CHAPTER THREE

Synthesis and applications of Pd-TiO_2-SiO_2 nanocomposite

This chapter deals with synthesis and characterization of Pd-TiO_2-SiO_2 nanocomposite further investigations have been made to verify the quality of present nanocomposite material in the development of electrochemical sensor for ascorbic acid.

3.1. INTRODUCTION

The requirement of nanomaterial in electrochemical sensors design has great significance from technological angles, because nanomaterial have better physical and chemical properties such as high catalytic activity, specific optical and mechanical properties in comparison to bulk material [Rahman et al., (2013)]. Titanium dioxide is the most extensively studied metal oxide semiconductor, discussed in literature, which is primarily owing to its excellent photocatalytic properties and chemical stability [Hwang et al., (2012); Liu, Shengwei et al., (2010a); Shang et al., (2012)]. It is utilized not only as a photocatalyst but also in solar cells [Braga et al., (2011); Kim, Hui-Seon et al., (2013)] and water splitting [Wang, Gongming et al., (2011)], because light induces charge separation on the surface of the semiconductor, resulting in the generation of electrons and holes on the surface. Nano sized titanium oxide have efficient photocatalytic properties for pollution degradation [Liu, Tong-xu et al., (2010b); Yuan et al., (2012)], water splitting [Asai et al., (2014)], antibacterial activity [Chen, Wei-Yu et al., (2010b)], decomposition of dyes [O'Regan et al., (2000)], solar cells [Kim, Hyunjin, (2010)], sensors [Qiu et al., (2011); Singh, Sujatha et al., (2012b); Wang, Guang-Li et al., (2009); Wu et al., (2014)] and electrochromic devices [Chen, Jing-Zhi et al., (2012a)] and also used in self-cleaning windows [Wilkinson et al., (2013)].

Noble metals are high-effective oxidation catalysts and this ability can be used to enhance the reactions on surfaces of electrochemical sensors. A wide diversity of methods, including impregnation, sol-gel, sputtering and thermal evaporation, has been used for introducing noble metal additives into oxide semiconductors. Different doping states can be obtained by different methods. Mixture of noble metal particles and metal oxides may be obtained by sol-gel method, while metal oxides modified by noble metal particles on the surface are possibly obtained by sputtering or thermal evaporation. There have been many reports for enhancement of sensitivity modified by noble metals, such as Pt, Au, Pd, Ag, etc. [Nie et al., (2013); Wang, Chengxiang et al., (2010); Zhang, Jun et al., (2012b); Zhu et al., (2012)].

M@TiO_2 (M = Ag, Pd, Au, Pt) nanocomposite particles with a diameter of 200–400 nm can be synthesized on a large scale by a clean photochemical route. The sizes of Pt, Au, and Pd nanoparticles formed on the surface of TiO_2 particles are about 1 nm, 5 nm, and 5 nm, respectively, and the diameter of Ag nanoparticles is in the range 2–20 nm. Moreover, the noble metal nanoparticles have good dispersity on the particles of the TiO_2 support, resulting in excellent catalytic activities [Chen, Shao Feng et al., (2010a)]. The coreshell nanocomposites of M@TiO_2 (M = Au, Pd, Pt) have been synthesized successfully via a facile hydrothermal treatment of TiF_4 precursor and noble metal colloid particles [Zhang, Nan et al., (2011)]. They also studied the incorporation of metal core into the shell of TiO_2 will inhibit the photocorrison behaviour and provide much better photocatalytic stability of M@TiO_2 (M = Au, Pd, Pt) nanocomposites than the bare TiO_2.

The metal oxide/silicon oxide nanocomposites were easily prepared through novel sol-gel process in which the metal oxide is the major component. In addition, due to the large availability of organically functionalized silanes, the silicon oxide phase can be used as a unique way of introducing organic additives into the metal oxide materials. In the course of preparation, particles obtained by hydrolysis have to be stabilized in order to prevent coagulation. Materials earlier used for stabilization were surfactants and microemulsions. For example, metal hydroxide nanoparticles may be synthesized in the aqueous medium enclosed in the droplets of microemulsions of the water/ oil type; the nanoparticles formed are protected from coagulation by the surfactant stabilizing the droplet, making possible the preparation of nanoparticles with diameters of 20–50 nm. TiO_2/SiO_2 nanocomposite also used as catalysts and photocatalyst for various reactions [Park et al., (2011)], annealed TiO_2 and SiO_2 used as anti-reflecting coating in high efficiency solar cell [Diedenhofen et al., (2014)]. Incorporation of nano size palladium (Pd) significantly increases the catalytic activity of materials and has been one of the attractive requirements for generating materials for electrochemical sensors design and has been one of the active areas of material preparation [Chen, Xiaomei et al., (2011); Zhang, HUI et al., (2012a); Zhao, Jiayue et al., (2011)].

We have studied the interaction of palladium chloride and 3-Glycidoxypropyltrimethoxysilane where Pd was reduced resulting Pd-linked 3-glycidoxypropyltrimethoxysilane [Pandey et al., (2001a)] and has been used for making organically modified silicate based electrocatalytic sensors. The reaction product of palladium chloride and 3-glycidoxypropyltrimethoxysilane is found compatible with the reaction product of titanium isoporpoxide and could be used for making nanocomposite of Pd/TiO_2/SiO_2 through sol-gel processing. Accordingly it was planned to prepare a composite of hydrolyzed reaction product of titanium isopropoxide and Pd-linked 3-glycidoxypropyltrimethoxysilane via sonication and calcination at optimum temperature that may form Pd/TiO_2/SiO_2 nanocomposite suitable for designing modified electrode as such material may facilitate electrocatalysis of AA oxidation which has been undertaken in present investigation.

Several approaches are used in the design of electrochemical sensor for detection of ascorbic acid. Recently a nonenzymatic amperometric detection of ascorbic acid (AA) using a glassy carbon (GC) disk electrode modified with hollow gold/ruthenium (hAu-Ru) nanoshells, which exhibited decent sensing characteristics [Jo et al., (2014)]. A new electrochemical sensor based on carbon-supported $NiCoO_2$ nanoparticles was prepared for selective detection of ascorbic acid (AA) [Zhang, X. et al., (2014)]. The sensor also exhibited successfully application in the determination of AA in real samples, including vitamin C tablet and orange juices [Kong et al., (2014)]. The simultaneous determination of ascorbic acid (AA), dopamine (DA), uric acid (UA) and tryptophan (TRP) was conducted on multi-walled carbon nanotubes bridged mesocellular graphene foam nanocomposite (MWNTs/MGF) modified glassy carbon electrodeLi, H. et al., (2014). The streptavidin-conjugated alkaline phosphatase (SA-ALP) was linked to the biotinylated aptamer II and catalyze hydrolyzation reaction of ascorbic acid 2-phosphate to produce ascorbic acid, which was detected by differential pulse voltammetry [Xu, F. et al., (2013)]. Some highly responsive ascorbic acid (AA) sensor utilizing over Palladium nanoparticles (PdNPs) composites was reported [Shi et al., (2012); Wang, X. et al., (2013)].

Electrode modified with metal oxide and their nanocomposites have also been studied for the determination of ascorbic acid [Kurihara et al., (2004); Mazloum-Ardakani et al., (2010)]. However, there is still a lack of reports available in the literature concerning the work based on TiO_2 with organically modified silicate and nanometal for the analysis of AA. Since the determination of ascorbic acid (AA) in biological fluids using electrochemical sensors is the subject of wide interest due to its consumption on a large scale as an antioxidant in food, beverages and in medicines [Jo et al., (2014); Kong et al., (2014); Reddaiah et al., (2013)]. Accordingly, in the present section, the biocompatibility of Pd-TiO_2-SiO_2 nanocomposite has directed our attention to understand the electroanalysis of biologically active analyte. It was planned to understand the electrocatalysis of ascorbic acid at Pd-TiO_2-SiO_2 modified electrode which has been reported in the present investigation. The application in the electrocatalytic oxidation of ascorbic acid based on cyclic voltammetry and amperometry measurements are discussed here.

3.2. EXPERIMENTAL

3.2.1. Materials

All the reagent used were analytical grade and used without further purification including Titanium isopropoxide (Aldrich), $PdCl_2$ (Aldrich), 3-Glycidoxypropyltrimethoxysilane (United Chem. Technol. Inc., Pertach^{TM}), Isopropanol [Thomas Baker (Chemical) Ltd. Mumbai], HNO_3 (Merk) and L-Ascorbic acid (Sisco Research Laboratories Pvt. Ltd. Mumbai), graphite powder (particle size 1–2 μm) and Nujol oil (density 0.838) were obtained from Aldrich Chemical Co. The water used in experiments is double distilled-deionized water (Alga water purification system). All electrochemical experiment were conducted in 0.1 molar phosphate buffer solution (pH 7.0) containing 0.5 M KCl.

3.2.2. Preparation of Pd-TiO_2-SiO_2 nanocomposite

Preparation of TiO_2 nanoparticle: Titanium isopropoxide was diluted in isopropanol and added in 0.3 M HNO_3 dropwise and let to be peptized 24 hours. The precipitate (titanic acid gel) was collected by filtration and washed with double distilled-deionized water three times to remove the iso-propanol solvent. The obtained gel was dried at 120 ºC followed by calcination at temperatures of 600 (Figure 3.1a) and 900 ºC for 3 h [26].

Preparation of Pd-TiO_2-SiO_2 nanocomposite: 0.5 M solution of titanium isopropoxide diluted in isopropanol was added drop-wise to 0.3 M HNO_3 aqueous solutions. The resulting titania sol (500 ml) was mixed with 75 μL palladium linked 3-glycidoxypropyltrimethoxysilane and stirred for 10 min followed by ultrasonication for 30 min. Palladium linked 3-glycidoxypropyltrimethoxysilane was made by adding 25 mL aqueous solution of palladium chloride (1 mg/mL) in 50 mL of 3-glycidoxyp ropyltrimethoxysilane. The resulting sol was washed several time to remove the solvent and dried at 120 ºC followed by calcination at temperatures 600 and 900 ºC (Figure 3.1b) for 3 h.

3.2.3. Instruments

Transmission electron microscopy (TEM) studies were performed using Hitachi 800 and 8100 electron microscopes (Tokyo, Japan) with an acceleration voltage of 200 kV. Energy dispersive spectroscopic (EDS) analysis was conducted with ZEISS SUPRA 40 (oxford) operating at 20 keV to perform the quantitative analysis of material. The X-ray powder diffraction patterns were obtained on Rigaku miniflex diffractometer using nickel filtered Cu Kα (λ= 0.15406 nm) radiation. Identification of the phase was made with the help of the JCPDS files. FTIR Spectra were performed on Perkin Elmer spectrum 100 in the range of 400 cm^{-1} to 4000 cm^{-1}. UV-Visible spectra were obtained through Ocean optics HR 2000 spectrophotometer assembled with DT 1000 CE power source. Cyclic voltammetry and amperometry were performed on an electrochemical workstation CHI 660B (CH Instruments, USA) in a three-electrode cell configuration with a working volume of 3 mL. An Ag/AgCl electrode (3 M KCl saturated with Ag/AgCl) and a platinum plate electrode served as reference and counter electrode respectively. All potentials given below were relative to the Ag/AgCl. The working electrode was a graphite paste electrode.

3.2.4. Preparation of modified electrode

The graphite paste electrode body used for the construction of modified electrode was obtained from Bio analytical systems (West Lafayette, IN; (MF 2010)). The well of electrode body was filled with active paste made by mixing graphite powder, TiO_2, and Pd-TiO_2-SiO_2 powder using nujol. The composition of active paste was TiO_2 and Pd-TiO_2-SiO_2 = 1% (w/w), graphite powder = 69% (w/w) and nujol oil = 30% (w/w). The mixture was homogenized in the blender and stored in a stoppard glass vial at room temperature or at 4°C in case of enzyme electrode when not in use. The paste surface was manually smoothened on a clean paper.

3.3. RESULT AND DISCUSSION

3.3.1 XRD Analysis

XRD was used for the identification of crystalline structure of the TiO_2 and Pd-TiO_2-SiO_2 nanocomposite. The gel of TiO_2 calcined at 600 °C exhibited well known peaks at 2θ = 25.22°, 37.78°, 47.82°, 53.82°, 54.86°, 62.5° which is denoted to the (101), (004), (200), (105), (211), (204) planes of anatase TiO_2 (Figure 3.2 a), and at 900 °C peak at 2θ= 27°, 36°, 41.5°, which is denoted to the (110), (101), (111), planes of rutile TiO_2 (Figure 3.2 a). The gel of Pd-TiO_2-SiO_2 nanocomposite calcined at 600 °C shows amorphous nature (Figure 3.3 a) of composite material and at 900 °C exhibited all the peaks of anatase shows in

Figure 3.3 b but peaks of rutile phase of TiO_2 was diminished and represent the phase transformation of composite material, The characteristic peaks of Pd nanoparticles at 40.1°, 46.6° and 68.1°, which corresponded to (111), (110) and (100) crystalline plane of Pd, were merged with the characteristic peaks of TiO_2.The XRD represent the some amorphous nature of composite material due to the presence of SiO_2 content.

3.3.2. Morphology and Chemical nature of Pd-TiO_2-SiO_2 nanocomposite

The morphology of Pd-TiO_2-SiO_2 nanoparticles was analysed by transmission electron microscopy (TEM). Characterisation shows the microstructure of Pd-TiO_2-SiO_2 nanoparticles calcinated at 900 °C. It can be seen that the average size of Pd-TiO_2-SiO_2 spherical nanoparticles was about 100 nm (Figure 3.4 b). Whereas TEM of TiO_2 nanopaticles calcined at 900 °C shows average particle size of 50 nm (Figure 3.4 a). The shape of TiO_2 nanoparticle shows spherical geometry, however agglomeration of nanoparticle occurs. The agglomeration decreases due to presence of SiO_2 matrix in Pd-TiO_2-SiO_2 nanoparticles and shows well-ordered spherical geometry. Figure 3.5 shows the SEM images of TiO_2 nanoparticles (a) and Pd-TiO_2-SiO_2 nanocomposite (b) also confirmed the particular performance of large surface-to-volume ratio. The chemical nature of material represented in EDS (Figure 3.6) and described in Table 3.1 from elemental composition of the composite material have Pd 0.46 % w/w.

Table 3.2. EDS data of Pd-TiO_2-SiO_2 nanocomposite.

Element	Weight %	Atomic %
O K	59.18	73.61
Si K	21.52	15.25
Ti K	27.00	11.22
Pd L	0.46	0.06
Total	118.16	

3.3.3. FTIR spectral analysis

IR spectra of Pd-TiO_2-SiO_2 composite shown in Figure 3.7 represents the peaks at 815 cm^{-1} corresponding to symmetrical stretching vibration of the SiO_2, Ti-O stretching in TiO_2 correspond to peak at 713 cm-1 and vibration of the Si-O-Ti and Si-OH at 952 cm^{-1}.The Pd-TiO_2-SiO_2 composite was made having similar ratio of TiO_2 and SiO_2, the corresponding peaks at 952 and 1026 cm^{-1} represent equal composition and is confirmed by EDS data (Table 3.1.). The peaks at 1600 and 3400 cm-1 correspond to bending vibration of adsorbed H_2O molecule.

3.3.4. Electrochemical analysis

We studied the electrochemistry of Pd-TiO_2-SiO_2 and pure Pd electrodes in 1M H_2SO_4 and the results are shown in Figure 3.8 (a) and (b). Figure 3.8 (a) shows that of the pure Pd whereas Figure 3.8(b) shows the cyclic voltammogram (CV) of Pd-TiO_2-SiO_2. In both cases CV was performed over a carbon paste electrode containing 1 %of the respective materials as modifiers. The voltammograms shown in Figure 3.8 a and b justify that CV of pure Pd shows a well defined redox couple of oxygen adsorption (at~ 0.538 V) and stripping (at ~ 0.418 V) during anodic and cathodic scans respectively. These results are consistent with that reported for electrodeposited Pd in H_2SO_4 [Guerin and Attard, (2001)]. The CV of Pd-TiO_2-SiO_2 (Figure 3.8 b) also shows redox behaviour at identical potential values as that in Figure 3.8 (a) but this is not as prominent as that of the former which may be due to the interaction of Pd with TiO_2 and SiO_2 followed by composite formation. However, in both the cases the redox process observed is extremely sensitive to pH of the medium and disappears at neutral or even lower acidic pH. We did not observe this redox process at pH 7 which was the working medium for the analysis of AA.

Figure 3.1. Photograph of TiO_2 nanoparticle **(a)** and Pd-TiO_2-SiO_2 Nanocomposite **(b)**.

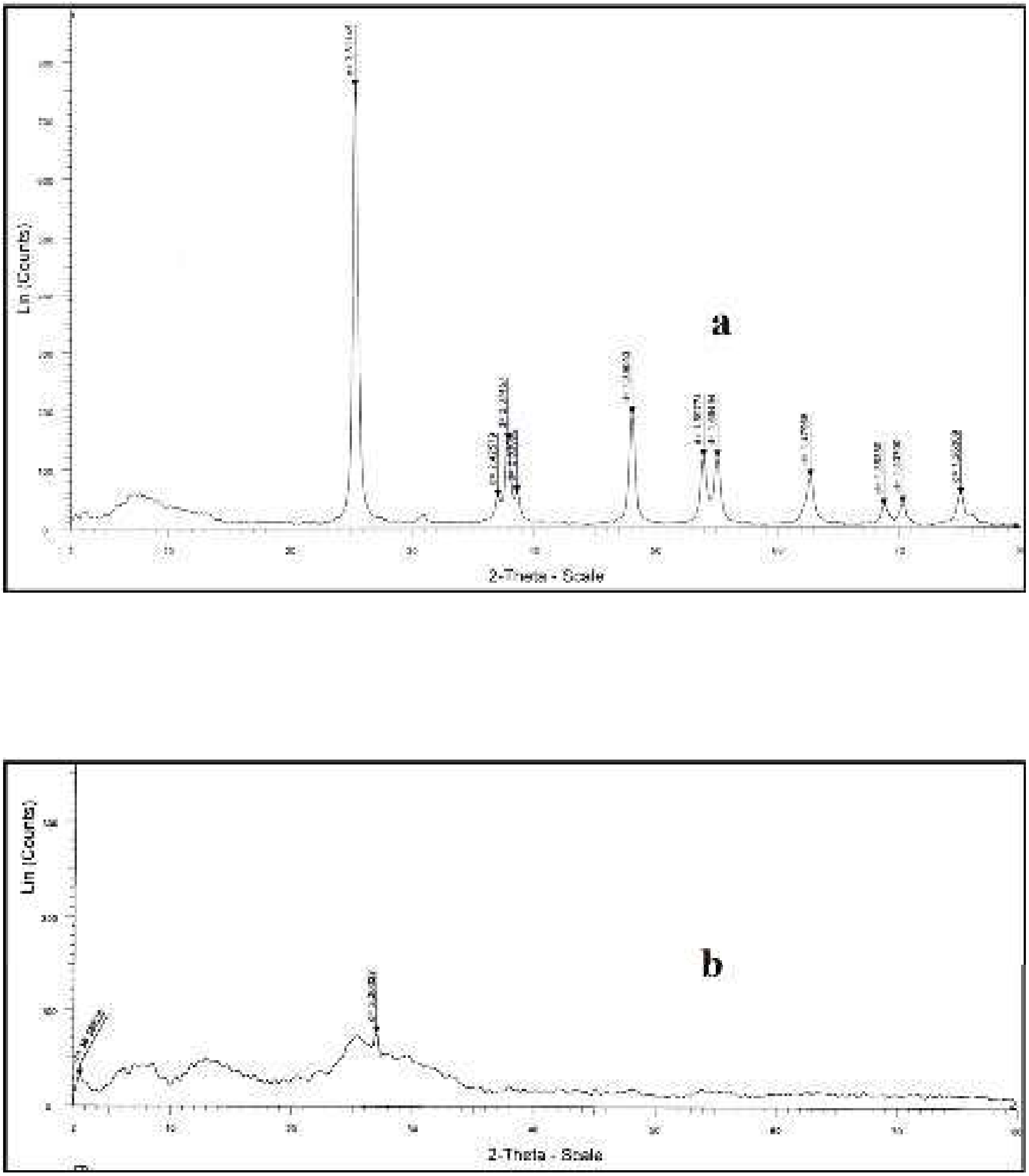

Figure 3.2. XRD of TiO_2 nanoparticle at 600 ºC **(a)** and Pd-TiO_2-SiO_2 nanocomposite at 600 ºC **(b)**

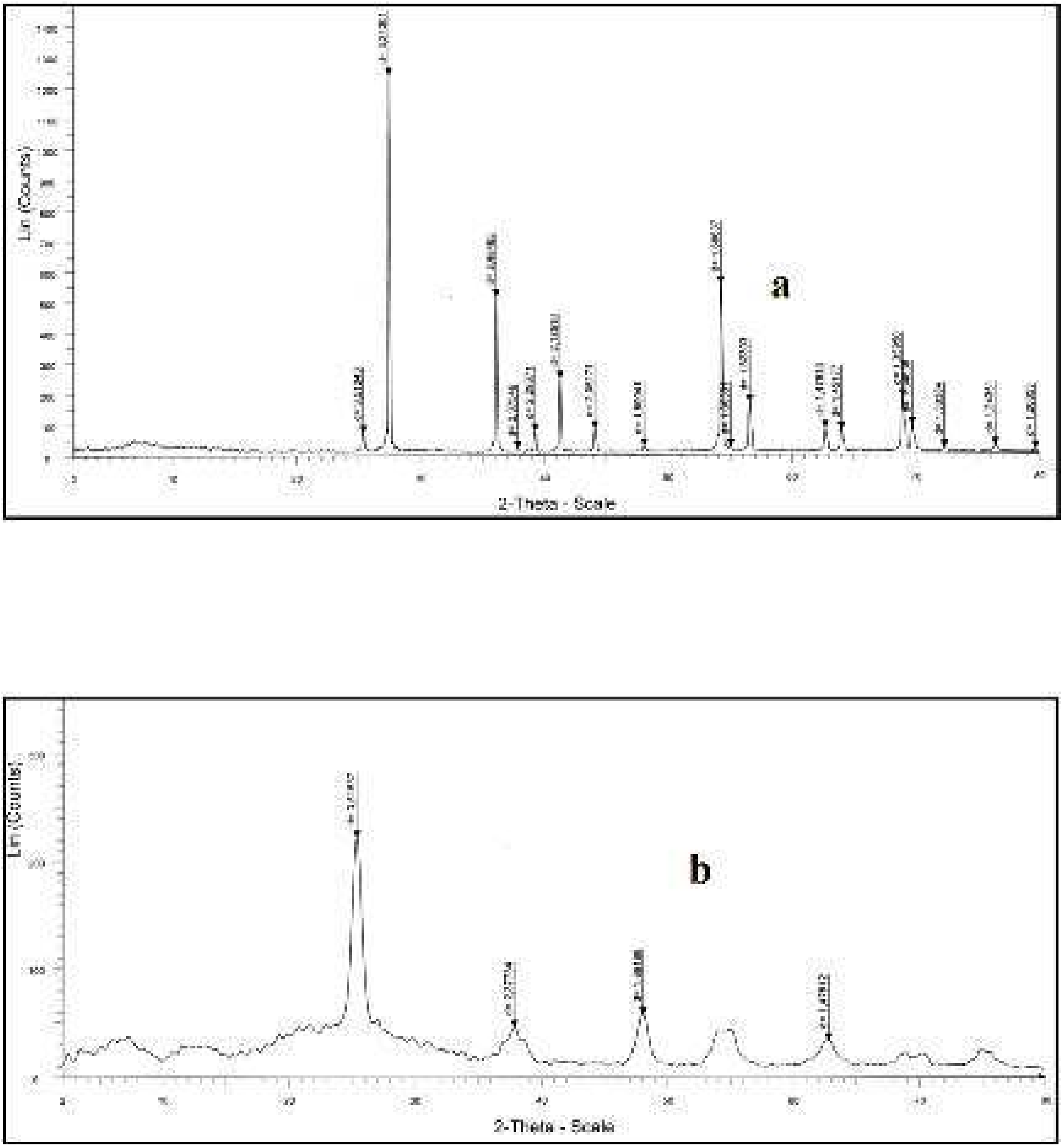

Figure 3.3. XRD of TiO_2 nanoparticle at 900 ºC **(a)** and Pd-TiO_2-SiO_2 nanocomposite at 900 ºC **(b)**

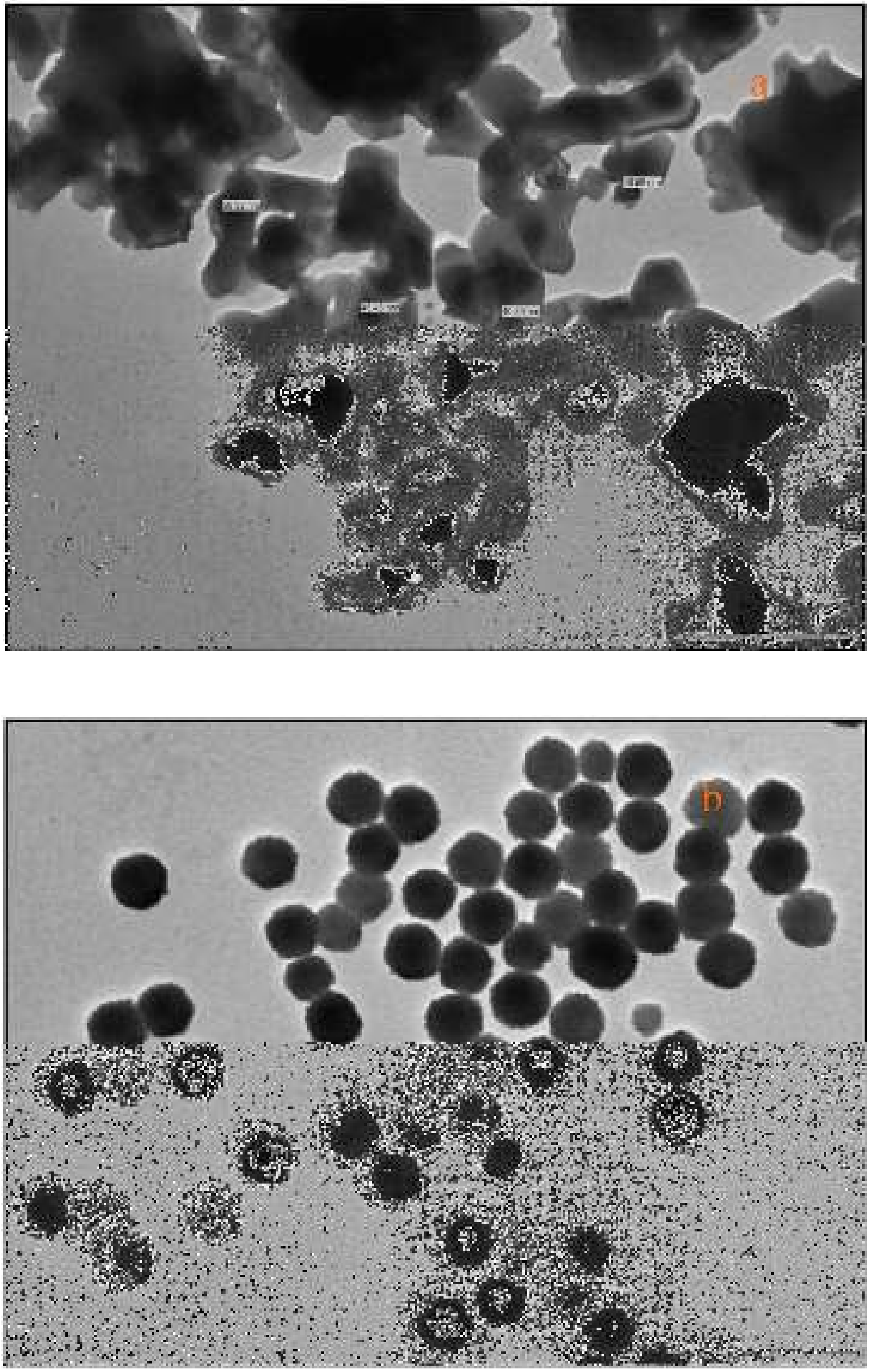

Figure 3.4. TEM image of TiO$_2$ **(a)** and Pd-TiO$_2$-SiO$_2$ **(b)** nanocomposite calcinated at 900°C.

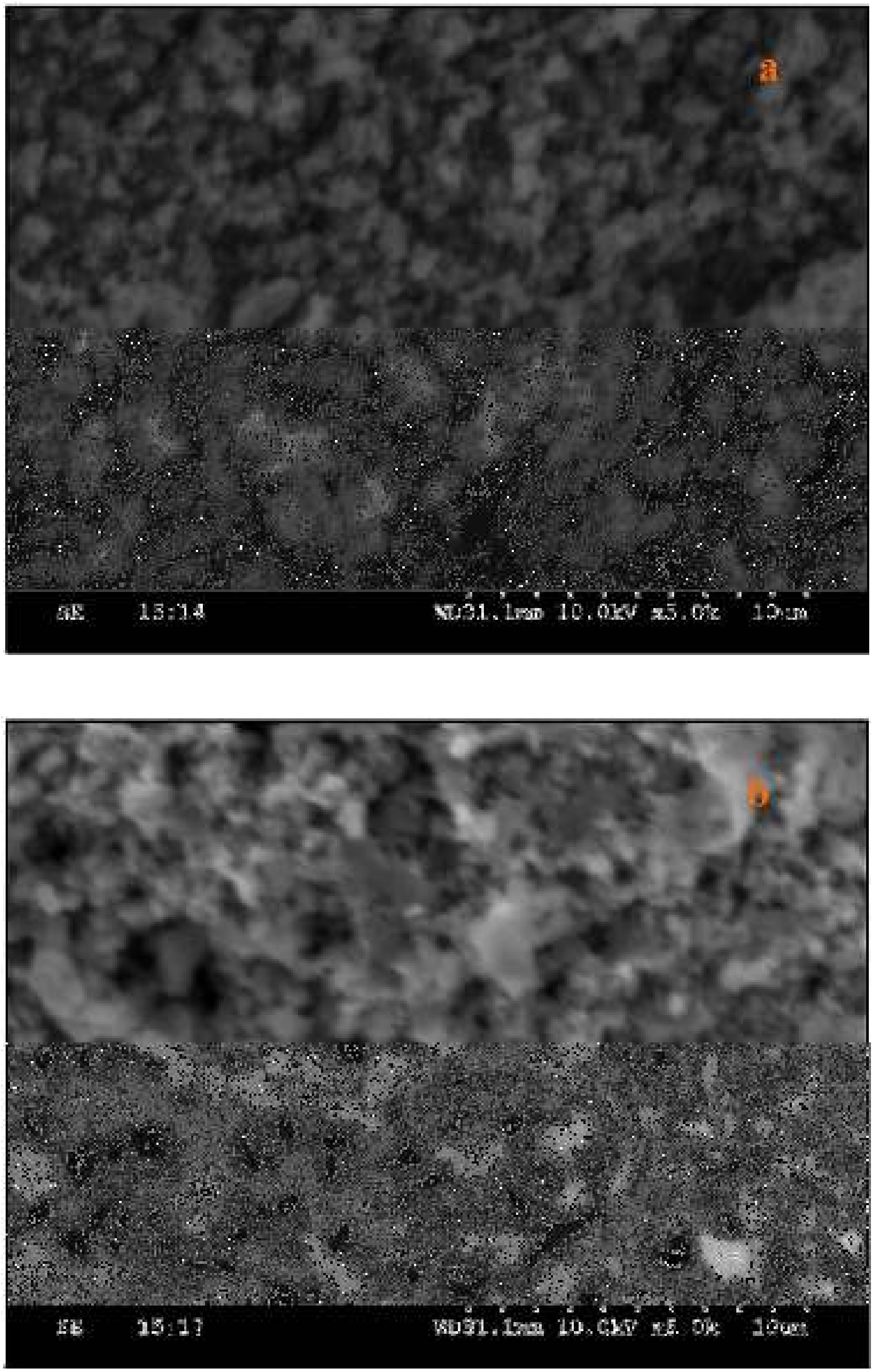

Figure 3.5. SEM image of TiO_2 nanoparticle **(a)** and Pd-TiO_2-SiO_2 nanocomposite **(b)**.

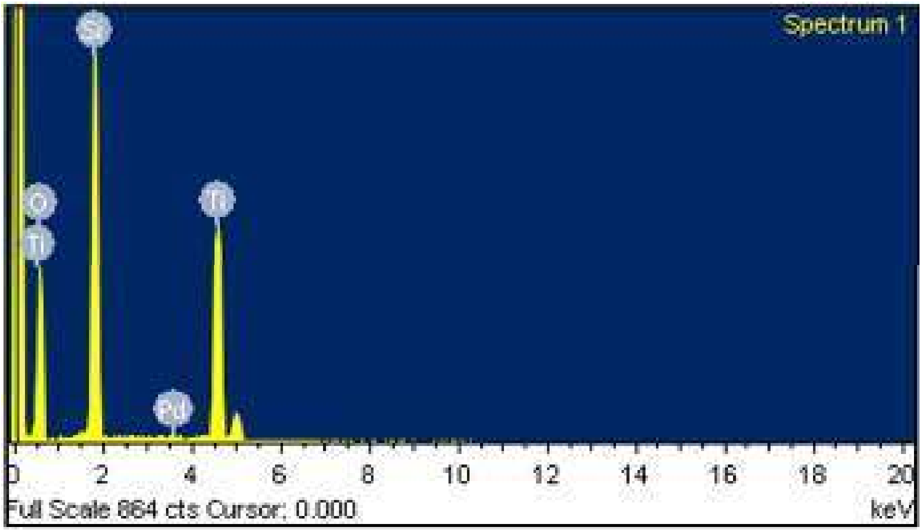

Figure 3.6. EDS spectra of Pd-TiO_2-SiO_2 nanocomposite.

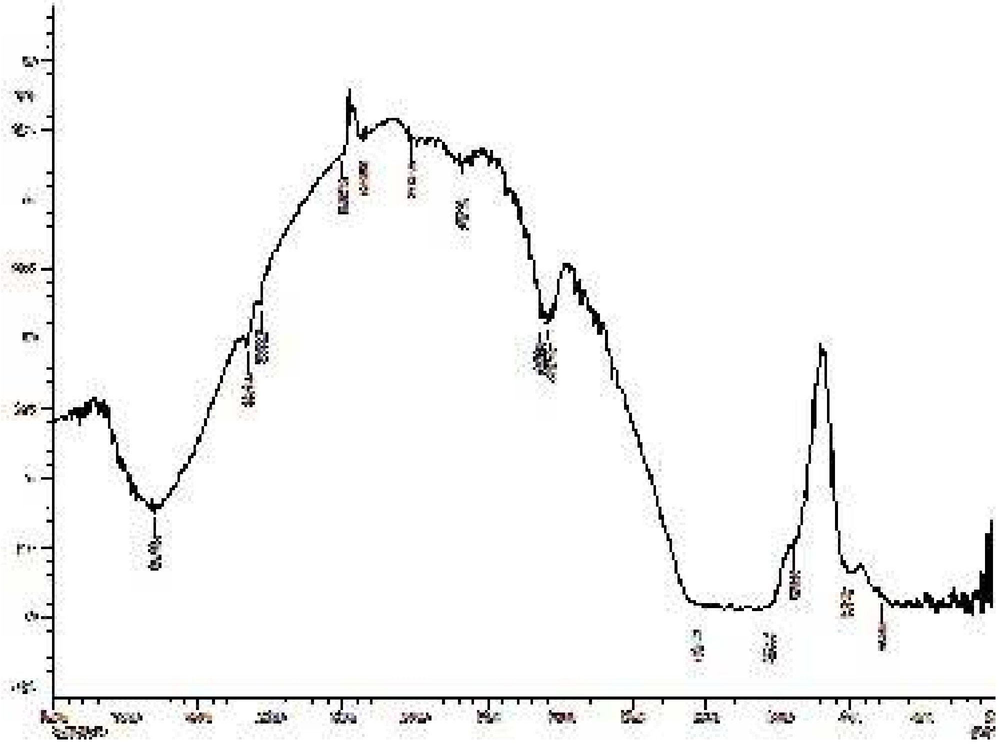

Figure 3.7. FTIR spectra of Pd-TiO_2-SiO_2 nanocomposite.

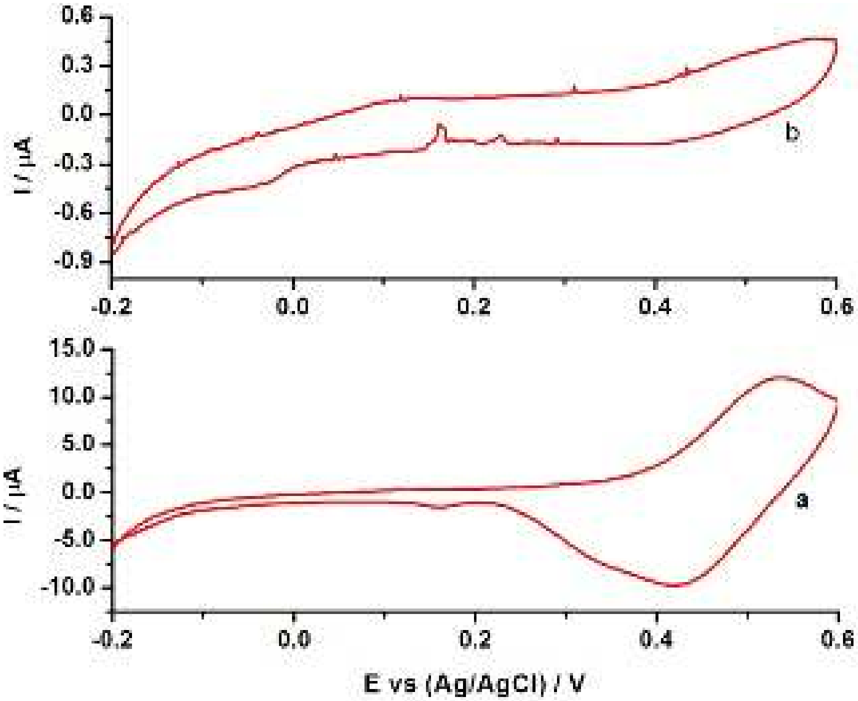

Figure 3.8. Cyclic voltammograms of pure Pd (a), Pd-TiO_2-SiO_2 (b) modified electrode in 1M H_2SO_4.

3.3.5. Electrocatalytic oxidation of ascorbic acid over modified electrode

3.3.5.1. Cyclic Voltammetry

The nanocomposite of Pd-TiO_2-SiO_2 does not show reversible redox electrochemistery in buffer however, the material acts as an efficient electrocatalyst for several analytes of biological significance. As an example we investigated the sensing ability of the Pd-TiO_2-SiO_2 nanocomposite modified graphite paste electrode towards AA and compared with bare and only TiO_2 modified graphite paste electrode. The voltammograms recorded for these three modified electrodes are shown in Figure 3.9 in the absence (a) and on the addition of 1 mM ascorbic acid (b). The values of peak currents in the presence of 1 mM ascorbic acid are found to be 3.65, 9.93 and 11.38 μA respectively for bare, only TiO_2 and Pd-TiO_2-SiO_2 modified graphite paste electrode respectively. The occurrence of remarkable variation in peak current value justifies the introduction of electrocatalysis of titanium oxide nanoparticle and Pd-TiO_2-SiO_2 nanocomposite. In the above electrocatalysis surface reaction takes place where Pd enhances the catalytic nature of TiO_2.

3.3.5.3. Amperometry

In order to study the quantitative determination of AA, the amperometric responses curve for the bare, only TiO_2 and Pd-TiO_2-SiO_2 modified graphite paste electrode were recorded on the addition of varying concentrations(1 μM to 1 mM) of AA in the phosphate buffer (0.1 M, pH= 7.0) at working potential of at 0.1 V vs Ag/AgCl (Figure 3.11). It should be noted that at such operating potential (0.1 V) the interfering analyte like uric acid does not undergo electrochemical oxidation and their contribution during amperometeric sensing of ascorbic acid is negligible (Figure 3.10). It is very much clear from the Figure 3.11 that the response was highest in case of Pd-TiO_2-SiO_2(a) followed by only TiO_2 and bare modified GP electrode again suggesting the excellent electrocatalytic behaviour of composite material towards the oxidation of AA. The calibration curves of AA detection by amperometry for bare, only TiO_2 and Pd-TiO_2-SiO_2 modified graphite paste electrodes were constructed using average currents recorded at three individual electrodes for each concentration point. Figure 3.12 shows the calibration curves for AA for bare (curve 1), for only TiO_2 (curve 2) and for Pd-TiO_2-SiO_2 (curve 3). The sensitivities towards AA was found to be 0.19 μA/mM for bare (curve 1), 0.54 μA/mM for TiO_2 (curve 2) and 2.72 μA/mM for Pd-TiO_2-SiO_2 (curve 3) modified graphite paste electrodes. The Figure 3.12 also shows the linear range for AA detection from 1μM - 1mM. Moreover, the Pd-TiO_2-SiO_2 nanocomposite sensor exhibited a linear dependence on AA concentration (R^2= .9993) with a linear range of 1μM - 1mM. These results justified the advantages of present nanocomposites in electrocatalysis.

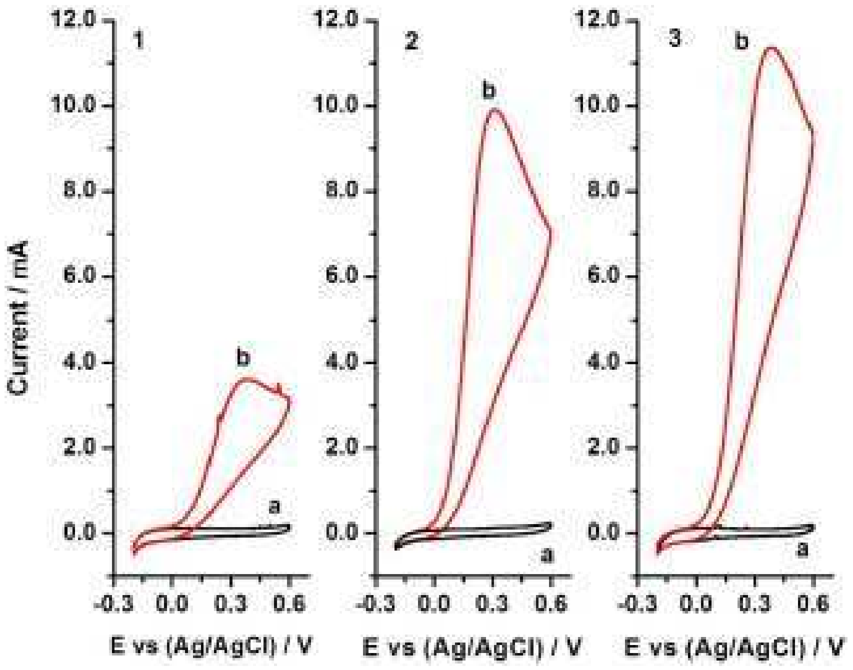

Figure 3.9. Cyclic voltammograms of bare graphite paste electrode **(1a)**, TiO_2 modified electrode **(2a)**, Pd-TiO_2-SiO_2 modified electrode **(3a)** in 0.1 M phosphate buffer, pH 7.0 at 25 0C and their response in 1 mM Ascorbic Acid **1b, 2b,3b** respectively.

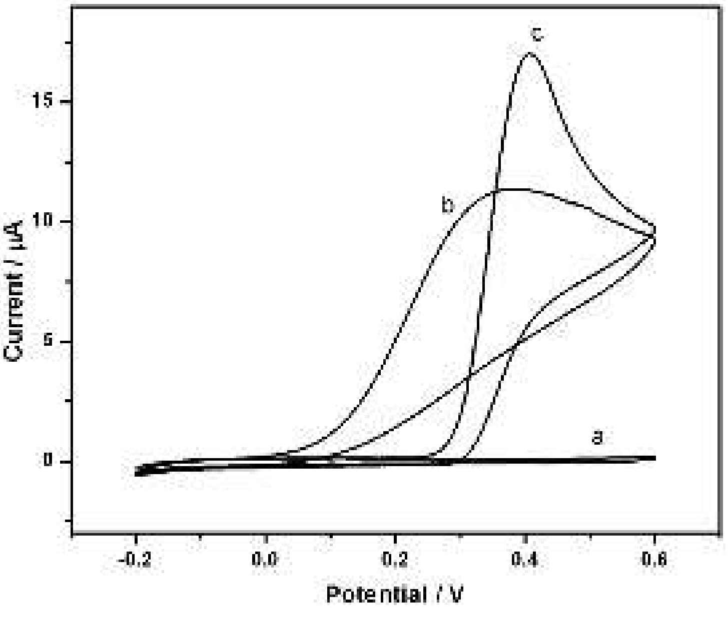

Figure 3.10. Cyclic voltammograms of bare Pd-TiO_2-SiO_2 modified electrode **(a)** in 0.1 M phosphate buffer, pH 7.0 at 25 ^{0}C and their response in 1 mM Ascorbic Acid **(b)** and response in 1 mM Uric Acid **(c)**.

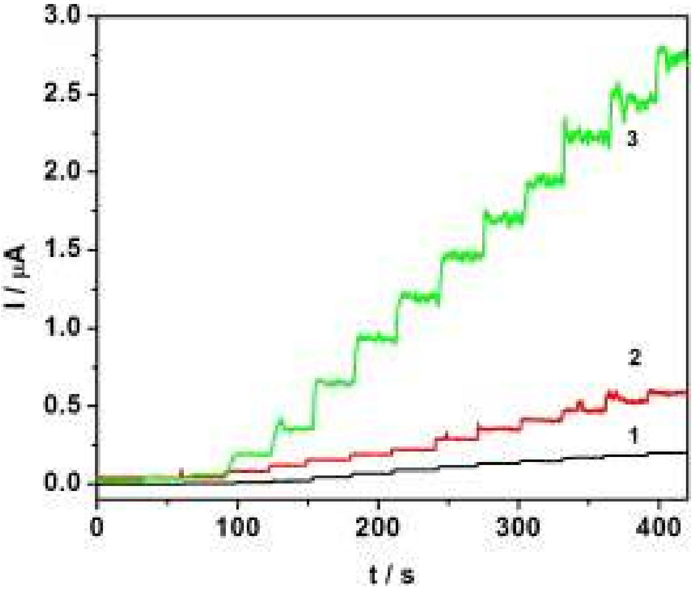

Figure 3.11. Typical amperometric responses of the bare graphite paste electrode **(a)**, TiO_2 modified electrode **(b)**, Pd-TiO_2-SiO_2(a) modified electrode **(c)** on the addition of varying concentrations (1 to 1000 µM) of ascorbic acid in 0.1 M phosphate buffer, pH 7.0 at 25°C and at 0.1 V vs Ag/AgCl.

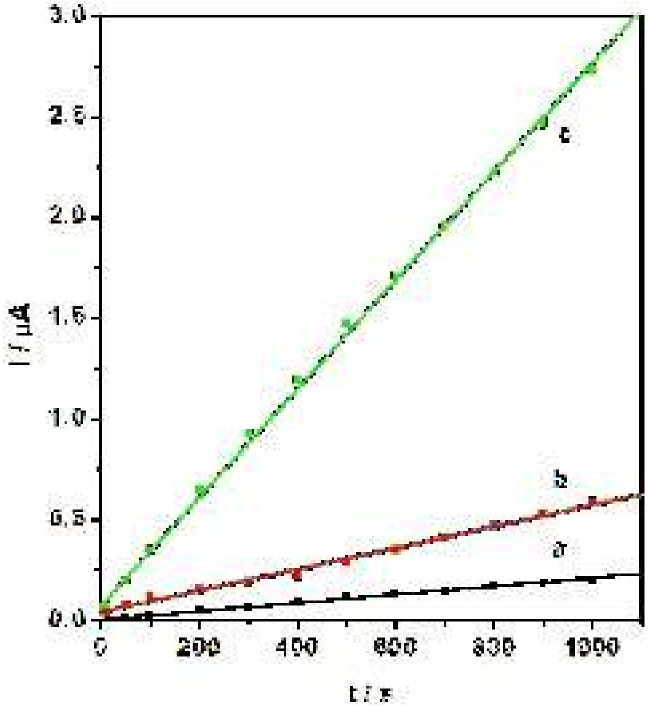

Figure 3.12. Calibration curves for the analysis of ascorbic acid using bare graphite paste electrode **(a),** TiO_2 modified **(b)** and Pd-TiO_2-SiO_2 modified **(3)** systems respectively.

3.3.5.4. Stability and reproducibility

The reproducibility of the electrode was examined by cyclic voltammetry of AA at the surface of Pd-TiO_2-SiO_2 electrode after twenty repetition cycles at 10 mV s^{-1}. Results shows that the oxidation peak potential of AA was not changed and anodic peak current was decreased by less than 2.8%. The storage stability of sensor was evaluated over a period of 30 days by storing the sensor inthe phosphate buffer (0.1 M, pH= 7.0) at room temperature. No obvious amperometric changes were observed after storing. It retained 91.6 % of its initial current after the 30 days storage.

3.4. CONCLUSION

We report in this chapter the preparation of Pd-TiO_2-SiO_2 nanocomposite having a particle size of approximate 100 nm with spherical morphology. Phase transform of TiO_2 (rutile to anatase) at 900 ºC in composite material preparation has been observed through X-ray differaction pattern in Pd-TiO_2-SiO_2 nanocomposite. The spherical morphology of nanocomposite showing in image collected by transmission electron micrography resembles the effect of SiO_2 in spite of only TiO_2 nanoparticle. The electrocatalytic activity for the oxidation of AA on TiO_2 nanoparticle and Pd-TiO_2-SiO_2 nanocomposite modified graphite paste electrode are reported in this chapter. The results based on cyclic voltammetry and amperometry justify the role of resulting Pd-TiO_2-SiO_2 modified electrode exhibits excellent electrocatalytic activity for the oxidation of AA with major findings as compared to bare and only TiO_2 modified GP electrode: (1) Pd enhances the electrocatalytic activity of TiO_2 nanoparticle (2) Pd-TiO_2-SiO_2 nanocomposites significantly increased the anodic current to the order of 11.38 μA as compared to bare and only TiO_2 modified graphite paste electrode 3.65 and 9.93 μA respectively for the oxidation of AA (3) An increase in the sensitivity of AA analysis was found to the order of 2.72 μA/mM within a linear range of 1μM -1mM at 0.1 V vs Ag/AgCl. (4) the modified electrodes posses high stability for more than 30 days with good reproducibility. Excellent sensitivity, improved detection limit and good stability and reproducibility of the present electrochemical sensor provide scope for practical application.