Electronic Supplementary Material (ESI) for RSC Advances.

Pristine carbon nitride as active material for high-performance metal-free supercapacitors: simple, easy and cheap

(Supplementary Information)

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S.I.1 - UREA XRD AND FTIR SPECTRA

As described in the experimental part, the XRD pattern and FTIR spectrum were obtained for the urea used as starting material to produce the C_3N_4. Figure S.1a presents the diffraction peaks for this material, with is according to the literature for a polycrystalline urea pattern[1]. In addition, Figure S.1b shows the vibrational spectrum with the characteristic bands for this material as reported in the literature[2,3].

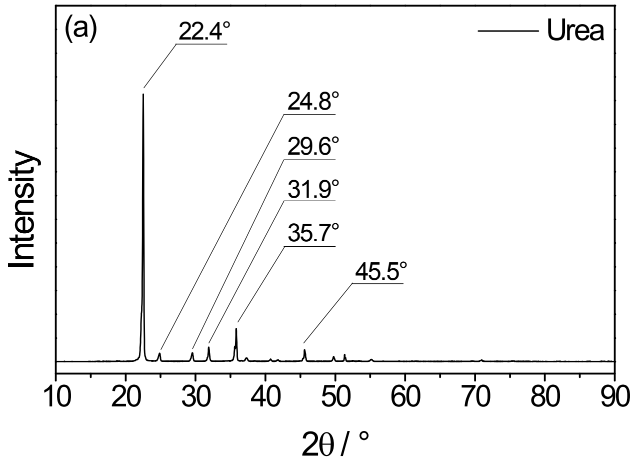

Figure S.1: Urea (a) x-ray diffractogram and (b) infrared spectrum.

Figure S.2 present the comparison between the urea and the exfoliated C_3N_4 diffractograms and infrared spectra. For a better visualization, the carbon nitride data had to be multiplied by 100 to be comparable to the urea one. In addition, it is possible to see that the characteristic peak of urea in 22.4° does not appear in the nitrate diffractogram and not even as peaks with very low intensities. On the other hand, infrared spectra, although having certain characteristics in common, due to the chemical bonds present in both materials, mainly the bands around 300 cm^{-1} related to C−H bonds cannot be seen in the C_3N_4 spectrum, suggesting that all the urea used as a precursor was converted to carbon nitride.

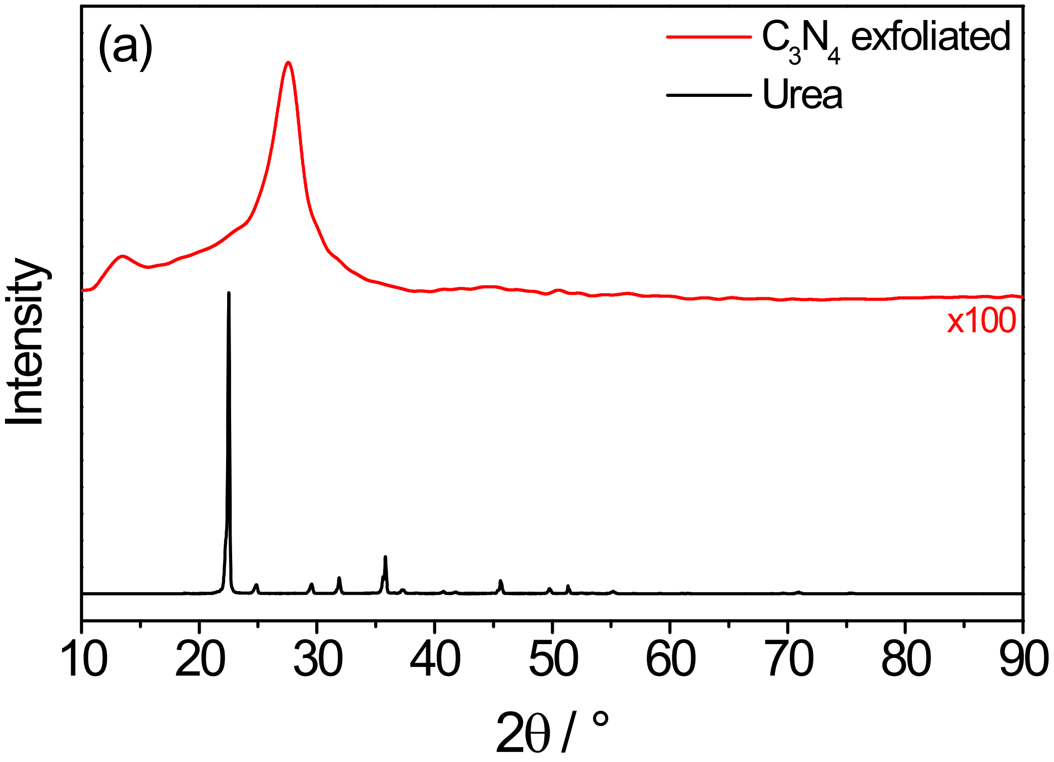

Figure S.2: Urea (a) X-ray diffractogram and (b) infrared spectrum.

S.I.2 - THERMAL GRAVIMETRIC ANALYSIS

The thermal analysis of the urea and carbon nitride were performed to verify the thermal behavior of these two materials and aiming to analyze the presence of undecomposed urea in the carbon nitride sample. Figure S.3 shows the weight loss curve plotted together with the first derivative (DTG) of the TGA curve, which makes it possible to see how many and at what temperatures each transformation occurs. Thus, the urea weight loss curve shows two distinct events in which the first one occurs from 150 °C to 275 °C and the second in the range from 275 °C to-475 °C. Furthermore, the DTG curves shows two endothermic peaks centered at 234 °C and 364 °C, being the first event assigned to the formation of biuret compound and the second one assigned to the formation of melamine [4,5].

The carbon nitride weight loss curve shows two distinct events, in which the first one occurs in the range from 50 °C to 150 °C being assigned to the desorption of physically adsorbed water molecules. The second weigh loss event occurs in the range from 525 °C to 775 °C (centered at

688 °C) is assigned to the degradation of carbon nitride structure, as already reported in the literature [6,7].

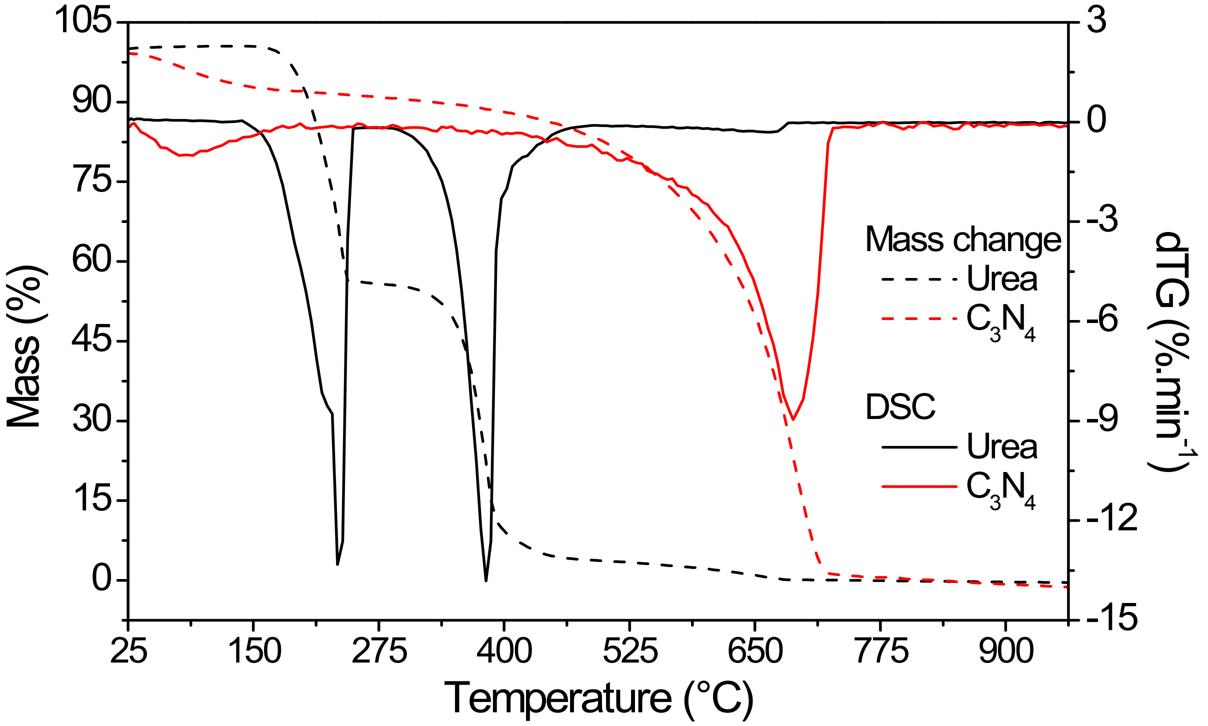

Figure S.3: Weight loss curve and fist derivative of the DTG for urea and C_3N_4.

S.I.3 - ENERGY DISPERSIVE X-RAY SPECTROSCOPY

To ensure the purity of the obtained carbon nitride and the complete conversion of the urea, was performed an elemental characterization using Energy Dispersive X-ray (EDX) of both, urea and C_3N_4. This measurement allowed obtains the atomic composition of the samples. Figure S.4 shows the energy spectra, where is possible to observe that was not found any O peak on the urea sample while in the carbon nitride there is just C and N as expected.

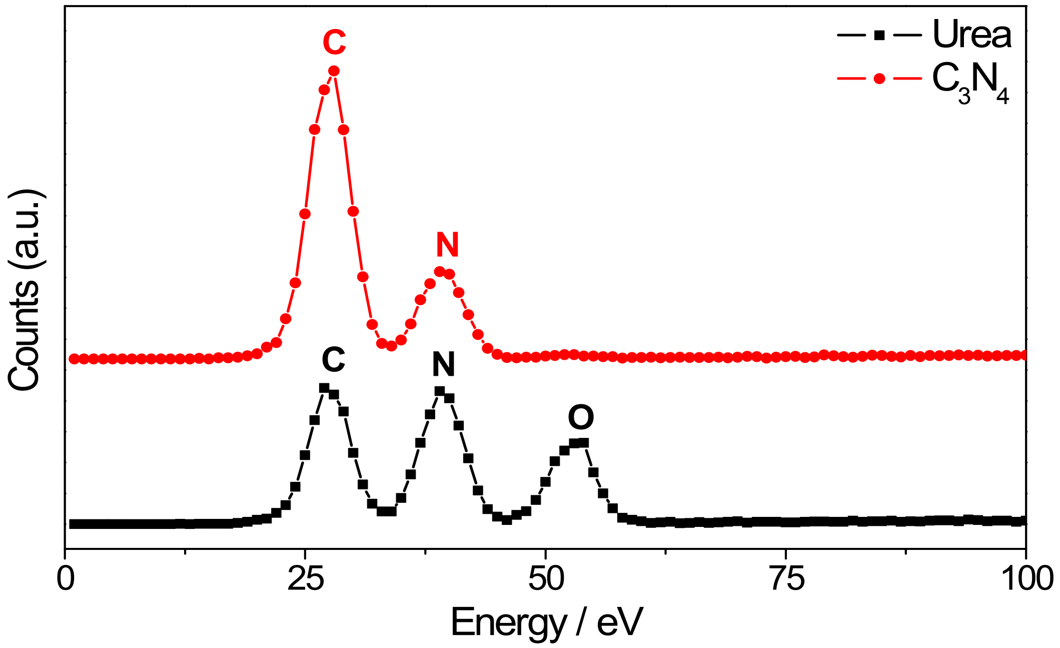

Figure S.4: Energy dispersive x-ray spectra for urea and exfoliated C_3N_4.

In addition, Table S.1 resumes the proportion of elements in the samples with the calculated standard deviation calculated considering different regions of the same sample. The urea empirical formula of urea is CH_4N_2O, it means that the proportion C:N:O is 1:2:1; while carbon nitrides present the empirical formula as C_3N_4 and proportion C:N:O, 3:4:0. Thus, as calculated by the EDS data was found the proportions for urea and carbon nitride 0.96**:**1.87**:**1.17 and 2.84**:**4.16**:**0.0, respectively. These results are in perfectly agreement with the expected for the C_3N_4 precursor and for urea-free carbon nitride.

Table S.1: Atomic proportions of carbon, nitrogen and oxygen obtained by EDS.

Elements	**Urea**	**Carbon nitride**
Carbon (%)	24.0±0.18	40.6±0.78
Nitrogen (%)	46.6±0.28	59.4±0.78
Oxigen (%)	29.4±0.10	-
Total	*100%*	*100%*

S.I.4 - N_2 SORPTION MEASUREMENTS

The nitrogen adsorption-desorption measurements (Figure S.5) were performed in order to obtain insights regarding the textural properties of the bulk g-C_3N_4 and the exfoliated material. Both materials presented type IV isotherms, typical of mesoporous solids in which the nitrogen adsorption proceeds via multilayer adsorption followed by capillary condensation[8]. Furthermore, the hysteresis loops of both materials are classified as H3 type, characteristic of layered materials with slit-shaped pores as a consequence of the aggregation of the flake shaped particles[8,9].

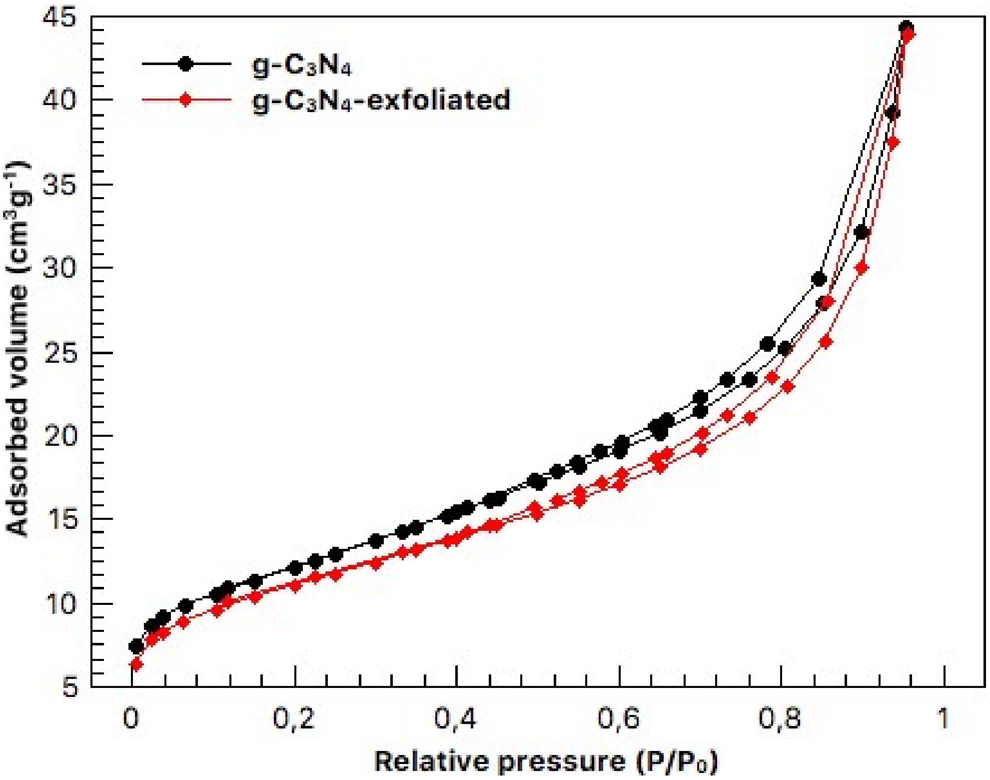

Figure S.5: Adsorption-desorption N_2 isotherms for the g-C_3N_4 and exfoliated C_3N_4.

Interestingly, the specific surface area of the non and exfoliated carbon nitride materials were similar, as evidenced in Table S.2. This behavior is assigned to the reversibility of the exfoliation method employing isopropanol, in which the exfoliated morphology is kept in solution and the drying procedure led to the re-stacking of graphite-like C_3N_4 layers in a disordered way as a consequence of the solvent evaporation[10]. Furthermore, the re-stacking is followed by a slightly increase in the volume and diameter of the slit-shaped pores, as observed in the Table S.2.

Table S.2: Textural properties of the g-C_3N_4 and the exfoliated C_3N_4.

Sample	$S_{B.E.T.}$ (m^2g^{-1})	$D_{B.J.H.}$ (nm)	V_P (cm^3g^{-1})
g-C_3N_4	36.7	6.7	0.04
C_3N_4 exfoliated	38.5	8.0	0.06

S.I.5 - EIS MODEL AND PARAMETERS BEHAVIOR VERSUS CYCLES NUMBER

As described in the manuscript, Figure S.6a shows the transmission line model used to fit the impedance data. To understand the aging behavior of the film, the parameters obtained from the model was plotted in function of the charge/discharge cycles. The capacitance of the double-layer decreases (Figure S.6b) almost five times due the cycles number, these parameters associated with the decrease in the pore resistance (Figure S.6d), could suggest that the film is lixiviated from the electrode, since the normal behavior is increase with the number of cycles. In addition to the film show a slightly increase resistance (Figure S.6e). This supposition can also explain the other curves obtained, with a less amount of electroactive film weight, both capacitance value decreases and the intercalation process (Figure S.6c) also occur in minor extension.

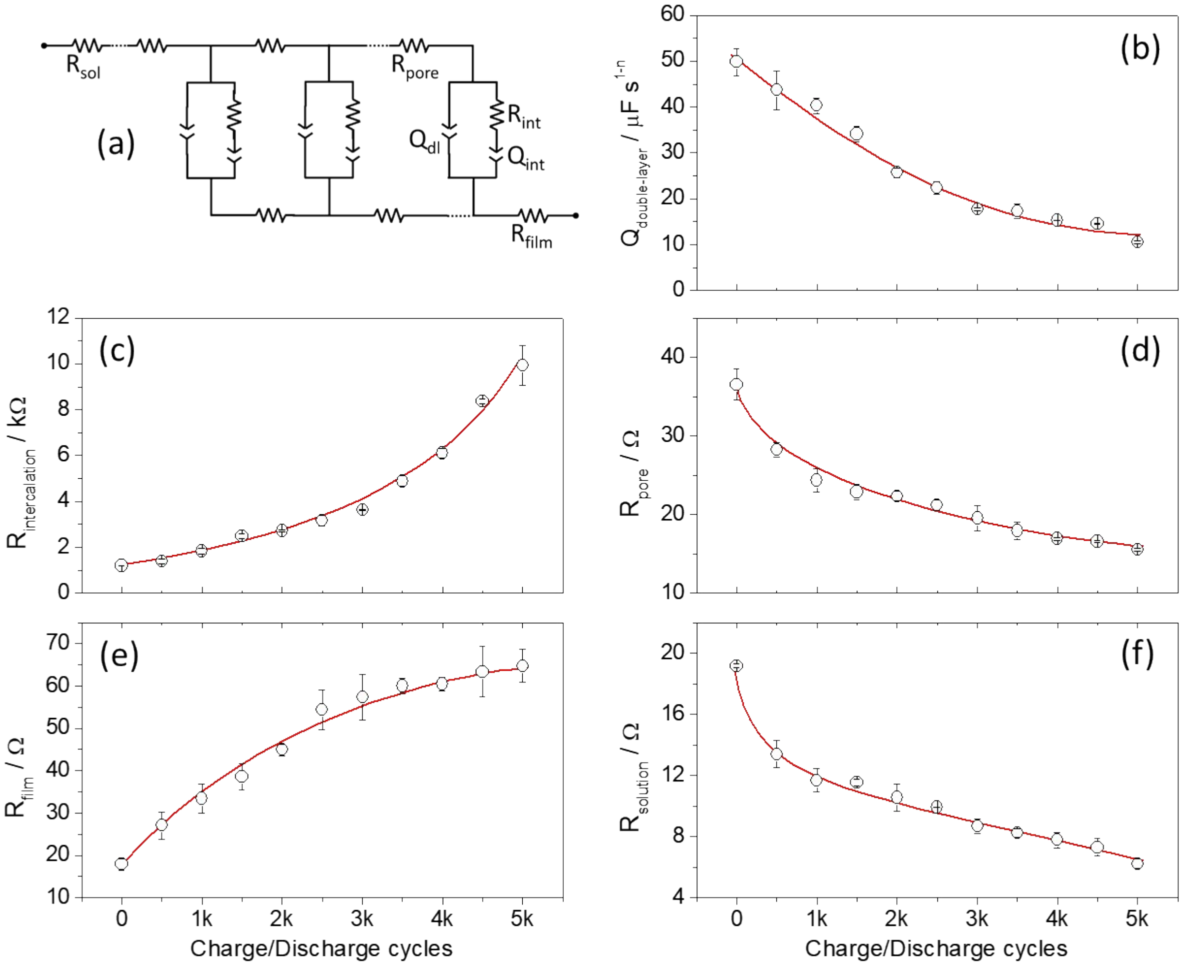

Figure S.6: (a) Model used to fit the EIS data; (b) double-layer capacitance, (c) intercalation (mas transport) resistance, (d) pore resistance, (e) film (C_3N_4) resistance and (f) solution resistance versus charge/discharge cycles.

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