Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

High voltage electrochemical exfoliation of graphite for high-yield graphene production

Sarah Roscher, * René Hoffmann, Mario Prescher, Peter Knittel and Oliver Ambacher

Fraunhofer Institute for Applied Solid State Physics, Tullastraße 72, 79108 Freiburg, Germany

* Corresponding author

Email: sarah.roscher@iaf.fraunhofer.de

Determination of the graphene yield

The yield of FLG flakes from our method was determined by Raman spectroscopic analysis. In order to do so, the whole material after the electrochemical treatment was extracted (subjected to thermal annealing for dehydrogenation) and investigated. There was no sample preparation that may favour graphene over graphite involved. Evaluating over 800 spectra of that material we can conclude from the sampling to the whole material and thus determine a yield.

Additionally, in order to determine a yield as defined by weight of the FLG flakes divided by weight of the starting material, we carried out a separation process based on careful decantation. The extracted material was dispersed and then allowed to settle until the thicker and heavier graphite flakes settled down while the lighter graphene flakes remained dispersed. The dispersed flakes were then decanted. The success of the separation was controlled by Raman spectroscopy. The precipitate consisted of mostly graphite (~ 95 %). The supernatant consisted of mostly FLG with ~ 5-10 % graphite. The complete separation of pristine graphene flakes is difficult due to its similar dispersion behaviour as graphite. Without functionalisation dispersion and sedimentation are largely dependent on size of the flakes, which is similar for graphene and graphite around 10 layers. However, the graphite in the supernatant and the graphene in the precipitate can be accounted for by correcting the measured weight with the respective percentage determined by Raman spectroscopy. With that we determined a yield by weight ratio of ~ 80 % graphene. This is in accordance with the yield obtained by Raman measurements of over 800 spectra of the whole material, as described above and in the article. Slight deviations may also arise due to small material losses during handling.

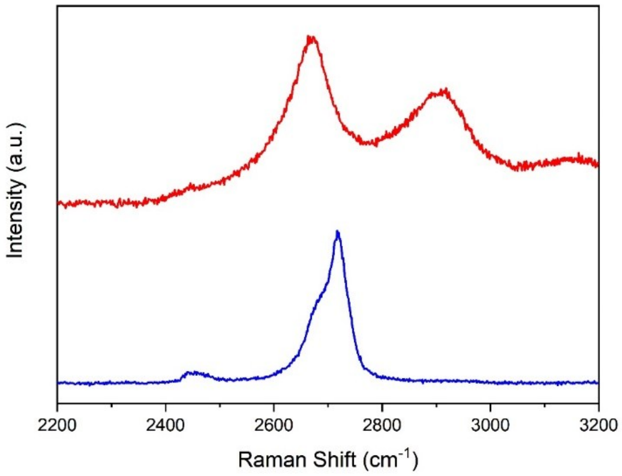


Figure S1: Raman spectra of the graphite flakes before (black) and after (red) electrochemical treatment showing the 2D band and the D+D' band evolution due to hydrogenation of the graphene lattice.

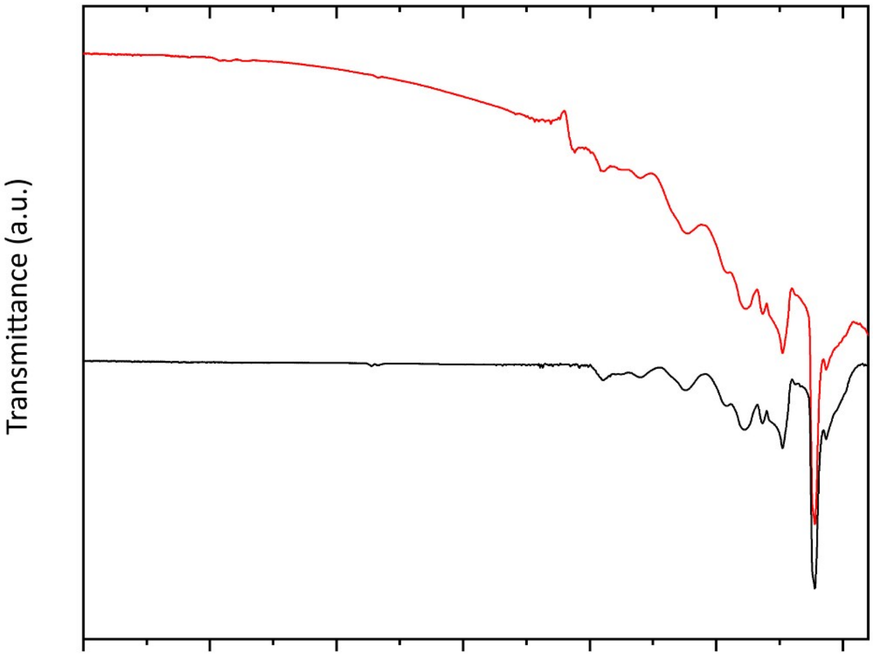


Figure S2: FTIR spectra of graphene on a silicon substrate (red) and the silicon substrate (black) without any baseline corrections.

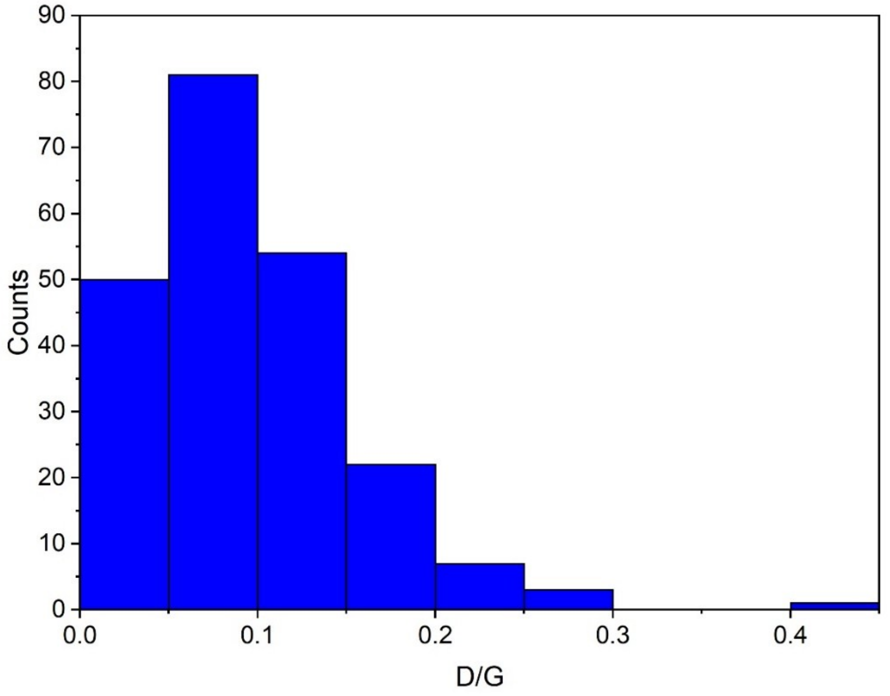


Figure S3: Histogram of the Raman D/G ratio of the pristine graphite flakes.

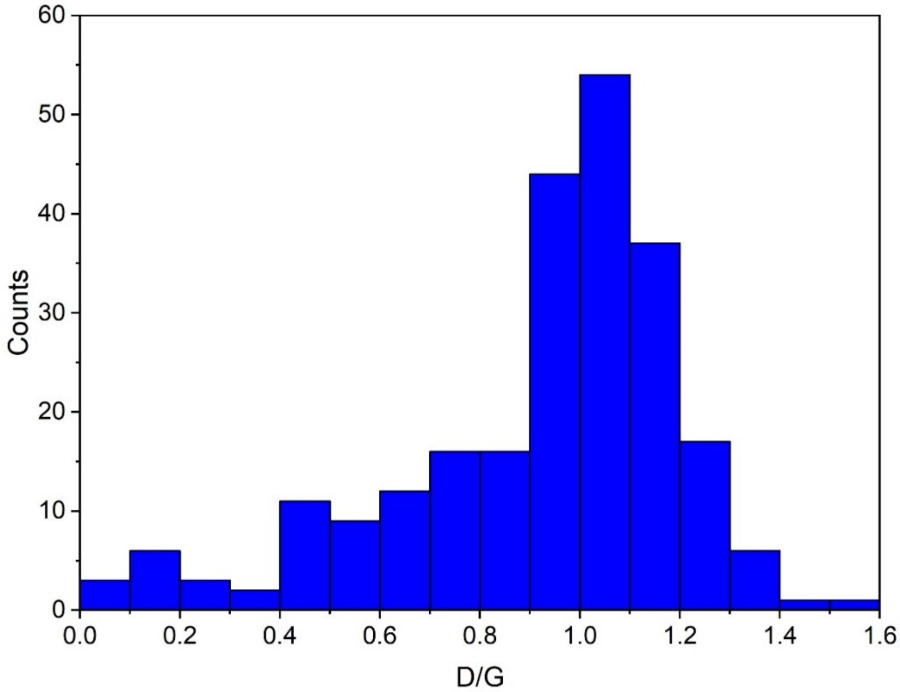


Figure S4: Histogram of the Raman D/G ratio of the electrochemically produced graphene flakes.

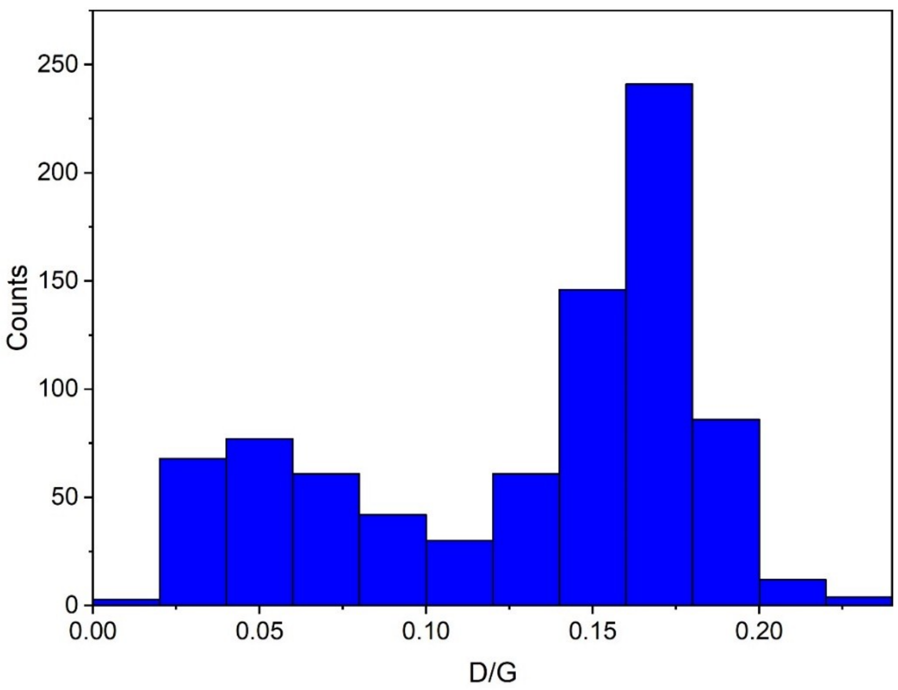


Figure S5: Histogram of the Raman D/G ratio of the annealed graphene flakes, i.e., after dehydrogenation.

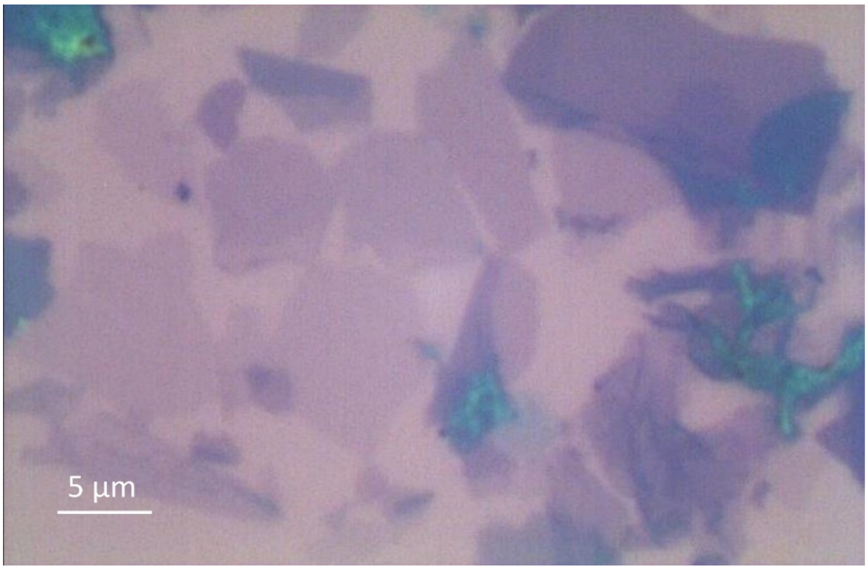


Figure S6: Example of an optical microscope image of the graphene flakes on SiO_2 (300 nm)/Si substrate that was used for the analysis of the graphene flake size. Flakes that are folded or agglomerated like, e.g., the ones at the bottom right were not used for evaluation.

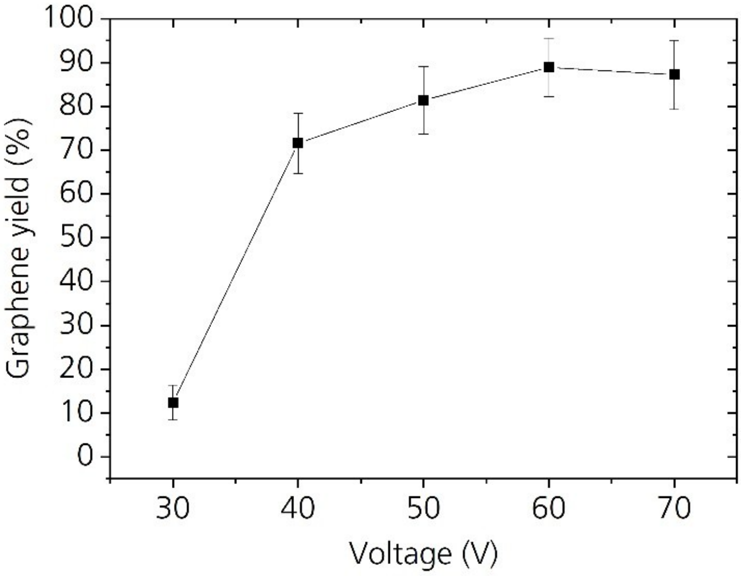
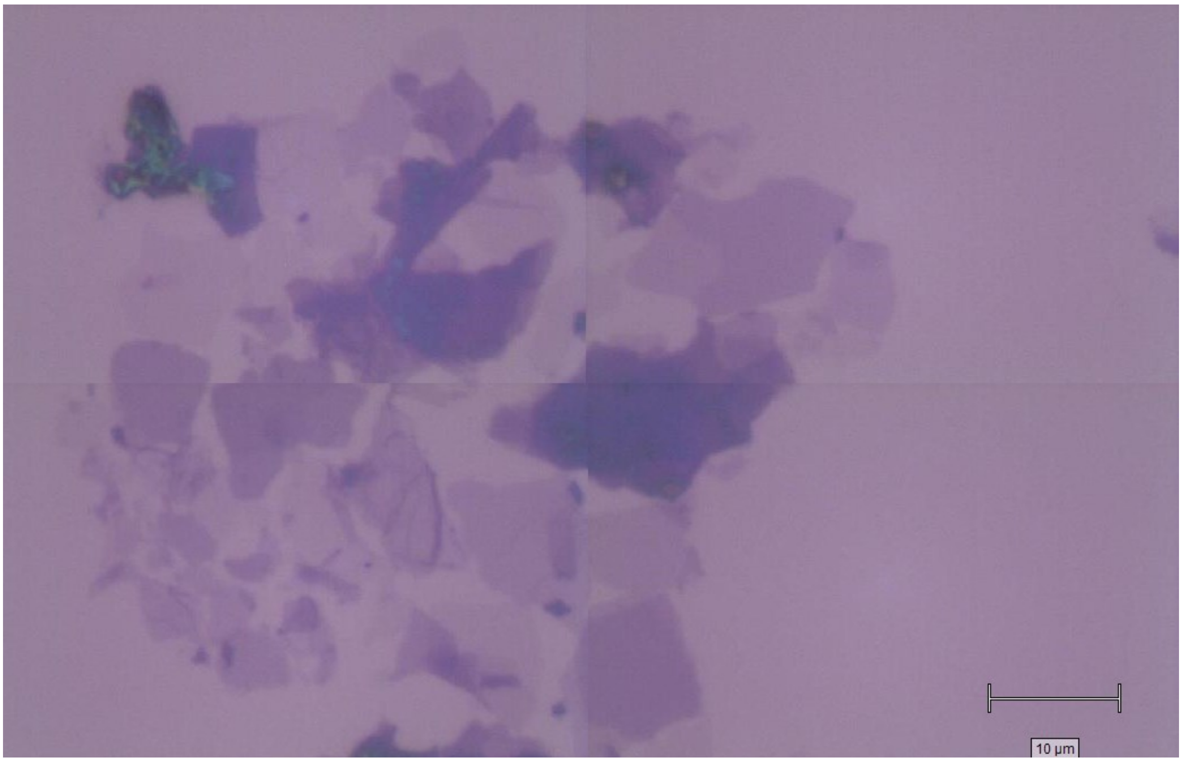


Figure S7: Graphene yield for different applied voltages (each for the duration of 24 h).

a)



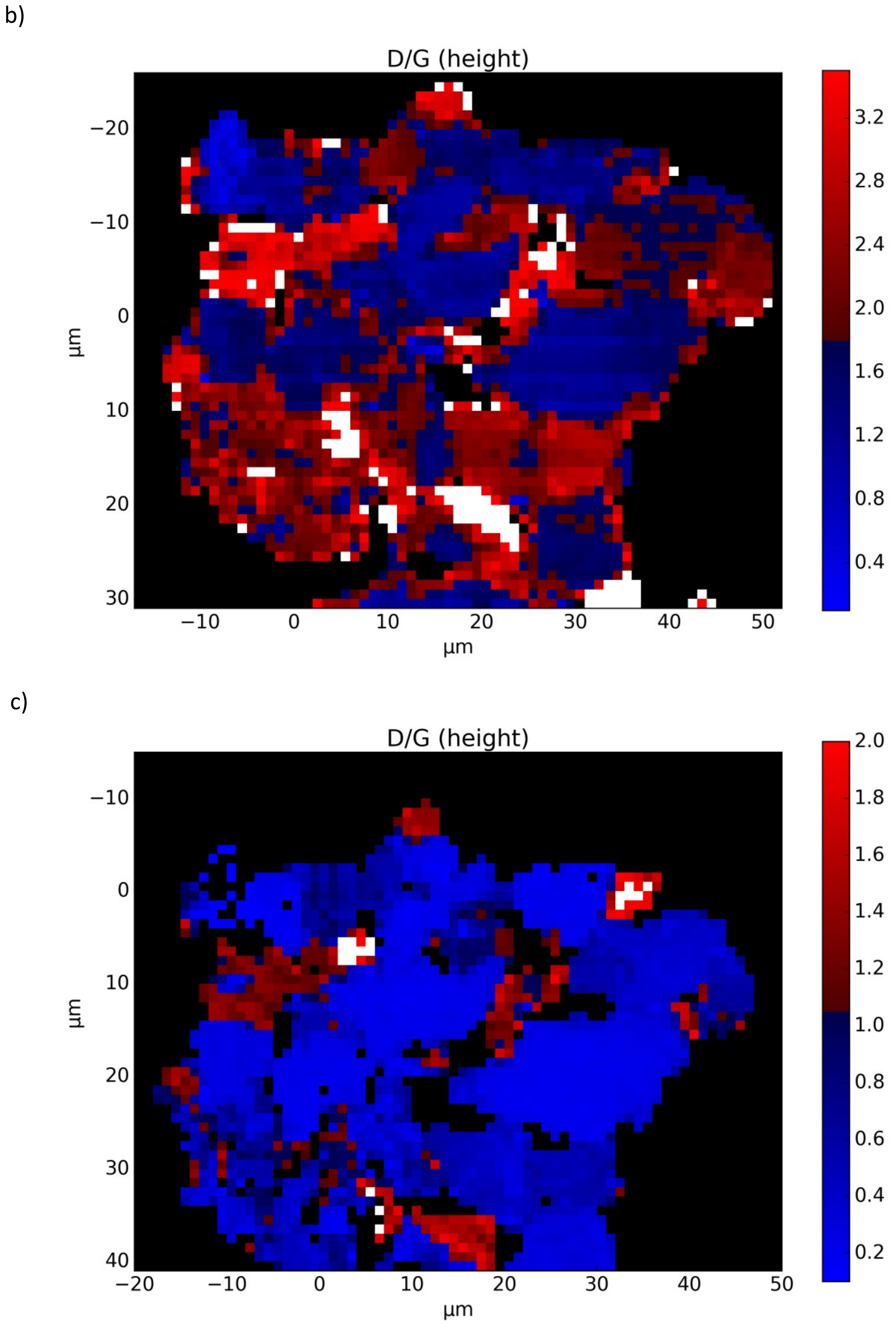


Figure S8: Raman mapping of graphene flakes on SiO_2 (300 nm)/Si with a spatial resolution of 1 µm. a) shows the optical microscope image of that area. b) and c) show the Raman D/G intensity ratio before and after annealing at over 600°C for dehydrogenation respectively. As can be seen, the D/G ratio strongly decreases upon dehydrogenation. In same small areas the D/G remains higher, which is likely caused by limited diffusion due to the small space between flake and substrate in those areas [1]. As mentioned in the article some flakes showed very flat and smooth morphology indicating better adherence to the substrate. In those cases hydrogen desorption may be hindered.

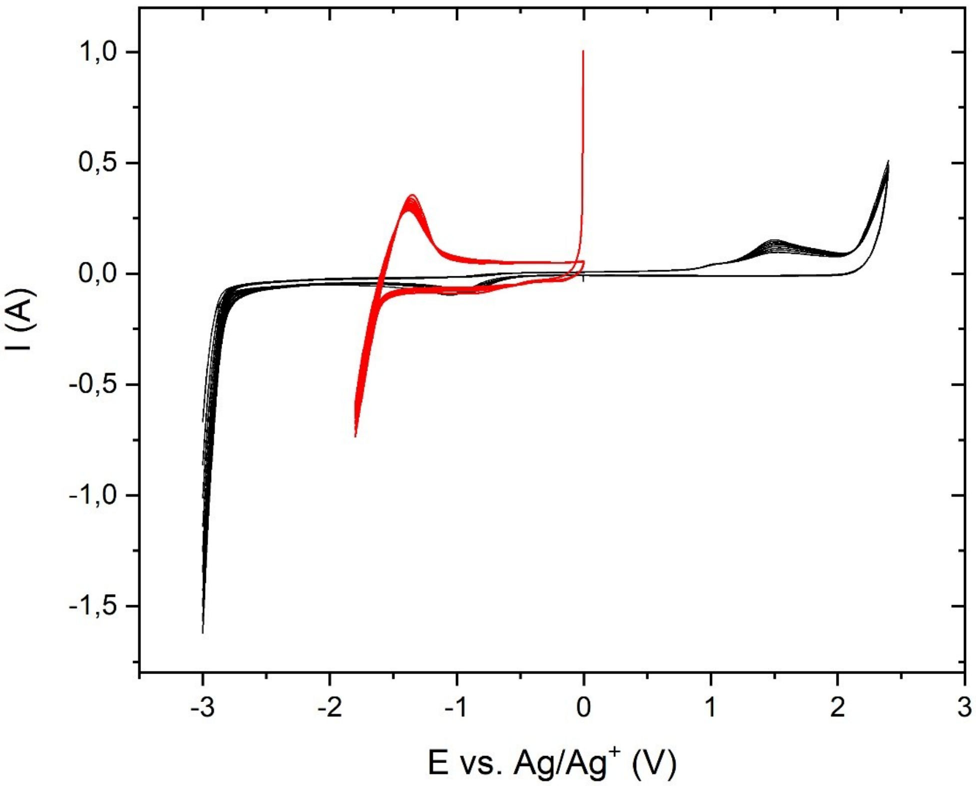


Figure S9: Cyclic voltammogram of the employed electrolyte 0.1 M $TBAPF_6$/PC with graphite (red) and BDD (black) working electrode (WE) vs an Ag wire as reference electrode (RE) and BDD counter electrode. The curve with graphite WE show the intercalation of the TBA-cations into the graphite layers under negative potentials with the de-intercalation peak at reverse scan direction. On the BDD WE no intercalation can take place. At more negative potentials the electrolyte decomposes.

References

1 J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead and P. L. McEuen, *Nano letters*, 2008, **8**, 2458–2462.