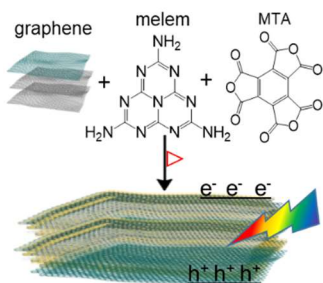


Enhanced Photodegradation of Methylene Blue Utilizing Tri-s-Triazine and Mellitic Triimides Heterostructures: Achieving High Activity in the Visible Spectrum

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Tri-s-triazine species, especially graphitic carbon nitride (g-C₃N₄), have aroused great interest in metal-free photocatalysts. However, the activity of these species is still limited, making it necessary to develop new materials with enhanced properties. In this work, six heterostructured photocatalysts were prepared through thermal polycondensation of different mass proportions of melem, mellitic trianhydride (MTA), graphene and g-C₃N₄. According to the results, the heterostructures produced with melem and MTA are formed by mellitic triimide (MTI) and tri-s-triazine species (g-C₃N₄ and melem) layers. These materials showed high photocatalytic activity under blue and violet light irradiation to decompose methylene blue (MB), as a model compound. The g-g-m20 heterostructure, with the highest percentage of MTI, showed the highest degradation rate of MB in both radiations, highlighting the influence of the number of MTI units to improve the charge stabilization on the photocatalytic properties of heterostructures.

Introduction

g-C₃N₄ has raised broad interest in photocatalysis because of its chemical stability, earth-abundant chemical composition, and eco-friendly character. However, the performance of bulk g-C₃N₄ is considered insufficient for large-scale applications due to its high charge recombination and insufficient visible-light utilization [1]. Various strategies have been presented for the synthesis of g-C₃N₄-based to optimize its photocatalytic activity. Among them, the heterostructure construction have been proposed to enhance the visible-light response and the charge migration [2]. The coupling of g-C₃N₄ with another metal-free semiconductor such as graphene is considered a reliable and effective method to improve its activity [3]. The charge transfer at the interface and the enhanced electron conductivity may improve photocatalytic efficiency. Recently, low band gap heterostructures produced by doping of MTI units into g-C₃N₄ showed significant improvements in photo-oxidative potential and red-shift absorption of metal-free photocatalysts. Condensation of three-directional melem and MTI units produced condensed sheets, which promote efficient intra-interlayer migration of photogenerated charge carriers and exhibits high electrical conductivity [4]. Therefore, in this study we report metal-free hybrid photocatalysts consisted of tri-s-triazine species, graphene and MTI. We evaluated how MTI ratio and presence of graphene as a cocatalyst in heterostructures may affect the decomposition of MB under visible radiation.

Material and Methods

Melem and g-C₃N₄ were obtained by direct thermal polycondensation of melamine at 420 °C and 520 °C (4 h, 5 °C min⁻¹), respectively. Mellitic acid tri-anhydride (MTA) was prepared by reflux of mellitic acid in acetic anhydride for 16 h. Six heterostructures were developed using different precursors (melem, g-C₃N₄, MTA and graphene), in different mass proportions, as shown in

Table 1. The g-C₃N₄-graphene (g-g) was prepared using the sonochemical method (60 min at 40 °C). The g-C₃N₄-MTI (g-m) and g-C₃N₄-graphene-MTI (g-g-m) heterostructures were prepared by thermal condensation (275 °C, 4 h, 7 °C min⁻¹) under N₂ flow. Photodegradation of MB was carried out to evaluate the photocatalytic performance. Tests were performed under visible-light irradiation from two LED light sources: violet (λ = 395 nm) and blue (λ = 450 nm), and the kinetics of MB decolorization was followed using UV-vis (λ=664 nm).

Results and Discussion

XRD and FTIR analyzes were used to verify the structural characteristics of the materials produced. The diffractograms of the heterostructures (Fig. 1a) reveal crystalline structures more similar to melem than to g-C₃N₄. However, the peaks identified at 13.0 and 27.5° are more intense in all heterostructures, indicating an increase in the spacing of the tri-s-triazine species. This behavior may be related to the condensation of melem suggesting that heptazine structures in hybrid materials are also in the graphitic carbon nitride form [5,6].

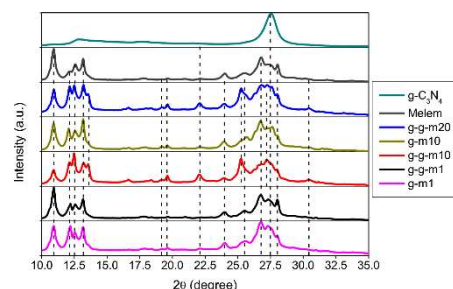


Figure 1. XRD patterns of g-C₃N₄, melem, and heterostructures.

The existence of MTI in the heterostructures can also be observed in the diffractograms. In g-g-m20, material with

a higher MTI ratio, peaks related to polyimide structure are seen centered at 19.1, 19.7 and 30.3° [4]. Additionally, peaks related to MTI show more intensity the greater amount of MTA used in the synthesis, confirming the presence of MTI in the materials [4,7]. In FTIR spectrum of g-g-m20 (Fig. 2), the most intense bands are characteristic of tri-s-triazine structures, similar to the observed for melem and g-C₃N₄. Bands associated with the imide functional group are identified with low intensity due to the small proportion of MTA used to prepare the hybrid materials. [7,8].

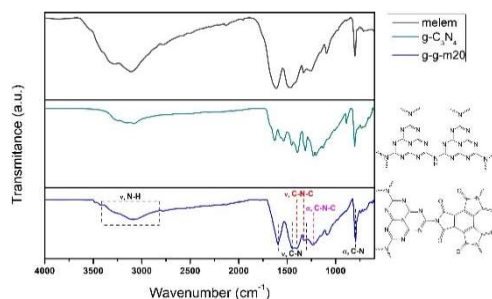


Figure 2. FTIR spectra of g-C₃N₄, melem and g-g-m20.

The photocatalytic performances of hybrid materials were evaluated by MB degradation in aqueous solution. The heterostructures showed high MB adsorption and photo-response under visible light, indicating that adsorption and photocatalysis process occur simultaneously for MB removal. For all photocatalysts, a greater MB removal was observed under violet radiation (Fig. 3a). The decrease in activity of most materials under blue radiation (Fig. 3b) can be explained by the bandgap energy values found by DRS analysis (Table 1), which makes them active at wavelengths shorter than the blue source used (450 nm).

The only photocatalyst that exhibited a similar response in both violet and blue radiations was the material with graphene and the highest percentage of MTI, g-g-m20, with 97.10% and 99.07%, respectively. This percentages of MB removed during photocatalysis was higher than that found in the literature for pure C₃N₄ [9] and may be explained by the low BG presented for this heterostructure when compared with g-C₃N₄ and with other materials developed in this work.

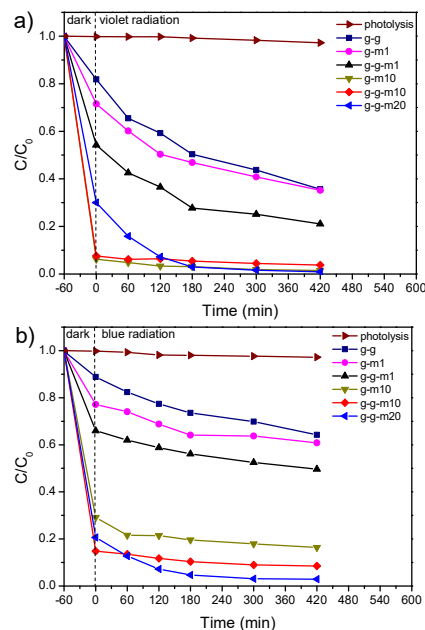


Figure 3. MB photodegradation in a) violet and b) blue radiation.

Table 1. Nomenclature and BG of the prepared heterostructures and the composition of each precursor used in the synthesis (% wt).

Heterostructure	g-g	g-m1	g-m10	g-g-m1	g-g-m10	g-g-m20
Description	g-C ₃ N ₄ -graphene	g-C ₃ N ₄ -MTIx		g-C ₃ N ₄ -graphene-MTIx		
MTA (% molar)		1%	10%	1%	10%	20%
g-C ₃ N ₄	99%					
graphene	1%			1%	1%	1%
Melem		98.7%	87.2%	97.7%	86.4%	74.5%
MTA		1.3%	12.8%	1.3%	12.6%	24.5%
Bandgap (eV)	2.80	2.90	2.76	2.84	2.65	2.54

x = molar percentage of MTA in the heterostructure synthesis.

Conclusions

The method employed to prepare heterostructures with MTI units incorporated into tri-s-triazine species proved efficient. The hybrid material g-g-m20 presented the highest MB degradation rate in both radiations, confirming that the number of MTI units and presence of graphene directly influence the photoactivity and electronic properties of heterostructures.

Acknowledgments

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