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A simple and efficient process for the synthesis of 2D carbon nitrides and related materials.

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Abstract.

This manuscript describes a new process for the synthesis of very high quality 2D Covalent Organic Frameworks (COFs), such as C₂N and CN carbon nitrides. This process relies on the use of a metallic surface as both a reagent and a support for the coupling of small halogenated building blocks. The conditions of the assembly reaction are chosen so as to leave the inorganic salts by-products on the surface, to further confine the assembly reaction on the surface and increase the quality of the 2D layers. We found that under these conditions, the process directly returns few layers material. The structure/quality of these materials is demonstrated by extensive cross-characterisations at different scales, combining optical microscopy, SEM/TEM, EDX, etc... The availability of such very large, high quality layers of these materials opens interesting perspectives, for example in photochemistry and electronics (intrinsic transport properties, high gap substrate for graphene, etc...).

Introduction.

The first preparation of graphene by Geim and Novoselov in 2004 [1,2] sparked an ever increasing interest in 2D materials. Indeed, along with graphene, dichalcogenides such as MoS₂ or WoS₂ [3,4], silicene [5,6], phosphorene [7,8,9], hexagonal boron nitride [10,11]... are also being investigated all over the world, due to their fascinating physical [12,13,14,15] and chemical properties [16,17,18].

More recently, 2D COFs (Covalent Organic Frameworks), a family of 2D materials, has received a growing interest [19,20,21,22,23,24]. Currently, most (not to say all) the current syntheses of COFs are relying on the assembly of small, multifunctional building units (Figure 1a, modified/adapted from [25]).

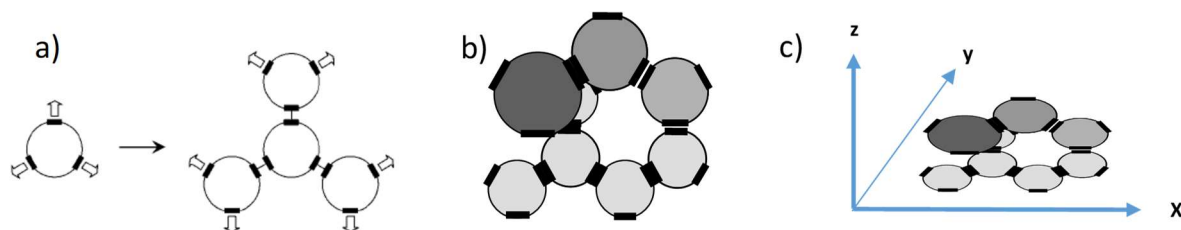


Figure 1: general synthesis of 2D materials

The main difficulty to be tackled here is the occurrence of such defaults as the one shown in Figure 1b. In this case, the connection between two adjacent units is missed, resulting in the formation of 3D, defective materials. It is thus clear that reducing the degree of freedom of the system along the « z »

axis (i.e. perpendicular to the average plane of 2D network, Figure 1c) should limit the occurrence of such defaults. A common approach is to adsorb the molecular building units on a surface and condense them by means of different bond-forming reactions [26, 27, 28]). Many examples of this strategy are to be found in literature, for example by using reactive Cu surfaces in combination with halogenated aromatics [26]. This strategy returned many beautiful 2D materials but often obtained and studied (for example by STM/AFM) under UHV conditions (i.e. impossible to get on a preparative scale). It would thus be interesting to use the same approach under more conventional conditions. An examination of the different metallic surfaces-assisted reactions in solution drives to the conclusion that the well known Fittig reaction [29] is ideal.

First, this reaction uses reactive metals (such as potassium or sodium) to promote the formation of a C-C bond between two (aromatic) halides (ex. : chlorides), with the concomitant formation of insoluble Na or K salts as by-products (Figure 2a).

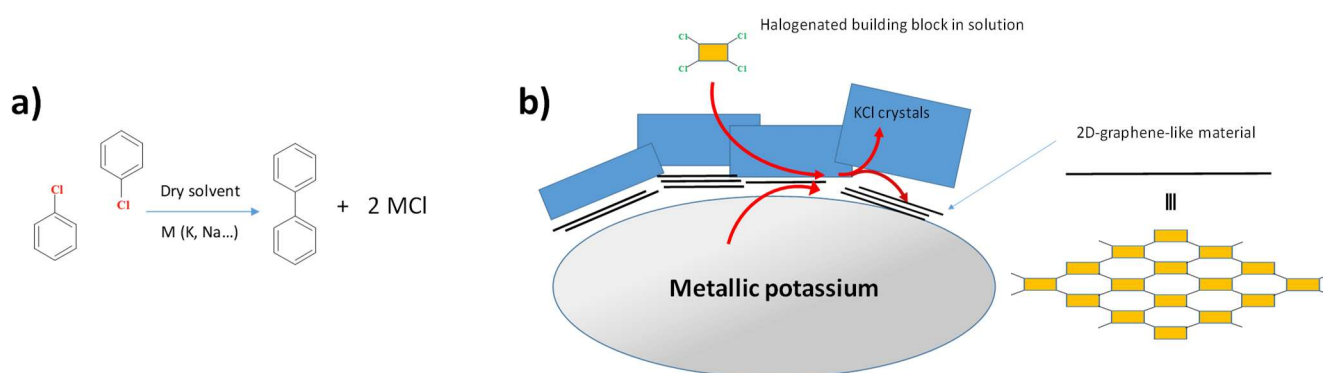


Figure 2: a) The Fittig reaction ; b) confining the growth of layered materials by both a surface and a metallic salt.

Second, as neither the starting products nor the final ones are soluble in potassium or sodium, this reaction is thus fundamentally a surfacic process. It is thus an appealing tool towards 2D materials.

Third, The Fittig reaction is far more reactive than more conventional couplings (ex. Ullman and variations), and there's no need for organometallic catalysts (Ni or Pd).

Last, the starting products are either commercially available or readily synthesised.

The by-product of this reaction (KCl in the example shown in Figure 2b) is insoluble in the reaction media, and thus precipitates on the surface of the metal. Under these conditions, the reaction may continuously runs in a thin layer of liquid sandwiched between the metal and the halide. As the thickness of this layer is automatically reduced by the presence of the upper KCl (or KBr) deposit, two confinements effects may act cooperatively:

- a first one is due to the fact that the involved reaction is intrinsically a surfacic process, and :
- the presence of a KCl or KBr precipitate, restricting the degree of freedom of the growing layers along the « z » axis (Figure 1c) adds a second confinement effect.

In this work, we wish to propose three examples of this double confinement strategy, that improves the quality of synthetic graphene-like 2D materials.

Results

Since the pioneering work of Xinhe Bao and Chuanbao et al. [30 31 32 33], the synthesis of 2D materials by alkali metal-promoted reduction of halogenated precursors was left largely unexplored. Seeking for simple synthesis, that could be performed using common lab equipment, we designed a protocol that runs under close to ambient conditions. To favor a 2D-confined reaction, the solvent used is chosen so as to dissolve the reactant (i.e. allows for the diffusion of the halogenated species to the metallic surface), but neither the final 2D material, nor the inorganic by-products (or any other metal-containing species), to reinforce the confinement effect.

A) : synthesis of CN carbon nitride.

We decided to perform a first experiment targeting a carbon nitride with the general formula CN (Figure 2A) [28, 29, 30, 34 35]. Indeed, carbon nitrides of various stoichiometries are promising for a plethora of applications [36 37 38]. Moreover, the envisioned starting product, cyanuric chloride, is a cheap, commercially available one.

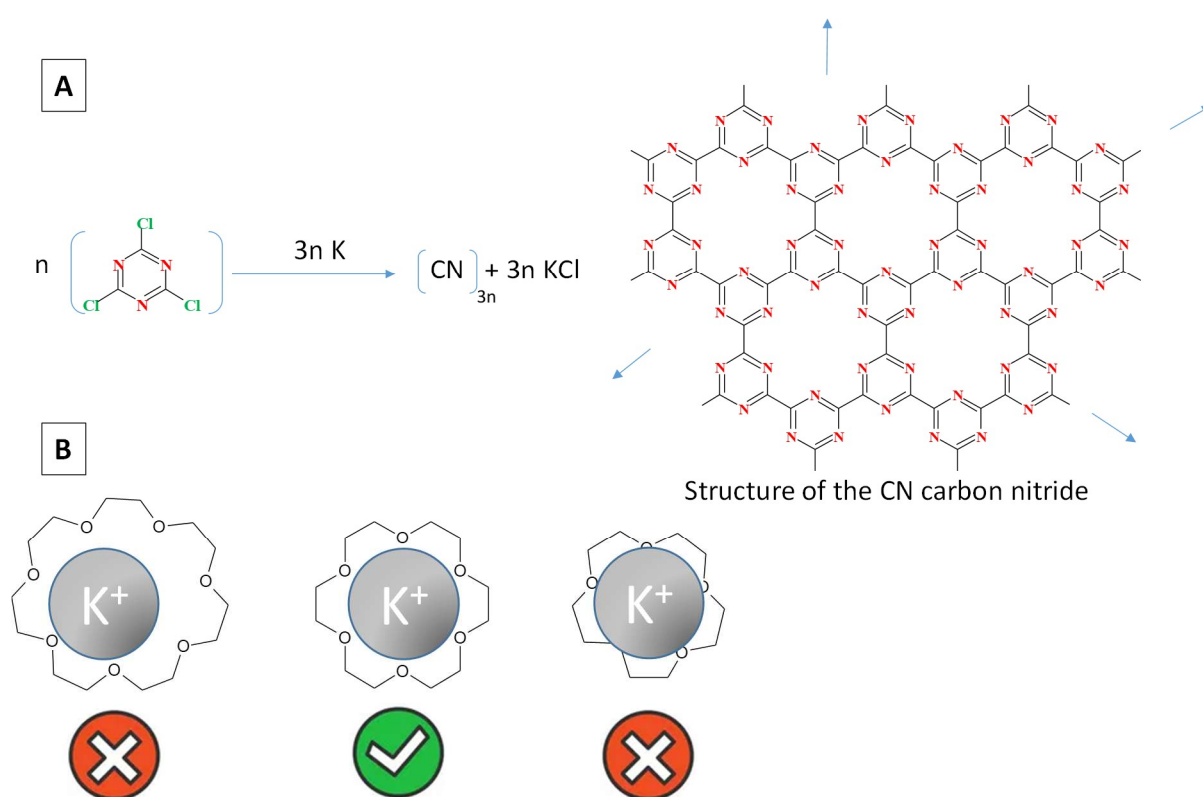


Figure 2: A) synthesis of CN carbon nitride ; B) fit of different macrocyclic cavities with the potassium ion.

Last, potassium was chosen as the reactive metal, because the targeted carbon nitrides do contain coordinating cavities with 6 inward-pointing nitrogen ligands [39]. The study of the complexation of K^+ ions with various oxygen-containing macrocycles indeed shown that K^+ ions has a high affinity for such 6-membered cavities, in comparison with other ones with 5 or 8 coordinating atoms (Figure 2B) [40]. It can thus be guessed that this cation will template the selective formation of six-membered cavities, thus further reinforcing the selectivity towards the formation of the targeted carbon nitrides.

Results.

The details of the synthetic process are to be found in the Supporting Informations (S1), along with a sequence showing the evolution of the reaction media as the reaction goes by (S1A→E).

Crude material analysis

First, an analysis of the crude reaction media (supernatant and solid separately) was performed to qualitatively assess the yield of the reaction.

The amount of remaining organics in the supernatant was found negligible (less than 100 mg). The presence of left residual starting product and/or partial reaction products can thus be considered as rather low.

Then, a sample of the solid obtained after the filtration step (i.e. the removal of soluble residual organics) was directly analysed by XPS spectroscopy (S1H). The Cl 2p spectra can be deconvoluted in two main components, at 197.74 and 199.26 eV. The first one is attributed to KCl (inorganic chloride), and the second one to organic chloride, i.e. to C-bonded chlorine. This later component may be attributed to incompletely reduced species.

The relative surfaces of these two components (along with the very low amount of recovered soluble species) drives to the conclusion that the yield of the reaction is over 80%.

The deconvolution of the N 1s signals shows two components, at 399.21 and 400.57 eV. The 399.21 eV component is attributed to triazinic nitrogens [41, 42, 43, 44]. The higher energy component is attributed to nitrogens bonded to included species, such as metallic cations or H-bonded species. In accordance with the presence of inorganic chloride, strong signals associated with K⁺ ions are also observed

Water-washed sample analysis

A final washing with water is necessary, to remove the water-soluble KCl by-product (see SI). CN is obtained as a light brown solid (Figure 3A), easily redispersed in water (Figure 3B).

An optical microscopy analysis of a water suspension shows this material as made of thin, very large flakes (some of them exceeding 500 μm (Figure 3C)). Characteristic features of 2D objects (such as foldings) are clearly observed (Figure 3D). More images are provided in the SI (Figures S1F→G).

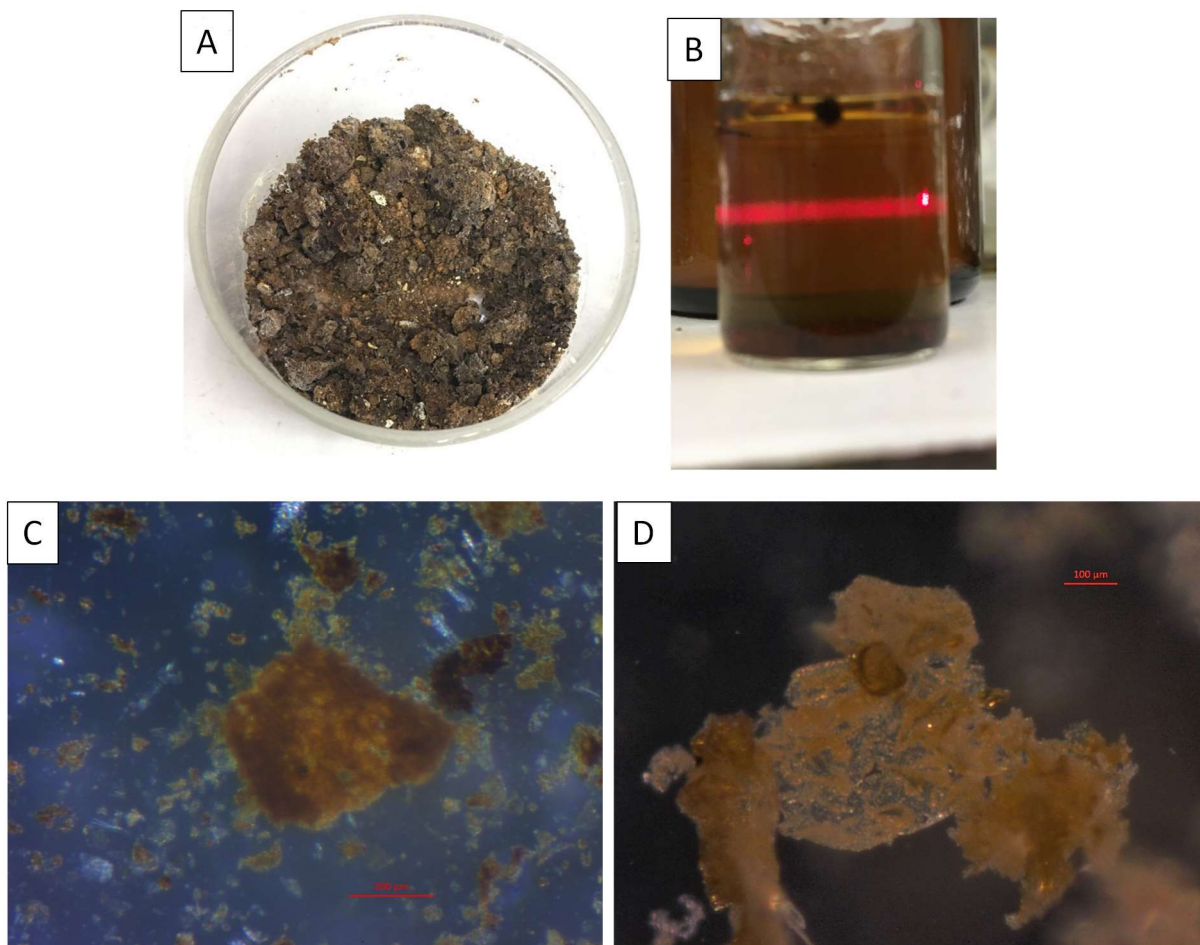


Figure 3. A) the crude CN material; B) water suspended CN, showing the Tyndall effect; C and D) optical microscopy analysis.

Some hollow spheres are also sometimes observed, probably the result of a molding of melted potassium droplets (Figure S1G).

These optical microscopy analyses were also performed using polarised light (Figure 4), with flakes suspended in dispersion oil. Under these conditions, some flakes appear alternatively bright and dark as a function of the relative angles between the polarizer and the sample. This shows that these flakes are crystalline. The fact that different domains appear inside the flake is attributed to foldings (Figures 4 D and E). Other flakes appear as uniformly bright, regardless of the angle. This could be attributed to the fact that they are constituted of several stacked layers, without orientational correlations between them. The presence of extensive crumpling may also be a plausible explanation, as these foldings may also change the polarisation angle of the transmitted light. A handling experiment of this flake is shown in the SI (Figure S1L) along with one more example of polarised light analysis of a CN flake (S1M).

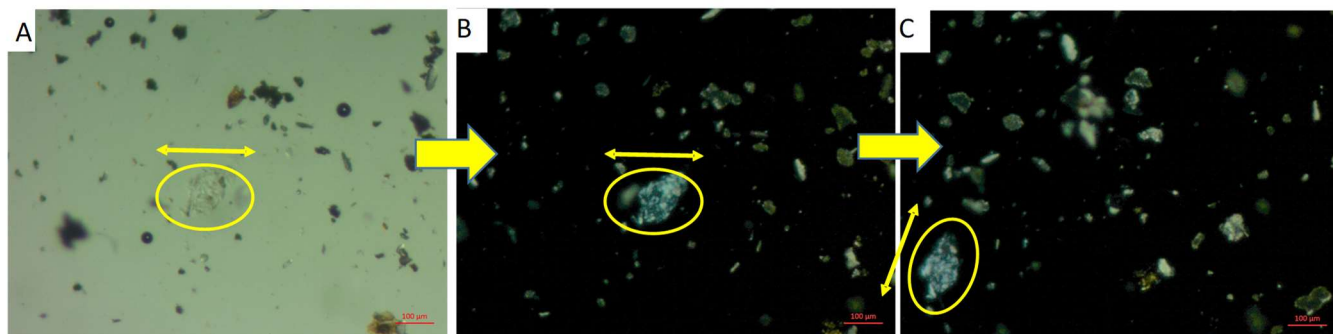


Figure 4: polarized optical microscopy analysis of a CN flake (yellow circle). A) normal light; B) and C) polarised light. The brightness of the flake changes as a function of the angle, evidencing its crystallinity.

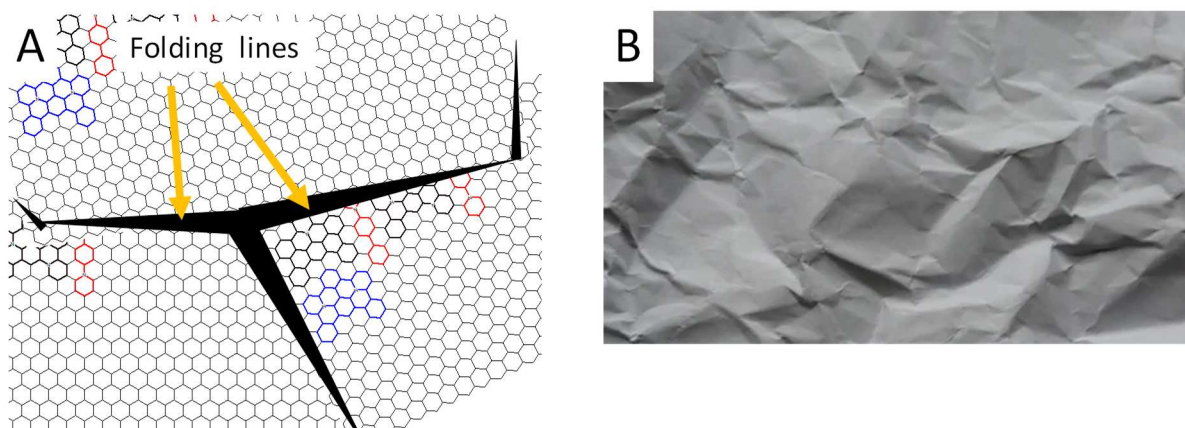


Figure 4: A) a simple model showing how foldings may give rise to different domains inside a single crystal flake. B) analogy with a folded sheet of paper.

Infrared spectroscopy

An IR spectra of CN is provided in the Supporting Informations, and compared with reference ones of triazine (Figure S1NA) and starting cyanuric chloride (Figure S1NB). It first shows the absence of signals associated with C-H bonds, thus excluding the existence of defaults in the structure that may have resulted from overreduction of CN. This also shows the absence of significant amounts of contamination (ex. residual solvents), systematically exhibiting strong signals in this wavenumber range. Second, the characteristic vibrations of the triazine aromatic ring are observed, confirming the proposed structure of the CN COF [45]. Signals are also observed around 2100 cm^{-1} , that could be ascribed to protonated nitrogen species [46]. The presence of these protonated species may explain the presence of high energy component in the XPS spectra of both N and C (see below).

A comparison between CN and the starting cyanuric chloride (Figure S1NB) shows the complete disappearance of the otherwise strong signal associated with the C-Cl bond at 850 cm^{-1} . This confirms the conclusions returned by XPS spectroscopy (see below), indicating the absence of significant amounts of chlorine in CN.

SEM/EDS

A SEM microscopy analysis of CN is shown on Figure 5.

Large flakes (Figure 5A), that tend to roll (Figure 5B) are observed. These features confirm the formation of a layered material.

An EDS analysis (Figure 5C) confirms the presence of the expected elements, along with residual KCl. Oxygen is also observed, probably as trapped/adsorbed species.

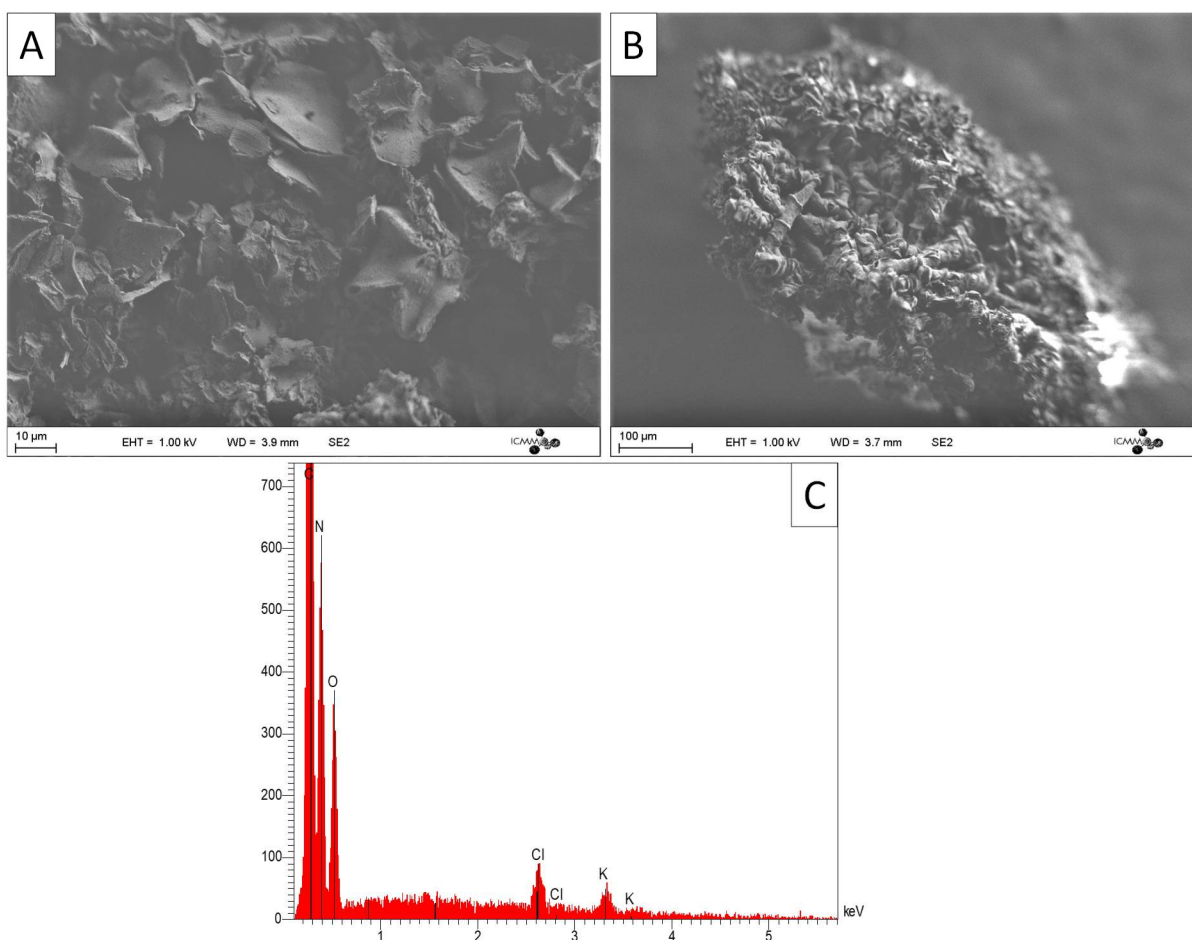


Figure 5. SEM (A and B) and EDS (C) analysis of CN.

XPS

An XPS analysis of a washed sample of CN is shown on **Figure 6**.

Analysis of the Cl 2p core-level spectrum revealed the presence of two spin-orbit doublets whose Cl 2p_{3/2} components are located at 201.3 eV and 198.2 eV. The higher binding energy component is attributed to traces of residual C-Cl bonds while the lower BE component may be related to chloride ions as remaining KCl and CaCl₂. Indeed, EDS analyses also confirms the presence of both potassium and calcium (see below, EDS analyses and **S1i→J**). The very low intensities of the C-Cl signal confirms the low amount of defects in the material. The deconvolution of C 1s signals shows three main components. The first one at 285eV corresponds to carbon contamination, ubiquitously encountered in such analyses. The two other main components can be attributed to triazinic carbons. The presence of these two signal may result from the interaction of some triazinic N-atoms with guest species (such as metallic cations or H-bonded, adsorbed species). This would in turn increase the polarity of the C=N bonds and thus increase the 1s binding energy of the directly attached carbons.

Regarding the N 1s signal, two main components are observed at 399.91 and 401.35 eV [38, 39, 40, 41]. The high energy component, has strongly decreased compared with the crude sample of CN. This confirms the attribution of this high energy peak to nitrogens interacting with included species, such as metallic cations. This may also be the result of partial protonation of pyridine nitrogens, as concluded from the IR study (see above discussion). Oxygen is still observed in the material, showing the presence of

included, oxygen-containing species. This is coherent with our interpretation of the N 1s signals. Such a tendency to absorb invited species is not surprising, considering the open structure of this material. Similar effects have already been observed with related carbon nitrides [43, 46, 52]. The C/N intensity ratio between normalized, 1s peaks from the relevant carbon signals (i.e. those with the highest binding energy, belonging to C=N bonds) and nitrogen is 1.2, close to the expected value of 1.

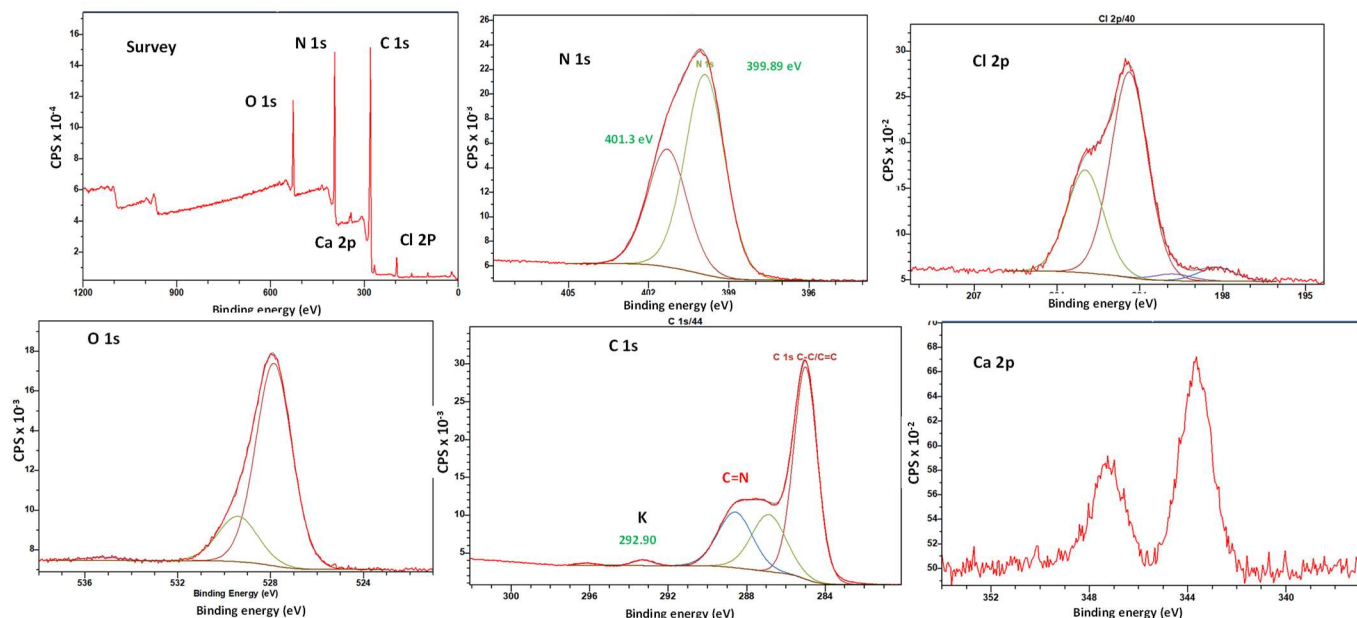


Figure 6. XPS analysis of CN.

XRD

A compared XRD analysis of a crude and washed CN sample was performed. The results are shown on **Figure 7**.

The crude sample (**Figure 7A**, red) only shows signals from the by-product of the reaction, i.e. KCl. No others peaks are visible.

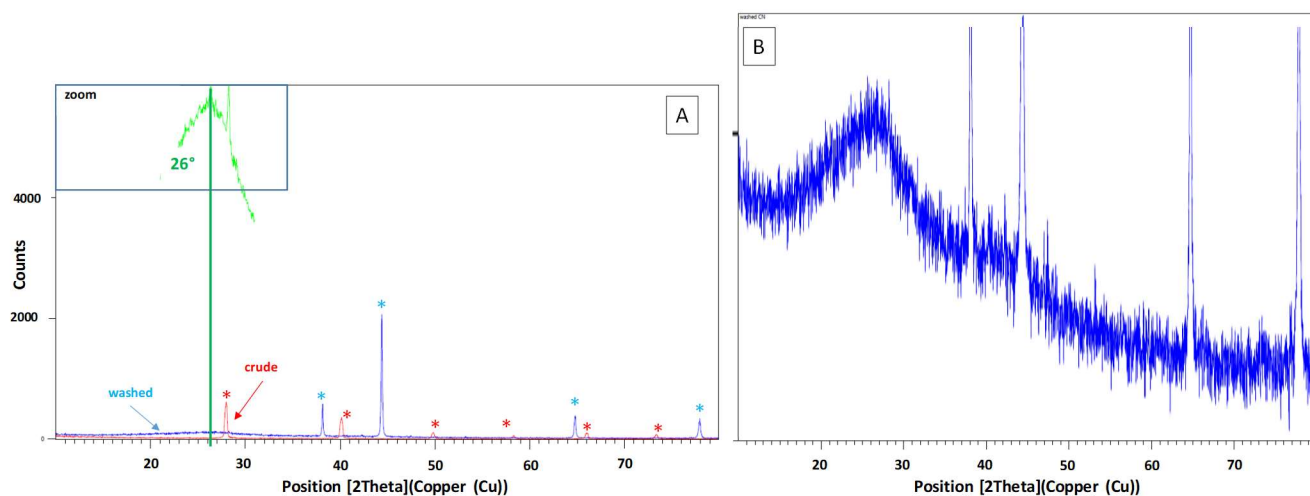


Figure 7: A) compared powder X-ray diffractograms of a crude (red) and washed (blue) CN samples (same batch). Insert (green): zoom over the blue curve. B) Powder X-ray diffractogram of a washed CN sample Blue stars : signals from the aluminum sample holder ; red stars : signals from KCl by-product.

Interestingly, strong evolutions of the same sample are observed upon washing (Figure 7A, blue). Along with the disappearance of the KCl-related signals, a broad peak, centered at 26° appears (Figure 7A, green insert), that was absent from the crude sample. As this peak is characteristic of the interplane spacing of graphenic materials, it can thus be concluded that the flakes mostly exist as individual/few layers objects in the crude material. These flakes are probably kept apart inside a KCl matrix. Upon washing and removal of KCl, these flakes then get aggregated, resulting in the appearance of the 26° peak. Another conclusion that is to be drawn from this comparative study is that the 2D layers are likely to grow as single/few layers aggregates during the synthesis.

TEM

The resulting analyses are shown on Figure 8. The images are shown at increasingly high magnifications, to assess the quality of the flakes over different scales.

The material appears as constituted of very large flakes, in accordance with SEM and optical microscopy images. These flakes are very homogeneous and thin, most of them seemingly constituted of bilayers (Figure 8C). They appear quite smooth, with very few visible defects (Figure 8D→F). The well-known affinity of planar, hexacoordinated ligands for uranyl ions was used to load CN with this ion, in order to increase contrasts (Figure S1K-A). TEM analysis of an isolated flake (Figure S1K-B→E) shows the presence of Moiré effects on top of superimposed layers, thus evidencing their crystallinity.

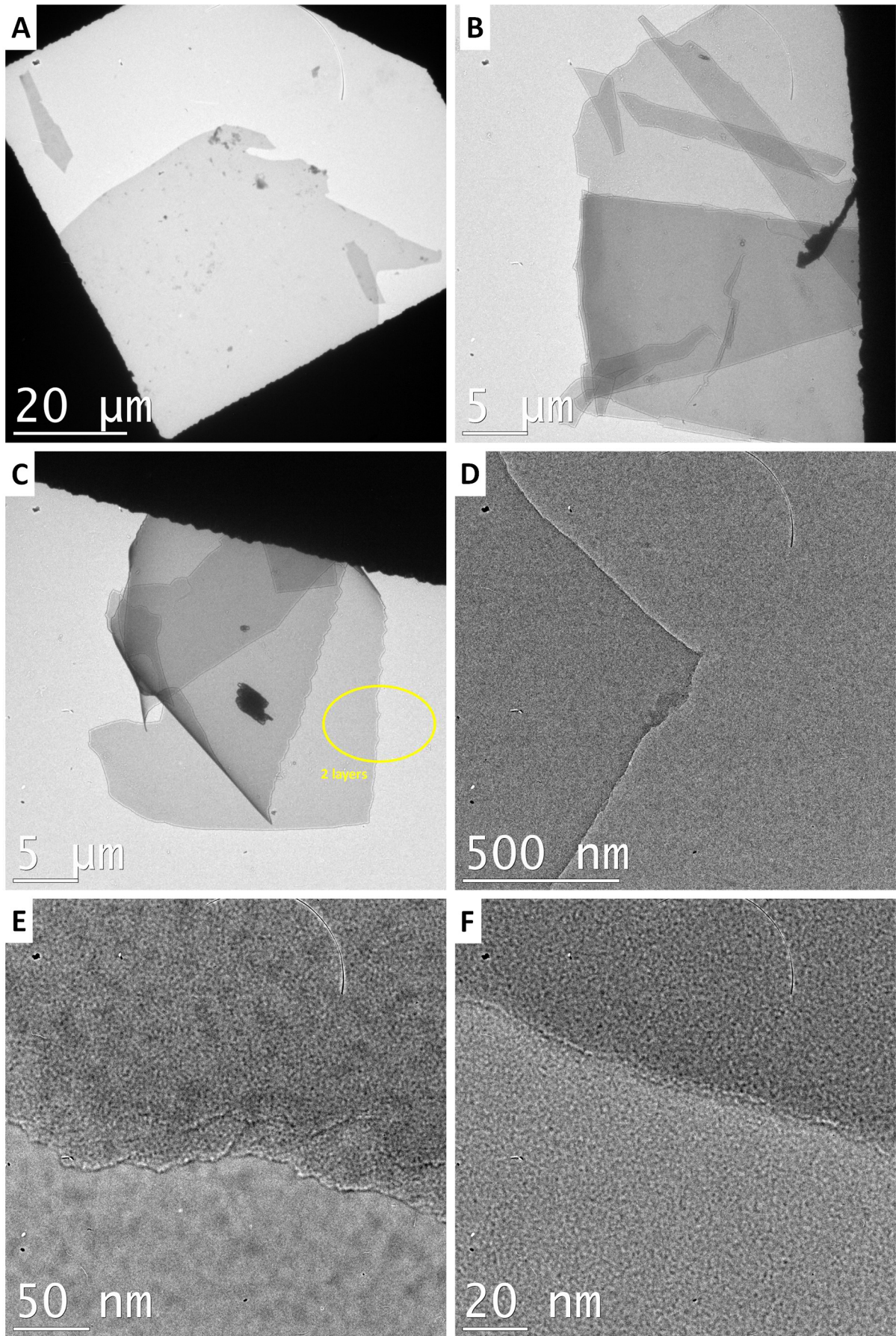


Figure 8. A→F: TEM images of CN flakes at increasing magnifications.

EDS

EDS analyses were also performed on this material. **Figure 9** shows a detailed analysis at the N-K edge.

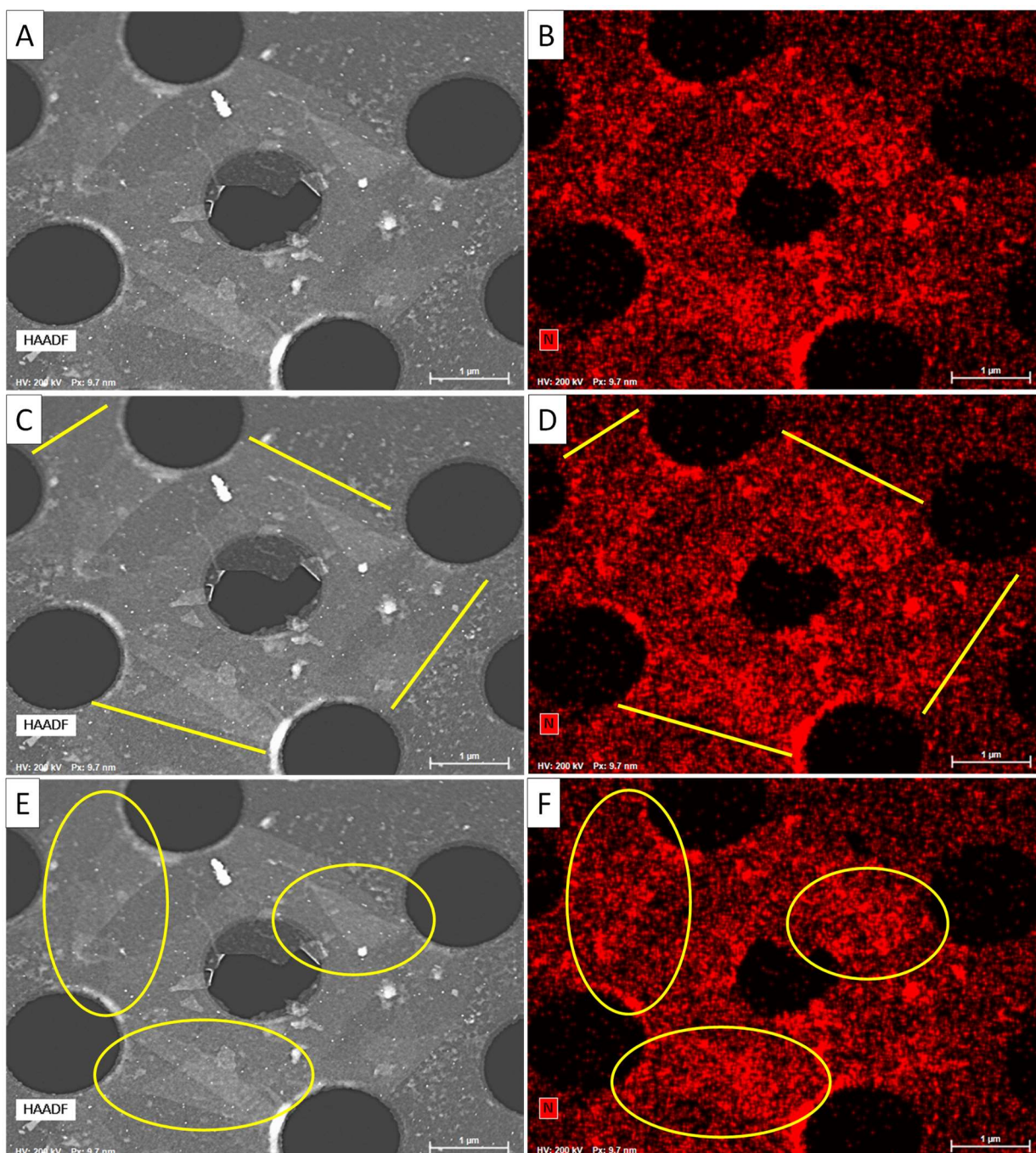


Figure 9. A,B) EDS map of CN at the N-K edge, C→F): highlight of the N-rich areas. The yellow lines /circles are provided as a guide to the eye.

The HAADF micrograph shows the presence of very thin flakes (**Figure 9A**). A comparison between this image (**Figures 9A** and **9C**) and the corresponding N mapping (**Figures 9B** and **9D**) shows a correlation between the shape of the flake and the intensity of the N signal. Moreover, the intensity of this signal increases where thicker flakes are observed (foldings), as evidenced on **Figures 9E** and **9F** (yellow circles). These observations are showing that the flakes are made of a nitrogen-rich material, as expected. This EDS analysis also shows the presence of K and Ca (**Figure S1i→J**), in accordance with EDS, XPS and EELS (see below) analyses.

EELS

An EELS analysis of this material (Figure 10) shows the presence of the expected elements C and N. Ca is also observed as an impurity from the starting metallic potassium. The structure of the C 1s and N 1s edges shows a fine structure that is characteristic of extended π -delocalisation [47], in accordance with the expected structure of CN.

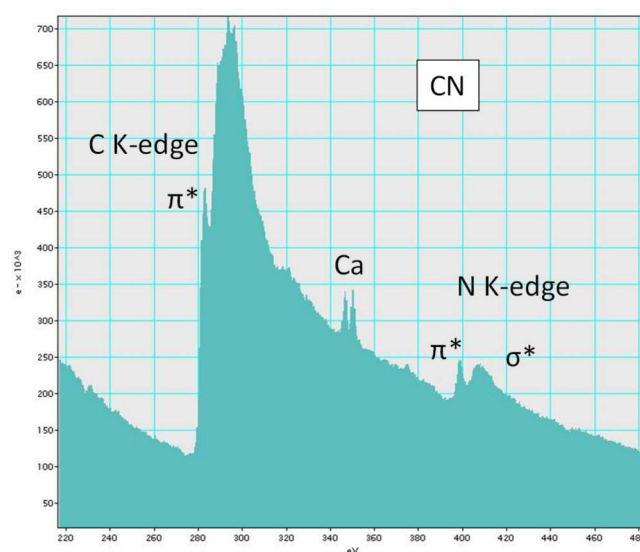


Figure 10. EELS analysis of CN.

All these analyses do show the presence of residual metals (K and Ca) in the material, most probably as cations included inside the coordinating cavities of CN. This may explain the presence of the different signals observed for N 1s by XPS analysis. Indeed, the direct coordination of the N to the positively charged cations probably gives rise to the observed higher energy component.

B) : synthesis of C_2N carbon nitride.

These very encouraging results prompted us to generalise our synthetic strategy. As a second example, we have chosen to synthesise a well documented 2D material, the « C_2N » carbon nitride (Figure 11). Since its discovery in 2015 [48], this material is under the spotlight, due to its tremendous properties in many different fields [49, 50, 51, 52, 53, 54, 55]. Only a handful of synthetic approaches are described so far, all relying on the condensation of complementary carbonyl and amine containing reagents under different conditions [45, 56], or high temperature pyrolysis of organic precursors [57]. In our work, the targeted carbon nitride is obtained by reduction of tetrachloropyrazine using potassium.

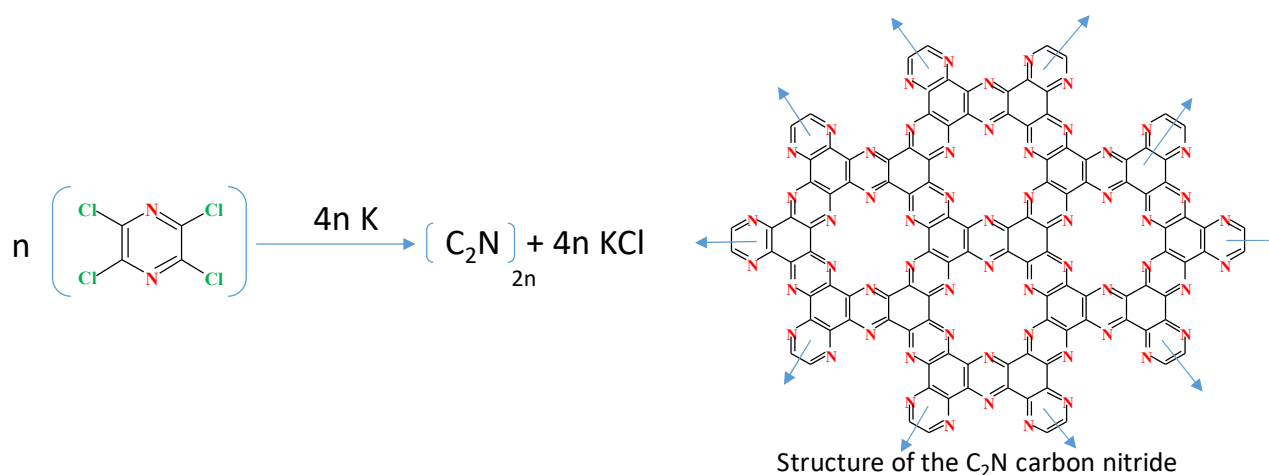


Figure 11. Synthesis of C_2N .

The detailed synthetic procedure is to be found in the Supporting Informations (S2).

Crude material analysis

We first performed an analysis of the crude material, to qualitatively estimate the yield of the synthesis. The reaction media was filtered, and the resulting black solid washed with acetone (see S2A→E). All the organic phases were combined and evaporated to dryness on a vacuum line, leaving a very small amount (50mg) of a dark brown residue. A sample of the solid black material left after filtration was then analysed. An XPS analysis of this crude sample is shown on Figure S2F. It shows the presence of strong potassium signals (Figure S2F-D) as cationic species. Analysis of the corresponding Cl 2p signals (Figure S2F-B) shows the presence of two different kinds of chlorine atoms. The one with the lowest binding energy is characteristic of anionic chlorine, and is thus ascribed to KCl. This is confirmed by the measured 1/1 K/Cl ratio. A second Cl component with a higher binding energy is attributed to organic chlorine (i.e. bonded to carbon atoms). A comparison of the relative areas of these two species (along with the very small amount of soluble material (50mg), see previous paragraph), shows that the yield of the reaction is above 90%.

An analysis of the N 1s signals (Figure S2F-C) reveals two components attributed to pyridinic-type nitrogens [38, 39, 40, 41]. The higher energy one probably belongs to metallic cations-bonded nitrogens. As already mentioned, strong signals of potassium ions (along with a few percent of calcium) are also observed.

Washed sample analysis

The purified C₂N material is obtained as a fluffy, black powder, (Figures 12A and B).

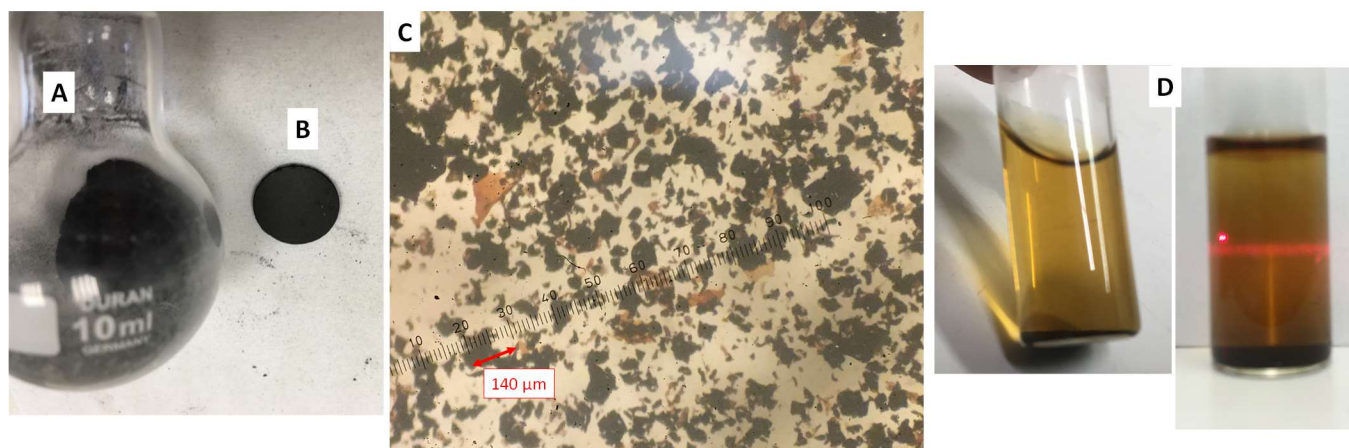


Figure 12: washed C₂N. Optical microscopy (A); (B) same material as a compressed pellet ; C): optical microscopy of an HCl dispersed C₂N sample; D) orange-colored HCl suspension of C₂N showing the Tyndall effect.

An observation of the same material as an acidic (1M HCl) water suspension shows it to be constituted of large, variously aggregated and folded flakes, with sizes ranging from a few tens to 300 μm (Figures 12C and 12D). The color of the thinnest flakes appears as deep orange, rapidly turning to black with increasing thickness (S2j). The bright orange color of acidic C₂N suspensions confirms that a significant amount of the material is made of single/few layers flakes (Figure 12E). In some instances, tubular (S2H) or shell-shaped objects (S2i) were also observed. In the later case, this is likely to be the result of a molding of melted potassium droplets, getting encapsulated during the growth of C₂N around them.

Interestingly, we also found that some flakes (thin enough and not too folded/crumpled) do rotate the polarisation plane of incident polarised light, as expected for single crystals. One example is shown on Figure 13. Other examples are provided in the SI (Figures S2K→S2M). The flakes (after washings) were dried on a glass plate overnight and diluted in dispersion oil to ease their observation and handling.

These extremely thin flakes are nearly invisible (even with the microscope). They can only be detected due to their changing brightness under polarized light. As the flakes get thicker, the effect disappears, probably due to: i) the absence of correlation of the orientation of the layers inside thick flakes, ii) their increasing absorbance and iii) the presence of foldings, that tend to average the effect on polarised light (see Figure 4). Note that the observation of single layer graphene using polarised light has already been reported [58, 59].



Figure 13: polarised light study of thin C₂N 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.

Infrared spectroscopy

The IR spectra of C₂N was compared with two reference compounds: starting tetrachloropyrazine on the one hand, and the building unit pyrazine on the other hand (Figure S2N). As observed for CN, the absence of C-H peaks for C₂N rules out the presence of: 1) structural defaults resulting from overreductions, and 2) significant amounts of contaminating species.

Second, signals attributed to characteristic vibrational modes of the pyrazine ring are observed (stretching C=C and C=N along ring deformation), confirming the proposed structure of C₂N [45] (Figure S2NA). As observed for CN, signals are also observed around 2100 cm⁻¹. These peaks may correspond to protonated, pyridinium-nitrogens, that are usually observed in this wavenumber area [46].

The IR spectrum of the starting tetrachloropyrazine shows a very strong C-Cl peak at 655 cm⁻¹, absent in C₂N (Figure S2NB). This confirms the success of the assembly reaction and reinforces the conclusions drawn from XPS analysis (see below), regarding the absence of chlorine in our material.

XRD.

A compared XRD analysis of a crude and washed C₂N sample was performed. The results are shown on Figure 14.

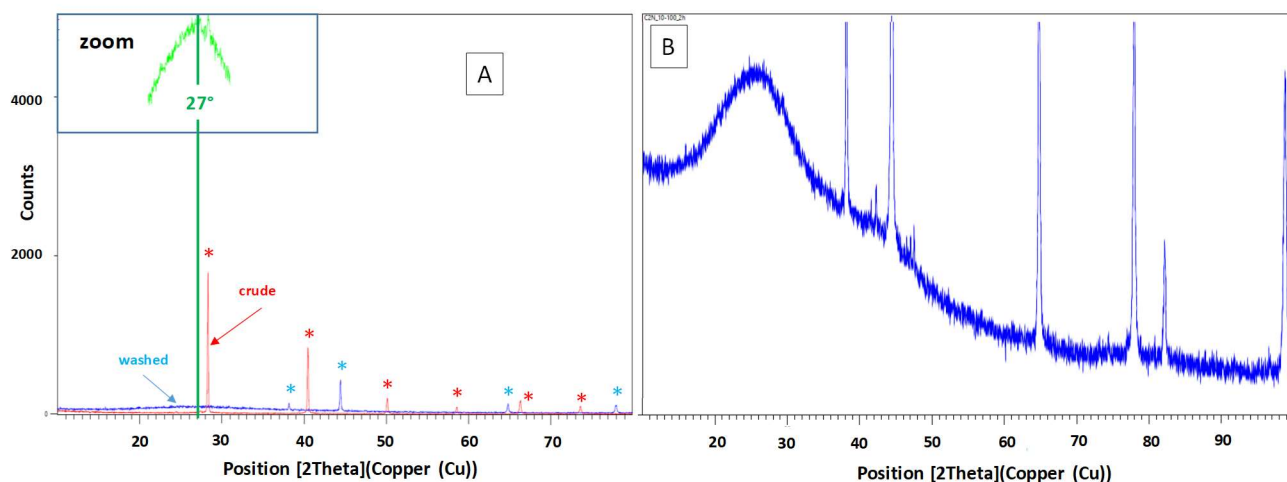


Figure 14: A) compared powder X-ray diffractograms of a crude (red) and washed (blue) C₂N samples (same batch). Insert (green): zoom over the blue curve. Blue stars : signals from the aluminum sample holder ; red stars : signals from KCl by-product. B) : Powder x-ray diffractogram of the washed C₂N sample. Black stars : signals from the aluminum sample holder.

The same trends as the ones observed with CN are evidenced. The crude sample (Figure 14A, red) only shows signals from the KCl by-product. However, the same sample shows a broad peak, centered at 27° (Figure 14A, insert) after washings (Figure 14A, blue). This signal was absent from the crude sample. Once again, it can thus be concluded that i) the flakes mostly exist as individual/few layers objects in the crude material, getting aggregated during washings, and ii) they are thus likely to grow individually during the synthesis.

Figure 14B shows the powder X-ray analysis of the washed sample. The presence of the peak around $2\theta=27^\circ$ shows that the material has a layered structure. The broadness of the peak evidences an irregular spacing between the sheets. Indeed, as the sheets get aggregated during washing, some foldings and/or inclusion of residual solvents occurs between the layers, resulting in a broad distribution of interplane spacings. A shoulder around $2\theta=40$ degrees corresponds to the in-plane signal [46, 52].

XPS

The composition of washed samples was assessed by XPS analysis (Figure 15). A survey shows the presence of the expected elements, C and N. A prominent peak of oxygen is also observed. It may be due to the presence of trapped oxygen-containing species, a commonly observed feature with this type of material [43, 46, 51, 52].

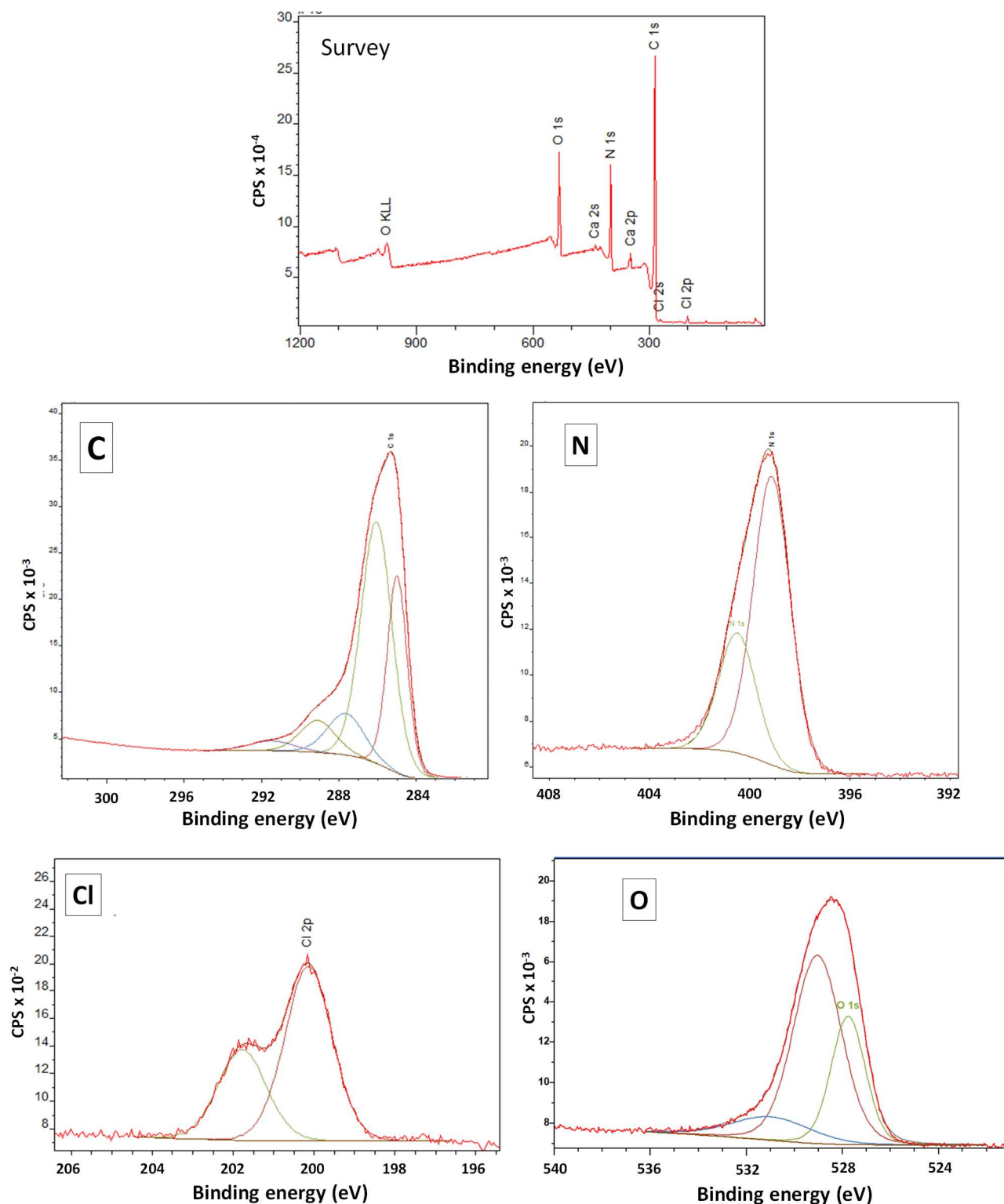


Figure 15 : XPS analysis of a washed C₂N sample.

The deconvolution of the C 1s peak shows two main components, at 285,9 eV (C=N) and 284,9 eV (C-C). This later peak, ubiquitous, may originate from contamination. The former one is associated with the C=N bonds of the 2D framework. Minor peaks at higher binding energies are from C=O containing adsorbed contamination, commonly encountered in XPS analyses. These may also originate from the interaction between N and included species (protons, as the material was washed with HCl, or remaining metallic cations), in line with the observed features of the N 1s signals. Indeed, the

corresponding electron-withdrawing influence may affect as well the adjacent N-bonded carbon atoms (see below).

Regarding the N 1s signal, it may be deconvoluted in two components, at 399.12 and 400.46 eV. The first one is attributed to pyridinic-type N, commonly observed between 398 and 399 eV, as discussed in the previous paragraph. [42-45]. Indeed, our synthesis does not involve any kind of NH₂ -type species (that appear in the same binding energy range), thus ruling out this possible attribution. Moreover, the dark black appearance of our material excludes any kind of reduction reaction (that could result in the formation of N-H or C-H species), that would break the conjugation of the network, rendering the material colorless. IR spectroscopy also rules out this possibility (see above discussion (infrared spectroscopy »). Moreover, tetrachloropyrazine was introduced in close to stoichiometric amount vs. potassium. It thus excludes a possible overreduction of the C₂N backbone to N-H containing species, as this would need significant amounts of excess metal. Moreover, as the post-synthesis workup was done under ambient conditions, such adventitious reduced species would have been re-oxidized to the main C=N ones (especially under the acidic conditions used for the redispersion of the material).

The High energy component (400.46 eV) may be attributed at first sight to residual tetrachloropyrazine. However, this interpretation is ruled out, as the amount of remaining C-Cl in the product is very low (Figure 15, survey). The first interpretation also seems unlikely, as these by-products are recovered in the supernatant and the corresponding amount of materials was found to be very low. This high energy component is better attributed to the interaction of pyridinic nitrogens with included, remaining metallic cations or hydrogen-bonded impurities that appeared during post-synthesis workup. Indeed, it was shown that the exact value of the position of the N 1s peak is strongly dependant on the environment of the corresponding nitrogens [42-45]. This last interpretation is in line with the presence of oxygenated species (Figure 15, O1s analysis) and remaining potassium and calcium. The C/N ratio is 3, higher than the expected value of 2. This may be ascribed to commonly observed carbon contamination of the sample. As said before, traces of chlorine are also observed (Figure 15), with binding energies associated with C-bonded chlorine. This confirms the very small amount of defaults lefts in the flakes, as only a very small amount of unreacted pyrazinic C-Cl bonds are present in the material.

SEM/EDS

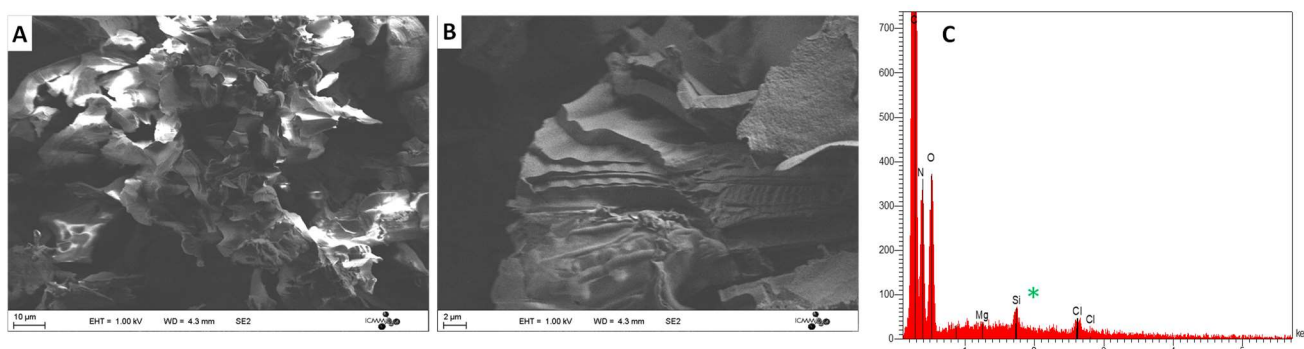


Figure 16: SEM imaging (A and B) and EDS analysis (C) of a C₂N sample (after washings). Green star: artifact from the substrate

SEM observation of an as-prepared sample (Figure 16) shows the presence of large flakes (>10µm). Their layered structure after washing and drying is in accordance with the expected one for C₂N [48]. EDS (figure 16C) shows the presence of the expected elements, along with SiO₂ from the substrate. **TEM.**

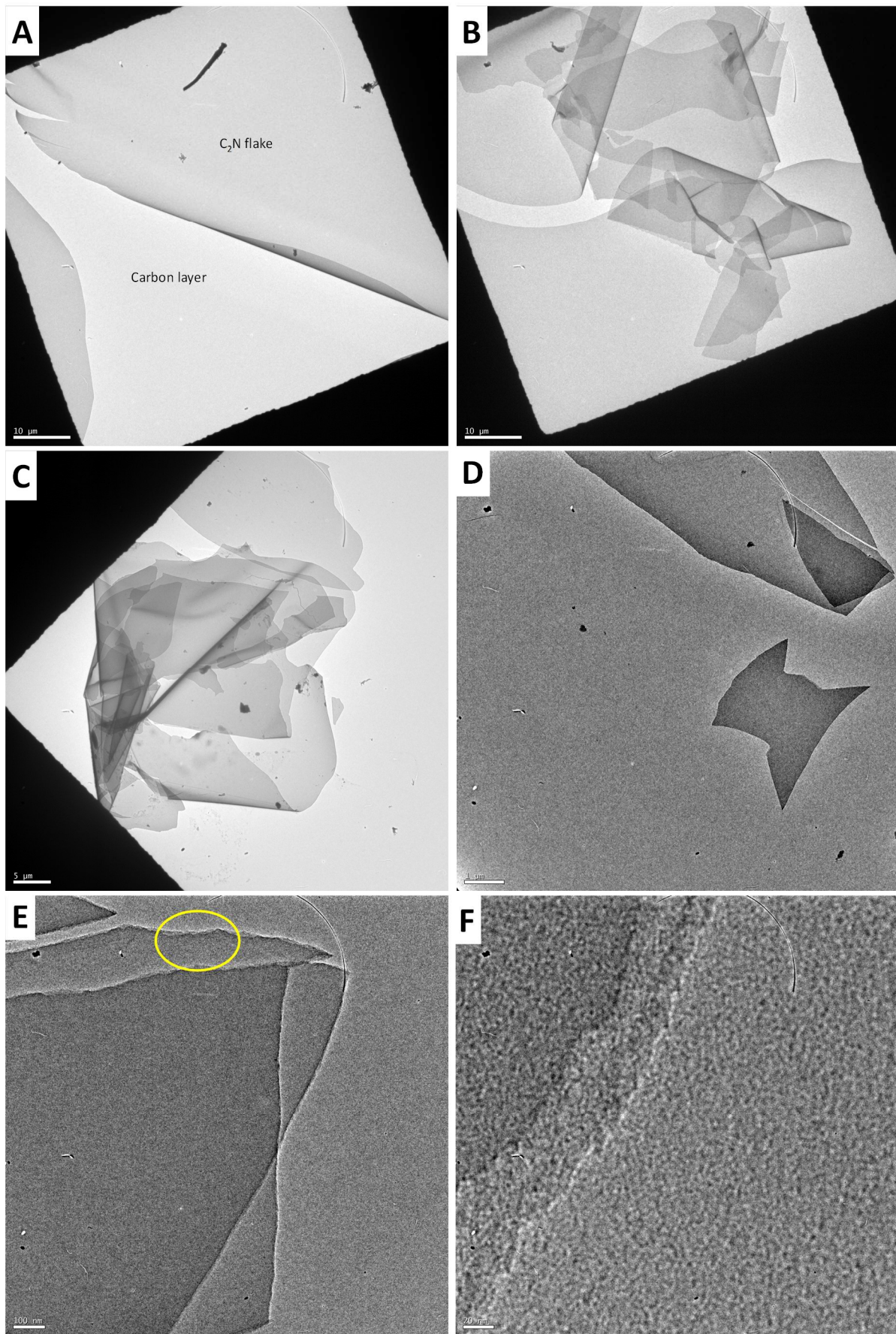


Figure 17 : A→F: TEM analysis of a C_2N sample at increasing magnifications.

Extensive TEM analyses were performed with washed samples. Different solvents were tested to optimise the dispersions (see supporting informations, Figure S2G). Figure 17A shows a typical image of a C₂N sample, washed according to the following sequence : 1) acetone, 2) water ; 3) HCl (see S2). HCl was shown to be the best choice for the redispersion of the different materials, in accordance with previous observations [60]. The images on Figure 17 are shown at increasingly high magnifications, to assess the quality of the flakes over different scales. Very large and smooth flakes are observed, with sizes exceeding 100 μm (Figures 17A and B, others micrographs of HCl-dispersed samples are provided in S2G-c). Some flakes are so large that they were first misinterpreted as broken carbon films from the TEM grid. However, a detailed analysis of the micrographs showed that: i) some typical features of carbon grids next to the flakes are still observed, and ii) the contrasts next to different flakes on different squares were found similar, thus proving that the carbon film was still present. The flakes are rather thin, being quite transparent to the e-beam. A detailed observation of the edges of these flakes shows that they're made of few layers. (Figures 17E and F yellow circle). These flakes appear as defects-free over very large areas (even at high magnifications, (Figures 17D→F)), assessing their structural quality. In some cases, these flakes were found to roll, forming tubular structures reminiscent of carbon nanotubes (Figure S2H).

The obtained C₂N material thus exhibits similar characteristics compared with the ones of the previously described CN.

A detailed observation of the edges of the flakes (Figure 18A, yellow circle) shows a regular pattern (Figure 18B, zoom Figure 18C), exhibiting a characteristic distance around 0.5 nm (Figure 18C). Note that this pattern is observed all the edge of the flake long (Figure 18B).

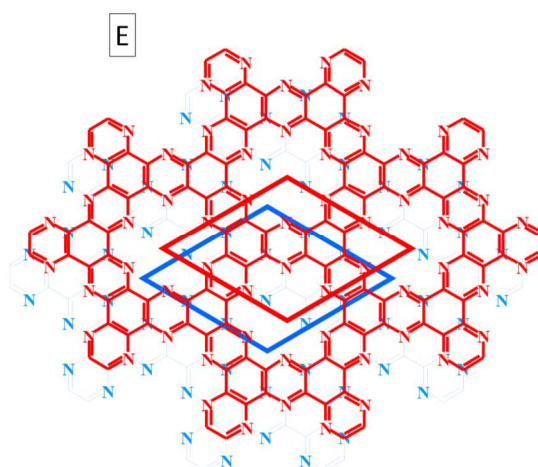
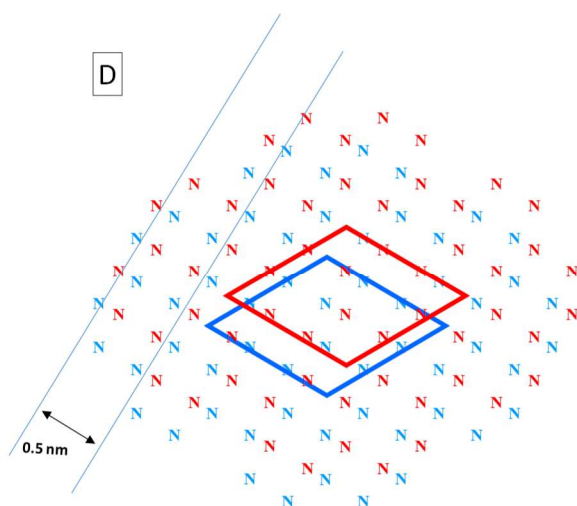
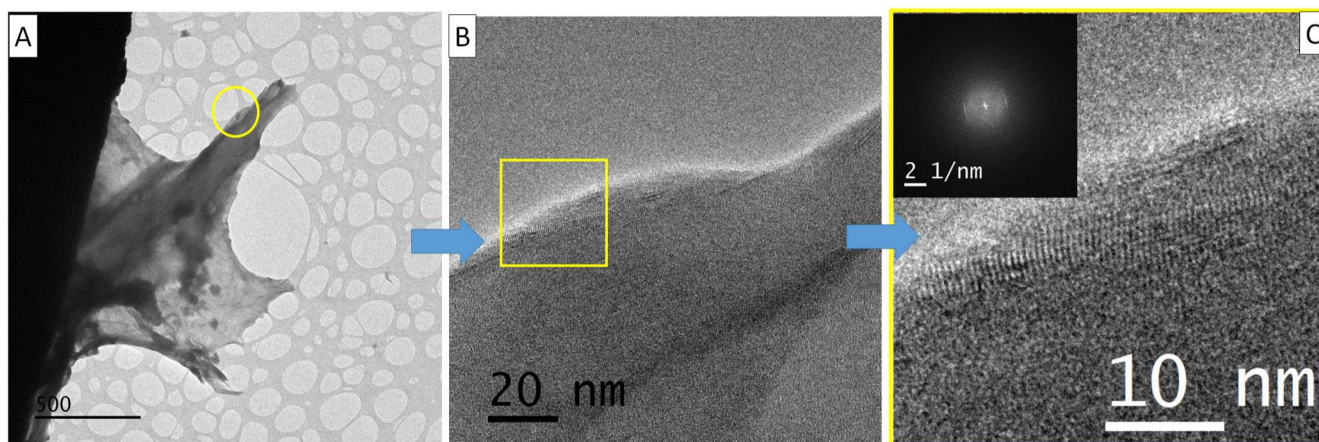


Figure 18 : TEM analysis of a C₂N flake showing a moiré effect. A) the observed flake; B) zoom over the yellow circle figure A; C) zoom over the yellow square Figure B (insert: FFT of the image); D) two stacked C₂N layers (blue and red, only nitrogen atoms shown for clarity, unit cells of the two stacked layers shown as rhombus) exhibiting the observed 0.5 nm distance.

This pattern is attributed to a moiré effect between few superimposed layers. One possibility is exemplified on **Figure 18D**, with two superimposed layers with an AB type stacking. This moiré effect evidences the crystallinity of the whole flake, as there's no reason for it to be more crystalline at its edges. Note that the material degraded very rapidly under the influence of the e-beam. Such an instability of 2D materials under TEM analyses is well documented in literature [61]. **Figure 18E** details the observed stacking mode. Note that it appears quite similar to the one expected from simulations [62].

We were not able to get convincing electron diffractions patterns from this material. This may be due to the previously mentioned instability of the material under electron irradiation. In some instances, clear diffraction patterns were observed (one example **Figure S2N**). However, these were finally considered as artifacts as i) the characteristic distance associated with the [100] plane was not observed, and ii) the brightness of the spots was too high to be associated with few layers flake. These artifacts may be due to remaining inorganics trapped inside the material. Great care should thus be taken while analysing the SAED of layered 2D materials.

EELS

An EELS analysis of a C₂N thin flake is shown on **Figure 19**. The presence of nitrogen is only observed on the flake (**Figure 19B**), not on the carbon grid (**Figure 19A**). C₂N appears as oxygen-free (**Figure 19C**). This confirms that the oxygen signals observed by XPS analysis are probably due to contamination, or to adventitious oxygen-containing species trapped between aggregated flakes. The near edge structures observed for the C and N signals confirms that these elements are sp² hybridized in the material [63].

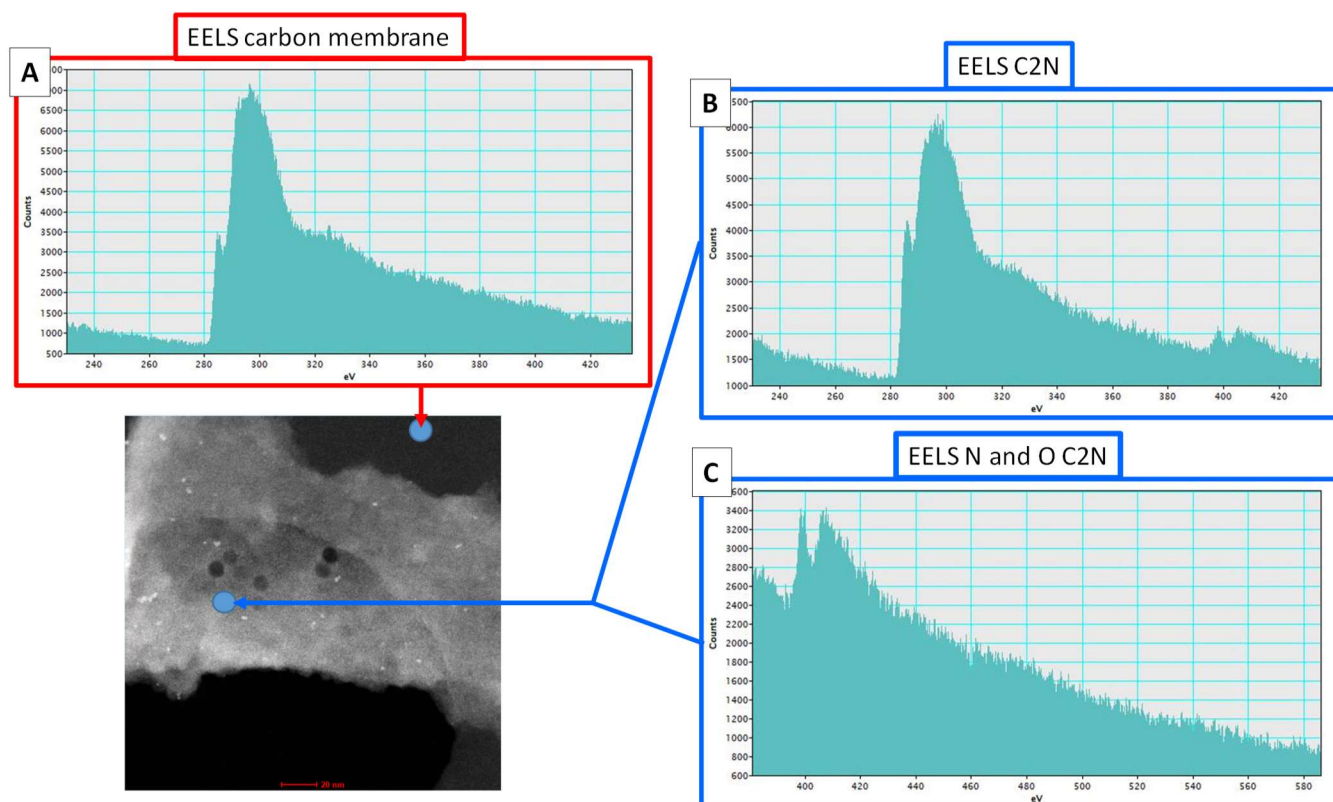


Figure 19 EELS analysis of a single C₂N flake suspended on holey carbon grid. A): carbon grid analysis, B) and C): C₂N sample. The regular, circular holes observed on the sample are due to electron-beam-induced damages.

C) : synthesis of a triazine-based COF

The potassium-promoted reduction of polyhalogenated aromatic building blocks thus appears as a very efficient tool for 2D materials synthesis. We then decided to further expand the scope of this process through a third example, sketched on **Figure 20**. This material belongs to the so-called Covalent Triazine Frameworks (CTF) family. These materials are indeed receiving an ever increasing interest, due to their interesting properties for example in the field of photocatalysis [64 65 66].

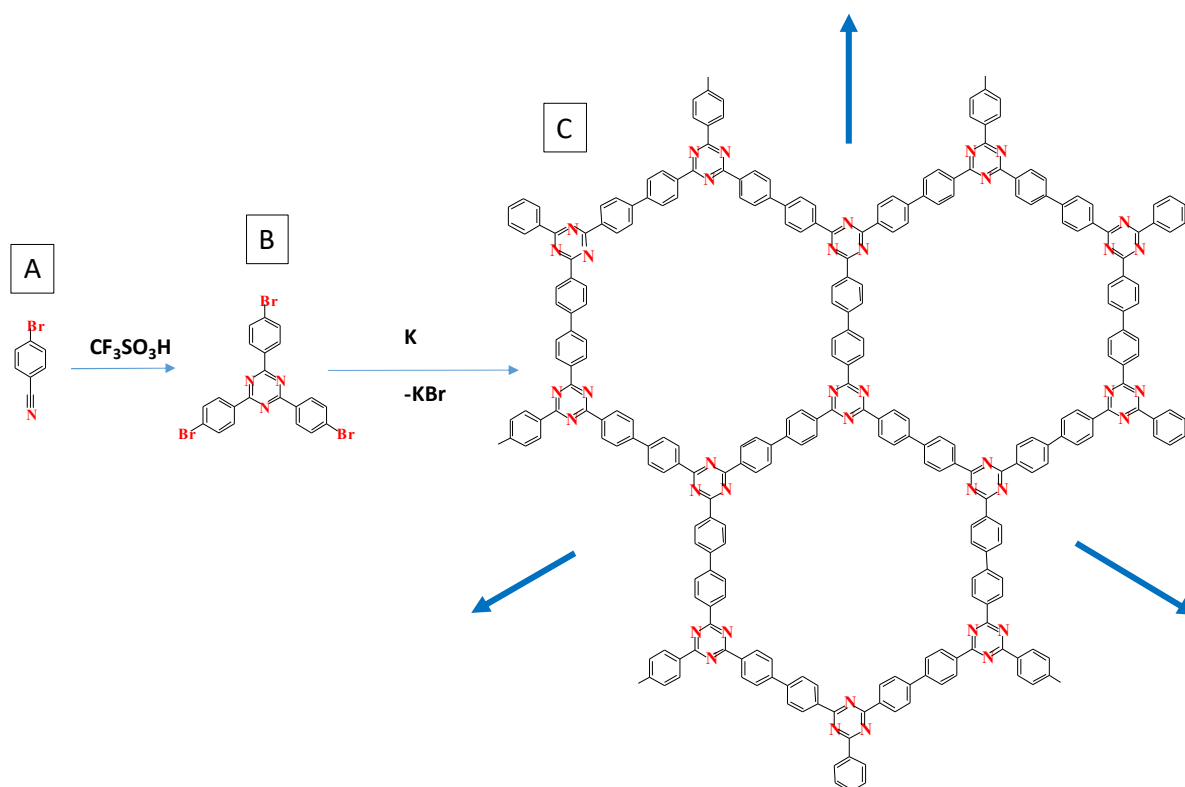


Figure 20: Synthesis of 2D material by reduction of a polyhalogenated triazine derivative.

The starting tris(bromophenyl) triazine **B** was synthesised by acid-promoted trimerisation of 4-(bromo)benzonitrile **A** [67]. The synthesis/purification of CTF-2D material is detailed in the Supporting Informations (S3).

Interestingly, a detailed observation of the surface of the solid material during the reaction (S3A→E) shows that it grows in a bark-tree like fashion (S3F, orange circle), along with KBr scales (S3F, yellow circles), both visible with the naked eye. This concomitant formation of layered KBr / CTF (see below) strongly supports our initial assumption that the inorganic by-product (KBr in this case) is likely to favor the confined growth of 2D materials.

Optical microscopy

The CTF material is obtained as a green-brown powder after drying, washing with dichloromethane and water (Figure 21A).

An observation of this material (as a water suspension) by optical microscopy shows it to be made of very large, thin flakes, with sizes ranging from a few μm to 500 μm (Figure 21B). More images are provided in the Supporting Informations (S3G→i). The characteristic features of 2D materials (such as foldings) are easily observed (Figure 21C, center image). The flakes appear as nearly transparent, evidencing their small thickness and large bandgap. Their yellow-green color is quite similar to the one observed using a different synthesis of this material [59]. Needle-like crystals of the starting material are sometimes observed (Figure 21C, yellow circle), as this starting tris(bromophenyl)triazine is highly insoluble and difficult to remove completely.

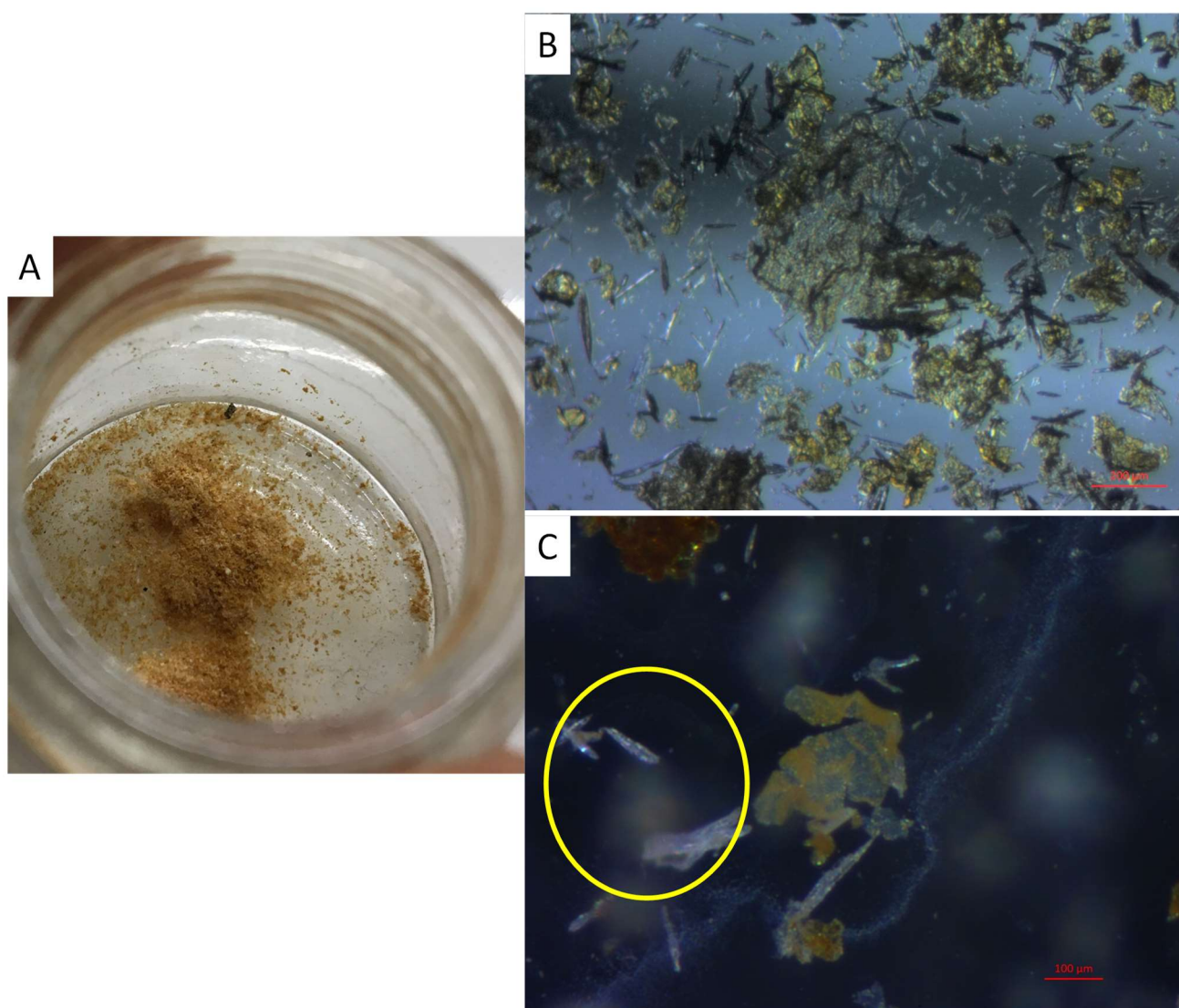


Figure 21: A) crude CTF 2D material ; B) and C) optical microscopy of CTF 2D material, yellow: starting product.

As for the previously described materials, we also found that some flakes (thin enough and not too crumpled), suspended in dispersion oil do rotate the polarisation plane of incident polarised light, as expected for single crystals. One example is shown on Figure 22. Another example is shown on S3M. These extremely thin flakes are nearly invisible (even with the microscope). They can only be detected due to their changing brightness under polarized light.

Note that the observation of other 2D materials such as single layer graphene using polarised light has already been reported [53, 54].



Figure 22: polarised light study of a thin CTF 2D flake (yellow circle). 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.

Infrared spectroscopy

An IR spectra of CTF is provided in the Supporting Informations, and compared with a reference one of the starting tribromotriazine derivative (Figure SXX). The signals attributed to the characteristic vibrational modes of the triazine and phenyl rings are observed (stretching C=C and C=N and ring deformation), in the same wavenumber range compared with the starting product. This confirms the proposed structure of CTF.

Another interesting feature is the complete disappearance of the strong signal at 540 cm^{-1} , attributed to the C-Br bond, on going from tribromotriazine to CTF. It confirms the occurrence of the expected coupling reaction, and thus the structure of the product. It also confirms the conclusions drawn from XPS experiments.

SEM

Figure 23 shows an SEM image of CTF-2D material. The presence of large, folded flakes is clearly evidenced. An EDS analysis of such a flake shows the presence of C, N and oxygen-containing contamination (Figure 23). Note that the N signal is absent from the carbon substrate used for this experiment (Figure 23A). The low relative intensity of the N signal is ascribed to i) the low intrinsic relative amount of carbon in the material ($C/N_{\text{theo}}=7$), and ii) the presence of the underlying carbon substrate.

In the same way, an EDS analysis of the needle-shaped objects sometimes observed with the CTF flakes shows the presence of bromine along with C, N and O. This confirms the attribution of these needle-shaped objects to the starting product (S3i). A comparison between the EDS analyses of CTF-2D material and the starting product shows that the relative C/N ration is close in both cases, as expected.

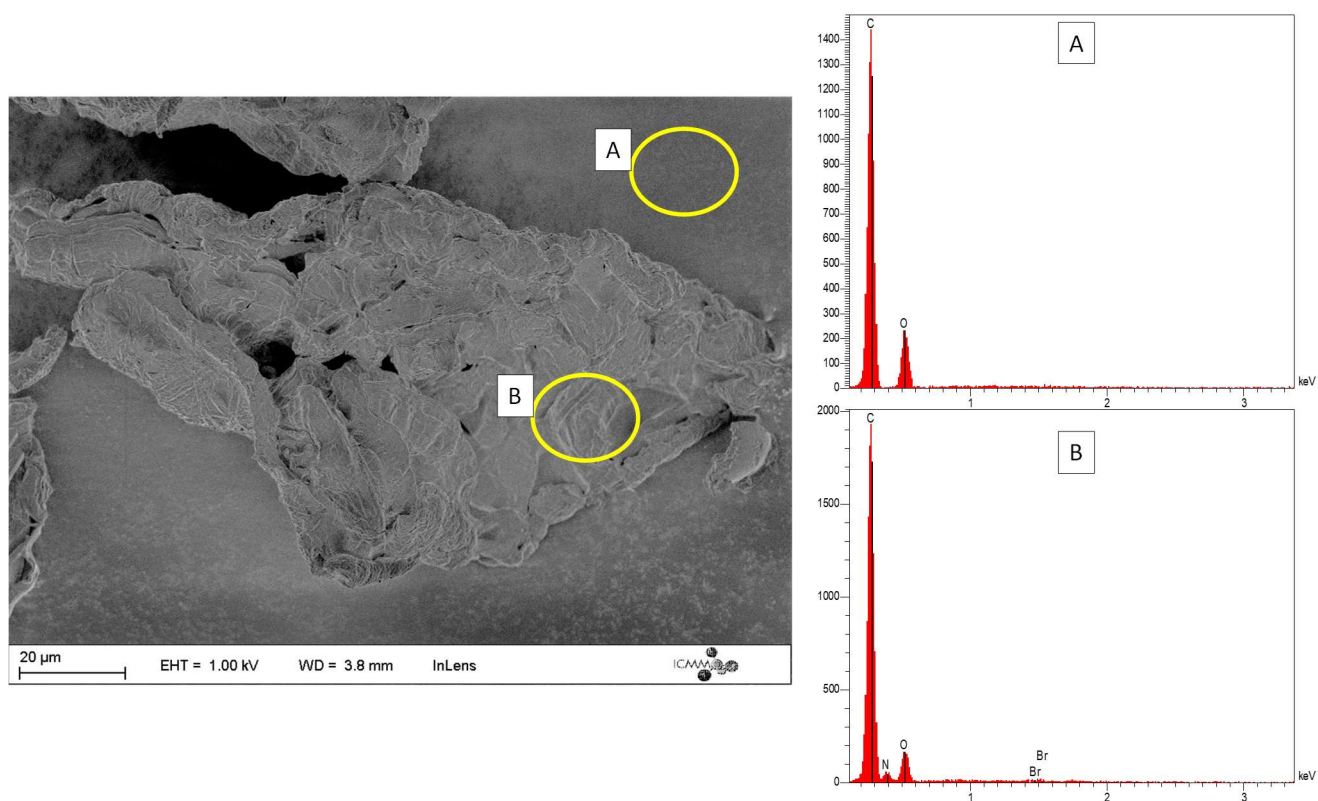


Figure 23: SEMM/EDS analysis of CTF-2D material. A) carbon substrate, B) CTF.

TEM

Figure 24 shows a TEM analysis of the CTF 2D material. As for the two previous materials, the images are shown at increasingly high magnifications, to assess the quality of the flakes over different scales. It confirms CTF material to be made of very thin and large flakes, with length sometimes exceeding 100 μm (**Figures 24A** and **B**). The flakes appear as very homogeneous and seemingly defect-free, even at large magnifications (**Figures 24C** and **D**). In a few places, some contamination by what seems to be needle-shaped crystals of the starting product are however observed (**Figures 24E** and **F**), in accordance with optical (**Figure 21C**) and EDS (**S3i**) observations.

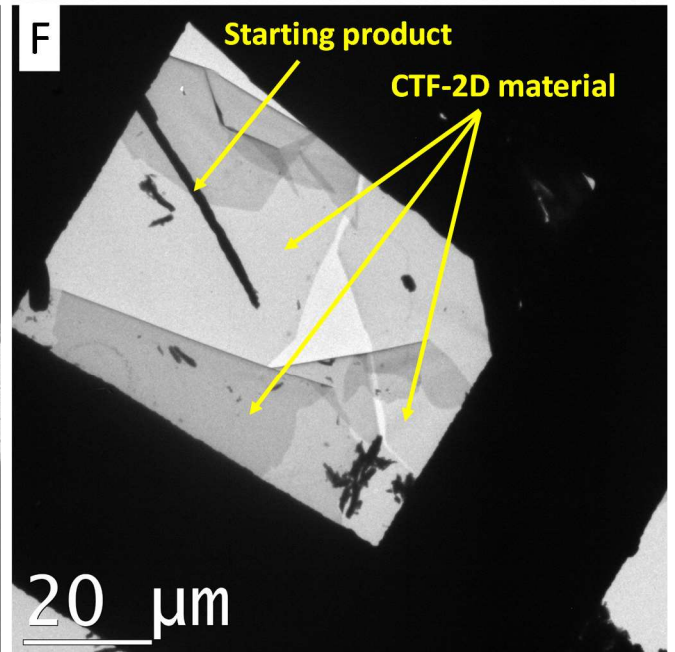
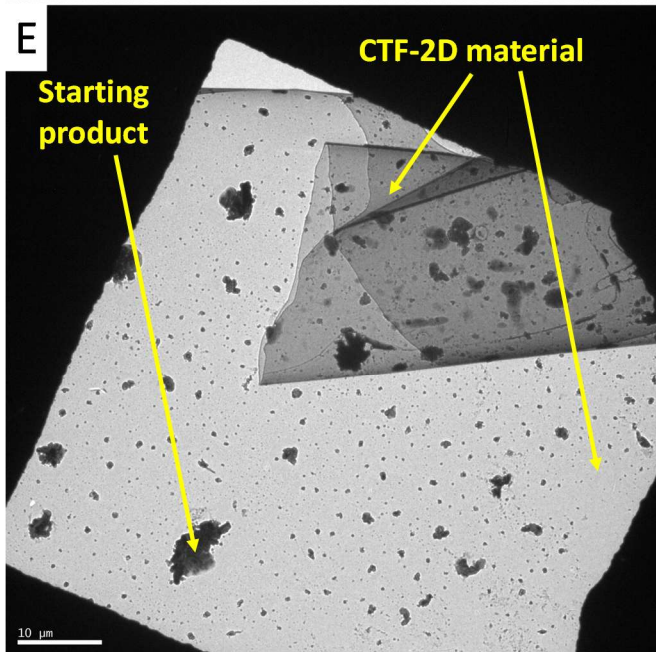
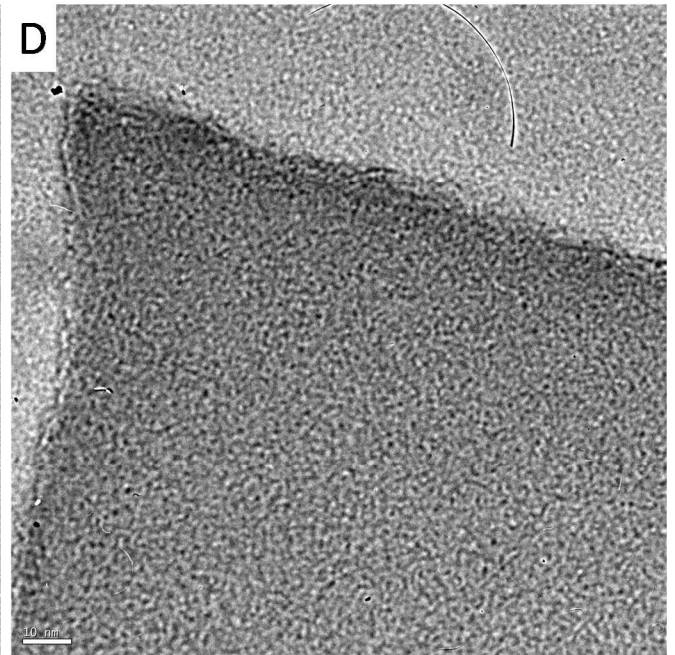
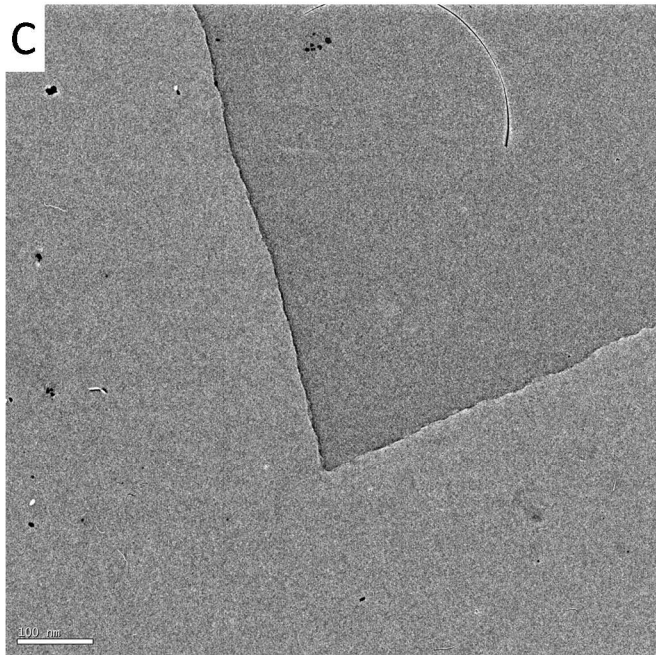
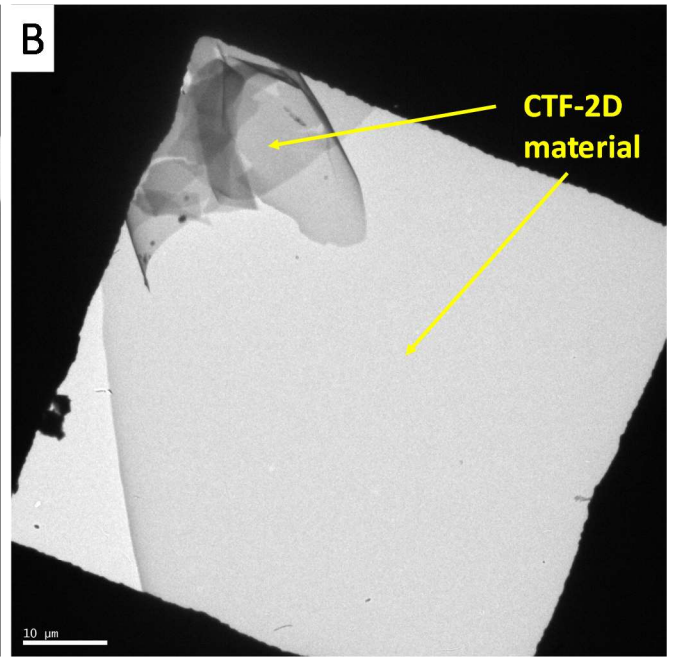
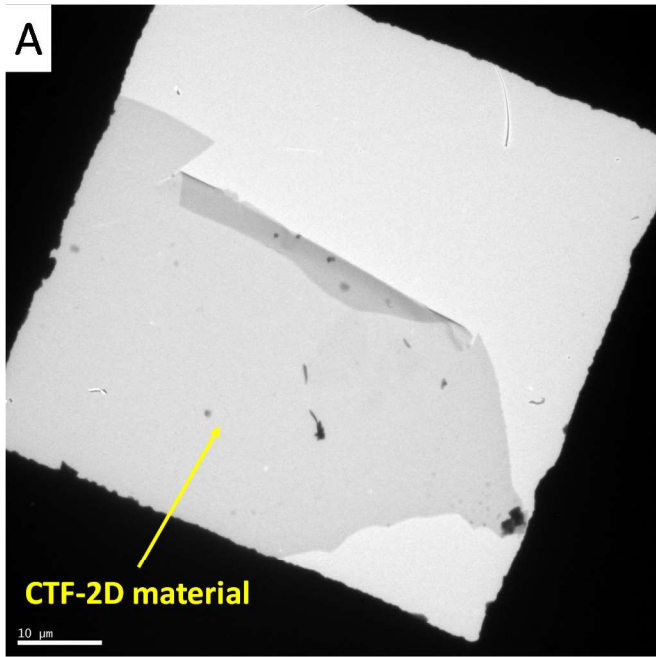


Figure 24: A→F: TEM analysis of CTF-2D material at increasing magnifications.

Some rare, highly folded CTF flakes were sometimes observed. A careful examination of the corresponding high resolution TEM micrograph (one example [Figure S3j](#)) over foldings allows to get a rough estimate of the thickness of the flakes. The obtained values fall between 1.5 and 3 nm, corresponding to 5 to 10 2D layers.

Some rare tube-shaped object were also observed ([Figure S3k](#)), reminiscent of a bamboo-like growth of carbon nanotubes [\[68\]](#). This may be due to a molding of potassium droplets during the growth

[Figure 25B](#) shows the SAED pattern obtained from the flake shown on [Figure 25A](#). This pattern shows the characteristic distance of 2.2 nm expected for the [100] plane of TPTZ. In the same way, a distance of 6 angströms along the z axis is observed (corresponding to the thickness of two conjugated layers) indicative of an AB type stacking.

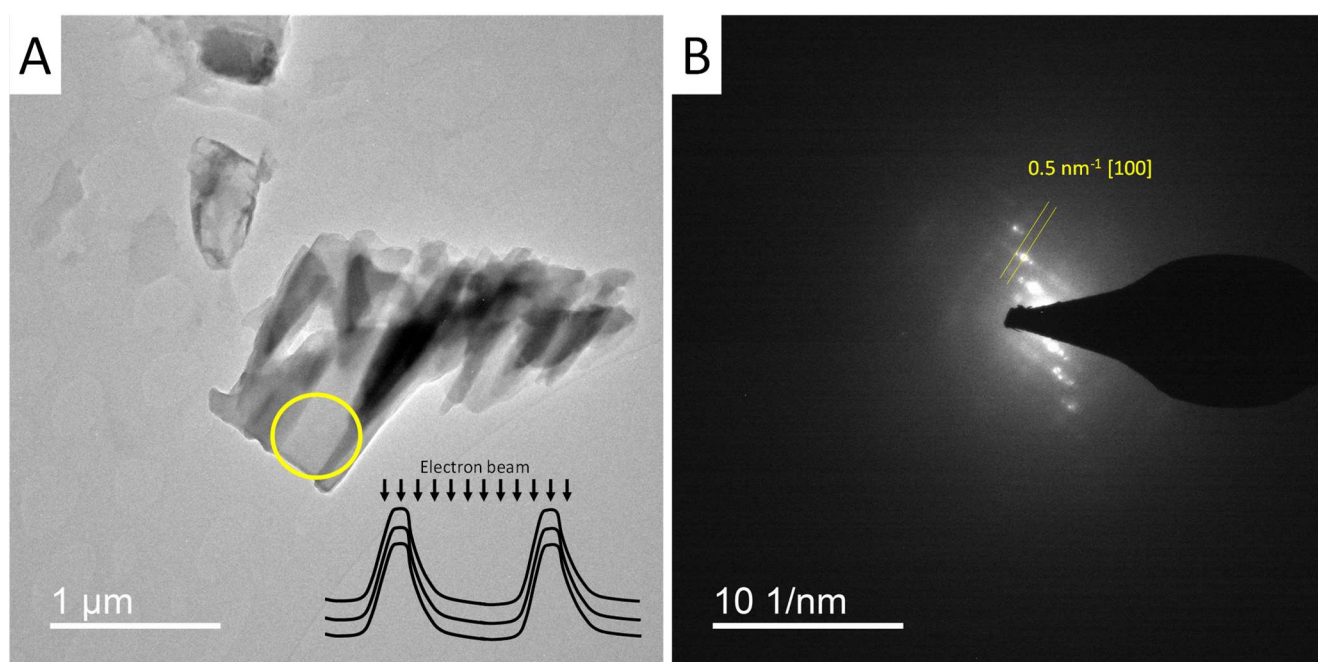


Figure 25: A) TEM analysis of CTF-2D material. Yellow circle: SAED analysed area. Insert: model of the analysed area; B) corresponding SAED analysis.

Such a pattern is observed during SAED analyses of 2D materials where several crystalline, stacked layers are parallel to the incident electron beam ([Figure 25A](#), insert) [\[69\]](#). It was not possible to observe diffraction on flat-lying sheets, presumably due to their small thickness and the very porous structure of CTF-2D layers. It is likely that in the present case, the observed pattern [Figure 25B](#) originates from the folded sides of the studied area ([Figure 25A](#), insert). This experiment confirms that the CTF flakes are crystalline.

Note that (as for the two previous 2D materials) artifacts were commonly observed during SAED experiments (some examples [Figure S3l](#)). They were finally discarded after careful analyses, as the characteristic distances expected for the [100] plane were never observed. These artifacts may originate from trapped inorganic salt, or remaining starting product.

XPS

[Figure 26](#) shows an XPS analysis of CTF-2D material. It shows the presence of strong signals from oxygen and silicon (with a relative O/Si intensity=2), from the silicon wafer used as the substrate for

the analysis. All the expected elements are observed, essentially carbon and nitrogen, with a relative C/N intensity of 12, the expected value being 7. This excess carbon is likely to be due to commonly encountered contamination. Only traces of bromine are observed, from remaining, unreacted starting product.

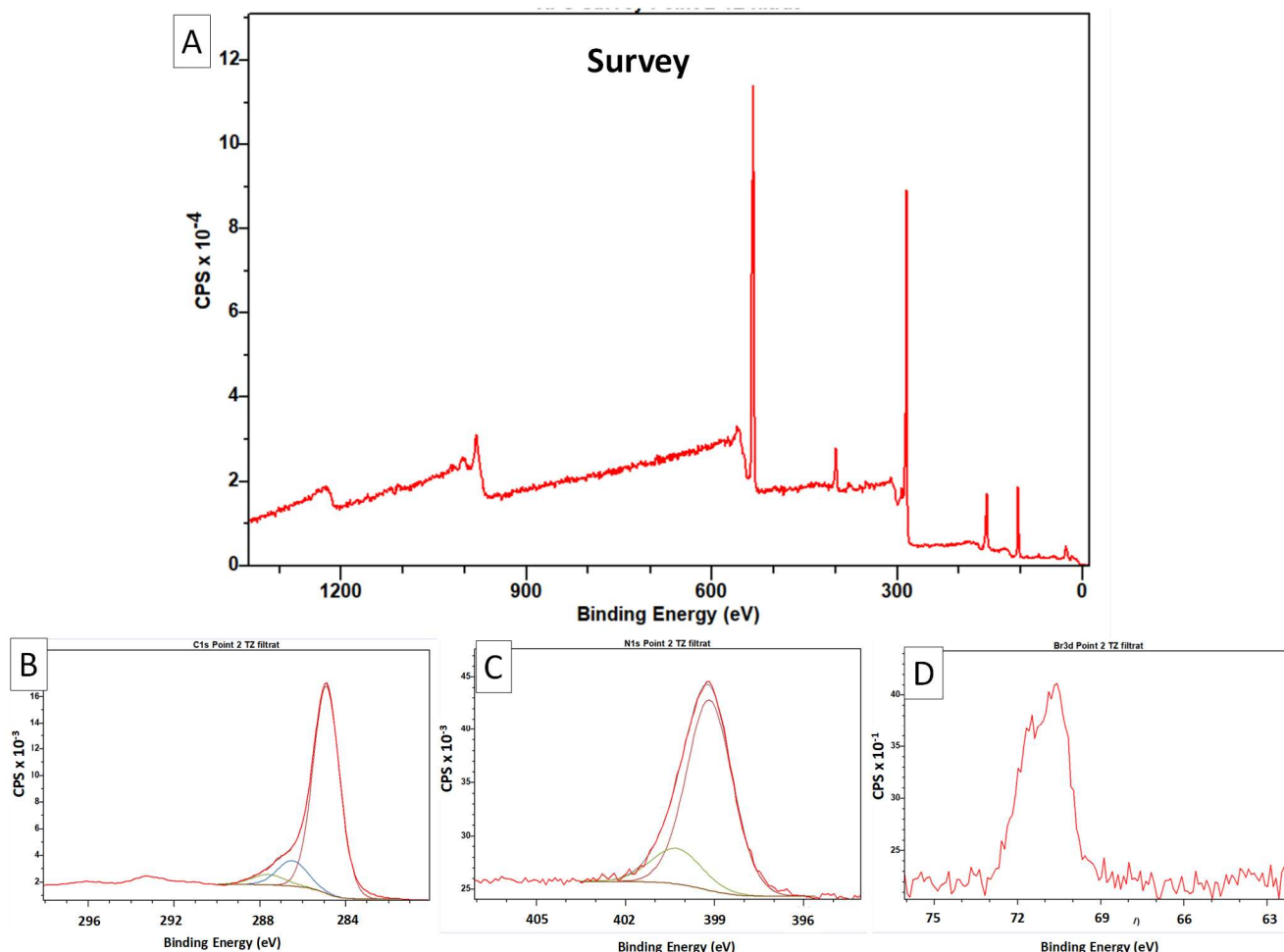


Figure 26: XPS analysis of CTF-2D material. A) : survey ; B) C) and D) C1s, N1s and Br3d respectively

D) Synthesis of C₂N using mercury/potassium amalgam

In line with the « double confinement » strategy, the synthesis of the C₂N carbon nitride (Figure 11) was also realised using another kind of reactive metal interface, the mercury/potassium amalgam. Indeed, the propensity of mercury to form liquid alloys with many metals, including alkaline ones is well known. We reasoned that under these conditions, the metallic interface should be more stable, as mercury itself is not reactive towards tetrachloropyrazine. This could in turn favor the formation of even higher quality 2D layers. Moreover, the liquid nature of the mercury/potassium amalgam should allow for a continuous supply of metallic potassium to the organic solvent/metal interface thus compensating for its consumption during the formation of the C₂N 2D network. Last, the inorganic by-product (KCl) is completely insoluble in the solvent used for the reaction (toluene), thus increasing the confinement effect. The details of the process are to be found in the Supporting Informations (S4A).

The initially shiny mercury interface rapidly gets covered with an orange-greenish deposit (S4A). The amalgam is removed using a pipette, and the supernating solid is washed with ethanol and water. The material is obtained as a light brown/orange powder, with many orange scales easily visible with the naked eye (Figure 27, yellow circles).

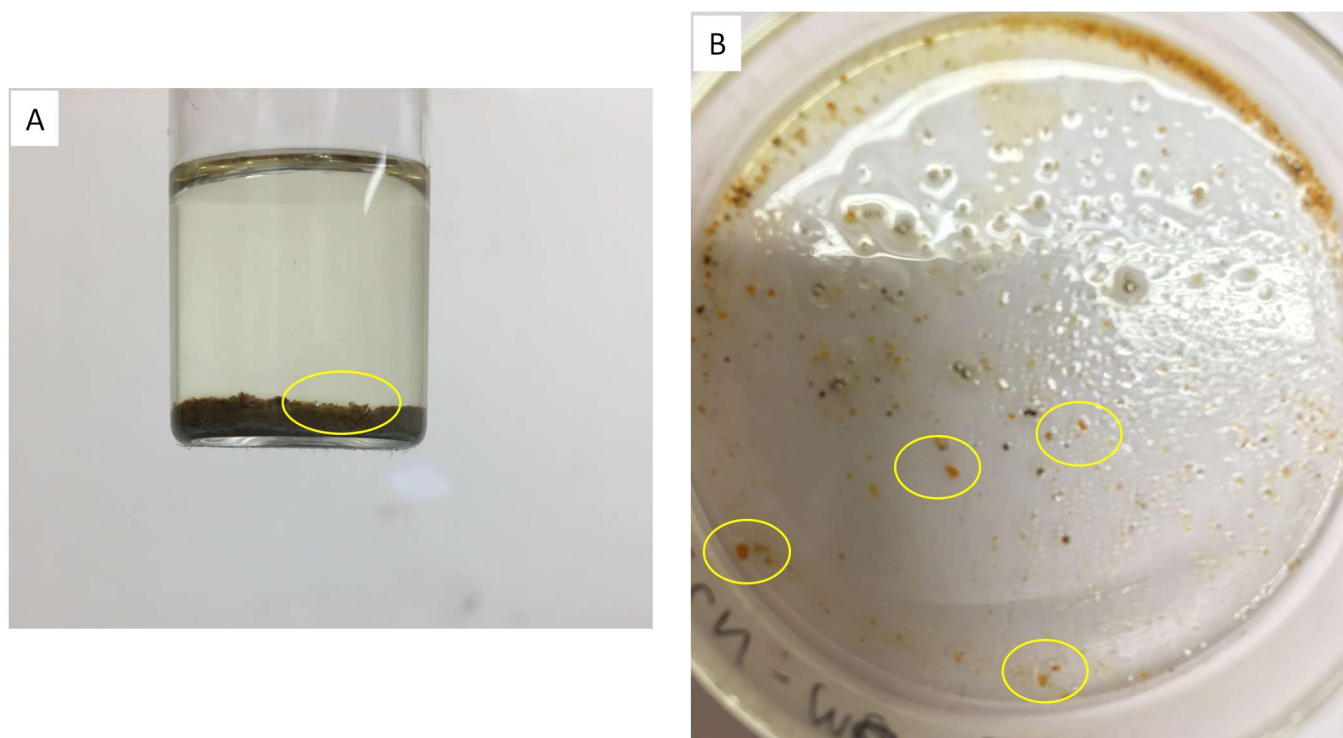


Figure 27: Hg/K-based synthesis of C_2N material. A) crude product, B) after spreading of a droplet of the previous material.

Optical microscopy analysis

Figure 28 shows an optical microscopy analysis of this material (as an EtOH/HCl suspension). Others images are provided in the SI (S4B).

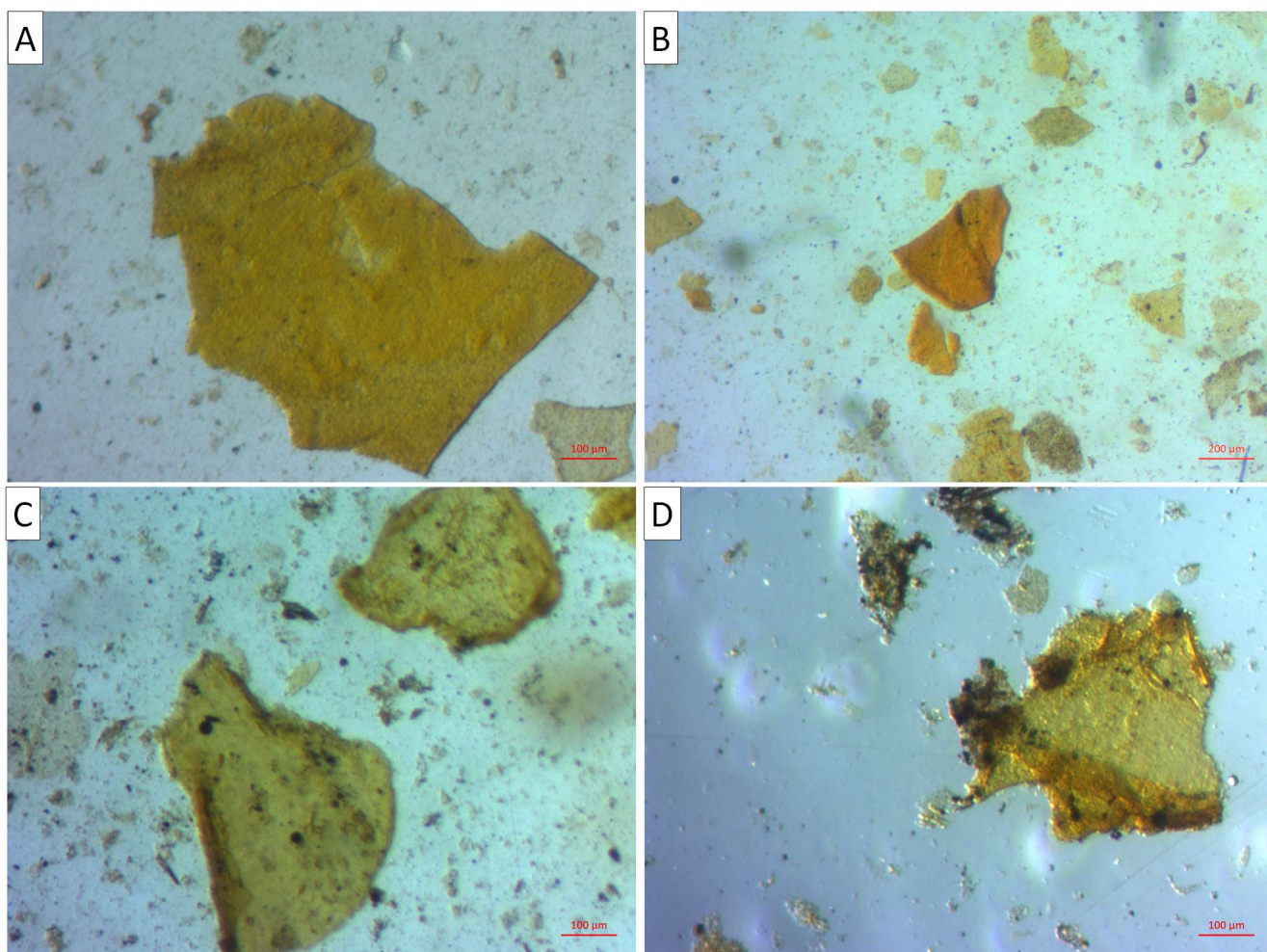


Figure 28: A→D: optical microscopy analysis of C_2N obtained using Hg/K amalgam. The flakes were suspended in a 1 : 2 / EtOH : HCl 2M (v/v) solution.

It shows the presence of very thin (transparent), very large flakes (often mm sized, [Figure 28A](#)), all exhibiting the characteristic orange color shades previously observed for thin C_2N flakes. This confirms that the mercury amalgam-based synthesis indeed mostly results in single/few layers flakes. Only a small amount of black materials (strongly aggregated/folded flakes) is observed.

A polarised light analysis of these flakes shows them to be quite crystalline, as they alternatively appear bright/dark as a function of the angle between the polarizers ([Figure 29](#)). One more example is shown in [S4C](#).

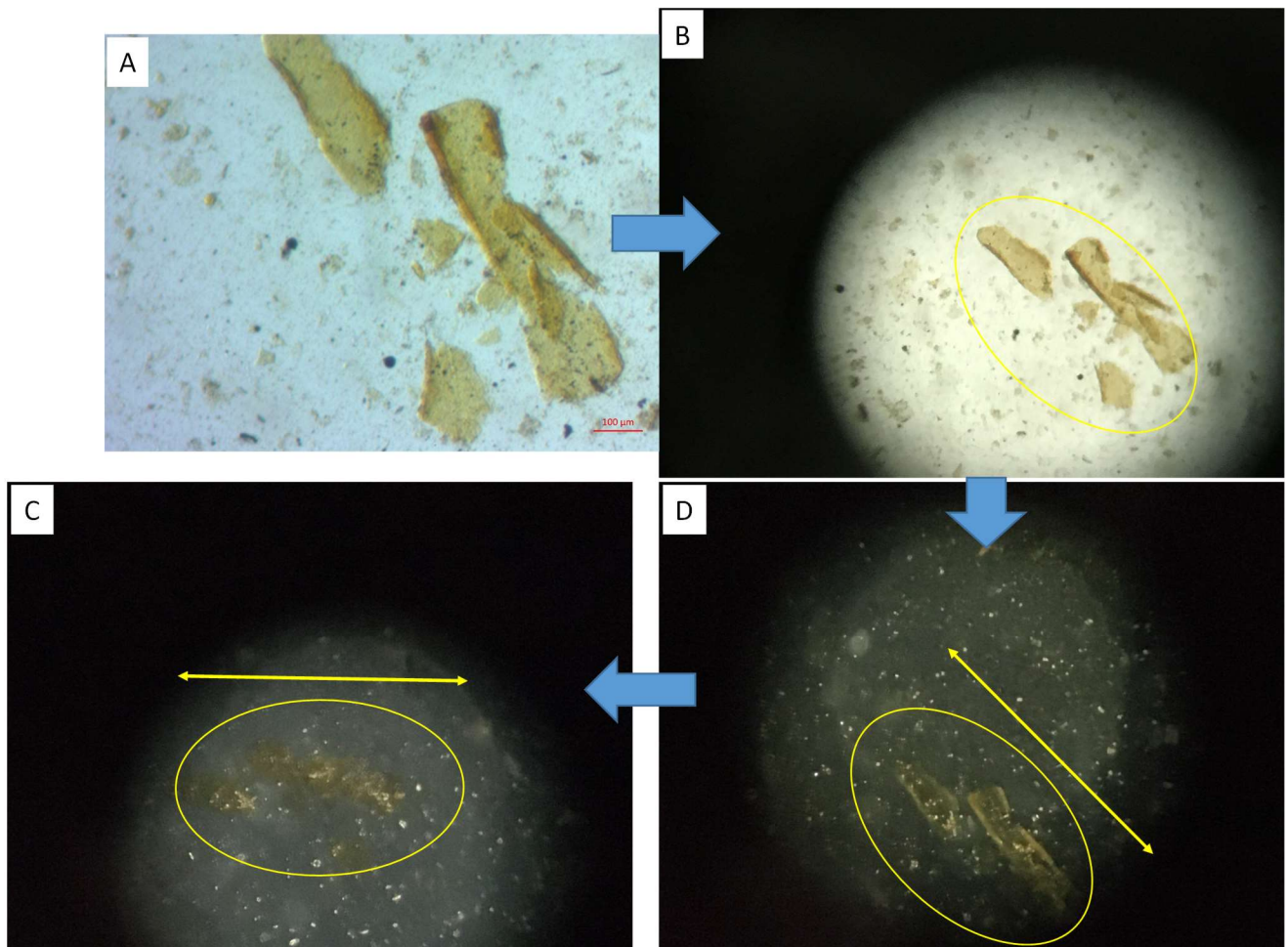


Figure 29: polarised optical microscopy analysis of a broken, tube-shaped C_2N flake. A) and B): normal light. C and D): evolution of the appearance of the flake as a function of the angle between polarizers. The flakes were suspended in a 1 : 2 / EtOH : HCl 2M (v/v) solution.

If kept in suspension for several days, the flakes tend to fold and roll, but are still crystalline (S4D).

TEM

Figure 33 shows a TEM analysis of C_2N obtained using the K/Hg amalgam. As for the previous materials, the best suspensions were obtained in acidic media. In line with the previous C_2N synthesis, very large and smooth flakes are observed, with few visible defects even at high magnifications (Figure 33E→F). An examination of the edges of these flakes clearly shows their layered structure (Figure 33E→F, yellow circles).

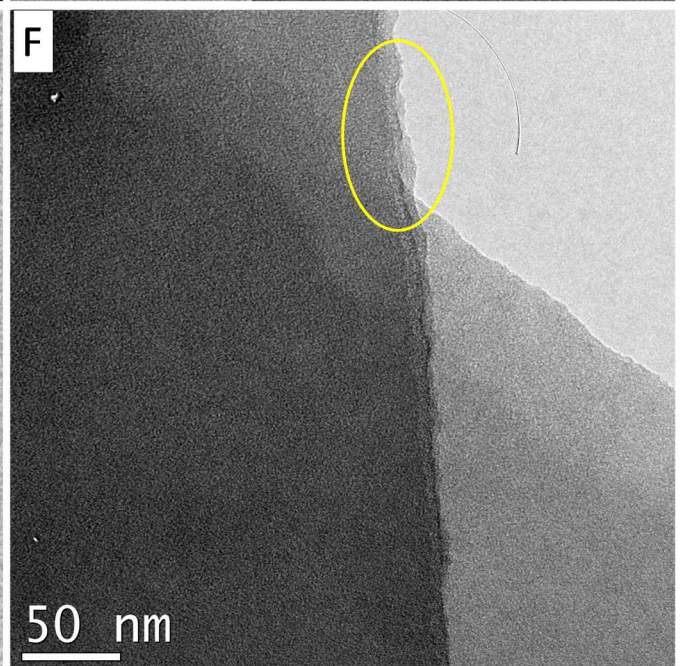
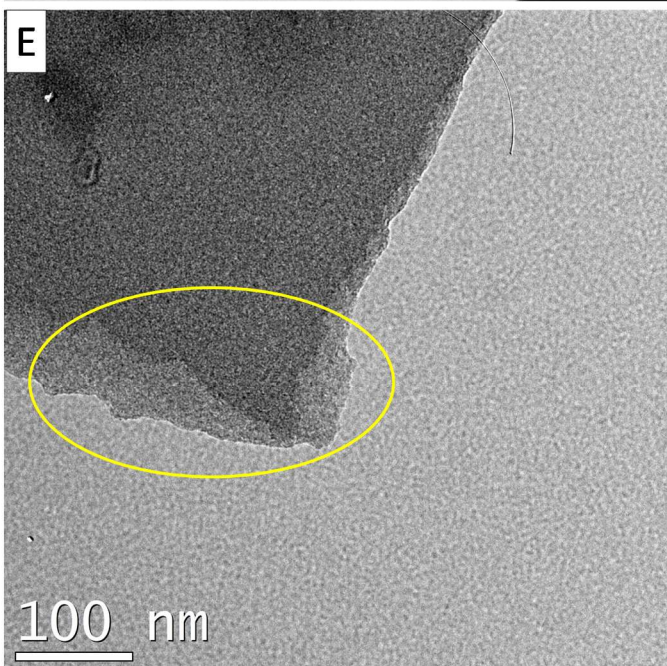
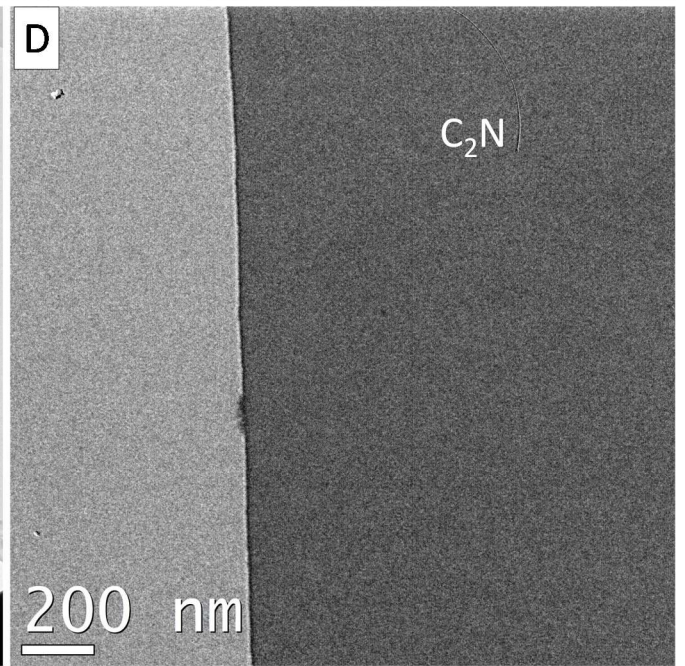
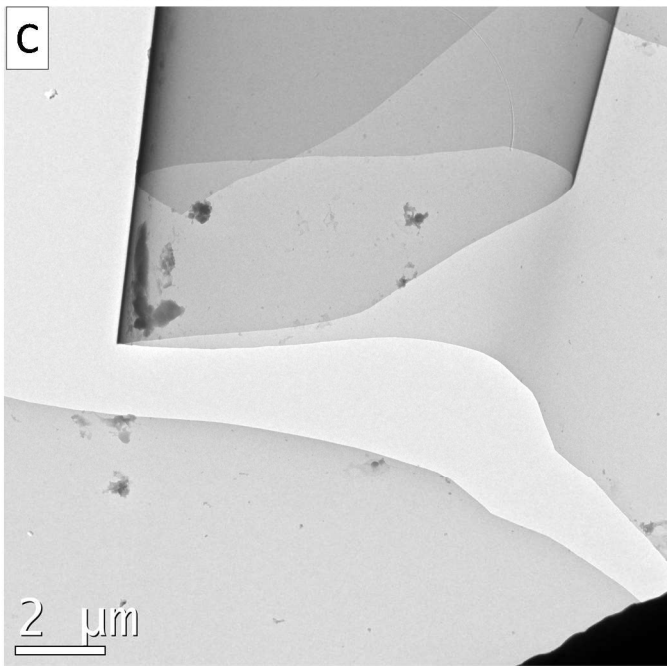
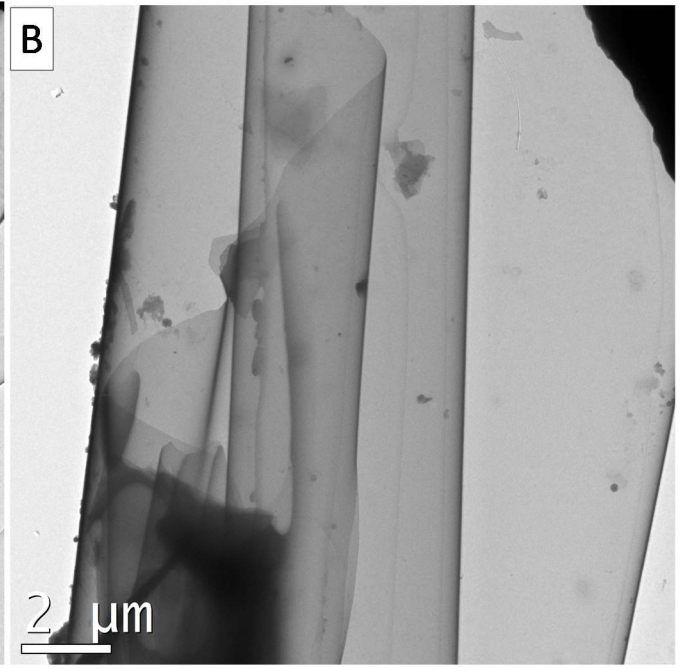
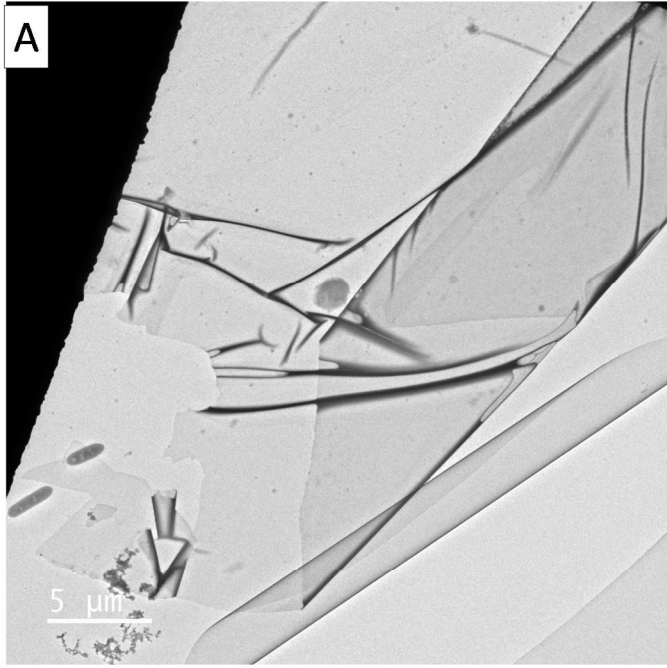


Figure 33 A→F: TEM analysis of K/Hg amalgam-promoted C₂N synthesis. The flakes were suspended in a 1 : 2 / EtOH : HCl 2M (v/v) solution.

In order to insure that the observed objects are not artifacts (broken carbon film from the grid), a TEM analysis of the same sample was performed using a holey carbon grid (Figure S4E). It indeed confirms the presence of very large flakes. Some expands over several squares on the TEM grid (Figure S4E-A→E). All are showing the characteristic features of sheet-like materials (folds, overlaps, etc...).

Figure S4F shows a TEM micrograph of a folded, thicker flake, clearly evidencing its layered structure.

Some rare, highly folded C₂N flakes were sometimes observed. A careful examination of the corresponding high resolution TEM micrograph (two examples Figure S4G) over foldings allows to get a rough estimate of the thickness of the flakes. The obtained values fall between 4 and 9 nm, corresponding to 10 to 20 2D layers.

XPS

Figure 34 shows the XPS analysis of one single C₂N flake (Figure 34A) deposited onto a silicon wafer. It first shows the presence of strong signals from oxygen and silicon (Figure 34B) (with an O/Si atomic ratio of 2), from the native SiO₂ layer of the silicon wafer. Carbon and nitrogen are observed (Figures 34C and 34D) as expected. Regarding the N 1s signal, only one single peak is observed, with a binding energy characteristic of pyridinic-type nitrogen atoms [38, 39, 40, 41]. The observed relative C/N intensity is 3, higher than the expected value of 2. This is likely to be due to commonly encountered carbon contamination. This is confirmed by the presence of a strong signal around 285 eV on the C 1s spectra (Figure 34D). Note that this C/N ratio is the same as the one measured for the previously described synthesis of C₂N (using potassium only as a reducing agent). Remnants of mercury (1 atomic %, Figure 34E) and potassium (3 atomic %, Figure 34D) are also observed, due to left starting products/by products. Chlorine is also observed as chloride ions, in a close to 1-to-1 atomic ratio vs. potassium, indicative of the presence of remaining KCl. This confirms the absence of significant amounts of left C-Cl bonds, and thus the formation of a continuous, defaults-free C₂N network. The signal of mercury steadily decreases during vacuuming (Figure 34E), confirming its presence as a metal.

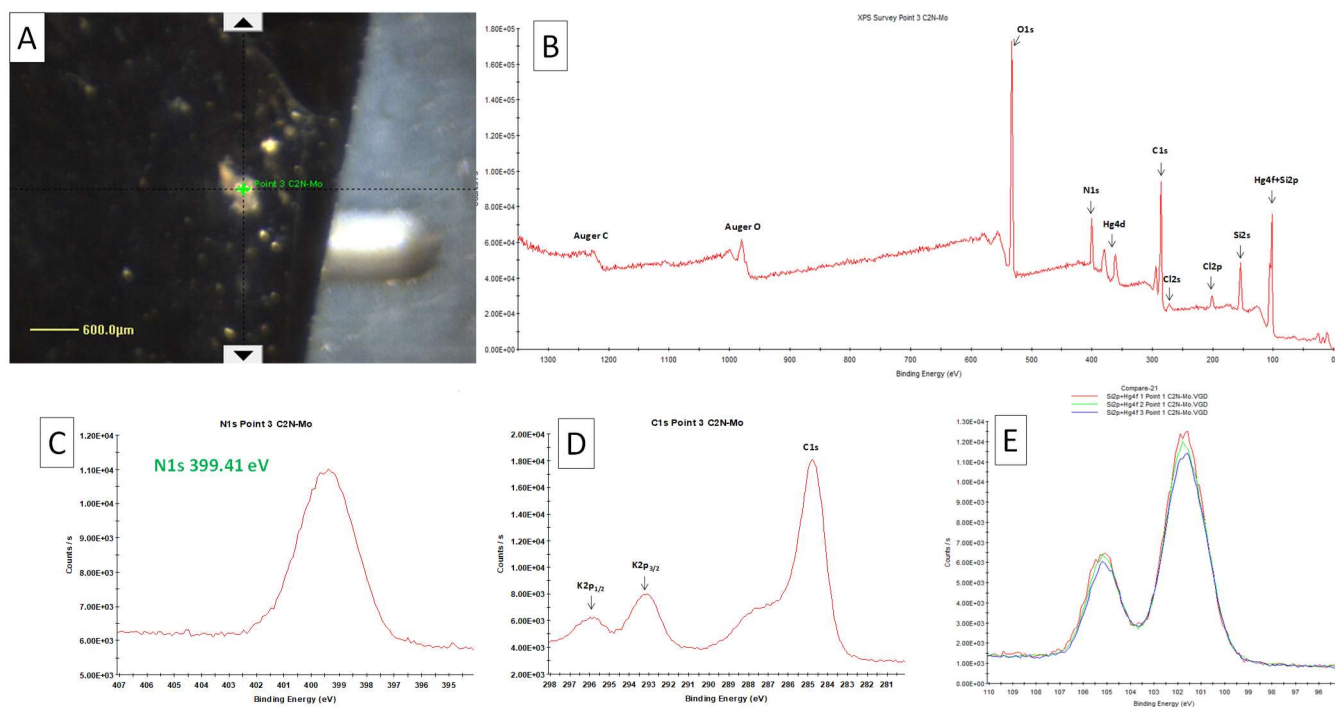


Figure 34: XPS analysis of K/Hg amalgam-promoted C₂N synthesis. A): the analysed flake; B): survey and C)→D): high resolution analyses. The flakes were suspended in a 1 : 2 / EtOH : HCl 2M (v/v) solution. E): evolution of the signal of Hg at the same place as a function of time.

Discussion.

The structure and composition of all three COFs described in this work are assessed by extensive cross-analyses (optical microscopy/XPS/XRD/SEM/TEM/EDS/IR). The conclusions are as follows:

- 1) XPS and XRD show the presence of high amounts of potassium halides in the crude materials (that are completely removed upon washing with water), as expected if the Fittig coupling reaction occurred (Figure 1) ;
- 2) the nearly complete absence of halogens in our final, (washed) materials confirms that the assembly reaction occurred cleanly (Figure 1), i.e. the (quasi) absence of remaining C-Cl or C-Br bonds);
- 3) the presence of strong signals associated with pyridinic-type nitrogens in all our materials as evidenced by XPS;
- 4) EELS experiments confirm point 3, as observed C and N signals are typical of species belonging to conjugated structures;
- 5) the crystallinity of our materials, confirmed by TEM (with SAED for one them) and optical microscopy experiments;
- 6) The compositions are very similar to literature-reported ones;
- 7) Infrared spectroscopy shows the presence of their expected, respective aromatic constituting units for all three COFs.

Taken together, all these conclusions clearly demonstrate the success of our synthetic strategy.

In the case of CN and C₂N, DRX shows the presence of the characteristic peak associated with interplane spacing [43, 46, 51, 52]. However, this peak exhibits some specific features. First, it only appears after washing the samples. Second it is quite broadened. As TEM demonstrates the very high quality of the flakes, we consider that the broadness of the peak is likely to be due to a broad distribution of interplane spacings. This originates from the fact that the layers grow individually, getting stacked during the washing steps. Indeed, TEM analyses (Figures SXX, SXX and SXX) show all three materials made of flakes with thicknesses ranging from 4 to 10 nm. This may induce an irregular spacing after drying. This may also ease the inclusion of metallic cations inside the coordinating holes. Indeed, a few percents of remaining K and Ca (a commonly observed impurity in commercial-grade potassium) are present in our CN and C₂N samples. The fact that our materials are directly obtained as single/few layers ones confirms the occurrence of very efficient mechanisms limiting its extension along the « z » axis (Figure 1c). This confirms the proposed double confinement effect by 1) the surface of the potassium and 2) the insoluble metal salts on top.

The first example of COF we describe (CN carbon nitride) has already been synthesised using a related protocol (reduction of cyanuric chloride with sodium under high pressure, solvothermal conditions in the presence of nickel as a catalyst [28, 29, 30]). However, the morphology of the material we obtained appears as very different. In our case, very large, well defined and seemingly defect-free 2D layers are obtained. These differences might be related to the differences in reactions conditions. Indeed, running the reaction under harsh, solvothermal conditions is likely to continuously remove the NaCl by-product deposit from the surface of sodium metal. This is an indirect evidence of the occurrence of a double-confinement effect in our case. The smaller ionic radii of Na⁺ (Na being the reducing agent used in the solvothermal syntheses) vs. K⁺ (in our case) may also play a role.

The same features were observed for all three COFs described in the present work, i.e. very large, and seemingly defect-free flakes with good composition analyses. Accordingly, a comparison between the EDS and XPS analyses of CN, C₂N, and CTF shows a continuous decrease of the relative amount of nitrogen from CN to CTF, in accordance with the corresponding respective theoretical nitrogen contents in their structures.

For the first time, the flakes described in our work are sufficiently large and defect-free to behave as single-crystals, as evidenced by polarised light microscopy analyses.

TEM confirms the exceptional quality/crystallinity of the 2D layers of all three COFs. The best dispersions (thinnest and largest flakes) were observed upon treatment of the as prepared materials with HCl, in comparison with the other dispersant that we used. Aqueous HCl is thus the best choice for the suspension/processing of these materials, in line with previous observations [55]. This may be due to partial protonation of embedded nitrogen atoms, inducing electrostatic repulsions between flakes. This is attested by the observation of signals that could be attributed to (N-H)⁺ bonds on the infrared spectra of CN and C₂N. This may also explain the presence of higher binding energy components in the N 1s / C 1s XPS analyses.

Interestingly, thin flakes of the three COFs that we synthesised exhibit different intrinsic colors, brown for CN, greenish-brown for CTF, whereas C₂N exhibits a deep orange one. This evidences the smallest bandgap of the later.

It should be underlined here that for all the COFs that we synthesised, the whole materials are made of flakes such as the ones shown on the different figures (both on the paper and in the SI). Indeed, all the observed areas on several TEM grids from different syntheses do show similar objects.

Improving the stability of the metallic interface by using potassium-mercury amalgam considerably improves the quality of the C₂N flakes, as expected for a surface-confined growth process. For the first time, millimeter-scale flakes of C₂N were obtained, an exceptional feature in the field of COFs.

The successful synthesis of three different 2D networks, using very different building blocks shows that our metallic potassium based process appears as quite general. This opens the door towards the synthesis of COFs with more complex structures.

Conclusion.

A simple protocol for the synthesis of graphene-related COFs was designed, and exemplified on three different examples.

The exceptional quality of the resulting materials (in terms of flakes sizes and defect-free nature) shows that the proposed « double confinement strategy » approach appears interesting for the synthesis of high quality 2D materials. This high quality, along with the soft conditions used and common laboratory equipments makes our process a significant improvement in the field.

The fact that the characteristic X-ray diffraction peak around 26° is only observed on washed samples tend to indicate that the growth of these 2D materials occurs as single/few layers, a new feature for wet syntheses of 2D materials.

These materials hold great promises in the field on nanoelectronics (high band gap support for graphene, transport studies, etc...). They're also interesting for photophysics, due to: i) the large size of the crystalline domains, ii) their low defects content and iii) their direct synthesis as highly exfoliated sheets. These studies are underway, and will be reported in due course.

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