Investigating the voltammetric reduction of methylviologen at gold and carbon based electrode materials. Evidence for a surface bound adsorption mechanism leading to electrode 'protection' using multi-walled carbon nanotubes

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Cyclic voltammetry was recorded in an aqueous solution of 1,1′-dimethyl-4,4′ bipyridinium dichloride ("methylviologen" or "paraquat") at a variety of electrode materials namely gold, boron doped diamond (BDD), edge (eppg) and basal plane (bppg) pyrolytic graphite electrode. Previous mechanisms reported in the literature to describe the observed voltammetry are critically assessed and an alternative mechanistic interpretation is presented involving evidence for surface adsorption of intermediate species in the redox behaviour of methylviologen (MV) rather than any disproportionation or comproportionation as was previously claimed for the specific case of gold electrodes. Various electrodes were then modified with multi-walled carbon nanotubes (MWCNTs) where the formation of solid MV^0 on the electrode surface was prevented due to preferential adsorption of MV^0 on the MWCNTs. Thus coating an electrode with MWCNTs can protect the electrode surface from "fouling", providing scope for diffusion dominated voltammetry at electrodes where surface inhibition has hitherto dominated.

1. Introduction

1,1′-Dimethyl-4,4′-bipyridinium dichloride (also known as methylviologen or paraquat) is commonly used as a non-selective contact herbicide due to its extreme toxicity linked to its redox potential.[1,2] The compound has attracted considerable attention from electrochemists over the past years due to its favourable redox properties resulting in many possible electrochemical applications.[3] The electrochemical kinetics of methylviologen in aqueous solution have been extensively studied in the past, and several different mechanisms have been proposed to explain the observed voltammetry on numerous electrode materials.[3–7]

As shown on Scheme 1, methylviologen exist in three main oxidation states, namely $MV^{2+} \rightleftarrows MV^{+} \rightleftarrows MV^{0}$.[3] It has been widely agreed in the literature that on a gold electrode, two voltammetric peaks exist in the cathodic scan at *ca.* −0.7 V and −1.2 V *vs.* SCE, corresponding to the formation of the cation:

$$MV^{2+} + e^{-} \rightarrow MV^{+} \quad (1)$$

and the neutral species:

$$MV^{+} + e^{-} \rightarrow MV^{0} \quad (2)$$

respectively.[1–6,8–14] In the anodic process, a "poorly defined" peak may be observed at *ca.* −0.9 V and has been suggested to arise from the electrode reaction:

$$2MV^{0} \rightarrow (MV)_2^{2+} + 2e^{-} \quad (3)$$

and the oxidation peak at −0.65 V is explained by the re-oxidation of the MV^{+} species:

$$MV^{+} \rightarrow MV^{2+} + e^{-} \quad (4)$$

A sharp peak appears between the two peaks stated above at −0.75 V which has been previously identified as the two-electron oxidation of the radical cation dimer:

$$(MV)_2^{2+} \rightarrow 2MV^{2+} + 2e^{-} \quad (5)$$

formed by the comproportionation of MV^0 on the electrode with MV^{2+} in solution.[7]

In this work, the voltammetric behaviour of several electrode materials (namely gold, boron doped diamond (BDD) edge and basal plane pyrolytic graphite (eppg and bppg) and glassy carbon (GC)) toward methylviologen is reported where we critically re-examine previous claims of comproportionation and, in particular, present evidence for an alternative surface bound stripping mechanism on a gold electrode. This adsorption mechanism is also observed on carbon electrodes excepting that no adsorption occurs when the working electrodes are modified with multi-walled carbon nanotubes (MWCNTs). In this case the MV molecules preferentially defuse to the MWCNTs and hence fouling of the electrode caused by a build up of solid MV^0 on the electrode surface is prevented.

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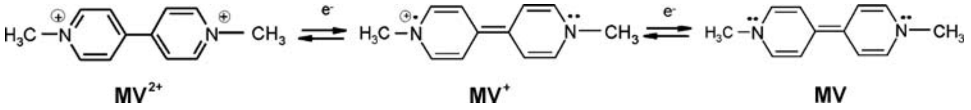

Scheme 1 Structure of methylviologen at different oxidation states.

2. Experimental

2.1 Reagents and equipments

All chemicals were obtained from Aldrich with the highest grade available and were used without further purification. All solutions were prepared using deionised water from a Vivendi UHQ grade water system (Vivendi) with a resistivity of not less than 18.2 MΩ cm at 298 K. Methylviologen stock solution (1 mM) was prepared from methylviologen dichloride in water with 0.1 M potassium sulfate as background electrolyte.[10] A solution volume of 10 cm^3 was used through out, and all solutions were degassed for 20 min with pure N_2 (BOC gases, Guildford, UK) prior to any electrochemical measurement being performed. Bamboo-like multi-walled carbon nanotubes with purity of greater than 95% was purchased from Nanolab Inc (Brighton, MA, USA).

Electrochemical measurements were recorded using a computer controlled μ-autolab potentiostat (Eco Chemie, Utrecht, Netherlands) with a standard three electrode configuration. Either a gold macrodisk electrode with a geometric area of 0.008 cm^2, a basal plane pyrolytic graphite electrode (bppg, 4.9 mm diameter, Le Carbone Ltd, Sussex, UK), an edge plane pyrolytic graphite electrode (eppg, 4.9 mm diameter, Le Carbone Ltd, Sussex, UK) or a boron doped diamond electrode (BDD, 3 mm diameter, Windsor Scientific, Slough, UK) was used as the working electrode. A platinum wire as counter electrode and a saturated calomel reference electrode (SCE, Radiometer, Copenhagen, Denmark) completed the cell assembly. The working electrodes were polished on soft lapping pads (Kemet Ltd, UK) with 3.0, 1.0 and 0.1 μM diamond spray before use.

2.2 Preparation of MWCNTs modified electrodes

The working electrodes (gold, BDD, eppg GC) were modified by first dispersing 10 mg of the MWCNTs in 10 mL of chloroform and sonicating the suspension for 30 min. 20 μL of the suspension was than placed onto the electrode surface, and the solvent was allowed to evaporate at room temperature, thus immobilising the MWCNTs onto the electrode surface.

3. Results and discussion

3.1 Voltammetric behaviour of methylviologen at a gold electrode surface

The cyclic voltammetric response of a gold macroelectrode in 1 mM methylviologen and 0.1 M of K_2SO_4, scanned from −0.3 V to −1.3 V at a scan rate of 10 mV s^{-1}, is presented in Fig. 1. In the figure, peaks II and II′ which occur at −0.67 V and −0.72 V *vs.* SCE, respectively are associated with the redox couple:[3]

$$MV^{2+} + e^- \rightleftarrows MV^+ \qquad (6)$$

A second redox couple (peak I and I′) occurs at −1.04 V and −0.90 V *vs.* SCE which also exhibits diffusion controlled voltammetric behaviour (see below) corresponding to the process generating neutral molecules in solution:[3]

$$MV^+ + e^- \rightleftarrows MV^0 \qquad (7)$$

Fig. 2(a) shows the cyclic voltammogram of MV at a gold electrode with different scan rates in the range 5–1000 mV s^{-1} and two oxidative peaks were observed at −1.04 V and −0.67 V *vs.* SCE. Fig. 2(b) shows the resulting plot of the Randles–Sevčik analysis performed on these peaks where it is clear that the peak currents observed for both peaks have a linear dependency on the square root of the scan rate[15] which implies that these peaks arise from a diffusion controlled process.[16]

Peak III, which appears at −0.75 V *vs.* SCE has previously been assigned in the literature as being due to a comproportionation process:[6,11,12]

$$MV^0 + MV^{2+} \rightleftarrows (MV)_2{}^{2+} \qquad (8)$$

In order to test this hypothesis, cyclic voltammetry was next performed with the same gold electrode in 1 mM methylviologen solution at a scan rate of 5–1000 mV s^{-1} from −0.3 V to −1.3 V with the potential held at −1.3 V for 15, 30 and 60 s before reversing the scan direction. Fig. 3 shows the resulting voltammograms at a scan rate of (a) 5 mV s^{-1} and (b) 200 mV s^{-1} where the electrode was held at −1.3 V for 15, 30 and 60 s before the anodic process took place. As a result, peak currents for I′, II′ and I did not change when the electrode was held at −1.3 V for increasing lengths of time, whereas peak III increased in size significantly in proportion to the period of holding at −1.3 V.

This observation suggests that peak III is likely to be associated with the surface bound process:

$$MV^0{}_{(ads)} \rightarrow MV^+{}_{(aq)} + e^- \qquad (9)$$

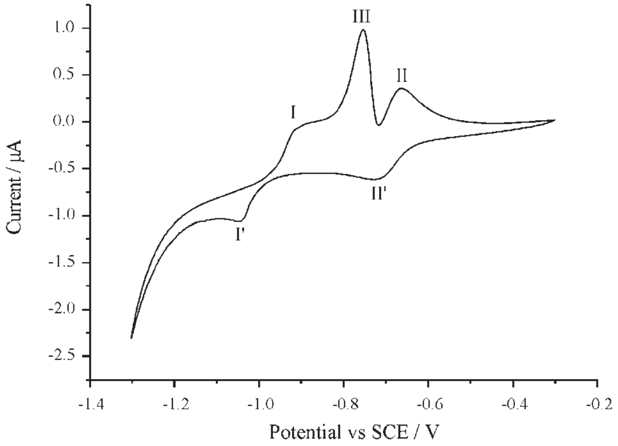

Fig. 1 Cyclic voltammogram of 1.0 mM methylviologen and 0.1 M K_2SO_4 at a gold electrode, v = 5 mV s^{-1}.

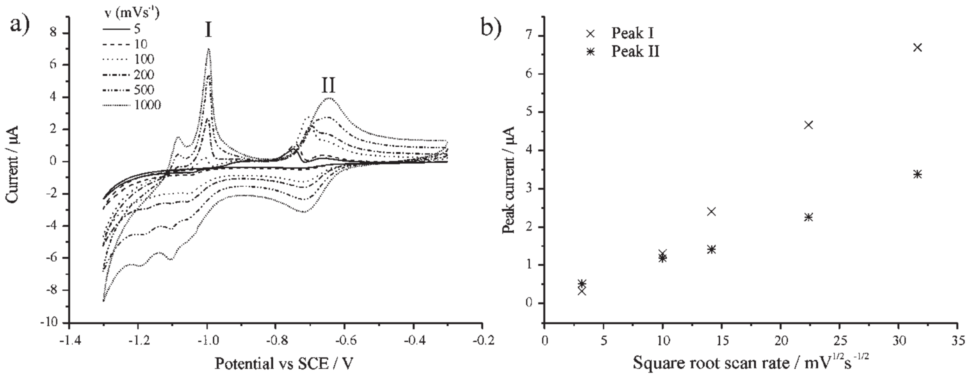

Fig. 2 (a) Overlaid cyclic voltammograms of 1 mM methylviologen in 0.1 M K_2SO_4 solution at a gold electrode, v = 5–1000 mV s^{-1} (b) Randles–Sevčik plot of peak I and II observed in (a).

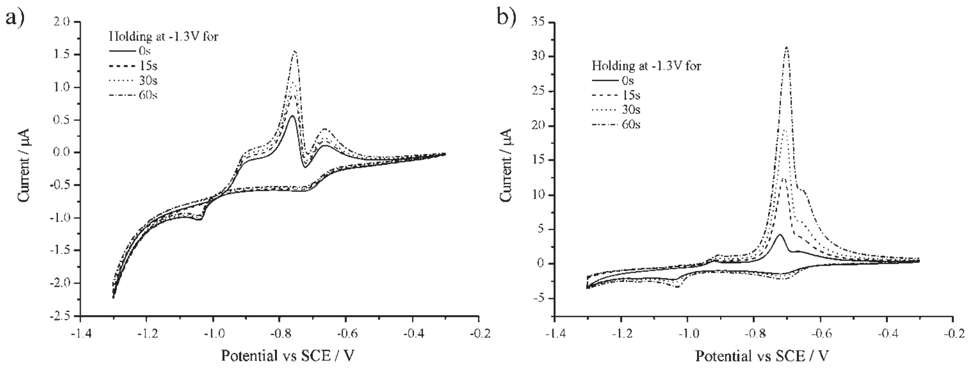

Fig. 3 Overlaid cyclic voltammograms of 1.0 mM methylviologen and 0.1 M K_2SO_4 at a gold electrode with the electrode held after scanning reductively at −1.3 V *vs.* SCE for different amounts of time: (a) v = 5 mV s^{-1}, (b) v = 200 mV s^{-1}.

Note that the fact that peak III occurs at more positive potentials than peak I suggest that $MV^0{}_{(ads)}$ is stabilised compared to $MV^0{}_{(aq)}$ due to surface adsorption interaction. The size of peak II also increased slightly with time due to the MV^+ concentration in the solution immediately adjacent to the electrode surface increasing temporarily as MV^0 is oxidised in peak III to form MV^+ which is then oxidised to MV^{2+} before the MV^+ has time to diffuse away. This effect is also illustrated in Fig. 3 where the height of peak II increased with increasing scan rate because less time was available for the MV^+ to diffuse away to the bulk solution.

In order to prove that peak III is the only surface bound process taking place, further experiments were carried out. The same gold electrode was held in 1 mM methylviologen solution for 5 min with an applied potential of −1.3 V *vs.* SCE before being removed from the cell (under the applied potential) and gently rinsed with water. A scan was then performed with this electrode from −1.3 V to −0.3 V in 0.1 M K_2SO_4 containing no MV in the solution at a scan rate of 200 mV s^{-1} and the result is shown in Fig. 4. A stripping peak is observed at around −0.7 V comparable to the large peak shown in Fig. 3(b). This indicates that peak III was indeed the oxidation of the MV^0 from the electrode surface to MV^+ into the solution. In the light of this experiment, the previous comproportionation mechanism cannot be correct since no methylviologen exists in the solution.

3.2 Voltammetric behaviour of methylviologen at carbon based electrode materials

Having elucidated a mechanism to explain all the features of MV voltammetry at a gold electrode, cyclic voltammetric behaviour of MV was then investigated in several other carbon based electrode materials, namely boron doped diamond (BDD), eppg, bppg and

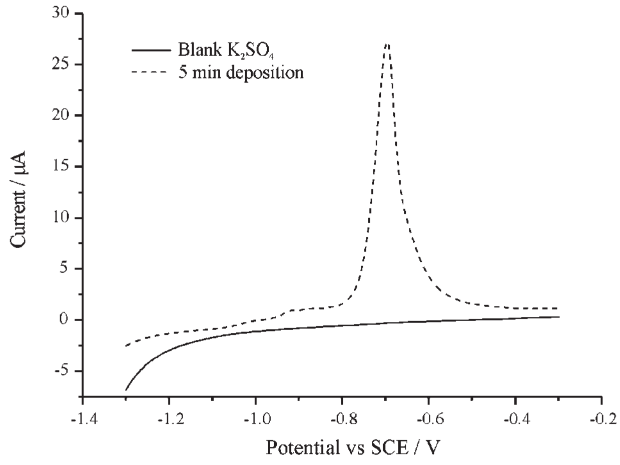

Fig. 4 Linear sweep voltammogram of a gold electrode in 0.1 mol dm^{-3} K_2SO_4 after holding at −1.3 V *vs.* SCE in 1 mM methylviologen solution for 5 min.

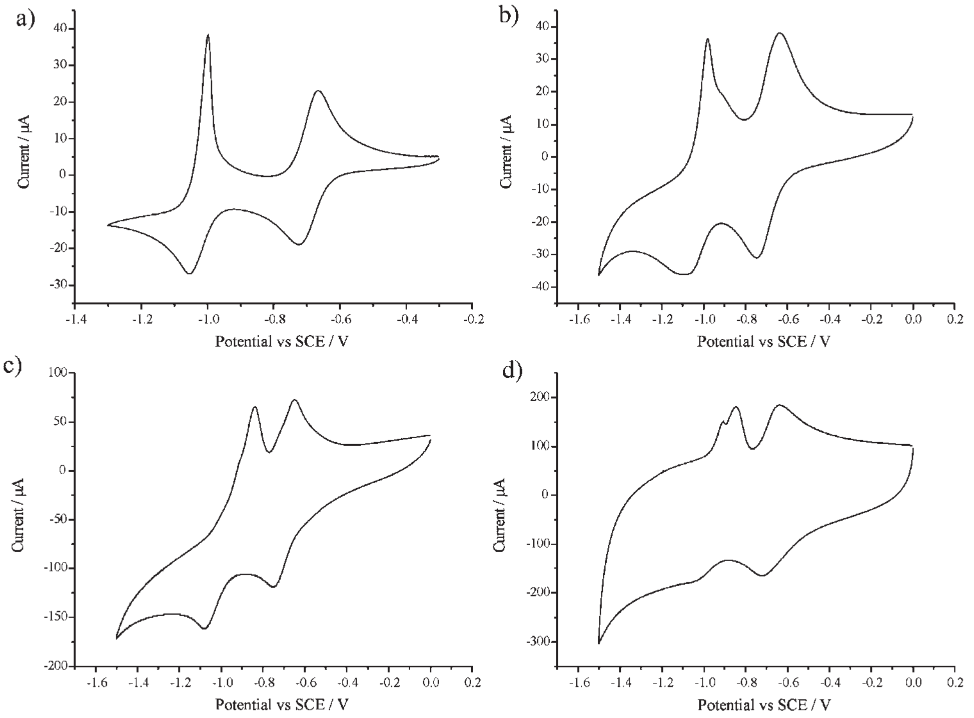

Fig. 5 Cyclic voltammogram of 1.0 mM methylviologen in 0.1 M K_2SO_4 at a (a) BDD, (b) GC, (c) bppg, (d) eppg electrode; $v = 200$ mV s^{-1}.

GC, the resulting voltammograms are shown in Fig. 5. Two cathodic peaks were observed with all four electrodes at −1.1 V and −0.75 V *vs*. SCE which are understood as the reduction process of the MV^{2+} and MV^{+} in eqn (6) and (7), respectively.[17,18] In the anodic process, two peaks were observed at *ca.* −0.67 V and *ca.* −1.0 V *vs*. SCE with GC and BDD electrode and at *ca.* −0.67 and −0.9 V for bppg electrode, whereas eppg electrode shows a similar behaviour to the gold electrode where the latter peak possess a shoulder at −1.0 V. The anodic peaks has been identified[19,20] as a combination of mass transport and surface adsorption process where the sharp peak at *ca.* −0.9 and −1.0 V correspond to the MV_0 on the electrode surface being

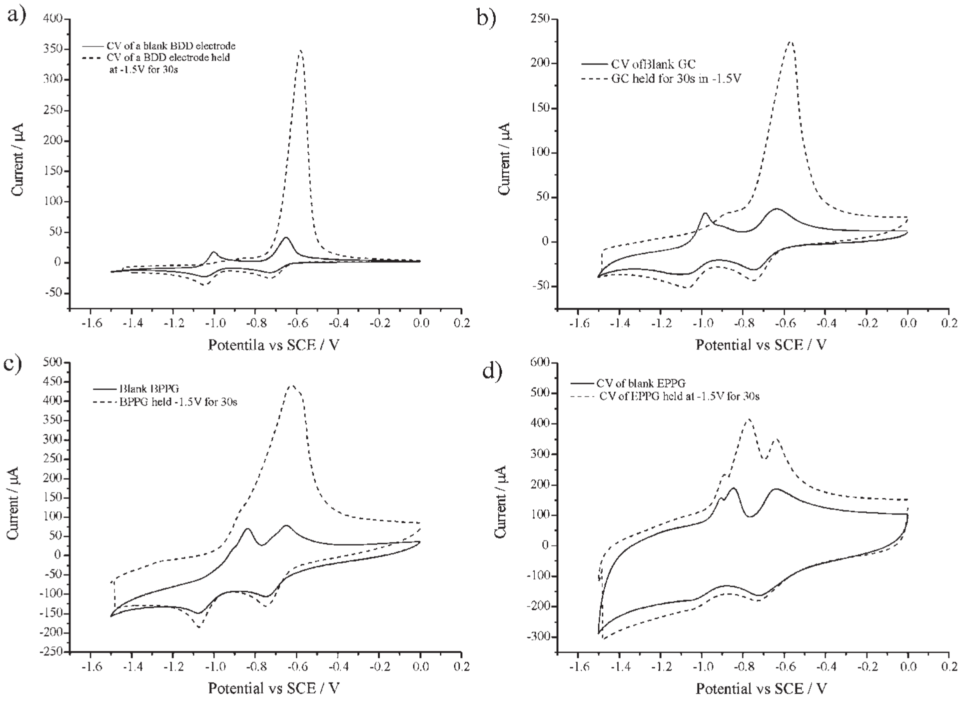

Fig. 6 Cyclic voltammogram of 1.0 mM methylviologen in 0.1 M K_2SO_4 at (a) BDD, (b) GC, (c) bppg, (d) eppg electrode with the electrode held after scanning reductively at −1.5 V *vs*. SCE for 30 s; $v = 200$ mV s^{-1}.

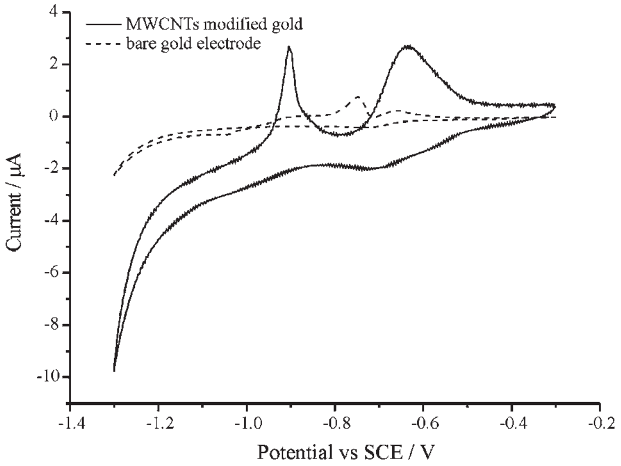

Fig. 7 Cyclic voltammogram of 1.0 mM methylviologen and 0.1 M K_2SO_4 at a gold electrode compared to a MWCNTs modified gold electrode; v = 5 mV s^{-1}.

stripped off the surface of the electrode to form MV^+ in the solution, and the more positive peak at −0.67 V *vs.* SCE arises from the further oxidation of MV^+ to MV^{2+}.[19–21]

To further investigate the voltammetric behaviour of these electrodes, experiments were carried out where the electrodes were again held at −1.5 V for 30 s before the reverse scan took place and the resulting voltammogram are shown in Fig. 6. A large stripping peak was observed at −0.65 V *vs.* SCE for the BDD, bppg and GC electrodes, whereas the eppg electrode again shows a similar response to the gold electrode, in that the size of the peak at −0.9 V has significantly increased and the peak at −0.65 V is also enhanced. This behaviour is due to the formation of a more stable crystalline form of MV^0 with time[21] which is only stripped off at a more positive potential, *via* a two-electron oxidation process at −0.5 V *vs.* SCE.

$$MV^0 \rightarrow MV^{2+} + 2e^- \qquad (10)$$

From Fig. 6, the stripping peak is sharper and better defined with the flatter BDD and GC electrode, compare to the broader peak observed at the bppg electrode where the surface is less uniform. Although, the stripping peak observed at the eppg electrode has now increased in size and shifted from −0.9 V to −0.8 V suggesting the formation of a more stable MV^0 layer at the electrode surface, no stripping peak at −0.65 V is observed.

3.3 Voltammetric behaviour of methylviologen on multi-walled carbon nanotubes (MWCNTs)

Having ascertained the voltammetric response of methylviologen on carbon materials, the behaviour of MWCNTs was investigated by dispersing a layer of MWCNTs onto a gold electrode with the procedure described in section 2.3. Fig. 7 shows a cyclic voltammogram of MV at a MWCNTs modified gold electrode compared to the voltammogram of MV at a bare gold electrode at scan rate of 10 mV s^{-1}. While similar peak potentials and shapes were observed in the cathodic processes, major differences were observed in the anodic scan where the stripping peak at −0.75 V *vs.* SCE is absent but with two distinct peaks appearing at *ca.* −1.0 V and *ca.* −0.6 V *vs.* SCE. Fig. 8(a) shows the cyclic voltammetric response of MV at the MWCNTs modified gold electrode with different scan rate. Randle–Sevčik analysis was carried out on both anodic peaks and the results are shown on Fig. 8(b). A linear response of peak current against the square root of scan rate was observed, which suggests that both peaks are diffusion controlled. This behaviour is comparable to peak I and peak II observed at a bare gold electrode, and corresponds to the oxidative processes listed in eqn (6) and (7). It is interesting to note that although methylviologen appears to be adsorbing on the gold and various carbon electrode materials studied, no adsorption is observed when the MWCNT are present except possibly at the very lowest scan rate used. Fig. 9 shows the cyclic voltammogram of MV at various MWCNTs modified electrodes (gold, eppg, GC and BDD) where the potential was held at a sufficiently low voltage for the MV deposition to occur for 0 and 30 s. Unlike the other electrode materials, the cyclic voltammetric response remained unchanged by this step. It is observed that the large stripping peak previously observed is absent after the deposition step, which suggests that MV molecules diffuse only to the MWCNTs without forming any solid MV^0. Hence, fouling of the electrode by the product of MV reduction is prevented.

4. Conclusions

Voltammetric evidence is presented which questions a previous mechanism proposed in the literature to describe MV voltammetry involving a comproportionation step. Instead we propose a mechanism involving a "stripping" step removing

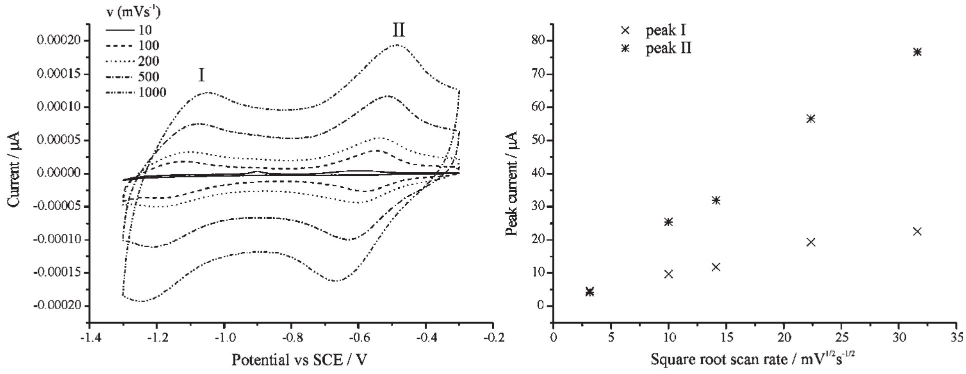

Fig. 8 (a) Overlay of cyclic voltammogram of 1 mM methylviologen and 0.1 M K_2SO_4 in water using a MWCNTs modified gold electrode, v = 10–1000 mV s^{-1} (b) Randles–Sevcik plots of peak I and II observed in (a).

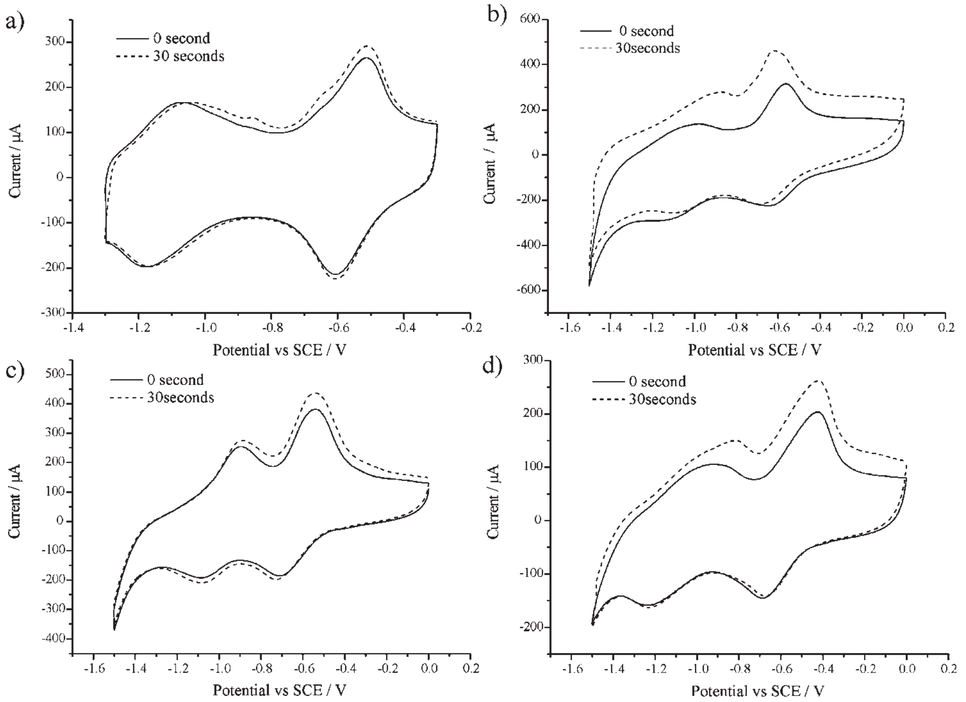

Fig. 9 Cyclic voltammogram of 1.0 mM methylviologen and 0.1 M K_2SO_4 at a MWCNTs modified (a) gold, (b) eppg (c) BDD, (d) GC electrode with the electrode held after scanning reductively at −1.3 V *vs.* SCE for different amounts of time; v = 200 mV s^{-1}.

MV^0 adsorbed on the electrode surface. This surface bound wave is also convoluted with the re-oxidation of MV^0 in solution which, perhaps, is the reason why previous researchers were misled into proposing a comproportionation mechanism. Similar voltammetric behaviour was observed on a variety of carbon electrodes (GC, BDD and bppg). On eppg electrodes, no stripping peak is observed, possibly due to the surface structure/roughness of the electrode preventing the formation of a structured MV^0 layer.

When these electrodes are modified with a layer of MWCNTs, no stripping of MV^0 is observed, and instead we observe two diffusion controlled redox couples corresponding to only solution phase MV voltammetry. After holding the modified electrode at a low potential, no distinct increase in the size of the oxidative peak was observed on any electrode tested, due to the preferential adsorption of MV on MWCNTs. Thus, the presence of MWCNTs can provide protection to an electrode from surface fouling by MV.

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