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Enhanced Electrocatalytic Activity of TiO_2 Nanotubes Modified with Pt and Pd Nanoparticles: Electro-oxidation of Dopamine, Uric Acid and Ascorbic Acid

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Abstract- *TiO_2 nanotubes electrode was fabricated by anodizing Ti sheets in F^- contained solution. The final modified electrode was then prepared by electrochemical pulse deposition of Pd and Pt nanoparticles onto the surface of tubes. The morphological characterization of the modified electrode suggested a uniform and regular tubular structure which was decorated by metal nanoparticles. The performance of the modified electrode was characterized by cyclic voltammetry and differential pulse voltammetry methods. The Pt-Pd-TiO_2 NTs modified electrode represented a relatively high sensitivity towards detection of dopamine in 0.1 M phosphate buffer solution (pH 7.00) as base solution. Over a wide concentration range of 2.0×10^{-7} to 1.0×10^{-4} M dopamine, the electro-oxidation peak currents of dopamine experienced two limits of linearity. However the sensitivity of the Pd- TiO_2 NTs was not acceptable for detection of dopamine. Furthermore, the Pt-Pd-TiO_2 NTs modified electrode was able to distinguish the oxidation response of dopamine, uric acid and ascorbic acid in mixture solution of different acidity.*

Keywords: TiO_2, Nanotubes, Anodizing, Pt-Pd nanoparticles, Dopamine, Uric acid, Ascorbic acid

1. Introduction

Nanotubular structures of TiO_2 have possessed potential applications in field of photo-electrochemical solar cells, photocatalysts, biocompatible materials and different type of sensors (Ghicov and Shmuki, 2009) and (Xiao et al., 2007). There are several reports of using modified structures of TiO_2 nanotubes in electrochemical biosensors (Mahshid et al., 2011a) and (Pan et al., 2009). Nowadays detection of dopamine (DA), an important neurotransmitter, has attracted much attention. In the extra-cellular fluid of the central nervous system the concentration of dopamine is very low. The loss of dopamine-containing neurons may result in serious neurological diseases, such as Parkinson's disease and schizophrenia (Niu et al., 2008) and (Wang et al., 2010).

The major problem and difficulties in the determination of dopamine is the coexistence of ascorbic acid (AA) and uric acid (UA) with a similar oxidation potential and concentrations much higher than dopamine (Zhao et al., 2005). Considering all these conditions, a sensitive and accurate electrode for detection of dopamine in the presence of uric acid and ascorbic acid is needed. There are several works on using modified materials such as metal nanoparticles (Ulubay et al., 2010) and (Atta et al., 2010), carbon nanotubes (Rubianes et al., 2010), metal oxides (Mazloum-Ardakani et al., 2010) and polymers (Chen et al. 2009) to improve the sensitivity, selectivity and stability of the bare electrode. Among them, metal nanoparticles such as Pt and Pd modified electrodes have attracted much attention due to their high surface area, effective mass transport and catalytic activity. According to the literatures, the most widely used bare electrodes are GCE (glassy carbon electrode) (Wu et al., 2003) and (Cao et al., 2008) and Metal electrodes such as Au and Pt (Mazloum -Ardakani et al., 2010). However, TiO_2 nanotubes electrodes possess an extra large surface area that prepares a suitable substrate for electrodeposition of metal nanoparticles. In our previous paper we have shown that the carbon-Pt modified TiO_2 nanotubes have possessed great catalytic activity towards dopamine. It is also shown that TiO_2 modified electrode is a sensitive electrode for detection of limited amount of dopamine (Mahshid et al., 2011b). In the following paper Pd and Pt nanoparticles has been used as the modifiers to prepare the final TiO_2 nanotubes electrode. It is shown that Pd nanoparticles are able to uniformly deposit onto the surface of TiO_2 nanotubes, preparing a conductive and uniform surface for deposition of Pt nanoparticles and also improve the conductivity of the whole modified electrode. Pt and Pd nanoparticles were electrodeposited from their single bath using electrochemical pulse deposition method. The catalytic activity of the final Pt-Pd-TiO_2 NTs modified electrode towards oxidation of dopamine was determined.

2. Experiments

Titanium foil (Aldrich, 99.8% pure, 0.127mm thick,) was cut into 1×3 cm pieces and then cleaned in HF solution. The cleaned Ti sheets were immediately anodized in a solution containing 0.1 M NaF and 0.5M $NaHSO_4$ for almost 2 h. The anodizing cell was a three- electrode configuration with a Pt sheet (Aldrich, 99.9% purity, 1 mm diameter) as the counter, SCE (saturated Calomel) as the reference and Ti sheet as the working electrodes. After anodization, samples were rinsed several times with distilled water and dried in an air stream. Pd and Pt nanoparticles were electrodeposited onto TiO_2 nanotubes using ZAHNER (IM6ex, Germany) working station and pulse electrodeposition method at -2 V for 1200 ms Pd and Pt nanoparticles were electrodeposited separately from their 1 mM single-bath solutions.

Electrochemical characterization was carried out in a CHI 660D (CH Instruments Inc., Austin, TX) electrochemical working station using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The electrocatalytic activity of the modified electrode was determined in single-bath solutions of 1mM dopamine (DA), 1mM uric acid (UA) and 1mM ascorbic acid (AA). The supporting electrolyte in all electrochemical investigations was 0.1M pH 7 phosphate buffer solutions (PBS). Solutions of dopamine, uric acid and also ascorbic acid were prepared daily using double distilled water and then directly used for the detection. All the experiments conducted at room temperature. The final topography of the electrode was studied using a scanning electron microscope (HITACHI S-4000, Japan).

3. Results and Discussion

3. 1. Electrocatalytic Activity of Pd-TiO_2 NTs and Pt-TiO_2 NTs for Detection of Dopamine

It is necessary to individually clarify the characteristics of Pd and Pt nanoparticles in final modified electrode. Under the same electrodeposition condition, Pd and Pt nanoparticles have shown different catalytic behaviour on the surface of amorphous and crystalline TiO_2 NTs electrode. It is known that the as-prepared TiO_2 nanotubes are amorphous, while after heat treatment at 500 °C for 3 h in the air it is going to be crystalline (Mahshid et al. 2011b). Figure 1 shows the cyclic voltammetry results of 1 mM dopamine oxidation in 0.1M pH 7.0 PBS at (1) Pd-cryTiO_2 NTs, (2) Pd-TiO_2 NTs, (3) Pt-TiO_2 NTs and (4) Pt-cryTiO_2 NTs electrodes in which 'cry' stands for crystalline. As it is obvious, the Pd modified electrodes have shown electrochemical response towards oxidation of dopamine in both crystalline (curve 1) and non-crystalline (curve 2) TiO_2 NTs. Moreover the oxidation peak possesses almost the same potential (E_p= 0.185V) and currect response (I_p= 341.4 μA). It suggests that, the catalytic behaviour of Pd modified TiO_2 nanotubes, is not vigorously depended on the crystallinity of the substrate. However, there are controversial results in case of Pt modified electrodes. Obviously, there is no electrochemical response to oxidation of dopamine on the surface of Pt-TiO_2 NTs electrode (curve 3), comparing to crystalline TiO_2 NTs electrode (curve 4).

It is believed that the controversial results are due to the different tendency of Pd and Pt nanoparticles for electrodeposition on the surface of non-crystalline TiO_2 nanotubes. Microstructure investigations (figure not shown) showed that Pd nanoparticles have uniformly deposited onto TiO_2 nanotubes and formed a chain-like structure of nanoparticles. This uniform electrodeposited Pd nanoparticles is responsible for high conductivity and catalytic activity towards detection of dopamine. However, there was no evidence for uniform electrodeposition of Pt nanoparticles on the surface of non-crystalline TiO_2 NTs.

It seems that Pd nanoparticles are better choice for modification of amorphous TiO_2 NTs. Since a lot of time and energy is spent for heat treatment of TiO_2 nanotubes, the amorphous TiO_2 nanotubes electrode is preferably used as the substrate in such a way that Pd nanoparticles are initially electrodeposited onto the tubes. Further modification of the structure is continued by electrodeposition of Pt nanoparticles onto the Pd-TiO_2 NTs electrode. Further morphological characterization of the modified electrode in section 3.3, obviously revealed the successful deposition of both Pt and Pd nanoparticles in the final structure.

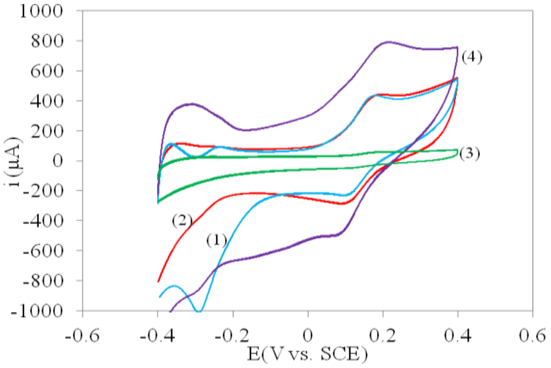

Fig. 1. Cyclic voltammetry obtained for 1mM DA in 0.1M pH 7.00 PBS with a scan rate of $100 mVs^{-1}$. (1) Pd- cryTiO_2 NTs, (2) Pd-TiO_2 NTs, (3) Pt-TiO_2 NTs and (4) Pt-cryTiO_2 NTs.

3. 2. Electrocatalytic Activity of Pt-Pd-TiO_2 NTs for Detection of Dopamine, Uric Acid and Ascorbic Acid

In this section the catalytic activity of TiO_2 nanotubes modified with both Pd and Pt nanoparticles are going to be discovered. Considering the previous results, it is expected to have an enhanced catalytic activity on the surface of Pt-Pd-TiO_2 NTs modified electrode. The necessity of modification with Pt nanoparticles will be more discussed in section 3.4, where the sensitivity of the electrode has measured.

Figure 2 shows the cyclic voltammetry results of (A) dopamine, (B) uric acid and (C) ascorbic acid oxidation at Pt-Pd-TiO_2 NTs modified electrode in 1.0×10^{-3} M dopamine 0.1M pH 7.0 PBS, 1.0×10^{-3} M uric acid 0.1M pH 7.0 PBS and 1.0×10^{-3} M ascorbic acid 0.1M pH 7.0 PBS, respectively. Since all these organic compounds are coexisted in human body, the simultaneous detection of them (as going to be discussed in section 3.4) is an important aspect of an electrode. However, it is first required to investigate the electrode respond to the individual detection of dopamine, uric acid and ascorbic acid from their single-bath solution. In order to have a better understanding of the role of Pt nanoparticles in the modified electrode, the cyclic voltammetry result of Pd-TiO_2 NTs modified electrode has been also taken into account.

Considering figure 2A, a pair of redox peaks was observed after modification of the electrode with Pd nanoparticles, representing the electro-catalytic activity of Pd towards dopamine oxidation (curve 1) with oxidation peak current (I_p) of 0.25 mA. As discussed before, the uniform deposition of Pd nanoparticles facilitates the electron transfer and enhances the conductivity. The performance of the electrode was much more improved by modification with Pt nanoparticles (curve 2). Here, the conductivity has a significant raise, which is ascribed to the high conductivity and catalytic activity of Pt, while there is hardly small shift in redox peaks potential.

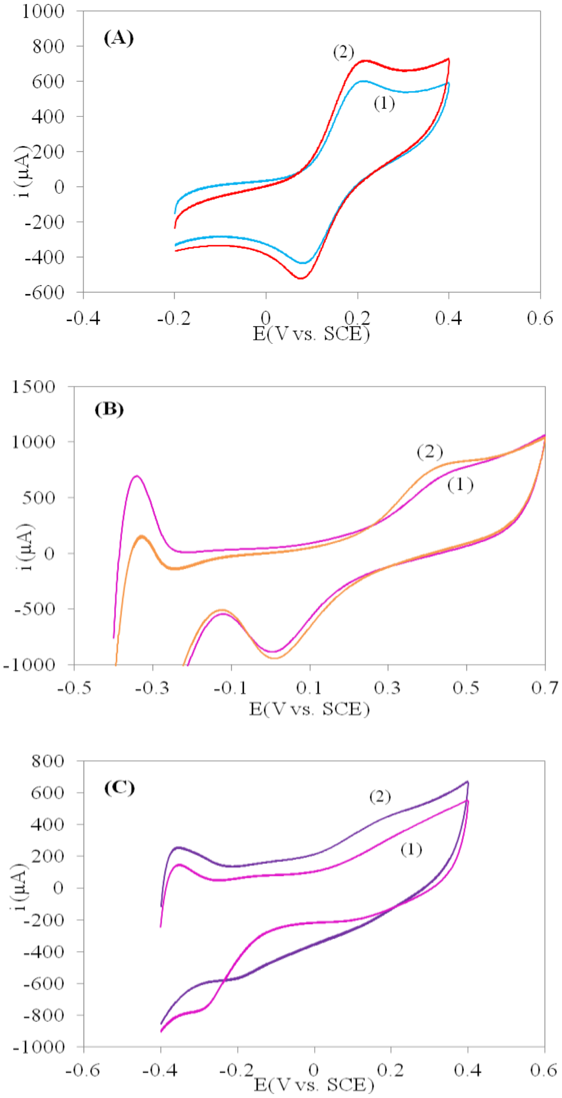

Fig. 2. Cyclic voltammetry obtained for (A) 1mM DA, (B) 1mM UA and (C) 1mM AA in 0.1M pH 7.00 PBS with a scan rate of $100 mVs^{-1}$. (1) Pd-TiO_2 NTs and (2) Pt-Pd-TiO_2 NTs

An almost same behaviour observed in cyclic voltammetry results of 1mM uric acid solution. According to figure 2B, the TiO_2 modified electrode shows electrochemical respond towards oxidation of uric acid on both Pd (curve 1) and Pt-Pd (curve 2) modified electrodes. As it is obvious, the Pd-TiO_2 NTs modified electrode has successfully recognised the oxidation and reduction reaction of uric acid at about 0.45 V and 0.01 V respectively. However, after modification with Pt nanoparticles the oxidation peak potential of uric acid has obviously shifted to more negative potentials accompanying a sharp rise in oxidation peak current (I_p).

Further experiments in 1 mM ascorbic acid solution also revealed the electrocatalytic activity of TiO_2 nanotubes modified electrode towards oxidation of ascorbic acid in figure 2C. Obviously the oxidation and reduction peaks are not sharp enough comparing to those obtained from dopamine and uric acid solutions. However, the effective role of Pt nanoparticles has obviously shown in the figure. Here, the cyclic voltammetry result of 1 mM ascorbic acid solution has shown a significant increase in oxidation peak current response of Pt-Pd-TiO_2 NTs modified electrode (curve 2) comparing to that of Pd-TiO_2 NTs modified electrode (curve 1). It is again ascribed to the high conductivity and catalytic activity of Pt nanoparticles, which is responsible for a raise in oxidation peak current response (I_p) as well as an observable negative shift in oxidation peak potential (E_p), respectively.

3. 3. Morphological Characterization of Pt-Pd-TiO_2 NTs

The morphological characteristic of TiO_2 nanotubes electrode, before and after modification with Pd and Pt nanoparticles has been shown in figure 3A and 3B, respectively. It is obvious that tubular structure of TiO_2 has been regularly formed by using anodizing method (figure 3A). This nano structure suggests a very large surface area for further modifications. Using the electrochemical pulse deposition method, the metal nanoparticles are deposited onto the surface of the tubes as shown in figure 3B.

As described before, Pd nanoparticles were primarily electrodeposited onto the nanotubes surface by pulse electrodeposition technique, followed by electrodeposition of Pt nanoparticles under the same condition. Uniform deposition of Pd nanoparticles is responsible for an impeccable final microstructure where the agglomeration of nanoparticles is prevented. In this case, the electrodeposition condition was chosen in a way that less possibility of nanoparticles coagulation on surface of the tubes could be observed.

According to the Energy Dispersive X-ray Spectrometer (figure 3C), both Pd and Pt nanoparticles are present in the final structure. Here the nanoparticles with average size of 15- 20 nm have uniformly deposited on tubes edge. There is also evidence of their presence inside the tubes. Considering both deposition sites, it could be expected that the final Pt-Pd-TiO_2 NTs modified electrode possessed a high catalytic activity, due to the presence of large amount of Pd and Pt nanoparticles.

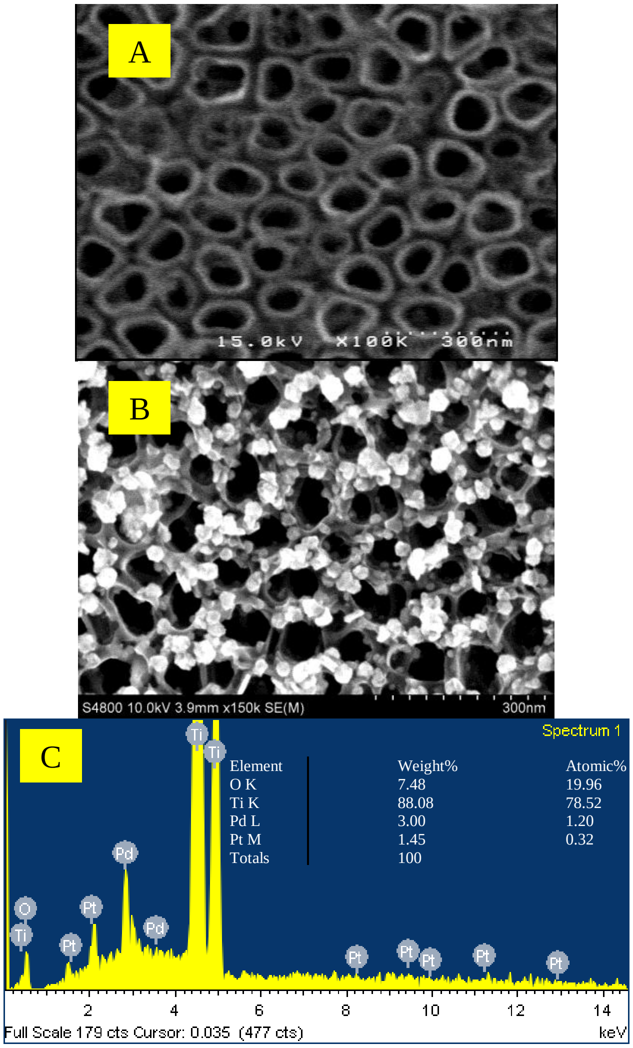

Fig. 3. Scanning electron microscopy images of TiO_2 nanotubes electrode: A) Before, B) After pulse electrodeposition of Pd and Pt nanoparticles and C) EDS spectrum of the Pt-Pd-TiO_2 NTs modified electrode.

3. 4. Differential Pulse Voltammetry on the Surface of Pt-Pd-TiO_2 NTs

The electrocatalytic behaviour of Pt-Pd-TiO_2 NTs electrode was studied, using differential pulse voltammetry method (DPV) in dopamine contained solution. For better comparison, the DPV result of dopamine oxidation on the surface of Pd-TiO2 NTs has also studied.

Figure 4 shows the DPV results of dopamine oxidation at (A) Pd-TiO_2 NTs and (B) Pt-Pd-TiO_2 NTs electrode in 0.1M pH 7.0 PBS contained various concentration of dopamine. In figure 4A, the oxidation peak potential of dopamine on Pd-TiO_2 NTs electrode experiences severe changes. Furthermore, there is no regular trend in oxidation peak current versus dopamine concentration in range of 8×10^{-7} to 3×10^{-6}M. However, a linear trend (slope: 1.386 μA/μM) between oxidation peak currents of dopamine and its concentration over 4.0×10^{-6} to 1.0×10^{-5}M dopamine is observed. These fluctuations suggest poor sensitivity of the Pd-TiO_2 NTs electrode towards detection of dopamine.

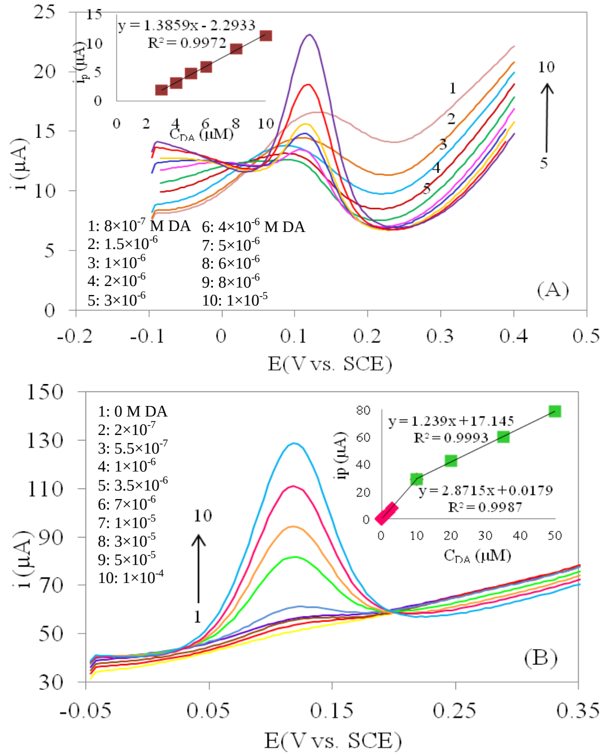

Fig. 4. Differential pulse voltammetry of DA at (A) Pd-TiO_2 NTs and (B) Pt-Pd-TiO_2 NTs in 0.1MpH 7.00 PBS with scan rate $20mVs^{-1}$ and pulse amplitude 50 mV. (Insets) calibration plot of oxidation peak current versus accumulated concentration of DA in each step.

According to figure 4B under optimised condition the oxidation peak potential of dopamine occurred at 0.120V for all concentrations of dopamine in range of 2.0×10^{-7} to 1.0×10^{-4}M. As shown in figure 4B (inset), the oxidation peak currents of dopamine experience two limits of linearity in this range of concentration. The oxidation peak currents of dopamine follow a sharp linear rise with slope of 2.87 μA/μM in range of 0- 1.0×10^{-5} M dopamine, suggesting a high sensitivity towards detection of dopamine in this range. Increasing the concentration of dopamine from 1.0×10^{-5}-1.0×10^{-4} M, the oxidation peak currents experience a slow rise with slope of 1.239 μA/μM. The whole experience suggests that the Pt-Pd-TiO_2 NTs possesses a relatively high sensitivity towards oxidation of dopamine in concentration range of 2.0×10^{-7} to 1.0×10^{-4}M. However, the sensitivity slightly decreases above 10^{-5} M dopamine, which limits its application.

It is known that simultaneous determination of dopamine, ascorbic acid and uric acid was always a great problem due to their similar oxidation potentials, which caused overlapped peaks on most common electrodes. Using DPV technique, selectivity of Pt-Pd-TiO_2 NTs modified electrode towards simultaneous oxidation of dopamine, uric acid and ascorbic acid was examined at three different acidities (figure 5). In this regard, a series of experiments obtained in a mixture of 1.0×10^{-4} M dopamine, 1.0×10^{-4} M uric acid and 2.0×10^{-4} M ascorbic acid. As usual, the base solution was 0.1M pH 7 PBS while H_2SO_4 was added to adjust pH to 4.5 and 3. Obviously, at pH 7 the oxidation peak potential of dopamine and uric acid has been occurred at 0.12 V and 0.35 V, respectively. Whereas the oxidation peak of ascorbic acid has been appeared as a small curve before that of dopamine at 0.08 V. It is obvious that Pt-Pd-TiO_2 NTs modified electrode could hardly separate the oxidation peak potential of ascorbic acid and dopamine at pH 7. However, increasing the acidity of the solution to pH 4.5, the oxidation peak potential of ascorbic acid and dopamine were completely separated from each other at 0.20 V and 0.36 V respectively. Comparing these results, the oxidation peak potential of all three components experienced obvious shift to more positive potentials. Almost similar trend was observed as the pH of the solution decreased to 3, resulting in complete separation of ascorbic acid and dopamine peak potential at 0.26 V and 0.42 V respectively. The peak separation between ascorbic acid and dopamine became greater at acidic solutions. At pH 4.5 and 3, the maximum separation of ascorbic acid and dopamine was obtained. Therefore simultaneous determination of ascorbic acid and dopamine on the surface of Pt-Pd-TiO_2 NTs electrode would be possible in acidic environments.

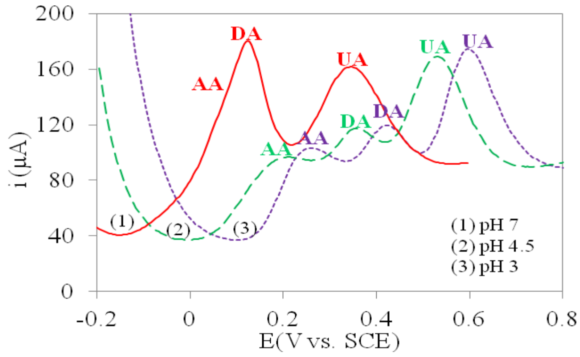

Fig. 5. Differential pulse voltammetry obtained in the simultaneous presence of 1×10^{-4} M DA+ 1.0×10^{-4} M UA+ 2.0×10^{-4} M AA at 1) pH 7, 2) pH 4.5 and 3) pH 3. The modified electrode was Pt-Pd-TiO_2 NTs under optimal condition of scan rate $20mVs^{-1}$ and pulse amplitude 50 mV.

4. Conclusion

The electrocatalytic behaviour of TiO_2 nanotubes electrode which is modified with Pd and Pt nanoparticles has been studied. First, the modified TiO_2 NTs electrode was fabricated by uniform deposition of Pd and Pt nanoparticles from their single-bath solutions using pulse electrodeposition method. The morphological characterization of the Pt-Pd-TiO_2 NTs suggested a uniform and regular deposition of metal nanoparticles. Pd nanoparticles were initially electrodeposited on the surface of amorphous TiO_2 to prepare a conductive and uniform surface for further modification with Pt nanoparticles. The performance of the modified electrode towards individual detection of dopamine, uric acid and ascorbic acid was characterized by cyclic voltammetry from their single-bath solutions. Differential pulse voltammetry method was also used to investigate the sensitivity of the Pd- TiO_2 NTs and Pt- Pd- TiO_2 NTs modified electrodes. The sensitivity of the Pd- TiO_2 NTs was not acceptable for detection of dopamine. However, the Pt-Pd-TiO_2 NTs modified electrode represented a relatively high sensitivity towards detection of dopamine in 0.1 M phosphate buffer solution (pH 7.00). Over concentration range of 2.0×10^{-7} to 1.0×10^{-4} M, the electro-oxidation peak currents of dopamine experience two limits of linearity which suggest a slight decrease of sensitivity. Furthermore, differential pulse voltammetry method was applied for simultaneous detection of the three compounds in a solution containing 1×10^{-4} M dopamine, 1.0×10^{-4} M uric acid and 2.0×10^{-4} M ascorbic acid. It was revealed that the Pt-Pd-TiO_2 NTs modified electrode was able to distinguish the oxidation response of dopamine, uric acid and ascorbic acid in mixture solution of different acidity.

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