

Photocatalytic Activity of Various g-C₃N₄ Materials Over The Removal of Ciprofloxacin

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The characterization techniques shows that the synthesized materials through pyrolysis (CN-P), thermal exfoliation (CN-E) and hidrothermal (HCN) combined with supramolecular agent (HCN-AC) was g-C₃N₄. It should be noted that the specific surface area from HCN-AC was superior (81.64 m² g⁻¹) to the other materials (under 36.36 m² g⁻¹) and its morphology was also different. HCN-AC exhibit a polyhedral morphology with flat faces as a result of the ordered stacking of thin layers, whereas, HCN show a more defined geometry than CN-P (agglomerated structures) and CN-E (thinner sheets and some hollow structures). All the materials were photocatalytically evaluated for the degradation of ciprofloxacin, being HCN-AC whom eliminate a higher percent (80%) in the first hour due to its high specific surface area and a greater presence of nitrogen vacancies.

Introduction

Heterogeneous photocatalysis is an Advanced Oxidation Process (AOPs) capable of eliminate organic pollutants [1]. It requires the presence of a semiconductor material that absorbs light to initiate a serie of surface reactions under environmental conditions to generate reactive oxygen species and electron vacancies [2].

A promising material is the graphitic carbon nitride (g-C₃N₄); but its aplicación is limited by the recombination of photogenerated species and low specific surface area, which is related to the synthesis technique [3]. The pyrolysis method (calcination of nitrogen rich precursor), resulted in a material with low specific area (below 10m²/g), few active sites and inefficient load transportation [4]. To overcome this situation, the thermal exfoliation can enhance its photocatalytic activity; while the combination of hydrothermal method with supramolecular agent increase the specific surface area and allows to control the composition and morphology as a function of reaction time.

For this reason, this work seeks to investigate the effect of g-C₃N₄ synthesized by pyrolysis, thermal exfoliation and hydrothermal method using cyanuric acid as a supramolecular agent for the degradation of ciprofloxacin in water.

Material and Methods

Pyrolysis: 8 g of melamine were calcinated at 550°C for 4 h in a high alumina crucible (CN-P). Thermal exfoliation: 2 grams of CN-P were placed in the high alumina crucible for calcination again at 550°C for 4

h (CN-E). Hydrothermal with supramolecular agent: 4 g of melamine along and 4 g of cyanuric acid (AC) were put into the hydrothermal reactor with 80 ml of deionized water to carry out the reaction at 180°C for 24 h, then it was calcined at 550°C for 4 h (HCN-AC), a material was synthesized without the AC for comparative purpose (HCN). All the materias were characteried by: XRD, FTIR XPS, DRS, BET, SEM. And evaluated in the photocatalytic degradation of ciprofloxacin (20 mg L⁻¹).

Results and Discussion

The synthesized materials exhibit the characteristic signals of g-C₃N₄ at 13.1° and 27.5° [4], which correspond to the (100) and (002) crystal planes, respectively (data not shown). The first is associated with the presence of graphite layers that constitute the structure of heptazine or tris-s-triazine due to the effect of hydrogen bonds, while the second is related to the stacking of the layers due to Vander Waals forces generated by aromatic rings [4]. The intensity of the (002) plane shows the following order: CN-E>CN-P>HCN>HCN-AC, with a similar trend for the (001) plane. Therefore, the synthesis method directly influences the number of layers formed, their extension and the interplanar distance in their stacking. FTIR confirms XRD results (data not shown) by the signals corresponding to the stretching of primary and secondary amines, as well as the structural vibrations of the C-N and C=N bonds coming from the heterocycles in the structure, along with the formation of triazine and tris-s-triazine which are characteristics of g-C₃N₄ [4].

The C1s region in XPS presents a signal that is attributed to the N=C-N₂ bonds belonging to the tri-s-triazine structure; while in the N1s region, three signals were observed corresponding to the C=N-C bonds, to the tertiary atom in the N-C₃ or H-N-C₂ bonds and to the C-N-H amino functional group, respectively (data not shown). It is reported that the intensity ratio between C=N-C/N-C₃ provides information about the nitrogen vacancies in the material [5], with HCN-AC being the smallest value in table 1, it has the highest number of nitrogen vacancies. Table 1 also contain the band gap and the specific surface area along with the pore diameter information from the synthesized materials. The morphology of CN-P exhibit layers stacked without order that form agglomerated structures (Figure 1a). Thermal exfoliation (CN-E) caused the formation of thinner sheets than those observed in CN-I and the presence of some hollow structures (Figure 1b). Regarding HCN, it presented an ordered geometry as a result of the stacking of thin flat sheets (Figure 1c). As for HCN-AC, the supramolecular agent contributed to obtaining a polyhedral morphology with flat faces as a result of the ordered stacking of thin layers (Figure 1d).

The photocatalytic evaluation show that supramolecular agent contributes to eliminate 80% of the initial compound during the first hour in comparison with all the other materials whom achieve a minor percent during the same time.

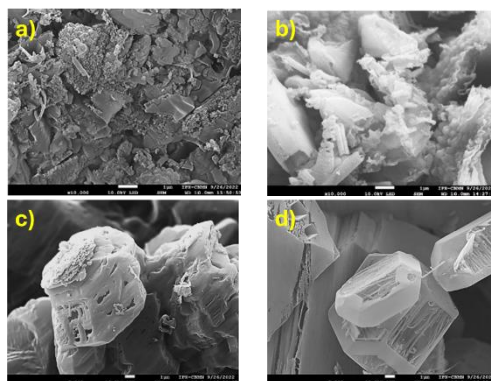


Figure 1. SEM images of a) CN-P, b) CN-E, c) HCN, d)HCN-AC.

Table 1. Characterization results from the synthesized materials from different methods

| Photocatalyst | C=N-C/N-C ₃ | Eg (eV) | Specific surface area (m ² g ⁻¹) | Pore diameter (nm) |
|---------------|------------------------|---------|---|--------------------|
| CN-P | 3.33 | 2.68 | 24.29 | 3.904 |
| CN-E | 3.57 | 2.66 | 28.08 | 3.885 |
| HCN | 3.70 | 2.64 | 36.36 | 3.884 |
| HCN-AC | 3.22 | 2.67 | 81.64 | 3.905 |

Conclusions

XRD, FTIR and XPS confirmed that g-C₃N₄ was synthesized by three different methods. Additionally, XRD, XPS and SEM demonstrate the effect of the synthesis method on the graphite layers that constitute the structure of heptazine or tri-s-triazine as well as the stacking of these layers, in correlation with the creation of nitrogen vacancies in the materials and the morphology obtained. Information that combined with the results of specific surface area and bandgap energy, shows that the addition of cyanuric acid as a supramolecular agent improves the photoactivity of HCN-AC compared to CN-E and CN-P.

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