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# The instructive redox behaviour of 4-ferrocenylcatechol on nanocrystalline titanium dioxide electrodes

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**An investigation into the redox behaviour of 4-ferrocenylcatechol bound to nanocrystalline $TiO_2$ electrodes identified a limitation to the use of catechol as an electron-transfer facilitating anchoring group. 4-Ferrocenylcatechol was adsorbed to transparent nanocrystalline $TiO_2$ electrodes. UV–visible spectra of the modified electrode were recorded in an acetonitrile-electrolyte solution. At an applied potential of +0.45 mV (vs Ag/AgCl/$Cl^-$) the ferrocenyl group oxidized to the ferrocenium cation and the catecholate group oxidized to the benzoquinone form. Subsequent application of a potential of 0 V reduced the ferrocenium to ferrocene but, owing to the irreversibility of the catechol oxidation in aprotic solvents, benzoquinone is not reduced to catecholate and subsequently desorbs and is lost due into solution. Electrochromic switching of the ferrocenyl electrochromophore on $TiO_2$ with aprotic electrolyte is, therefore, irreversible. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** titanium dioxide; ferrocene; catechol; electrochemistry

## INTRODUCTION

Devices containing functional molecules anchored to nanocrystalline titanium dioxide electrodes have attracted a significant amount of attention.[1–5] Nanocrystalline $TiO_2$ electrodes coated with light-absorbing dyes are fundamental components of dye-sensitized solar cells[6] and a number of display devices utilizing $TiO_2$ electrodes with adsorbed electrochromic compounds have been reported.[7] In each case, the redox chemistry of the bound molecular species is intimately involved with the device performance. It is important in these devices that the functional molecules are strongly bound to the metal oxide surface throughout the various redox cycles. Different binding groups have been investigated including, for example, carboxylic,[8] phosphonic[9,10] and boronic acids.[11] These groups are all redox inert. Catechol (1,2-dihydroxybenzene), on the other hand, is redox active and has been proposed as a non-innocent[12] anchoring group that could potentially facilitate electron transfer to metal oxide surfaces.[13–15] There are several reports of catechol-containing compounds bound to titanium dioxide particles.[16–19]

To investigate the behaviour of the catechol group acting as an anchor for electrochromophores, we examined the spectroelectrochemical behaviour of $TiO_2$ electrodes coated with a compound consisting of catechol covalently attached to the archetypal redox centre, ferrocene. Here we present an investigation into the redox behaviour of 4-ferrocenylcatechol (Fig. 1) bound to nanocrystalline $TiO_2$ electrodes. The results describe a limitation to the utility of catechol as an electron-transfer facilitating anchoring group.

## RESULTS AND DISCUSSION

We recently reported the electrochemical and spectroelectrochemical properties of 4-ferrocenylcatechol in solution.[20] Cyclic voltammetric measurements showed oxidation processes at −0.03 and +1.11 V (vs the $Fc^+/Fc$ couple). The first process is reversible on the cyclic voltammetric timescale and is assigned to the $Fe^{III/II}$ couple. The second oxidation is an irreversible two-electron process and corresponds to the

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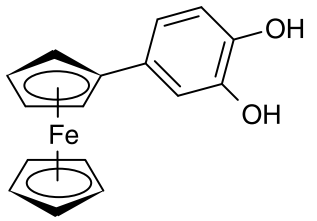

**Figure 1.** 4-Ferrocenylcatechol.

proton (pH)-dependent oxidation of the catechol group to the corresponding 1,2-benzoquinone. The assignments of these processes were confirmed by spectroelectrochemical measurements, during which it was observed that in unbuffered, aprotic acetonitrile solution the first oxidation process is not completely reversible. Upon reduction of the oxidized species, the 4-ferrocenium-catechol cation, significant amounts of 4-ferrocenyl-1,2-benzoquinone (up to 20%) were detected.[20] This immediately suggested to us that catechol-centred oxidation might be a limitation to the use of catechol anchors to oxide surfaces. This was tested in the current work.

4-Ferrocenylcatechol was readily adsorbed to transparent nanocrystalline $TiO_2$ electrodes from methanol solution. The modified electrode was placed in a quartz cuvette together with reference and counter electrodes and $LiClO_4$ (0.1 M)–[$n$Bu$_4$][PF$_6$] (0.1 M) in acetonitrile as supporting electrolyte. UV–visible spectra were recorded while a potential was applied using a potentiostat. Figure 2(a) shows the changes in the UV–visible spectrum that occur upon oxidation of the bound 4-ferrocenylcatechol at an applied potential of +0.45 V (vs Ag–AgCl). The starting spectrum was very similar to that of 4-ferrocenylcatechol in solution.[20] The weak band at 450 nm was assigned to a symmetry-forbidden Fe ($a_{1g}$) → Fe ($e_{1g}$) transition.[5]

As the oxidation proceeded, a strong band at ~445 nm and a weaker band in the NIR developed (the maximum of which is at a wavelength outside the range of the instrument employed). The spectrum of the oxidation product is characteristic of ferrocenium-aryl species.[20] Figure 2(b) shows spectra recorded immediately after those shown in Fig. 2(a) at an applied potential of 0 V, which is sufficient to reduce the ferrocenium group back to the starting ferrocene. The intensity of the band at ~445 nm decreases while a broad band at ~690 nm appears that identifies formation of 4-ferrocenyl-1,2-benzoquinone. The characteristic 690 nm band arises from a ferrocenyl donor to quinone acceptor charge transfer transition,[20] and thus is observed only after reduction of ferrocenium back to ferrocene. Noteworthily, the overall intensity of the electronic spectrum eventually decreases, indicative of desorption of the complex from the $TiO_2$ surface. At more negative potentials, the starting spectrum could not be recovered indicating that the system is irreversible.

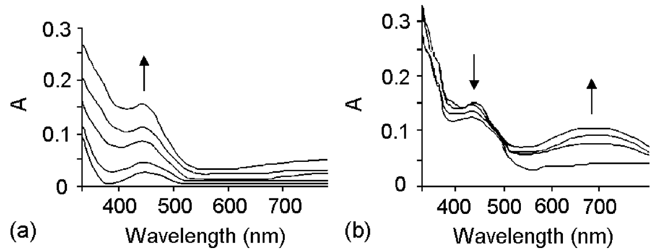

**Figure 2.** UV–vis spectroelectrochemistry for 4-ferrocenylcatechol adsorbed on a $TiO_2$ electrode: (a) oxidation at +0.45 V (vs Ag/AgCl/Cl$^-$); (b) reduction of the oxidation product at 0 V.

Figure 3 shows schematically the processes that are indicated by the experimental data. At an applied potential of +0.45 mV, the ferrocenyl group is oxidized to the ferrocenium cation and the catecholate group is oxidized to the benzoquinone form. Recent work by Curulli *et al.*[21] using $TiO_2$ electrodes modified with ferrocene monocarboxylic acid or catechol showed that catechol is oxidized at a potential ~100 mV lower than that for ferrocene carboxylic acid. Interestingly, the catechol oxidation was found to be reversible in buffered solution. In the current work, subsequent application of a potential of 0 V reduced the ferrocenium centre to ferrocene centre but, owing to the irreversibility of the catechol oxidation, a result of the

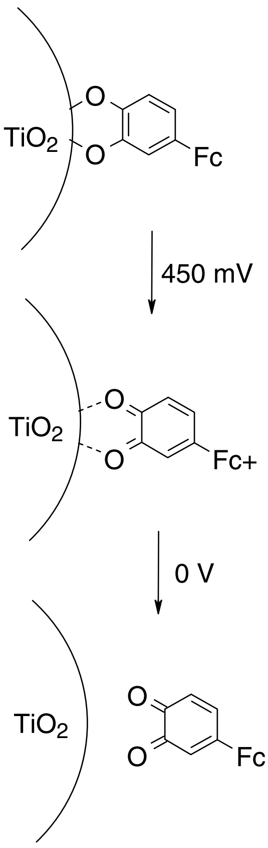

**Figure 3.** Diagram showing processes occurring at the 4-ferrocenyl-coated $TiO_2$ electrode.

pH dependence of this process, any ligand oxidized to the labile *ortho*-quinone form stays so, and subsequently desorbs and is lost due to diffusion into solution. Owing to this process, any electrochromic switching of the ferrocenyl electrochromophore is irreversible. This appears to be the first example of the process occurring in an oxide-bound organometallic catechol complex.

In conclusion, these results highlight an important aspect of the catecholate anchoring group in aprotic environments; oxidation of catechol, which may occur at potentials at or below those used to switch electrochromophores, gives the labile (poor-donor) 1,2-benzoquinone. In the absence of a proton source, this process is irreversible.

## EXPERIMENTAL

4-Ferrocenylcatechol was prepared using a literature procedure.[20]

### Nanocrystalline titanium dioxide electrodes

Glass slides coated with F-doped $SnO_2$ (TEC 10, 10 Ω/sq, Hartford Glass, USA) were washed with Pyroneg (Johnson Diversey) in water in a sonicator for 30 min. They were then washed with absolute ethanol in a sonicator for 30 min before being dried at 120 °C in an oven. A colloidal suspension of titanium dioxide (9 nm particle size, Solaronix) was deposited on the conducting side of the glass slide and a smooth film was formed using a draw bar. The film was dried in air before being placed in an oven at 450 °C for 30 min. The electrodes were allowed to cool before being immersed in a 1.3 M methanol solution of 4-ferrocenylcatechol for 1 h. The electrodes were then rinsed thoroughly with solvent to remove any unbound complex and used immediately for spectroelectrochemical experiments.

### Spectroelectrochemical measurements

A three-electrode system was used with the coated glass slide as the working electrode, a Pt gauze counter electrode, and an $Ag/AgCl/Cl^-$ reference electrode. The supporting electrolyte was $LiClO_4$ (0.1 M)–$[n\text{Bu}_4][PF_6]$ (0.1 M) in acetonitrile. The electrodes were arranged in a 1 cm path-length quartz cuvette and placed in the sample compartment of a Cary 500 spectrophotometer. Potentials were applied using a Pine AFCBP1 bipotentiostat. Spectra were recorded while the electrolysis potential was applied. A baseline spectrum was obtained using an uncoated $TiO_2$ electrode.

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