Microcrystalline Materials on Electrodes

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We show that the amperometric response of redox couples can be amplified at electrodes covered with microcrystalline solids and the corollary, that the electrorelease of surface materials can be triggered by solution molecules.

Electrodes modified with covalently, ionically, or polymerically bound redox species have received much attention in the context of molecular electronics, electrocatalysts, photoelectrochemical devices, sensors, and displays.[1] Here we show that modification by simple deposition of microcrystalline, non-conducting materials can confer novel properties onto an electrode. These are (i) amplification of the amperometric response of a solution species, (ii) triggered release of surface material by solution redox catalysts, and (iii) control of the overpotential for the electroreleasing by solution molecules.

The reduction of the cationic diazoalkane complex $[WF(NNCH_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$, **A**$^+$, which may be conveniently represented by $[FWN_2CH_2]^+$, **W** = $[W(Ph_2PCH_2CH_2PPh_2)_2]$ on platinum, glassy carbon, or gold electrodes in methyl cyanide containing 0.2 M $[NBu_4][BF_4]$ gives a bright yellow microcrystalline deposit of the binuclear diazenide **B**[2] $[FWN_2CH_2CH_2WF]$, which adheres to the electrode surface, Figure 1 and Scheme 1.

Diazenide species which are closely related to **B** oxidise reversibly in solution near −0.5 V relative to ferrocinium/ferrocene (fc^+/fc)[3] but there is little redox activity of the bulk deposit of **B** at potentials in this vicinity; the material is not electronically conducting, and the W^{II} redox state is effectively trapped in the crystalline solid, Figure 2a.

However, close to E° for the reversible one-electron oxidation of the parent cation **A**$^+$, massive dissolution of the surface material takes place with concomitant amplification of

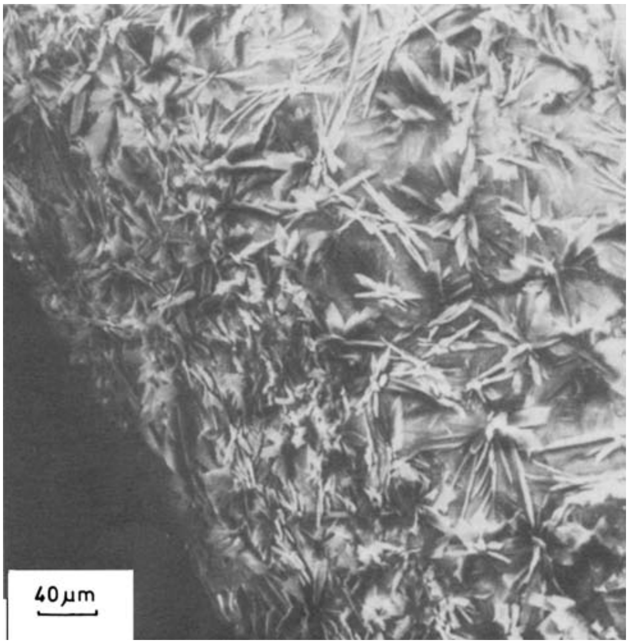
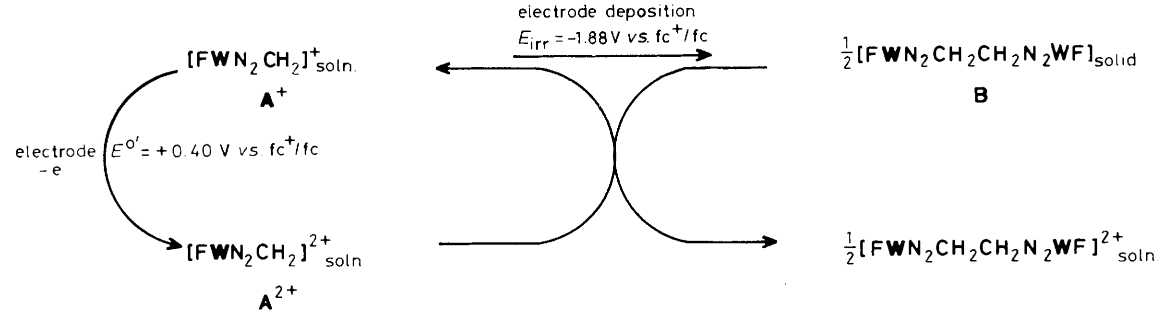


Figure 1. Microcrystalline deposit on platinum wire electrode. Deposition time 3 min from 2 mM solution of **A**$^+$ in 0.2 M $[NBu_4][BF_4]$–MeCN.



Scheme 1. Electrocatalysed dissolution of diazenide, **B**; **W** represents $[W(Ph_2PCH_2CH_2PPh_2)_2]$.

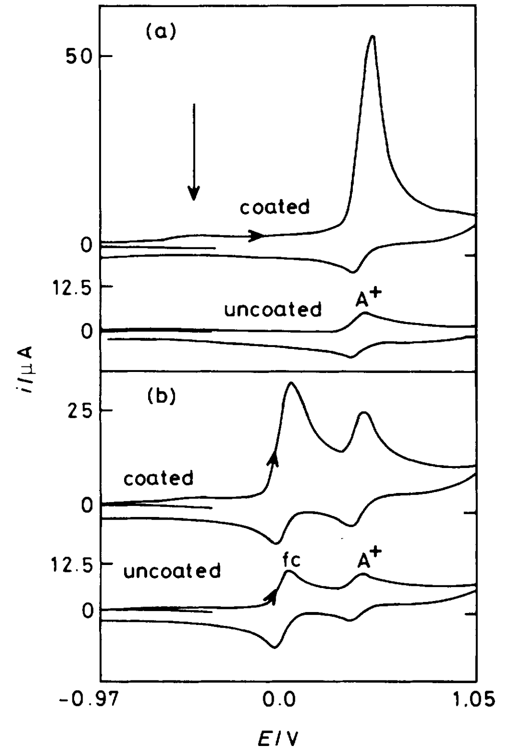


Figure 2. Voltammetric responses at coated and uncoated electrodes. (a) Diazoalkane, **A**$^+$. The arrow locates the slow surface oxidation of **B**. (b) Electrorelease of **B** electrocatalysed by fc$^+$/fc. **B** was electrodeposited for 1 min on a polished vitreous carbon disc of area 0.73 mm^2 by reduction at −2.0 V *vs.* fc$^+$/fc of a 2 mM solution of **A**$^+$ in 0.2 M $[NBu_4][BF_4]$-MeCN; fc concentration 2.4 mM. Scan-rate for both (a) and (b) was 0.25 V s^{-1}.

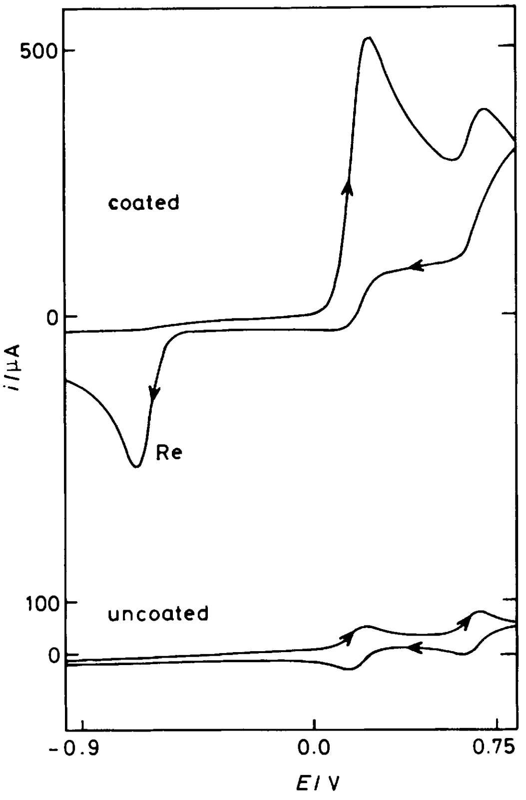


Figure 3. Voltammetric response of dpab (1.2 mM in 0.2 M $[NBu_4]$-$[BF_4]$-MeCN) at a Pt-wire electrode of area 14.5 mm^2 coated with *trans*-$[ReCl_2(Ph_2PCH_2CH_2PPh_2)_2]$. Peak Re corresponds to the detection of electroreleased *trans*-$[ReCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ which undergoes a one-electron reduction. Beneath is shown the response of the same solution of dpab at the same Pt electrodes after removal of the surface coating. Both voltammograms were recorded at a sweep-rate of 0.3 V s^{-1}.

the peak-current for the oxidation of the diazoalkane, Figure 2a. Chronocoulometric measurements show that the ratio Q_{in}/Q_{out} *i.e.* (charge injected during deposition/charge out during dissolution) is about 1.2.

We can account for the amplification and the electroreleasing[4] of oxidised material in the following way. The microcrystalline deposit is porous and this allows the diffusion of solution species within it. The solution cation **A**$^+$ is oxidised to the dication at the electrode surface and reduced back at the crystal surfaces of **B**. In this fashion **B** is electrocatalytically oxidised to a soluble form by the shuttling of the **A**$^+$/**A**$^{2+}$ couple, Scheme 1.

If this mechanism is correct then foreign couples should also stimulate the dissolution of the surface material, provided their E^o-values are sufficiently positive of that for the primary oxidation of the diazenide **B**. That this is the case is evident by the amplification of the voltammetric peak-current for the oxidation of ferrocene, Figure 2b: the magnitude of the amplification with ferrocene is about half of that observed for the diazoalkane because the E^o of the latter encompasses the secondary irreversible oxidation of **B**.[3]

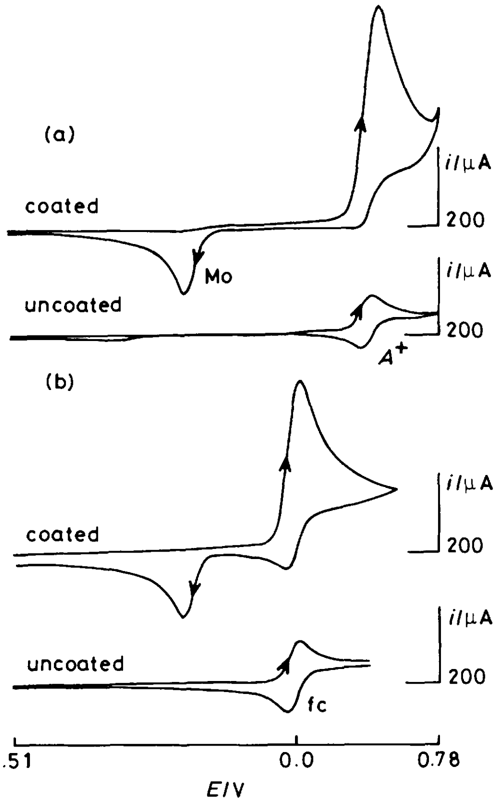


Figure 4. Overpotential for electroreleasing of *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ is controlled by solution redox catalyst: (a) A^+ (2 mM, scan-rate 0.24 V s^{-1}) at molybdenum chloride coated and uncoated Pt-electrode (area, 14.5 mm^2); (b) ferrocene (0.75 mM, scan-rate 0.15 V s^{-1}) at coated and uncoated electrodes in 0.2 M $[NBu_4][BF_4]$–MeCN. Peak Mo in (a) corresponds to the reduction of electroreleased *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$.

It is possible mechanically to prepare electrodes with surface coatings of other microcrystalline materials which display electrochemical properties analogous to the composite described above. Mulls of *trans*-$[ReCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ and *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ were prepared by grinding samples of the halides in MeCN, dip-coating onto platinum wire electrodes, and drying in air. The dramatic amplification of the voltammetric response of 1,4-bis(diphenylamino)benzene (dpab) at an electrode coated with the Re-complex is illustrated by Figure 3: soluble *trans*-$[ReCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ is electroreleased into solution and is detected upon scan-reversal.

That the overpotential for the dissolution of the surface material is determined solely by the redox catalyst is clearly shown by the voltammograms of A^+ and ferrocene at electrodes coated with *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$,[5] Figure 4.

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