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Silver nanoparticles dispersed in polyaniline matrixes coated on titanium substrate as a novel electrode for electro-oxidation of hydrazine

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Abstract Silver nanoparticles dispersed in polyaniline matrixes coated on titanium substrate, as a novel electrode, was easily synthesized by electro-polymerization of aniline on titanium and then electrodeposited silver nanoparticles on PAni electrode. The electrochemical behavior and electro-catalytic activity of silver nanoparticles/PAni/Ti electrodes were characterized by cyclic voltammetry. The morphology of silver nanoparticles on PAni/Ti electrodes were characterized by scanning electron microscopy and energy-dispersive X-ray techniques, respectively. Results indicated that silver nanoparticles with a diameter of about 40–70 nm were homogeneously dispersed on the surface of polyaniline film. The silver nanoparticles/PAni/Ti electrodes were examined for electro-catalytic activity toward oxidation of hydrazine. The results show that these modified electrodes are highly active for electro-catalytic oxidation of hydrazine.

Introduction

The development of inorganic/organic composites has recently received increasing attention due to their wide range of potential uses [1, 2]. Composites of conducting polymers and inorganic nanoparticles have received a lot of attention because of their usefulness in several applications [3, 4]. Various approaches have been used to prepare conducting polymer/metal composites. Many studies have been devoted to the dispersion of metal particles in thin films of various polymers [5–16]. Among these polymers, the polyaniline (PAni) is one of the most important conducting polymers because of its high conductivity, ease of preparation, good environmental stability, and large variety of applications such as electrochromic devices, secondary batteries, catalysis, and corrosion protection coatings [17–20]. Silver nanoparticles are potential electro-catalysts for fuel cells [21], electrolysis of brine [22], and for the reduction of organic halides [23] due to the high catalytic activity. In the application as electro-catalysts, the silver nanoparticles are required to be finely discrete states, where the size and the shape are critical parameters to be controlled [24]. Hydrazine has been recognized as a neurotoxin, carcinogenic mutagenic [25], and hepatotoxic substance, which has adverse health effects such as liver, brain [26], DNA damage [27], creation of blood abnormalities, and irreversible deterioration of the nervous system [25]. On the other hand, these materials have wide applications in industry and agriculture, as explosives, antioxidants, photographic developer, oxygen scavengers, and insecticides. Hydrazine is also considered as a base fuel in fuel cells. Because of the great importance of hydrazine, its accurate and economical determination is still a challenging research in analytical chemistry. Among numerous techniques that have been reported for the determination of hydrazine, electrochemical techniques offer the opportunity for portable, economical, sensitive, and rapid methodologies. Therefore, the electro-oxidation of hydrazine compounds is a reaction of practical importance. Immobilization of the metal nanoparticles in an active matrix may enhance the overall reactivity of the catalytic metal centers. For example, our recent studies on the electro-catalytic properties of Pt/TiO_2/Ti, Au/TiO_2/Ti, and Au/PAni/Ti electrodes have shown that the immobilization of the metal nanoparticles in an active matrix improves the electro-catalytic activity to a great extent

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[28–31]. To date, the variety of researches has been focused on the using of nanoparticles and nanocomposites in the electrochemistry fields [32–35]. The aim of the present work was to investigate the electro-oxidation of hydrazine on silver nanoparticles dispersed in polyaniline matrixes and analyze the effect of their morphologies on the electro-catalytic characteristics of this modified electrode. The polyaniline films were obtained by applying cyclic voltammetry scans on titanium substrates. Ag nanoparticles dispersed on the polyaniline films by cathodic electrodeposition. The electro-oxidation of hydrazine on silver nanoparticles/PAni/Ti electrodes was carried out using cyclic voltammetry and the results are discussed on the basis of differences in their surface area. The surface morphology and element analysis of silver coating on polyaniline films were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively.

Experimental

Chemicals, solutions, and electrochemical equipment

Hydrazine (Merck, >99%), $AgNO_3$ (Merck, 99.8%), and Na_2SO_4 (Merck, >99%) were used as received. All other chemicals were of analytical grade and used without further purification. Aniline was distilled under reduced pressure and then stored at low temperature before use. All electrochemical experiments were carried out at room temperature and distilled water was used throughout. The electrochemical experiments were performed in a three-electrode cell assembly. 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 electrode (SCE). Electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical System run by Powersuite Software.

Polyaniline synthesis

Electro-polymerization of polyaniline from an acidic solution was conducted on titanium electrode. Titanium discs were cut from a titanium sheet (purity 99.99%, 1 mm thickness) and mounted using polyester resin. The deposition of conducting polymers on spontaneously passivating metals such as titanium and aluminum usually requires a pretreatment of the substrate in order to remove natural oxides, which cover the metal surface. Prior to electropolymerization of aniline, the titanium electrodes were first mechanically polished with different grades of abrasive papers, rinsed in a run of distilled water, then chemically etched by immersing in a mixture of volumetric 1:4:5 of $HF:HNO_3:H_2O$. The last step of pretreatment was rinsing with deionized water. After the pretreatment, electropolymerization of aniline was conducted in solution of 0.1 M aniline and 0.5 M H_2SO_4 through 30 successive cyclic voltammetry scans in the potential range of −0.5 and 1.5 V at a scan rate of 10 mV s^{-1}.

The electrodeposition of silver nanoparticles on polyaniline matrixes coated on titanium substrate

After rinsing with water, the PAni/Ti electrodes were immerged into the bath to electrolytic deposition, the distance of the two electrodes was 2 cm. Deposition of silver nanoparticles on PAni/Ti electrodes was performed under galvanostatic conditions with a current density of 10 mA cm^{-2} for 5 min, in a bath containing 1.76×10^{-3} M $AgNO_3$ + 0.1 M $KClO_4$. The temperature is maintained at 25 °C.

Physical characterization

The morphology and composition of silver nanoparticles on the polyaniline films were characterized with a scanning electron microscope (Philips, Model XL30) and energy-dispersive X-ray spectroscopy (EDX).

Results and discussion

Preparation of polyaniline coating on titanium electrode

Figure 1 shows cyclic voltammograms recorded during electro-polymerization of polyaniline on titanium electrode in 0.5 M H_2SO_4 solution containing 0.1 M aniline at a scan

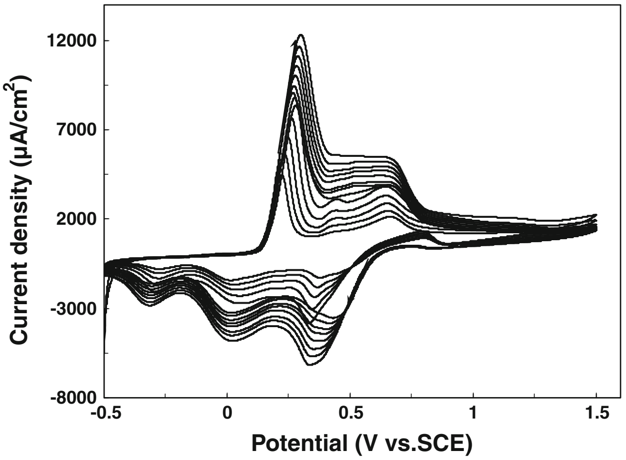

Fig. 1 Cyclic voltammograms during polymerization in 0.5 M H_2SO_4 solution containing 0.1 M aniline at a scan rate of 10 mV s^{-1}

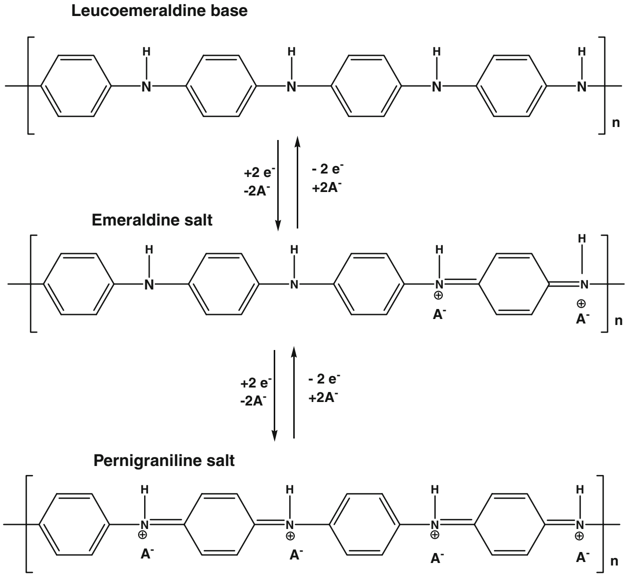

Fig. 2 Generalized scheme of electrochemical reactions of various polyaniline oxidation forms

rate of 10 mV s^{-1}. First anodic peak occurring at a potential of about +0.25 V could be attributed to the doping of sulfate anions via transition of leucoemeraldine form of polyaniline to emeraldine salt, while further increase of the potential above +0.65 V denotes transition of emeraldine salt to pernigraniline salt. Between these two well-defined anodic peaks, small peak at potential of about +0.45 V could be assigned to degradation reaction of the polyaniline. Different forms of polyaniline oxidation states are schematically represented in Fig. 2 [36].

Morphology of silver nanoparticles on polyaniline matrixes coated on titanium substrate (on PAni/Ti electrodes)

Figure 3 shows the SEM micrographs of silver nanoparticles electrodeposited on the polyaniline film. It can be seen that the silver nanoparticles with diameters about of 40–70 nm are distributed in an almost homogeneous manner at the surface of the polyaniline film. Figure 4 shows the EDX spectrum of silver nanoparticles/PAni/Ti after 5 min electroplating of silver on PAni/Ti electrode. EDS result confirms the presence of silver nanoparticles in the displaced films.

Cyclic voltammetric study of hydrazine electro-oxidation on the electrodes

In order to compare silver nanoparticles/PAni/Ti electrode with flat silver electrode, the method of cyclic voltammetry was used to estimate the electro-catalytic behavior of the electrodes. Figure 5A presents cyclic voltammograms of

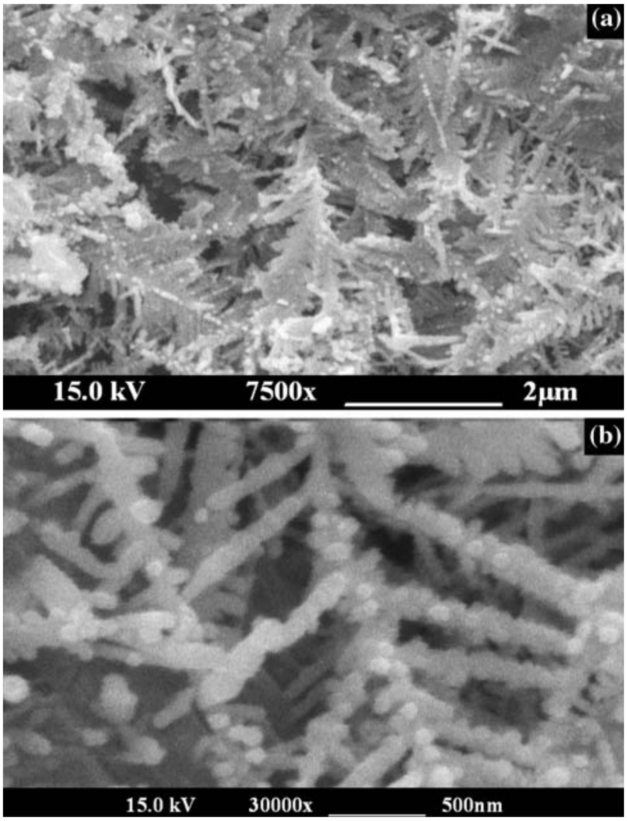

Fig. 3 Scanning electron microscopic (SEM) images of the silver nanoparticles on the PAni/Ti electrode with different magnifications (**a**, **b**)

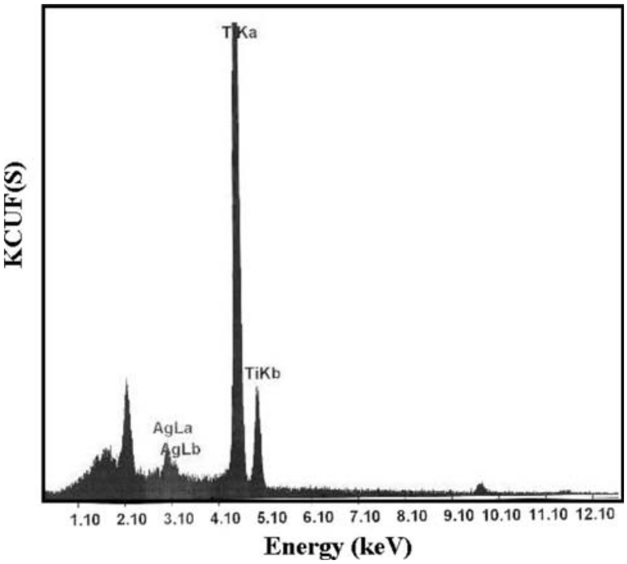

Fig. 4 Energy dispersive X-ray (EDX) of silver nanoparticles/PAni/Ti electrode

1 cm^2 flat silver electrode in 0.1 M Na_2SO_4 aqueous solution, at a scan rate of 100 mV s^{-1} without hydrazine (a) and at present 10 mM $N_2H_4 \cdot H_2O$ (b). Cyclic

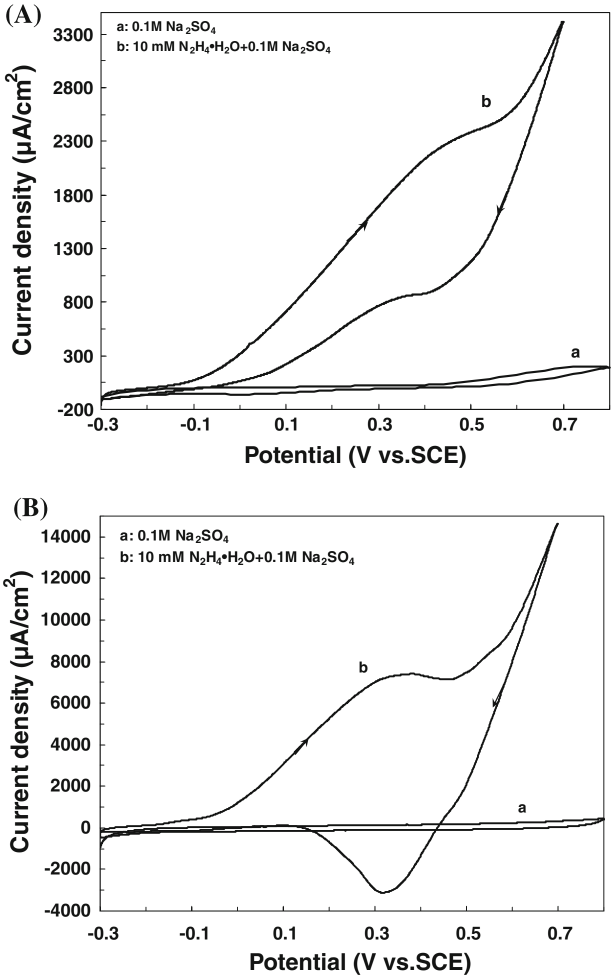

Fig. 5 Cyclic voltammograms of flat silver electrode (**A**) and silver nanoparticles/PAni/Ti electrode (**B**) in 0.1 M Na_2SO_4 aqueous solution without hydrazine (*a*) and at present 10 mM $N_2H_4{\cdot}H_2O$ (*b*) at 25 °C with a scan rate of 100 mV s^{-1}

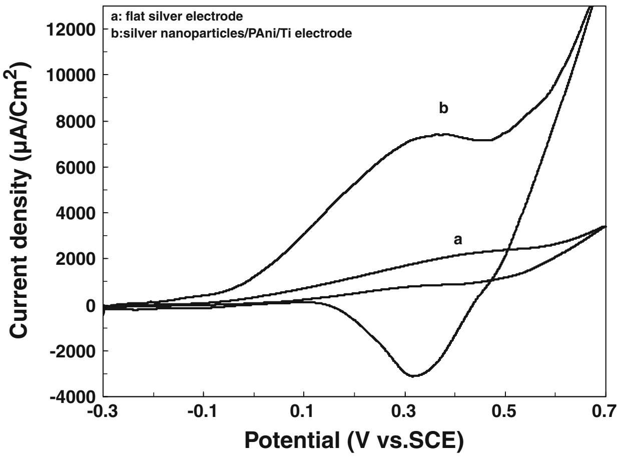

Fig. 6 Cyclic voltammograms for silver nanoparticles/PAni/Ti and flat silver electrodes in 10 mM $N_2H_4{\cdot}H_2O$ + 0.1 M Na_2SO_4 at 25 °C with a scan rate of 100 mV s^{-1}

voltammetry data were recorded for 1 cm^2 silver nanoparticles/PAni/Ti electrode in 0.1 M Na_2SO_4 aqueous solution, at a scan rate of 100 mV s^{-1} without hydrazine (a) and at present 10 mM $N_2H_4{\cdot}H_2O$ (b) as shown in Fig. 5B. Figure 6 shows the comparison of oxidation hydrazine on flat silver electrode and silver nanoparticles/PAni/Ti electrode. It can be seen from Fig. 6 that the current density for hydrazine oxidation on silver nanoparticles/PAni/Ti electrode is greater than that observed for flat silver electrode, indicating the surface area of silver nanoparticles/PAni/Ti electrode was enlarged by dispersion silver nanoparticles in polyaniline matrix. In addition to clarify if the increase of the specific area is the only factor to explain the increase of the oxidation current or the modification of the electrode provides new reaction pathways, decreasing the activation energy barrier of the reaction; the temperature dependency of hydrazine oxidation on flat silver electrode and silver nanoparticles/PAni/Ti electrode were investigated in the temperature range of 278–318 K by the method of differential pulse voltammetry (DPV) and Arrhenius plots for the anodic current of hydrazine oxidation on both electrodes showed a linear correlation is obtained between ln *i* and 1/*T*, the apparent activation energy for silver nanoparticles/PAni/Ti electrode was found to be lower than flat silver electrode. Thus, increasing of the specific area and decreasing of activation energy are two parameters that increased the oxidation current.

Effect of scan rate

To study the electro-oxidation mechanism of hydrazine on silver nanoparticles/PAni/Ti electrode, the cyclic voltammetric curves were recorded at different scan rates in 10 mM $N_2H_4{\cdot}H_2O$ + 0.1 M Na_2SO_4 aqueous solutions in the potential range of −300 mV to +700 mV as shown in Fig. 7. It can be seen that the peak current is proportional to the potential scan rate. To investigate the electro-catalytic reaction mechanism of hydrazine oxidation on silver nanoparticles/PAni/Ti electrode, diagram of peak current i_p versus square root of scan rate $v^{1/2}$ was constructed. As known in the precondition semi-infinite linear diffusion, peak current i_p was related to scan rate through the following equation:

$$i_p = \left(2.99 \times 10^5\right) n (\alpha n_a)^{1/2} A C_o D_o^{1/2} v^{1/2} \tag{1}$$

where i_p: peak current, v: scan rate, n: number of electrons transferred, α: coefficient of electron transfer, C_o: bulk concentration of substrate, D_o: diffusion coefficient, A: the electrode surface area. If the concentration C_o is hold constant, the peak current i_p is linearly proportional to the square root of scan rate $v^{1/2}$. While the scan rate is kept

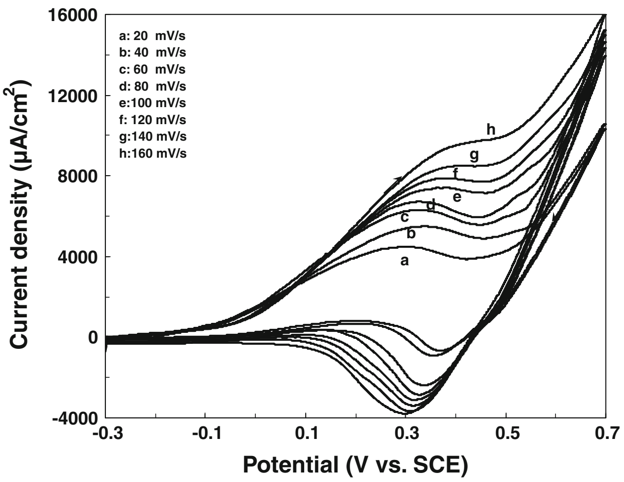

Fig. 7 The cyclic voltammograms for silver nanoparticles/PAni/Ti electrode in 10 mM $N_2H_4 \cdot H_2O$ + 0.1 M Na_2SO_4 at different scan rate

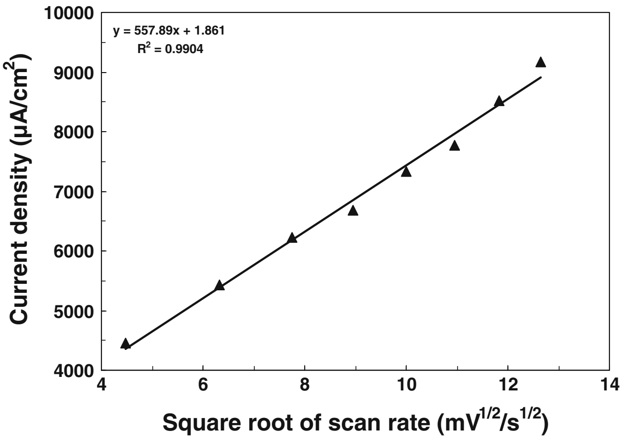

Fig. 8 The plot of hydrazine oxidation peak current on the silver nanoparticles/PAni/Ti electrode versus $v^{1/2}$

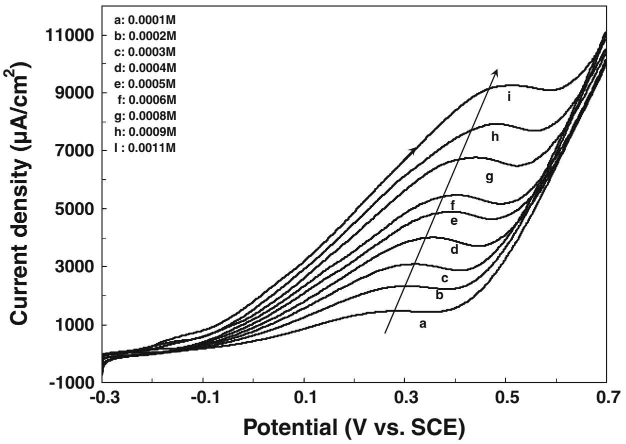

Fig. 9 The linear-sweep voltammograms of silver nanoparticles/PAni/Ti electrode in 0.1 M Na_2SO_4 solution with different concentrations of hydrazine (from 0.1 to 1.1 mM)

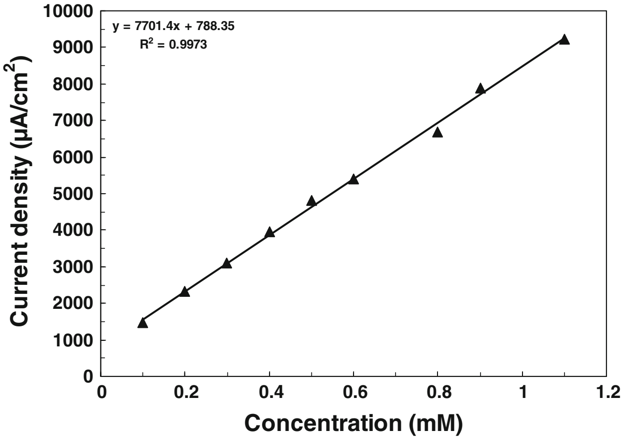

Fig. 10 The plot of hydrazine oxidation peak current on the silver nanoparticles/PAni/Ti electrode versus concentration of hydrazine

constant, the peak current i_p is linearly proportional to the concentration C_o, which indicates that the reaction is controlled by diffusion. It is seen from Fig. 8 that the peak current i_p is linearly related to the square root of scan rate $v^{1/2}$ and the correlation coefficient is $R^2 = 0.99$, which ensures that the oxidation process of hydrazine on the silver nanoparticles/PAni/Ti electrode is a controlled diffusion process.

Electro-catalytic determination of hydrazine

Effect of hydrazine concentration on the linear-sweep voltammetric response of silver nanoparticles/PAni/Ti electrode was investigated. Figure 9 shows the linear-sweep voltammograms of the silver nanoparticles/PAni/Ti electrode at the presence of various concentrations of hydrazine. The observed anodic peak current increases with increasing hydrazine concentration in the solution. This catalytic peak current shown a linear relationship with the concentration of hydrazine in the range of 0.1–1.1 mM with a correlation coefficient of $R^2 = 0.99$ (Fig. 10). Compared to modified carbon electrodes requiring tedious preparations and pretreatment procedures, silver nanoparticles/PAni/Ti electrode can easily be prepared without any further need to modification, thus from a practical point of view can be applied for the quantitative determination of hydrazine.

The effect of temperature on hydrazine oxidation at silver nanoparticles/PAni/Ti electrode

Temperature is one of the most important factors affecting the reaction rate. In order to study electro-catalytic performance of silver nanoparticles/PAni/Ti electrodes on the

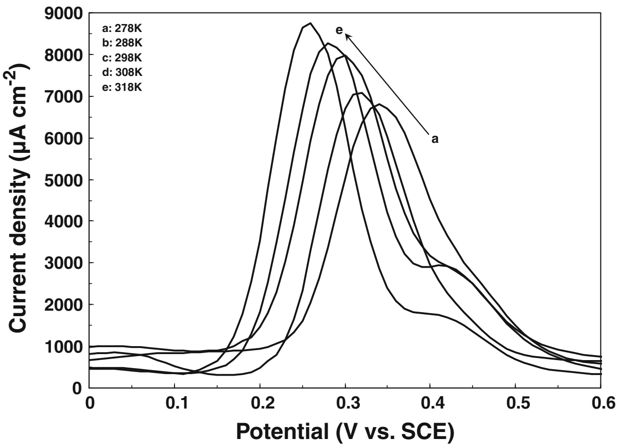

Fig. 11 The effect of temperature on differential pulse voltammograms of hydrazine oxidation on silver nanoparticles/PAni/Ti electrode in the range of 278–318 K

electrolyte temperature (T_{el}) and determination of activation energy, the temperature dependency of hydrazine oxidation on silver nanoparticles/PAni/Ti electrode was investigated in the temperature range of 278–318 K by the method of DPV. From Fig. 11, it can be seen that anodic current increase with temperature. Also, as can be seen from Fig. 11, increase in temperature leads to a shift of anodic peak toward more negative potentials due to the more feasibility of oxidation at elevated temperatures. Figure 12 presents the relationship between the experimental temperature and the hydrazine electro-oxidation current density. As the temperature increases, the electro-oxidation current density increases. This is attributed to the increase in the rate of charge transfer at electrode/electrolyte interface. At the same time, high temperature will decrease the increases diffusion phenomena, so higher electro-oxidation currents could be obtained. Figure 13 shows Arrhenius plot for the anodic current of hydrazine oxidation on silver nanoparticles/PAni/Ti electrode. Linear correlation is obtained upon plotting ln *i* versus 1/*T*. According to following equation [37]:

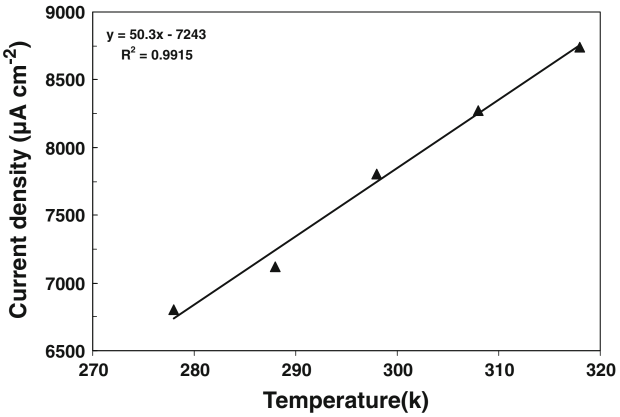

Fig. 12 Relationship between electro-oxidation current density and temperature

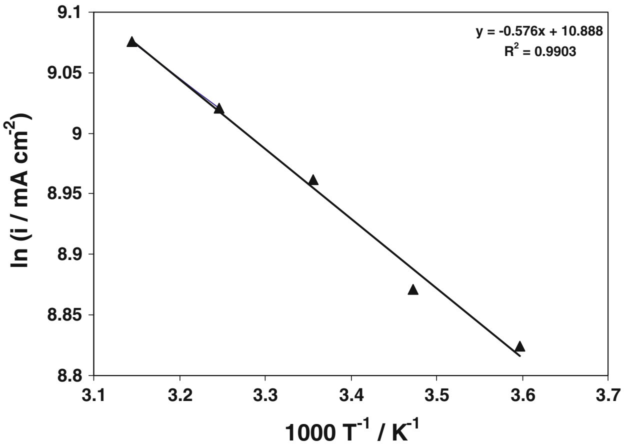

Fig. 13 Arrhenius plot for the anodic current of hydrazine oxidation on silver nanoparticles/PAni/Ti electrode

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

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

From plotting ln *i* versus 1/*T*, slope = $-E_a/R$.

And as well as in Fig. 13 for silver nanoparticles/PAni/Ti electrode, we have; slope = $-\mathrm{E_a}/R = -0.576$, so $E_a = 4.789\ \mathrm{kJ\ mol^{-1}}$.

Conclusion

A novel synthesis route for preparing silver nanoparticles highly dispersed on the surfaces of PAni/Ti electrode has been developed with the aim of the electro-oxidation of hydrazine. The electro-catalytic activity of the silver nanoparticles/PAni/Ti electrodes and pure silver toward hydrazine oxidation was evaluated through cyclic voltammetry. The electrochemical evaluations showed that PAni/Ti electrodes modified with silver nanoparticles are highly active for electro-catalytic oxidation of hydrazine. The oxidation kinetic of hydrazine was also studied by varying the potential scan rate. The results indicated that the oxidation process is mass transfer controlled. Finally, the oxidation current of hydrazine Silver nanoparticles/PAni/Ti electrodes was used for the determination of hydrazine in aqueous solution and a linear calibration curve was found in the range of 0.1–1.1 mM with a correlation coefficient of 0.99.

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