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1 Influence of synthesis parameters on g-C<sub>3</sub>N<sub>4</sub>  
2 polysulfides trapping: a systematic study.

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18 **KEYWORDS:** lithium sulfur battery, double-layer, carbon nitride, polysulfides trapping

## 1 ABSTRACT

2 Beyond Li-ion batteries, one of the most promising technology is the Lithium-Sulphur (Li-S) not  
3 only for its higher theoretical energy density (about 2600 Wh kg<sup>-1</sup>) but because sulfur is relatively  
4 inexpensive and non-toxic. However, the Li-S battery suffers from “shuttle effect” of polysulfides.  
5 Thus, restricting shuttling means increasing cell performance and durability. DFT calculations  
6 showed that graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) exhibits strong interactions with Li<sub>2</sub>S (*e.g.* superior to  
7 graphene-like carbon) and acts as polysulfides trapping agent. In this work, the role of g-C<sub>3</sub>N<sub>4</sub>,  
8 synthesized from different precursor and at different polycondensation temperatures was  
9 systematically studied, using a double layer approach for the electrode preparation, which ensures  
10 direct interaction between g-C<sub>3</sub>N<sub>4</sub> and soluble lithium-polysulfides.

11 This systematic study confirms the importance of the morphological and superficial properties of the  
12 material. In particular, carbon nitride from urea precursor remarkably improves the performance of  
13 the sulphur cathode, increasing the specific capacity of the cell by 25% and improving its useful life  
14 over 500 cycles. According to the morphological characterization and the XPS analysis, benefits are  
15 achieved from polycondensation of urea at 550 °C. The obtained g-C<sub>3</sub>N<sub>4</sub> shows the highest proportion  
16 of -NH<sub>2</sub> species on the surface, which favours the interaction with polysulfides.

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## 20 1. INTRODUCTION

21

1 Lithium-ion batteries (LIBs) are well established energy storage devices for electronic,  
2 transportation and renewable-energy applications. Unfortunately, the current Li-ion technology is  
3 reaching its intrinsic limits in terms of energy density and specific capacity as a consequence of the  
4 intercalation/insertion-compounds chemistry [1]. At the same time, to meet the ever-increasing  
5 energy storage demand for electrical mobility and smart grids, future batteries have also to guarantee  
6 sustainable and cheaper solutions. Alternative systems that can deliver higher capacities and energy  
7 densities need to be developed and implemented [2].

8 Beyond Li-ion battery, one of the most promising next-generation energy storage system is the  
9 lithium-sulphur (Li-S) battery. Sulphur offers many advantages compared to traditional LIBs active  
10 materials at the cathode. From a commercial perspective, sulphur is earthly abundant, geographically  
11 well-distributed, non-toxic and can be produced from desulphurization processes from oil and gas  
12 industries. This means that the overall battery price and the environmental impact can also be reduced  
13 [3][4]. From the electrochemical point of view, Li-S technology is expected to achieve 2-3 times  
14 higher (about 2600 Wh kg<sup>-1</sup>) energy density than the actual LIBs, thanks to the particular chemistry  
15 of the system, which involves the reaction of sulphur ( $\alpha$ -S<sub>8</sub>) to Li<sub>2</sub>S, through the formation of lithium  
16 polysulfides (LiPSs) intermediates [5]. The peculiarity of Li-S system is that the discharge products  
17 have different physical properties. Typically, S<sub>8</sub> and Li<sub>2</sub>S are solid and insoluble in the common  
18 electrolytes, while the intermediate LiPSs are soluble in organic solvents. As a matter of fact, the  
19 huge number of intermediate species and the complex reaction mechanism are responsible for the  
20 drawbacks of the system. Indeed, commercialization of the lithium-sulphur technology is still limited  
21 by some key challenges that have to be addressed [6]. Elemental sulphur has very low electronic  
22 conductivity ( $5 \times 10^{-30}$  S cm<sup>-1</sup> at 25 °C.) [7]. The insulator nature of both sulphur and Li<sub>2</sub>S results in  
23 large polarization and slow kinetic processes, limiting sulphur utilization. For this reason, sulphur  
24 needs to be intimately mixed with a conductive additive such as carbon, which inevitably reduces the

1 energy density of the system. At the same time a huge volume expansion occurs during the solid-  
2 liquid-solid transition process, causing structural and morphological changes of the cathode [7][8][5].

3 However, the most important issue of Li-S system is related to LiPSs dissolution. On one hand,  
4 dissolution of LiPSs is beneficial to achieve full active-material utilization because new bulk sulphur  
5 can be continuously exposed to the electrolyte and participate to the reaction [4]. On the other hand,  
6 the dissolved long chain polysulfides can diffuse out of the cathode and migrate towards the anode,  
7 where they directly react with metallic lithium creating nonconductive and insoluble  $\text{Li}_2\text{S}$  precipitate  
8 on its surface. This process is known as “polysulfides shuttle effect”, which results in both anode  
9 corrosion and irreversible loss of active material, with consequent low capacity retention and low  
10 Coulombic efficiency [7]. Moreover, during cell resting, sulphur reacts directly with lithium ions in  
11 the electrolyte producing soluble lithium polysulfides with consequent self-discharge of the cell  
12 [5][7][8].

13 In the last years, different approaches and methods have been adopted to solve these issues with  
14 the purpose to achieve a widespread introduction of this technology in the market [8].

15 Research attempted to design and develop suitable cathode nanocomposites, with conductive  
16 carbon scaffolds and/or conducting polymers in order to increase the electrical conductivity and  
17 provide structural integrity of the S cathode [5]. Moreover, novel electrolyte formulations have been  
18 implemented with the aim of creating a passivating and protective film on metallic lithium anode,  
19 limiting polysulfide shuttle effect [3][4][8]. Another important strategy is LiPSs confinement. In  
20 general, this is realized by immobilizing LiPSs species within the cathode via physical or chemical  
21 adsorption [9][10][11][12]. However, physical adsorption cannot confine polysulfides completely,  
22 while materials that carry out chemical bonding have the general disadvantage of low specific surface  
23 area, thus low sulphur loadings can be achieved. Therefore, physical or chemical processes taken

1 individually show limited improvements, while their combination creates synergies and is the most  
2 promising strategy to address shuttle effect [9].

3 In the last five years, g-C<sub>3</sub>N<sub>4</sub> has been studied as suitable polysulfides trapping agent in Li-S  
4 battery. Many investigations have been focused on understanding the origin of the strong interaction  
5 between carbon nitride and lithium polysulfides [13]. The existence of a strong electrostatic affinity  
6 between carbon nitride and LiPSs was confirmed and validated [14][15][16] both by density  
7 functional theory (DFT) simulations and experimental data. These studies pointed out a strong  
8 contribution of g-C<sub>3</sub>N<sub>4</sub> in the kinetics of LiPSs redox reactions due to the high surface polarization  
9 of carbon nitride, which alters the molecular configurations of the adsorbed LiPSs, affecting the  
10 electron transport and increasing the rate of the redox conversion reaction. The combination of DFT  
11 calculations and spectroscopic studies highlighted that the binding energy between Li<sub>2</sub>S<sub>2</sub> (or Li<sub>2</sub>S<sub>4</sub>)  
12 and g-C<sub>3</sub>N<sub>4</sub> increases by increasing the concentration of doped N in g-C<sub>3</sub>N<sub>4</sub>. This means that  
13 accessible pyridinic nitrogen adsorption sites are the key factor for the improvement of  
14 electrochemical performance. [17][18][19].

15 Starting from theoretical predictions, many different strategies were adopted to properly exploit  
16 the g-C<sub>3</sub>N<sub>4</sub> properties as LiPSs trapping agent. Carbon nitride was largely investigated as sulphur  
17 host, often coupled with graphene to increase the conductivity. Alternatively, many studies were  
18 oriented to modify polyolefin-based separators with g-C<sub>3</sub>N<sub>4</sub> or create novel interlayer architectures  
19 [18][19]. Recently, a selective double layer structure of the cathode was investigated to mitigate  
20 LiPSs diffusion. This was obtained by simply coating the surface of a S/C cathode with a thin  
21 laminated graphene-based or polymer-based interlayer [20][21][22]. Following the same strategy Qu  
22 *et al.* [23] developed a 2D laminated composite of graphene and g-C<sub>3</sub>N<sub>4</sub> nanosheets (g-C<sub>3</sub>N<sub>4</sub>/GS),  
23 directly spread on the sulphur cathode surface.

1 As a matter of fact, many types of doping, morphologies, and different precursors of carbon nitride  
2 were reported in various studies. To date though, no systematic study comparing the role of different  
3 carbon nitride precursors as well as the different synthesis temperatures was carried out. In fact, most  
4 of the reported investigations are difficult to compare, because of the different adopted strategies and  
5 test parameters (*e.g.* sulphur mass loading, electrolyte uptake *etc.*) employed.

6 For this reason, this work investigates the role of g-C<sub>3</sub>N<sub>4</sub>, synthesized from different precursors and  
7 at different temperatures, using a double layer cathode approach. The designed double layer cathode  
8 guarantees good interaction between LiPSs and the carbon nitride, since the carbon nitride, which has  
9 neither an optimal mesoporosity nor an optimal electronic conductivity, is not directly mixed with  
10 sulphur. Hence the cathode is composed of two layers. In the first layer, sulphur is intimately mixed  
11 with the conductive carbon, which is a good electron conductor for the electrochemical reaction. In  
12 the second layer the good distribution of carbon nitride allows the material to better exert its trapping  
13 action towards LiPSs.

## 16 2. EXPERIMENTAL SECTION

### 18 2.1. Material preparation

19 In order to investigate the effects of different physicochemical properties of g-C<sub>3</sub>N<sub>4</sub> towards LiPSs  
20 trapping, three different carbon nitride materials were prepared starting from urea ( $\geq 98$  % Sigma  
21 Aldrich), dicyandiamide (DCDA,  $\geq 99.0$  % Sigma Aldrich) and melamine (MLM,  $\geq 99$  % Sigma  
22 Aldrich), respectively. It is important to note that urea, dicyandiamide and melamine are nontoxic,  
23 cheap and easily available precursors [24].

1 In a typical condensation process 6 g of urea, dicyandiamide or melamine were put into a semi-  
2 closed alumina boat and heated to 550 °C in a tubular furnace for 3 h with a heating rate of 2.5 °C  
3 min<sup>-1</sup>. After the reaction, the furnace was cooled to room temperature and the resultant g-C<sub>3</sub>N<sub>4</sub>  
4 samples were grounded into powder, washed several times with water and ethanol and centrifuged at  
5 10000 - 12000 RPM for 15 minutes. The different g-C<sub>3</sub>N<sub>4</sub> powders prepared starting from urea,  
6 dicyandiamide, melamine, were named as: CN-U, CN-D, CN-M, respectively.

7 In the second part of the work, urea was treated at three different annealing temperatures: 450, 550,  
8 and 650 °C, respectively. All the obtained samples discussed in this section were labelled as CN-U-  
9 x, where x refers to the specific annealing temperatures.

10

## 11 **2.2. Material characterization**

12 XRD analysis was carried out by a PANalytical X'Pert (Cu Ka radiation) diffractometer. Data  
13 were collected with a 2D solid state detector (PIXcel) from 10 to 80° 2θ with a step size of 0.026 2θ  
14 and a wavelength of 1.54187 Å.

15 Fourier Transform Infrared Spectroscopy (FTIR) was measured with a Nicolet™ iS50 FTIR  
16 spectrometer (Thermo Scientific™) equipped with ATR tool. 32 scans were collected with a  
17 resolution of 4 cm<sup>-1</sup> from 4000 to 400 cm<sup>-1</sup>.

18 Thermogravimetric analysis was performed on a Linseis TGA PT 1600 instrument by heating the  
19 composite at 10 °C min<sup>-1</sup> from room temperature to 800 °C in air.

20 FESEM analysis was carried out by Zeiss SUPRA™ 40 with Gemini column and Schottky field  
21 emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 3 kV and  
22 working distance (WD) between 2.1 - 8.5 mm, with magnification up to 1000 KX.

1 The Brunauer-Emmett-Teller specific surface area (SSA) was determined by nitrogen  
2 physisorption at 77 K using a Micrometrics ASAP 2020 instrument. The specific surface area was  
3 calculated with the BET model in the relative pressure range of 0.07 - 0.30 by assuming 0.162  
4 nm<sup>2</sup>/molecule as the molecular area of nitrogen.

5 X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI Model 5000  
6 electron spectrometer equipped with an aluminium anode (1486 eV) monochromatic source, with a  
7 power of 25.0 W, and high-resolution scan with 11.75 eV pass energy. The instrument typically  
8 operates at pressures below  $5 \times 10^{-8}$  mbar.

9 For polysulfides adsorption tests, a solution 0.1 M of Li<sub>2</sub>S<sub>6</sub> was prepared directly reacting Li<sub>2</sub>S and  
10 S<sub>8</sub> (in the weight ratio 1:5) into a mixture of DME and DIOX (1:1 by volume) for 72 h at 70 °C, under  
11 continuous stirring in argon atmosphere. Li<sub>2</sub>S<sub>6</sub> was chosen as representative soluble long-chain  
12 polysulfide species. The resulting brownish-red Li<sub>2</sub>S<sub>6</sub> solution was then diluted to 1.0 mM for the  
13 polysulfide adsorption test. Then, a quantity of different carbon nitride equivalent to 0.5 m<sup>2</sup> surface  
14 area was added to 20 μL of 1.0 mM of Li<sub>2</sub>S<sub>6</sub> solution diluted in 2 mL of DME:DIOX 1:1 v/v mixture  
15 and left to interact for 12 hours [25].

16 The UV-Vis absorption spectra were detected by a UV-vis spectrophotometer (JENWAY, 6850  
17 UV/Vis. Spectrophotometer) within the spectral range of 200 - 500 nm.

18

### 19 **2.3. Electrochemical measurements**

20 All the working electrodes were prepared by solvent tape casting method. The so called  
21 “standard” sulphur cathode electrode (STD) was prepared using pure sulphur ( $\geq 99.5$  % Sigma  
22 Aldrich) as active material, Ketjenblack® (KjB, EC-300J, AkzoNobel), as conductive carbon additive  
23 and poly(vinylidenedifluoride) (PVdF, Solvay; 10 wt.% in N-methyl-2-pyrrolidinone solution) as

1 polymeric binder. The “standard” electrode composition (STD) was set up 60:30:10 wt.%,  
2 respectively for (S:KjB:PVdF), in all experiments. This ratio was chosen with the aim to obtain a  
3 cathode with reproducible sulphur loading, using a simple mixing procedure and taking into account  
4 that this is a simple and easily scalable procedure. The final mixture was mechanically deposited on  
5 the aluminium current collector by Doctor Blade technique. The blade was adjusted for a 200  $\mu\text{m}$   
6 deposition using an automatic film applicator (Sheen 1133N) with a speed of 50  $\text{mm s}^{-1}$ . After the  
7 slurry deposition the coated aluminium foil was dried at 50  $^{\circ}\text{C}$  in air. A similar procedure was used  
8 to obtain the double layer cathode. The dried standard electrode was first obtained following the  
9 previously mentioned procedure and was subsequently coated by a second layer containing carbon  
10 nitride. The ratio between CN, KjB and PVdF, contained in the second layer slurry was 80:10:10,  
11 with a blade thickness of 200  $\mu\text{m}$ . In the DL electrodes containing CN-U-550, the carbon nitride mass  
12 loading was about 0.9  $\text{mg cm}^{-2}$ . For all the DL electrodes the S/CN ratio was kept in the range of 0.9  
13 – 1.0, in order to have a comparable S/CN ratio.

14 After solvent evaporation in air, disks of 2.54  $\text{cm}^2$  were punched out, vacuum dried at 40  $^{\circ}\text{C}$  (in a  
15 Büchi Glass Oven B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraum  
16 Labstar,  $\text{H}_2\text{O}$  and  $\text{O}_2$  content < 1 ppm) for cell assembly. The active material loading of the “standard”  
17 sulphur cathode (STD) was  $\sim 1 - 1.2 \text{ mg cm}^{-2}$ . It is worth noting that the obtained electrodes have  
18 been carefully selected according to their weight and morphology.

19 The electrodes were assembled in 2032 coin-type cells with lithium disk (Chemetall Foote  
20 Corporation,  $\varnothing$  16 mm) as counter electrode and PP polymeric membrane (Celgard 2500, 25  $\mu\text{m}$   
21 thickness,  $\varnothing$  19 mm) as separator. The electrolyte was a solution of 1,2-dimethoxyethane (DME) and  
22 1,3-dioxolane (DIOX) 1:1 (v/v) with 1.0 M lithium bis(trifluoromethanesulfonyl)imide  
23 ( $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{CF}_3$ , LiTFSI) and 0.25 M lithium nitrate ( $\text{LiNO}_3$ ,  $\geq 99.9\%$  Sigma Aldrich). The  
24 solution was stored in argon filled glove box for at least 12 h before the use. The electrolyte amount

1 for each kind of experiment never exceeded 20  $\mu\text{L}$ , corresponding to  $\sim 10 - 11 \mu\text{L mg}^{-1}$  (referred to S  
2 quantity).

3 The cycling performances of the cathodes were investigated by means of galvanostatic discharge-  
4 charge cycling (GC) using an Arbin LBT-21084 battery tester at room temperature. Galvanostatic  
5 discharge-charge tests were carried out in the potential interval 1.8 - 2.6 V vs.  $\text{Li}^+/\text{Li}^0$  at different  
6 current rates. The C-rate was calculated using the theoretical capacity of sulphur ( $1672 \text{ mAh g}^{-1}$ ). For  
7 cyclic voltammetry (CV), the electrode potential was reversibly scanned between an extended range  
8 of potential from 1.7 to 2.8 V vs.  $\text{Li}^+/\text{Li}^0$  at  $0.1 \text{ mV s}^{-1}$ .

9 Electrochemical Impedance Spectroscopy tests (EIS) were performed with Bio-Logic® VSP-3e  
10 multichannel potentiostat, equipped with impedance modules. Each spectrum was recorded in the  
11 frequency range of 100 kHz to 10 mHz, with an excitation potential of 5 mV and 10 points per decade.

12

13

### 14 **3. RESULTS AND DISCUSSION**

15

#### 16 **3.1. Morphological characterization**

17

18 Graphitic carbon nitride can be easily prepared by the direct pyrolysis of various organic precursors  
19 (Figure 1a). The intrinsic physicochemical properties of  $\text{g-C}_3\text{N}_4$ , including morphology, thermal  
20 stability, surface area, pore volume, and yield are closely related to the precursor [24].

21 The morphological characterization of the prepared samples was performed by FE-SEM  
22 investigation. The FE-SEM images of  $\text{g-C}_3\text{N}_4$  samples are depicted in Figure 1. All the  $\text{g-C}_3\text{N}_4$

1 particles exhibit wrinkles and irregular shapes. In particular, CN-D and CN-M consist of large  
2 amounts of dense and thick nanosheets with irregular shape assembled together, resulting in a  
3 condensed morphology (Figure 1a, d and b, e). On the contrary, CN-U shows dispersed smooth and  
4 thin irregular flakes with characteristic higher porous morphology (Figure 1c, f), respect to the other  
5 two. The typical higher porous structure is due to the different reaction pathway of urea respect to  
6 melamine and dicyandiamide, as discussed below [26][27].

7

8

*Please insert here Figure 1*

9

10 Elemental analysis was carried out to evaluate the C/N ratio for the different samples (Table S1).  
11 The three carbon nitride samples showed a C/N ratio of 0.57 - 0.58, which is less than the theoretical  
12 value of 0.75 and less than the average value usually reported in literature (*e.g.* 0.70) [28]. The similar  
13 C/N ratio of the different carbon nitride confirms the excess of nitrogen in all samples, if compared  
14 to theoretical values. These observations are attributed to the incomplete condensation of amino  
15 groups, which is related to the small, but significant, amounts of hydrogen that is still present in the  
16 compounds [29]. This explains why the general formula  $C_xN_yH_z$  is usually assigned to carbon nitride  
17 [28]. In some cases, determination of C:N:H ratios is affected by the presence of other elements *i.e.*  
18 exposure to air or moisture, which can be incorporated into the samples [28]. For example, the evident  
19 missing amount reported for CN-U in Table S1 can be attributed to oxygen or moisture, which is still  
20 present in the sample.

21 XRD patterns (Figure 2b) of the three g- $C_3N_4$  samples clearly show two peaks at  $27.6^\circ$  and  $13.5^\circ$ ,  
22 which are assigned to (002) and (100) planes, respectively. The main peak at  $27.6^\circ$  (002) is attributed  
23 to the strong interplanar stacking of the conjugated aromatic systems while the less pronounced peak

1 at  $13.5^\circ$  is due to the in-plane tri-s-triazine units, which form one-dimensional (1D) melon units [24].  
2 These two diffraction peaks are consistent with the XRD patterns of g-C<sub>3</sub>N<sub>4</sub> (JCPDS 87-1526). No  
3 particular difference is seen in the position of XRD peaks for g-C<sub>3</sub>N<sub>4</sub> powders prepared from different  
4 precursors, confirming identical crystal structures [26]. The interplanar d-spacing was calculated  
5 considering the strong peak at  $27.6^\circ$  and was around 3.26 Å for all samples. In the XRD spectra of  
6 CN-U, the two main peaks are broader and have lower intensity as a consequence of smaller  
7 crystalline domains [27]. The possible explanation for the different peak shapes in CN-U can be  
8 attributed to the alternative polycondensation route [26]. In fact, during the thermal condensation of  
9 urea, the heptazine-based structure might not be completely formed and some structural defects can  
10 be present in the final product [27]. The FWHM of the Bragg lines of g-C<sub>3</sub>N<sub>4</sub> powders, was calculated  
11 in order to compare the size of the crystallites. The average crystallites sizes are 13.18, 40.94 and  
12 31.02 nm for CN-U, CN-D and CN-M, respectively. To summarize, the XRD patterns all belong to  
13 g-C<sub>3</sub>N<sub>4</sub> structure but both the intensity and breadth of the peaks are strictly related to the different  
14 nanostructures and morphologies of the as-prepared g-C<sub>3</sub>N<sub>4</sub> samples [24].

15 The FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub> are shown in Figure 2c. All samples showed some evident groups of  
16 signals centred in three different regions of the spectra: at 3000 – 3500 cm<sup>-1</sup>, 1200 – 1700 cm<sup>-1</sup> and  
17 700 – 800 cm<sup>-1</sup>. The absorption peaks in the 700 – 800 cm<sup>-1</sup> region are typically assigned to the  
18 bending vibration mode of carbon nitride heterocycles, in particular the band at 801 cm<sup>-1</sup> is  
19 characteristic of out of plane bending vibration mode of the triazine units [24]. The bands in the 1200  
20 – 1650 cm<sup>-1</sup> region correspond to the typical stretching vibration modes of the heptazine heterocyclic  
21 ring (conjugated C=N). The 2172 cm<sup>-1</sup> peak is only observable in the CN-U spectra and is assigned  
22 to C≡N triple bond. The presence of this peak indicates that the aromatic unit of g-C<sub>3</sub>N<sub>4</sub> was partly  
23 broken and defected [30]. Another interesting difference among the samples is seen in the 3000 –  
24 3500 cm<sup>-1</sup> region. The absorption band at 3170 cm<sup>-1</sup> is assigned to the stretching mode of O-H while

1 the band at  $3336\text{ cm}^{-1}$  belongs to the N-H vibration mode [30]. This indicates the existence of  
2 uncondensed amino groups and absorbed  $\text{H}_2\text{O}$  molecules in all samples. However, the peaks intensity  
3 of CN-U is stronger than that of CN-D and CN-M, indicating that urea improves the polycondensation  
4 of  $\text{g-C}_3\text{N}_4$  [24]. Nonetheless, all samples basically retain the carbon nitride structure.

5 All the synthesized samples have similar nitrogen adsorption-desorption isotherms (Figure 2d),  
6 which belong to the Type IV isotherm with H3 loop corresponding to monolayer coverage and  
7 multilayer adsorption, typical of non-rigid aggregates of plate-like particles [31]. The specific surface  
8 areas were 4.5, 5.1 and  $44.8\text{ m}^2\text{ g}^{-1}$  for CN-D, CN-M and CN-U, respectively while the pore volume  
9 lets us suppose that all samples have negligible microporosity and some disordered interparticle  
10 mesoporosity (Figure 2e). CN-U has the highest specific surface area and highest porosity, confirming  
11 its different morphology.

12 More precisely, both the specific surface areas and pore volumes of CN-U are one order of  
13 magnitude higher than those of CN-D and CN-M, as reported in Table S2. The different  
14 morphological characteristics for CN-U are due to the particular synthetic route of carbon nitride  
15 from urea, which induces the formation of large amount of gas such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , favouring the  
16 expansion of the packing layers and higher porous structures. In particular, the presence of oxygen  
17 heteroatom in urea affects the thermal condensation process, originating water vapour, which can act  
18 as “soft template” producing porous structures and inducing the expansion of carbon nitride layers  
19 [27]. As previously observed, higher porosity specific surface area of the urea-derived  $\text{g-C}_3\text{N}_4$  can  
20 enhance the electrochemical properties of the carbon nitride [27]. In particular, the high surface area  
21 facilitates the mass transfer providing more active sites for surface-dependent reactions. At the same  
22 time structural defects resulting from the lack of a proper s-triazine structure can generate more  
23 catalytic active sites for LiPSs interaction [27].

24

1 *Please insert here Figure 2*

2

3 To better investigate the chemical state of the different elements and the surface composition and  
4 functionalization, samples were analysed by X-ray photoelectron spectroscopy (Figure 3). The  
5 comparison of the survey spectra reveals that all samples predominantly contain C, N and O elements  
6 (Figure S1). No significant shift in the binding energy of C1s, N1s and O1s signals is detected,  
7 showing that the chemical state on the surface of the g-C<sub>3</sub>N<sub>4</sub> is almost the same in the various samples.  
8 Moreover, the similar intensity of C1s and N1s peaks suggests that the amount of C and N is almost  
9 the same in each sample. Table 1 reports the relative percentage of C and N for CN-D, CN-M and  
10 CN-N calculated by high resolution XPS spectra deconvolution. Unfortunately, the quantitative XPS  
11 analysis of C is hindered by the presence of “adventitious” C1s signals deriving from the carbon  
12 tape used to mount the samples. However, a small signal of silicon was also detected and used to  
13 evaluate the contribution of the carbon tape in the C1s spectra. For samples CN-M and CN-U, the  
14 C1s core level spectra (Figure 3a, b, c) was deconvoluted into four components: sp<sup>2</sup> hybridized C  
15 atoms (284.8 eV), C–O (286.2 eV), N–C=N (288.0 eV) and C=O (288.9 eV). The C1s spectrum of  
16 CN-D (Figure 3a), was deconvoluted in five components. The additional peak centred at 290.2 eV is  
17 ascribed to O=C–O. As previously mentioned, the carbon tape signals can interfere in the analysis,  
18 these peaks are located at 284.8 eV for main C–C interaction, at 286.1 eV (C–O) and at 288.7 eV (O–  
19 C=O) due to surface oxidation of the carbon film [28]. For this reason, the high resolution N1s  
20 spectrum (Figure 3d, e, f) helps to obtain more information on the carbon nitride surface chemistry.  
21 The N1s spectra were deconvoluted into three main components. In particular, the peak at 398.5 eV  
22 was attributed to hybridized nitrogen in C–N bonds (C=N–C) of triazine rings, which is consistent  
23 with the peak at 288 eV of sp<sup>2</sup> bonded C atoms in the C1s spectrum. The peak at 399.6 eV refers to  
24 the central N atoms bridging between three heptazine rings (N–(C)<sub>3</sub>). The peak at 401.1 eV is

1 indicative of C–N–H uncondensed amino groups (H–N–(C)<sub>2</sub>) [28]. No signals were detected at 403  
2 eV due to N–O species.

3 As reported in Table 1, the different surface functionalities of CN-U, respect to CN-D and CN-M  
4 is particularly evident. In fact, the surface of carbon nitride obtained from urea is particularly rich of  
5 pyridinic nitrogen, which is the major adsorption sites of LiPSs. This is in good agreement with  
6 similar conclusions achieved by other studies, combining theoretical calculations with experimental  
7 analysis [17][18][19][32].

8

9 *Please insert here Figure 3*

10 *Please insert here Table 1*

11

12 To further evaluate the polysulfide adsorption capability of the various carbon nitrides, a visual  
13 adsorption test under argon atmosphere was performed. After adding g-C<sub>3</sub>N<sub>4</sub> to the Li<sub>2</sub>S<sub>6</sub> solutions  
14 the colour appears yellow for all samples, as depicted in Figure 4a. The solution containing CN-U  
15 appears paler, due to the intrinsic colour of carbon nitride obtained from urea, which is closer to pale  
16 yellow. After resting for 12 hours without stirring, only the solution containing CN-U is transparent  
17 (Figure 4a). On the contrary, the solution containing CN-M shows no colour fading, while the one  
18 with CN-D shows only a mild discolouration. Accordingly, the interaction between CN-U and LiPSs  
19 is the strongest one. The consistent colour fading, clearly observable after 12 hours, confirms the  
20 strong interaction between lithium polysulfides and carbon nitride, especially for CN-U. According  
21 to SSA analysis, it is worth noting that, the added amount of 0.5 m<sup>2</sup> for CN-U is definitely lower in  
22 comparison to the others, so the active sites accessibility is particularly important for a good physico-  
23 chemical interaction. We also show a comparison at 0 hours and after 12 hours among the pure Li<sub>2</sub>S<sub>6</sub>

1 reference solution, the  $\text{Li}_2\text{S}_6$  solution with  $0.5 \text{ m}^2$  of KJB and the  $\text{Li}_2\text{S}_6$  solution with  $0.5 \text{ m}^2$  of CN-U  
2 (Figure 4b). The LiPSs solution with CN-U showed an evident discoloration after 12 hours,  
3 confirming that carbon nitride has relevant adsorption capability for LiPS. On the contrary no  
4 discoloration is seen with KJB, confirming that the interaction of KJB is weak and not sufficient for  
5 high sulphur loadings.

6 Regarding the electrochemical characterization of the double-layer electrodes, cyclic voltammetry  
7 and galvanostatic cycling were performed for all the samples.

8 Figure 4c shows the cyclic voltammetry profiles at a scan rate of  $0.1 \text{ mV s}^{-1}$ , within the cut-off  
9 potentials of 1.6 - 2.8 V. All the CV curves demonstrate typical sulphur cathode behaviour. As  
10 expected, the two peaks detected during the initial cathodic reduction, correspond to two different  
11 redox processes. The first reduction peak at 2.23 V refers to the reduction of sulphur ( $\text{S}_8$ ) to soluble  
12 long-chain lithium polysulfide ( $\text{Li}_2\text{S}_x$ ,  $4 < x < 8$ ), while the second reduction peak centred at 1.95 V  
13 is assigned to the further conversion of long-chain LiPSs to insoluble short-chain lithium polysulfides  
14 ( $\text{Li}_2\text{S}_2$  or  $\text{Li}_2\text{S}$ ). By contrast, during the oxidation process, two overlapping anodic peaks at 2.45 V  
15 and 2.55 V are observed. These peaks represent the formation of both higher order polysulfides and  
16 elemental sulphur, by the oxidation of low order LiPSs. The peaks potential of the double layer  
17 electrodes are shifted if compared to the peaks positions of the single layer electrode (STD). Precisely,  
18 in double-layer electrodes the two reduction peaks are shifted toward lower potentials while the  
19 oxidation peaks move towards higher potentials if compared with STD cathode.

20 Generally, the broader shape observed for the DL electrodes is attributable to the presence of the  
21 second layer, and due to the consequent smaller ion diffusion typical for thicker electrodes, as already  
22 observed in previous work [33][34]. Secondly, the initial higher polarization can be related to the  
23 semiconducting nature of carbon nitride, which is widely distributed in the second layer. In fact, as  
24 possible to see in the FE-SEM micrographs (Figure S5), DL electrode containing CN-U shows a wide

1 distribution of carbon nitride into the top-layer. While the electrodes with CN-D and CN-M present  
2 a less homogeneous distribution of dense and thick agglomerates.

3 Carefully observing the voltammograms of DL cathodes, some accentuated anodic and cathodic  
4 peaks shoulders are detectable. The presence of different peaks/shoulders are attributable to the  
5 different reduction reactions involved in the Li-S discharge process. The presence of evident and  
6 well-defined shoulders for the DL electrodes, lets us suppose that carbon nitride shifts some  
7 polysulfides conversion reactions. In fact, the broader profile can, also, indicate the presence of  
8 numerous species undergoing the anodic reaction, over a wide range of potentials. Similar CV  
9 voltammograms were also reported by Yao *et al.* [35].

10 The galvanostatic charging and discharging behaviour of the cathodes was compared at C/5 for 200  
11 cycles, after three activation cycles at C/10.

12 Figure 4e shows the first-cycle galvanostatic voltage profiles at C/10 of the STD and of the double-  
13 layer electrodes, which all exhibit the typical two plateau discharge curves. The first plateau at 2.3 V  
14 is related to the reduction of sulphur to long-chain LiPSs, and the second, at 2.1 V, corresponds to the  
15 reduction into short-chain LiPSs. The four cathodes delivered an initial discharge capacity at C/10 of  
16 about 780, 870, 1010 and 1150 mAh g<sup>-1</sup> for STD and double layer STD+CN-D, STD+CN-M,  
17 STD+CN-U electrodes, respectively. The initial higher capacity of STD+CN-x electrodes can be due  
18 to the additional contribution to the discharge capacity of about 93.6 mAh g<sup>-1</sup> due to g-C<sub>3</sub>N<sub>4</sub> [23]. A  
19 second explanation can be a partial rearrangement of the active sulphur material after the initial  
20 charge-discharge cycle. In particular, the g-C<sub>3</sub>N<sub>4</sub> layer can reduce the capacity loss originating from  
21 the rearrangement of sulphur during the first cycles [23].

22 After 200 cycles (Figure 4d), the discharge capacity at C/5 was 340 mAh g<sup>-1</sup> for STD electrode and  
23 406, 609 and 740 mAh g<sup>-1</sup> for STD+CN-D, STD+CN-M, and STD+CN-U, respectively. The capacity

1 retention (for the 1<sup>st</sup> and the 200<sup>th</sup> cycles at C/5) is higher for the double-layer electrodes, resulting  
2 88.1 % for STD+CN-U and 73.9 %, 58.0 %, 52.6 % for STD+CN-M, STD+CN-D and STD,  
3 respectively. This means that the capacity fade of the STD+CN-U is only 0.06 % per cycle. The  
4 Coulombic efficiency at the 200<sup>th</sup> cycle is higher than 99 % for all samples (Figure S6, Table S3).

5 The overpotential of the electrodes was calculated measuring the voltage hysteresis ( $\Delta E$ ) between  
6 charge and discharge curves at 50 % of the total discharge capacity (Q1/2) at the 1<sup>st</sup> cycle (Figure  
7 S7a). The STD cathode showed an initial polarization of 0.17 V, whereas in the double layer cathode  
8 the polarization was 0.23 V. The large overpotential observed in first cycles should be ascribed to the  
9 initial wetting process between the cathode and the electrolyte, and this is particularly true for the  
10 double-layer electrode, where sulphur is confined in the bottom layer, thus the electrolyte needs more  
11 time to reach it. Moreover, the layer of g-C<sub>3</sub>N<sub>4</sub> decreases the conductivity of the cathode and increases  
12 the overpotential. At the 1<sup>st</sup> cycle, for STD the capacity of the upper (Q1) and the lower (Q2) plateaux  
13 were 269 and 510 mAh g<sup>-1</sup> respectively, corresponding to a total discharge capacity of about 779  
14 mAh g<sup>-1</sup>, which is definitely lower than sulphur theoretical value of 1675 mAh g<sup>-1</sup>. On the contrary,  
15 for the double-layer cathode Q1 was 374 mAh g<sup>-1</sup> and Q2 was around 808 mAh g<sup>-1</sup>, which summed  
16 together correspond to a total discharge capacity of 1182 mAh g<sup>-1</sup>, that is 34 % higher capacity than  
17 that of STD. The corresponding Q1 and Q2 values of the single-layer electrode are approximately 35  
18 and 65 %, respectively, while they are 32 and 68 % for the double-layer, which means that the  
19 percentage contribution of upper-plateau discharge, due to long-chain LiPSs, is lower for the cathode  
20 containing carbon nitride.

21 Considering the charge/discharge curves from the 1<sup>st</sup> to 200<sup>th</sup> cycle (Figure S7b, c), for STD and  
22 STD-CN-U, the polarizations increase with the increase of the current density from C/10 to C/5.  
23 Larger polarization of double-layer electrodes is seen at higher C-rate, while the overpotential of STD  
24 cathode is quite constant at C/5. As depicted in Figure S7c, the polarization of STD + CN-U increases

1 from C/10 to C/5 (3<sup>rd</sup> to 5<sup>th</sup> cycle) but decreases from 5<sup>th</sup> to 200<sup>th</sup> cycle at constant C/5-rate. This  
2 means that after some “activation” cycles, the initial polarization effect is mitigated, due to the  
3 presence of carbon nitride. The decrease of specific capacity ( $\Delta Q$ ) related to the upper plateau,  
4 between the 1<sup>st</sup> and 200<sup>th</sup> cycle, is around 147 mAh g<sup>-1</sup> for the STD and 115 mAh g<sup>-1</sup> for the STD +  
5 CN-U electrode. As known, the region of the upper discharge plateau is ascribable to the formation  
6 of soluble long-chain polysulfides. Therefore, it is possible to assume that the decrease of specific  
7 capacity ( $\Delta Q$ ) related to the upper plateau, is mainly due to the formation and diffusion of soluble  
8 polysulfides into the electrolyte, which induces the irreversible loss of active sulphur. For this reason,  
9 the values of  $\Delta Q$  can be directly correlated to the suppression of polysulfide diffusion [36]. The lower  
10  $\Delta Q$  observed for double layer cathode means a lower irreversible loss of active sulphur and  
11 consequently an effective lower LiPSs dissolution, thanks to the presence of carbon nitride. These  
12 results indicate that the carbon nitride layer not only enhances the specific capacity of the cell but  
13 also reduces the capacity loss originating from rearrangement of active sulphur during cycling.

14 To evaluate the self-discharge of the battery the STD cell and the STD+CN-U cell were cycled at  
15 C/10 for one cycle and then rested for 20 days (Figure 4f). During the rest phase, the open circuit  
16 potential (OCV) of the cells were measured once per minute then two charge/discharge cycles were  
17 performed at the end of the rest time. The measurement was performed to evaluate the static  
18 stabilization of Li-S cells and the decay of the open-circuit voltage due to polysulfides diffusion,  
19 which is related to the self-discharge of the cell with consequent irreversible capacity fading. Both  
20 the OCV and the capacity retention after the rest time were used to evaluate the effect of carbon  
21 nitride on the discharge behaviour of the cell. The STD electrode delivered an initial capacity of 780  
22 mAh g<sup>-1</sup> (at C/10), while the STD + CN-U delivered an initial capacity of 980 mAh g<sup>-1</sup>. After 20 days-  
23 rest, the specific capacity of STD was 650 mAh g<sup>-1</sup> with capacity retention of 83 %, while the STD +

1 CN-U successfully recovered up to  $910 \text{ mAh g}^{-1}$  with capacity retention of 93 %. After the long-time  
2 rest the STD cell exhibited severe capacity fading, 10 % higher than that of STD + CN-U.

3 Both cells demonstrated an initial voltage of 2.37 V after the first cycle at C/10. After resting for  
4 20 days, the STD cell voltage showed an OCV of about 2.227 V, indicating a voltage decay of 145  
5 mV. After the same rest time, the STD + CN-U cell showed a final voltage of 2.314 V, with a voltage  
6 decay of about 61 mV, which is consistently lower than the OCV decay of the STD. These results  
7 can be reasonably attributed to the polysulfides trapping action and the consequent self-discharge  
8 inhibition due to g-C<sub>3</sub>N<sub>4</sub> in the double-layer cathode.

9

10 *Please insert here Figure 4*

11

12 Thus, carbon nitride obtained from urea is the best candidate for lithium polysulfides trapping. The  
13 reason is twofold. First, we observed that morphology is a key factor, since the SSA of CN-U is one  
14 order of magnitude higher than that of the other samples. This increases the presence of active sites  
15 able to interact with LiPSs. Second, the different surface chemistry of CN-U, being particularly rich  
16 of pyridinic nitrogen, allows specific interactions with LiPSs species.

17 To better investigate and discriminate the role of surface chemistry and material morphology on  
18 LiPSs adsorption ability, the influence of the synthesis temperature was examined. Three different g-  
19 C<sub>3</sub>N<sub>4</sub> samples were synthesized by thermal condensation process, starting from urea, at the annealing  
20 temperatures of: 450°, 550° and 650 °C, respectively. The samples were labelled as CN-U-x, where  
21 x refers to the specific annealing temperature.

1 The FESEM micrographs of the prepared samples are shown in Figure 5a. At the process  
2 temperature of 450 °C, g-C<sub>3</sub>N<sub>4</sub> shows a regular morphology composed of wavy and smooth flakes  
3 with a low presence of visible pores. Increasing the temperature to 550 °C, the typical flakes are still  
4 present, but some rolled and conical structures start to appear, originating a visible porosity into the  
5 sample. The thermal degradation is particularly evident at 650 °C, where the original large flakes are  
6 seriously degraded, and highly porous structure is visible.

7 The structural characteristics of the samples are further analysed by X-ray diffraction and FT-IR  
8 spectroscopy (Figure 5b). The XRD pattern indicates that g-C<sub>3</sub>N<sub>4</sub> was already formed even at low  
9 annealing temperature of 450 °C and is still present 650 °C. This is consistent with the two typical  
10 diffraction peaks at around 13° and 27.5° corresponding to (001) and (002) planes, respectively  
11 (JCPDS file no. 87–1526). The main peak results slightly shifted from 27.26° to 27.52° in CN-U-550,  
12 if compared to CN-U-450, but it is around 27.36° for CN-U-650 sample. However, the interplanar d-  
13 spacing of the interlayer stacking of conjugated aromatic system is 3.25 Å and quite similar for all  
14 the samples.

15 The FT-IR analysis of the samples shows the typical absorption bands of carbon nitride, confirming  
16 the formation of g-C<sub>3</sub>N<sub>4</sub> at all temperatures (Figure 5c). The obtained spectra are similar to the ones  
17 previously described (Figure 2c) however, the peaks in the range of 3000 - 3700 cm<sup>-1</sup> are sharper for  
18 CN-U-650, indicating that more C–NH<sub>2</sub> groups and C–NH–C bridges between heptazine units are  
19 present in the structure [37]. This results in a greater fraction of small polymer segments containing  
20 only few heptazine units with -NH/NH<sub>2</sub> groups at the ends [37] and suggests that the higher  
21 temperature of polymerization promotes the planarization of the g-C<sub>3</sub>N<sub>4</sub> layers, weakening the  
22 interactions between two adjacent atoms, which are respectively located in two adjacent tri-s-triazine  
23 rings [38].

1 To confirm the different porosity and surface area of the synthesized samples, the nitrogen  
2 adsorption-desorption isotherms and pore size distribution (PSD) were evaluated by BET method.  
3 The pore size distribution denotes the mesoporous structure for all g-C<sub>3</sub>N<sub>4</sub> (Figure 5 d, e) [39][40].  
4 In particular, CN-U-450 and CN-U-550 have small mesopores at about 3-5 nm and some larger  
5 mesopores at about 35 - 45 nm. Interestingly, the CN-U-650 pore distribution is wider and more  
6 heterogeneous, presenting huge amount of mesopores of about 35-45 nm. Additionally, mesopores at  
7 3 - 5 nm and micropores at 2 nm, are present. This porosity is due to the splitting of the nanosheets  
8 layers during the thermal condensation and exfoliation process of carbon nitride. Particularly, small  
9 mesopores may be originated by the nanosheets splitting, while larger mesopores can be prevalently  
10 formed by the packing process of g-C<sub>3</sub>N<sub>4</sub> layers [39][40]. The characteristic PSS of CN-U-650 is the  
11 result of the thermal exfoliation occurring at high temperature and the consequent structure  
12 degradation, which originates a **higher number** of pores. The generation of **higher** porous structure  
13 allows a significant enhancement of specific surface area, which increases as the process temperature  
14 rises. The specific surface areas of CN-U-450 is about 42 m<sup>2</sup> g<sup>-1</sup>, similar to the one at 550 °C (48 m<sup>2</sup>  
15 g<sup>-1</sup>). In contrast, the specific surface area is twice for CN-U-650, which is about 84 m<sup>2</sup> g<sup>-1</sup>. In general,  
16 the BET surface area of g-C<sub>3</sub>N<sub>4</sub> increases with the polycondensation temperature, because the  
17 temperature increment promotes the separation of layers in g-C<sub>3</sub>N<sub>4</sub>. Over 600 °C, the decomposition  
18 of carbon nitride layer networks occurs, which creates additional pores in the structure and a  
19 characteristic “sponge-like” morphology.

20  
21 *Please insert here Figure 5*

1 The surface chemical composition of the synthesized samples was also evaluated by XPS analysis  
2 (Figure 6). The survey spectra for all g-C<sub>3</sub>N<sub>4</sub> samples revealed three main peaks, at 288, 400, and 532  
3 eV belonging to carbon, nitrogen and oxygen, respectively (Figure S8). The presence of oxygen is  
4 more pronounced in CN-U-550 and CN-U-650 samples due to some adsorbed moisture and/or air.

5 For all samples, the C1s spectra (Figure 6a, b, c) were deconvoluted in four main peaks, as  
6 previously reported. In particular, the peak at 284.8 eV arises from the adventitious carbon of the  
7 carbon tape (Csp<sup>2</sup>, Csp<sup>3</sup>) [41], while the weak peak at 286.2 eV is due to nitrogen-related defects of  
8 g-C<sub>3</sub>N<sub>4</sub> (N-CH=N or C-O bonding). The intense peak around 288.1 eV was identified as the typical  
9 sp<sup>2</sup>-hybridized carbon (N-C=N) in the aromatic s-heptazine ring and the other peaks at 289 - 290.1  
10 eV are assigned to C=O or O=C-O species. The high-resolution N1s spectra (Figure 6d, e, f) were  
11 deconvoluted into three peaks, centred at 398.5, 399.6, and 401.1 eV, respectively. The peak at 398.5  
12 eV corresponds to sp<sup>2</sup>-hybridized nitrogen in triazine rings (C-N=C), while the peak at 399.6 eV is  
13 due to tertiary nitrogen N-(C)<sub>3</sub> groups. The weaker peak at 401.1 eV can be attributed to quaternary  
14 N (H-N-(C)<sub>2</sub>) [39][42].

15

16 *Please insert here Figure 6*

17

18 The ratio between C=N-C and N-(C)<sub>3</sub> was calculated in order to evaluate the influence of synthesis  
19 temperature on the surface chemical composition, and reported in Table 2. The CN-U-550 sample  
20 presents higher percentage of secondary nitrogen species (C=N-C ~ 47-56 %) and lower percentage  
21 of tertiary nitrogen species (N-(C)<sub>3</sub> ~ 25 - 38 %), while CN-U-450 shows similar percentage of both  
22 species. CN-U-650 shows higher amounts of N-(C)<sub>3</sub> compared to C=N-C and H-N-(C)<sub>2</sub> species  
23 (about 30 %). A ratio of 0.99, 1.3, and 0.6 for CN-U-450, 550, and 650, respectively, was measured.

1 A low value of the  $C=N-C/N-(C)_3$  ratio indicates the presence of nitrogen vacancy in the triazine  
2 rings site. The relative intensity of the two main peaks reveals that more tertiary nitrogen ( $N-(C)_3$ ),  
3 instead of pyridinic nitrogen ( $C=N-C$ ), is formed as the synthesis temperature increases [39][41].  
4 Therefore, XPS analysis indicates that, by increasing the temperature up to 650 °C, a chemical  
5 transition from pyridinic nitrogen to tertiary nitrogen occurs with consequent degradation of g- $C_3N_4$   
6 sheets.

7  
8 *Please insert here Table 2*

9  
10 Since substantial differences were noticed between CN-U-450 and CN-U-650, we expect  
11 differences in LiPS trapping capabilities.

12 To evaluate the LiPSs adsorption capability 20  $\mu$ L of 1.0 mM of  $Li_2S_6$  solution diluted in 2 mL of  
13 DME:DIOX 1:1 v/v mixture were directly added to a quantity equivalent to 0.5  $m^2$  surface area of  
14 CN 450, 550, and 650 (Figure 7a). After resting the samples for 12 hours, both solutions with CN-U-  
15 550 and CN-U-650 showed colour fading, although the latter is of lower intensity. CN-U-450 still  
16 showed a yellowish **coloration**, demonstrating lower interaction with  $Li_2S_6$ .

17 **The UV-Vis absorption test of carbon nitride obtained from urea at 550 °C is reported in Figure**  
18 **S9. It is well recognized that LiPSs “ $Li_2S_x$ ” ( $2 < x < 16$ ) present three main absorption regions at 400**  
19 **nm, 300 nm, and 200 nm [43][44][45]. In particular,  $Li_2S_4$ ,  $Li_2S_6$  and  $Li_2S_8$  species produce**  
20 **characteristic peaks in the region above 300 nm, respectively at 400, 430, and around 500 nm [46],**  
21 **while elemental sulphur exhibits strong absorption below 300 nm [46]. More in general, the large**  
22 **absorption band between 300 and 400 nm can be assigned to a mixture of  $Li_2S_x$  ( $1 < x < 8$ ) species**

1 and/or radicals [45]. Observing the UV-Vis spectra, the absorbance of the solution containing CN-U-  
2 550 is much lower than pure polysulfides solution, which is consistent with the colour fading  
3 observed in the solution after 12 h. The remarkable absorption intensity decrease, in the range  
4 between 350 – 500 nm, suggests the effective LiPSs entrapment capability of carbon nitride.

5 To further verify the nature of the chemical interaction between g-C<sub>3</sub>N<sub>4</sub> and LiPSs, XPS analysis  
6 was performed on the carbon nitride powder after the LiPSs adsorption test Figure S10. Concerning  
7 high resolution XPS spectra of nitrogen (N1s), the peak attributable to pyridinic bond (C=N–C)  
8 shifted slightly from 398.5 to 398.9 eV, indicating the existence of a chemical interaction between g-  
9 C<sub>3</sub>N<sub>4</sub> and polysulfides species [47]. This was confirmed also by the amount reduction of this  
10 functional group passing from 47.9 to 25 %. At the same time the peaks of high-resolution spectra of  
11 C1s are shifted at lower binding energy, this can be due to the strong chemical interaction between  
12 g-C<sub>3</sub>N<sub>4</sub> and LiPSs [48][49]. In addition, a peak centred at 285.4 eV was detected, which can be  
13 assigned to C–S bond [48]. In the high resolution XPS spectra of sulphur, the peak centred at 162.8  
14 is associable to Li–S bonds of LiPSs or, according to Fan *et. al*, it may also be ascribed to C–S binding  
15 between g-C<sub>3</sub>N<sub>4</sub> and LiPSs [47]. The peak centred at 169.1 V could be attributed to SO<sub>x</sub> species  
16 derived from sulphur oxidation in air [48]. It is important to note that, in the range of 166 - 170 eV,  
17 are generally detectable the peaks corresponding to the formation of thiosulfate and/or polythionate,  
18 which are considered effective polysulfide mediators to limit the diffusion of polysulfides [25][50].  
19 Lastly, the symmetric peak at 55.45 eV in all Li1s spectra is attributed to Li–S bond. Therefore, XPS  
20 analysis demonstrates that g-C<sub>3</sub>N<sub>4</sub> obtained from urea at 550 °C can effectively adsorb LiPSs, thus  
21 enhancing the cycling stability of the batteries.

22 In Figure 7b the specific charge and discharge capacities were compared for each sample, for the  
23 first 10 cycles. The cells were cycled at C/10 for the initial 3 cycles and then cycled at C/5. All the  
24 double-layer (STD + CN-U-x) cathodes displayed higher specific capacities than the STD electrode.

1 The initial specific capacity of the STD cathode was  $800 \text{ mAh g}^{-1}$  at C/10, which is significantly  
2 lower if compared to STD + CN-U-x cathodes, which is more than  $1000 \text{ mAh g}^{-1}$  for all samples. On  
3 the contrary, increasing the current at C/5, the specific capacity of STD + CN-U-650 rapidly decreases  
4 to lower values than the STD. At the same time, as shown in Figure 7c, the specific capacity of STD  
5 + CN-U-450 decreases after 30 cycles, reaching a value comparable to the STD.

6 Figure 7d depicts and compares the charge/discharge curves at the first cycle (at C/10). The  
7 characteristic plateaus are well discernible, and the polarization is similar for all the samples. All STD  
8 + CN-U-x electrodes show slightly higher polarization than STD. This behaviour is due to the  
9 intrinsic nature of carbon nitride double-layer, as previously explained.

10 After 200 cycles (Figure 7c), the STD + CN-U-550 cathode delivered  $750 \text{ mAh g}^{-1}$ , which is  
11 significantly higher than that of STD ( $345 \text{ mAh g}^{-1}$ ). Both STD+CN-U-450 and STD+CN-U-650  
12 showed very low specific capacities after long-cycling test. In particular, STD+CN-U-450 cell failed  
13 after 195 cycles, while STD+CN-U-650 cell delivered a specific capacity of  $250 - 300 \text{ mAh g}^{-1}$  after  
14 200 cycles at C/5.

15 To understand the real behaviour of the double-layer in STD+CN-U-x electrodes and discern the  
16 contribution of the different g-C<sub>3</sub>N<sub>4</sub> structures, the specific capacity at 5<sup>th</sup> and 200<sup>th</sup> cycles are reported  
17 in Table S4, with the corresponding capacity loss (% per cycle) at C/5. The capacity loss between the  
18 5<sup>th</sup> and the 200<sup>th</sup> cycle is 0.23 % per cycle for STD cathode. A similar capacity loss is observed for  
19 STD + CN-U-450, while for STD + CN-U-550 it is about a third of that of the STD. The low capacity  
20 loss observed for both STD+CN-U-450 and STD+CN-U-550 reflects their good capacity retention.  
21 The capacity trend of STD + CN-U-650 is highly instable, which means that the capacity decrease is  
22 not constant during cycling, making it more difficult to determine the capacity retention.

1 Figure S11 compares the Coulombic efficiencies (CE) of the cathodes. The CEs of STD and STD  
2 + CN-U-550 are close to 100 %, reflecting good charge and discharge efficiency in each cycle. The  
3 unsteady CE values for STD + CN-U-650 can be assigned either to parasitic reactions or to the  
4 occurrence of shuttle mechanism responsible for longer charge.

5 All cells were cycled for more than 500 cycles at C/5, in order to evaluate both the long cycling  
6 stability and the capacity retention (Figure 7e). The final capacity of STD + CN-U-550 was 570 mAh  
7 g<sup>-1</sup>, meaning 55 % of the initial capacity at C/5 and corresponding to 0.9 mAh g<sup>-1</sup> loss per cycle.

8

9 *Please insert here Figure 7*

10

11 EIS measurements were performed at OCV, after three formation cycles at C/10 for both STD and  
12 STD+CN-U-550.

13 The EIS spectra consist of a depressed semicircle at high to medium frequency regions and a  
14 bended line in the low-frequency region (Figure 8). In general, the depressed semicircles result from  
15 the superposition of many semicircles, corresponding to several parallel contributions [51]. Typically,  
16 the Nyquist plot of a Li-S cell can be described by an equivalent electrical circuit consisting of an  
17 initial ohmic resistance ( $R_{el}$ ) in series with one or more R//CPE elements (connected in parallel).  $R_{el}$   
18 is the bulk electrolyte resistance, which can be strongly influenced by polysulfides dissolution. CPEs  
19 and  $R_s$  can be attributed to the surface double layer capacity and surface resistance of lithium and  
20 sulphur electrodes, respectively. While  $CPE_{ct}$  and  $R_{ct}$  are assigned to the pore double layer capacity  
21 and the charge transfer resistance, respectively.  $W$  is the Warburg impedance due to the diffusion of  
22 the polysulfides within the cathode [52].

1 The initial  $R_{el}$  and  $R_{ct}$  values are comparable in both electrodes, confirming a good filling and  
2 diffusion in the double-layer by the electrolyte. Therefore, despite of the second layer, g- $C_3N_4$  with  
3 high surface area guarantees fast electrolyte permeation. A lower value of  $R_s$  was calculated for the  
4 double-layer electrode, meaning a lower surface resistance for this electrode. The higher  $R_s$  observed  
5 for the single-layer standard cathode, after only three cycles, can be attributable to a more pronounced  
6 passivation layer formed on both the anode and cathode surfaces, and to a higher amount of  $Li_2S$ .

7

8 *Please insert here Figure 8*

9

10 These results confirm that the differences in terms of specific surface area, pore distribution and  
11 general morphology can inevitably contribute to the final electrochemical performances. However,  
12 the different surface chemistry, in particular the amount of nitrogen species, is reasonably the major  
13 factor affecting the electrochemical behaviour. The huge amount of tertiary nitrogen in CN-U-650  
14 and the concomitant low amount of pyridinic nitrogen is probably one of the most relevant cause of  
15 the low electrochemical performance.

16

#### 17 **4. CONCLUSIONS**

18

19 To limit the shuttle effect, a double-layer approach based on carbon nitride-was investigated in this  
20 work. The adoption of the double-layer approach allows carbon nitride to directly interact with  
21 lithium polysulfides while the interaction between sulphur and conductive mesoporous carbon black

1 is guaranteed. The double-layer electrodes showed good cycle performances, suggesting enhanced  
2 interaction between the polysulfides and carbon nitride. In particular, the electrode containing carbon  
3 nitride synthesized from urea showed the best performances in terms of specific capacity, capacity  
4 retention and coulombic efficiency. This suggested that urea improves the chemical and  
5 morphological features of g-C<sub>3</sub>N<sub>4</sub> towards LiPSs trapping compared to dicyandiamide and melamine.

6 We also discussed how the different temperatures of polycondensation of urea affect the specific  
7 surface area and the surface functionalities of the final g-C<sub>3</sub>N<sub>4</sub>. In particular, the greater amount of  
8 pyridinic nitrogen is a basic parameter for achieving excellent electrochemical performances since it  
9 is recognised as active site for the interaction with polysulfides. Carbon nitride obtained at 550 °C  
10 showed the best electrochemical results, increasing the cell specific capacity by 25% and improving  
11 its useful life over 500 cycles.

12 In summary, a layer of carbon nitride, directly coated on the cathode surface is a successful strategy  
13 to increase the electrochemical performances of sulphur-based electrodes. Moreover, the shuttle  
14 effect can be effectively restricted inserting carbon nitride with optimized morphological properties  
15 and surface functionalities. Finally, the double-layer strategy resulted a versatile technique for future  
16 optimizations and industrial scale-up of S-based cathodes.

17

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3 The processed data required to reproduce these findings will be provided upon request to the  
 4 corresponding authors.

5

6 **Table 1.** Relative percentage of C and N species area of CN-D, CN-M and CN-N calculated by  
 7 high resolution XPS spectra deconvolution.

<i>BINDING ENERGY (EV)</i>	<i>Specie</i>	<i>CN-D</i>		<i>CN-M</i>		<i>CN-U</i>	
		<i>Area %</i>	<i>Area relative%</i>	<i>Area %</i>	<i>Area relative%</i>	<i>Area %</i>	<i>Area relative%</i>
<b>398.5</b>	C=N-C	38.25	10.74	37.37	10.82	60.14	22.36
<b>399.6</b>	N-(C) <sub>3</sub>	40.04	11.24	47.74	13.82	29.75	11.06
<b>401.1</b>	H-N(C) <sub>2</sub>	21.71	6.10	12.65	3.66	7.47	2.78
<b>403.0</b>	N-O	-	-	-	-	-	-
<b>284.8</b>	Csp <sup>2</sup> Csp <sup>3</sup> Cadv	49.32	35.47	50.31	35.75	37.79	23.74
<b>286.3</b>	C-O	12.32	8.87	9.56	6.79	13.71	8.61
<b>288.1</b>	N-C=N	10.35	7.44	14.06	9.99	39.54	24.84
<b>288.9</b>	C=O	22.37	16.09	26.07	18.53	8.96	5.63
<b>290.1</b>	CO <sub>3</sub> <sup>-2</sup>	5.62	4.04	-	-	60.14	22.36
	%N	32.48		35.25		37.18	
	%C*	67.52		64.75		62.82	
	<b>N/C</b>	<b>0.48</b>		<b>0.54</b>		<b>0.59</b>	

8

9

1 **Table 2.** Relative percentage of C and N species area of CN-U obtained at different temperatures,  
 2 calculated by high resolution XPS spectra deconvolution.

<i>BINDING ENERGY</i>  ( <i>EV</i> )	<i>Specie</i>	<i>CN-U-450</i>		<i>CN-U-550</i>		<i>CN-U-650</i>	
		<i>Area</i>	<i>Area</i>	<i>Area</i>	<i>Area</i>	<i>Area</i>	<i>Area</i>
		<i>%</i>	<i>rel</i>	<i>%</i>	<i>rel</i>	<i>%</i>	<i>rel</i>
<i>398.5</i>	C=N-C	16.07	41.81	16.32	47.91	8.03	27.25
<i>399.6</i>	N-(C)3	16.26	42.31	12.86	37.77	12.56	42.66
<i>401.1</i>	H-N( C)2	5.44	14.17	3.96	11.64	8.54	29.01
<i>403.0</i>	N-O	16.07	41.81	1,32	47.91	8.03	27.25

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### Captions to Figures

8 **Fig. 1.** FESEM **micrographs** of STD+CN-D (a, d), STD+CN-M (b, e) and STD+CN-U (c, f) at 25  
 9 and 50 KX respectively.

10 **Fig. 2.** Synthesis scheme (a), XRD patterns (b), FT-IR/ATR spectra (c) N<sub>2</sub> adsorption-desorption  
 11 isotherms (d) and pore-size distribution with specific surface area (inset) (e) comparison for the g-  
 12 C<sub>3</sub>N<sub>4</sub> samples prepared starting from different precursors.

13 **Fig. 3.** XPS high resolution C1s of CN-D (a), CN-M (b) and CN-U (c) and high resolution N1s of  
 14 CN-D (d), CN-M (e) and CN-U (f).

15 **Fig. 4.** Lithium polysulfides adsorption test (a, b), cyclic voltammetry comparison at 0.1 mVs<sup>-1</sup> (c),  
 16 galvanostatic charge/discharge cycling comparison (d), first cycle galvanostatic charge/discharge

1 profiles comparison at C/10 (e) between single-layer cathode and double-layer cathodes and self-  
2 discharge comparison of single-layer standard electrode and CN-U based double-layer electrode (f).

3 **Fig. 5.** FESEM **micrographs** at 50 KX (a), XRD patterns (b), FT-IR/ATR spectra (c) N<sub>2</sub> adsorption-  
4 desorption isotherms (d) and pore-size distribution (e), comparison of carbon nitride powder obtained  
5 at different temperatures.

6 **Fig. 6.** XPS high resolution C1s of CN-U-450 (a), CN-U-550 (b) and CN-U-650 (c) and high  
7 resolution N1s of CN-U-450 (d), CN-U-550 (e) and CN-U-650 (f).

8 **Fig. 7.** Lithium polysulfides adsorption test (a), galvanostatic charge/discharge cycling for the first  
9 10 cycles (b) and for 200 cycles (c), first cycle galvanostatic charge/discharge profiles at C/10 (d),  
10 comparison for double-layer cathodes with g-C<sub>3</sub>N<sub>4</sub> obtained at different temperatures. Galvanostatic  
11 charge/discharge long cycling for double-layer containing CN-U-550 (e).

12 **Fig. 8.** Nyquist plot comparison of single-layer and double-layer cathode and adopted equivalent  
13 circuits.

14

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