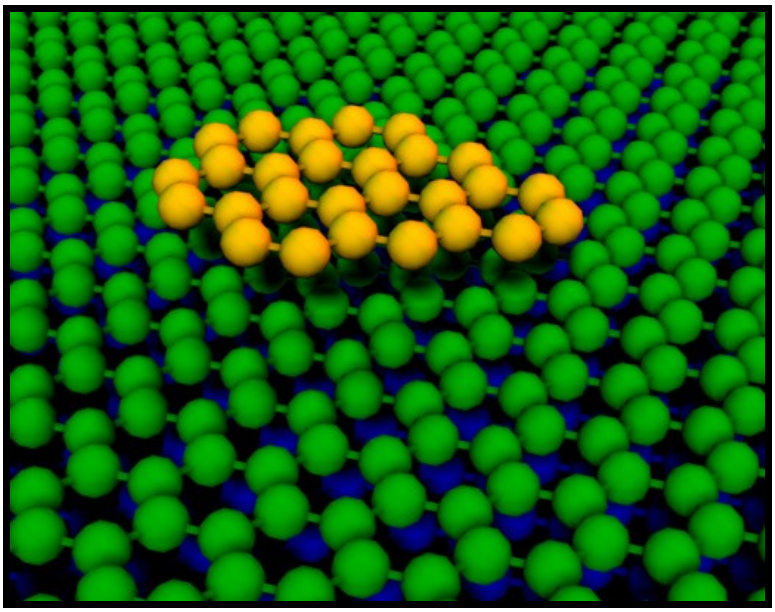
Project work

NANOFLAKES

Interactions with surfaces
134.114



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Motivation

The task of this project was to develop a method to prepare ultrasmall graphite flakes (nanoflakes).

Introduction

Graphite flakes with size of 100 nm and less were produced by different methods.
Size determination was performed with TEM (at USTEM) and powder diffraction (at the TU chemistry department, Prof. F. Kubel).

Graphite

Graphite is a layered crystal.
Each of these layers has a hexagonal structure, with a unit cell side length of about 0.14 nm. Each atom has 3 nearest neighbours in this distance.
The distance between two layers is 0.34 nm. The layers are shifted against each other in a way that only a half of the atoms lie exactly below and above an atom of a neighbouring layer, the other half of the atoms lie between the middle of hexagons of the neighbouring layers (which are empty).
This is the reason why the forces between the atoms of one layer are much stronger than between neighbouring layers.
We can imagine graphite as a pile of paper. Each sheet of paper is relatively stable and not easily destroyable, but the sheets can easily slide against each other or even can be separated.

In physics terms, the bindings within one layer are covalent, and the bindings between two layers are van der Waals. A single layer of graphite is called graphene. High quality graphite with few flaws in the crystal structure is known as highly ordered pyrolytic graphite (HOPG). For this project only HOPG was used.

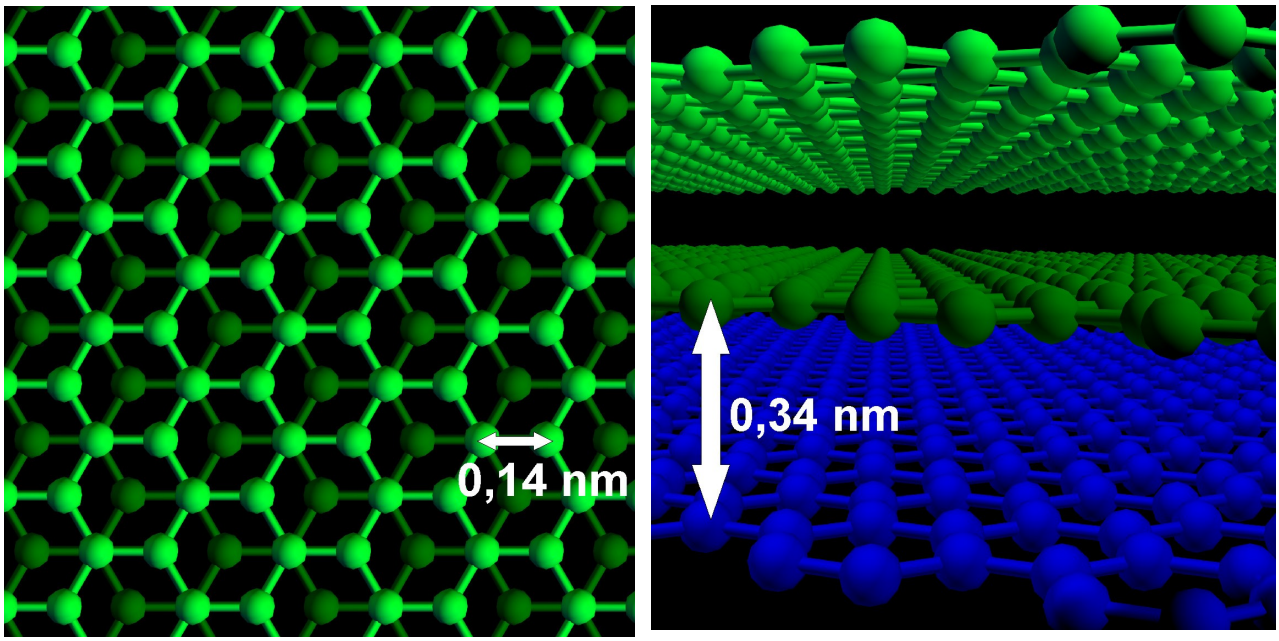


Fig.1: Visualisation of graphite:
left: 001 as projection plane
right: from between the layers

TEM

(Transmission electron microscopy)

In this microscopy method, a beam of electrons is shot at a thin sample.
The electrons interact with the sample depending on thickness, element and crystal structure.
Behind the sample transmitted electrons are detected and displayed on a screen.

The resolution of such a microscope is theoretically limited only by the de Broglie wavelength of the electrons. But because the quality of the magnetic lenses is not perfect, such high resolution cannot be reached.
In the microscopes that were used in this study, the wavelength of the electrons is of the order of 10^{-12} m (acceleration voltage: 200kV), but actually the maximum resolution is just of the order of 10^{-10} m.

For the analysis of my sample the microscopes FEI TECNAI G20 and FEI TECNAI F20 were used. The main difference is that the G20 uses a LaB6 cathode, while the F20 uses a FEG (field emission gun), which provides a better electon beam and thus better resolution.

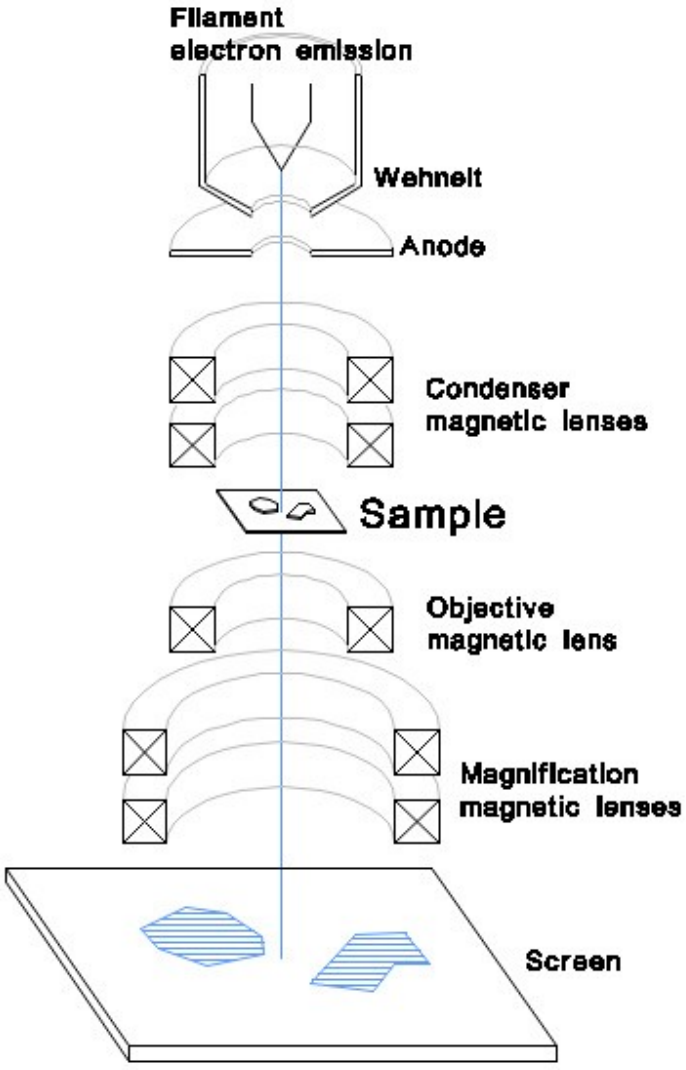


Fig. 2: Schematic TEM

TEM samples

For transmission electron microscopy, samples have to be very thin, below 100 nm, better in the order of 10 nm.
For these measurements TEM grids were used, which are copper grids of about 3 mm diameter. The copper wires are completely opaque for the TEM. On the copper grid, a very thin layer (coat) is placed that transmits the electrons. The coat has an amorphous structure to minimally interfere with the measurement. There can be holes in the coat, so that the coat does not interfere at all with the measurement of particles lying over a hole.

In the initial investigations of the current experiments a coat of amorphous graphite was used, which had holes of about 2.8 µm diameter.
HOPG pieces lying on this coat could be detected, and resolved down to a size of about 10 nm. Smaller pieces and probably also pieces that were too thin could not be detected anymore, because the coat was interfering too much with the measurement.
Above the holes, atomic resolution could be reached in the HOPG nanoflakes, however only large particles could lie over a hole, the smaller ones would fall through.

In the later investigations of the current experiments a Silicon monoxide (SiO) coat was used. This coat had no holes, but nevertheless slightly improved the resolution, because now graphite on SiO had to be investigated and not graphite on graphite.
Because of this experimental setup, atomic resolution could not be reached. However in one case the SiO coat was ripped by accident, opening a small cleft of about 30 nm, allowing atomic resolution on the HOPG nanoflake.

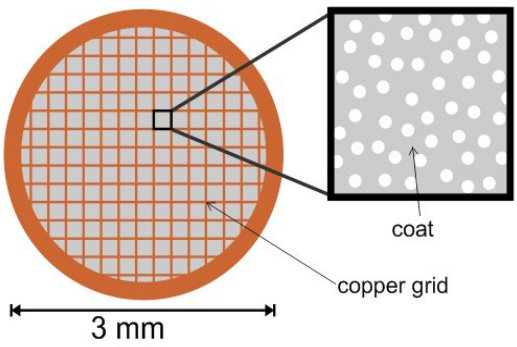


Fig. 3: TEM grid with holed coating

X-ray powder diffraction:

Powder diffraction is a technique to determine the crystallic structure of solids. The solid is pulverized, so that it consists of a multitude of minuscule crystal particles, which in the ideal case are oriented randomly in different directions.
The X-rays are reflected (Bragg condition $n\lambda=2d \sin\theta$) by the crystal lattice planes.

A monocrystalline substrate has to be rotated in order to get different angles θ and thus to get different reflections.
In the case of a powder, which is inherently multicrystalline, no rotation of the sample is needed, since the crystallites point in each possible direction. Thereby all the different reflections from different angles θ are achieved
An angle dependent intensity diagram is obtained, the peaks being reflections from different lattice planes (different d in the Bragg equation) and of different order n.
This intensity diagram can now be compared with diagrams of known crystal structures, or with theoretically calculated diagrams, and so conclusions about the crystal structure, the grain size and other information can be drawn.

Texturing effect
With layered crystals such as graphite, texturing can appear, that means that the particles do not orient randomly, they are flat and tend to lay down in layers.
A method to avoid texturing is mixing the layered powder with another non-layered powder, for example Si. The flat particles will orient randomly around the Si particles, like leaves in a box of blueberries.
The intensity diagram of Si is well known, so it can easily be "subtracted" from the intensity diagram of the whole sample, and the intensity diagram of the layered crystal remains and can by analysed.

The measurements were performed with
Pulverdiffraktometer PANalytical X'Pert PRO (XP-2), Cu(LFF)-Anode, (K1)=1.5406, (K2)= 1.5444Å. Bragg-Brentano-Goniometer; Röhrenleistung 40 kV, 40 mA, Theta/Theta -Scans, Messbereich 5-90°, Messzeit 30 Min

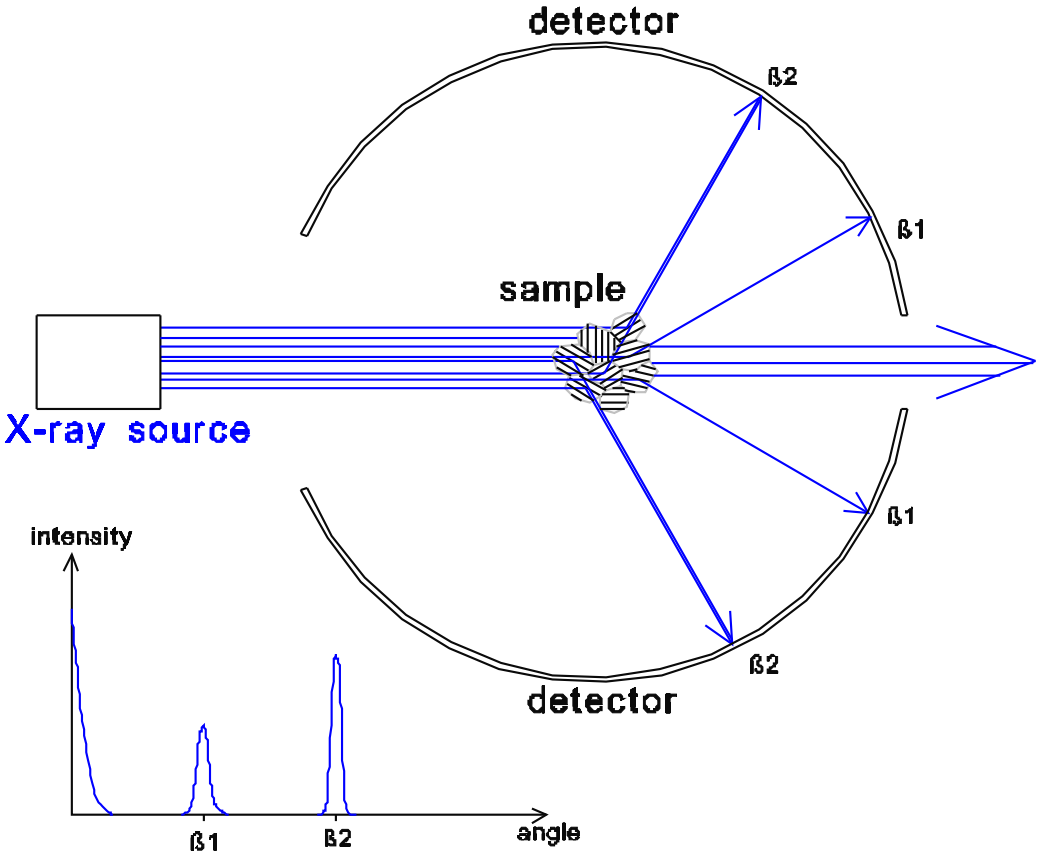


Fig. 4: Schematic X-ray powder diffractometer

Preparation of the sample

Several preparation methods were tried.
An issue was that the particle density often was quite low, and searching in TEM for the particles (hoping that there are any) was like looking for the needle in the haystack.

1. <u>Scotch tape method</u>

The HOPG was cleaved with the use of adhesive tape. While cleaving, not only large pieces of graphite detach, but also some small ones. The tape with layers of graphite sticking on it was put over the TEM grid , or the TEM grid was put upside down onto the tape. Small pieces, if there were any, and dust, were supposed to fall onto the TEM grid or respectively to attach to it by friction forces.

<u>Advantages:</u>
The only advantage is that the preparation is not very complicated and specific equipment is not required.
<u>Disadvantages</u>
- Very low particle density (not more than 3 particles could be found on the whole grid).
- The particles are rather large (100 nm and more, no smaller particles found).
- Contamination because of the preparation method.
- The coat of the TEM grid can easily be destroyed if it sticks to the scotch tape.

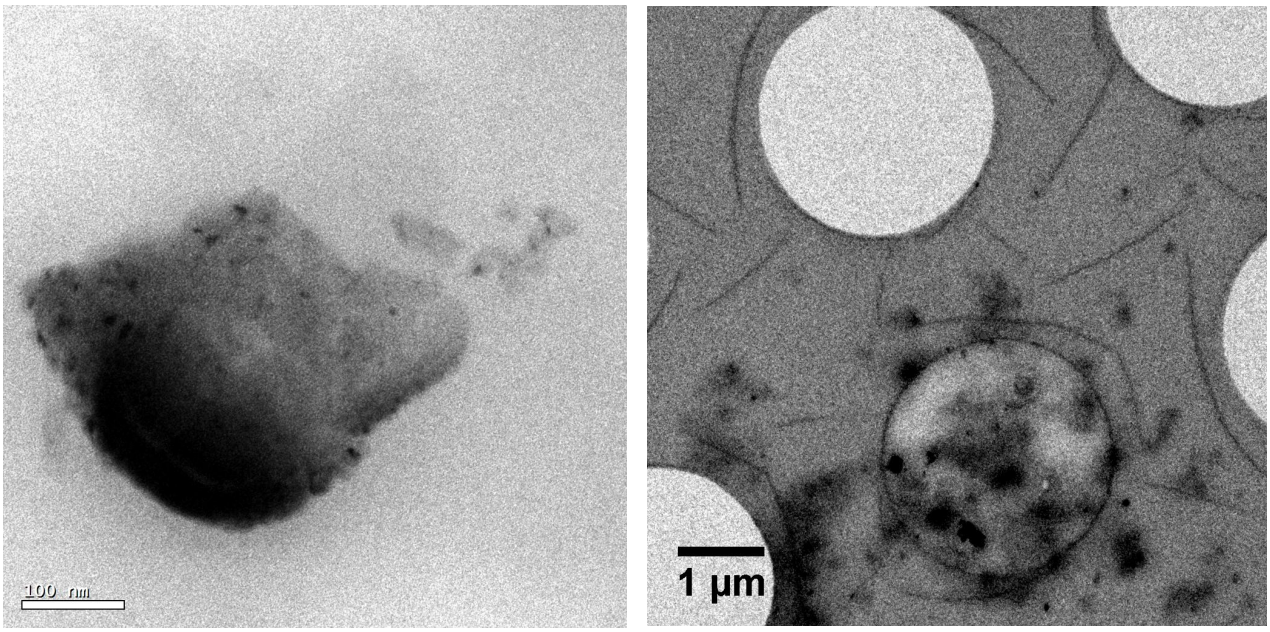


Fig.5a: HOPG nanoflakes prepared with method 1 (scotch tape).
Fig.5b: Here the holes of the carbon coat are visible (bright circles). The dark spots are HOPG flakes. The lines are part of the amorphous carbon coat.

2. <u>Rubbing between two flat planes</u>

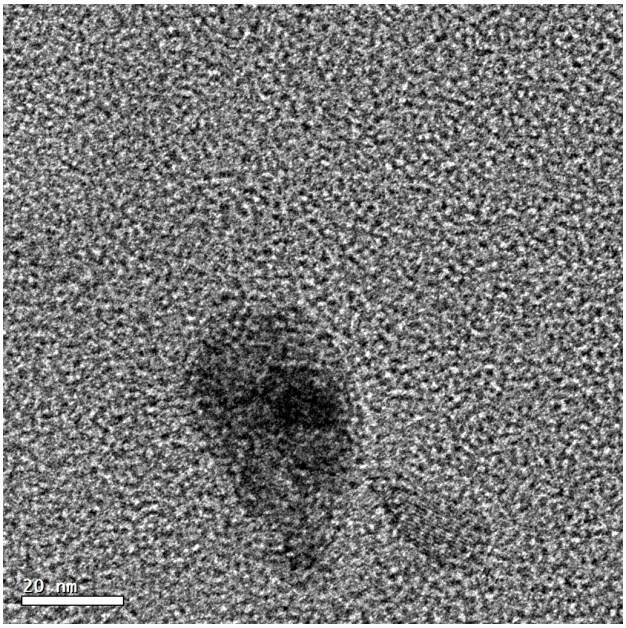
A small piece of HOPG graphite is put between either two pieces of silicon wafer, or glass microscope slides. They are rubbed against each other for about 10-15 min. With the glass slides, it can be directly observed how the piece of HOPG turns into a stain of dust, with one or two bigger particles remaining uncrushed.

With an optical microscope one can see that there are a lot of differently sized pieces. There is a good chance that there are even smaller particles, visible only in TEM.
To get the graphite onto the TEM grid, acetone is dropped onto the silicon or glass plane, the graphite dust is thereby washed off and can be dropped onto the TEM grid.

<u>Remark:</u>
Acetone was a bad choice, because it is polar and graphite is not, so that the graphite flakes stay on the surface of the acetone droplet rather than immersing into the liquid.
Later for other preparation methods, Chloroform ($CHCl_3$) or CCl_4 was used. Graphite could immerse much better.

<u>Advantages:</u>
- The amount of particles is a bit larger, and could be further improved by repeating the process (dropping several times).
- Very small particle sizes could be reached (many particles <100 nm, some of the order of 10-20 nm)

<u>Disadvantages:</u>
- Debris from the liquid and from the rubbing planes.
- The distribution of particles was not regular, the particles were located mostly in one area at the border of the TEM grid. The reason could be a bad choice of solvant.



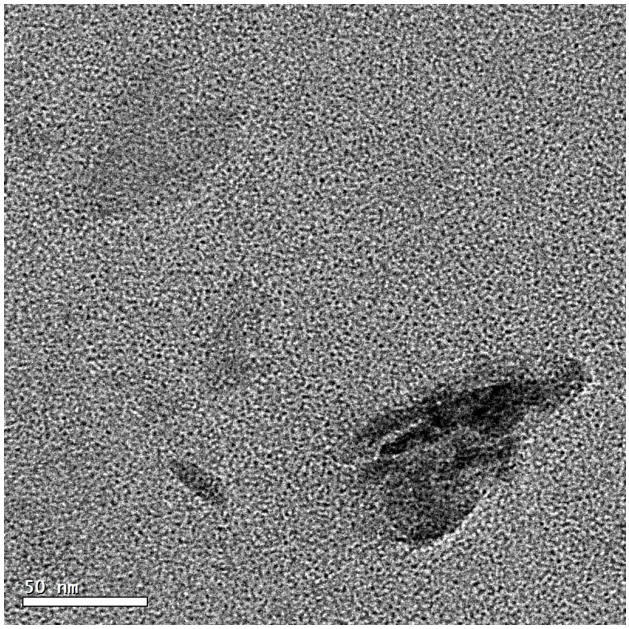


Fig. 6a: Particles prepared with method 2. On the smaller particle on the right side, faint lines are visible, probably rows of atoms.
Fig. 6b: Four particles. The two upper particles on the left side are hardly visible, they are probably very thin. Sometimes it was hard to say whether something was a particle or just background noise.

3. <u>Ultrasonic bath</u>

A piece of graphite is put into a watch glass with Chloroform or CCl_4. The piece is rubbed with a needle against the glass. Smaller pieces of graphite and dust detach and become visible on the surface of the watch glass.
Now the liquid with the dissolved graphite can be poured into a small jar and put into ultrasonic bath, in order to further dismember the graphite.
Now it can be dropped onto a TEM grid.

<u>Advantages</u>
- The ultrasonic bath separates the graphine layers from each other quite well.

<u>Disadvantages</u>
- Too low particle density.
- The particle size seemed rather large (mostly > 100 nm), however one piece of 20 nm was found. Perhaps a higher density would show more small particles.

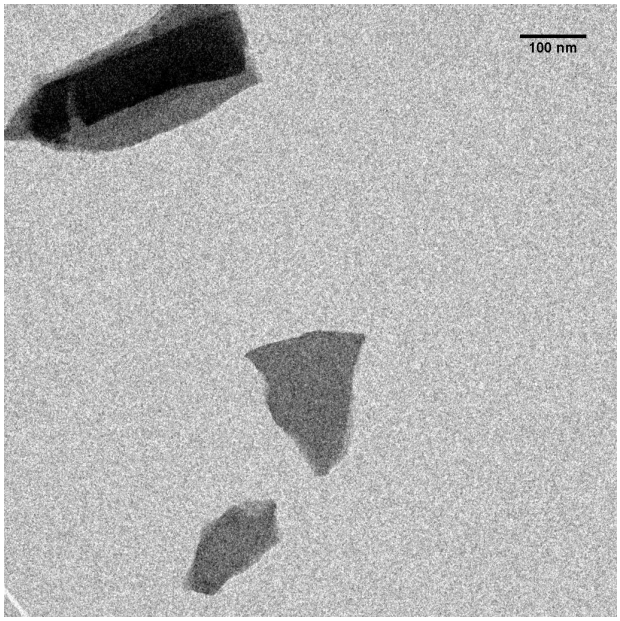
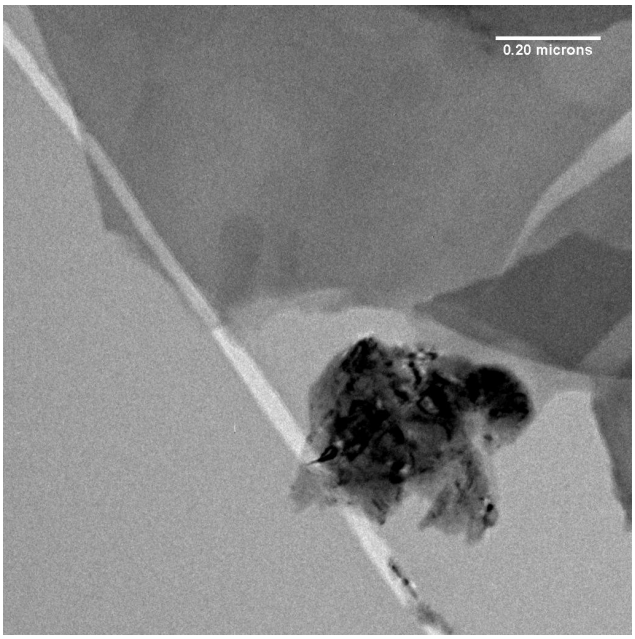


Fig. 7: Some HOPG flakes produced with method 3.



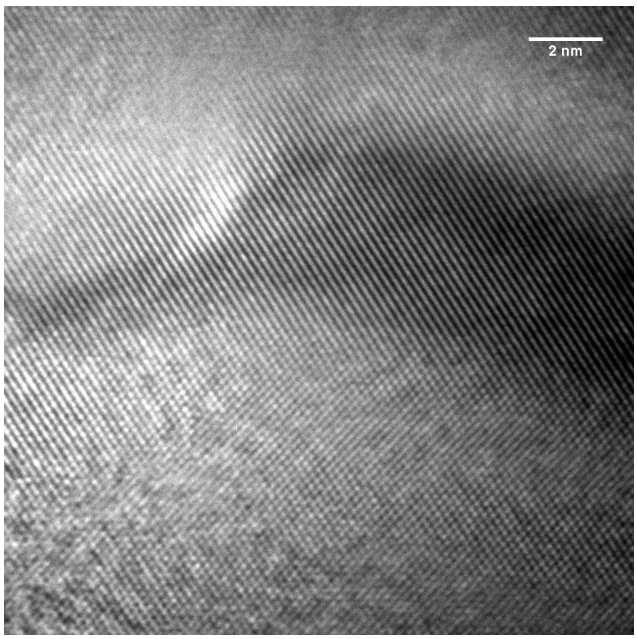


Fig. 8a: On places like this, where the SiO coat was ripped by accident (diagonal bright line), high resolution could be achieved over that cleft.
Fig. 8b: High resolution image over the cleft.

4. <u>Mortar and pestle</u>
The piece of graphite is crushed with some Si with an agate mortar and pestle for about 20 min. The Si is added for two reasons:
- Si is quite a hard material and helps to break the graphite down in very small parts
- With such a sample, not only TEM investigation, but also powder diffraction can be performed. In powder diffraction, Si helps against the texturing effect of graphite.

The powder is dissolved in Chloroform or CCl_4 and put in a small jar into an ultrasonic bath. It is put to rest for at least 20 min (better for several hours), in order to let the bigger pieces of graphite and also the silicon sink towards the ground (both graphite and silicon have a higher density than the liquid). Small graphite particles remain in the upper region of the liquid because of diffusion.

Two ways of depositing the graphite on the TEM grid were attempted:
a.)
From the upper part of the liquid a small amount is put onto the TEM grid with a dropper. The dropping can be repeated several times in order to reach higher graphite densities on the grid.
b.)
The TEM grid is placed on an empty watch glass. From the upper part of the liquid an amount is put onto the watch glass with the dropper so that the grid becomes almost invisible behind the dissolved graphite dust (this guarantees a decent density). The liquid evaporates and on the grid remain small pieces of graphite and some Si debris.

Advantages:
- High density
- Very uniform particle distribution especially with method b.)
- The density can be varied:
    a.) by changing the number of drops on the sample
    b.) by changing the height of the liquid in the watch glass.
- Large amounts of graphite powder can be produced that way.

Disadvantages:
- Silicon debris in the sample
- Small particles cannot be unambiguously identified as either Si or graphite
- High waste of material in the lower part of the jar
- The dropper can stir up the liquid when it is immersed.
- Problems to pick up the grid from the watch glass with tweezers.

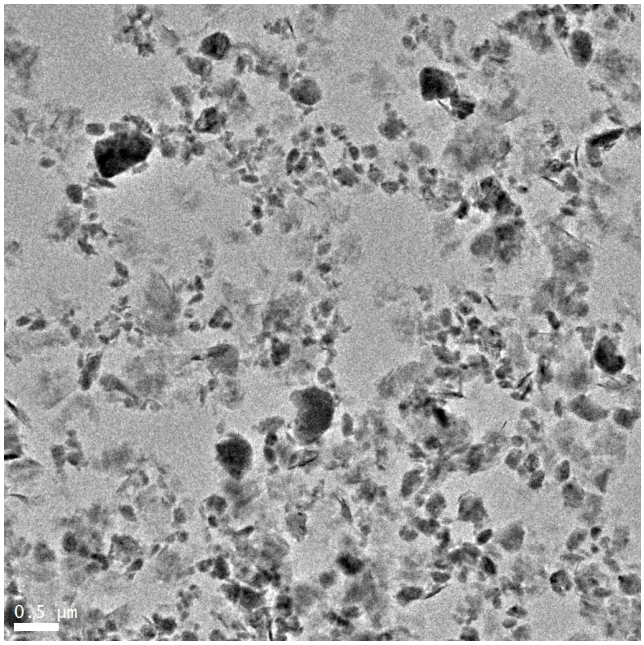


Fig. 9: High density of particles could be reached with method 4. The darker spots are most probably Si debris.

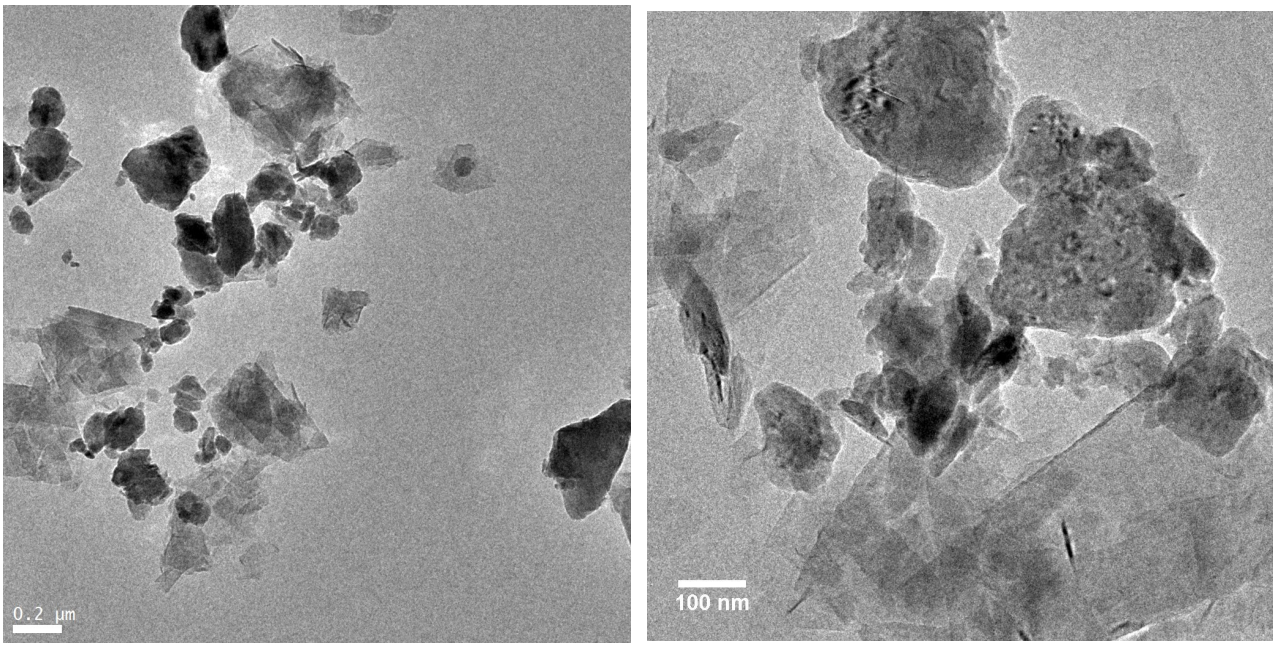


Fig. 10a,b: Two different particle types can be recognized. The rounded, dark things are Si. The flat, layered particles are graphite.

Size determination

The size was determined in two different ways:

1.) <u>TEM size determination</u>

Measurements were performed with TEM, searching for pieces, imaging them, and measuring the diameter for statistical analysis.

Challenges while measuring:
- Small particles (diameter < 10 nm) are not measurable in TEM if they are thin (they give too small contrast)
- Particles around 10 - 100 nm are measurable, but it is hard to prove whether they are graphite or not.
- Very small droplets of the solvent remain on the grid. They appear similar to the graphite but sublimate at higher magnifications due to the heating effects of the electron beam.
- Other debris

The TEM pictures were imported into the program ImageJ (http://rsb.info.nih.gov/ij/), the particles were selected one by one by hand, the size was determined by the program and written into a list.

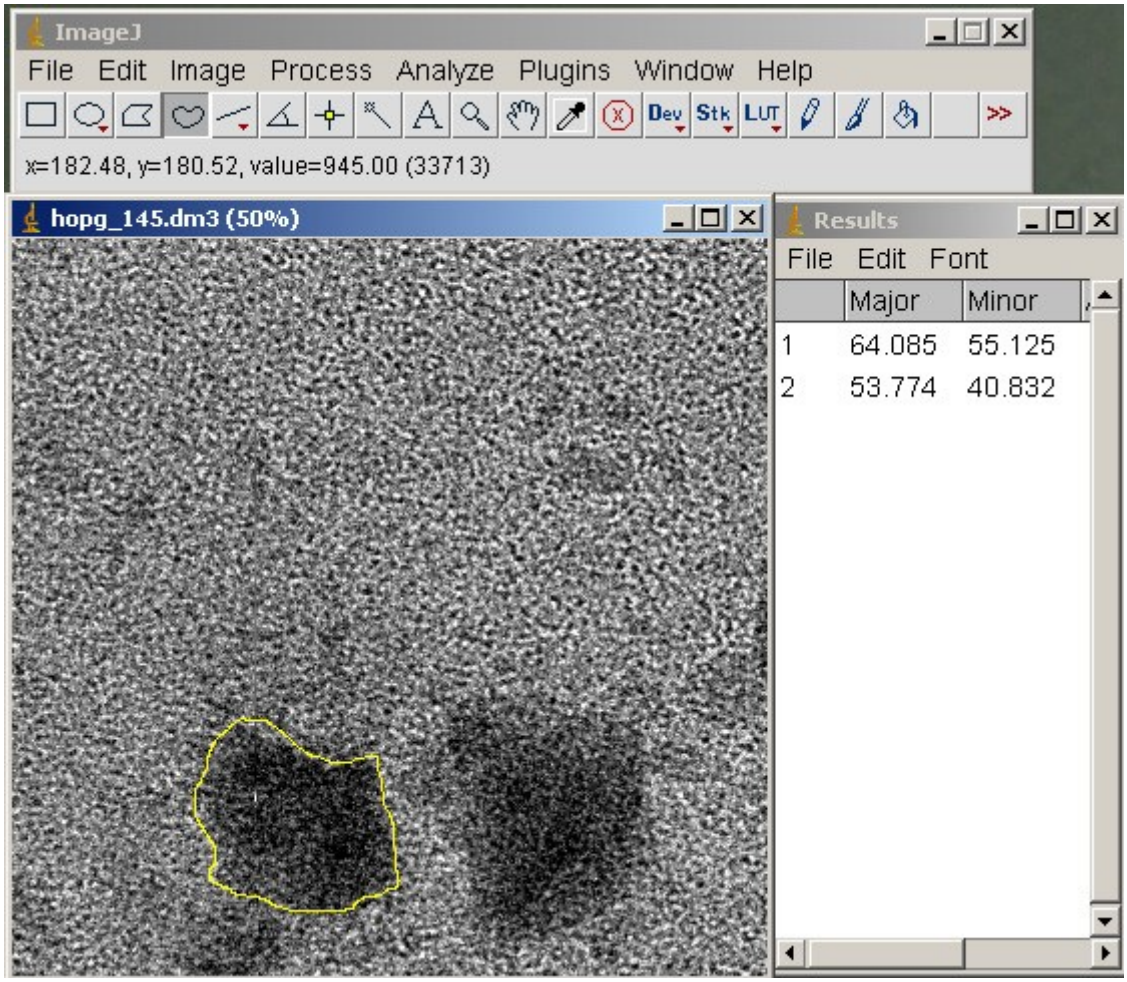


Fig. 11: Determination of particle size with ImageJ. Yellow: currently selected particle.

2.) <u>Powder diffraction size determination</u>

The graphite-silicon powder was put into a powder diffractometer and measured.
Apart from the size and structure of the unit cell, also the crystallite size could be determined.
The measurement took 30 min.

Challenges while measuring:
- Texturing effect

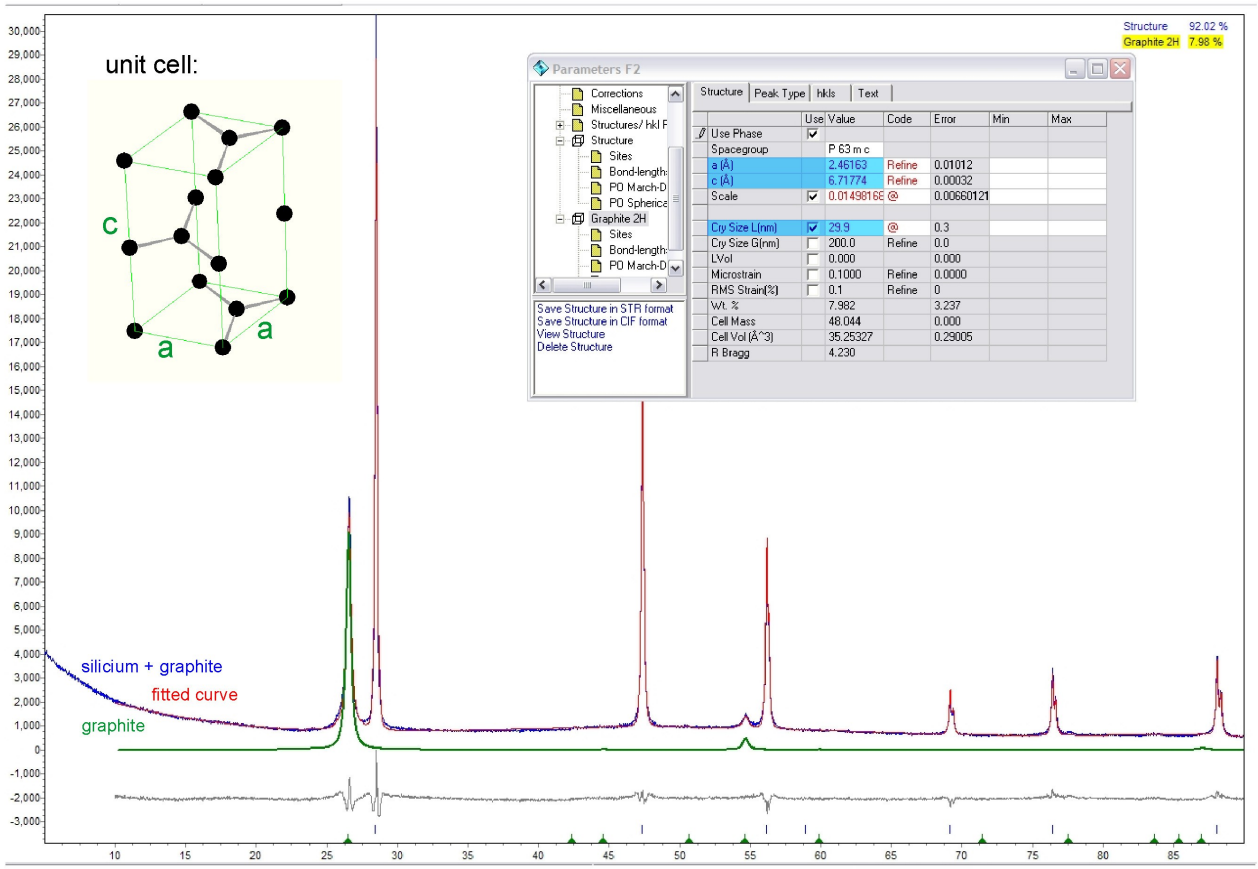


Fig.12: Fitting a curve to the powder diffraction measurement result.

Results

1.) TEM results

Remarks:
- Measurement 2b was performed with the F20 TEM, while the measurements 4a and 4b were performed with the G20 TEM. With the F20, better magnifications could be reached, but that microscope was not available for the measurements 4a and 4b.
- The percentages relate to all counted particles. As the particles with low diameters were counted on a smaller area with higher magnification than the big particles, their actual total percentage is most probably higher for the small particles.

Method 2b:
(rubbed between glass microscope slides, washed onto the TEM grid)
Total amount of found particles: 74
Diameters:
<20 nm: 29%
20<d<40 nm: 23%
40<d<60 nm: 21%
60<d<80 nm: 12%
80<d<100 nm: 4 %
> 100 nm: rest

Very large particles were not considered (no picture made, no size measured), but were there too.
The particles were very hard to find because of a low particle density.
Solvant debris was confusing the experiment.

Method 4a (mortar and pestle, dropped onto the TEM grid sample) :
Total amount of considered particles: 101
<100 nm : 16% of the particles
100-200 nm: 28 % of the particles
>200 nm: rest
Very good particle density (in the order of 10 particles/µm² throughout the whole sample)

Method 4b (mortar and pestle, put onto the watch glass)
Total amount of considered particles: 136
<100 nm: 24% of the particles
100-200 nm: 23% of the particles
>200 nm: rest
Very good particle density (in the order of 10 particles/µm² throughout the whole sample)

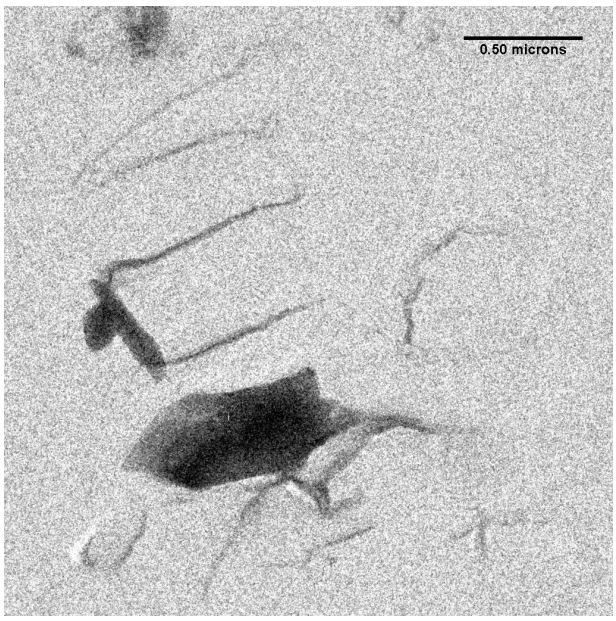
2.) Powder diffraction results

average particle size:
29,9 ± 0,3 nm

Additional information:
crystallographic group: P 63 m c
size of unit cell:
a = b = 0.246 ± 0.001 nm
c = 0.671774 ± 0.000032

Anomalies

On one of the samples from mortar, structures resembling carbon nanotubes were found. It could be a carbon nanotube that formed in the chloroform solution, or a carbon particle which had a very strange shape (this is rather improbable), or some debris of another substance.



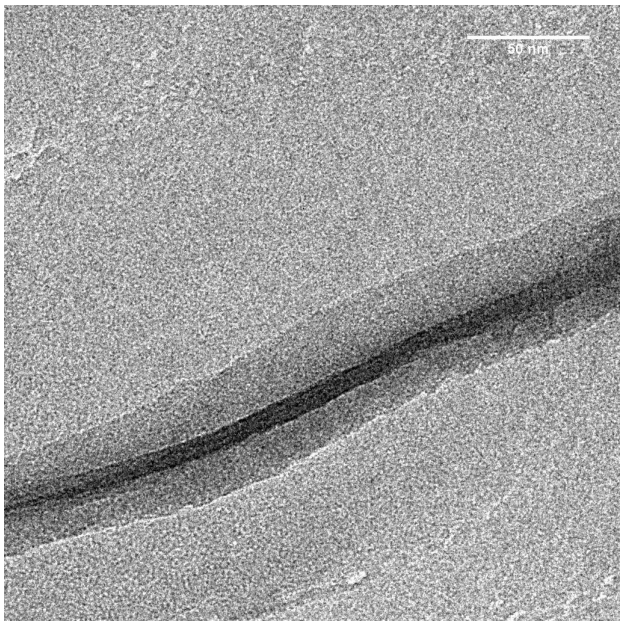
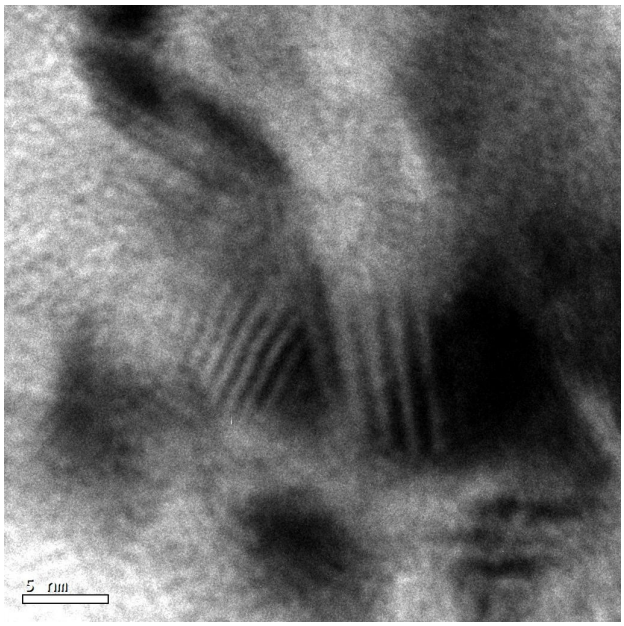
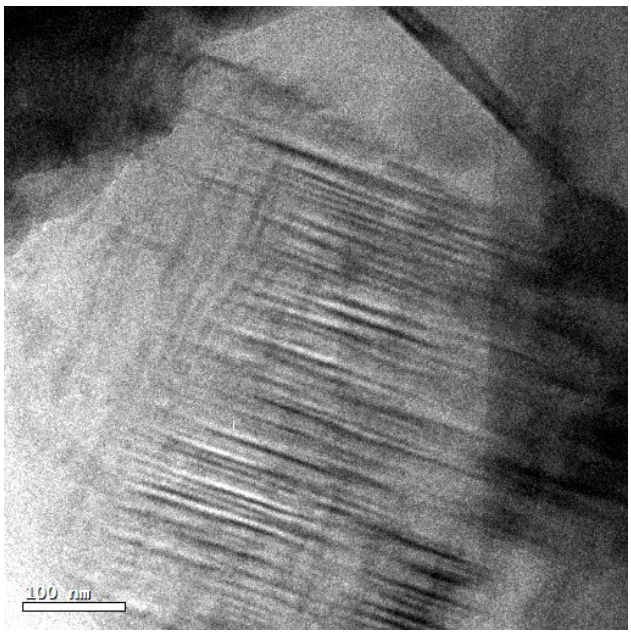


Fig. 13a: Thin elongated objects were found.
Fig. 13b: A closeup shows a structure which resembles a carbon nanotube.

On one of the scotch tape samples and on the sample rubbed between glass microscope slides, fringes were found. They could be stacked graphite layers visible not from top, but from the side. (Fig.14a)

Also on the Scotch tape sample, a "wrinkled" structure was found. (Fig. 14b)





Discussion and Outlook

The method using mortar and pestle turned out to be best suited for the purposes of this study. Further investigations without using Si shall be performed.

A novel method to prepare flawless surfaces shall use these nanoflakes as rafts.

Acknowledgements

I would like to thank my supervisor Ille Gebeshuber for her time and her efforts,
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Structure and electronic properties of graphite nanoparticles

Yon Ju-Nama and Jamie R. Lead
Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications