



# A comparative photophysical and photoelectrochemical study of undoped and 2-aminothiophene-3-carbonitrile-doped carbon nitride



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## ABSTRACT

Introducing molecular dopants in carbon nitride has been shown to dramatically modify its electronic structure, resulting in efficient charge separation and improved photocatalytic efficiency. Herein, we have studied the effect of doping carbon nitride with 2-aminothiophene-3-carbonitrile. A fundamental photoelectrochemical characterization has been performed comparing the behavior of the resulting material (ATCN) with undoped carbon nitride (CN). On the one hand, it is shown that the photocurrent onset shifts with the pH up to a value of 8 for both materials, as expected theoretically. On the other, ATCN, which benefits from additional light absorption, shows an improved photoactivity toward hydrogen evolution. In addition, it displays intriguing photoluminescence properties that can be additionally engineered by modulating the potential. In a more general vein, this study illustrates how to shed light on the effects of introducing molecular dopants in the CN matrix.

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## 1. Introduction

Global warming and energy crisis are among the main problems that challenge a future viable and sustainable human society. In this context, photocatalytic and photoelectrochemical devices are promising solutions because of their potential to produce H<sub>2</sub> from H<sub>2</sub>O by harvesting solar energy [1–3]. In fact, solar hydrogen would be an excellent alternative fuel since it would be clean, cheap and renewable [4].

Among the different photoactive materials, recently carbon nitride (CN) has attracted much interest for its impressive properties. It stands out due to its thermal and chemical stability, its two-dimensional structure, easy fabrication and semiconductor character, being at the same time a low-cost nontoxic material [5–8]. It is of particular interest that CN features a band gap of about 2.7 eV, with suitable band positions for both water reduction and oxidation [9]. It was first used as a visible light photocatalyst for hydrogen generation by Wang et al. [10]. Since then, a number of publications have appeared demonstrating the interest of this material in photocatalysis [11–17]. However, a low photocatalytic activity has been measured in all cases due to a restricted light

absorption and particularly, due to fast charge recombination. The latter has been related with a low surface area, limited charge mobility and the presence of a high density of grain boundary defects [17–19]. However, seeking new strategies to diminish charge recombination or increase light absorption has been a worldwide continuing endeavor and today a number of general approaches have demonstrated to effectively increase the CN limited photoactivity [20]. Namely, doping with metallic or nonmetallic elements [21], copolymerizing with other organic compounds (see below), performing surface modification (mainly constructing heterojunctions) and nanostructuring are the main successful approaches to increase light absorption and/or favor charge separation.

Carbon nitride is based on covalent networks of tri-s-triazine (heptazine) or triazine units linked by —N= or —NH— groups generating a two dimensional geometry. Being an organic polymer-like material, it can be easily modified through grafting other organic groups in its structure [12,20,22–24]. Among the different possibilities, thiophene-based- $\pi$ -conjugated molecules have attracted great interest as these motifs can act as strong electron donors and also as chromophoric centers to harvest photons. On this basis, Wang and coworkers [25–28] have investigated a variety of co-monomers as building blocks to red-shift the optical absorption and promote exciton splitting and charge separation. Among the different co-monomers, 3-aminothiophene-2-carbonitrile has been explored and it has been

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demonstrated to be particularly promising [25–28]. Its introduction into the CN matrix modulates the electronic structure [25], apparently narrowing the band gap and tuning the LUMO and HOMO positions. This provokes an enhancement in the photocatalytic activity for not only water reduction [25,26,28], but also for the photooxidation of alcohols [27].

Experimentally, this copolymerization takes place simply by heating at 550 °C the co-monomer with the CN precursor (such as urea, dicyandiamide, etc.). The fact that the co-monomer is introduced in extremely small amounts (about 0.1%) allows us to consider such a copolymerization as a form of molecular doping. In this regard, doping CN with sulfur has also been studied [29–32]. This element has been introduced using a sulfur atmosphere and also, using organic precursors containing sulfur. Upon doping, an apparent reduction of the band gap is observed as in the case of thiophene-doping. It is expected that sulfur substitutes nitrogen atoms in the CN lattice, changing its electronic structure [33].

In this work, we have prepared carbon nitride via one-pot condensation of urea and sulfur-doped carbon nitride (ATCN) using 2-aminothiophene-3-carbonitrile as a co-monomer. Such a feasible and economic approach leads to chemically improved carbon nitride sheets, as expected. In this contribution, we have tried to shed some light on the main causes that enhance carbon nitride photochemical properties. For such a purpose, we have combined photoelectrochemical and spectroelectrochemical measurements. Our results evince the importance of the disorder degree of the heptazine units in the final behavior, including the possibility of reversibly tuning the luminescence of ATCN samples. The latter fact points to the presence of new electronic states in ATCN that can act as electron traps. These results also disclose new challenges and opportunities for the future development of CN-based materials.

## 2. Experimental

Nanoporous carbon nitride electrodes were prepared on commercial fluorine-doped tin oxide (FTO) glass substrates 1 ( Pilkington, TEC15) by spin-coating. Carbon nitride powder was obtained by treating 10 g of urea (purity 99.5%+, Aldrich Chem. Co.) in a closed crucible at 550 °C for 2 h (heating ramp of 4 °C·min<sup>-1</sup>). On the other hand, ATCN was obtained by stirring 10 g of urea and 10 mg of 2-aminothiophene-3-carbonitrile (purity 99.99%+, Aldrich Chem. Co.) in 10 mL of ultrapure water for 12 hours. Subsequently, the suspension was heated to 80 °C until complete solvent evaporation and thermally treated as described above for the undoped carbon nitride.

Suspensions of the corresponding powders were prepared (5 mg/mL in dimethyl formaldehyde) and spin-coated on FTO using a two-step program: 900 rpm for 9 s and 2000 rpm for 60 s. Afterward, the samples were annealed at 150 °C in air for 10 minutes. The deposition procedure was repeated twice to obtain the desired film thickness (1.8 μm as measured with a mechanical profilometer KLA-Tencor Alpha Step D-100). Finally, the electrodes were post-annealed at 150 °C in air for 40 minutes to partially sinter the particles among them and with the substrate.

A Bruker D8-Advance X-ray diffractometer operating with Cu-K $\alpha$  radiation at 40 kV and 40 mA was used to obtain the X-ray diffraction patterns. The composition of the electrodes was analyzed by X-ray photoelectron spectroscopy (XPS) using a K $\alpha$  ThermoScientific spectrometer. The nanoparticle morphology was studied by means of a JEOL JEM-1400 transmission electron microscope (TEM), while the electrode surface morphology was observed with a JEOL JSM-840 scanning electron microscope (SEM).

Photoelectrochemical measurements were performed at room temperature using a three-electrode cell provided with a fused

silica window and a computer-controlled Autolab PGSTAT30 potentiostat. In all cases, an Ag/AgCl/KCl(sat) electrode and a Pt wire were employed as a reference and as a counter electrode, respectively. The linear sweep voltammograms started from the positive potential limit, being the scan performed toward more negative potentials. Five different working electrolytes were used: 0.1 M NaOH, buffer solutions of pH 10.50, 8.0 and 4.7 (Table S1), 0.1 M Na<sub>2</sub>SO<sub>4</sub>, and 0.1 M HClO<sub>4</sub>. All of them were prepared with ultrapure water and N<sub>2</sub>-purged before the experiments unless otherwise mentioned. The illumination was carried from the electrode substrate side employing a 300 W Xe arc lamp (Thermo Oriol) equipped with a water filter. The light intensity was adjusted with a neutral density filter to 50 mW·cm<sup>-2</sup> as measured with an optical power meter (Thorlabs model PM100D).

UV-Visible diffuse reflectance spectra were measured with a UV-2401 PC Shimadzu spectrometer using an integrating sphere. Photoluminescence (PL) spectra were recorded using a Fluoromax-4 fluorometer. In-situ PL spectroelectrochemical measurements were performed by using an electrochemical cell fitted to a conventional fused silica cuvette. As in the case of the photoelectrochemical measurements, all the potentials were measured against an Ag/AgCl/KCl(sat) reference electrode and a Pt wire was used as a counter electrode. A computer-controlled Autolab PGSTAT30 potentiostat was also used for these experiments.

## 3. Results

To verify the structure of the as-prepared powders they were analyzed by XRD. The diffractograms of both CN and ATCN are very similar, as displayed in Fig. 1. The XRD patterns show two characteristic peaks at about 13° and 27.5° associated with graphitic stacked CN layers [1,34]. The peak at 13° can be indexed as the (100) plane corresponding to the in-plane structural packing motif of tri-s-triazine units, while the intense peak at 27.5° corresponds to the graphite-like interlayer (002) plane. It is worth noting that the XRD peaks are broad and relatively weak, indicating low crystallinity due to the presence of small ordered domains and/or a small nanoparticle size.

The sample morphology was characterized by electron microscopy. Representative SEM images of the corresponding electrodes, which are shown in Fig. 2A and B, indicate that both CN and ATCN samples are composed of porous aggregates. To obtain additional information about the building blocks of such aggregates, CN and ATCN were analyzed by TEM as shown in Fig. 2C and D. In both cases, a lamellar two-dimensional structure composed of wrinkled nanosheets is observed. From a morphological point of view, both samples are virtually identical.

XPS experiments were carried out to obtain additional information about the chemical composition of both samples

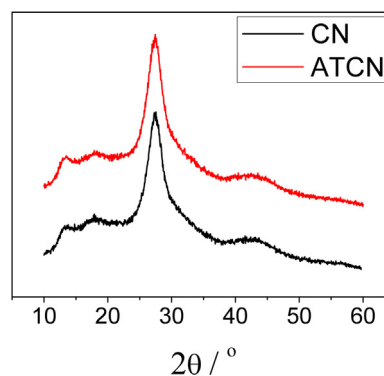


Fig. 1. XRD patterns for CN and ATCN powders.

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