Thin films of hydroxy-TEMPO-substituted TTF and of its charge-transfer complex with TCNQ

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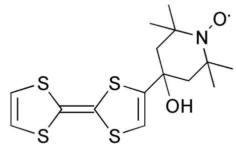
Received (in Montpellier, France) 20th December 2001, Accepted 19th February 2002
First published as an Advance Article on the web 31st May 2002

Thin films of 4-hydroxy-TEMPO-substituted TTF [TTF-(OH)TEMPO] were grown on *ex situ* cleaved KBr (001) using the high vacuum evaporation technique. Sub-micronic grains uniformly covering the KBr surface were evidenced by scanning electron microscopy (SEM). The films were also studied by infrared (IR), electron spin resonance spectroscopy (ESR) and X-ray photoelectron spectroscopy (XPS). Amorphous thin films of [TTF-(OH)TEMPO][TCNQ] were obtained on KBr pellets and on micro-rough Si(001) wafers using chemical vapour deposition (CVD). They were characterized by SEM, IR, XPS and ESR. SEM images on micro-rough Si(001) wafers evidenced micro-needles (0.5–2 μm in length, 0.1–0.2 μm in diameter), uniformly covering the substrate surface. CN stretching frequencies were in agreement with a reduced TCNQ moiety, thus indicating a charge transfer between the donor [TTF-(OH)TEMPO] and the acceptor (TCNQ) molecules (degree of charge transfer ~1).

Considerable effort has been recently devoted to the preparation of thin films based on organic materials. Diodes, light-emitting diodes, and field effect transistors are a few examples of reported devices using thin organic film technology.[1–5] The main techniques used for the preparation of thin films of molecule-based materials are Langmuir–Blodgett,[6] high vacuum evaporation,[7–9] electrochemical deposition,[10,11] molecular beam deposition,[12] and chemical vapour deposition (CVD)[13,14] methods. For instance, macroscopically ordered thin films of organic salts with large second-order hyperpolarizabilities for use in nonlinear optical devices have been grown by low-pressure CVD.[13] Thin oriented films of the organic radical *p*-NPNN[15] were obtained by thermal evaporation in high vacuum.[8] We have recently reported on the formation of CVD-grown films of molecule-based compounds exhibiting metal-like conductivity or magnetic ordering. In particular, the growth of thin films of the organic conductor [TTF][TCNQ][16] and of TCNE-based bulk ferro- or ferrimagnets[17] on various substrates (namely KBr pellets, Si wafers, and stainless steel with conversion coatings) was achieved. On the other hand, co-existence or interplay of conductivity and magnetism is now of great interest in the field of molecular materials science. For example, the coexistence of antiferromagnetic ordering and superconductivity in κ-$(BETS)_2FeBr_4$[18] and of ferromagnetism and metallic conductivity in $[BEDT\text{-}TTF]_3[MnCr(C_2O_4)_3]$[19] have been evidenced. A recent approach is to build up charge transfer complexes bearing stable radical unit(s) in either the donor or acceptor moieties or in both, and to arrange the unpaired electrons in a columnar structure.[20,21] Nakatsuji *et al.* have reported on the synthesis of 4-hydroxy-TEMPO-substituted TTF [TTF-(OH)TEMPO] and its use as a donor in charge transfer complexes with some acceptors (DDQ or $TCNQF_4$).[22] However, to our knowledge, charge transfer complexes based on TTF-TEMPO derivatives as donors and on tetracyanoquinodimethane (TCNQ) as acceptor have never been described. We report hereafter on the results of the preparation of thin films of TTF-(OH)TEMPO and of [TTF-(OH)TEMPO][TCNQ] using either high vacuum evaporation or CVD techniques.



TTF-(OH)TEMPO

Experimental

Commercial TTF and TCNQ were used without further purification. TTF-(OH)TEMPO was prepared following previously described procedures.[23] *Ex situ* cleaved KBr(001), KBr pellets (pressed from ~130 mg of dry powder using an IR die), and the non-polished surface of (001)-oriented Si wafers were used as substrates. To improve adsorption properties of the non-polished surface of Si, the wafers were dipped in a water–sulfuric acid bath (5% vol.) containing sodium thiosulfate (3 g L^{-1}) and HF (2 mol L^{-1}) at 60 °C for 60 min.

High vacuum evaporation procedure

TTF-(OH)TEMPO powder was introduced into a Cu crucible covered with a piece having a 1.5 mm exit hole. KBr(001) substrates were glued to a stainless steel sample holder with silver paint. The evaporation system was then pumped for 6 h and the resulting base pressure was better than 1×10^{-5} Pa. The powder was heated from room temperature to 443 K over 30 min. in a first ramp [during this period of time, the largest amount of TTF-(OH)TEMPO was evaporated] and from 443 to 523 K over 40 min. in a second ramp (in order to complete

DOI: 10.1039/b111662m

Table 1 Typical experimental CVD conditions for film formation

Precursor (mass/mg)	Vaporisation T/K	Helium flow rate/ sccm	Substrate (annealing) T/K	Pressure/ Pa	Deposition (annealing) duration/min.	Substrate	Atomic N/S ratio[a]	CN frequencies/ cm^{-1}	NO frequency/ cm^{-1}
TTF-(OH)TEMPO[b] (15)	443	—	223 (—)	8×10^{-3}	70 (–)	KBr(001)	0.30	—	1377
TTF-(OH)TEMPO[b] (10)	443	—	223, 293 or 333 (388)	7×10^{-3}	90 (240)	KBr(001)	N.D.	2225[c], 2172, 2116	1378
TCNQ[b] (3.3)	523	—							
TTF-(OH)TEMPO[d] (80)	463	87	333 (—)	230	150 (–)	KBr pellet or Si(001)	1.31[e]	2179[e], 2121[e] 2183[f], 2120[f]	1378[e,f]
TCNQ[d] (60)	433	87							

[a] Determined by XPS analyses of the films. [b] High vacuum evaporation technique. [c] Assigned to $TCNQ^0$. [d] CVD technique. [e] On KBr. [f] On Si(001).

precursor evaporation). The substrate temperature during deposition was 223 K (Table 1).

TTF-(OH)TEMPO and TCNQ were heated at evaporation temperatures of 443 and 523 K, respectively (Table 1). Co-evaporation was carried out on KBr(001) substrates (substrate temperature: 223, 293, or 333 K) for 90 min. The films thus obtained were then annealed at 388 K for 240 min.

CVD procedure

Thin films of [TTF-(OH)TEMPO][TCNQ] were deposited from TTF-(OH)TEMPO and TCNQ precursors, using a conventional hot-wall CVD apparatus. The glass crucibles were charged with the starting compounds inside an argon-filled glove box. The KBr pellets and the Si(001) wafers were placed on top of a glass slide inside the reactor and the CVD system was then pumped for 15 h down to $\sim 10^{-3}$ Pa, while the carrier lines were heated at 353 K and the reactor at 423 K. The precursors were vaporized at low pressure (Table 1), and transported by helium carrier gas to the mixing zone ($T = 448$ K) and then to the deposition zone ($T = 333$ K). The mixing zone was held at 448 K in order to avoid condensation of the starting compounds.

Characterization methods

Infrared spectra of thin films deposited on cleaved KBr(001) were obtained using an FT-IR spectrometer (Bomem MB-120) equipped with an IR-plan Spectra Tech microscope. Infrared spectra of thin films deposited on KBr pellets and on Si(001) wafers were recorded on a Perkin–Elmer 1725 FT-IR spectrometer. ESR spectra were recorded at 100 K using a Brücker ESP 300 spectrometer. SEM images of evaporated thin films were obtained on Hitachi S-570 equipment. SEM observations of CVD-grown thin films were realized on a Jeol Model JSM 840A microscope. XPS spectra of evaporated thin films were taken with a SPECS EA10P hemispherical analyzer using both non-monochromated Mg-Kα (1253.6 eV) and Al-Kα (1486.6 eV). XPS spectra of CVD-grown thin films were recorded using a VG Escalab Model MK2 spectrophotometer (Mg-Kα radiation: 1253.6 eV). X-ray diffraction (XRD) studies of evaporated thin films were performed using a Philips-MRD diffractometer (Cu-Kα radiation: 1.5418 Å) and XRD characterizations of CVD-grown deposits were run on a Seifert XRD 3000 TT diffractometer (Cu-Kα radiation: 1.5418 Å).

Results and discussion

Evaporated thin films

Thin yellow films were obtained by evaporating the TTF-(OH)TEMPO precursor in high vacuum using *ex situ* freshly cleaved KBr(001) as substrates, which were held at 223 K. The films were stored in air for several months without decomposition. As shown in Fig. 1, the evaporated films are made of very small grains (~0.1 μm) uniformly covering the substrate surface. XRD studies evidence that the films have an amorphous or nanocrystalline character. Thin molecular films of neutral TTF derivatives (such as TMTTF, EDT-TTF or BEDT-TTF) grown on NaCl(001) or KBr(001) substrates were found to be highly oriented and SEM and tapping mode atomic force microscope (TMAFM) images of these deposits showed rectangular crystallites exhibiting an in-plane incommensurate texture.[9] In our case, the crystallisation energy barrier is not overcome[9] and elevated annealing temperatures would lead to the desorption of the film in the high vacuum conditions in use.

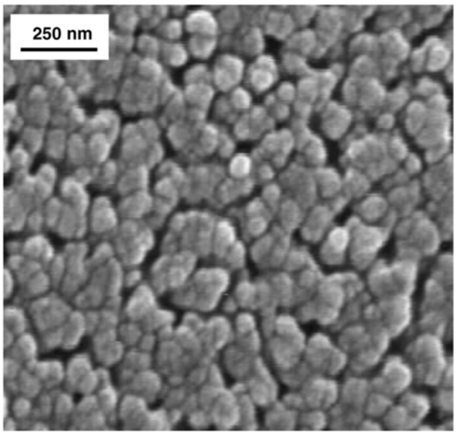


Fig. 1 SEM image of an evaporated thin film of TTF-(OH)TEMPO.

The IR spectrum of the films exhibits frequencies identical to those observed for TTF-(OH)TEMPO in powder form, but the bands are slightly broader due to surface effects (Fig. 2).[24] The stretching carbon–carbon double bond is at 1542 cm^{-1}, in good agreement with that of TTF (1555 cm^{-1}).[25] The nitroxide ($NO^{\bullet}$) part of the molecule is evidenced by a ν_{NO} stretching mode at 1377 cm^{-1}.

XPS analysis of the films gives an atomic N/S ratio of 0.30, quite close to the theoretical value (0.25). The photoemission spectrum of the N(1s) line is shown in Fig. 3. A least-squares fit deconvolution with Gaussians of the N(1s) signal gives two peaks at 398.9 and 401.0 eV binding energy, respectively, both with a full width at half maximum (FWHM) of 2.1 eV (this condition is imposed in the fit). The position of the main line (398.9 eV) is compatible with the position of the nitroxide group of *p*-NPNN (400.6 eV, FWHM = 1.2 eV)[8] and is thus attributed to the nitrogen of the $NO^{\bullet}$ group. Larger binding energy values for *p*-NPNN films could be due to the delocalisa-

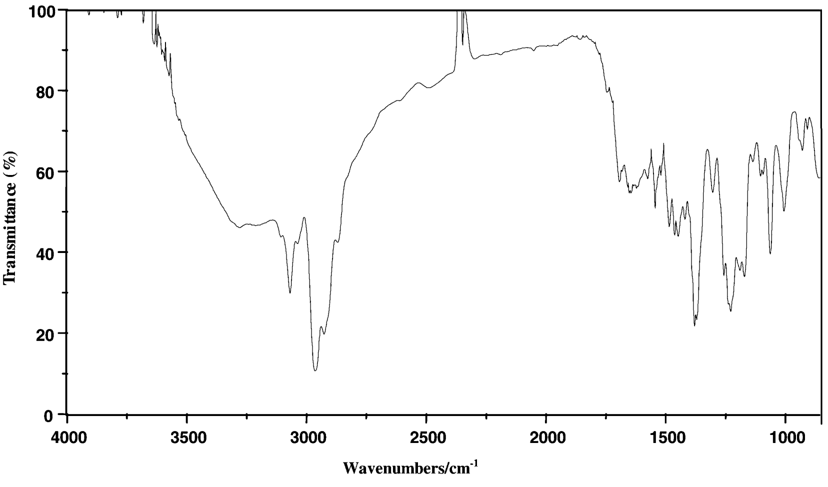


Fig. 2 IR spectrum of an evaporated thin film of TTF-(OH)TEMPO.

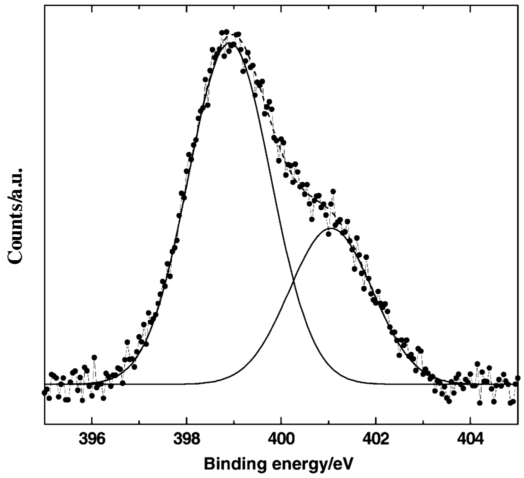


Fig. 3 XPS spectrum of the N(1s) electrons for an evaporated thin film of TTF-(OH)TEMPO.

tion of the unpaired electron in the O–N–C–N–O region, while in TTF-(OH)TEMPO, unpaired electrons are localised on the nitroxide moiety. The larger values of the FWHM in our films as compared to the highly ordered *p*-NPNN films are due to surface disorder. The shoulder observed at 401.0 eV, thus shifted by 2.1 eV to higher binding energies, may be assigned to a shake-up satellite[26] involving N–O bands in analogy to [TTF][TCNQ].[7] The binding energies of the S(2p) and S(2s) lines are 164.0 and 228.0 eV, respectively, in agreement with the values found for TTF derivatives.[27]

Further evidence of the nitroxide group is given by ESR spectroscopy. The ESR spectrum recorded at 100 K exhibits 3 lines at 2.024, 2.005, and 1.980 (Fig. 4, spectrum A). The central signal with a g factor of 2.005 coincides with that of TTF-(OH)TEMPO in powder form (2.006).[22] A three-component ESR signal has recently been observed by S. Hase *et al.* for phenol- and phenoxide-substituted nitronyl nitroxide biradicals in a glassy solution of toluene.[28] The two main features were assigned to randomly oriented triplet species ($S_{\text{total}} = 1$) and a weak central peak was attributed to a small amount of monoradical ($S = 1/2$) impurity. In our films, the two lines at 2.024 and 1.980 could be due to TTF-(OH)TEMPO radicals associated into dimers for which $S_{\text{total}} = 1$.

Amorphous pale-green thin films were grown on cleaved KBr(001) substrates by co-evaporating the TTF-(OH)TEMPO and the TCNQ precursors under high vacuum (substrate temperature: 223, 293 or 333 K). The IR spectra of the films exhibit a stretching CN absorption at 2224 cm^{-1}, identical to that of TCNQ^0. Thus, no charge transfer from TTF-(OH)TEMPO donor to TCNQ acceptor is observed. After annealing the films at 388 K in nitrogen, the colour turned from pale green to deep green. Three CN frequencies are detected in the IR spectrum: 2225(s), 2172(m), and 2116(s) cm^{-1}. The band at 2225 cm^{-1} is assigned to TCNQ^0, whereas the other bands are attributed to a reduced TCNQ moiety. Charge transfer from TEMPO-substituted TTF to TCNQ has thus occurred, as expected according to the redox behaviour of TTF-(OH)TEMPO, which is comparable to that of TTF.[22] However, the persistence of a strong CN band from zerovalent TCNQ, even after a long annealing time, suggests that, in this case, evaporation in high vacuum is perhaps not the most well-suited technique for the preparation of [TTF-(OH)TEMPO][TCNQ] films. More sophisticated evaporators with constant and calibrated molecular fluxes would indeed improve the preparation of such films in high vacuum although the substrate temperature during evaporation is limited to *ca.* 350 K due to desorption. Because such instrumentation is not available in our system, other alternatives have been explored.

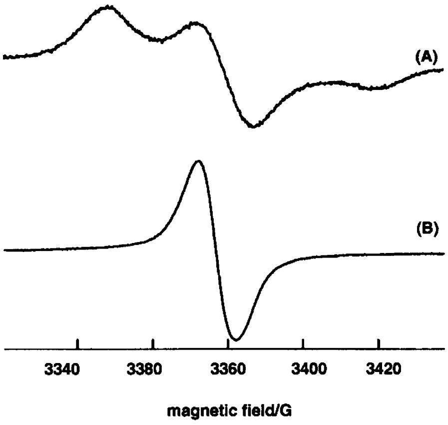


Fig. 4 ESR spectra at 100 K of (A) an evaporated thin film of TTF-(OH)TEMPO and (B) a CVD-grown film of [TTF-(OH)TEMPO][TCNQ] on KBr pellets .

CVD-grown thin films

Thin deep-green films of [TTF-(OH)TEMPO][TCNQ] were grown from TTF-(OH)TEMPO and TCNQ precursors on KBr pellets and micro-rough Si(001) wafers, using a CVD

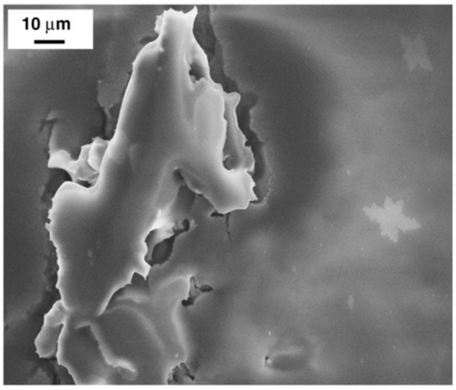


Fig. 5 SEM image of a CVD-grown film of [TTF-(OH)TEMPO][TCNQ] on a KBr pellet.

apparatus (substrate temperature: 333 K, see Table 1). Despite the hygroscopic character of the KBr pellets, the films are very stable. SEM images evidence a film uniformly covering the substrate surface. However, some defects are occasionally encountered (Fig. 5). XRD studies of these films show no reflections within the range $d = 7.5$–3.5 Å.

On the infrared spectrum of the films, three ν_{CN} bands appear at 2179(s), 2152(sh), and 2121(m) cm^{-1}, all consistent with reduced TCNQ (Fig. 6). Bloch *et al.* have drawn a linear relationship between the higher nitrile stretching frequency and the degree of charge transfer (ρ) for a series of 19 TCNQ salts.[29] In the case of our films, the higher ν_{CN} frequency appears as a strong band at 2179 cm^{-1}, and the corresponding degree of charge transfer is $\rho \sim 1$. This value is much higher than that for [TTF][TCNQ] ($\rho = 0.59$), and comparable to that of alkaline metal-TCNQ complexes.[29] It is also to be noticed that the higher ν_{CN} frequency for [TTF-(OH)TEMPO][TCNQ] films is in relatively good agreement with that for charge transfer complexes in which the donor part is the TEMPO radical itself and the acceptor part is $TCNQF_4$.[20] As mentioned in the introduction, [TTF-(OH)TEMPO][$TCNQF_4$] in powder form has been previously described and exhibits a ν_{CN} band at 2195 cm^{-1}.[22] The carbon–carbon double bond stretching mode of the donor is at 1505 cm^{-1}, a lower value than that observed for evaporated films of TTF-(OH)TEMPO (1542 cm^{-1}, see above). The cationic character of the donor is thus confirmed. The NO stretching mode appears as a broad band at 1378(s) cm^{-1} for CVD-prepared [TTF-(OH)TEMPO][TCNQ] films, indicating that the nitroxide portion of the molecule is not affected by the charge transfer [1377(s, br) cm^{-1} for TTF-(OH)TEMPO thin evaporated films, see above].

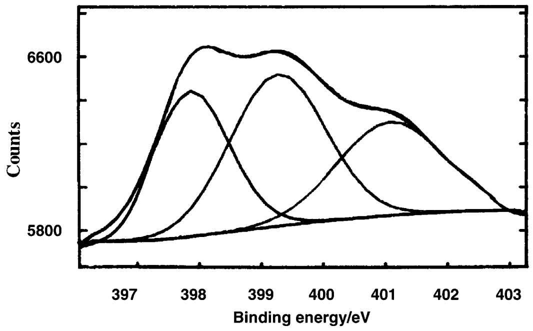


Fig. 7 XPS spectrum of N(1s) electrons for a CVD-grown film of [TTF-(OH)TEMPO][TCNQ] on a KBr pellet.

XPS analysis of the N(1s) region is shown in Fig. 7 where two main lines and a smaller shoulder at higher binding energy are observed. A least-squares fit deconvolution with Gaussians of the N(1s) signal gives the following peak positions (FWHM values are imposed in the fit): 397.9 (FWHM = 1.5), 399.3 (FWHM = 1.8), and 401.1 eV (FWHM = 2.0 eV). This three-component profile confirms the presence of both TTF-(OH)TEMPO and TCNQ moieties in the film. The first line at 397.9 eV is assigned to the nitrogen atoms from nitrile groups, by comparison with earlier data on [TTF][TCNQ] evaporated thin films, in which N atoms from CN groups have a binding energy at 398.1 eV.[7] The second line at 399.3 eV is attributed to the nitrogen atom of the nitroxide group [398.9 eV for evaporated thin films of TTF-(OH)TEMPO, see above]. The shoulder is assigned to both N atoms from CN groups of $TCNQ^0$ due to surface thermal vibrations (which induce the reduction of the surface charge transfer[30]) and to a shake-up satellite. Furthermore, the XPS analysis evidences a N/S atomic ratio of 1.31, in good agreement with a 1:1 stoichiometry for which theoretical N/S atomic ratio is 1.25. It is to be remarked that charge transfer complexes involving TTF-(OH)TEMPO as donor and DDQ or $TCNQF_4$ as acceptors are also 1:1 adducts.[22]

The ESR spectrum recorded at 100 K on a CVD-grown [TTF-(OH)TEMPO][TCNQ] thin film (Fig. 4, spectrum B) exhibits one line at 2.007, identical to that of TTF-(OH)TEMPO[22]. The presence of the nitroxide radical in the CVD-deposited charge transfer complex is thus confirmed. Conductivity measurements and magnetic susceptibility curves obtained from CVD-grown [TTF-(OH)TEMPO][TCNQ] thin

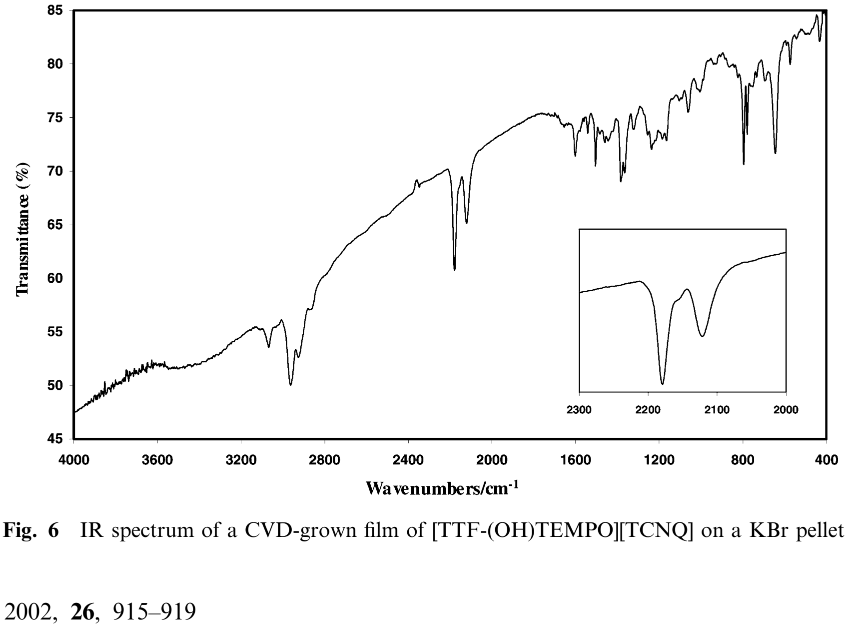


Fig. 6 IR spectrum of a CVD-grown film of [TTF-(OH)TEMPO][TCNQ] on a KBr pellet.

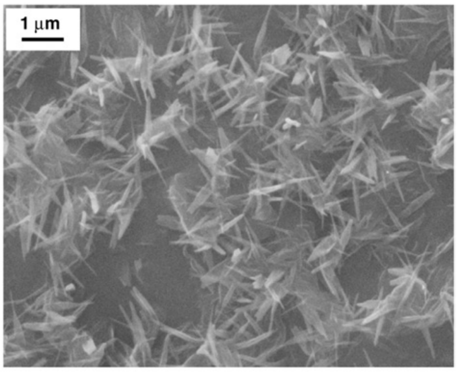


Fig. 8 SEM image of a CVD-grown film of [TTF-(OH)TEMPO][TCNQ] on Si(001).

films on KBr pellets were not interpretable, possibly due to the low amount of deposited material.

KBr substrates are not the most appropriate for electronic device applications. It seemed thus interesting to evaluate the use of Si(001) wafers as substrates. To improve the adsorption properties of the non-polished surface of Si(001), the wafers are dipped in an acidic aqueous solution of H_2SO_4–HF containing sodium thiosulfate. This treatment leads to a micro-rough structure uniformly deposited onto the honeycomb network of the non-polished surface of the wafers.[31] On these substrates, CVD-grown thin films of [TTF-(OH)TEMPO][TCNQ] are characterized by ν_{CN} frequencies similar to those observed on KBr pellets [2183(s), 2162(m), and 2120(sh) cm^{-1}]. XRD analyses show no reflections within the range $d = 7.5$–3.5 Å. SEM images evidence micro-needles (0.5–2 µm in length, 0.1–0.2 µm in diameter) and some platelets (Fig. 8). Such a SEM profile has previously been obtained on CVD-grown thin films of [TTF][TCNQ].[16]

Conclusion

For future electronic and magnetic devices, the preparation of molecule-based materials in a practical usable form (thin films, nanowires, micro-needles, *etc.*) is a major difficulty to overcome. In this paper, we have demonstrated the feasibility of processing thin adherent films of the radical donor TTF-(OH)TEMPO and of its charge transfer complex with TCNQ on various substrates [KBr(001), KBr pellets, micro-rough Si(001) wafers]. Evaporated thin films of TTF-(OH)TEMPO on KBr(001) were made of very small cauliflower-like grains and had an amorphous character. For CVD-grown deposits of [TTF-(OH)TEMPO][TCNQ], IR, XPS and ESR analyses revealed the presence of a reduced TCNQ moiety and demonstrated that the nitroxide radical was preserved within the films. Micro-rough Si(001) wafers have shown the ability to induce the formation of micro-needles. In the future, these substrates will be applied to the growth of other radical donors and to other conducting molecular systems.

Acknowledgements

We thank M. Reversat for the XRD experiments and SEM characterizations, G. Chatainier for the XPS results and A. Mari for ESR experiments. H. C. gratefully thanks Université Paul Sabatier for ATUPS financial support.

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15 Abbreviations used: *p*-NPNN = *p*-nitrophenyl nitroxide nitroxide; TTF = tetratiafulvalene; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane; TCNE = tetracyanoethylene; BETS = bis(ethylenedithio)tetraselenafulvalene; DDQ = 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone; $TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane; TMTTF = tetramethyltetrathiafulvalene; EDT-TTF = ethylenedithiotetrathiafulvalene; BEDT-TTF = bi-bis(ethylenedithio)tetrathiafulvalene; dmit = 1,3-dithiole-2-thioxo-4,5-dithiolate.
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27 XPS binding energies of sulfur lines ($n = 2$) of thin films of TTF-derivatives. S(2p): TMTTF (164.4 eV), EDT-TTF (163.9 eV), BEDT-TTF (163.6 eV), TTF-TCNQ (163.8 eV). S(2s): TMTTF (227.9 eV), EDT-TTF (227.8 eV), BEDT-TTF (227.8 eV), TTF-TCNQ (228.0 eV).
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