Characterisation of two distinctly different processes associated with the electrocrystallization of microcrystals of phase I CuTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane)†

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Received 23rd May 2006, Accepted 15th August 2006
First published as an Advance Article on the web 14th September 2006
DOI: 10.1039/b607290a

Semi-conducting phase I CuTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane), which is of considerable interest as a switching device for memory storage materials, can be electrocrystallized from CH3CN via two distinctly different pathways when TCNQ is reduced to TCNQ− in the presence of [Cu(MeCN)4]2+. The first pathway, identified in earlier studies, occurs at potentials where TCNQ is reduced to TCNQ− and involves a nucleation–growth mechanism at preferred sites on the electrode to produce arrays of well separated large branched needle-shaped phase I CuTCNQ crystals. The second pathway, now identified at more negative potentials, generates much smaller needle-shaped phase I CuTCNQ crystals. These electrocrystallize on parts of the surface not occupied in the initial process and give rise to film-like characteristics. This process is attributed to the reduction of Cu[T(CNQ)2]TCNQ] or a stabilised film of TCNQ via a solid–solid conversion process, which also involves ingress of Cu+ via a nucleation–growth mechanism. The CuTCNQ surface area coverage is extensive since it occurs at all areas of the electrode and not just at defect sites that dominate the crystal formation sites for the first pathway. Infrared spectra, X-ray diffraction, surface plasmon resonance, quartz crystal microbalance, scanning electron microscopy and optical image data all confirm that two distinctly different pathways are available to produce the kinetically-favoured and more highly conducting phase I CuTCNQ solid, rather than the phase II material.

Introduction

The synthesis and characterisation of CuTCNQ is of considerable interest1–6 because of the suggested use of this semiconducting solid as an electronic and optical switching device with potential applications in memory storage.7,8 It was recently established that CuTCNQ could be chemically synthesized in two distinct phases of significantly different conductivity, thereby furthering our understanding of the polymorphism of CuTCNQ.1 An electrochemical approach to the formation of bulk phase I and phase II CuTCNQ was demonstrated in the situation where solid TCNQ, which is highly insoluble in water (as is CuTCNQ), is adhered to an electrode surface and reduced while in contact with aqueous CuSO4 electrolyte media.2 Subsequently,3,6 we demonstrated that the more conductive phase I CuTCNQ can be electrocrystallized from acetonitrile solutions as well separated arrays of large needle-shaped branched crystals that nucleate at preferred sites on the electrode and grow rapidly into the bulk solution. Electrocrystallization was detected at potentials slightly more negative than those required for reduction of TCNQ to TCNQ− [Fig. 1(a)] containing [Cu(MeCN)4]2+ and occurred according to the scheme

$$\text{TCNQ}_{(\text{MeCN})} + e^- \rightarrow \text{TCNQ}^-_{(\text{MeCN})} \quad (1)$$

$$\text{TCNQ}^+_{(\text{MeCN})} + \text{Cu}^{2+}_{(\text{MeCN})} \rightarrow \text{CuTCNQ} \quad (2)$$

In these studies, it was noted that additional voltammetric features occurred at potentials between the TCNQ2+/− and TCNQ+−/− processes [Fig. 1(b)]. Results of this study now demonstrate that these additional Faradaic features provide an alternative route to the formation of closely spaced arrays of much smaller sized CuTCNQ phase I crystals, rather than phase II or other forms of copper-TCNQ material.

Voltammetric, electrochemical quartz crystal microbalance, surface plasmon resonance, optical and electron microscopy, spectroscopy and X-ray diffraction methods have been used to characterize the identity, phase and morphology of the product formed via this alternate electrocrystallization pathway that occurs at carbon, metallic (gold and platinum) and semiconducting [indium tin oxide (ITO) and boron-doped diamond (BDD)] electrode surfaces.

Experimental

Materials

98% Tetrakis(acetonitrile) copper(I) hexafluorophosphate ([Cu(MeCN)4]PF6) from Strem Chemicals; 98% TCNQ from

† Electronic supplementary information (ESI) available: scanning electron microscopy images of CuTCNQ electrocrystallization after voltammetry. See DOI: 10.1039/b607290a
Aldrich; and 99.99% acetonitrile from Omnisolv were used as provided by the manufacturer. Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$), used as the supporting electrolyte, was purified and recrystallized as described elsewhere.$^3$ 10 mM TCNQ (0.1 M Bu$_4$NPF$_6$) and 100 mM [Cu(MeCN)$_4$]PF$_6$ (0.1 M Bu$_4$NPF$_6$) stock solutions were prepared in acetonitrile. Two solutions were prepared from these stock solutions for voltammetric and electrocrystallization studies. Addition of 1 mL of the 100 mM Cu$^+$ solution to 10 mL of the 10 mM TCNQ solution produced a solution having equimolar 9.09 mM concentrations of both TCNQ and Cu$^+$ (MeCN). Addition of 0.33 mL of the 100 mM Cu$^+$ solution into 10 mL of the 10 mM TCNQ solution produced a solution having 9.66 mM TCNQ and 3.22 mM Cu$^+$ (MeCN).

Instrumentation and procedures

Voltammetric experiments were commenced after degassing the acetonitrile (0.1 M Bu$_4$NPF$_6$) electrolyte solutions with solvent saturated nitrogen for at least 10 minutes.

Electrochemical quartz crystal microbalance (EQCM) experiments were undertaken with an ELCHHEMA EQCN-701 quartz crystal nanobalance and a PS-205 potentiostat connected to a computer via an Advantech PCI-1711 DAQ, as reported elsewhere.$^3$

In situ optical video images were obtained with an Olympus SZ604STR-F Zoom stereomicroscope coupled to a DP-11 digital camera, as described elsewhere.$^6$ Ex situ optical microscope images were captured with an Olympus BX-51M optical microscope (10, 20 and 50× magnification) and a DM-12 digital camera.

Ex situ scanning electron microscopy (SEM) employed a Philips XL30 Field Emission Gun Scanning Electron Microscope or a JEOL JSM-460A, both with an Oxford Link energy dispersive X-ray (EDAX) system. Imaging of solids deposited on 3 mm glassy carbon (GC) electrodes was performed with the aid of a homebuilt aluminium electrode holder. Solution remaining on the electrode after removal from the electrochemical cell was carefully removed by use of tissue paper (Kimwipe). Electrodes were also gently bathed in acetonitrile and then in distilled water. This procedure greatly reduced the amount of Bu$_4$NPF$_6$ present on the electrode surface.

X-Ray powder diffraction (XRD) patterns of electrocrystallized CuTCNQ formed on ITO electrodes and diffuse reflectance infrared transform spectroscopy (DRIFT) data were obtained using the previously reported configuration.$^6$

In situ surface plasmon resonance (SPR) experiments were performed using an Autolab ESPRIT (ECO-Chemie) system in combination with the Autolab PGSTAT100 (ECO-Chemie) potentiostat. SPR substrates (gold coated glass) were placed onto a hemi-cylindrical lens with index matching oil (all supplied by ECO-Chemie). Linearly p-polarized light with a wavelength of 670 nm was directed through the lens forming a 2 mm$^2$ spot on the 50 nm thick gold film in the Kretschmann configuration. The gold film was used as the working electrode with the potential applied being versus a platinum wire quasi-reference electrode. The angle of minimum reflected light intensity was used to monitor the SPR signal during the course of voltammetric experiments.

Results and discussion

Cyclic voltammetry of TCNQ and Cu(MeCN)$_4$$^+$

Cyclic voltammetric studies describing the reduction of TCNQ to TCNQ$^-$ and TCNQ$^{2-}$, and the oxidation and reduction of Cu(MeCN)$_4$$^+$ in acetonitrile (0.1 M Bu$_4$NPF$_6$) at GC, gold, Pt, ITO and BDD electrodes have been described elsewhere.$^3,6$ TCNQ(MeCN)$^-$ dissolved in acetonitrile (0.1 M Bu$_4$NPF$_6$) exhibits two well-separated, one-electron diffusion controlled reduction processes. Cu(MeCN)$_4$$^+$ in acetonitrile (0.1 M Bu$_4$NPF$_6$) also exhibits two, one-electron processes, but in this case, one involves reduction and the other oxidation. The origins of the electrode processes are summarized in eqn 3–6.

![Cyclic voltamograms](image_url)

**Fig. 1** Cyclic voltammograms obtained at a 1 mm diameter Au electrode in acetonitrile (0.1 M Bu$_4$NPF$_6$) when 9.09 mM TCNQ is reduced in the presence of 9.09 mM Cu$^+$ (MeCN): (a) for process I when the potential is switched at −0.1 V vs. Ag/AgCl, and (b) when the potential is switched at −0.25 V vs. Ag/AgCl, at a scan rate of 100 mV s$^{-1}$ so that process I$'$ is also detected.
and the potential at which they occur provides information on the conditions needed to electrocrystallize CuTCNQ. Ref. 3 and 6 may be consulted for additional details.

\[
\text{TCNQ}^{\text{(MeCN)}} + e^- \rightleftharpoons \text{TCNQ}^{2-}(\text{MeCN}) \quad (3)
\]

\[
\text{TCNQ}^{2-}(\text{MeCN}) + e^- \rightleftharpoons \text{TCNQ}^{2-}(\text{MeCN}) \quad (4)
\]

\[
\text{Cu}^{+}(\text{MeCN}) + e^- \rightleftharpoons \text{Cu}^0(\text{Metal}) \quad (5)
\]

\[
\text{Cu}^2+(\text{MeCN}) \rightleftharpoons \text{Cu}^{2+}(\text{MeCN}) + e^- \quad (6)
\]

Cyclic voltammetry for reduction of TCNQ in the presence of Cu(MeCN)+

Reduction of TCNQ to TCNQ– in acetonitrile (Bu4NPF6) in the presence of Cu+(MeCN) at equal concentrations (9.09 mM) produces conditions at the electrode surface where the CuTCNQ solubility product of 4.9 × 10−7 M2 is substantially exceeded.3 Consequently, electrocrystallization of CuTCNQ may occur on the electrode surface at potentials where the formation of TCNQ2– commences, provided the kinetics of precipitation are fast enough [scan rate sufficiently slow, Fig. 1(a)] and nucleation sites are available for crystal growth to take place on the electrode surface.3,6 Studies on gold (Fig. 1, labelled as process I), platinum, carbon, ITO and BDD electrodes display an initial TCNQ0– reduction process with I_red and I_ox being associated with TCNQ reduction and TCNQ2– oxidation respectively, and I_strip representing the sharp stripping process for phase I CuTCNQ (the electrocrystallization of CuTCNQ by process I_red and its stripping process I_strip is termed I). Formation of CuTCNQ by process I occurs by nucleation at preferred sites on the surface,3,6 followed by a rapid growth process that produces large branched needle-shaped phase I crystals.3,6 On switching the scan direction, the presence of a symmetrical peak [labelled I_strip in Fig. 1(a)] may be observed. This is associated with partial stripping of CuTCNQ when the potential is returned to more positive values.3 More strongly adhered crystals were formed on the ITO surface, which are more difficult to strip from the electrode surface.6

At more negative potentials, but prior to the onset of reduction of TCNQ to TCNQ2–, a small Faradaic couple is detected [labelled as process I’ in Fig. 1(b)] with very sharp, symmetrical reduction (I’_red) and oxidation (I’_ox) peaks at all electrode surfaces examined. It is this second process (designated feature I’) which is of interest in this paper. It is important to note that process I’ was only observed in cyclic voltammograms when both TCNQ and Cu+(MeCN) were present in solution at concentrations that enabled the CuTCNQ solubility product limit of 4.9 × 10−7 M2 to be exceeded. Furthermore, cyclic voltammetric experiments performed with a GC electrode modified with an electrocrystallized film of CuTCNQ in the presence of TCNQ(MeCN)/background electrolyte, or Cu+(MeCN) did not exhibit any evidence of process I’, implying all of these components are required for process I’.

With a TCNQ concentration of around 9 mM, process I’ remains present when the Cu+(MeCN) concentration is varied over the range 3.22 to 11.76 mM [Fig. 2(a)]. The areas (charge) associated with processes I’_red and I’_ox are almost constant for this sequence of experiments. In contrast, the potential, defined as the average of the reduction and oxidation peak potentials, shifts to slightly less negative values with increasing Cu+(MeCN) concentration (Table 1). Lowering the concentration of TCNQ from 9.09 to 1 mM while having a 10-fold excess of Cu+(MeCN) resulted in a total absence of process I_strip when a sweep rate of 100 mV s−1 was employed. However, process I’ was still evident.

![Cyclic voltammograms obtained in acetonitrile (0.1 M Bu4NPF6) at a 3 mm diameter GC electrode using a scan rate of 100 mV s−1 for the reduction of 9.66 mM TCNQ in the presence of 3.22 mM Cu+(MeCN) as a function of switching potential.](image)

**Fig. 2** (a) Cyclic voltammograms obtained in acetonitrile (0.1 M Bu4NPF6) at a 3 mm diameter GC electrode using a scan rate of 100 mV s−1 for the reduction of 9.66 mM TCNQ in the presence of 3.22 mM Cu+(MeCN) as a function of switching potential. (b) Voltammograms in acetonitrile (0.1 M Bu4NPF6) at a 3 mm diameter GC electrode using a scan rate of 100 mV s−1 in the positive potential direction after holding the potential at −0.25 V vs. Ag/AgCl (more negative than for process I’) for 1, 5, 10, 20 and 30 s.

**Table 1** Cyclic voltammetric data obtained at a 3 mm diameter GC electrode using a scan rate of 20 mV s−1 for process I’ in acetonitrile (0.1 M Bu4NPF6) vs. Ag/AgCl at different Cu+ and TCNQ concentrations

<table>
<thead>
<tr>
<th>Cu+/TCNQ concentration/mM</th>
<th>E_p^red</th>
<th>E_p^ox</th>
<th>ΔE_p</th>
<th>E_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.22/9.66</td>
<td>−0.237</td>
<td>−0.144</td>
<td>0.093</td>
<td>−0.191</td>
</tr>
<tr>
<td>6.25/9.35</td>
<td>−0.214</td>
<td>−0.107</td>
<td>0.107</td>
<td>−0.161</td>
</tr>
<tr>
<td>9.09/9.09</td>
<td>−0.156</td>
<td>−0.093</td>
<td>0.063</td>
<td>−0.125</td>
</tr>
</tbody>
</table>
Experiments were performed with 9.66 mM TCNQ and 3.22 mM Cu$^{+}_{(MeCN)}$, and the potential was held at $-0.25$ V vs. Ag/AgCl for different lengths of time to induce process $I'_{\text{red}}$. This was then followed by sweeping the potential at a scan rate of 100 mV s$^{-1}$ in a positive direction in order to monitor process $I'_{\text{ox}}$ [Fig. 2(b)]. It can be seen quite clearly that the electrodeposition time does not significantly affect the current magnitude or shape of the $I'_{\text{ox}}$ process. The charge associated with this process at electrodeposition times up to 30 s remained almost constant (151 mC cm$^{-2}$) which suggests that this process is associated with the oxidation of a film or the stripping of a fixed amount of solid from the electrode surface (the charge associated with process $I'_{\text{red}}$ during cyclic voltammetry also has a similar value). In contrast, longer electrodeposition times lead to the emergence and then increase in magnitude of process $I_{\text{strip}}$. Clearly process $I'$ is mechanically very different from process $I$.

**Galvanostatic reduction of TCNQ in the presence of Cu(MeCN)$_4^{+}$**

Electrodeposition of CuTCNQ by constant cathodic current galvanostatic methods was undertaken (Fig. 3) at a gold electrode for 9.09 mM Cu$^{+}_{(MeCN)}$ with 9.09 mM TCNQ, and 3.22 mM Cu$^{+}_{(MeCN)}$ with 9.66 mM TCNQ. For 9.66 mM TCNQ in the presence of 3.22 mM Cu$^{+}_{(MeCN)}$, and with constant cathodic currents $\leq -16$ $\mu$A, the potential initially shifts negatively with time, and then remains constant until the end of the 30 s electrolysis period. Applying a more negative current results in a dramatic shift in the potential–time dependence. However, it can be seen [Fig. 3(a)] that a period of a constant potential of $-200$ mV vs. Ag/AgCl is obtained, whose lifetime is dependent on the magnitude of the applied current. The lifetime of this constant potential state decreases from 17 to 5 s when the applied cathodic current is increased from $-20$ to $-25$ $\mu$A. Analogously for 9.09 mM Cu$^{+}_{(MeCN)}$ with 9.09 mM TCNQ, a constant potential regime of $-200$ mV vs. Ag/AgCl is detected. However, this constant potential state is achieved with a smaller cathodic current ($17$ $\mu$A compared to $-19$ $\mu$A) and for a shorter time than for 3.22 mM Cu$^{+}_{(MeCN)}$ with 9.66 mM TCNQ [Fig. 3(b)].

The attainment of a constant potential of $-200$ mV vs. Ag/AgCl coincides with the potential for process $I'$ (Fig. 2). At smaller applied currents, it is assumed that electrocrystallization of CuTCNQ proceeds via process $I$. Thus, as in the case of controlled potential experiments, the mechanism for CuTCNQ electrocrystallization can be changed from the process $I'$ to the process $I'$ mode, but in this case via alteration of the current. At even larger applied cathodic currents, and particularly for 9.09 mM Cu$^{+}_{(MeCN)}$ with 9.09 mM TCNQ, an additional electrolysis route is introduced [Fig. 3(b), >$-18$ $\mu$A]. This is attributed to either copper electrodeposition [copper electrodeposition from Cu(MeCN)$_4^{+}$ occurs at $-0.50$ V vs. Ag/AgCl], reduction of TCNQ$^{-2}$ to TCNQ$^{-2-}$, or reduction of CuTCNQ.

**Probing of electrocrystallized solid by microscopy**

Ex situ SEM images of solid electrocrystallized via process $I'$ were obtained after reduction of TCNQ was carried out at $-0.25$ V for fixed periods of time, or the potential was cycled over the potential range $0.75$ V to $-0.25$ V, in order to ascertain if the morphology of the solid formed under these conditions corresponds to either of the known CuTCNQ phases. Images were compared with those obtained via process $I$, which is known to produce CuTCNQ phase I.$^{3,6}$

Electrocrystallization at a GC electrode when the potential is held at 0 V to form phase I CuTCNQ via process $I'$ gave rise to well separated regions of extensively branched needles, consistent with rapid growth of CuTCNQ (phase I) from preferred sites on the surface.$^{3,6}$ After 30 s, some crystals have grown up to 30 $\mu$m in length [Fig. 4(a)]. In contrast, deposition for short times at $-0.25$ V, which encompass the potential regime of process $I'$ [Fig. 4(b)], leads to detection of only a very few large needle-shaped crystals. Predominately a large number of much more closely spaced smaller crystals (<5 $\mu$m in length) are found. However, longer deposition times at $-0.25$ V lead to the growth of large needles, some of which have branched to such an extent that they have the appearance of dendrimers. A few of the smaller crystals also remain almost unchanged (images not shown). Analogous electrocrystallization experiments (followed by SEM imaging) were

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**Fig. 3** Potential–time plots obtained with a 1 mm diameter Au electrode in acetonitrile (0.1 M Bu$_4$NPF$_6$) for the reduction of TCNQ in the presence of Cu$^{+}_{(MeCN)}$ at (a) 3.22 mM Cu$^{+}_{(MeCN)}$ and 9.66 mM TCNQ with constant applied cathodic currents of $-5$, $-10$, $-15$, $-16$, $-17$, $-18$, $-19$, $-20$, $-21$ and $-25$ $\mu$A, and (b) 9.09 mM Cu$^{+}_{(MeCN)}$ and 9.09 mM TCNQ with constant applied cathodic currents of $-5$, $-10$, $-15$, $-16$, $-17$, $-18$, $-19$ and $-20$ $\mu$A.
also carried out on semi-conducting ITO electrodes at $-0.10 \text{ V}$ [Fig. 5 (a)] and $-0.30 \text{ V}$ [Fig. 5(b–d)] for 30 s. The applied potentials were slightly more negative than the case for the GC electrode, i.e. $-0.10 \text{ V}$ was used instead of $0 \text{ V}$ for process $I'$, and $-0.30 \text{ V}$ instead of $-0.25 \text{ V}$ was used for process $I''$, due to $IR_u$ drop effects associated with the large area ITO electrode. Again on the ITO electrode, the size of the crystals are much smaller and the packing density greater when a more negative deposition potential is used to induce solid formation via process $I''$.

SEM examination of a GC electrode surface after cycling the potential over the range from $+0.75 \text{ V}$ to $-0.25 \text{ V}$ at a scan rate of 100 mV s$^{-1}$ (Fig. S1) revealed the presence of the same needle-shaped crystals as generated by cycling the potential from $+0.75$ to $0 \text{ V}$, but with a much higher density. Scanning the potential back to $0 \text{ V}$ from $-0.25 \text{ V}$ after solid formation via process $I''$ had no significant affect on the crystals, but the crystals were removed from the electrode if the potential was scanned back to $+0.75 \text{ V}$. After 13 cycles of the potential over the range $+0.75$ to $-0.25 \text{ V}$, and finishing at $-0.25 \text{ V}$ [Fig. S1(c) and (d)], the branched needles were still present, as well as some very long 100 $\mu$m sized needles and a few cubic crystals. Scanning the potential back to $+0.75 \text{ V}$ (Fig. S1(e) and (f)) removed all of the smaller needles, leaving only a few large needles, and what appeared to be a cubic TCNQ crystal. EDAX analysis confirmed the presence of carbon, nitrogen and copper in representative needle-shaped crystals.

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Solvent removal could contribute to the morphology of the crystals detected. Thus, \textit{in situ} images obtained from optical video measurements (Fig. 6) were also recorded in order to monitor the course of the electrocrystallization process by pathways I' and I'' This required the use of vertically rather than horizontally oriented larger area ITO electrodes (ca. 0.25 cm\(^2\)). \textit{In situ} optical microscopy images of electrocrystallized CuTCNQ on ITO obtained \textit{via} constant potential (−0.10 V) deposition conditions (process I') show the growth of well spaced large dendritic-type crystals [Fig. 6(a)]. In contrast, when the potential is cycled into the I'\textsubscript{red} process region (lower limit −0.3 V) an extensive coating of small crystals is detected on all sections of the electrode, but not in the diffusion field of the initially formed larger crystals [Fig. 6(b)]. It is assumed that when the potential is in the region of process I', further growth of CuTCNQ also continues to occur in the case of the larger crystals generated in potential region I'. This process will consume TCNQ\(^-\) and so maintain a depletion zone around the region where large crystals are formed and hence produce a region on the electrode surface where no new TCNQ\(^-\) containing crystals are able to form.

**Infrared spectroscopy and X-ray diffraction measurements**

IR spectra obtained on solids deposited from 3.22 mM Cu\textsuperscript{+} (MeCN) with 9.66 mM TCNQ and 9.09 mM Cu\textsuperscript{+} (MeCN) with 9.09 mM TCNQ (no removal of Bu\textsubscript{4}NPF\textsubscript{6}) under conditions confined to process I' and I'' always exhibited characteristic bands at 2204, 2172, 1909 and 825 cm\(^{-1}\) associated with CuTCNQ phase I,\textsuperscript{1} but none indicating phase II formation\textsuperscript{1} (IR bands expected at 2214, 2172, 2141, 1940, 1896 and 825 cm\(^{-1}\)). No evidence for TCNQ was found\textsuperscript{10} (IR bands expected at 2226, 2173, 1996, 1861 and 1807 cm\(^{-1}\)). Characteristic Bu\textsubscript{4}NPF\textsubscript{6} IR absorption bands were detected.

Powder XRD data obtained on electrocrystallized solid obtained after potential step experiments (−0.30 V) at ITO electrodes also confirmed that exclusive formation of CuTCNQ phase I (phase II was not detected) takes place on ITO (see ref. 6 for details of XRD characterisation of CuTCNQ phases).

In summary, two distinctly different processes appear to be possible for the formation of phase I CuTCNQ. Potential region I' favours formation of large needle-shaped crystals, and region I'', much smaller, more densely packed crystals.

**EQCM studies**

EQCM data obtained at a gold electrode with 3.22 mM Cu\textsuperscript{+} (MeCN) and 9.66 mM TCNQ encompassing the region of processes I' and I'' are shown in Fig. 7. Data relevant to process I' are considered in ref. 3 and reflect the mass change encountered as CuTCNQ is deposited at (I\textsubscript{red}) and then stripped from the surface (I\textsubscript{strip}). It is now shown that process I'' also involves a mass change (assuming the Sauerbrey equation is valid). Under all conditions, on the first scan of the potential in the negative direction, only a minimal mass increase is detected at the potential where TCNQ reduction begins. On scanning into the I'\textsubscript{red} process region, a further small mass increase is detected. On switching to the positive potential scan direction, a very large mass increase is detected at potentials more positive than the I'\textsubscript{ox} process. This is the potential region where growth of the branched CuTCNQ crystals occurs.\textsuperscript{3} At the TCNQ\(^-\) oxidation peak, the rate of mass increase slows, since TCNQ\(^-\) is no longer being generated. When the potential of the stripping peak is reached, a very sharp mass loss is detected. However, upon completion of the first cycle of potential, the mass does not return to the initial or baseline value. This implies that a residue of solid remains adhered to the electrode, despite voltammetric evidence of a large stripping process.

Second and subsequent potential cycles show a rapid mass increase at potentials where TCNQ reduction to TCNQ\(^-\) commences. This is consistent with sites now being immediately present for rapid crystal growth as soon as a source of TCNQ\(^-\) becomes available. On the second cycle, a mass increase is also still detected at potentials where process I'\textsubscript{red} occurs. On completion of 13 potential cycles, the mass change associated with the electrocrystallization process I' almost ceases. At this stage it is possible that the needle crystals formed in this potential region have grown so large that their extremities become too far removed from the electrode surface to allow sufficient current to be transmitted in order to continue either the crystal growth or stripping processes. Alternatively, extensive dendritic crystal growth into the solution phase may have lowered the sensitivity of the EQCM response, as has been found previously in the case of TTFBr\textsubscript{0.7} electrocrystallization.\textsuperscript{11} In contrast, on repetitive cycles of the potential, the I'\textsubscript{red} process still exhibits a mass increase, and the I'\textsubscript{ox} process a mass decrease. The continued presence of a well defined I' process, and its mass increase/decrease, again suggests that this reaction resembles that expected from the presence of a rigid film on the electrode surface.

Cyclic voltammetric experiments at a gold microelectrode also indicate the presence of residual CuTCNQ on the electrode surface [Fig. 7(d)] after the completion of one potential cycle and the enhanced significance of process I' on repetitive cycling of the potential. As reported previously,\textsuperscript{5} on the first negative potential sweep a steady state response is observed for the reduction component of the TCNQ\(^0\)− process, whilst process I'' is not clearly discernible. In the reverse positive scan direction, the reductive current increases continually until it reaches a maximum value at potentials where formation of TCNQ\(^-\) ceases. As the positive direction scan is continued, a current crossover occurs at 300 mV [Fig. 7(d)], indicative of a nucleation–growth mechanism, and finally, at even more positive potentials, a stripping process is detected. The second cycle of the potential leads to distinctly different behaviour, in that a potential-independent limiting current region is not detected, even for the reduction component, implying that rapid growth of conductive crystals may now continue on sites that have been nucleated on the previous potential cycle. Furthermore, on the second cycle, process I'' can now be much more clearly seen. The significantly increased currents detected in the second cycle imply that residual phase I CuTCNQ is present on the microelectrode and, being semi-conducting, acts as an electrode itself and therefore increases the overall area of the microelectrode. The magnitude of the charge associated with the stripping
peak is also far less than that passed during the reduction component, again indicating only partial removal of CuTCNQ from the electrode in each cycle of the potential.

Surface plasmon resonance studies

SPR is another technique that can be used to monitor surface interactions with an electrode. The change in SPR response is due to the absorption of the evanescent wave generated at the electrode–solution interface when light is incident on its back face. SPR has mainly been used to monitor the mass change associated with protein and polymer voltammetry or film deposition.12–18 According to these studies, the SPR configuration used in this work should exhibit a shift in the angle of minimum reflected light intensity of 120 μrad with the adsorption of 1 ng mm⁻². However, it has also been found that changes in the electrode double layer during solution phase voltammetry and other factors can affect the SPR signal.19

In the present case, the SPR response [Fig. 8(a)] for the TCNQ⁰/⁻ reduction shows a reversible 120 μrad sigmoidal decrease in SPR angle while the TCNQ⁻/⁻² reduction is accompanied by a reversible 120 μrad sigmoidal increase. This is probably associated with large changes in the extinction coefficient when TCNQ⁻ is formed. Deposition of Cuₙ(metal) [Fig. 8(b)] gave a large 700 μrad increase in the SPR angle before the SPR signal went off scale with continued deposition. The SPR signal returned to the baseline value after the Cu stripping process at ~0.65 V vs. Ag/AgCl.

The electrorystallization of CuTCNQ from 3.22 mM Cu⁺(MeCN) with 9.66 mM TCNQ [Fig. 8(c)] also gives rise to a reversible 120 μrad sigmoidal decrease in the SPR angle at potentials where TCNQ is reduced to TCNQ⁻. However, in the I_red/I_ox region, there is now a very large reversible SPR angle shift of 900 μrad, increasing first on reduction and subsequently decreasing upon oxidation. Increasing the Cu⁺(MeCN) concentration [Fig. 8(d)] does not affect either of the reduction processes, but on switching the scan direction, as the solution phase TCNQ⁻/⁻² reduction occurs and the CuTCNQ stripping peak I_strip, the sigmoidal SPR response has shifted to more positive potentials with the voltammetry. The fact that the SPR signal showed no difference when TCNQ is reduced in the presence and absence of Cu⁺(MeCN) is most

![Fig. 7](a–c) EQCM data (current – black, mass – grey) obtained under conditions of cyclic voltammetry over the potential range 0.75 to ~0.40 V vs. Ag/AgCl at a scan rate of 100 mV s⁻¹ using a 5 mm diameter Au electrode for 3.22 mM Cu⁺(MeCN) and 9.66 mM TCNQ in acetonitrile (0.1 M Bu₄NPF₆); number of cycles are (a) 1, (b) 2 and (c) 13. (d) Cyclic voltammetry in acetonitrile (0.1 M Bu₄NPF₆) at a 5 μm diameter microdisc gold electrode using a scan rate of 100 mV s⁻¹ for the reduction of 9.09 mM TCNQ in the presence of 9.09 mM Cu⁺(MeCN).
likely due to the crystals forming at discrete points on the electrode surface, hence the expected 12–18 m° shift in the angle of minimum reflected light intensity equating to 1 ng mm⁻² is not applicable. The high sensitivity of the SPR to the I₀ couple, further implies the existence of film type behaviour on the electrode surface in this potential region.

Mechanistic considerations

The voltammetric, spectroscopic, and microscopic data all suggest that reduction of TCNQ at an electrode surface in the presence of Cu⁺(MeCN) leads to the electrocrystallization of CuTCNQ via two distinctly different processes, I' and I''. Process I', as shown previously, 3,6 follows a nucleation–growth mechanism which generates arrays of well spaced large branched needles. In this process CuTCNQ phase I formation occurs on the electrode surface at discrete sites, thereby allowing rapid electrocrystallization at potentials where TCNQ⁻⁻ is generated (eqn 7–9) and subsequently stripped off the electrode surface (eqn 10).

\[
\text{TCNQ}(\text{MeCN}) + e^- \rightleftharpoons \text{TCNQ}^- (\text{MeCN}) \tag{7}
\]

\[
\text{TCNQ}^- (\text{MeCN}) + \text{Cu}^+ (\text{MeCN}) \rightarrow \text{CuTCNQ(nucleating site)}_{(s)} \tag{8}
\]

Rapid crystal growth is then facilitated by the process

\[
\text{TCNQ(MeCN)} + \text{Cu}^+ (\text{MeCN}) + e^- \xrightarrow{\text{CuTCNQ(nucleating site)}} \text{CuTCNQ}_{(s)} \tag{9}
\]

\[
\text{CuTCNQ}_{(s)} \xrightarrow{\text{Stripping Process}} \text{Cu}^+ (\text{MeCN}) + \text{TCNQ(MeCN)} + e^- \tag{10}
\]

In contrast, process I'' produces much smaller phase I CuTCNQ crystals that cover most of the surface region where crystals derived from process I' are absent. The charge passed for process I'' is almost independent of precursor concentrations and electrodeposition times. This and other data imply that a finite amount of reactant is involved in this process. As the product is phase I CuTCNQ, the Faradaic current associated with process I'' cannot be due to copper ion or bulk TCNQ reduction, which occur at different potentials. One possible mechanism to explain process I'' involves the formation of [\text{TCNQ}^-\text{(TCNQ)}] anions stabilized by the presence of Cu⁺ and the subsequent reduction of this moiety to CuTCNQ generating the current associated with process I''. Other studies have reported the formation of [\text{TCNQ}^-\text{(TCNQ)}] anions and their reduction in polymer films in aqueous conditions\textsuperscript{20} and in acetonitrile\textsuperscript{21} under conditions where this moiety is generated via the voltammetry of TCNQ. In the polymer situation, three voltammetric
processes associated with reactions 11, 13 and 14 are detected; as opposed to the two charge transfer processes associated with reactions 3 and 4. The extra charge transfer process I’ (reaction 13) is due to the reduction of the \([\text{TCNQ}^-])\) anions

\[\text{TCNQ}_{\text{(MeCN)}} + e^- \rightleftharpoons \text{TCNQ}^-_{\text{(MeCN)}} \] (11)

\[\text{TCNQ}_{\text{(MeCN)}} + \text{TCNQ}^-_{\text{(MeCN)}} \rightleftharpoons \left[\text{TCNQ}^-\text{(TCNQ)}\right]_{\text{(MeCN)}} \] (12)

\[\left[\text{TCNQ}^-\text{(TCNQ)}\right]_{\text{(MeCN)}} + e^- \rightleftharpoons 2\text{TCNQ}^-_{\text{(MeCN)}} \] (13)

\[\text{TCNQ}^-_{\text{(MeCN)}} + e^- \rightleftharpoons \text{TCNQ}^2^-_{\text{(MeCN)}} \] (14)

which occurs at potentials between processes 11 and 14, as does process I’ in this study in the presence of Cu\(^+\). The \([\text{TCNQ}^-\text{(TCNQ)}]\) anion also is well known to be incorporated into crystal structures which are classed as mixed-valent or complex salts. A more extensively reduced TCNQ dimer is formed when LiTCNQ is dissolved in water or DMSO. At low concentrations, a LiTCNQ solution is green due to TCNQ\(^-\), but at high concentrations, blue \([\text{TCNQ}_2]^-\) dimers are present. Formation of \([\text{TCNQ}^-\text{(TCNQ)}]\) anion dimers provides a source of neutral TCNQ that may exist at more negative potentials than would otherwise be the case.

The absence of process I’ when Cu\(^+\) is not present in the solution, and the dependence of the potential of process I’ on Cu\(^+\) concentration would indicate that Cu\(^+\) stabilises the \([\text{TCNQ}^-\text{(TCNQ)}]\) anion. Reduction of Cu\(^+\)\([\text{TCNQ}^-\text{(TCNQ)}]\) would then produce sparingly soluble CuTCNQ which could then rapidly crystallize onto the electrode surface at all locations not occupied by crystals formed \textit{via} process I’. Consequently, this mechanism would be expected to generate arrays of closely spaced crystals, which have properties more like those expected for a film than would otherwise be the case. The reactions giving rise to process I’, according to this mechanism, are summarised in eqn 15–17.

\[\text{TCNQ}_{\text{(MeCN)}} + e^- \rightleftharpoons \text{TCNQ}^-_{\text{(MeCN)}} \] (15)

\[\text{TCNQ}_{\text{(MeCN)}} + \text{TCNQ}^-_{\text{(MeCN)}} + \text{Cu}^+_{\text{(MeCN)}} \rightleftharpoons \text{Cu}^+ \left[\text{TCNQ}^-\text{(TCNQ)}\right] \] (16)

\[\text{Cu}^+ \left[\text{TCNQ}^-\text{(TCNQ)}\right] + e^- \rightleftharpoons \text{CuTCNQ}\text{(phase I)}_{\text{(film)}} + \text{TCNQ}^-_{\text{(MeCN)}} \] (17)

where \(\text{Cu}^+ \left[\text{TCNQ}^-\text{(TCNQ)}\right]\) may be confined to the electrode surface, dissolved in the bulk solution or in an equilibrium between the two states. Indeed a stabilised Li\(^+\)\([\text{TCNQ}^-\text{(TCNQ)}]\) species has been reported previously in an on-line electrochemistry/electrospray mass spectrometry experiment.

The voltammetric characteristics of process I’ closely resemble those associated with the solid–solid conversion of TCNQ to CuTCNQ, as in eqn 18.

\[\text{TCNQ}_{\text{(film)}} + \text{Cu}^+_{\text{(MeCN)}} + e^- \rightleftharpoons \text{CuTCNQ}_{\text{(film)}} \] (18)

Indeed the nature of the voltammetric response associated with process I’ resembles that observed when a GC electrode modified with solid TCNQ is cycled in an aqueous solution of 0.1 M CuSO\(_4\) or other salts such as Na\(^+\), K\(^+\) and tetraalkylammonium cations. In this case, an inert zone between the oxidation \((E_{\text{p}}^{\text{ox}})\) and reduction \((E_{\text{p}}^{\text{red}})\) peaks \((E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}} = \Delta E_{\text{p}})\) of the order of 100 mV is detected, as found with process I’ (Table 1). The mid-point potential \((E_{\text{p}}^{\text{ox}} + E_{\text{p}}^{\text{red}})/2 = E_{\text{m}}\) of process I’ shifts to less negative potentials with the addition of Cu\(^+\) as expected on the basis of aqueous studies using TCNQ\(_{(s)}\) as an ion sensor (Table 1). However, quantitative analysis of this potential shift associated with process I’ is complicated by the presence of process I’.

Galvanostatic techniques allow the process of CuTCNQ formation to shift from predominantly process I’ to process I’ when the applied current is increased, as also occurs when the potential driving force is made more negative by potentiostatic means. Nevertheless, \textit{in situ} optical microscopy images clearly reveal that process I’, if allowed to occur under conditions of slow scan rate cyclic voltammetry, is influenced by process I’. Thus, large CuTCNQ crystals formed by process I’ create a depletion zone which retards formation of a film of CuTCNQ, \textit{via} process I’ in their immediate vicinity.

IR and XRD data are consistent with CuTCNQ phase I being present on the electrode surface, with no phase II evident. Hence a high purity CuTCNQ phase I film is created. The EQCM technique responds to the film behaviour in the potential region of process I’, but is not sensitive to the large crystals formed by process I’. However, since large crystals continue to be deposited by process I’ in the potential region where process I’ occurs, the apparent sensitivity of the EQCM response to the film mass changes is modified from that predicted by the Sauerbrey equation. The SPR response to the film deposition in process I’ is also considerably greater than for the electrocrystallization taking place in process I’. The SPR method therefore shows an ability to highlight changes associated with films over discrete depositions.

Conclusions

The reduction of TCNQ in acetonitrile at an electrode surface in the presence of Cu\(^+\) allows the electrocrystallization of sparingly soluble semi-conducting phase I CuTCNQ to occur \textit{via} two distinctly different pathways, namely, a nucleation–growth mechanism (eqn 7–9) that generates branched needles where nucleation probably occurs at discrete sites on the electrode surface and a “film” mechanism (eqn 15–18).

Rapid crystal growth \textit{via} mechanism I’ produces branched needles from discrete points. Some as large as 100 μm may be formed after 120 s of electrolysis or after extensive voltammetric cycling of the potential over the range 0.7 to −0.1 V vs. Ag/AgCl (excluding the potential region where process I’ occurs). Proceeding into the potential region of process I’ also produces needles of phase I CuTCNQ, but these are smaller and have a much higher packing density. The needle morphology, as well as IR and XRD data, indicate that CuTCNQ formed either \textit{via} mechanism I’ or I’ is of a high
purity and is the more conducting, kinetically favoured phase I material rather than thermodynamically stable phase II. Crystal growth kinetics also seem to favour formation of phase I in the chemical synthesis of CuTCNQ from TCNQ and CuI$^-$ and in the solid-state voltammetry of TCNQ in aqueous CuSO$_4$(aq) media. Presumably, the limited conductivity of phase II crystals minimizes their ability to grow rapidly. Small CuSO$_4$(aq) media.2 Presumably, the limited conductivity of phase II crystals minimizes their ability to grow rapidly. Small CuTCNQ crystals may be stripped from the electrode surface back to soluble Cu$^{+}(MeCN)$ and TCNQ by application of positive potentials as in eqn 10, under conditions where larger ones remain on the surface, possibly because of slow electron transfer rates over long distances or poorer ohmic contact.

This new process for forming phase I CuTCNQ allows us to create more uniform, high purity films than from process I and their ability to form switching devices is of great interest.

Acknowledgements

The authors wish to express their appreciation to the Monash Electron Microscopy and Microanalysis Facility for access to their SEM facilities. Financial support from the CSIRO Division of Manufacturing and Infrastructure Technology and the Australian Research Council is also gratefully acknowledged, as is the award of a grant from the American Electroplaters and Surface Finishers Society to ARH.

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