2/Ti electrode with flat gold electrode, the method of cyclic voltammetry was used to follow the electro-catalytic behavior of the electrodes. Figure 4A and B present cyclic voltammograms of gold and Au/TiO_2/Ti electrodes in 0.1 M Na_2SO_4 aqueous solution (a) and 0.1 M Na_2SO_4–0.5 mM dopamine aqueous solution (b), respectively. It can be seen from Fig. 4A and B that there is no redox peaks for Na_2SO_4 on both from Au/TiO_2/Ti and flat gold electrodes. Figure 4A and B is illustrated that the pure gold electrode exhibited no oxidation peak, but after replacing the pure gold electrode with Au/TiO_2/Ti electrode, distinguished peaks were observed in the cyclic voltammetry. Therefore, it is confirmed that the Au/TiO_2/Ti electrodes are electro-catalysts with very high activity for dopamine.

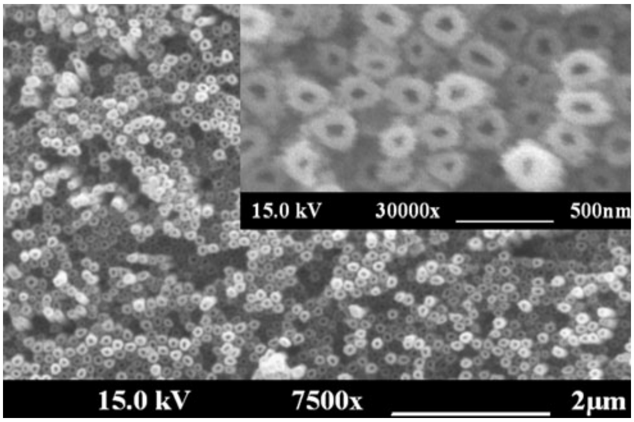

Fig. 1 The surface morphology of the titanium dioxide nanotubes prepared by titanium anodizing

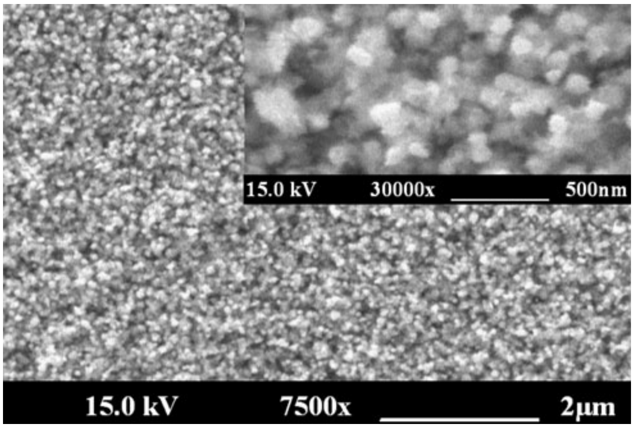

Fig. 2 The surface morphology of gold coating on the TiO_2/Ti electrode

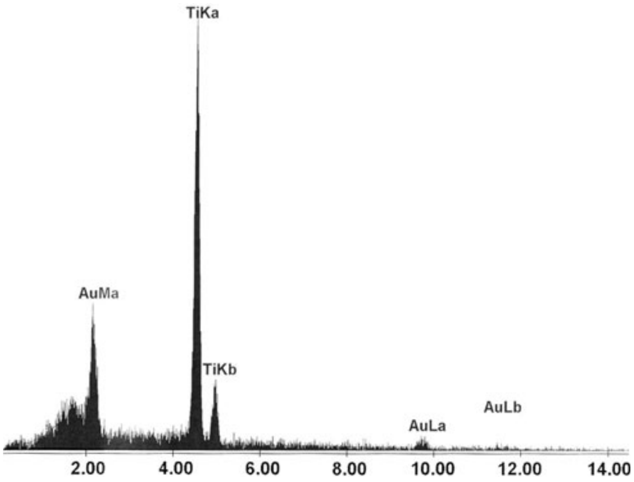

Fig. 3 EDAX of Au/TiO_2/Ti electrode after 10 min electroplating of gold on anodized titanium

3.3 Effect of scan rate and discussion on dopamine electro-oxidation mechanism

The effect of different scan rates on the electro-catalytic properties of Au/TiO_2/Ti electrode towards dopamine oxidation has been studied and the results were shown in Fig. 5. As can be seen, the increase in potential scan rate induced an increase in the electro-catalytic peak current. The obtained cyclic voltammograms were used to examine the variation of oxidation peak current versus scan rate. The oxidation current of dopamine increased linearly with the square root of scan rate in Au/TiO_2/Ti electrode with a correlation coefficient of $R^2 = 0.99$ (Fig. 6), which ensures that the oxidation process of dopamine on the Au/TiO_2/Ti electrode is a diffusion controlled process.

3.4 Electro-catalytic determination of dopamine

Effect of dopamine concentration on the cyclic voltammetric response of Au/TiO_2/Ti electrode was investigated. Figure 7 shows the cyclic voltammograms of the Au/TiO_2/

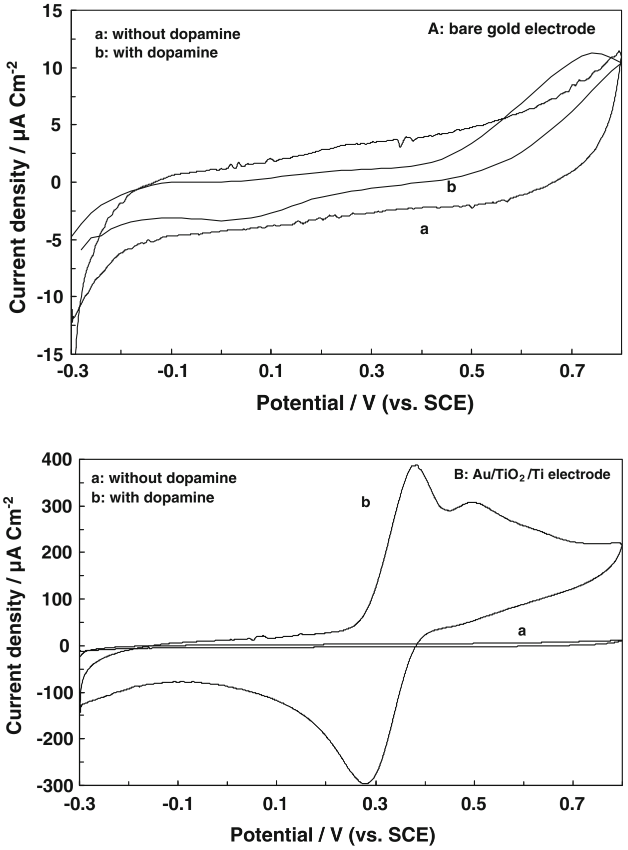

Fig. 4 Cyclic voltammograms of gold electrode (**A**); and Au/TiO_2/Ti electrode (**B**) in a 0.1 M Na_2SO_4 (*a*) and in a 0.1 M Na_2SO_4 + 0.5 mM dopamine (*b*) aqueous solutions at 25 °C with a scan rate of 100 mV s^{-1}

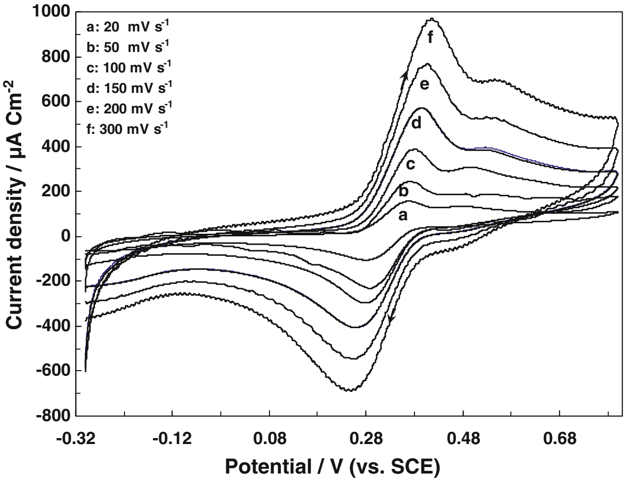

Fig. 5 The cyclic voltamograms of dopamine on Au/TiO_2/Ti electrode at different scan rate

Ti electrode at the presence of various concentrations of dopamine. The anodic peak current observed increases with increasing dopamine concentration in the solution. This catalytic peak current has a linear relationship with

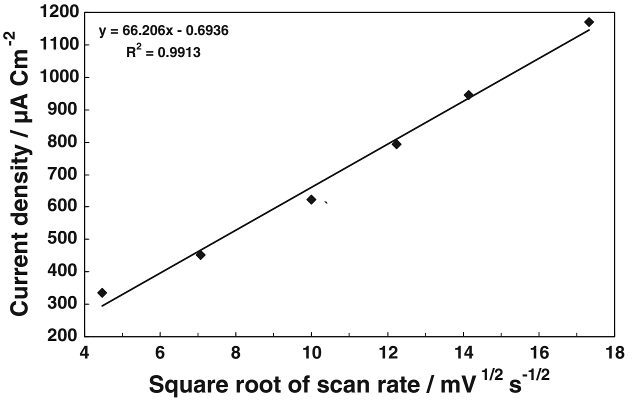

Fig. 6 The plot of dopamine oxidation peak current on the Au/TiO_2/Ti electrode vs. $v^{1/2}$

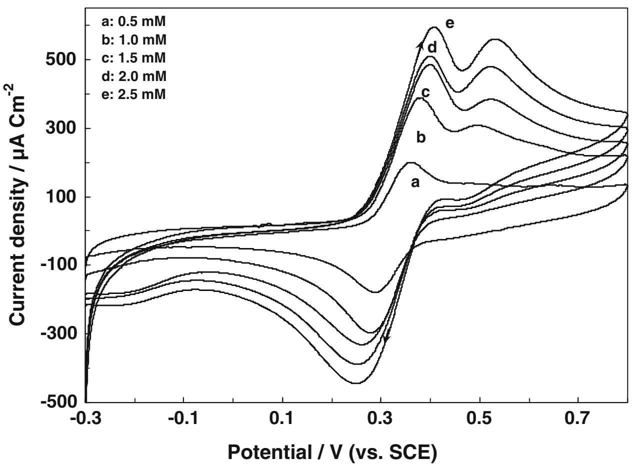

Fig. 7 The cyclic voltamograms of Au/TiO_2/Ti electrode in 0.1 M Na_2SO_4 solution with different concentrations of dopamine

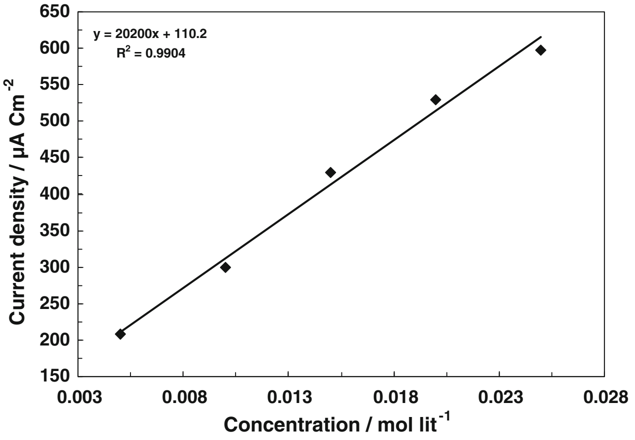

Fig. 8 The plot of dopamine oxidation peak current on the Au/TiO_2/Ti electrode vs. concentration of dopamine

the concentration of dopamine in the range of 0.5–2.5 mM with a correlation coefficient of 0.99 (Fig. 8). From these results, it can be concluded that the electro-oxidation of dopamine on these new modified electrodes can be used for quantitative determination of dopamine in samples. In Fig. 7, in range of 0.35–0.50 V versus SCE, two anodic peaks can be observed. The first peak can be attributed to oxidation dopamine to dopaminoquinone and the second one can be attributed to oxidation leucodopaminochrome to dopaminochrome (according to Fig. 13).

3.5 The temperature dependence of dopamine oxidation on Au/TiO_2/Ti electrode

In order to study the electro-catalytic performance of Au/TiO_2/Ti electrodes on the electrolyte temperature (T_{el}) and determination of activation energy, the temperature dependence of dopamine oxidation on Au/TiO_2/Ti electrode was investigated in the temperature range of 298–348 K by the method of cyclic voltammetry. From Fig. 9, it can see that anodic current increase with temperature increase. Figure 10 shows Arrhenius plot for the anodic current of dopamine oxidation on Au/TiO_2/Ti electrode. Linear correlation is obtained upon plotting ln i versus $1/T$. According to following equation [26]:

$$i = i_0 \exp(-E_a/RT) \tag{2}$$

$$\ln i = \ln i_0 - E_a/RT \tag{3}$$

From plotting ln i versus $1/T$, slop $= -E_a/R = -1.2868$; so $E_a = 10.69$ kJ mol^{-1}.

3.6 Effect of pH on the oxidation of dopamine

The electrochemical behavior of dopamine is dependent on the pH of the aqueous solution. It is known that variation in the electrolyte pH will result in variations of the formal potential of dopamine. Therefore, the thermodynamic

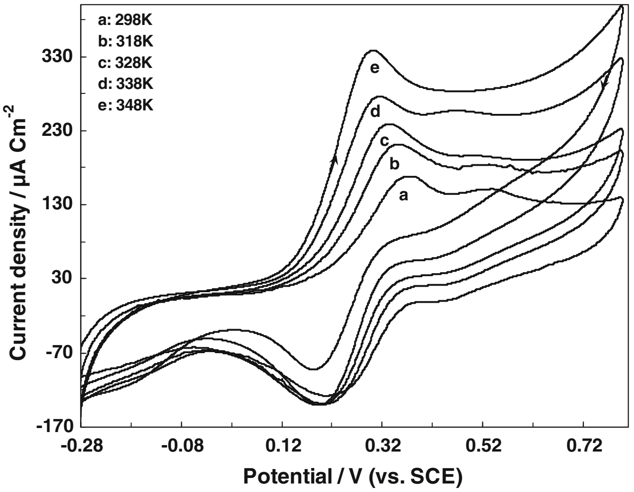

Fig. 9 The effect of temperature on cyclic voltammograms of dopamine oxidation on Au/TiO_2/Ti electrode in the range of 25–75 °C

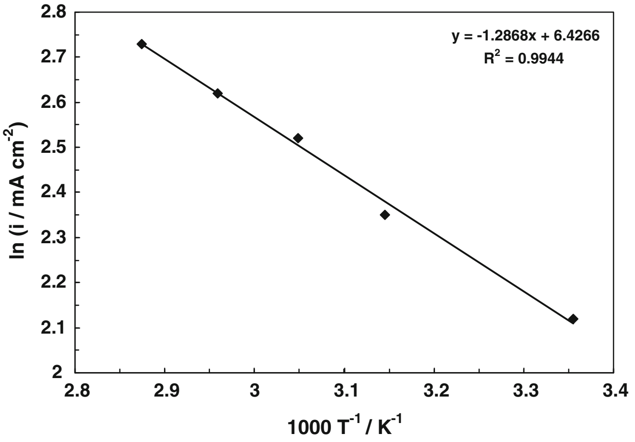

Fig. 10 Arrhenius plot for the anodic current of dopamine oxidation on Au/TiO_2/Ti electrode in a 0.1 M Na_2SO_4–0.5 mM dopamine aqueous solution

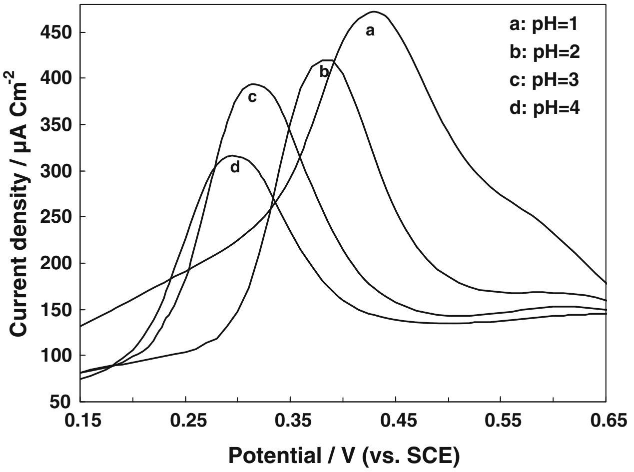

Fig. 11 Differential pulse voltammetry of Au/TiO_2/Ti electrode in 0.1 M Na_2SO_4–0.5 mM dopamine aqueous solution at various pH values 1, 2, 3 and 4 with scan rate 100 mV s^{-1}

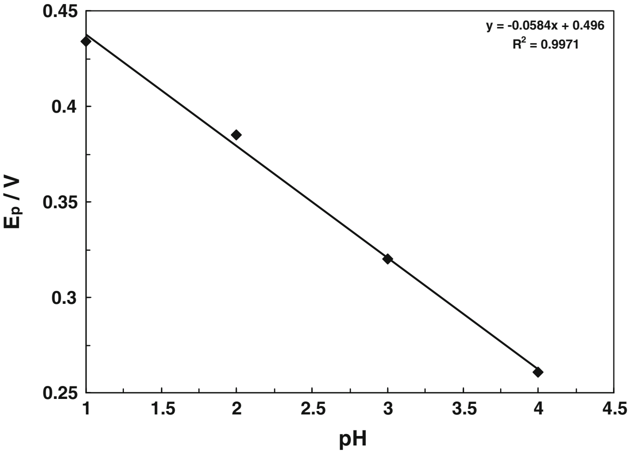

Fig. 12 Plot of anodic peak potential of dopamine oxidation vs. pH of solution

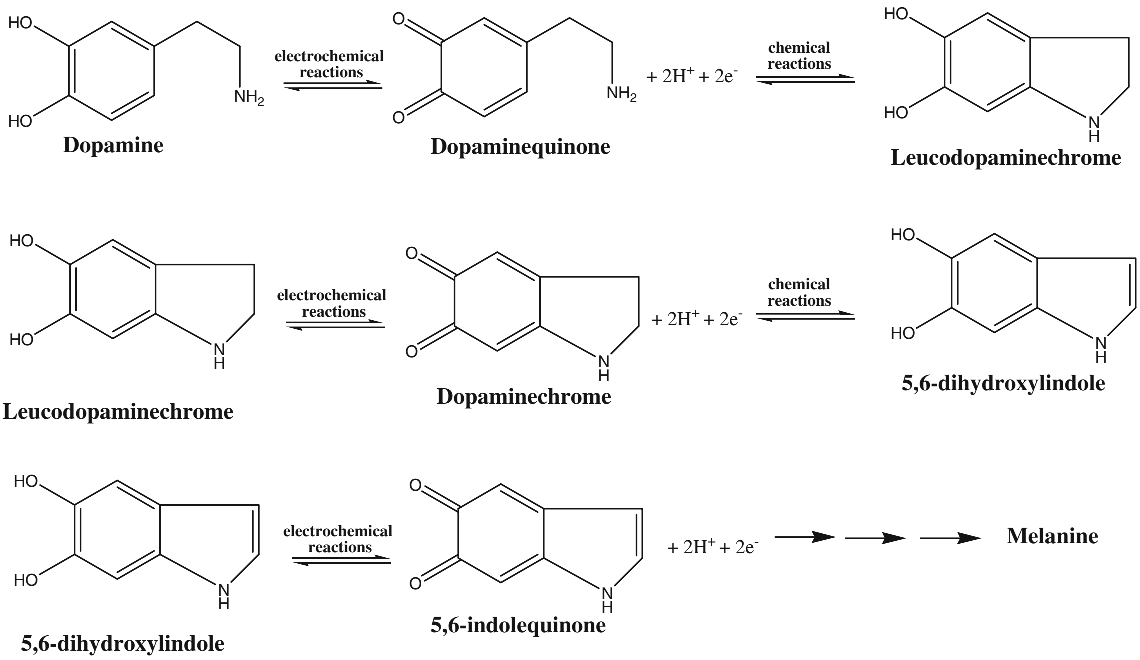

Fig. 13 Generalized scheme of dopamine oxidation mechanism

driving force for the catalysis will vary with pH, making the peak currents and the shapes of the cyclic voltammograms pH dependent. The effect of pH on the peak current and peak potential of the catalytic oxidation of dopamine was investigated by differential pulse voltammetry (DPV). As the results shown in Figs. 11 and 12, the peak potential for dopamine oxidation indicated a linear variation with the value of pH and it shifted to a more negative potential at higher pHs. There is a linear relationship between the anodic peak potential and pH of the solution with a slope about of −58.4 mV and $R^2 = 0.99$ which suggested that the total number of electrons and protons taking part in the charge transfer was the same and the intervention of protons in the reaction correlated with the mechanism displayed in the Fig. 13. Different steps of dopamine oxidation are schematically represented in Fig. 13 [2, 28, 29]. As illustrated in Fig. 13, dopamine oxidation is two electrons, two protons process. The results showed that the slope of E_p versus pH graph is −58.4 mV/pH unit over a pH range of 1–4 which is very close to the anticipated Nernstian value of 59.2 mV for a two electrons, two protons process.

4 Conclusion

Au/TiO_2/Ti electrode was prepared by a two-step process consisting of titanium anodizing followed by gold cathodic electrodeposition. The morphology and electro-catalytic performance of the electrode was investigated by scanning electron microscopy (SEM) and cyclic voltammetry (CV), respectively. The results indicated that gold particles were homogeneously deposited on the surface of TiO_2 nanotubes. These electrodes presented a good electro-catalytic activity toward the oxidation of dopamine. The electrocatalytic activity of the Au/TiO_2/Ti electrodes and pure gold toward dopamine oxidation was evaluated by electrochemical voltammograms. Results showed that the bare gold electrode is not suitable for the oxidation of dopamine. However, the Au/TiO_2/Ti electrode was shown to possess catalytic activity toward the oxidation reaction of dopamine. The oxidation kinetic of dopamine is also studied by varying the potential scan rate. The results indicated that the oxidation process is diffusion controlled. Finally, the oxidation current of dopamine Au/TiO_2/Ti electrodes was used for the determination of dopamine in aqueous solution and a linear calibration was found in the range of 0.5–2.5 mM with a correlation coefficient of 0.99. Therefore this modified electrode can be used for quantitative determination of dopamine in biological as well as pharmaceutical samples.

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