Electrochemical modification of chromium surfaces using 4-nitro- and 4-fluorobenzenediazonium salts†

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Chromium surfaces can be electrografted with organic surface films using 4-nitro- or 4-fluorobenzenediazonium salts, despite the fact that the surfaces are covered with a protective chromium oxide layer.

In many scientific and industrial applications metal surfaces are modified with organic materials to produce a variety of functional groups that define the final surface properties (water repelling, self cleaning, antibacterial, *etc.*). A promising method to conduct a surface modification with organic molecules is electrochemical reduction of vinylic,[1] diazonium[2] or iodonium salts[3] at the surface. Various metal surfaces have already been grafted successfully in this manner, *e.g.* Fe,[4] Ni,[5] Zn,[5] Co,[5] Cu,[5] Pt,[5] and Au.[4–6] However, so far no reports have appeared on the modification of chromium surfaces applying the diazonium route.

This work presents results showing that it is indeed possible to electrochemically graft 4-nitrobenzenediazonium tetrafluoroborate (NBD) onto chromium, despite the fact that the outermost part of the surface consists of chromium oxide which is electrically insulating.[7] The modified surfaces are analysed by cyclic voltammetry (CV), polarization modulated infrared reflection absorption spectroscopy (PMIRRAS), and X-ray photoelectron spectroscopy (XPS).

Two different chromium substrates were considered according to the specific purpose of the measurements. For PMIRRAS and XPS analyses relatively large surface areas were required, so in these cases chromium deposited on microscope glass slides (1.1 cm × 6 cm) by physical vapour deposition were used. To ensure consistency in the measurement series these electrodes were also employed in the appropriate CV experiments, although for routine electrochemical experiments the use of smaller electrodes prepared from chromium nuggets was found to be more suitable.

Fig. 1 illustrates the repetitive voltammograms recorded for NBD on the chromium-covered glass slide (see inset for a scanning electron microscopy image of the surface). On the initial cycle a broad irreversible wave is observed with a peak potential of −0.19 V *vs.* SCE corresponding to the reduction of NBD. This reduction results in a generation of the 4-nitrophenyl radical upon expulsion of N_2.[2]

The location of the peak as well as the broadness of the wave are similar to those observed for NBD on other metals such as Au, Pt, and Ni.[5,8] The second and, in particular, the third cycles are essentially featureless which can be interpreted in terms of a passivation of the surface occurring during the first sweep because of aryl radicals attacking and reacting with the surface. This method is expected to result in relatively thin, yet multilayered films.[9–11] The electrodes produced in this manner are denoted as Cr–NB. Performing a potentiostatic electrolysis at *e.g.* an applied potential of −0.5 V *vs.* SCE for 300 s rather than the three cycles in CV produces a relatively thicker film in the grafting procedure as evidenced by its complete blocking abilities towards 2,4,6-triphenylthiopyrylium tetrafluoroborate as mentioned in the ESI.†

A common electrochemical methodology employed for a first analysis of the properties of surface films is to measure charge transfer properties of a suitable redox probe. As demonstrated in the ESI,† the charge transfer for 2,4,6-triphenylthiopyrylium tetrafluoroborate becomes almost completely blocked upon electrografting, which is consistent with the formation of a relatively compact layer on the modified electrode surface.

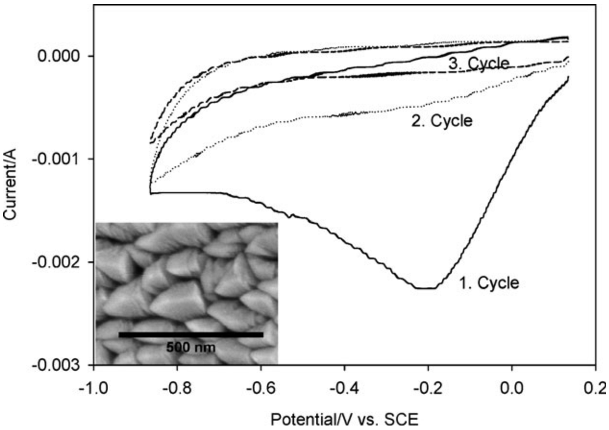

Fig. 1 Cyclic voltammograms of 2 mM solution of 4-nitrobenzenediazonium tetrafluoroborate in 0.1 M Bu_4NBF_4/CH_3CN recorded at a sweep rate of 0.1 V s^{-1} at a Cr electrode. Solutions were stirred in between cycles. Inset shows a scanning electron microscopy image of a Cr-covered microscopic glass slide.

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† Electronic supplementary information (ESI) available: Equipment, experimental procedures, synthesis of NBD, blocking experiments, PMIRRAS spectra at different substrate angles, XPS spectra. See DOI: 10.1039/b9nj00422j

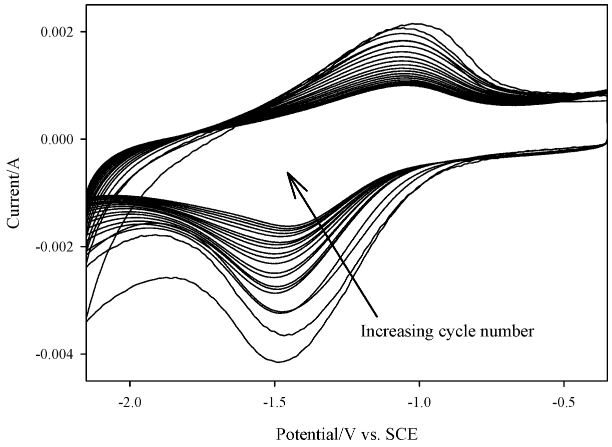

Fig. 2 Twenty successive cyclic voltammograms recorded on a Cr–NB electrode in 0.1 M Bu_4NBF_4/CH_3CN at a sweep rate of 2 V s^{-1}.

Further evidence of the presence of the nitrophenyl groups in the layer can be provided by exploiting their electroactivity. Fig. 2 shows successive voltammograms recorded on a Cr–NB electrode (ultrasonically rinsed) in a pure electrolyte solution. The first sweep shows a significant reduction peak appearing at −1.49 V *vs.* SCE and on the reverse sweep a somewhat smaller oxidation peak at −1.02 V *vs.* SCE. On subsequent cycles similar, yet smaller, appearances of what reasonably and in accordance with other studies[5,8] can be assigned to originate from the surface-attached $–C_6H_4NO_2/–C_6H_4NO_2^{\bullet -}$ redox couple.

The charge associated with the redox waves can be extracted from an integration of the current signal and on this basis the surface coverage can be easily calculated to be ~2.3 × 10^{-9} mol cm^{-2}. This value is about four times higher than those found for the grafting of 4- or 3-nitrobenzenediazonium on pyrolyzed photoresist film[10] and glassy carbon,[3,11] which presumably can be attributed to the fact that the actual area of the rough chromium slide is appreciably larger than the geometrical area (~3.5 cm^2 corresponding to the part of the slide immersed into solution).

The observed electrochemical deactivation, which occurs relatively slowly for an organic redox couple, is due to a chemical reaction, most likely a protonation of $–C_6H_4NO_2^{\bullet -}$ by the residual water always present in CH_3CN.[12] This, along with the observation that a film is still present after the extensive sweeping (as well as ultrasonic treatment) as revealed by a blocking experiment using 2,4,6-triphenylthiopyrylium tetrafluoroborate, makes it unlikely that desorption processes involving possible physisorbed species should contribute to the decline of the signal.

It is worth noting that the charge transfer process of surface-attached $–C_6H_4NO_2/–C_6H_4NO_2^{\bullet -}$ at the chromium surface is quasi-reversible as evidenced from the separation of the peaks by more than 400 mV. In comparison, there is little or no peak separation at all for *e.g.* Cu[5] and Ni.[5] This difference in the redox behavior can be attributed to the presence of a partly insulating layer of chromium oxide on top of the bulk chromium material, resulting in slower charge transfer processes.

To verify the presence of nitrophenyl groups on Cr–NB the PMIRRAS technique was applied. Because of the orientation of the chromium on the slides (see inset in Fig. 1) the orientation of the polarization of the light is shifted. This has the consequences[13] that absorption bands will point downwards (and not upwards as usual) and the intensity of the bands will be dependent on the sample orientation.

The IR spectrum obtained for Cr–NB is depicted in Fig. 3. Distinct bands observed at 1530 and 1350 cm^{-1} correspond to the asymmetric and symmetric stretch of the nitro group, respectively.[4,14,15] The minor band at 1600 cm^{-1} is consistent with aromatic ring stretching.[14] None of these bands are seen for an ungrafted chromium substrate (data not shown). According to the selection rules in PMIRRAS only vibrations with a transition mode having components normal to the surface of the substrate are detectable. Covalently attached nitrophenyl groups would indeed be expected to give PMIRRAS signals as they at least to a certain extent have to stand upright on the surface.[15–17] In contrast, physisorbed molecules which most likely would lay flat on the surface would give rise to no such signals.

Fig. 3 would seem to indicate that cyclic voltammetric sweeping on Cr–NB induces almost no change in the PMIRRAS spectra, but importantly a notable decline of the PMIRRAS signal is seen upon continued sweeping. Overall, this trend is therefore in line with the voltammetric analysis (see Fig. 2). In addition, the PMIRRAS spectra have no band from the diazonium group (~2300–2230 cm^{-1}; data not shown)[14] verifying that physisorption of NBD presents no problem. Hence, PMIRRAS confirms the presence of covalently attached nitrophenyl groups on the chromium surface.

The issue which remains to be resolved at this point is the nature of bonding in Cr–NB, *i.e.* does the chemisorption of nitrophenyl groups go through Cr–C or Cr–O–C linkages, taking into account that chromium surfaces are covered by a thin layer of chromium oxide.[7] Although it has been shown that aryl groups, in general, would prefer to be attached to the metal rather than metal oxides,[4,5] the Cr–O–C option should still be considered in the chromium case. A few examples involving the immobilization of aryl groups on oxides such as

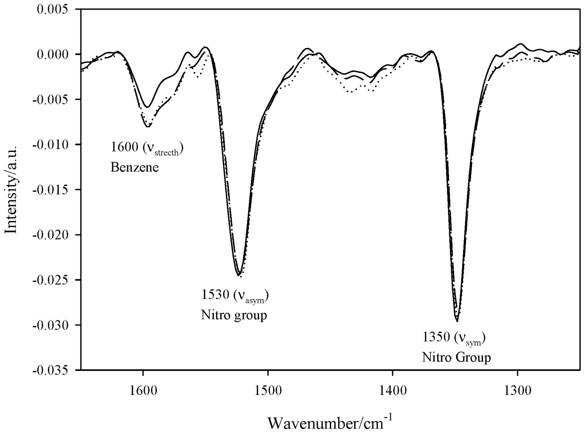

Fig. 3 PMIRRAS spectrum of a Cr–NB slide before sweeping (—) and after the 1st (---) and 2nd (···) cycle in CV.

titanium,[18] copper,[19] aluminium,[19] and indium tin oxides (ITO)[20] have been demonstrated previously. In these cases a covalent attachment is observed for copper oxide films whereas the linkage to indium tin oxide at present is unclear.

Relevant information in this respect was extracted from XPS measurements on Cr–NB. For comparative purposes an ungrafted as well as a 4-fluorobenzenediazonium grafted chromium slide (Cr–FB) prepared under the same conditions as Cr–NB were included in the analysis. Survey scans along with high-resolution spectra for Cr 2p and N 1s are available in the ESI.† These spectra show that a nitro group can be identified for Cr–NB,[21] the F signal is evident for Cr–FB, and for all samples a layer of chromium oxide is detectable on the surface.

In Fig. 4 high-resolution XPS spectra of C 1s and O 1s are collected. The carbon peak is broad for all measurements due to the almost unavoidable contamination of the surface with organic material (*i.e.* C–O, C=O, and aliphatic C–H groups) from the atmosphere as corroborated by the pronounced carbon signal obtained for an ungrafted slide. However, a more detailed elaboration of the C 1s spectrum for Cr–NB (included in the ESI†) reveals that ~91% of the signal can be attributed to C–NO_2 and aromatic C–H bonds. In addition, a broad peak at 291 eV corresponding to the $\pi \rightarrow \pi^*$ transition of the aromatic ring is evident. Importantly, no peak arising from a C–Cr bond, which would be expected to be at 282.4 eV,[22] can be identified for neither Cr–NB nor Cr–FB indicating that the nitrophenyl groups are not bound to the Cr surface through a carbide bond.

The high resolution O 1s spectra of the grafted and, in particular, the ungrafted slides show a pronounced signal at 530.4 eV originating from O–Cr (*i.e.* chromium oxide) in the outer layer.[22] Unfortunately, identification of an eventual Cr–O–C covalent bonding on the grafted samples is impossible, since the O–Cr bonding energy in Cr–O–C is expected to be located also in the region around 531 eV.[23] Interestingly, for the Cr–NB sample only, an additional peak is seen at 533 eV which can be assigned to oxygen in the nitro group.

Hence, XPS measurements show that nitrophenyl groups are present on the surface of Cr–NB and that the attachment does not go *via* direct metal–carbon covalent bonding. Knowing that the outerlayer of the metal surface consists of chrominium oxides leaves us with a covalent attachment mode based on Cr–O–C covalent bonding as the most plausible option. This interpretation is fully consistent with the observed low electron transfer rates associated with the surface-attached nitrophenyl redox system and the robustness of the organic surface film. A similar covalent attachment has been observed by McCreery for copper oxide films.[19]

This work demonstrates that it is possible to electrograft chromium surfaces with organic material using 4-nitrobenzenediazonium or 4-fluorobenzenediazonium salt, despite the fact that the surfaces are covered with a protective chromium oxide layer. Electrochemical measurements of the grafted and subsequently ultrasonically rinsed samples in the former case show that the surface is modified with covalently attached nitrophenyl groups. This is substantiated by PMIRRAS spectra in which the nitrophenyl groups give rise to large signals. Finally, XPS measurements exclude the possibility that a covalent attachment should go through a direct bonding of the aryl group to the chromium surface. Rather the results suggests that the aryl groups are attached to the surface *via* the oxide layer in terms of Cr–O–C linkages, although a direct detection of such a bond was precluded. We believe that this information will be pertinent in future studies on electrografted stainless steel surfaces.

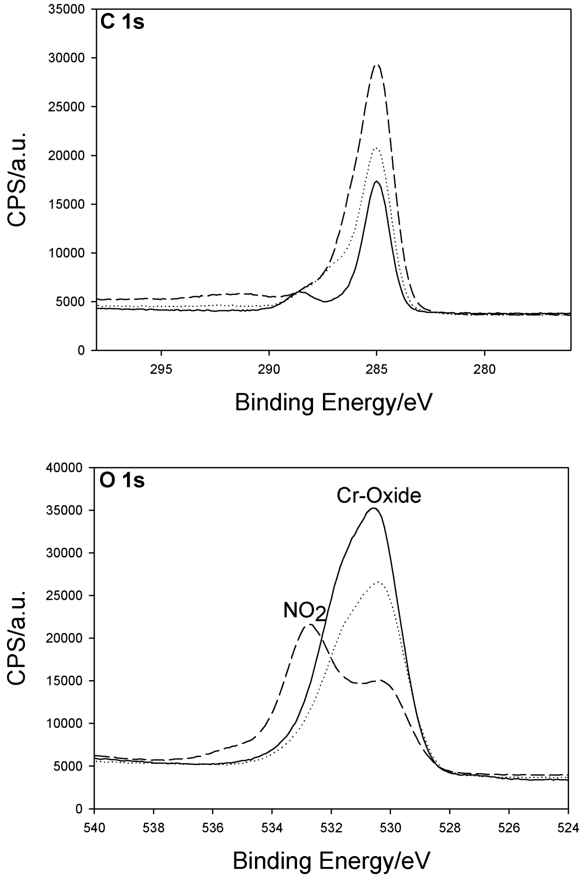

Fig. 4 High resolution XPS spectra, *i.e.* counts per second (CPS) *vs.* binding energy, of carbon (top) and oxygen (bottom) for the ungrafted (—), Cr–FB (···) and Cr–NB (---) slides.

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Experimental

Electrochemical grafting was performed by means of three successive voltammetric cycles from 0.15 to −0.85 V *vs.* SCE from a 2 mM 4-nitrobenzenediazonium tetrafluoroborate solution in 0.1 M Bu_4NBF_4/CH_3CN. The grafted surface was ultrasonicated for 10 min in various solvents before analysis by cyclic voltammetry, PMIRRAS, and XPS.

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