

Supporting informations

General

2, 3, 5, 6, tetrachloropyrazine was purchased from Chemieliva, and used as received. All other reagents were from TCI and used as received.

Toluene was dried over CaH_2 .

XPS results were acquired using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al $\text{K}\alpha$ (1486.6eV) X-ray source and a charge compensation system. Spectra were collected using a pass energy of 160eV for survey and 40eV for core levels.

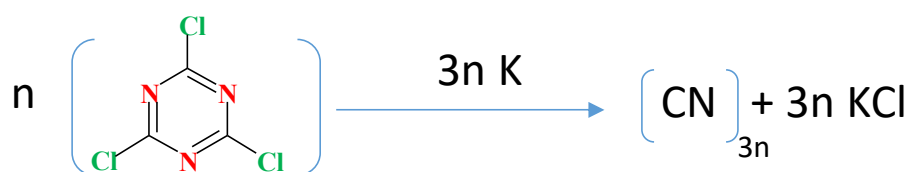
TEM samples were prepared by dropping one or two droplets of a water (or HCl/EtOH) suspension of the flakes onto the TEM grids previously deposited on absorbing paper, to rapidly flow out excess solution.

Most TEM studies were performed using a FEI-CM 20 microscope, operating at 200kV.

The sample shown on **Figure S1K** was studied by transmission electron microscopy (TEM) using a JEOL JEM-1400 microscope operating at 120 kV. The samples were stained using 2% uranyl acetate and deposited onto copper grids covered with formvar film (400 mesh). The excess liquid was blotted off using filter paper, and the grids were dried before observation. Images were acquired using a post-column high-resolution (9 megapixels) high-speed camera (RIO9; Gatan) and processed with Digital Micrograph (Gatan) and ImageJ (open source software, Research Services Branch, National Institute of Mental Health, Bethesda, MD).

The experiments **Figures 21, 27, S2N, and S3I** were realized using a TITAN3 G2 TEM within the MATMECA consortium at CentraleSupélec, partially funded by the French ANR under contract number ANR-10-EQPX-37

S1: Synthesis and characterisations of CN.

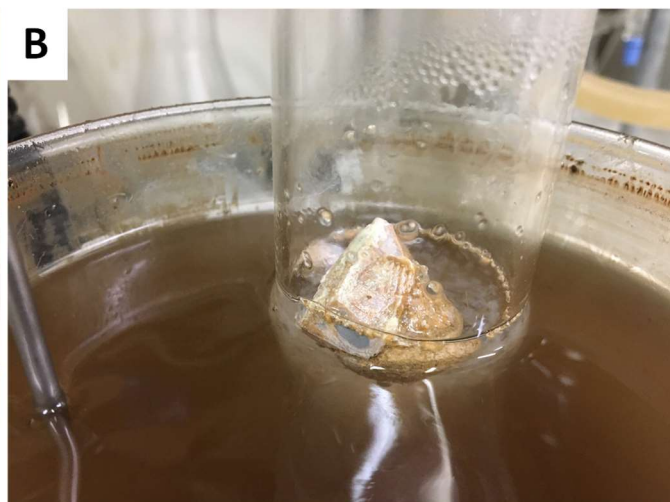
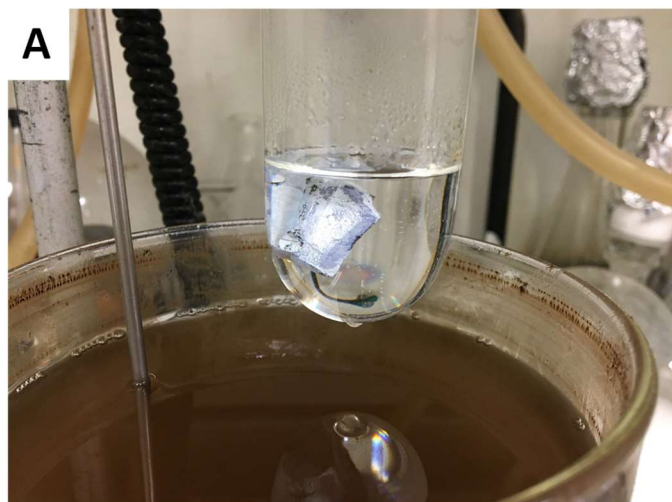


A chunk of metallic potassium (about 1g) is weighted in a closed vial under argon. 20mL of anhydrous benzene or toluene are then added, still under argon. A slight excess (vs. potassium) of cyanuric chloride (about 1.7 g) is then added, and the media is brought to reflux for 24 hrs under argon. Shortly after the beginning of the synthesis, the initially shiny potassium surface (S1A) rapidly gets wrapped by a light brown deposit (S1B). During the course of the reaction, this solid material expands considerably (S1C), the flask beeing nearly completely filled with a brown solid at the end of the synthesis (S1E).

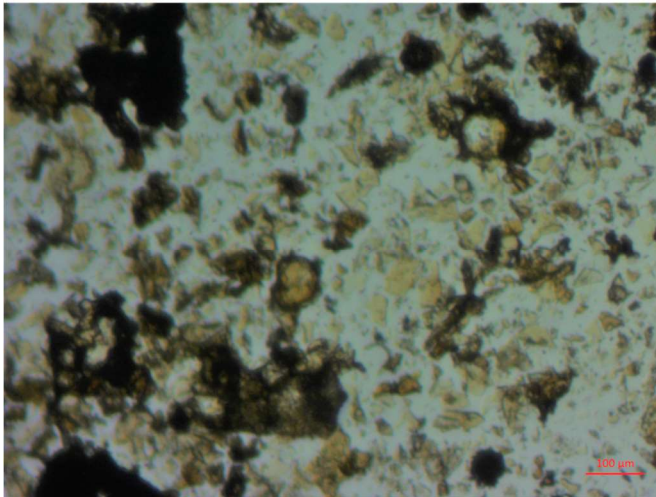
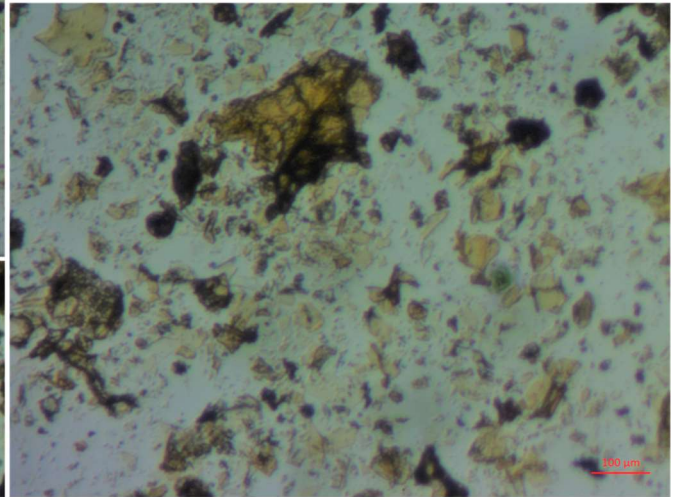
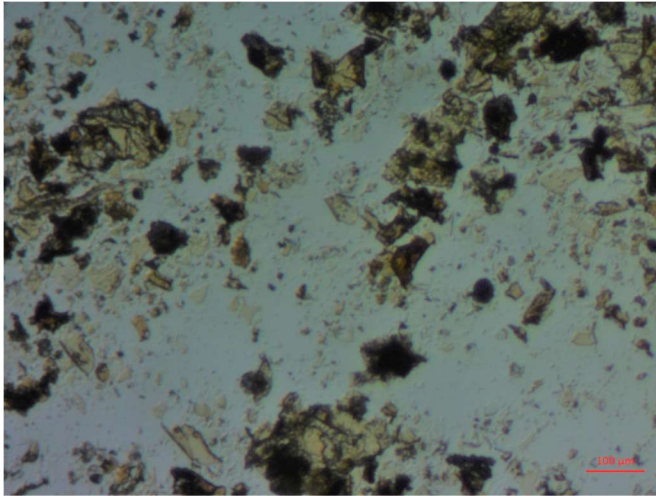
The material is filtered, and the solid is washed with acetone. These organic fractions are combined and evaporated. The resulting dark brown, oily material is weighted to estimate the yield of the reaction.

The complementary solid is then suspended in water, and filtered. This operation is repeated one more time. CN is obtained as a light brown solid.

S1 A→E: evolution of the reaction media during CN synthesis (solvent : benzene).



S1F : optical microscopy study of CN, showing the presence of large amounts of thin, transparent flakes of various sizes.



S1G : optical microscopy study of CN: hollow spheres (arrows) observed along with flakes.

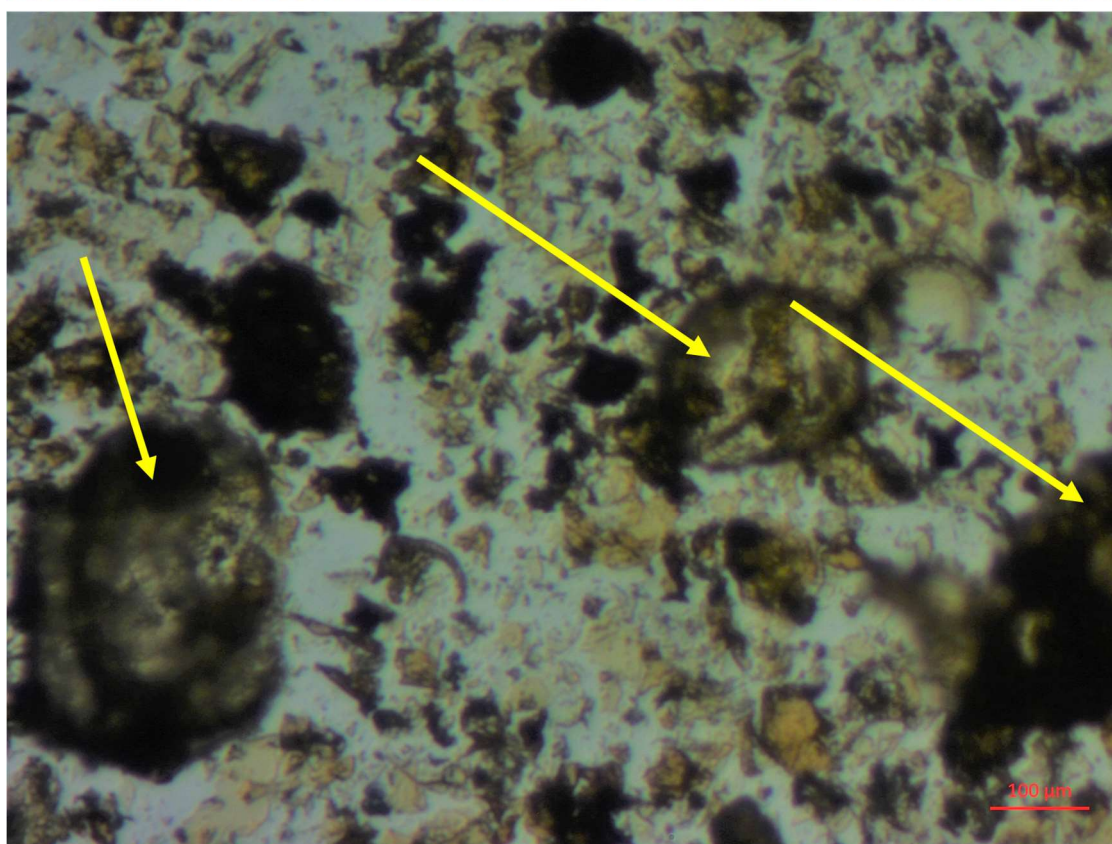
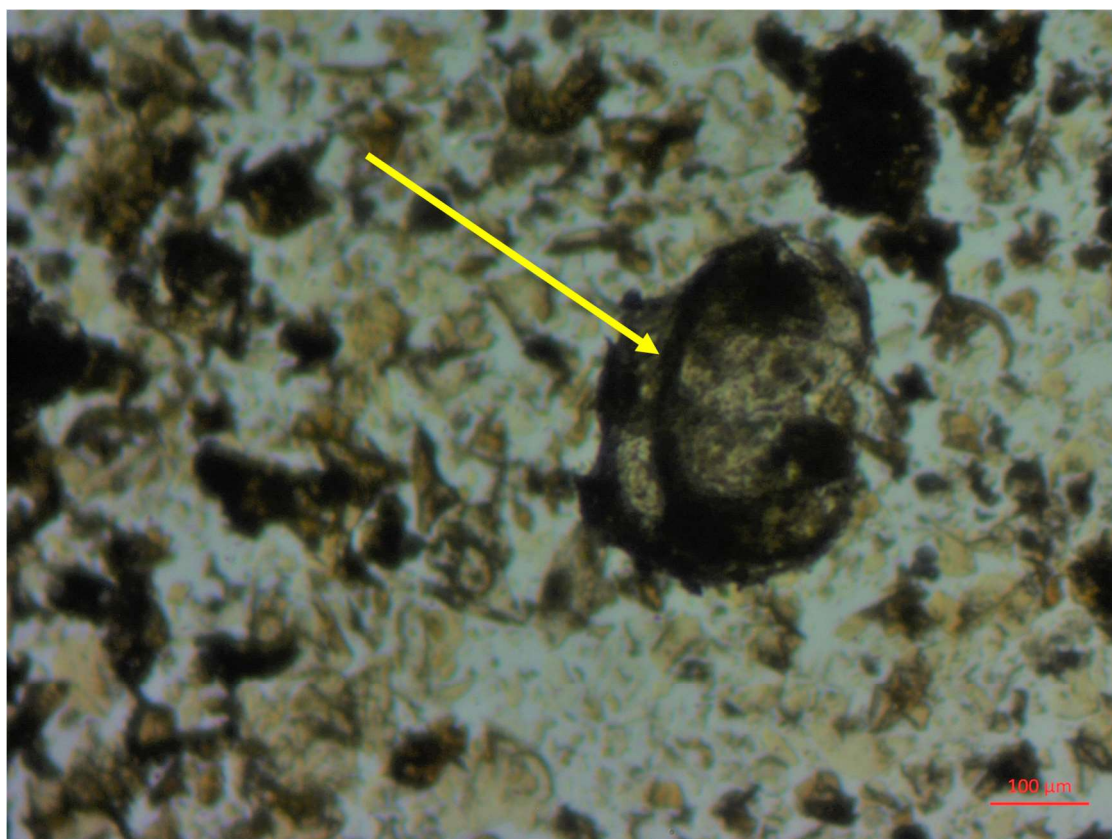


Figure S1H: XPS analysis of crude CN.

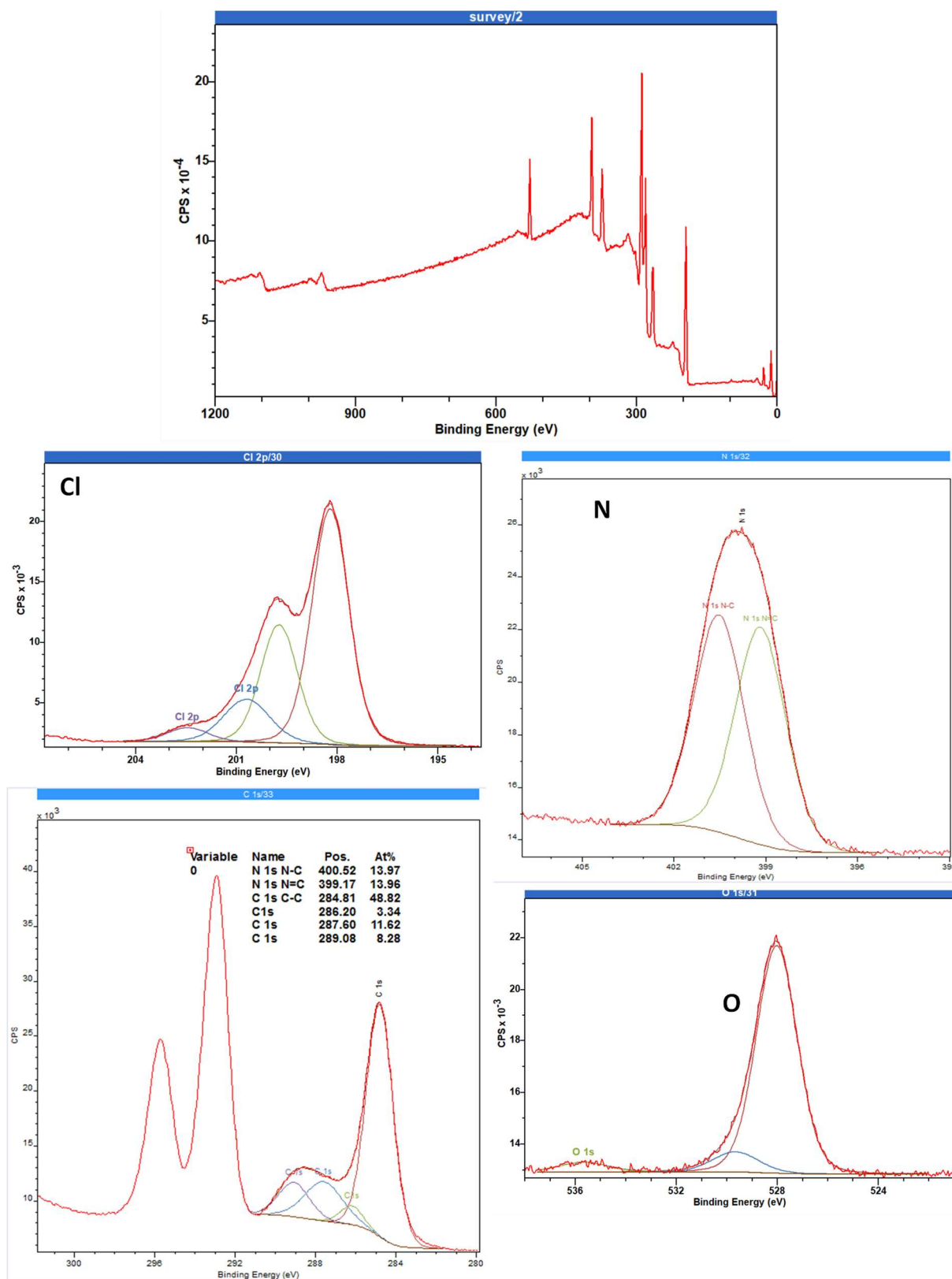


Figure S1i: EDS analysis at the Ca edge

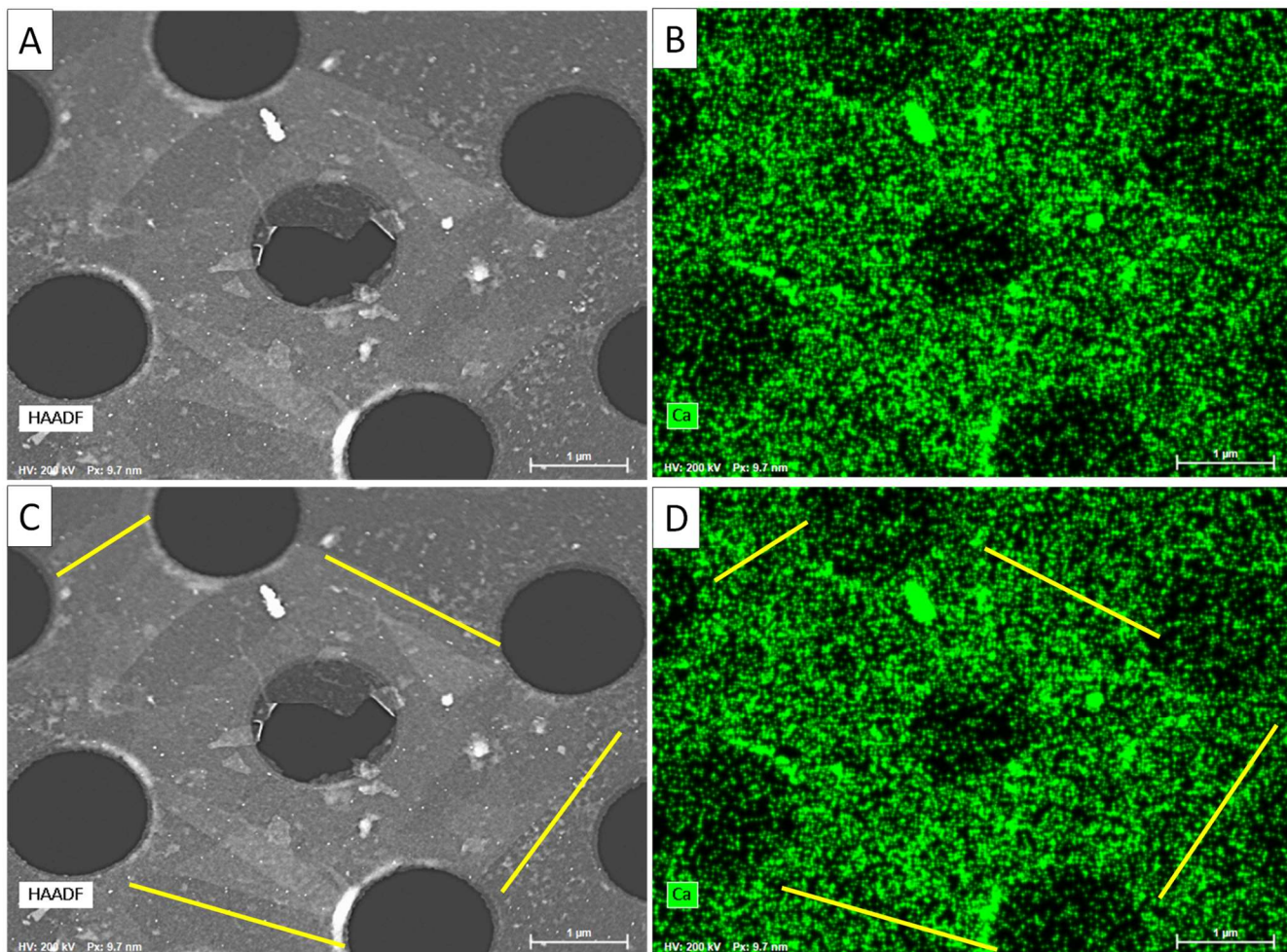


Figure S1j: EDS analysis at the K edge

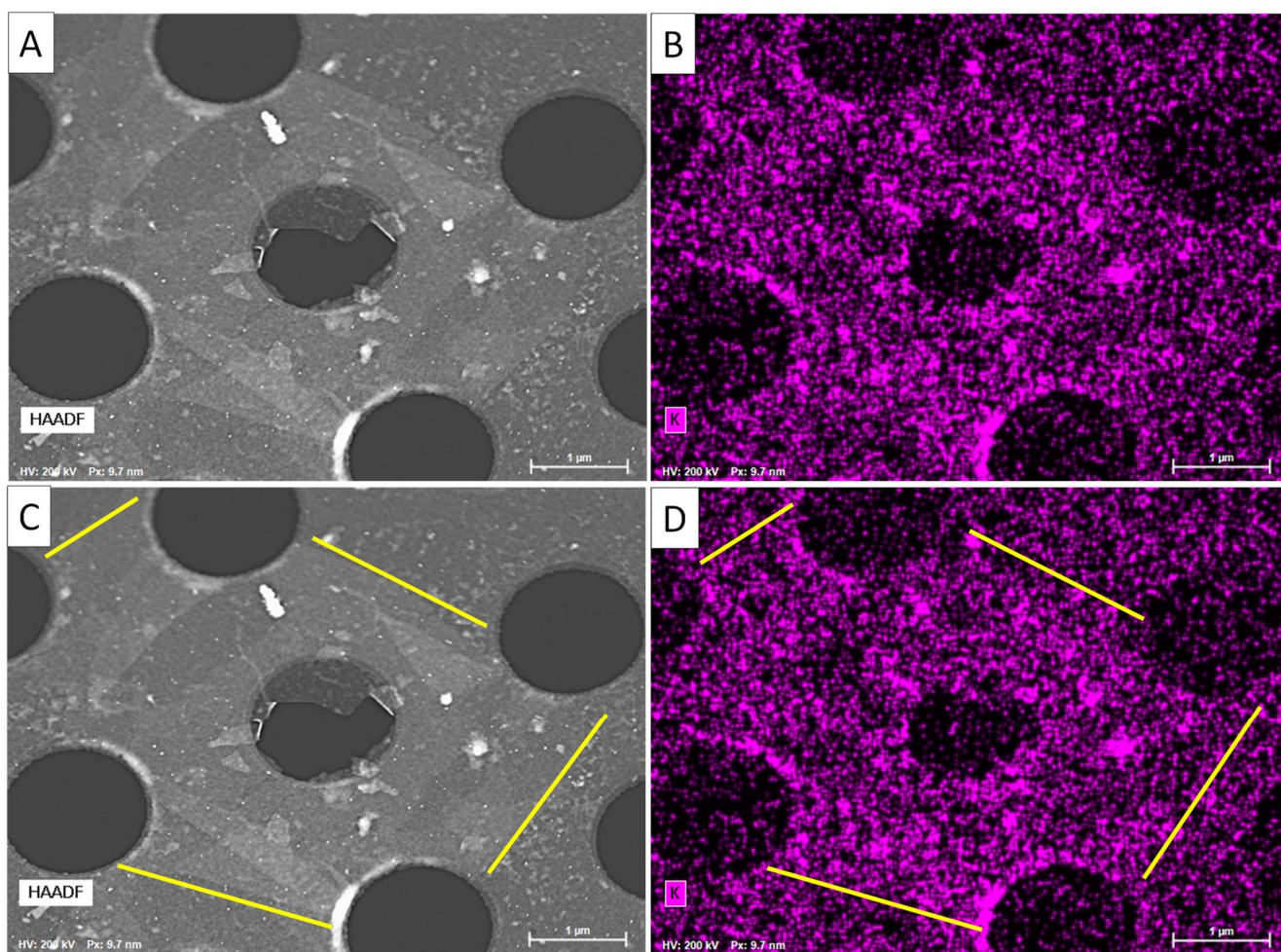
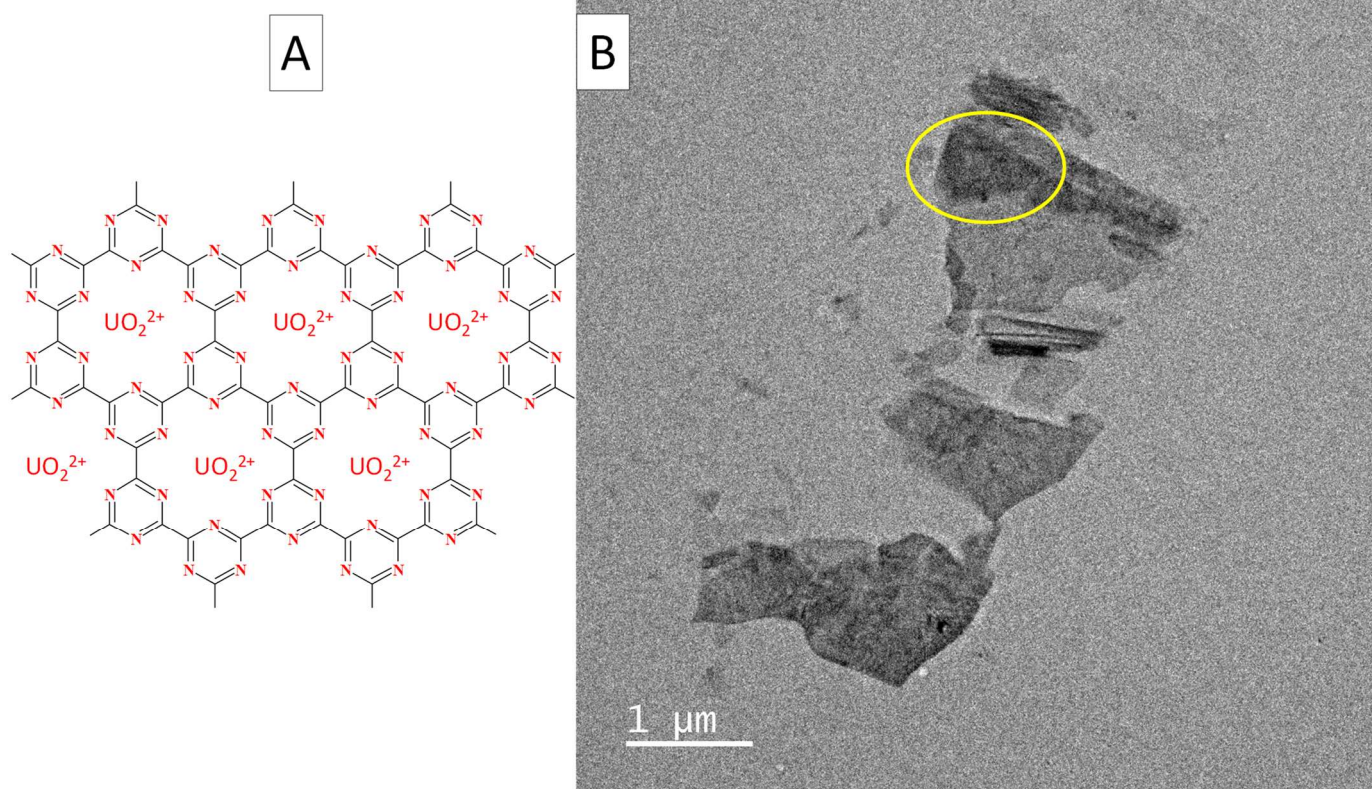
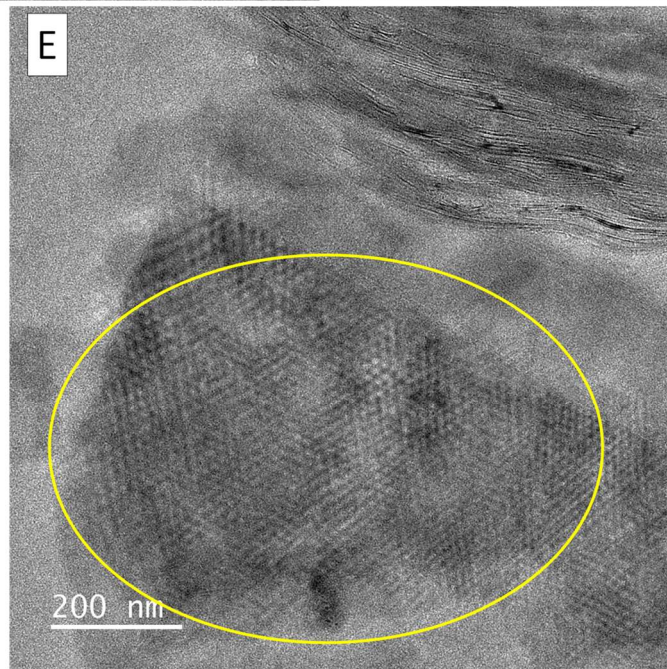
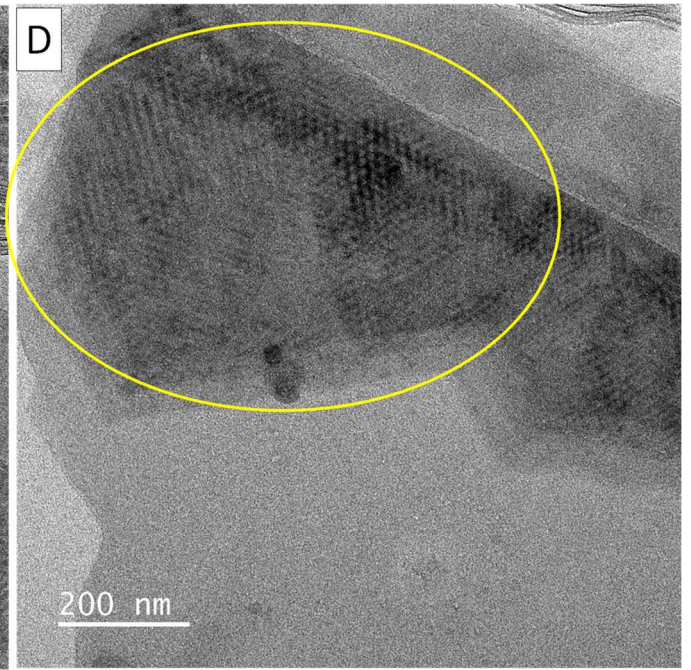
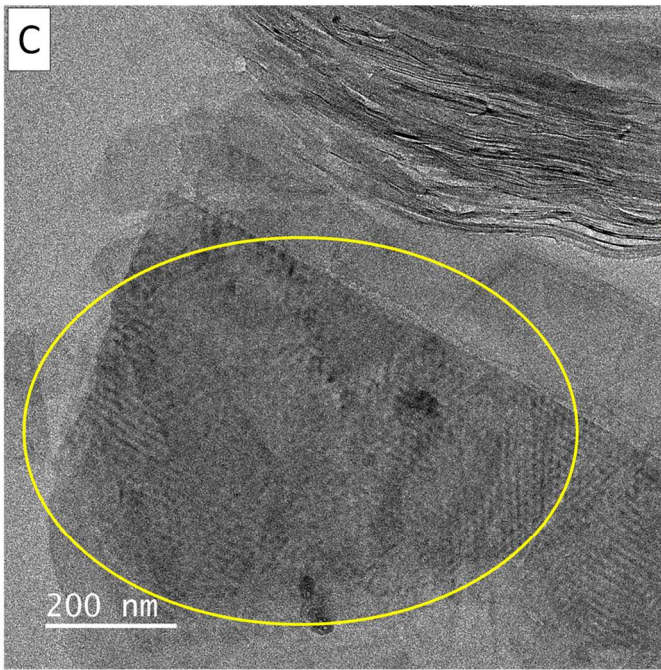
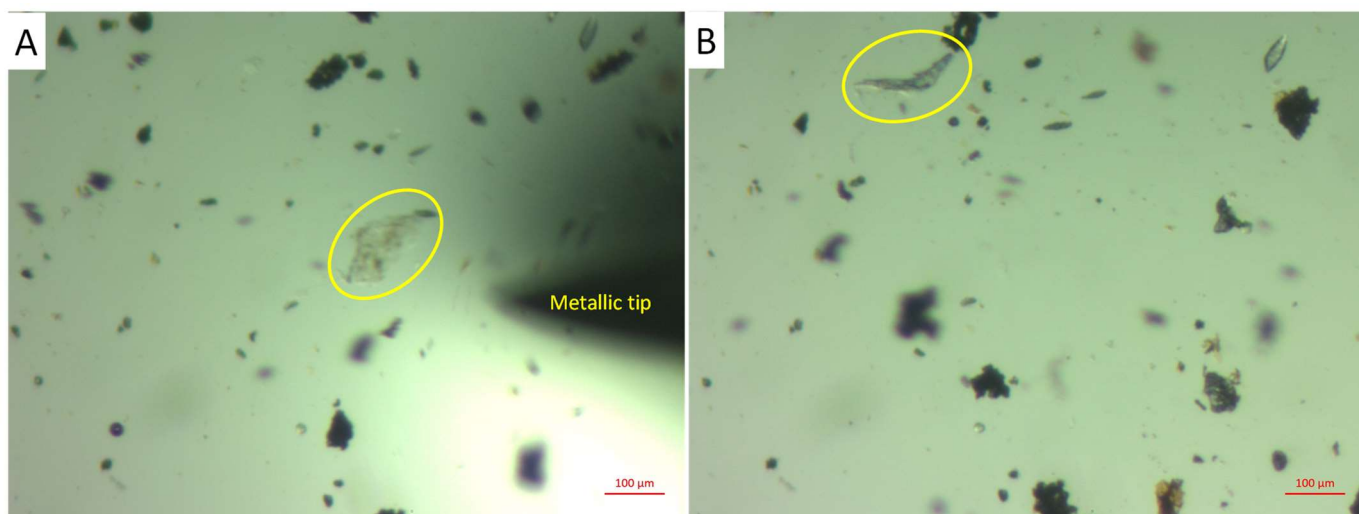


Figure S1K: TEM analysis of an uranyl ions loaded flake (uranyl acetate used, JEOL 1400 microscope operating at 120KV)

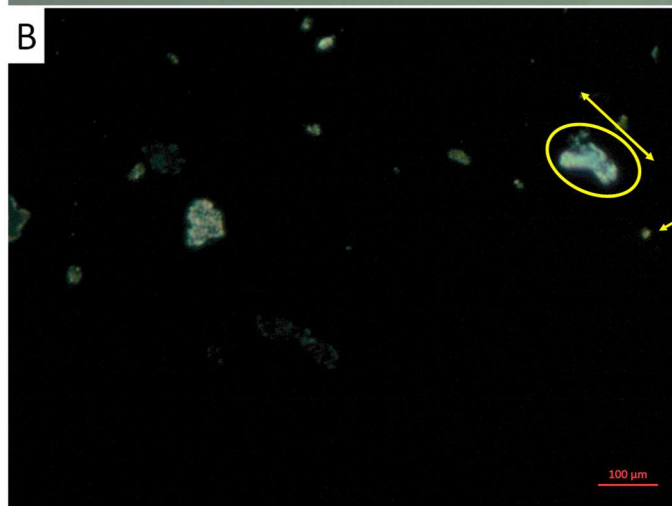
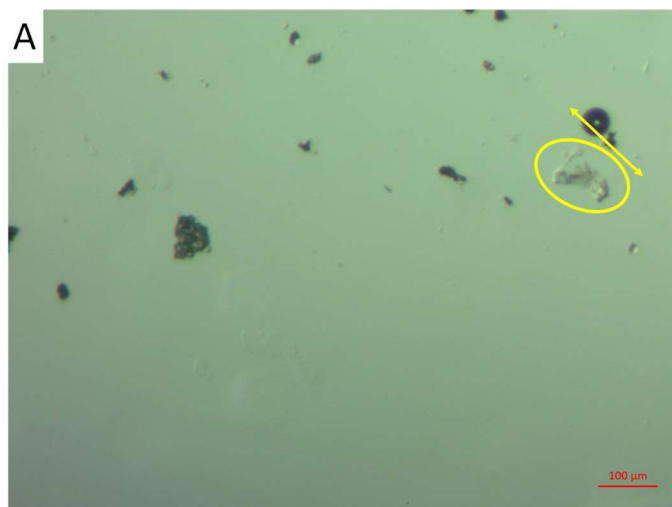




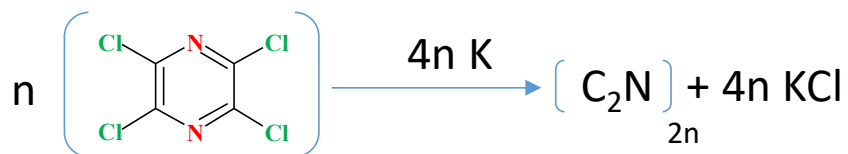
S1L : handling of a single CN flake. The highlighted flake is pushed and tilted using a metallic tip. Note that this flake is the same than the one shown on **Figure 5** in the main text of the article.



S1M: polarized optical microscopy analysis of a CN flake (yellow circle). A) normal light; B) and C) polarised light. The brightness of the flake changes as a function of the angle, evidencing its crystallinity.



S2: synthesis and characterisations of C₂N.



A chunk of metallic potassium (about 1g) is weighted in a closed vial under argon. 20mL of anhydrous benzene or toluene are then added, still under argon. A slight excess (vs. potassium) of tetrachloropyrazine (about 1.5 g) is then added, and the media is brought to reflux for 24 hrs under argon. Shortly after the beginning of the synthesis, the initially shiny potassium surface (S2A) rapidly gets wrapped by a solid black deposit (S2B). During the course of the reaction, the solid material considerably expands (compared with the initial size of the potassium chunk (S2C)), the flask being nearly completely filled with a black solid at the end of the synthesis (S2E).

The supernatant is filtered off, and the black solid is then washed with acetone. The organic solvent fractions are then combined and evaporated. The resulting dark brown oil is then weighted to assess the yield of the reaction.

The complementary black solid is then washed twice with deionised water, to remove soluble by-product (such as KCl).

Figure S2A→E: evolution of the reaction media during the synthesis of C_2N (solvent: benzene).

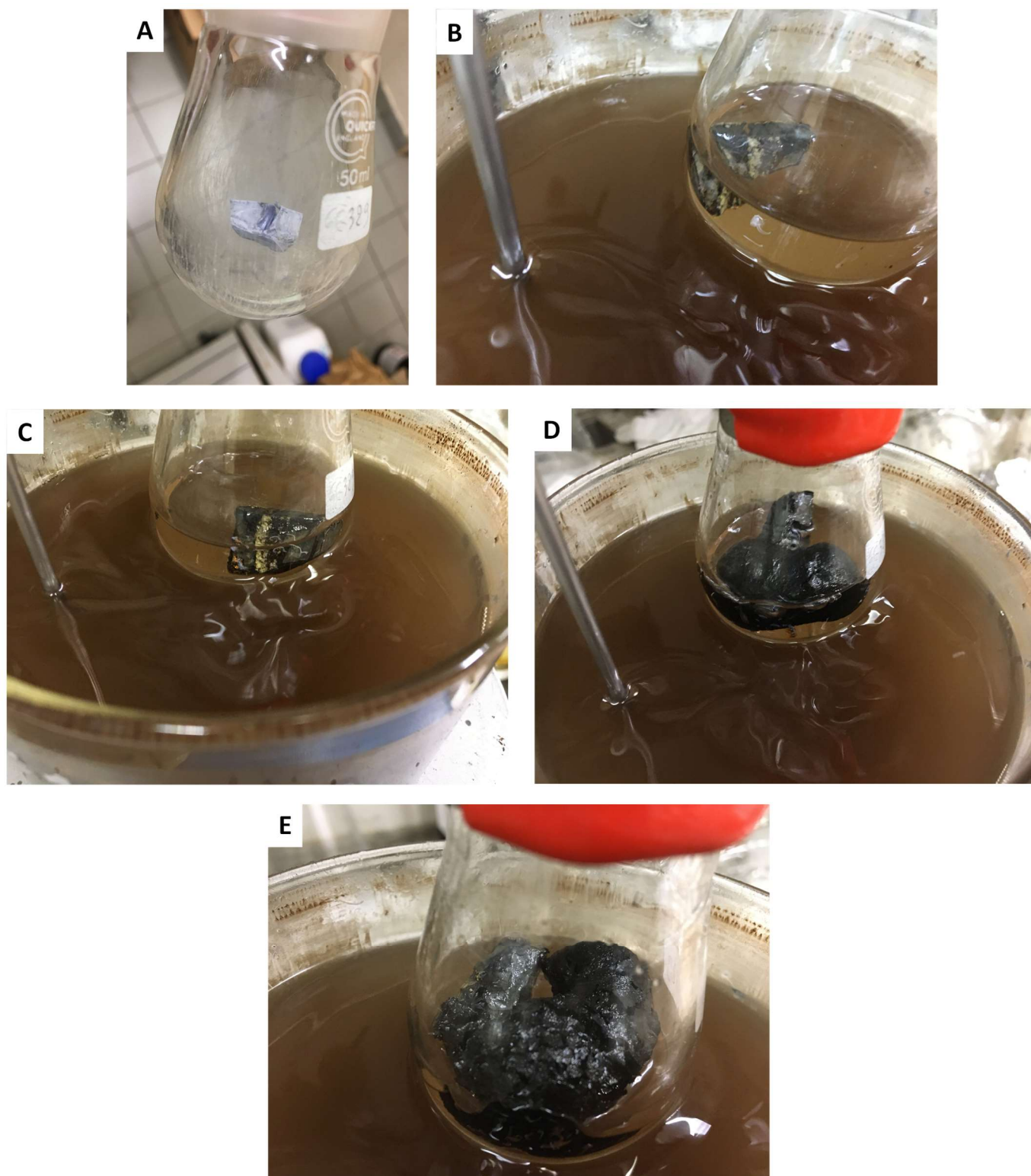
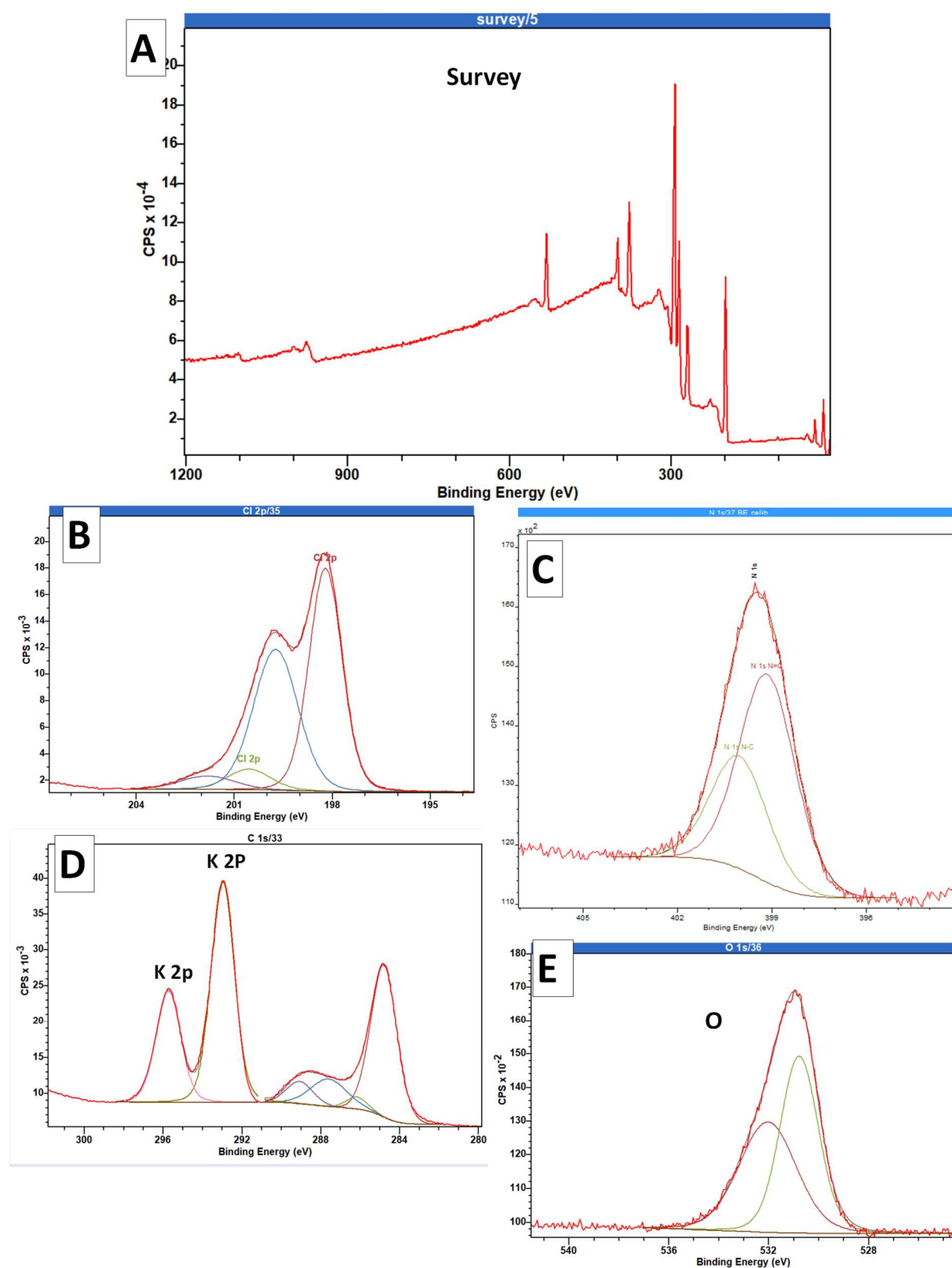


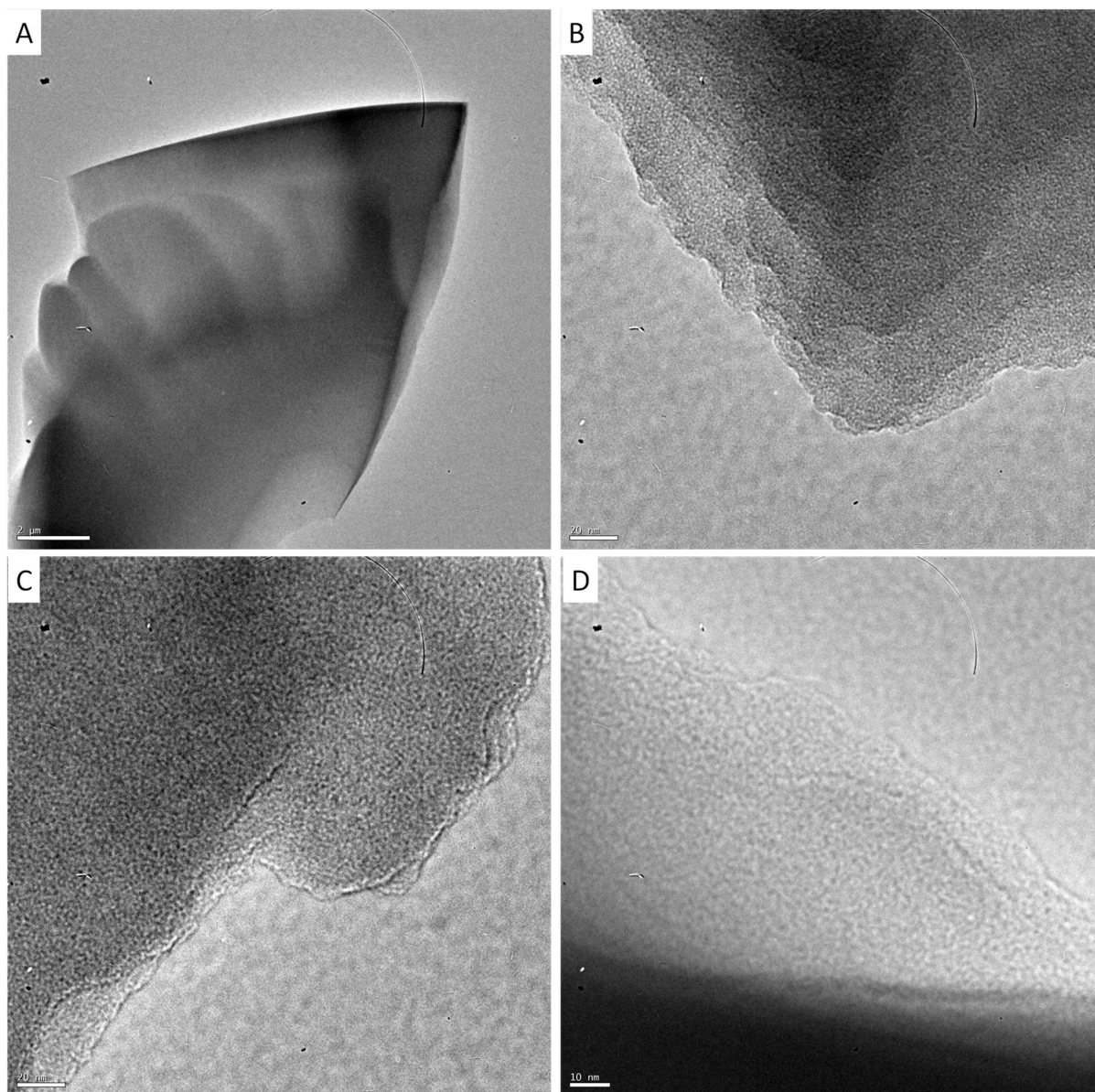
Figure S2F : XPS analysis of crude C₂N carbon nitride.



S2G: optimisation of the solvents used for dispersing the C₂N carbon nitride.

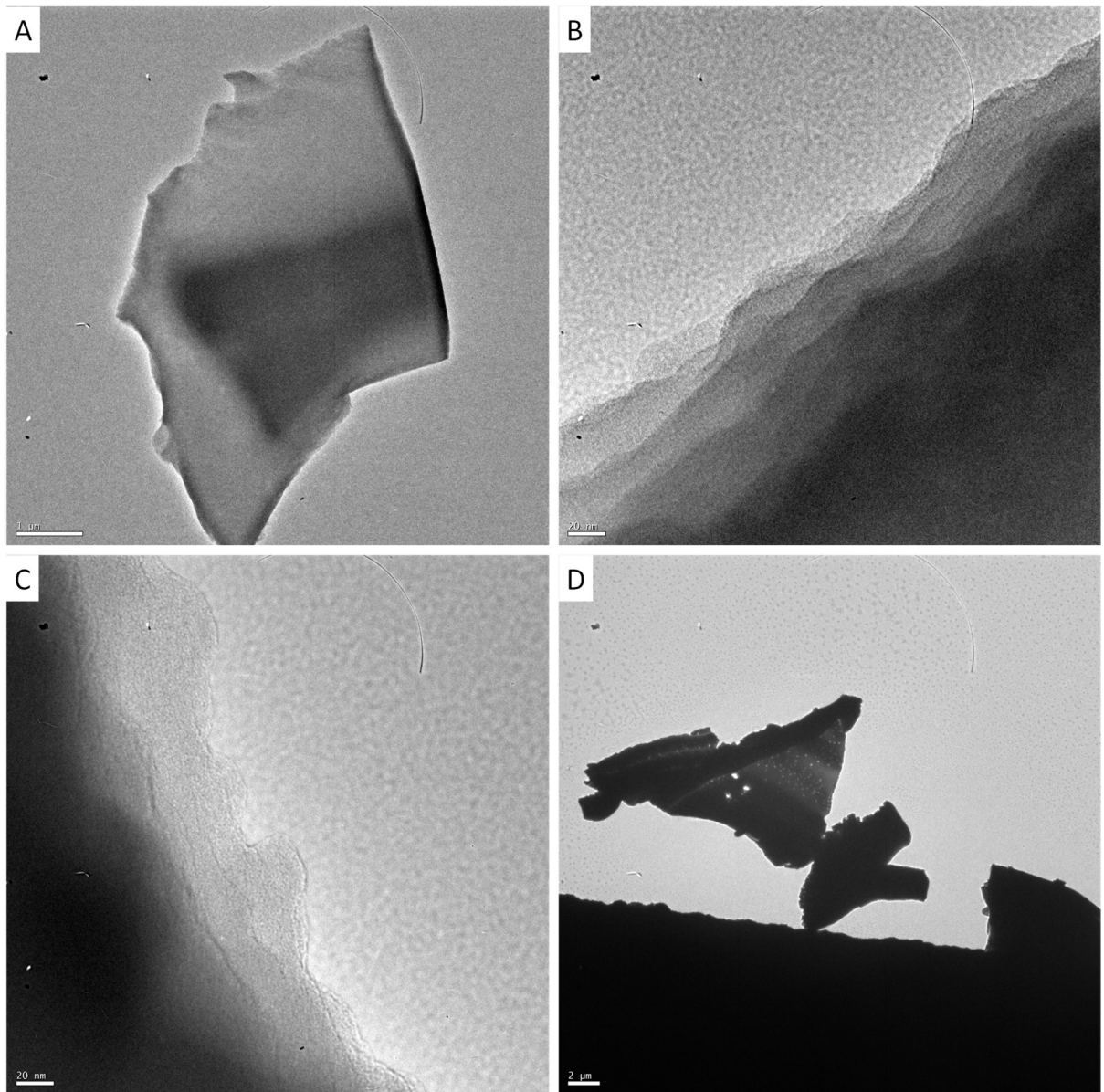
a) acetone dispersion.

Large, smooth flakes are observed. They appear as rather thin, being quite transparent to the e-beam.



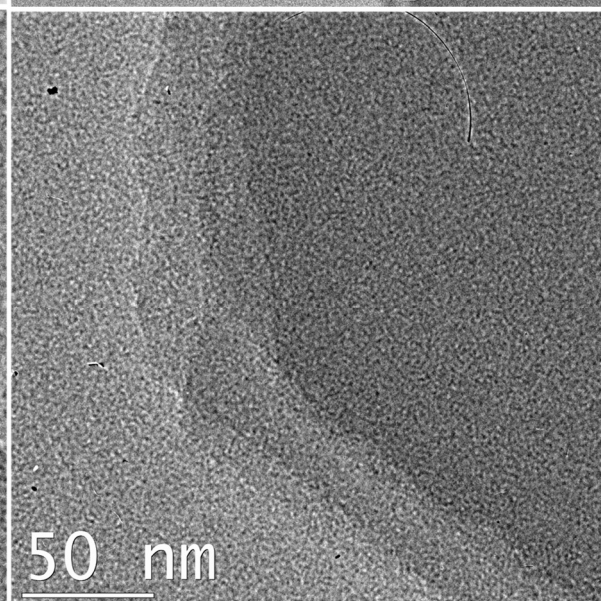
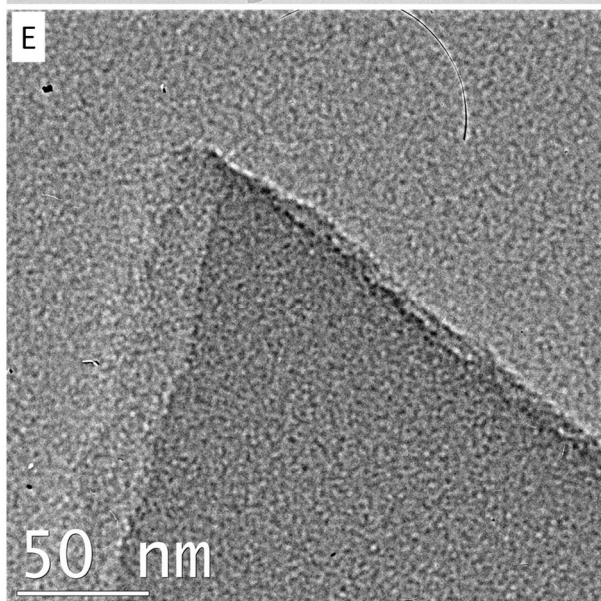
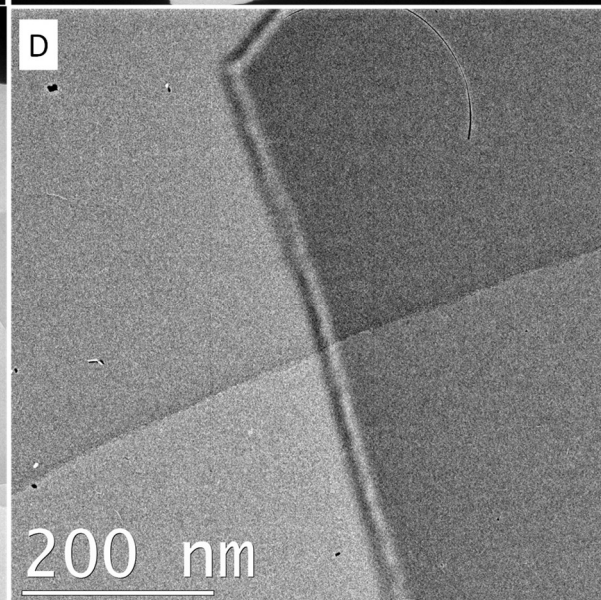
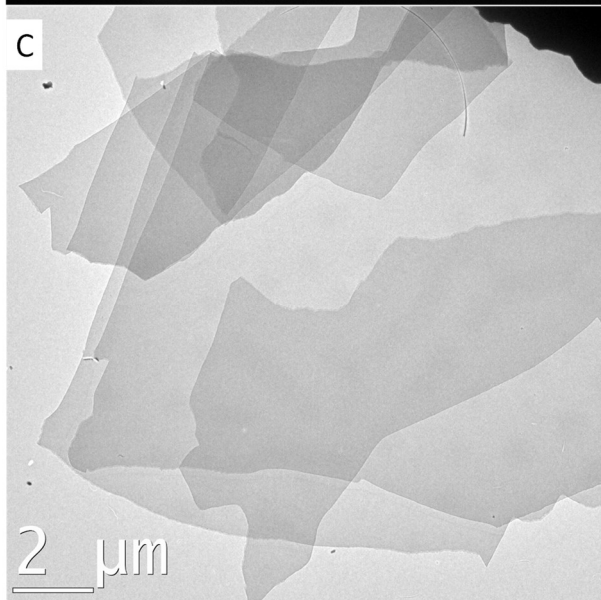
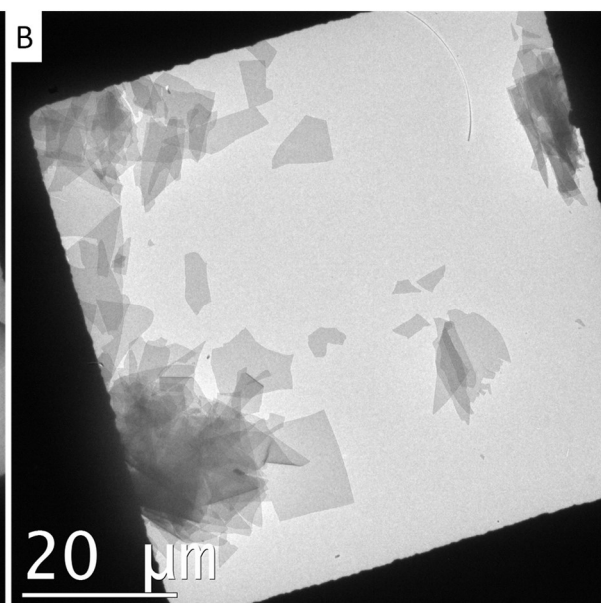
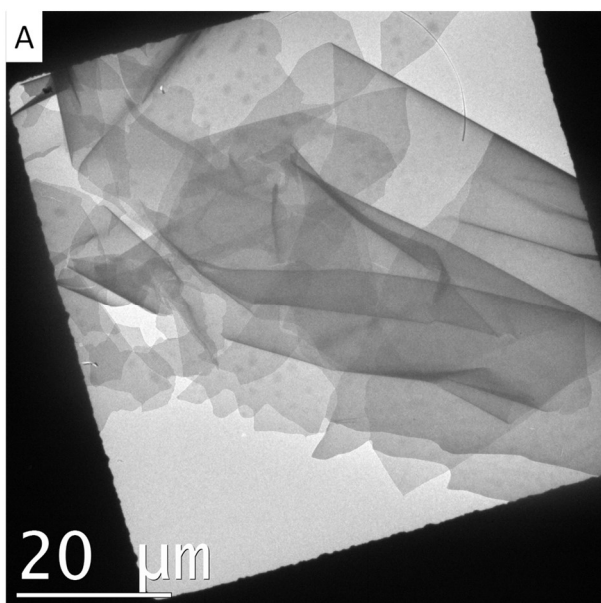
A detailed observation of the edges of these flakes shows that the material has a layered structure, in accordance with SEM observations. The layers appear as rather smooth, with few defects.

b) Ethanol dispersion.

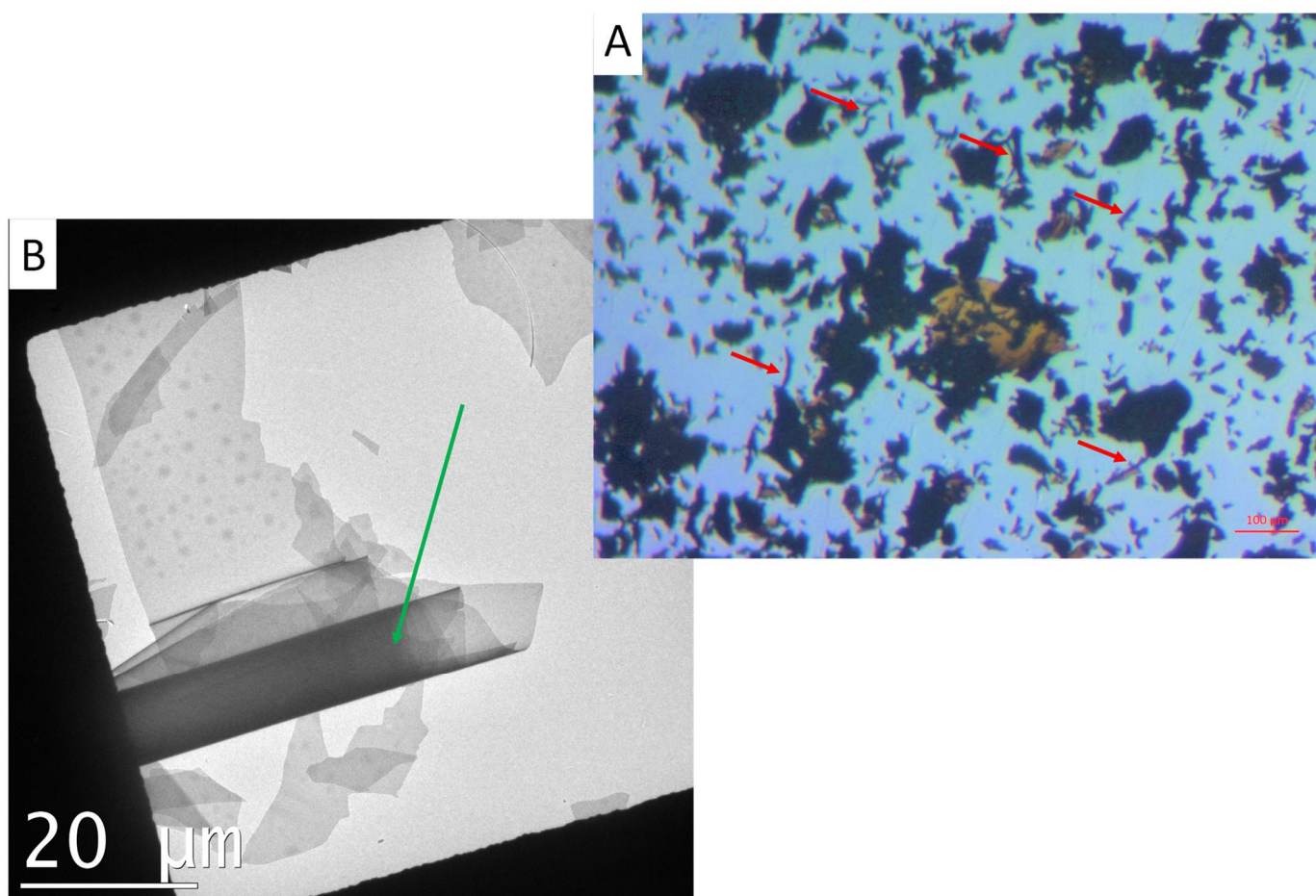


Once again, TEM shows the presence of layered, large flakes of various thicknesses.

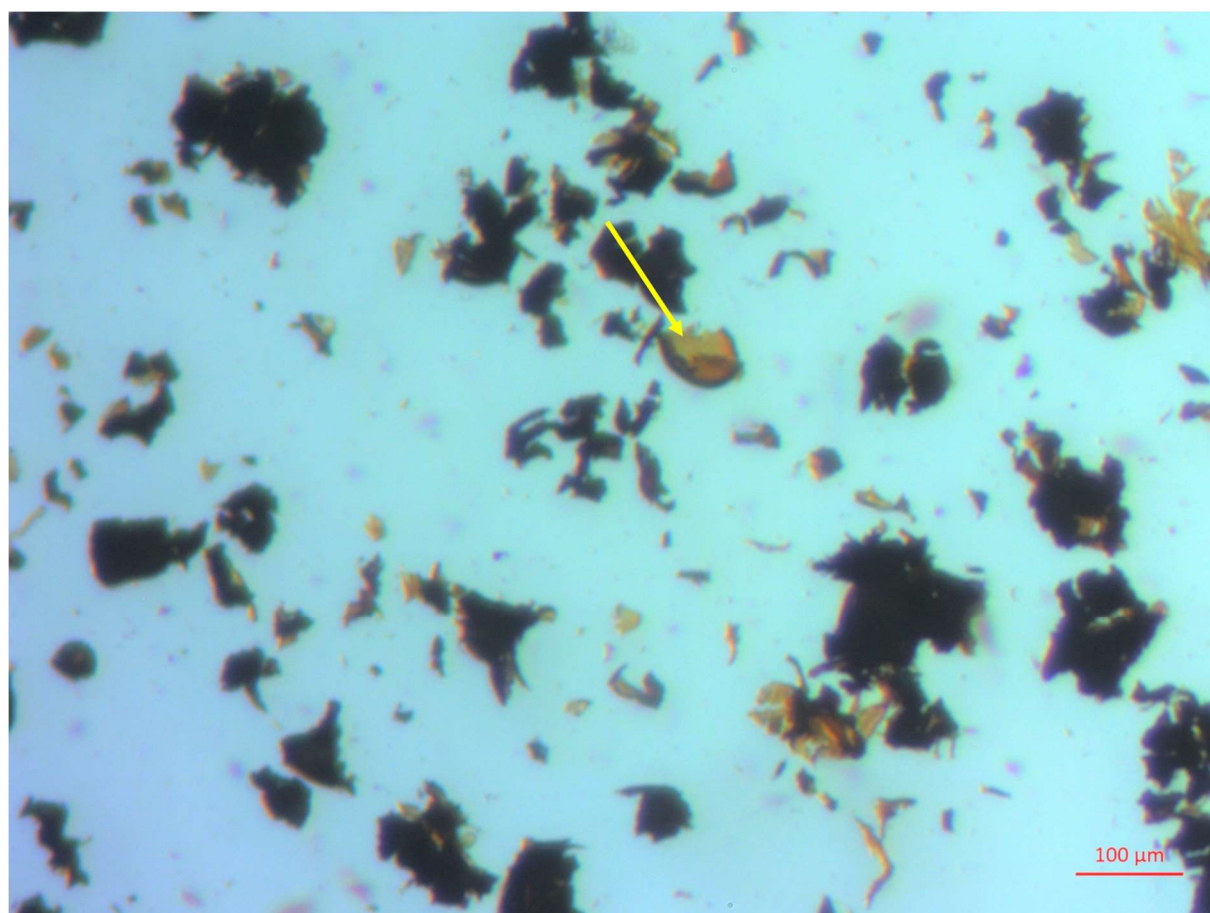
c) 1M HCl dispersion



S2H: combined optical microscopy (A) and TEM (B) observation of tube-shaped C₂N objects (green/red arrows).



S2i: optical microscopy observation of shell-shaped objects.



S2j: compared optical microscopy appearance of two large and flat flakes (yellow circles) as a function of their thickness: (A) thin and (B) thicker one.

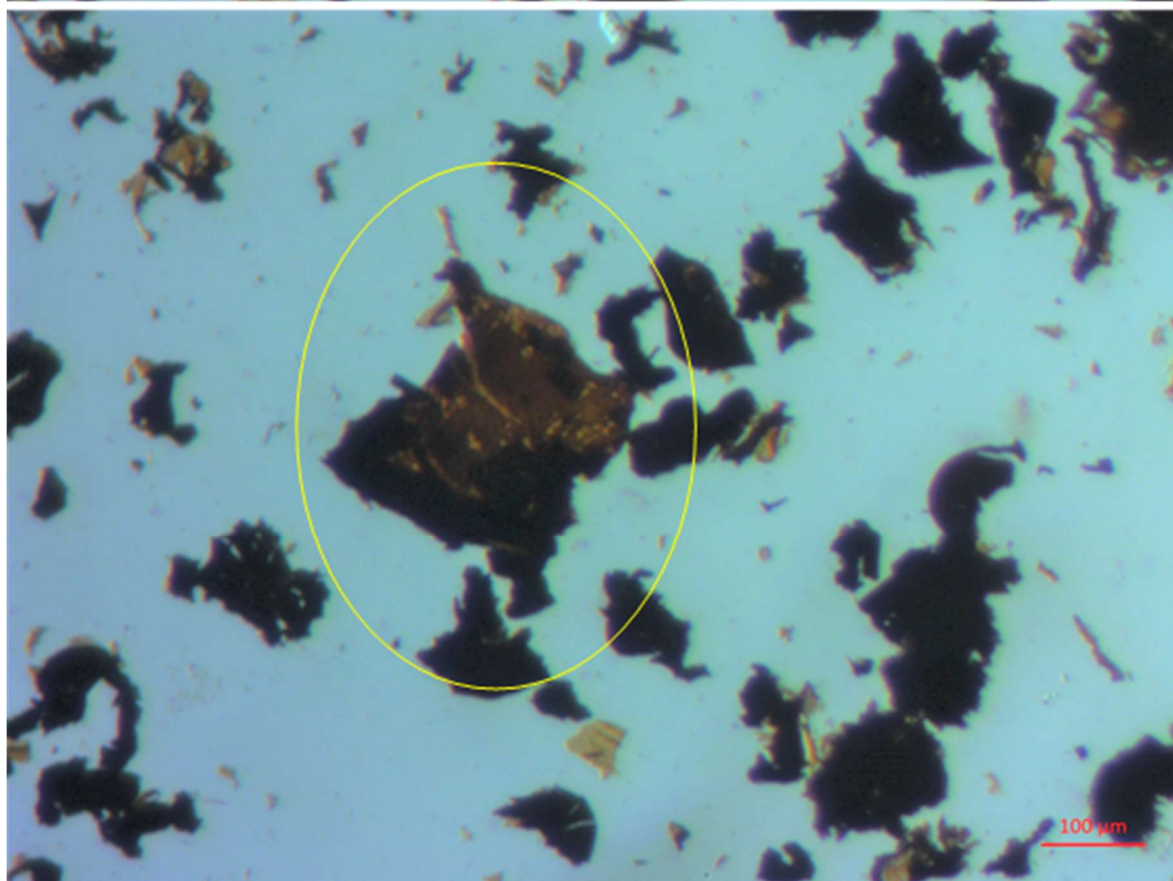
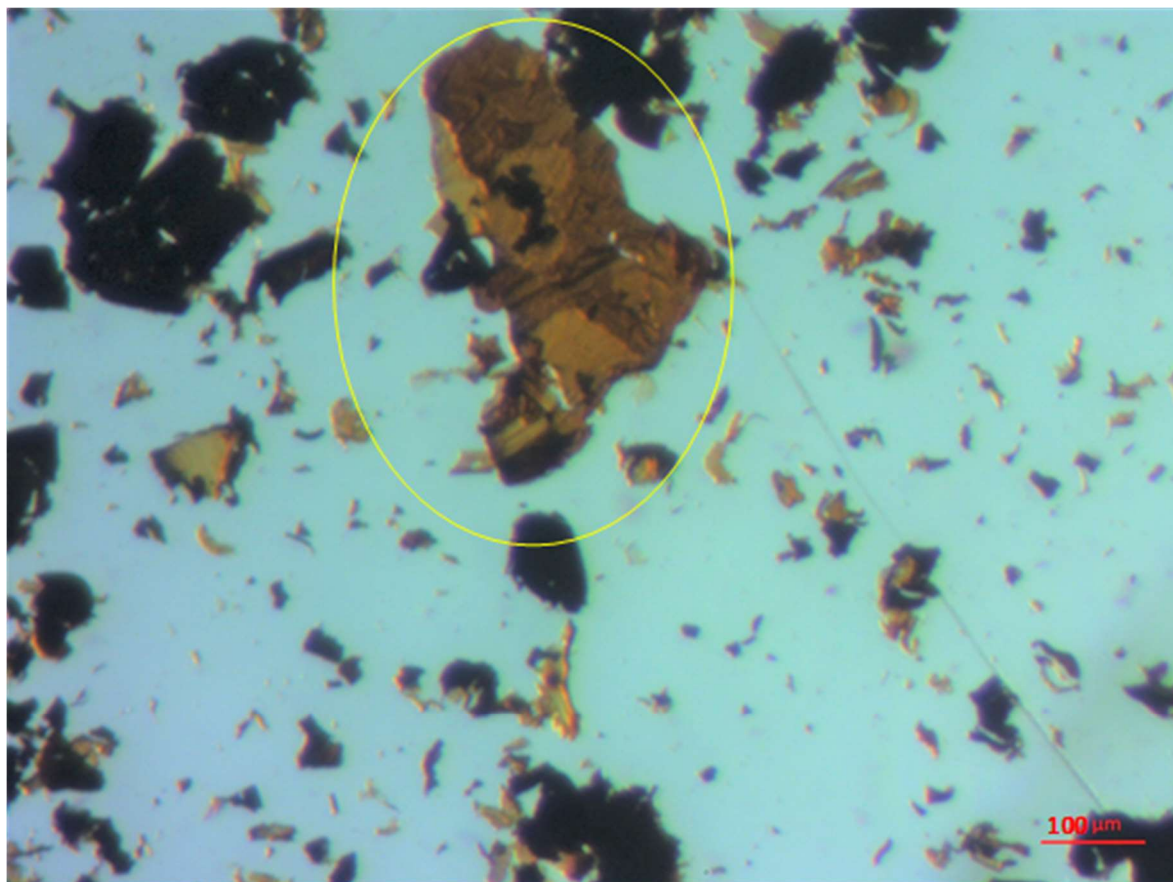


Figure S2K: polarised light study of thin C_2N flakes (yellow circles). A): normal light; B): same flakes under cross polarized light and C) same sample upon rotation. The appearance of the flakes alternatively goes brighter and darker as a function of the angle. D and E: foldings inside a single crystal flake induces the appearance of different crystalline orientations, resulting in different contrasts.

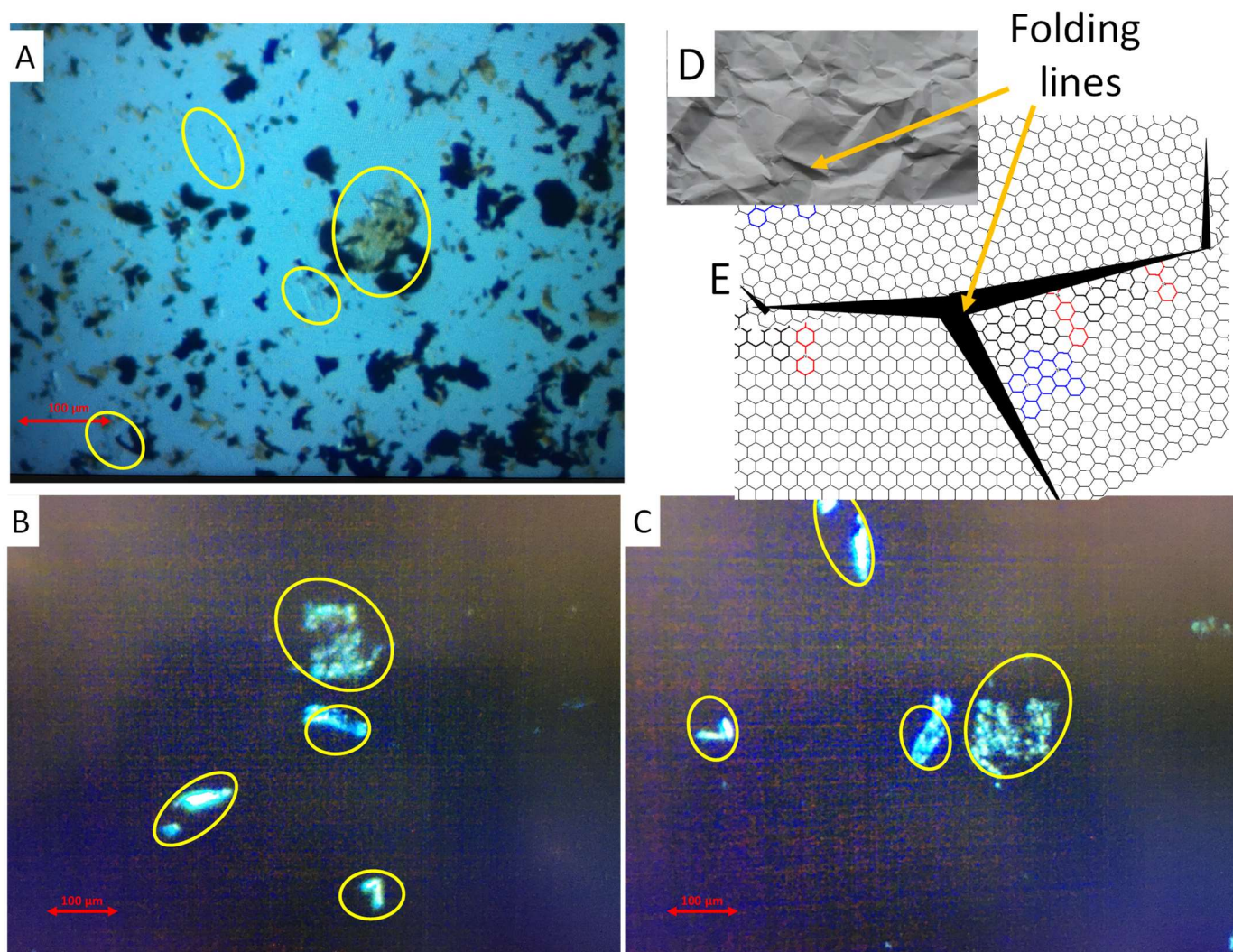


Figure S2L: polarised light study of a thin, folded C_2N flake (yellow circle). A): normal light; B): the same flake under cross polarized light and C) same sample upon rotation. The appearance of the flake alternatively goes brighter and darker as a function of the angle. D) and E), a simple model explaining the occurrence of different domains inside a single flake.

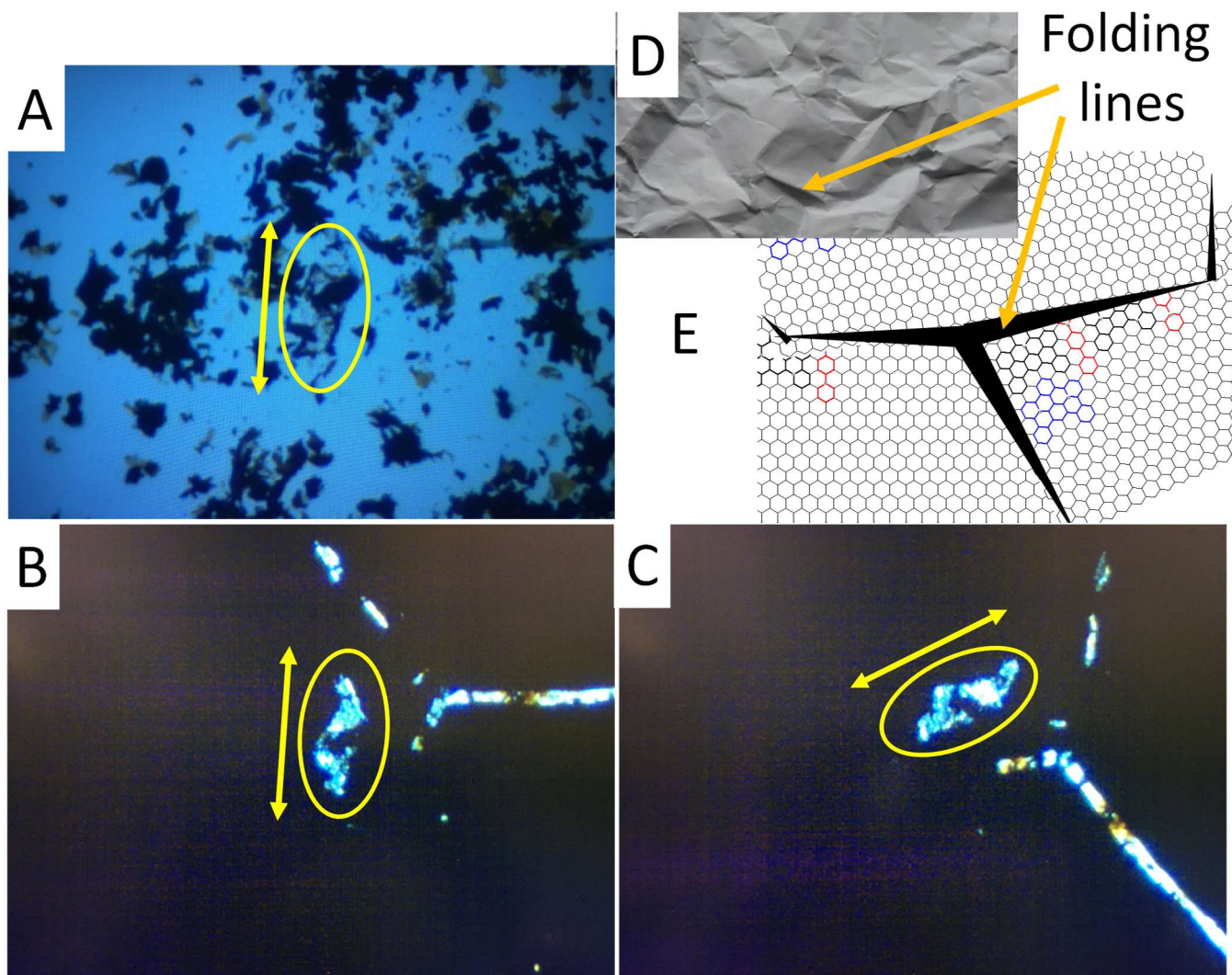
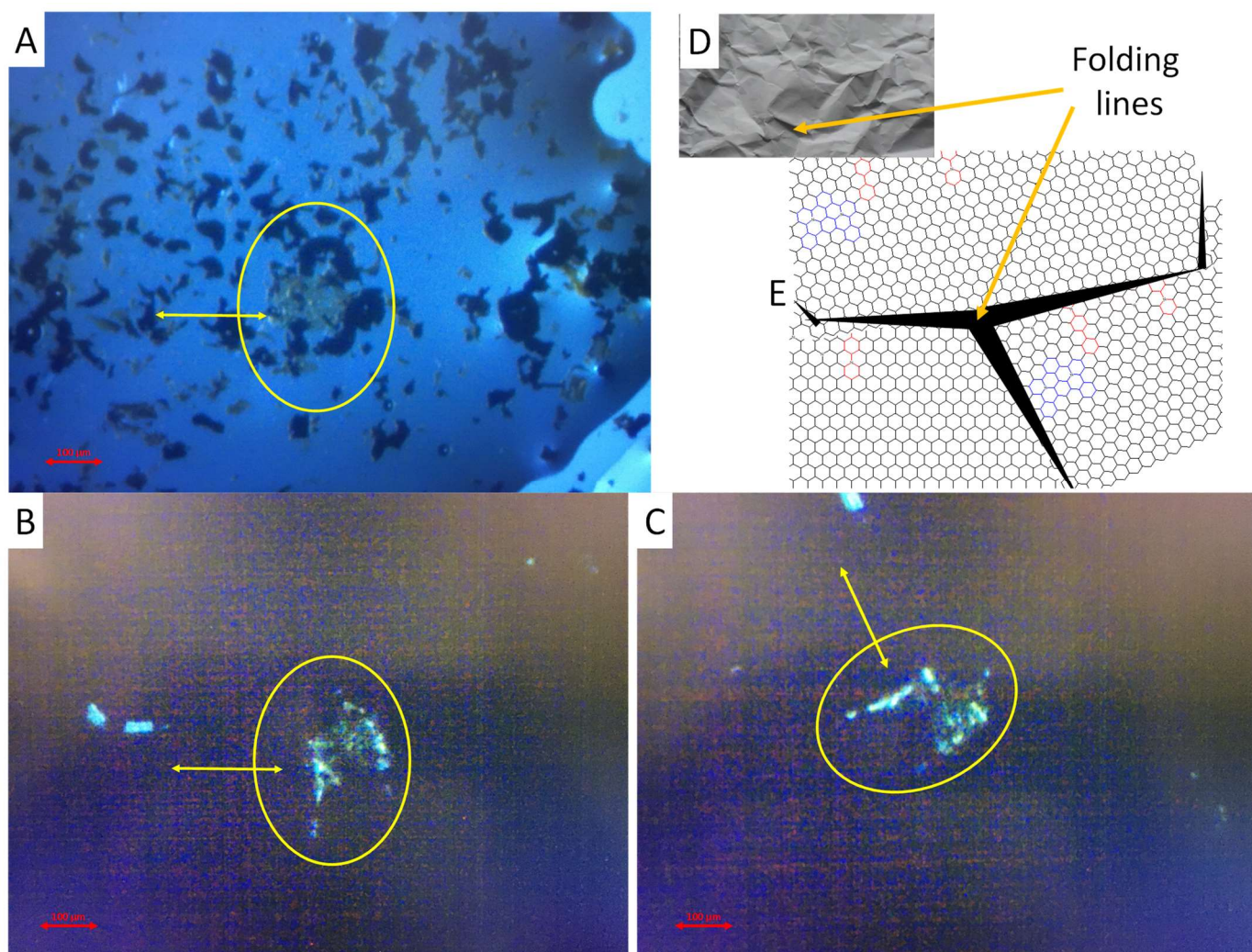
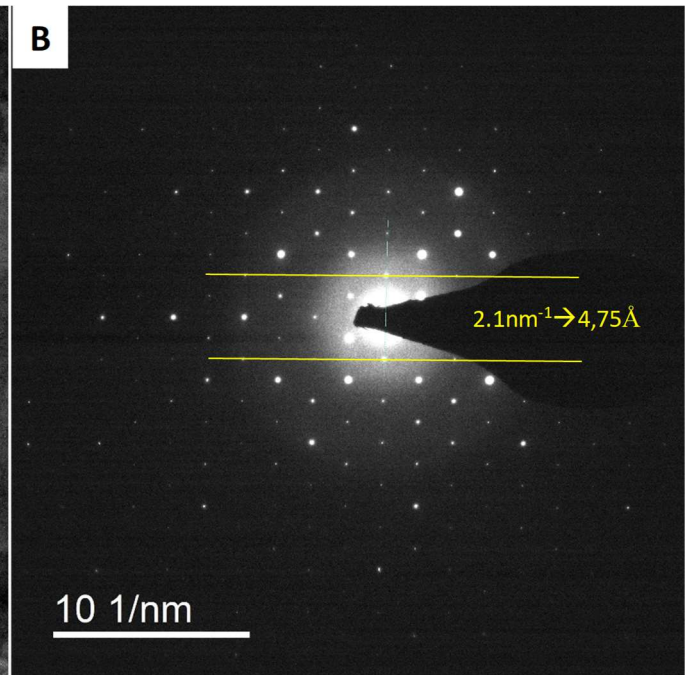
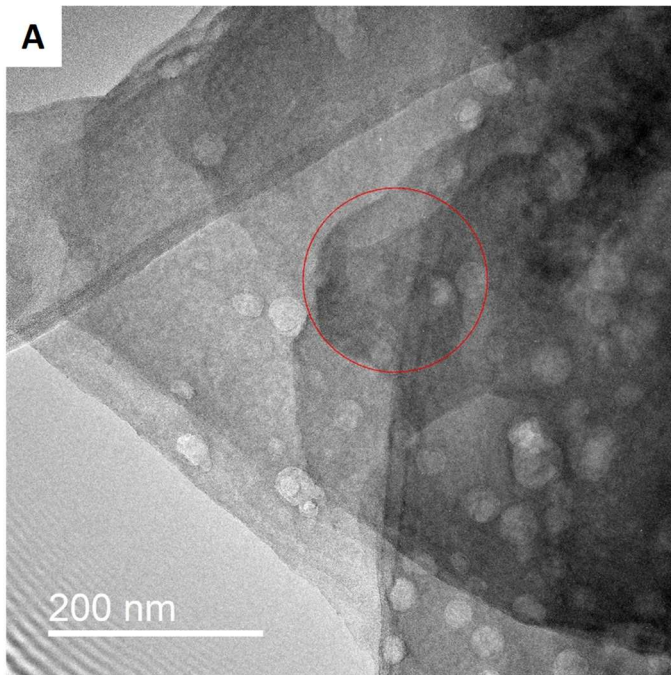


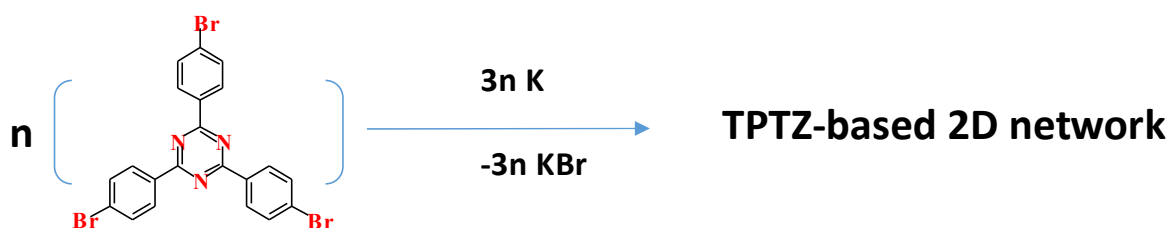
Figure S2M: polarised light study of a thin, crumpled C_2N flake (yellow circle). A): normal light; B): the same flake under cross polarized light and C) same sample upon rotation. The appearance of the flake alternatively goes brighter and darker as a function of the angle. D and E: foldings inside a single crystal flake induces the appearance of different crystalline orientations, resulting in different contrast.



S2N: example of artifacts observed during C₂N carbon nitride SAED analysis. Holey TEM carbon grid used, suspended sample.



S3: synthesis and characterisations of CTF 2D material.

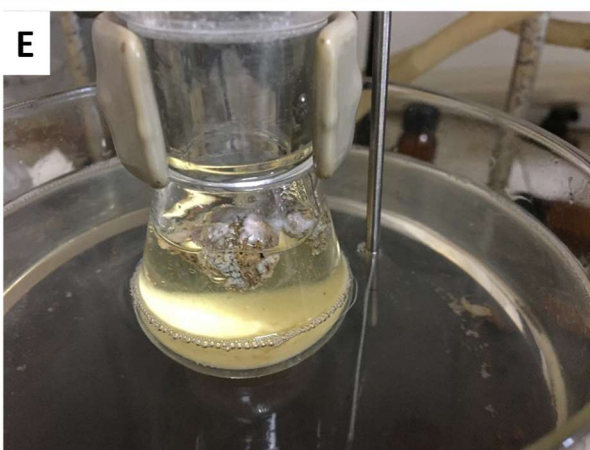
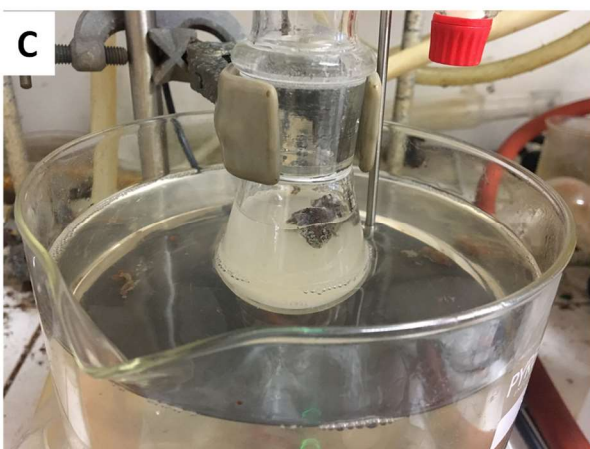


A chunk of metallic potassium (1g) is weighted in a closed vial under argon. 60mL of anhydrous benzene or toluene are then added, still under argon. Tris(bromophenyl)triazine (3.38 g) is then added, and the media is brought to reflux under argon for three days. Note that the media remains as a suspension, as the starting triazine product is poorly soluble. The initially shiny potassium surface rapidly gets purple, and then covers with a light brown solid. As the reaction goes by, the solid material considerably expands ([Figures S3A→E](#)).

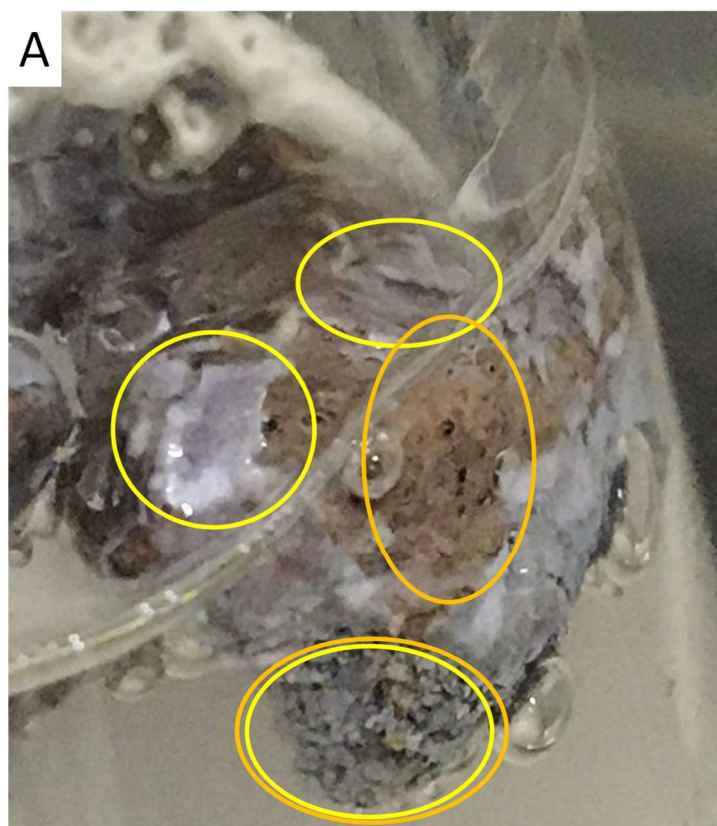
At the end of the refluxing period, remaining metallic potassium is quenched by slow addition of ethanol under argon.

The solid is filtered, washed with dichloromethane, acetone, and water. The precipitate is then suspended in o-dichlorobenzene, and centrifuged (10000 RPM, 3 mins). The precipitate (mostly unreacted starting product) is discarded. The supernatant is then filtered, leaving CTF-2D material as light greenish-brown powder.

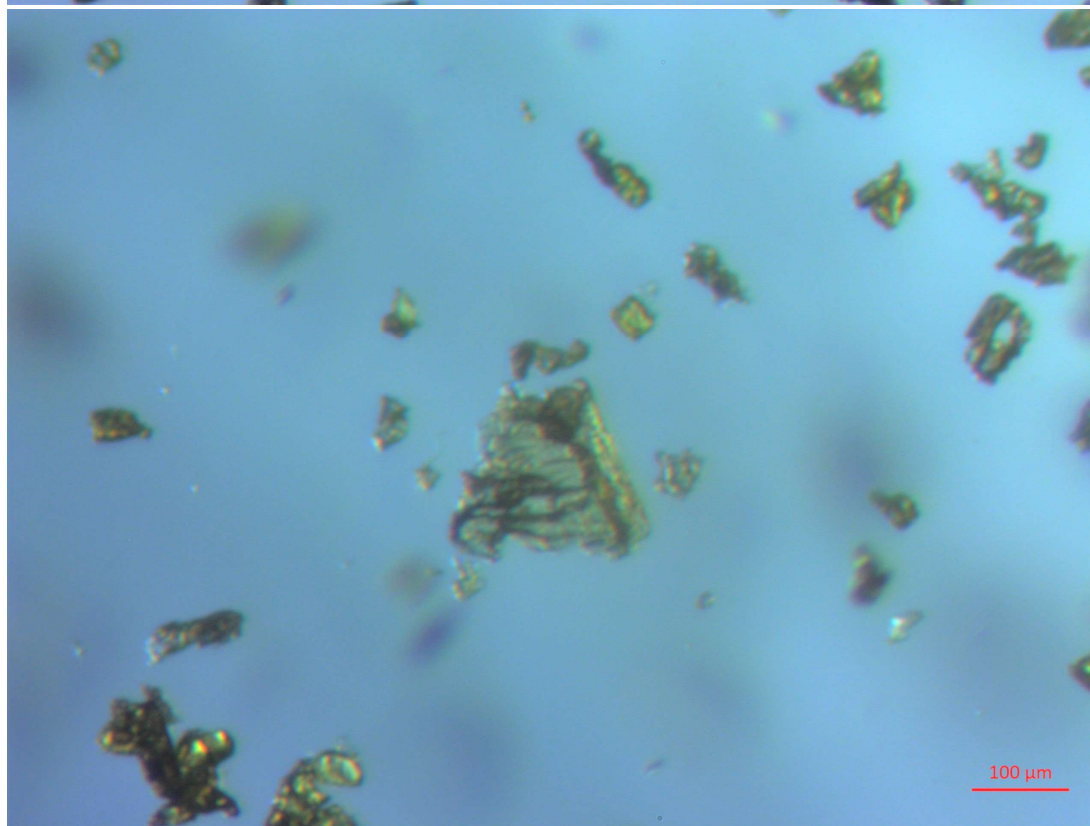
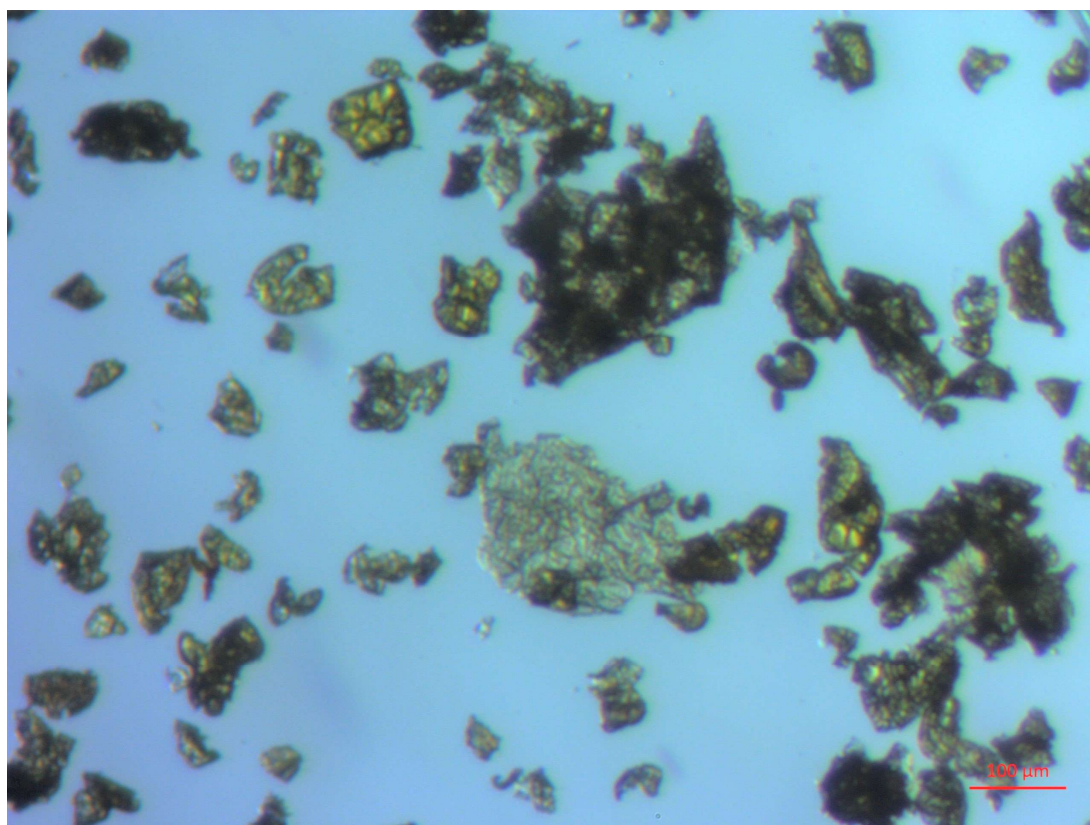
Figures S3A→E: evolution of the reaction media during the reaction.



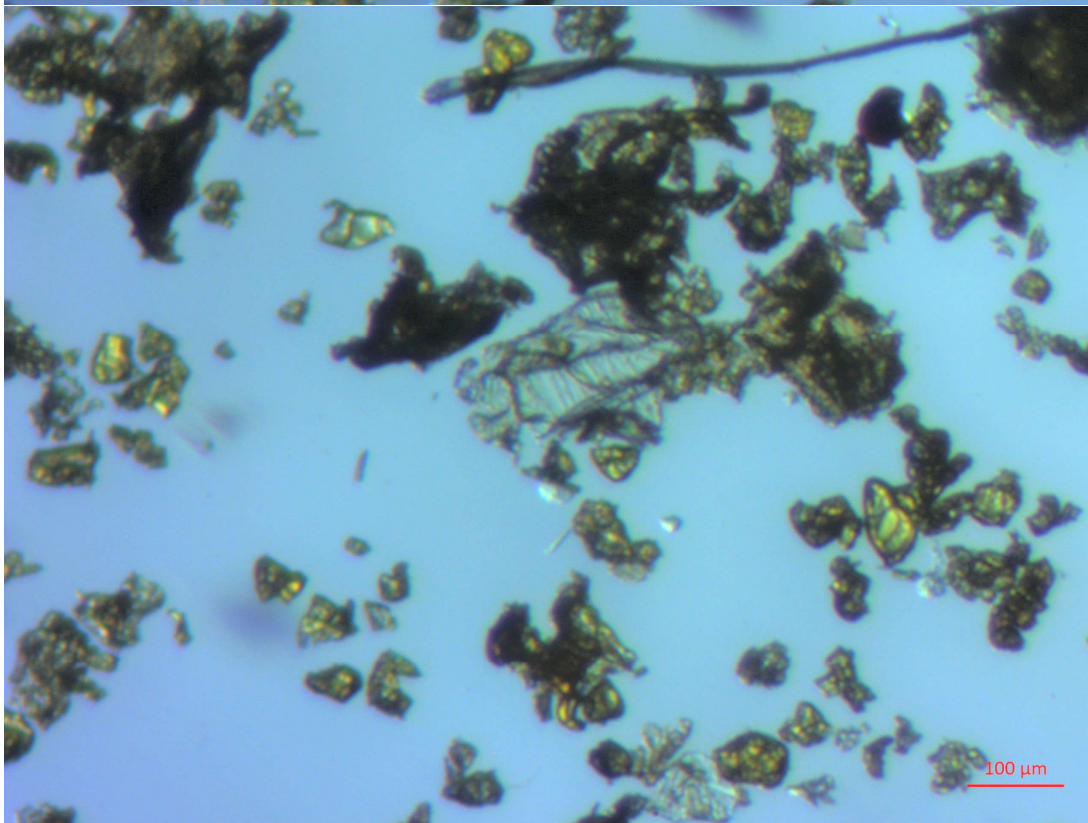
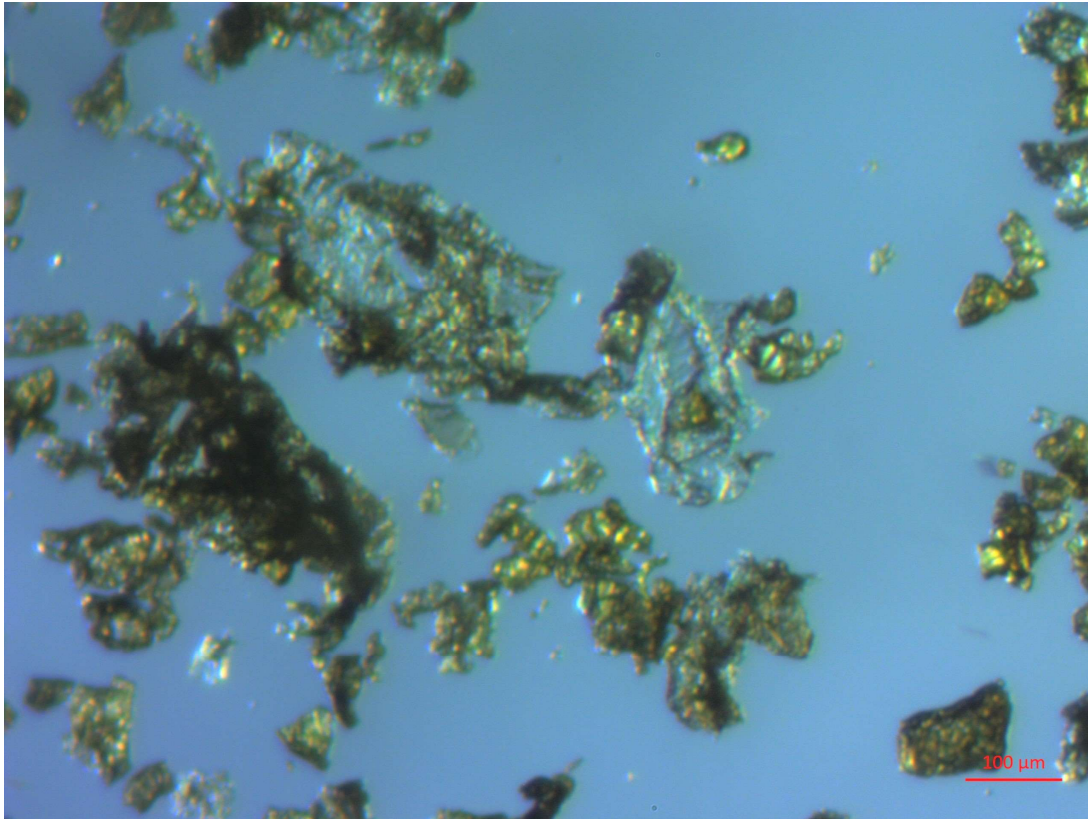
S3F: bark-type growth of CTF organic networks. A): KBr (yellow) and 2D CTF (orange) scales ; B): analogy with bark.



S3G→i: Optical microscopy analysis of CTF samples.



S3H



S3i

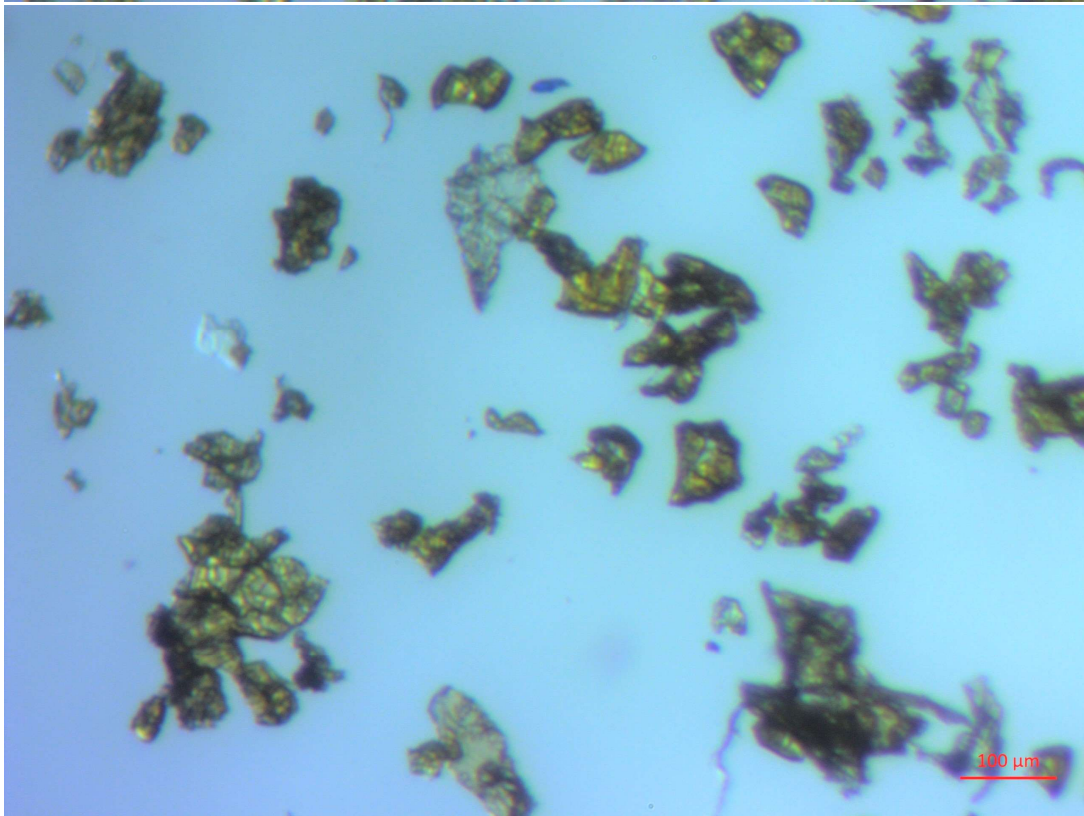
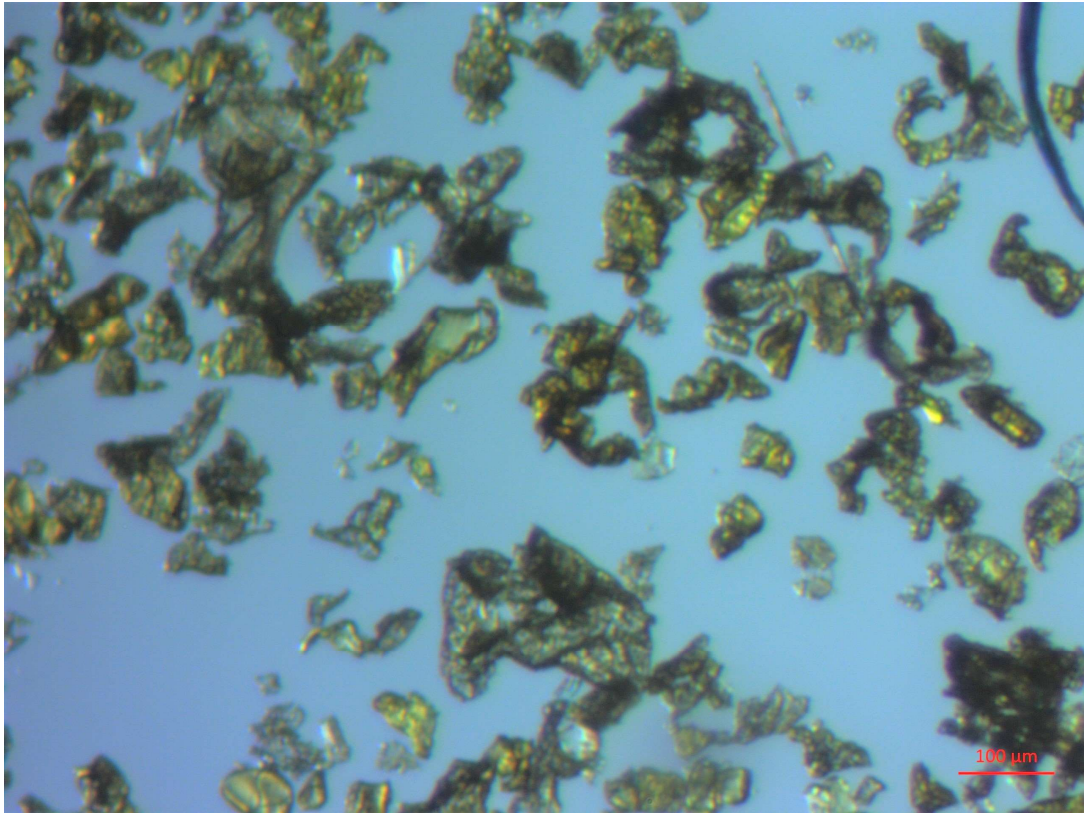


Figure S3i: analysis of a needle-shaped crystal of starting product.

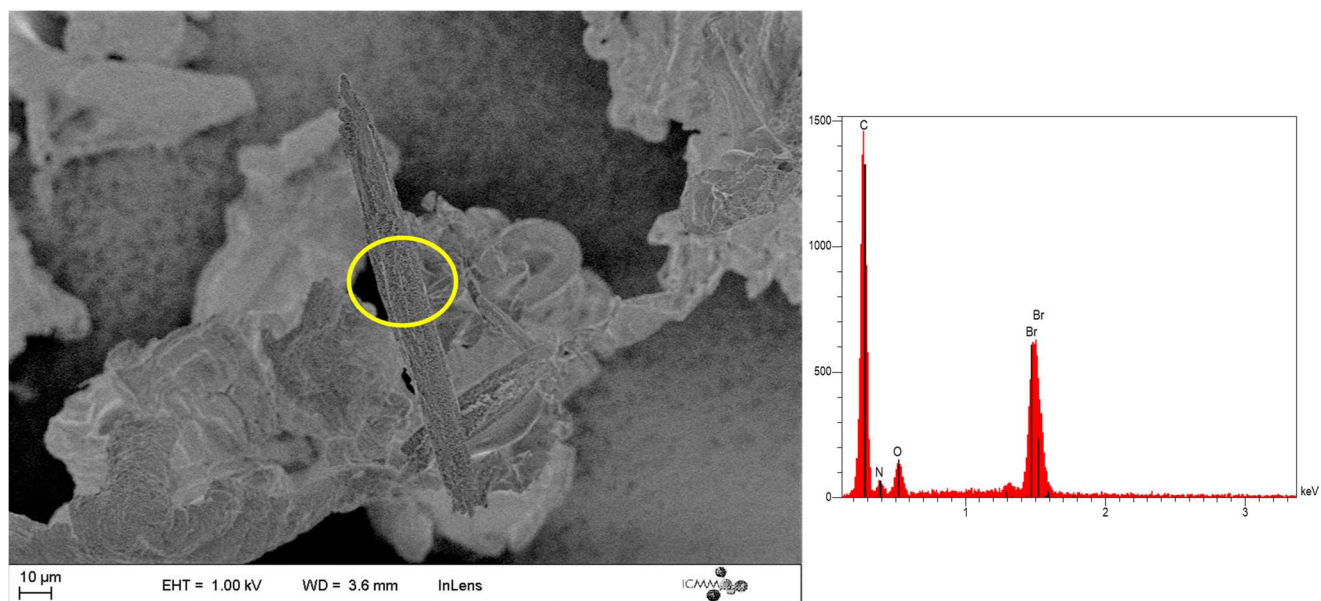


Figure S3j: High resolution (200 kV) TEM study of a highly folded CTF flake.

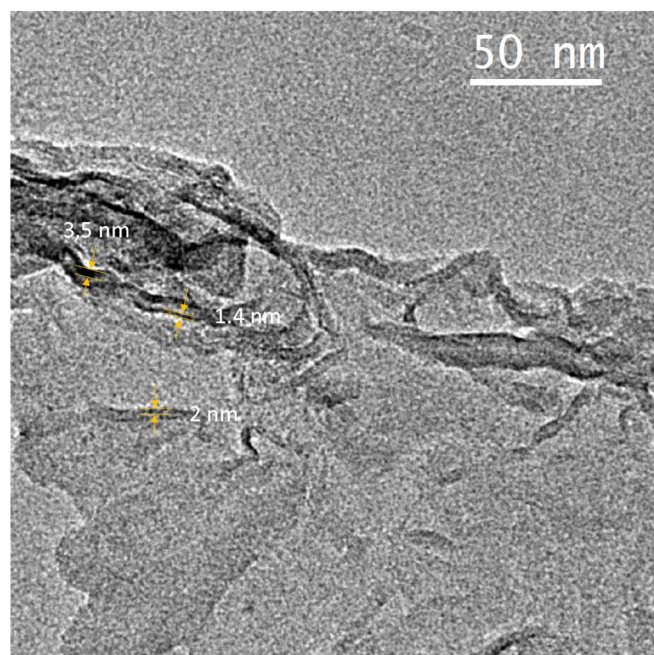
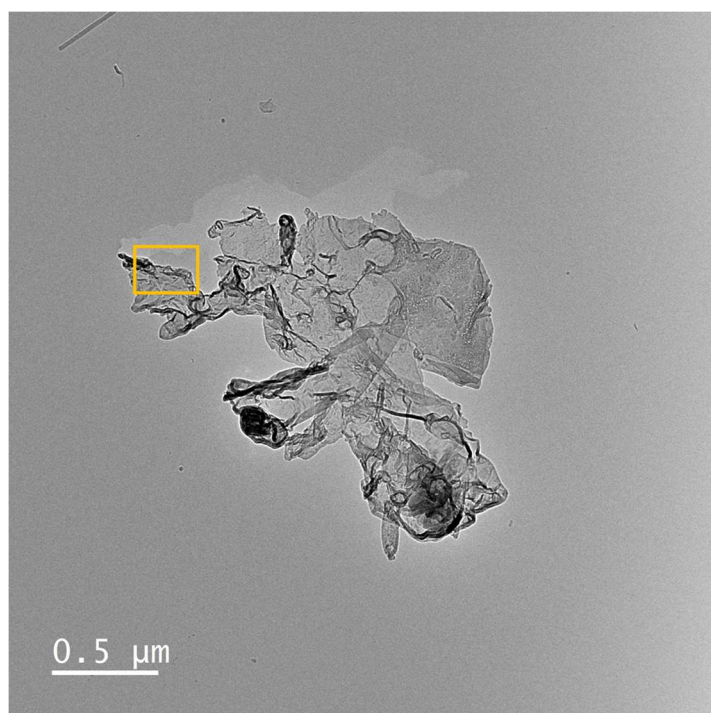


Figure S3k: High resolution (200 kV) TEM study of a tube-shaped CTF flake.

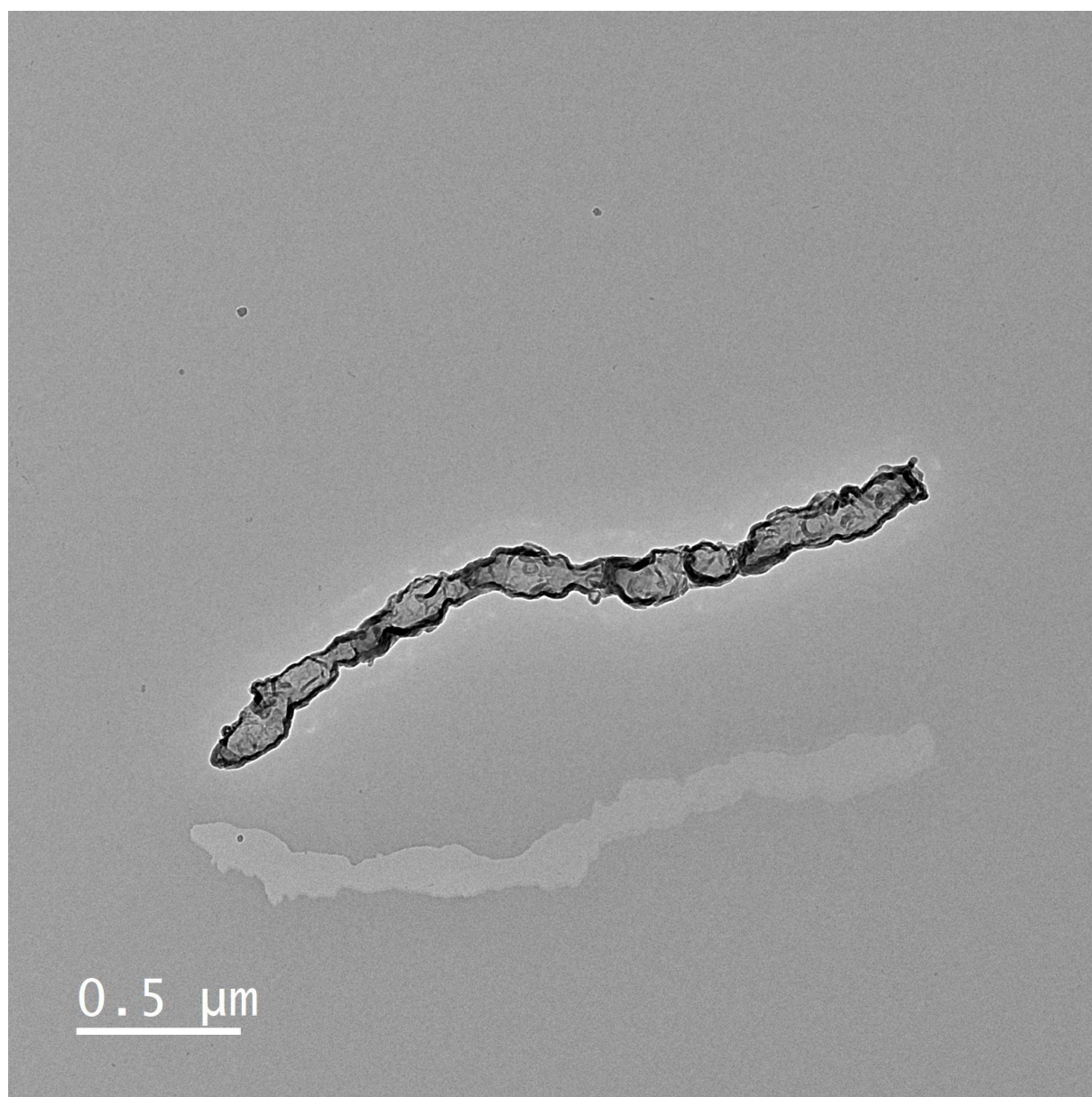


Figure S3I: artifacts observed during SAED analysis of triazine-based 2D network.

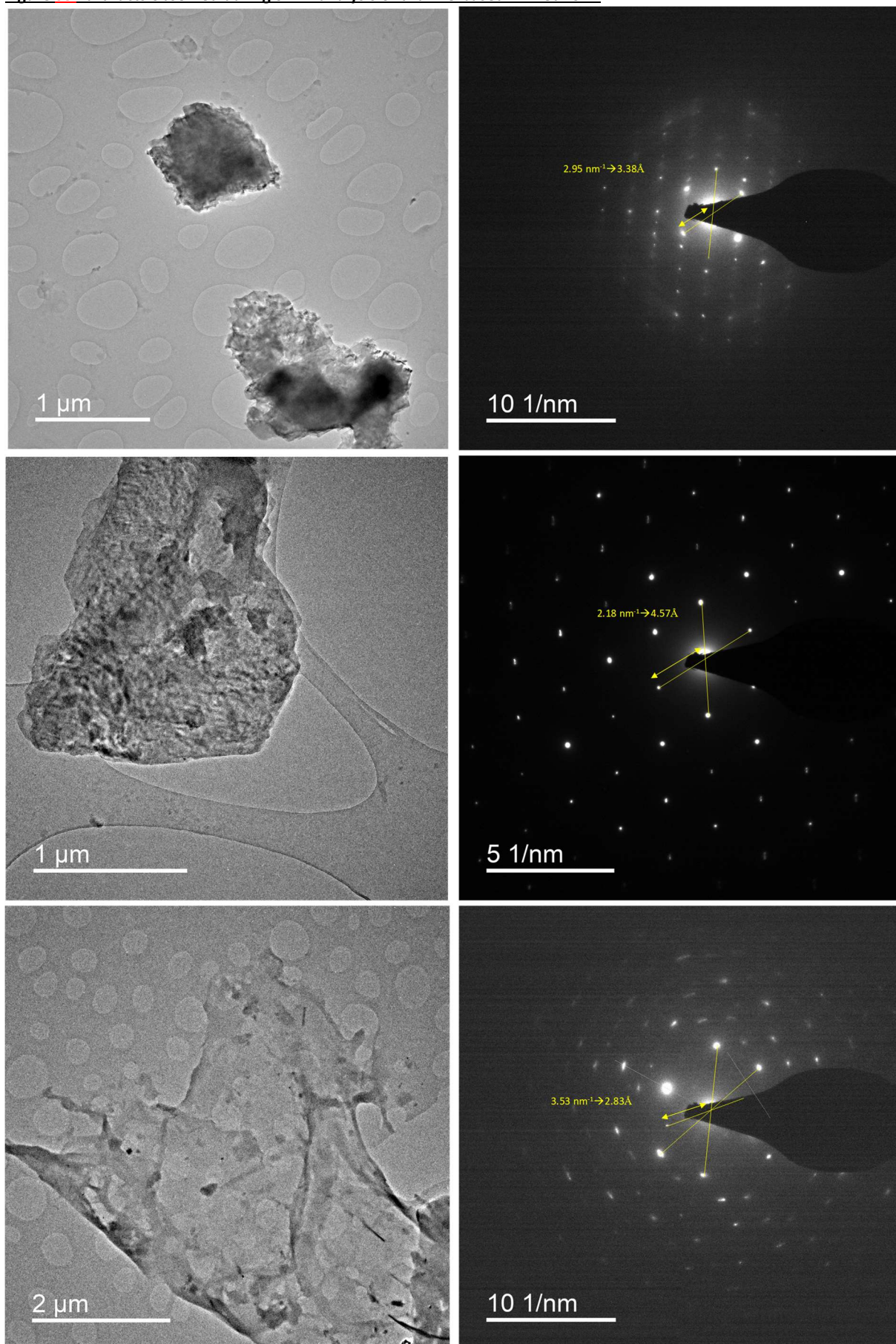


Figure S3K: polarised light study of a thin TPTZ 2D flake (yellow circles). A): normal light; B): the same flake under cross polarized light and C) same sample upon rotation (yellow arrows on B) and C) as a guide to the eye). The appearance of the flake alternatively goes brighter and darker as a function of the angle. Bright crystals of the starting product are also observed.

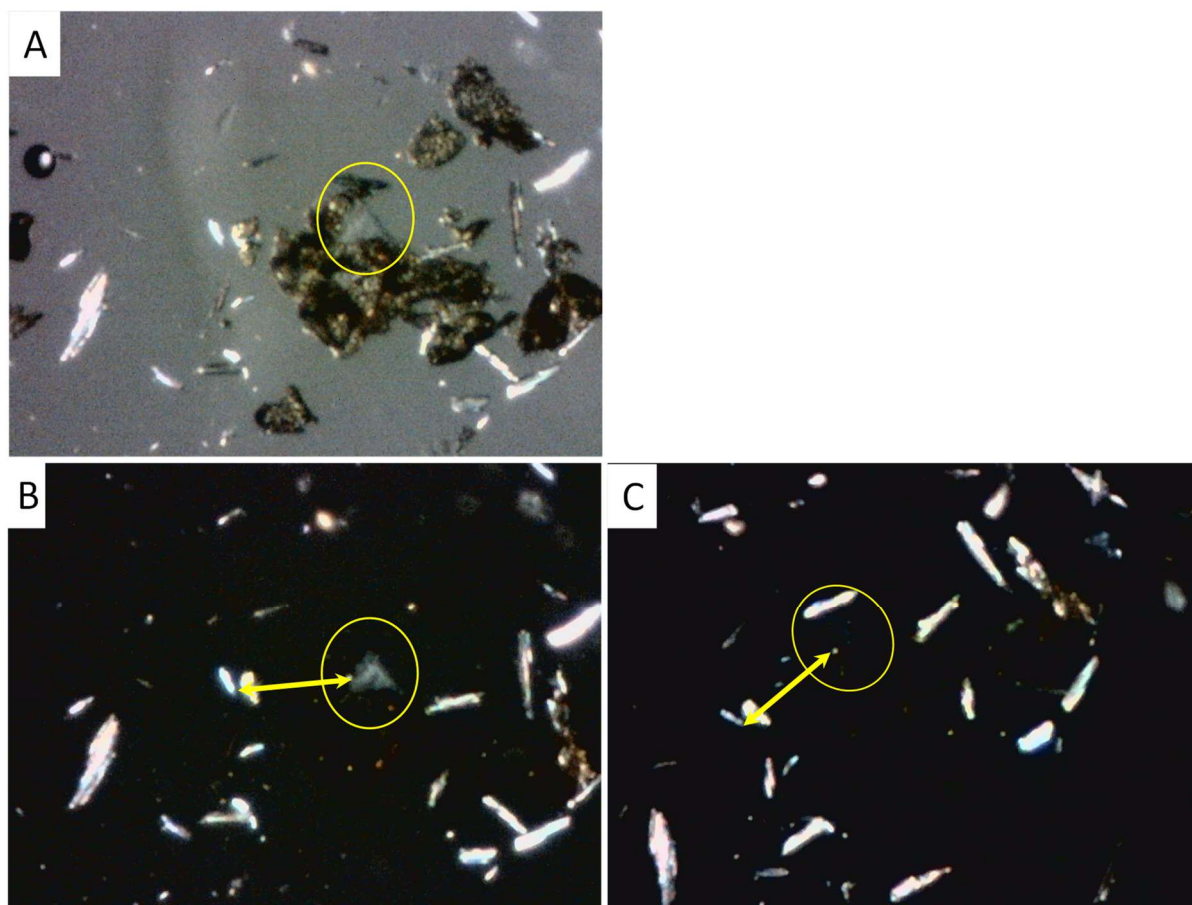


Figure S4A: Synthesis of C₂N carbon nitride network using mercury/potassium amalgam.

To a 10ml Schlenk tube flushed with argon, are added 0.345g of metallic potassium and 4mL of mercury at ambient temperature. The dissolution of potassium in mercury is complete within 30 mins.

The white solids that appeared during the process at the surface of the amalgam are wiped out, leaving a clean, shiny surface (Figure A). A solution of 0,49g of tetrachloropyrazine in 5mL of anhydrous toluene is then added. The reaction media is heated at 110°C under argon for 7 days, resulting in the formation of a brown deposit on the surface of the amalgam (Figure B).

After cooling the system down to ambient temperature, the liquid amalgam is removed (using a pipette), and the remaining brown powder is washed with ethanol and water under argon.

C₂N is obtained as a brown-orange powder.

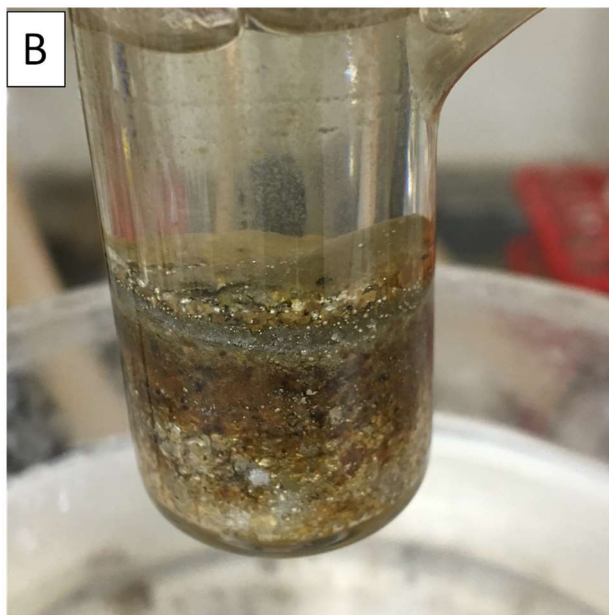
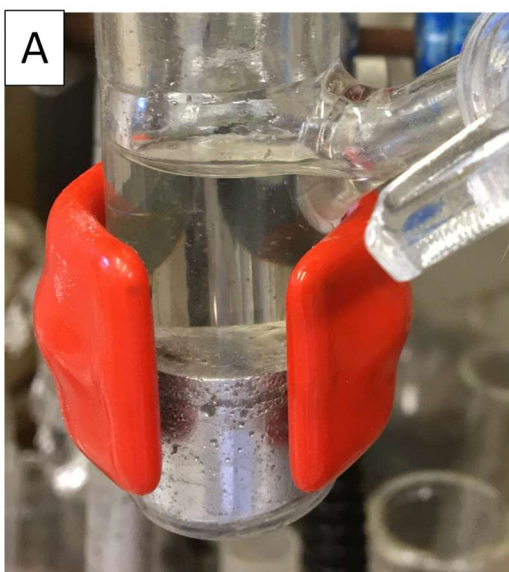


Figure S4B: optical microscopy analysis of a K/Hg amalgam-promoted synthesis of C_2N .

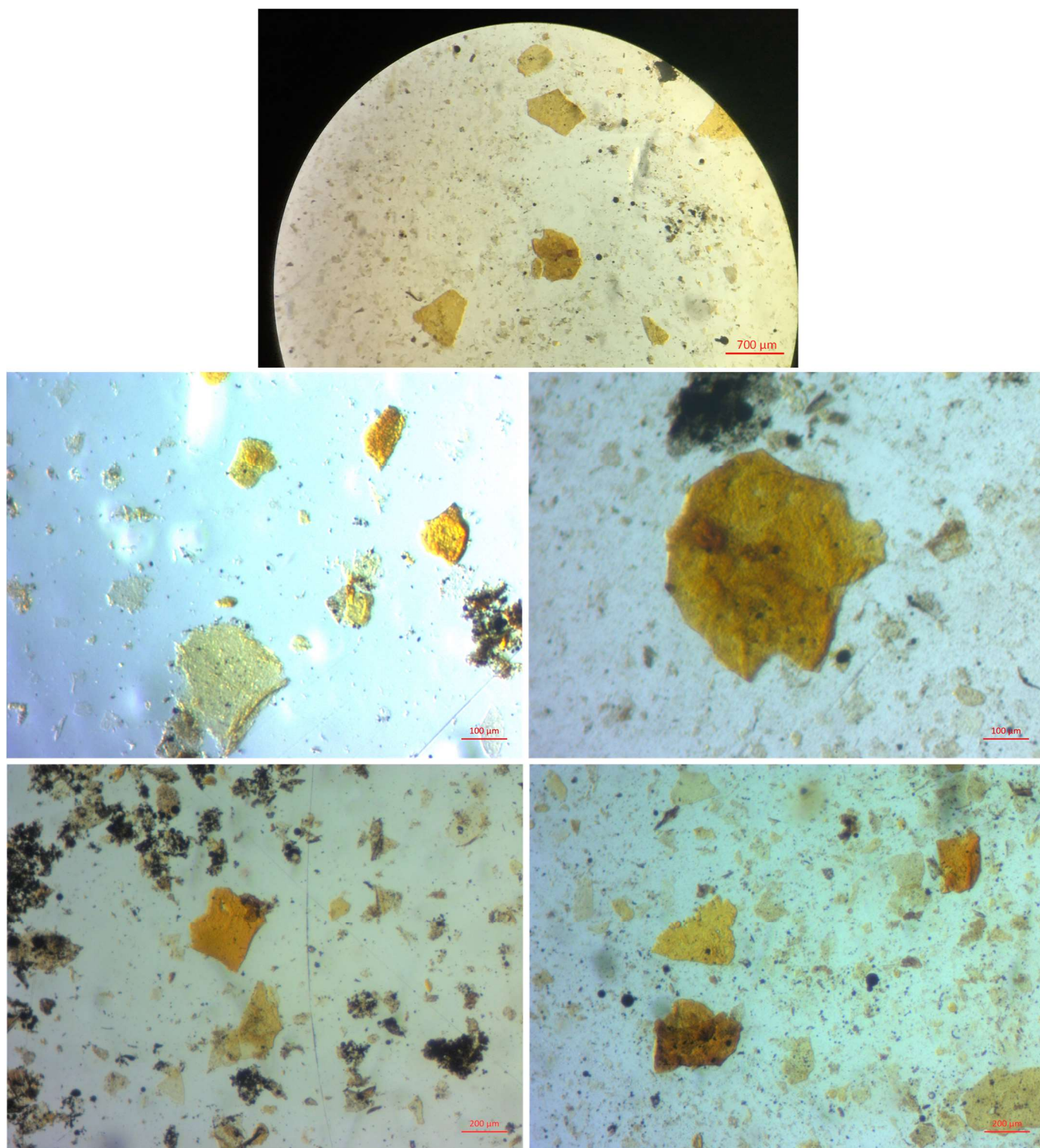
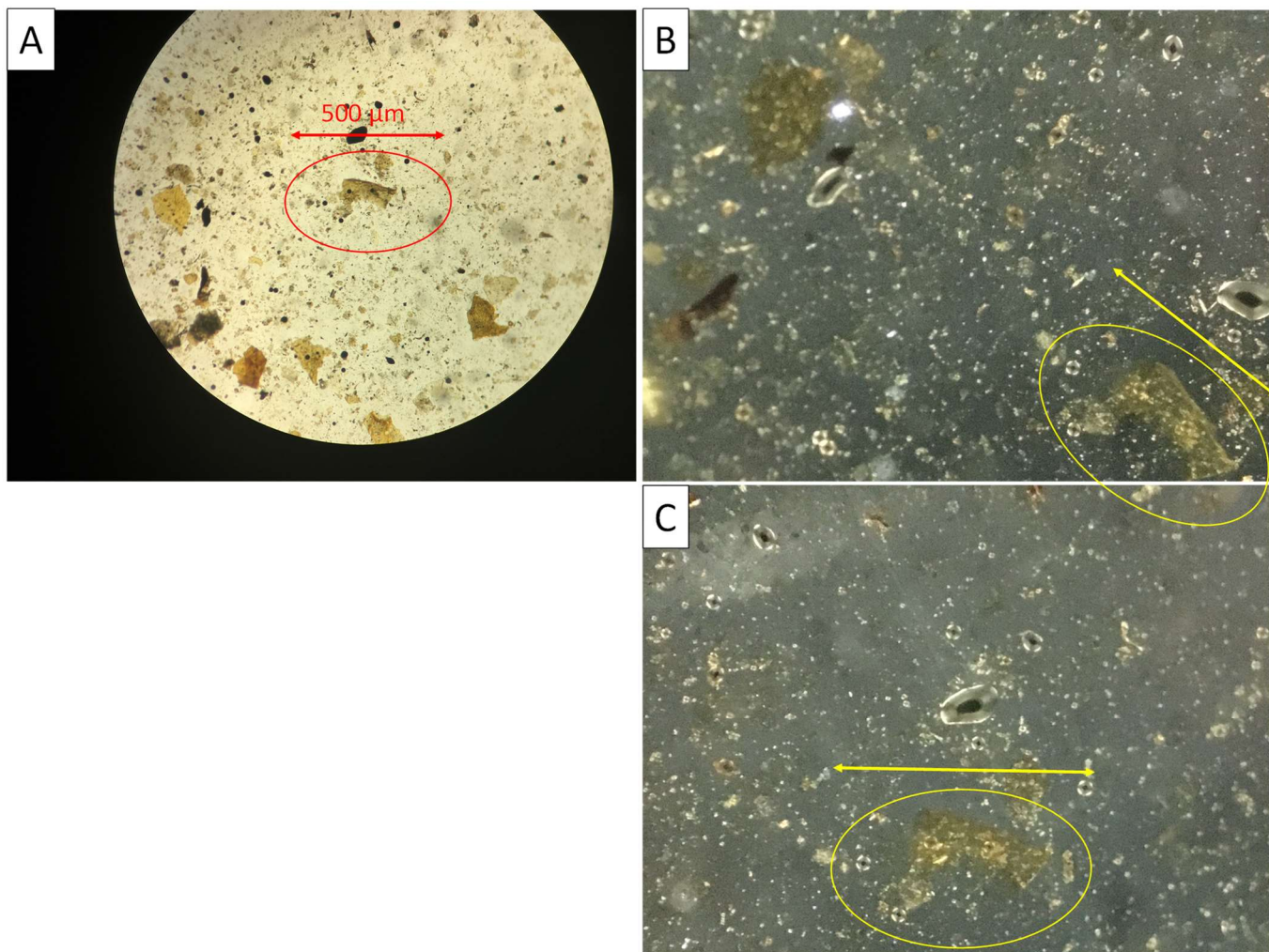
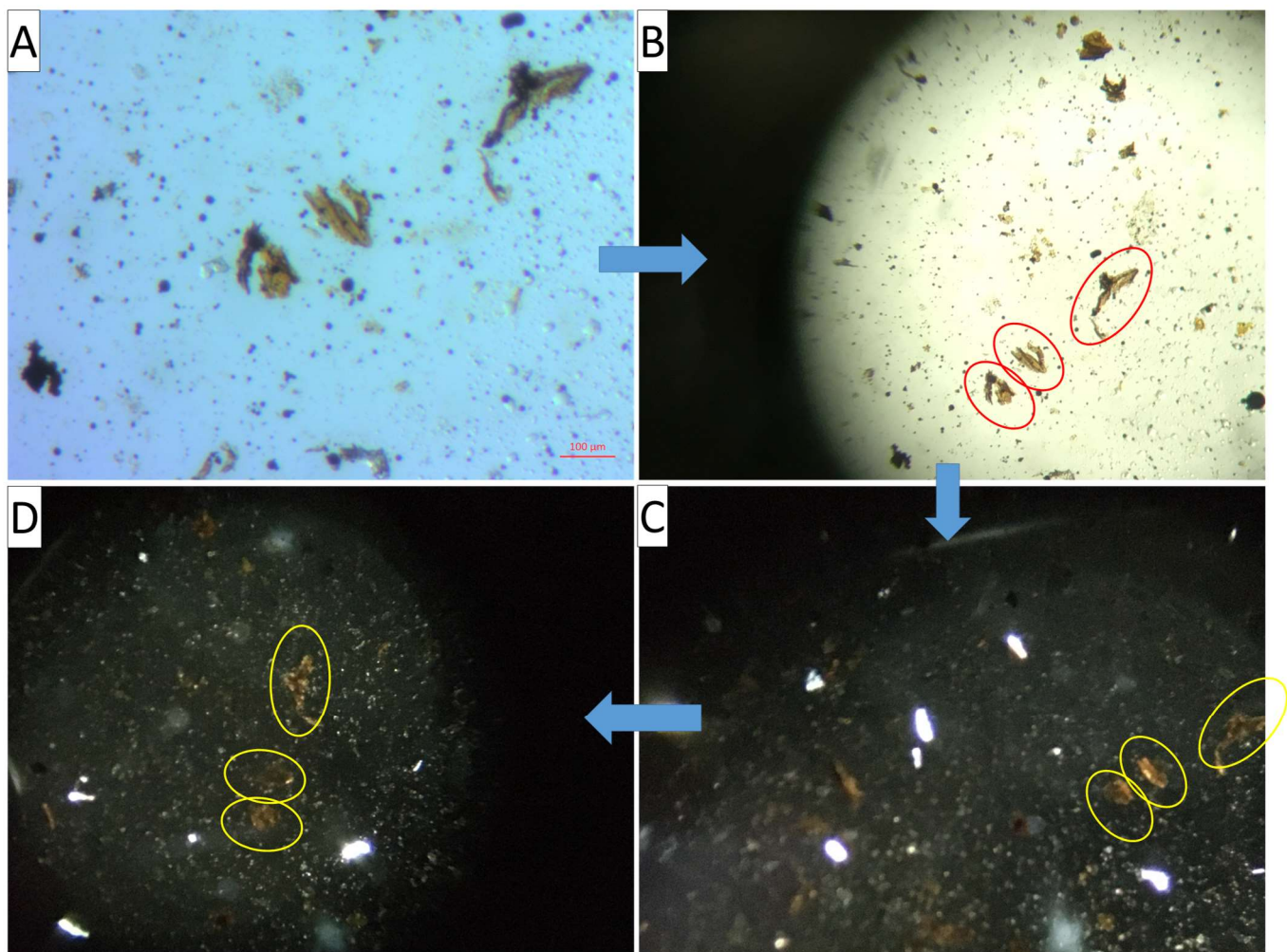


Figure S4C: polarised light study of a thin C_2N 2D flake (circles). A): normal light (red circle, 300); B): the same flake under cross polarized light and C) same sample upon rotation (yellow circles/arrows on B) and C) as a guide to the eye). The appearance of the flake alternatively goes brighter and darker as a function of the angle.

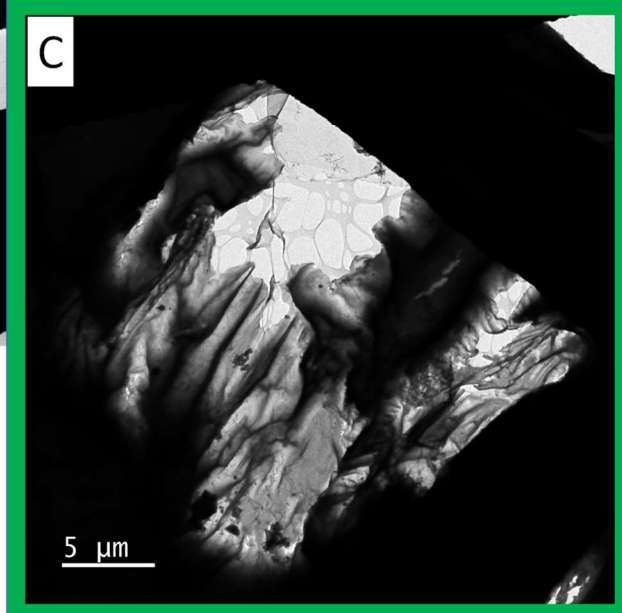
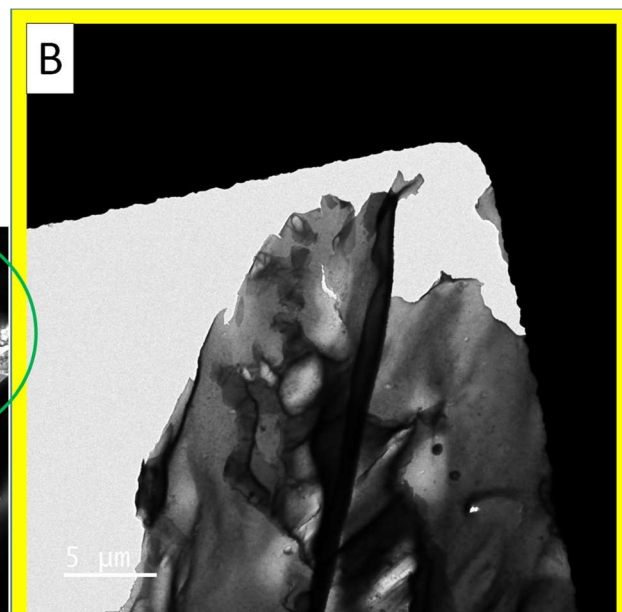
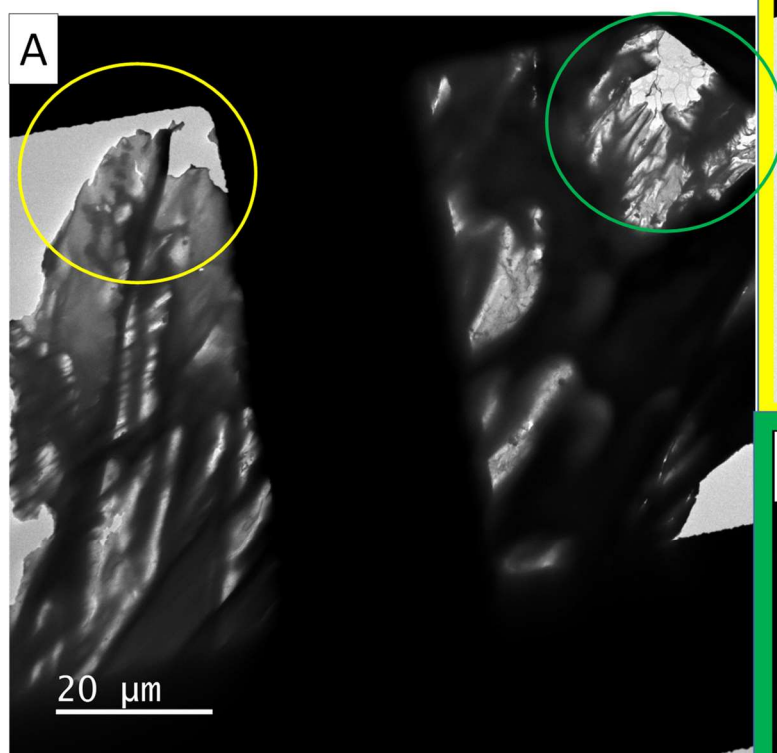


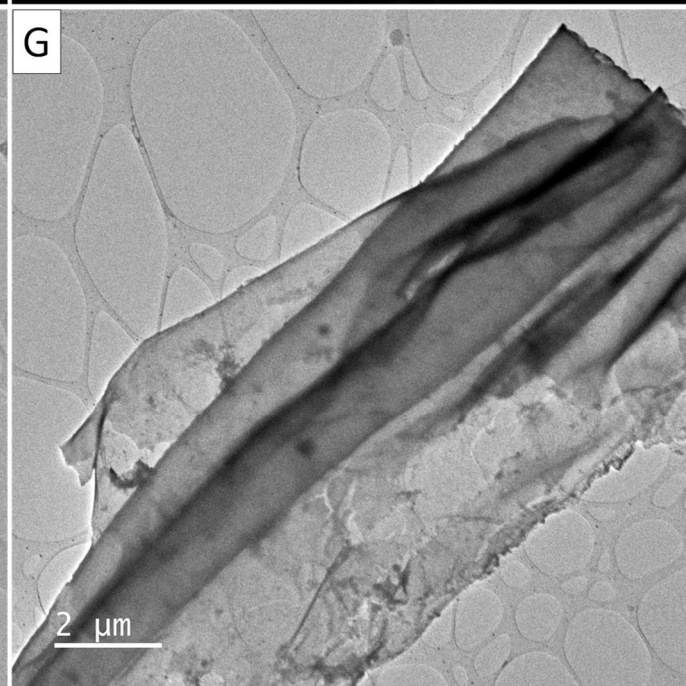
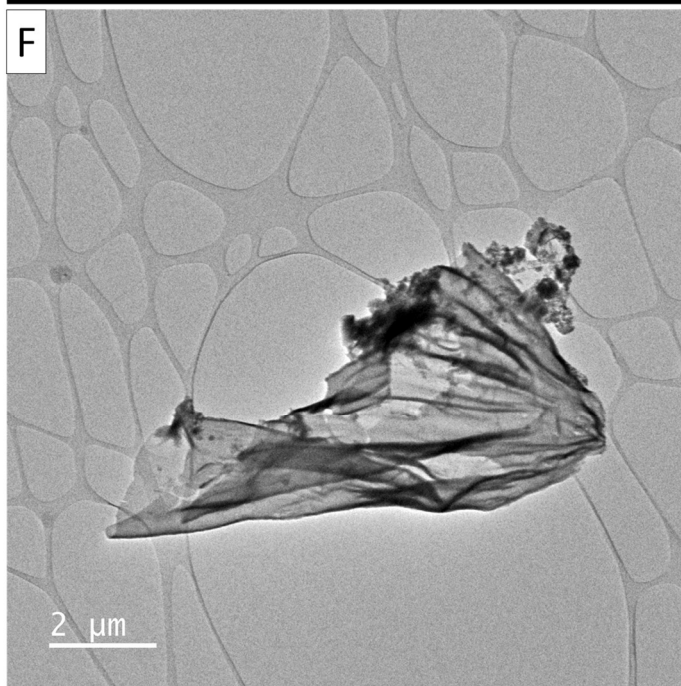
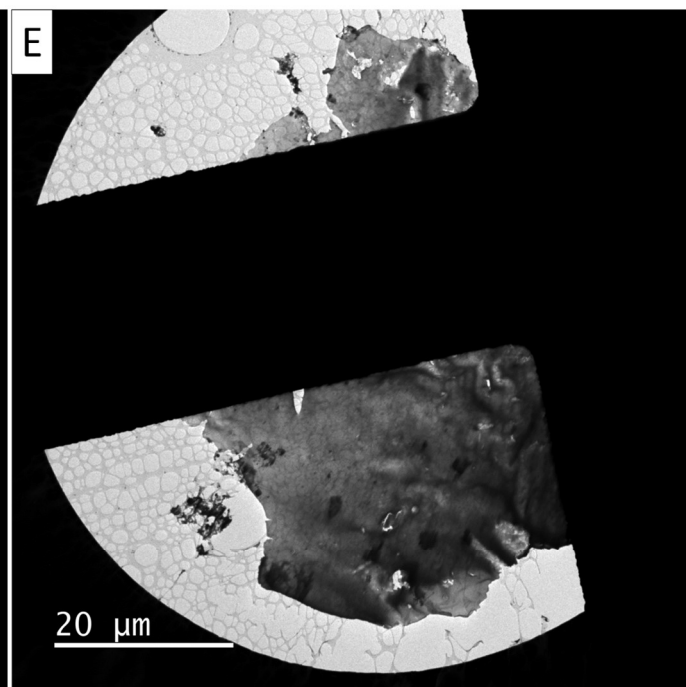
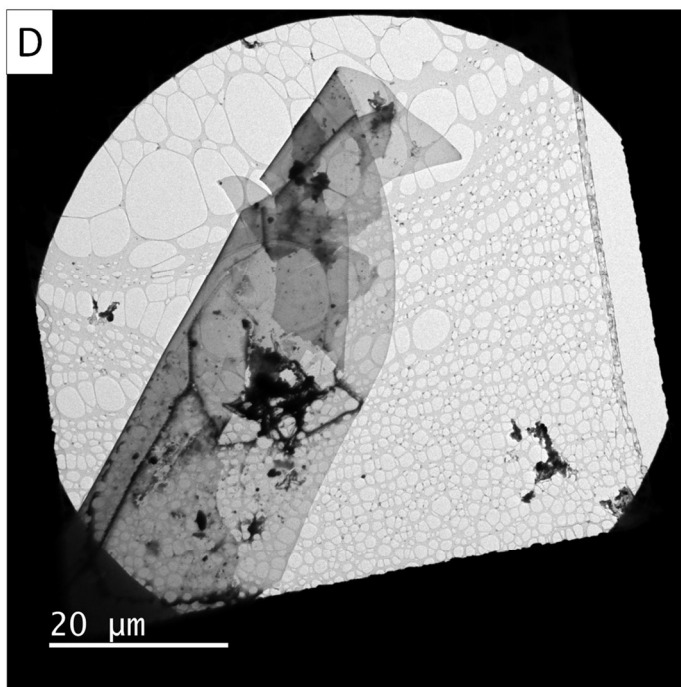
S4D: aged, folded flakes are still able to rotate polarised light.



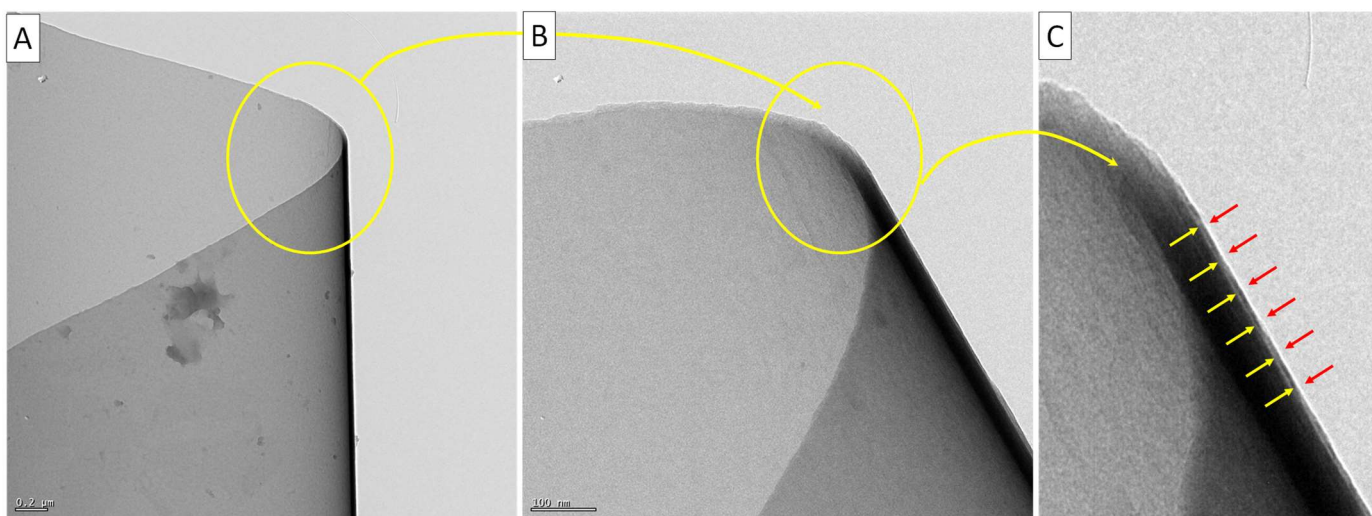
S4E: TEM study of C₂N deposited onto a holey carbon grid (HCl/EtOH dispersion).

Various sized flakes are visible, some of them spanning over several squares (S4E-A→E). Interestingly, the flake shown on S4E-F has been pined by a default on the grid while still being flushed by the dispersion media (acidic water/ethanol) during its deposition on the grid.





S4F: TEM study of a thick C₂N flake (HCl/EtOH dispersion).



S4G: High resolution TEM study (200 kV) of a folded C_2N flake (HCl/EtOH dispersion).

