Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Low-energy electron irradiation induced synthesis of molecular nanosheets: An influence of the electron beam energy

Christof Neumann,[a] Richard A. Wilhelm,[bc] Maria Küllmer,[a] and Andrey Turchanin[ad*]

[a] *Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany*
[b] *Institute of Applied Physics, TU Wien, 1040 Vienna, Austria*
[c] *Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany*
[d] *Jena Center for Soft Matter (JCSM), 07743 Jena, Germany*

*Address correspondence to andrey.turchanin@uni-jena.de

Derivation of the rate equation for conversion of a NBPT SAM into a CNM

We described the cross-linking of the SAM into a CNM using the following chemical equation:

$$[SAM] \xrightarrow{e^-} [CNM]$$

Here, [SAM] and [CNM] represent factions of the nitro groups and amino groups in the monolayer, respectively. We assume the reaction can be expressed by a first-order rate equation with the rate constant, κ, and the electron dose, ϕ:

$$\frac{d[SAM]}{d\phi} = -\kappa[SAM]$$

$$\Leftrightarrow \frac{d[SAM]}{[SAM]} = -\kappa d\phi$$

$$\Rightarrow \int_{[SAM]_0}^{[SAM]} \frac{d[SAM]}{[SAM]} = \int_0^{\phi} -\kappa d\phi$$

$$\Leftrightarrow ln([SAM]) \Big|_{[SAM]_0}^{[SAM]} = -\kappa\phi \Big|_0^{\phi}$$

$$\Leftrightarrow ln([SAM]) - ln([SAM]_0) = -\kappa\phi$$

Initially, the sample consist completely of a SAM and we can simplify using $[SAM]_0 = 1$:

$$ln([SAM]) = -\kappa\phi$$

$$[SAM] = e^{-\kappa\phi}$$

We conclude from our XPS results $[SAM] + [CNM] = 1$ leading to:

$$F(\Phi) = [CNM](\Phi) = 1 - e^{-\kappa\phi}$$

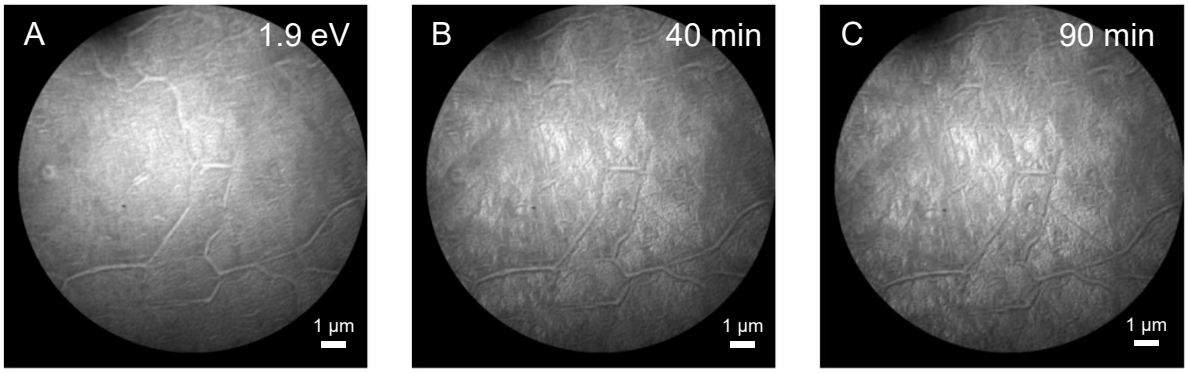

Figure S1: LEEM images acquired by continuous irradiation of a NBPT SAM using an electron energy of 1.9 eV. Image A shows the pristine SAM, whereby the images B and C are acquired after irradiation time 40 min and 90 min, respectively.

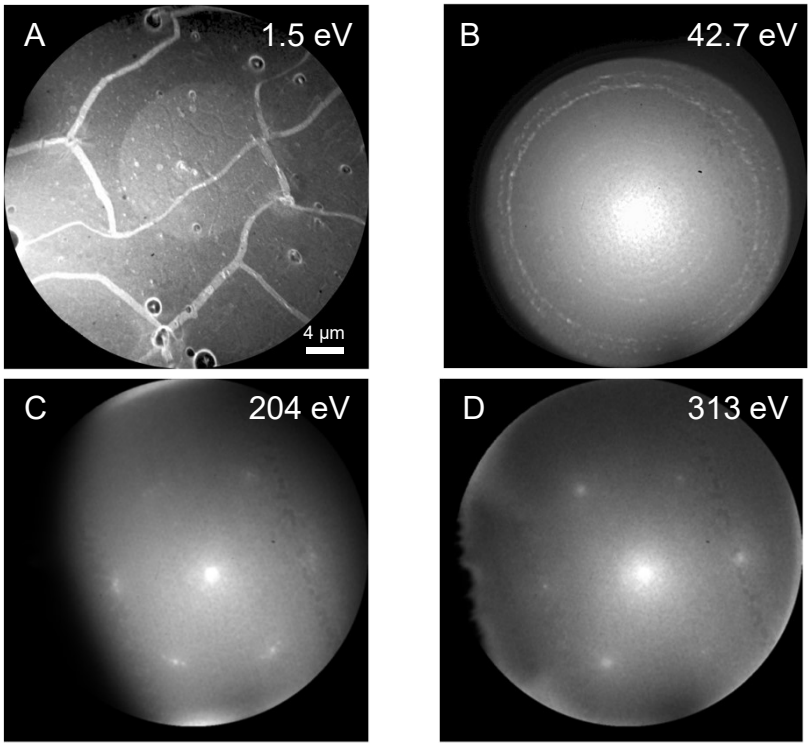

Figure S2: (A) LEEM image of a reference Au/mica sample showing different domains. The image was obtained without the contrast aperture. (B) µLEED pattern acquired from an Au/mica reference sample using an electron energy of 42.7 eV. The µLEED pattern was acquired within the circular region in the center of (A). (C-D) µLEED patterns acquired from an NBPT SAM/Au/mica using higher electron energies showing the pattern corresponding to a Au(111).

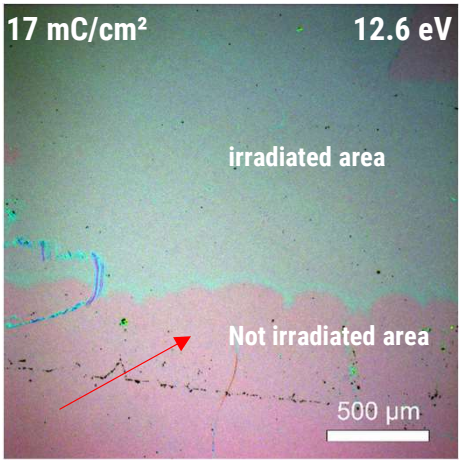

Figure S3: Optical microscope image of a transferred NBPT CNM after irradiation with 17 mC/cm² using an electron energy of 12.6 eV. The area marked with the red arrow was covered during electron irradiation by the sample holder.

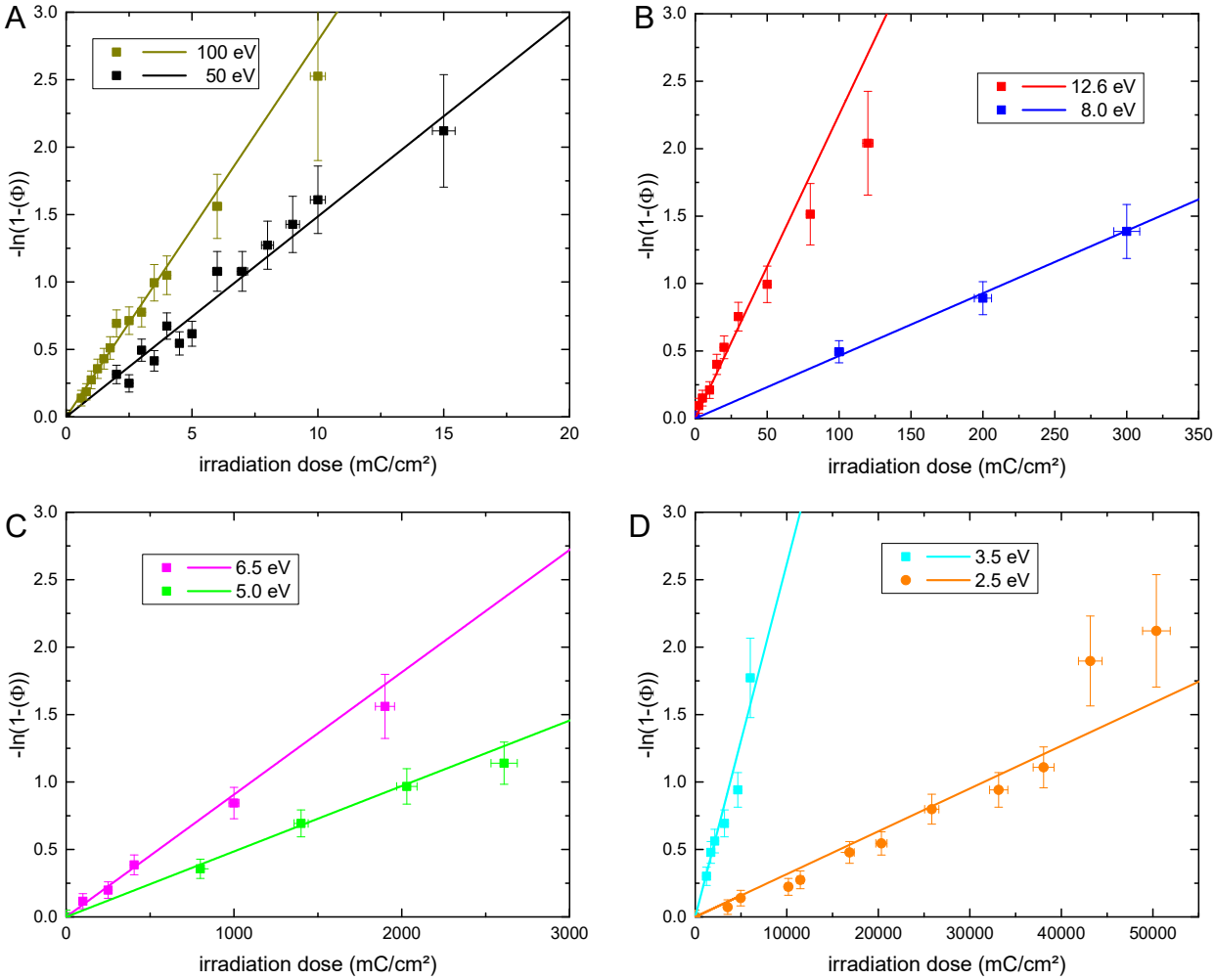

Figure S4: Experimental data presented in Fig. 5A and the linearized fit function $F(\Phi)$. For better visualization the data are presented for different electron energies separately in (A-D). The linearized fit functions show a good agreement with the experimental data.

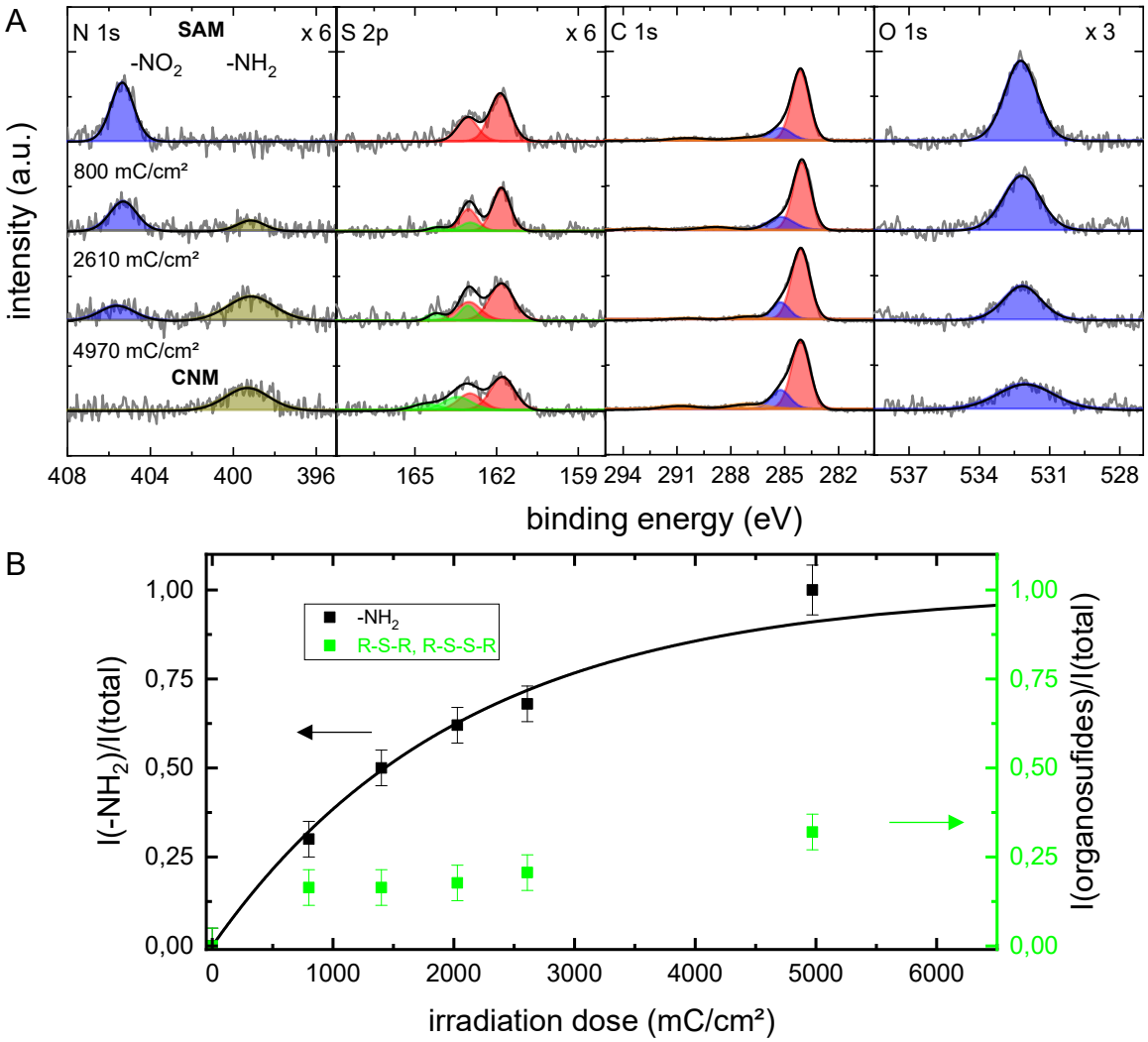

Figure S5 : (A) N 1s, S 2p, C 1s and O 1s XP spectra of a NBPT SAM which is stepwise irradiated with electrons with an energy of 5 eV and subsequently cross-linked into a carbon nanomembrane. For better representation, intensities of the N 1s, S 2p and O 1s spectra are multiplied by the factor presented in the figure. In (B) the fractions of $-NH_2$ and organosulfide (R-S-R and R-S-S-R) groups are presented as a function of the irradiation dose.

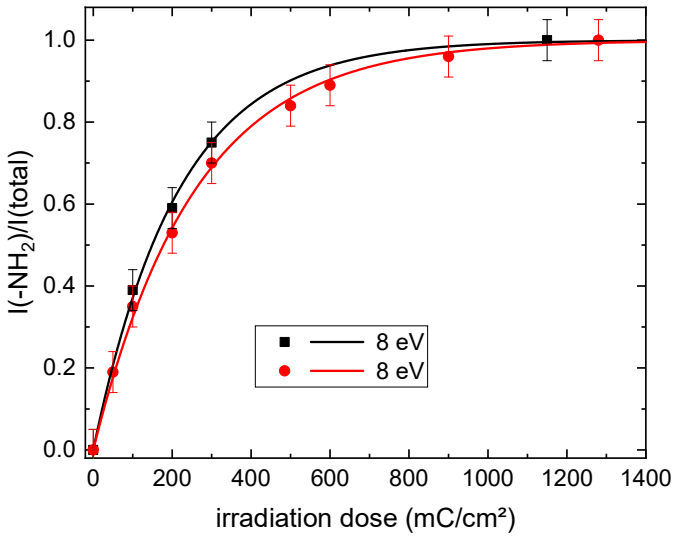

Figure S5: XPS analysis of the cross-linking of an NBPT SAM using a primary electron energy of 8 eV (black) and a primary energy of 12.6 eV which was retarded to 8 eV using a negative sample bias of - 4.6 V (red). The resulting fraction of amino groups as a function of the irradiation dose is identical for both samples.

Table S1: Coefficients of determination, R^2, of the linearized fit functions $F(\Phi)$ in Fig S4.

Electron energy (eV)	**100.0**	**50.0**	**12.6**	**8.0**	**6.5**	**5.0**	**3.5**	**2.5**
R^2	0.992	0.976	0.984	0.999	0.988	0.983	0.946	0.958

Table S2: Summary of the determined rate constants, κ, of the cross-linking. These values were used to calculate the effective cross-linking cross sections, σ_{eff}, and the cross section, σ_{eff}^*, corrected by the secondary electrons yield.

E (eV)	κ (cm²/mC)	σ (cm²)	σ* (cm²)
100.0	$(2.79 \pm 0.07) \times 10^{-1}$	$(4.47 \pm 0.11) \times 10^{-17}$	$(3.72 \pm 0.09) \times 10^{-17}$
50.0	$(1.49 \pm 0.06) \times 10^{-1}$	$(2.38 \pm 0.09) \times 10^{-17}$	$(1.90 \pm 0.08) \times 10^{-17}$
12.6	$(2.25 \pm 0.13) \times 10^{-2}$	$(3.61 \pm 0.20) \times 10^{-18}$	$(2.12 \pm 0.12) \times 10^{-18}$
8.0	$(4.64 \pm 0.10) \times 10^{-3}$	$(7.43 \pm 0.16) \times 10^{-19}$	$(4.64 \pm 0.10) \times 10^{-19}$
6.5	$(9.07 \pm 0.61) \times 10^{-4}$	$(1.45 \pm 0.10) \times 10^{-19}$	$(9.08 \pm 0.61) \times 10^{-20}$
5.0	$(4.85 \pm 0.31) \times 10^{-4}$	$(7.77 \pm 0.49) \times 10^{-20}$	$(3.89 \pm 0.25) \times 10^{-20}$
3.5	$(2.62 \pm 0.23) \times 10^{-4}$	$(4.19 \pm 0.37) \times 10^{-20}$	$(2.10 \pm 0.19) \times 10^{-20}$
2.5	$(3.17 \pm 0.21) \times 10^{-5}$	$(5.08 \pm 0.33) \times 10^{-21}$	$(2.54 \pm 0.17) \times 10^{-21}$

Table S3: Secondary electron yield (SEY) for primary electrons, n_p, with different energies adopted from Refs. [1-2]. For 50-100 eV only elastically scattered electrons are taken into account. The number of electrons, N, involved in the cross-linking process is calculated to $\mathrm{N} = n_p(1 + \eta_{SEY})$

Electron energy (eV)	**100.0**	**50.0**	**12.6**	**8.0**	**6.5**	**5.0**	**3.5**	**2.5**
η_{SEY}	0.2	0.25	0.7	0.6	0.6	1.0	1.0	1.0

[1] B. Völkel, A. Gölzhäuser, H. U. Müller, C. David and M. Grunze, *J. Vac. Sci. Tech. B:*, 1997, **15**, 2877-2881.

[2] L. A. Gonzalez, M. Angelucci, R. Larciprete and R. Cimino, *AIP Adv.*, 2017, **7**, 115203.

Video S1: Video of the *in operando* 12.6 eV μLEED diffraction pattern as a function of the applied the irradiation dose.