In-operando studies of Ag-TCNQ nanocrystals using Raman and soft x-ray microspectroscopy

Benedikt Rösner,1,3* Ute Schmidt,2 Rainer H. Fink1

1 Department Chemie und Pharmazie & ICMM, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, 91058 Erlangen, Germany.

2 WITec GmbH, Lise-Meitner-Str. 6, 89081 Ulm, Germany

3 Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland (current affiliation)

*benedikt.roesner@psi.ch

Abstract. We characterize individual Ag-TCNQ nanocrystals during switching their resistivity state in operando. Raman and soft X-ray absorption microspectroscopy are employed to disclose the electronic state of the organic component in dependency of applied voltage. Whereas Raman microspectroscopy offers qualitative insight into the conversion of negatively charged TCNQ molecules to their neutral counterpart, quantification of the neutral fraction can be achieved using X-ray absorption spectroscopy. These results allow a detailed investigation of resistivity switching in electrically bistable Ag-TCNQ nanocrystals.

1. Introduction
Electrically bistable Ag-TCNQ (TCNQ = 7,7’,8,8’-tetracyanoquinodimethane) nanowires have been under intense investigation for more than a decade with respect to their promising capabilities to undergo reversible transitions between two resistance states [1]. Although reverse charge transfer has been proposed being the reason for changes of the conductivity of metal-organic TCNQ-based salts [2], unambiguous proof of this concept has not been demonstrated in individual nanometre-sized crystals so far.

Microspectroscopic methods represent powerful tools for characterizing electronic properties of metal-organic and organic materials. Herein, we report on the potential of photon-based methods to conduct spectroscopy on these functional electronic materials in high spatial resolution down to the nanoscale [3]. We employed confocal Raman microscopy and scanning transmission X-ray microscopy (STXM) to keep track of the electronic changes, which occur in individual Ag-TCNQ crystals upon switching their resistivity state.

2. Experimental
Ag-TCNQ crystallites have been synthesized in wet-chemical environment as described elsewhere [4]. Commercial 100 nm thick silicon nitride membranes (Silson Ltd.) or silicon wafers (with a top 100 nm silicon oxide layer) were used as substrates. Individual wires suited for in operando experiments have been identified under the light microscope and contacted by thermal evaporation of 30 nm thick gold contacts.
Raman spectromicroscopy was conducted with a WITec alpha 500 R confocal Raman microscope. After mounting the contacted Ag-TCNQ wires on the microscope, the two gold electrodes were contacted with two gold-coated needles using micromanipulators. A constant negative voltage was applied to the Ag-TCNQ wire. The whole sample was then scanned together with the micromanipulator to ensure a stable electric contact. Arrays of Raman spectra were recorded while the current flow was monitored by a Keithley 4200-SCS parameter analyser. For different sets of spectra, the voltage was increased in several steps. In operando STXM experiments were performed using contacted samples mounted on a dedicated holder for in-situ experiments in the STXM at the PolLux beamline [3] at the Swiss Light Source (Figure 1) in a similar way. The X-ray beam was focused using a Fresnel zone plate with 35 nm outermost zone width and an order-sorting aperture with 70 µm diameter, and was detected using a photomultiplier tube.

3. Results and Discussion
In order to confirm the presence of electronic switching in Ag-TCNQ nanocrystals, we conducted a survey study probing several dozen wires with diameters between 30 nm and 380 nm inside a transmission electron microscope [5]. Quite important, the Ag-TCNQ crystals exhibit similar electrical switching characteristics over the whole diameter range, enabling to use wires with diameters between 100 nm and 400 nm diameter as model material for microspectroscopic in-situ experiments.

3.1. Raman spectroscopy
After the proposed reverse charge transfer [2] from the negatively charged TCNQ anion to the silver cations, the material provides a significantly different vibrational structure which can be probed using Raman spectromicroscopy. Experimental spectra of TCNQ, Na-TCNQ and Cu-TCNQ allow for distinguishing the neutral and the negatively charged TCNQ molecule as the latter shows a clear shift of the vibration band at 1457 rel. cm\(^{-1}\) to 1388 rel. cm\(^{-1}\), due to antibonding effects at a specific C=C double bond [6, 7].

Whereas Raman spectra recorded without voltage and with -1 V applied show clearly the clean spectrum of negatively charged TCNQ. The vibrational peak of the neutral molecule at 1457 rel. cm\(^{-1}\) starts to rise when the applied voltage is driven to negative values (Figure 2). This change proves qualitatively that reversed charge transfer takes place upon switching the resistivity state of an individual Ag-TCNQ wire. The pronounced evolution of the peak at -15 V furthermore demonstrates that a remarkable part of the material is converted. However, an absolute quantification of affected...
molecules based on Raman spectroscopy is rather than straightforward due to dissimilar polarizability tensors of neutral and negatively charged molecules [8].

Figure 2: Raman spectra of an individual Ag-TCNQ wire with different voltages applied. Reference spectra are shown for comparison.

Figure 3: Linear dichroism in Ag-TCNQ. a) NEXAFS spectra of Ag-TCNQ oriented differently with respect to the polarization vector of the X-rays. b) Scanning transmission X-ray micrograph showing different absorption contrast with respect to the orientation of Ag-TCNQ crystallites. c) Defined geometry for in operando STXM experiments.

3.2. Scanning transmission X-ray microspectroscopy

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy provides a complementary tool for disclosing the electronic structure of TCNQ. Whereas Raman spectroscopy shows a clear shift of one vibrational band, the NEXAFS spectra of TCNQ and TCNQ$^-$ both show several overlapping C 1s to $\pi^*$ absorption peaks between 283 and 289 eV. However, their intensities are much lower for the negatively charged species where an additional electron is already present in the unoccupied states. In addition, the peaks at 288.0 eV and 289.6 eV are distinctive for neutral TCNQ [9, 10].

For quantitative comparability, the absorption probability of differently oriented wires in NEXAFS spectroscopy has to be taken into account. Due to their very ordered crystal structure [11], Ag-TCNQ needles show a pronounced linear dichroism (Figure 3 a,b). We thus conducted all experiments with the E-vector of the X-rays oriented parallel to the crystals (see Figure 3 c) to ensure maximum absorption in the $\pi^*$ region.
Applying various negative voltage steps, the contacted Ag-TCNQ is switched and its X-ray absorption spectrum is recorded \textit{in operando}. The fraction of neutral TCNQ can then be derived expressing the experimental spectra as linear combination of the reference spectra of TCNQ and Ag-TCNQ (Figure 4). The experiments show remarkable fractions of the neutral TCNQ molecule up to 22.3\% when its resistivity is switched, enhancing the conductivity of the material remarkably \cite{5}. More important, the switched state seems to be maintained when the voltage is switched off for several minutes (red square in Figure 4b).

Figure 4: a) NEXAFS spectra of an individual Ag-TCNQ nanowire with 0, -5 and -10 V applied. The spectra can be expressed by a linear combination of the reference spectra of TCNQ (orange) and Ag-TCNQ (green), giving the percentage of neutral TCNQ contained in the material (b). The neutral TCNQ fraction stays present switching off the voltage for 5 min after measuring the spectrum at -7.5 V (red square).

4. Conclusions
Employing microspectroscopic probes in high lateral resolution offers exciting possibilities to investigate electronic organic building blocks \textit{in operando}. We are thus able to confirm and to quantify the effect of reverse charge transfer in individual Ag-TCNQ nanocrystals upon resistivity switching. These experiments enable important insights into charge-induced processes on the nanoscale, which is crucial in ongoing miniaturization of electronic devices.

References
[1] Fan Z, Mo X-L, Lou C, Yao Y, Wang D, Chen G-R and Lu J G 2005 IEEE Trans Nanotech 4 238-41
[2] Potember R S, Poehler T O and Cowan D O 1979 Appl Phys Lett 34 405-7
[3] Raabe J, Tzetkov G, Flechsig U, Böge M, Jaggi A, Sarafimov B, Vernooij M G C, Huthwelker T, Ade H, Kilcoyne D, Tyliszczak T, Fink R H and Quitmann C 2008 Rev Sci Instrum 79 113704
[4] Rösner B, Späth A and Fink R H 2013 J Cryst Growth 380 34-8
[5] Ran K, Rösner B, Butz B, Fink R H and Spiecker E 2016 Nanotechnology accepted
[6] Khatkale M S and Devlin J P 1979 J Chem Phys 70 1851-9
[7] Umbach T R, Fernández-Torrente I, Ruby M, Schulz F, Lotze C, Ruraili R, Persson M, Pascual J I and Franke K J 2013 New J Phys 15 083048
[8] Machado H J S and Hinchliffe A 1997 Electron J Theor Chem 2 49-55
[9] Bäsßler M, Fink R H, Buchberger C, Väterlein P, Jung M and Umbach E 2000 Langmuir 16 6674-81
[10] Koshino M, Kurata H and Isoda S 2004 J Electr Spectr Rel Phen 135 191-200
[11] Shields L 1985 J Chem Soc, Faraday Trans 2 81 1-9