Chapter 4

Simultaneous Detection of AZT and NVP on 2D Materials Pd@rGO Decorated with MoS_2 Quantum Dots Modified SPGE

4.1 Introduction

HIV-1 infections or AIDS treatment is based on chemotherapy, mainly inhibiting the replication of HIV reverse transcriptase whose main function is virus replication. There are various types of drug categories available NRTI, NNRTI, protease inhibitor etc. to cure HIV-1 infections. In chemotherapy, two or more drugs are combined either from the same category or from different category because it relies on highly active anti-retroviral therapy (HAART) [Rao *et al.*, 2009]. A recent finding is to give two or more drugs in combinations to overcome various side effects of a single drug. AZT is the first NRTI drug used for the treatment of persons infected with HIV-1 infections [Hirsch *et al.*, 1993; Barone *et al.*, 1991; Hoetelmans *et al.*, 1996; Font *et al.*, 1999; Clercq *et al.*, 1994; Warnke *et al.*, 2007]. Further, this drug is given in combination with other NNRTI drugs like NVP [Rao, *et al.*, 2009; Adkins *et al.*, 1998; Hollanders *et al.*, 2000]. But due to accumulation of their by-products inside the body, there is a strong need to develop a single sensing platform to determine the concentration of both the drugs simultaneously or develop a sensor showing bifunctional activity to determine both the drug simultaneously.

Various techniques have been utilised in the literature for simultaneous detection of these drugs like HPLC, HPTLC etc. But these techniques are time consuming and complicated. So, there is a strong need to develop an electrochemical sensor which can be used to determine both the drugs with high sensitivity and also provide portability to the developed sensor. Various sensing platform are developed for the simultaneous

detection of different drugs, but there is not any report available for the simultaneous determination of anti-HIV drugs like AZT and NVP using electrochemical techniques which are frequently given in combinations to HIV patients.

In the present work, we developed a novel sensor for electrochemical determination of NVP and AZT simultaneously based on Pd@rGO/ MoS_2 QDs modified GCEs and SPGE based on our earlier work as narrated in chapter 2 and 3. The electro-catalytic activity of Pd@rGO/ MoS_2 QDs composite synergistically enhanced the oxidation of NVP and reduction of AZT resulted in the detection limit of NVP and AZT up to 10 µM concentration. The developed sensor showed a linear relationship between the oxidation peak current and drug concentrations in the wide range 10 µM – 80 µM under optimized conditions. Further, the proposed method is also employed for detection of both the drugs in complex system (human serum) samples.

4.2 Experimental section

All the experimental setups used as discussed in chapter 3.

4.3 Results and discussion

Characterisation of Pd@rGO/ MoS_2 QDs is same as discussed in chapter 3.

4.3.1 Electrochemical detection of NVP on Pd@rGO decorated MoS_2 QDs SPGE

Electrochemical sensing of NVP is performed on Pd@rGO/ MoS_2 QDs modified SPGE in PBS (pH 10) by CV and DPV techniques as shown in Figure 4.1.

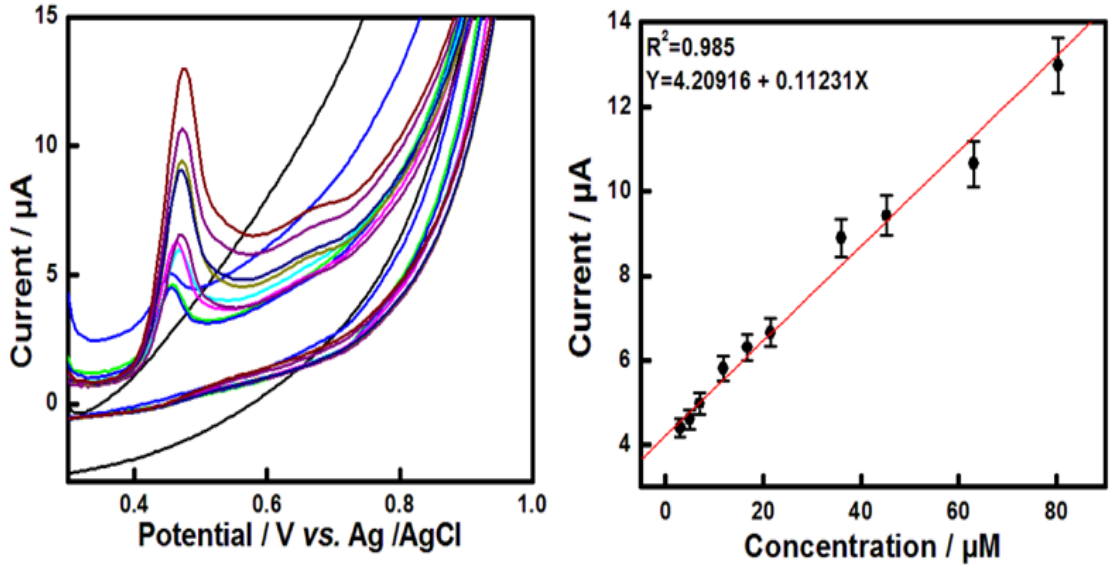

Figure 4.1 CV response of NVP (from 1 µM conc. to 80 µM) on Pd@rGO decorated with MoS_2 QDs SPGE and its corresponding calibration plot.

Pd@rGO/ MoS_2 QDs modified SPGE show oxidation peak potential of NVP at 0.45 V *vs.* Ag/AgCl. On increasing the concentration of NVP there is an enhancement of oxidation peak current. The plot between NVP conc. and oxidation peak current is showing linearity with regression coefficient value of 0.985 with good sensitivity from 1 µM to 80 µM concentration. NVP electrochemical determination is also performed by DPV as shown in Figure 4.2. Pd@rGO/ MoS_2 QDs modified SPGE is showing better resolution of peak potential by DPV with regression coefficient value of 0.986 and 0.086 µA /µM sensitivity from 1 µM to 80 µM concentrations at S/N:3.

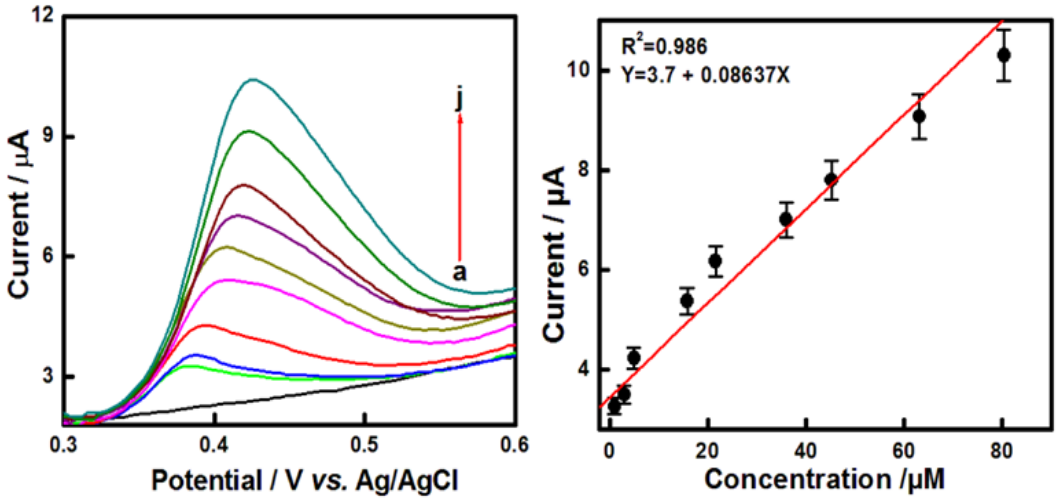

Figure 4.2 DPV response of NVP (from 1 µM conc. to 80 µM) on Pd@rGO decorated with MoS_2 QDs SPGE and its corresponding calibration plot.

Figure 4.3 exhibits CVs of Pd@rGO/ MoS_2 QDs modified SPGE at different scan rates at a fixed concentration of NVP in PBS (0.1 M, pH = 10). The oxidation peak current increases in a linear fashion with the square roots of the scan rates in the range of 10 - 100 mV/s. This shows that oxidation of NVP on modified electrode surface is diffusion controlled and exhibits fast electron transfer rate kinetics for oxidation of NVP. The shift of oxidation peak potential with increasing scan rate towards higher potential side in CV indicates chemically irreversible oxidation of NVP.

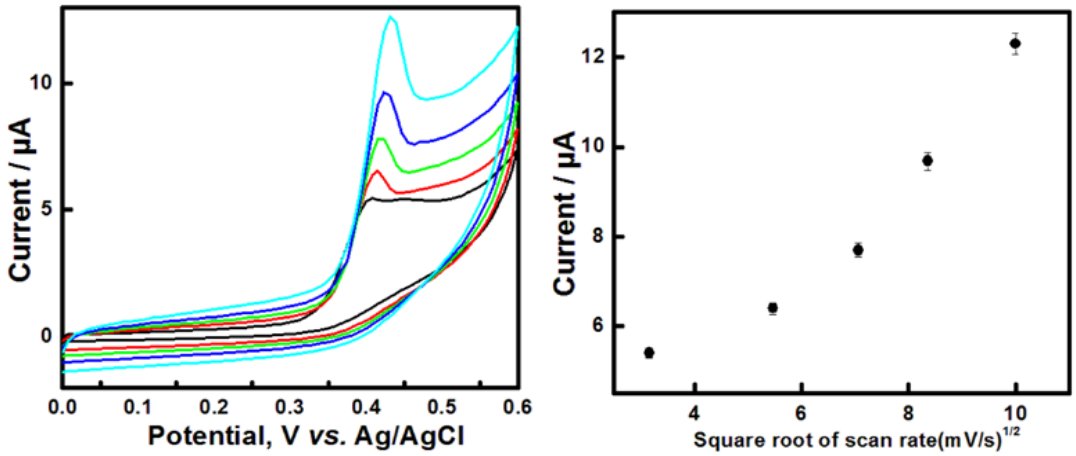

Figure 4.3 Effect of scan rates (10, 30, 50, 70, 100 mV/s) on NVP oxidation over Pd@rGO/ MoS_2 QDs modified SPGE and calibration plot between square root of scan rate and current.

4.3.2 Electrochemical detection of AZT on Pd@rGO decorated MoS_2 QDs SPGE

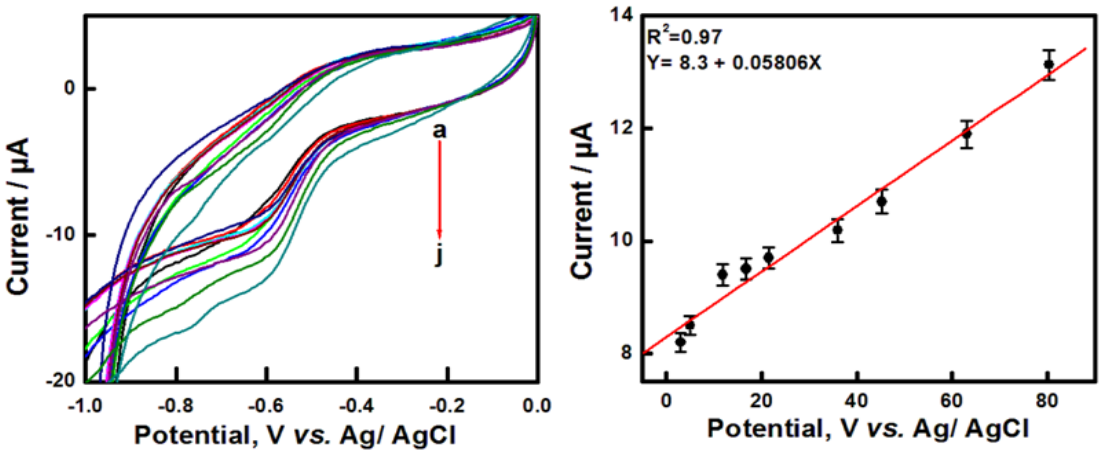

Figure 4.4 CV response of successive AZT additions (10 - 80 µM) over Pd@rGO decorated with MoS_2 QDs modified SPGE and its corresponding calibration plot.

Electrochemical detection of AZT is performed using Pd@rGO/ MoS_2 QDs modified SPGE in PBS (pH 10) using cyclic voltammetric techniques as shown in Figure 4.4

from 5 µM to 80 µM concentration with regression coefficient value of 0.97 and 0.058 µA/µM sensitivity at S/N:3.

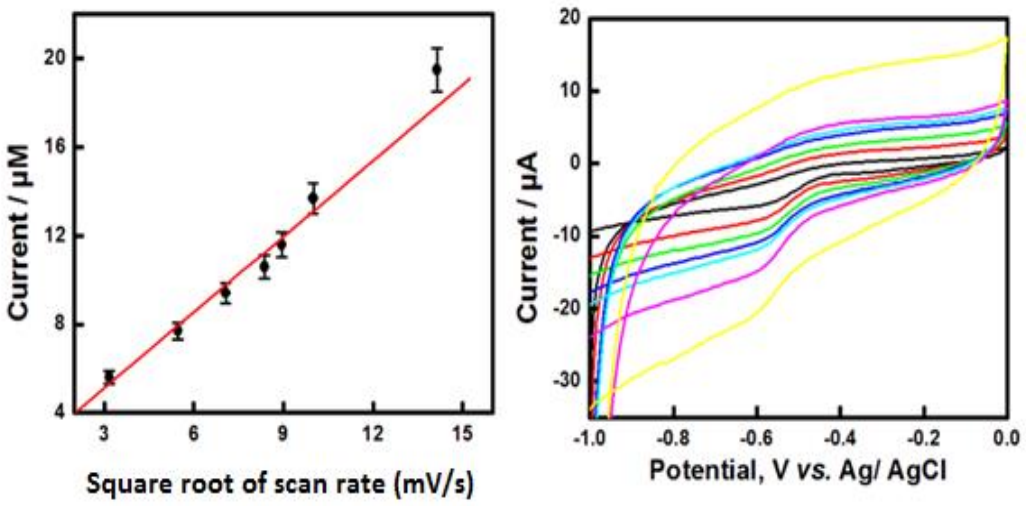

Figure 4.5 Effect of scan rates (10, 30, 50, 70, 80, 100, 200 mV/s) on AZT sensing and plot between Square root of scan rate and current.

The modified electrode exhibits a well defined reduction peak potential at 0.59 V. With increasing the concentration of AZT reduction peak current increases linearly as shown in Figure 4.4. It shows that the modified electrode surface is highly catalytic towards reduction of AZT.

Figure 4.5 exhibits the CVs of Pd@rGO/ MoS_2 QDs modified SPGE at different scan rates at a fixed concentration of AZT in PBS (0.1 M, pH = 10). The oxidation peak current increases in a linear fashion with the square roots of scan rates in the range of 10 - 200 mV /s. This shows that oxidation of AZT on modified electrode surface is diffusion controlled and exhibits fast electron transfer rate kinetics for reduction of AZT. The shift of reduction peak potential with increasing scan rate towards more negative potential side in CV indicates chemically irreversible reduction of AZT.

4.3.3 Simultaneous detection of NVP and AZT on Pd@rGO decorated with MoS_2 QDs SPGE

Pd@rGO/ MoS_2 QDs modified SPGE shows electro-catalytic effect towards oxidation of NVP and reduction of AZT as explained above. Further, Pd@rGO/ MoS_2 QDs modified SPGE is used for simultaneous detection of both the drugs. Catalytic effects of Pd@rGO/SPGE, MoS2 QDs/SPGE, Pd@rGO/ MoS_2 QDs modified SPGE are checked towards simultaneous detection of both the drugs in PBS (pH 10). It has been observed that in all the cases, oxidation peak of NVP and reduction peak of AZT are well observed. Pd@rGO/ MoS_2 QDs modified SPGE is highly catalytic towards oxidation of NVP and reduction of AZT as shown in Figure 4.6. Pd@rGO/ MoS_2 QDs modified SPGE shows oxidation of NVP and reduction of AZT at lower potentials as compared to modified Pd@rGO/SPGE and MoS_2 QDs/SPGE. In bare SPGE, we didn't get any oxidation peak but reduction peak is observed which may be due to the interference of oxygen.

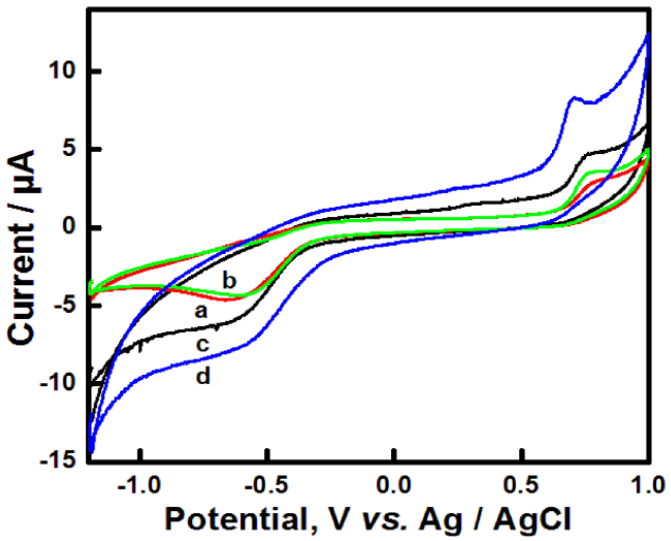

Figure 4.6 Effect of modification towards NVP oxidation and AZT reduction a) Bare SPGE, Modified SPGE with b) MoS_2 QDs c) Pd@rGO d) Pd@rGO/ MoS_2 QDs.

So, Pd@rGO/ MoS_2 QDs modified SPGE is showing highest current at lowest potential as compared to others due to synergistic interaction between both components at a fixed concentration of both the drugs. This causes a huge increment in peak current as compared to other electrodes. Figure 4.7 exhibits schematic representation of simultaneous detection of both the drugs in PBS at pH 10 on Pd@rGO/ MoS_2 QDs modified SPGE. Pd@rGO/ MoS_2 QDs modified SPGE exhibits bifunctional activity, which facilitates the conversion of azido group of AZT into amine and formation of a dimerized product of radical cation of NVP resulting into their simultaneous determination on a single nanostructured platform.

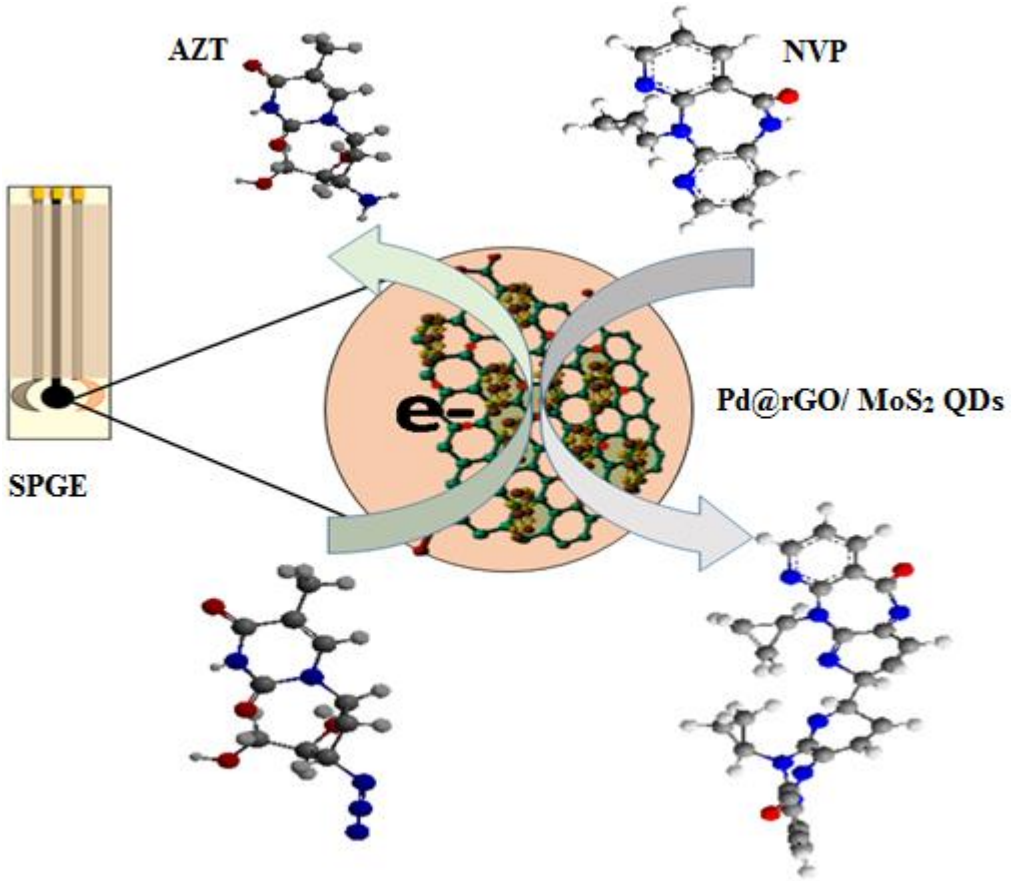

Figure 4.7 Schematic representations of NVP oxidation and AZT reduction using a Pd@rGO/ MoS_2 QDs modified SPGE.

Pd@rGO/MoS_2 QDs modified SPGE is used for simultaneous determination of both drugs from 10 µM to 80 µM concentration by CV in PBS (pH 10). With increasing the concentration, peak currents of both drugs increase in a linear fashion which is shown in Figure 4.8 with corresponding calibration plots of both the drugs. Oxygen causes some interference in reduction of AZT.

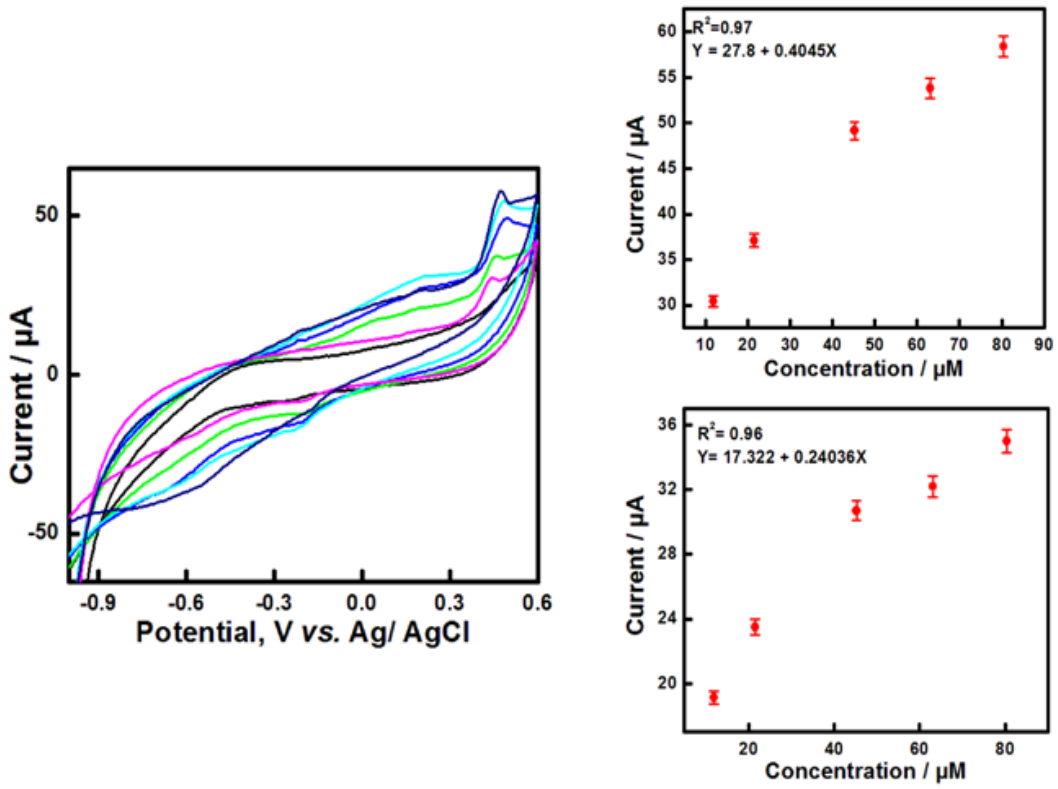

Figure 4.8 Pd@rGO/ MoS_2 QDs modified SPGE towards electrochemical detection of AZT and NVP (from 10 µM to 80 µM) and its corresponding calibration plots.

Figure 4.9 exhibits the CVs of Pd@rGO/ MoS_2 QDs modified SPGE at different scan rates at a fixed concentration of NVP and AZT in PBS (0.1 M, pH = 10). The oxidation peak current of NVP and reduction peak current of AZT increase in a linear fashion with the square roots of scan rates in the range of 10-100 mV /s. This shows that oxidation of NVP and reduction of AZT on modified electrode surface are diffusion

controlled and exhibit fast electron transfer kinetics for oxidation of NVP and reduction of AZT.

The shift of oxidation peak potential with increasing scan rate towards higher potential side in CVs indicate chemically irreversible oxidation of NVP and reduction of AZT.

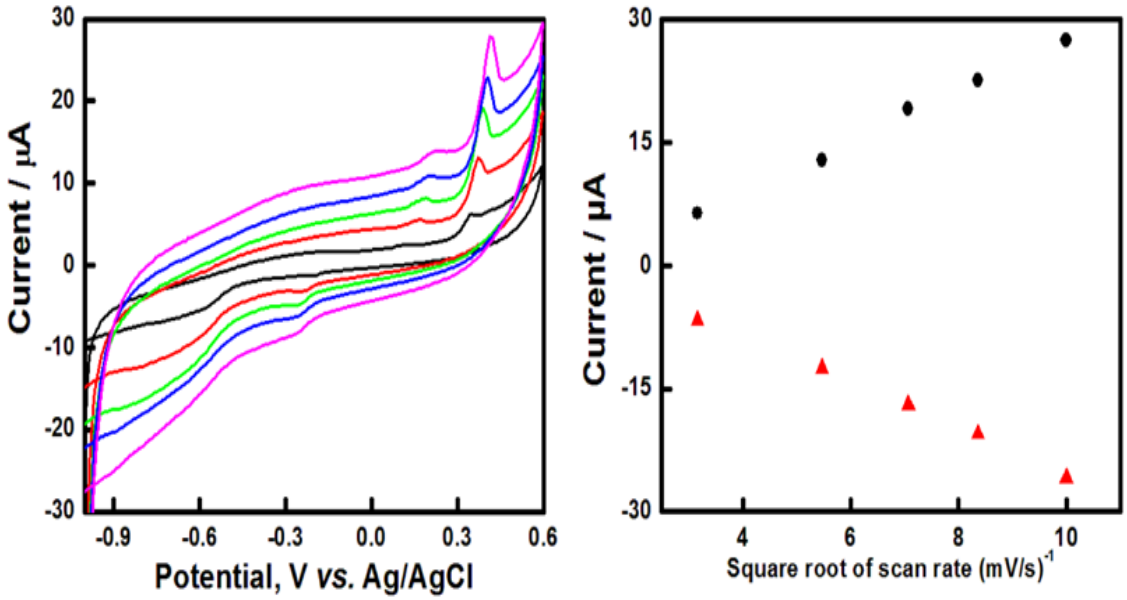

Figure 4.9 Effect of scan rates (10, 30, 50, 70, 100 mV/s) on NVP oxidation and AZT reduction.

4.4 Conclusions

Pd@rGO/ MoS_2 QDs modified SPGE platform is successfully utilized for simultaneous determination of AZT and NVP. Modified SPGE exhibits bifunctional activity towards AZT reduction and NVP oxidation. Effect of scan rate confirms that both processes are diffusion controlled on the modified electrode surface.