



# Effect of exfoliation and surface deposition of $\text{MnO}_x$ species in $g\text{-C}_3\text{N}_4$ : Toluene photo-degradation under UV and visible light



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## ABSTRACT

A relatively low surface area graphitic carbon nitride produced by a standard melamine calcination procedure was subjected to an exfoliation process and/or surface deposition of Mn-containing species. The resulting catalysts were characterized using X-ray diffraction and photoelectron spectroscopies, transmission electron microscopy, UV–vis and infrared spectroscopies, and porosimetry. The photocatalytic properties of the materials were tested in the gas-phase degradation of toluene under UV, visible and Sunlight-type illumination and their performance assessed through the measurement of the materials optical properties and subsequent calculation of the true quantum efficiency. The numerical analysis of the efficiency parameter evolution throughout the above mentioned carbon nitride samples provides quantitative estimation of the catalytic effect resulting from the exfoliation process and/or the surface deposition of Mn-containing species. Such analysis allows thus to compare the activity significance of each one of the carbon nitride modifications explored as well as the synergistic effect originated by the combined action of such modifications.

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## 1. Introduction

The high levels of pollution originated by industrial and mobile source emissions, together with the ever-higher standards for emission control of many industrialized countries, have driven the current interest in environmental protection processes, leading to a high scientific and technological activity in this area. In this context, much attention has been focused on advanced oxidation processes and in particular heterogeneous photocatalysis. Heterogeneous photocatalysis is an advanced oxidation process that uses semiconductors, broadly applied in the degradation/transformation of organic pollutants as well as biological microorganisms [1–4]. Its most significant advantage with respect to other remediation technologies could be the use of the solar energy, a free and renewable energy source. Obviously, the efficiency of this process depends directly of the photocatalyst performance upon solar irradiation conditions.

Undoubtedly,  $\text{TiO}_2$  has been the most studied photocatalyst. For such material, many studies reported relatively high activity. Addi-

tionally, its low cost and stability makes this material particularly interesting for a wide variety of applications [1,5–8]. However, the limited utilization of the visible and infrared regions of the solar spectrum precludes its wide potential application as a solar photocatalyst. Such limitation comes from the high band gap inherent by all titania polymorphs, around 3.0–3.5 eV [1,7,9–13]. Thus, and despite the significant use of  $\text{TiO}_2$ -based heterogeneous photocatalysts, it is especially important the development of new, alternative semiconductors focusing in the effective utilization of the sunlight. This involves unavoidably the improvement of the visible light use as this region accounts for ca. 43% of the intensity of the solar spectrum.

One of the materials potentially interesting for sunlight-driven photocatalytic applications is the graphite like carbon nitride ( $g\text{-C}_3\text{N}_4$ ). Its good electronic and chemical properties and thermal stability have allowed the use of the  $g\text{-C}_3\text{N}_4$  material as a free metal catalysis for many photochemical reactions such as organic photodegradation, water splitting or alcohol reforming [14–19]. In order to optimize the carbon nitride catalytic properties for target-specific applications, several modifications of bare  $g\text{-C}_3\text{N}_4$  have been conducted, including the surface modification using metals such as Ag, Au, Pt [20–30], and different oxides or hydroxides, among which we can highlight  $\text{ZnO}_2$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Co}(\text{OH})_2$  and  $\text{MnO}_x\text{OH}_y$  [31–41]. Another possible modification consists

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in obtaining exfoliated systems. This greatly increases the surface area of the g-C<sub>3</sub>N<sub>4</sub> bulk. The limited surface area presented by the bulk material, typically 10–40 m<sup>2</sup>g<sup>-1</sup>, is a consequence of the stacking of the g-C<sub>3</sub>N<sub>4</sub> layers and can be significantly increased by the mentioned exfoliation process [15,20,30,42,43]. Moreover, many authors report that exfoliated g-C<sub>3</sub>N<sub>4</sub> nanomaterials can modify positively the photo-charge handling capability of the material with respect to the bulk counterpart [16,44–46]. There are several methods of exfoliating g-C<sub>3</sub>N<sub>4</sub>. One of the simplest is the ultra-sonication assisted by water. In this case, the exfoliated g-C<sub>3</sub>N<sub>4</sub> material presents high stability and lacks toxic impurities (common by other preparation methods), which make them a promising material for photocatalytic processes [44].

In this contribution we combine two strategies related to the exfoliation and surface modification by Mn-containing species to obtain a new material which enhanced catalytic properties with respect to the bare, bulk-type g-C<sub>3</sub>N<sub>4</sub>. Mn-containing species have attracted particular attention due to their significant influence in photoactivity through the efficient handling of hole-related species while exfoliation appears, as mentioned, as a general way to improve photo-performance [39]. We tested such materials in the photodegradation of gas phase toluene. In order to fully analyze the potential of the materials in utilizing efficiently the sun as the energy source of the photodegradation process, the study was carried out using three light sources, this is; UV, sunlight-type and visible type. The characterization of the samples was performed using X-ray diffraction, X-ray photoelectron, infrared, and ultraviolet spectroscopy, transmission electron microscopy and N<sub>2</sub> physisorption. Additionally, the study includes the modelling of the light-matter interaction, necessary for determining the true quantum efficiency values and compare samples in quantitative basis. Using the true quantum efficiency parameter and a simple mathematical procedure we carried out a quantitative analysis of the beneficial effects induced by the exfoliation process of the carbon nitride and/or the presence of Mn-containing species in the photoactivity of the materials.

## 2. Materials and methods

### 2.1. Samples preparation

The graphitic carbon nitride was obtained by calcination of melamine (Aldrich), in a semi-closed system to prevent sublimation, at 580 °C for 4 h using a heating ramp of 5 °C min<sup>-1</sup> [20,39,47]. The exfoliated g-C<sub>3</sub>N<sub>4</sub> material was prepared by ultrasonication for 4 h using as-prepared bulk g-C<sub>3</sub>N<sub>4</sub> in deionized water (1 mg cm<sup>-3</sup>). The suspended part after 18 h of sedimentation was selected as the exfoliated part of the material and obtained after evaporation of the water at 80 °C. The carbon nitride component modified with manganese oxide was prepared using an impregnation method. For this, the g-C<sub>3</sub>N<sub>4</sub> or the exfoliated one and the manganese precursor (Manganese (II) nitrate tetrahydrate, Aldrich) were added to a deionized water solution. After 2 h under magnetic stirring the liquid was evaporated at 110 °C for 15 h. The final MnO<sub>x</sub>-carbon nitride composites were obtained by calcination at 350 °C, with a heating ramp of 5 °C min<sup>-1</sup> maintaining this temperature for 2 h. The final MnO<sub>x</sub> loading was 2 wt.%, confirmed with an error below 5% using ICP-AAS (induced couple plasma and atomic absorption spectroscopy) spectrometry.

Samples names are g-C<sub>3</sub>N<sub>4</sub> or g-C<sub>3</sub>N<sub>4</sub>/MnO<sub>x</sub> when prepared from the initial powder extracted from calcination of melamine and E-g-C<sub>3</sub>N<sub>4</sub> or E-g-C<sub>3</sub>N<sub>4</sub>/MnO<sub>x</sub> when prepared from the powders subjected to the exfoliation procedure.

### 2.2. Characterization and analytical methods

The BET surface areas and average pore volumes and sizes were measured by nitrogen physisorption (Micromeritics ASAP 2010). XRD profiles were obtained using a Seifert D-500 diffractometer using Ni-filtered Cu Kα radiation with a 0.02° step. UV-vis diffuse-reflectance spectroscopy experiments were performed on a Shimadzu UV2100 apparatus using nylon as a reference. The Fourier transform infrared spectra were taken in a Bruker Vertex 80 FTIR spectrometer using a MCT detector. XPS data were recorded on 4 × 4 mm<sup>2</sup> pellets, 0.5 mm thick, prepared by slightly pressing the powdered materials which were outgassed in the prechamber of the instrument at room temperature up to a pressure <2 × 10<sup>-8</sup> Torr remove chemisorbed water from their surfaces. The SPECS spectrometer main chamber, working at a pressure <10<sup>-9</sup> Torr, was equipped with a PHOIBOS 150 multichannel hemispherical electron analyser with a dual X-ray source working with Ag Kα (hν = 1486.2 eV) at 120 W, 20 mA using C 1s as energy reference (284.6 eV). Transmission electron microscopy images were recorded on a JEOL 2100F TEM/STEM microscope.

### 2.3. Photo-catalytic experimental details

Gas-phase photo-oxidation of toluene (≥99% Aldrich) was carried in a continuous flow annular photoreactor containing ca. 0.4 mg cm<sup>-2</sup> of photocatalyst as a thin layer coating on a pyrex tube. The scheme of the reaction system is presented in Fig. 1 and has been presented and detailed in previous works [48,49]. The reacting mixture (100 ml min<sup>-1</sup>) was prepared by injecting toluene into a wet (ca. 75% relative humidity) 20 vol.% O<sub>2</sub>/N<sub>2</sub> flow before entering to the photoreactor, yielding an organic inlet concentration of ca. 700 ppmv. Fluorescent UV (Sylvania F6WBTL-65; 6 W) and sunlight-type lamps (Sylvania F6W/D; 6W) were used for the photoreaction experiment. For the visible light experiments, we used a flexible polyester filter made from a deeply dyed PET material to absorb ultraviolet rays. The material allows less than 10% transmission below 390 nm. Reaction rates and selectivity were evaluated under steady-state conditions, typically achieved after ca. 6–10 h from the irradiation starting. The concentration of toluene and the reaction products were analyzed using an on-line gas chromatograph (Agilent GC 6890) equipped with a TCD (for CO<sub>2</sub> measurement) and FID (organics measurement) detectors.

### 2.4. Light-matter interaction modelling and quantum efficiency calculation

#### 2.4.1. Local superficial rate of photon absorption

The local superficial rate of photon absorption ( $e^{a,s}$ ) is defined by Eq. (1) [31,50]. In this equation  $F_{As}$  is the fraction of light absorbed by the sample and  $q_{sup}$  the radiation flux at each position ( $X_s, Y_s, Z_s$ ) of the catalytic film (See Fig. 1).

$$e^{a,s}(\underline{x}) = q_{sup}(\underline{x}) F_{As} \quad (1)$$

To obtain the radiation flux on the surface of the samples, we calculate first the impinging radiation flux from the lamps ( $q_n$  in Fig. 1). Considering the coordinated system presented in Fig. 2 and the geometry of the reactor (annular multilamp), the  $q_n$  can be determined by Eq. (2) [31].

$$q_n(X_s, Y_s, Z_s) = \sum_{L=1}^{L=4} \sum_{\lambda} \int_{\varphi_{\min,L(x,y)}}^{\varphi_{\max,L(x,y)}} \int_{\theta_{\min(x,y,\varphi)}}^{\theta_{\max(x,y,\varphi)}} \frac{P_{\lambda,L}}{2\pi R_L Z_L} \sin^2 \theta \left( \left( \frac{X_s - X_L}{R} \right) \cos \varphi + \left( \frac{Y_s}{R} \right) \sin \varphi \right) d\varphi d\theta \quad (2)$$

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