Integrating theory and experimental: Insights into $g-C_3N_4$ structures for enhanced photocatalysis

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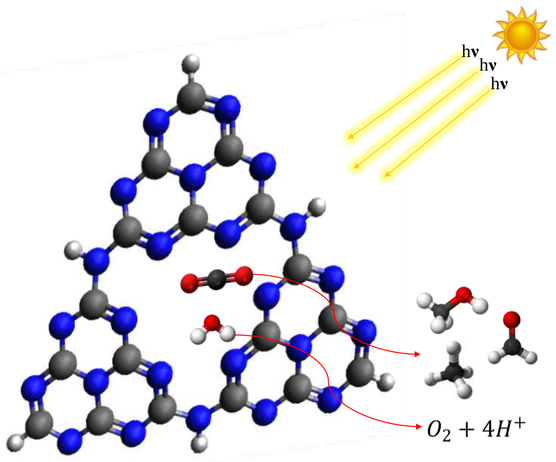
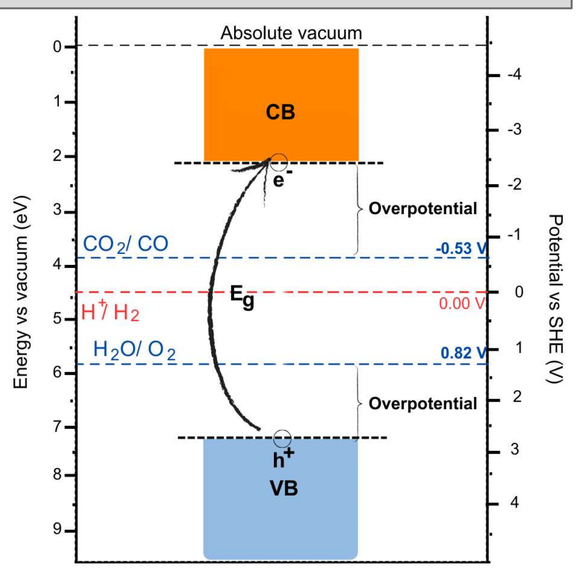
In this study, we investigated the properties of g-C_3N_4, focusing on its standard melamine structure and polymeric form for application in photocatalysis. Photocatalysis involves five essential steps: (1) optimal absorption of light, preferably in the UV spectrum to maximize solar efficiency; (2) effective charge separation, promoting the separation of electrons and holes to increase the recombination rate; (3) selective absorption of substances such as H_2O and CO_2; (4) oxidation; and (5) reduction of these substances. We are conducting detailed theoretical and experimental analyses. Theoretical calculations included geometry optimization and electronic structure characterization, followed by excited state calculations using the TD-DFT/M06/def2-SV(P) method. We also performed experimental analyses, starting with the preparation of g-C_3N_4, where 1g of melamine was heated at different temperatures (400°C, 450°C, 500°C and 550°C) for 4 hours, with a temperature increase of 5°C per minute. The first sample was melamine and after the maximum temperature (550°C) we observed the formation of the polymer. To study the chemical composition and molecular structure of the samples, we used infrared spectroscopy (FT-IR) on Perkin Elmer's Frontier equipment, in UATR mode, covering the spectral range from 4000 to 400 cm-¹, with 32 accumulations. We observed that higher temperatures favored the formation of the polymeric phase. The properties of the structures showed little variation with shape change, fulfilling the essential thermodynamic criteria for photocatalysis in the reduction of water and CO_2.

INTRODUCTION:





Mains steps for photocatalyst:

- Light absorption
- Charge separation
- H_2O / CO_2 absorption
- Oxidation-reduction reactions
- Product desorption

Reactions:	E°(Volts vs. SHE)
$CO_2 + H^+ + 2e^- \rightarrow HCOOH$	-0.61
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$	+0.82

METHODOLOGY:

THEORETICAL:

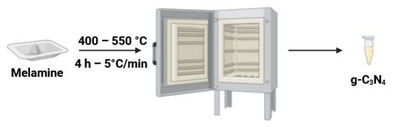
- G09
- DFT/TD-DFT
- M06/DEF2/SV(P)
- Geometry optmization
- Excited state analysis
- Characterization of eletronic properties
  Ionization potential calculations

EXPERIMENTAL:

Melamine: 1g

Heating:
- Temperatures: 400°C, 450°C, 500°C, and 550°C.
- Duration: 4 hours
- Heating rate: 5° C/min

Chemical Composition
- Analysis Technique: FT-IR (UATR)
- Scanning range: 4000-$400cm^{-1}$

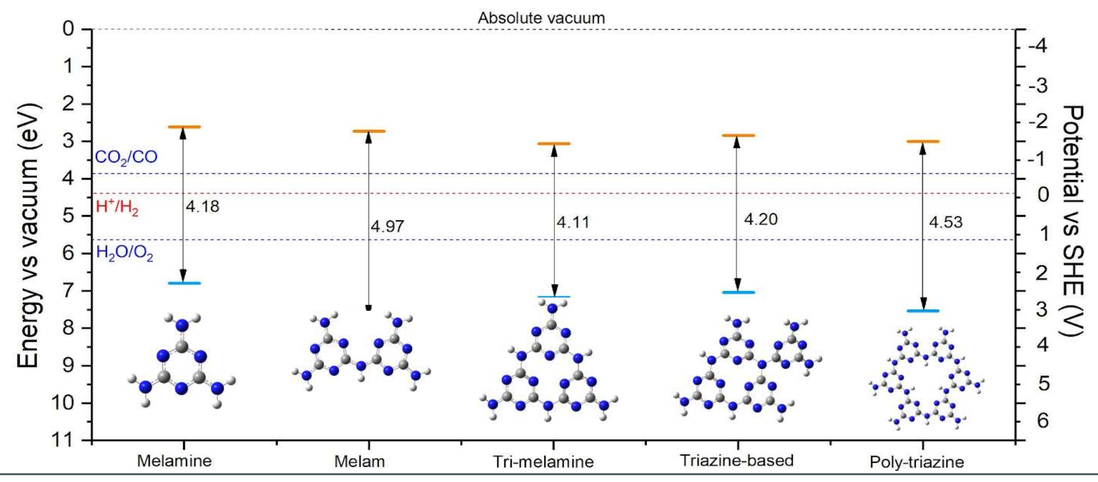


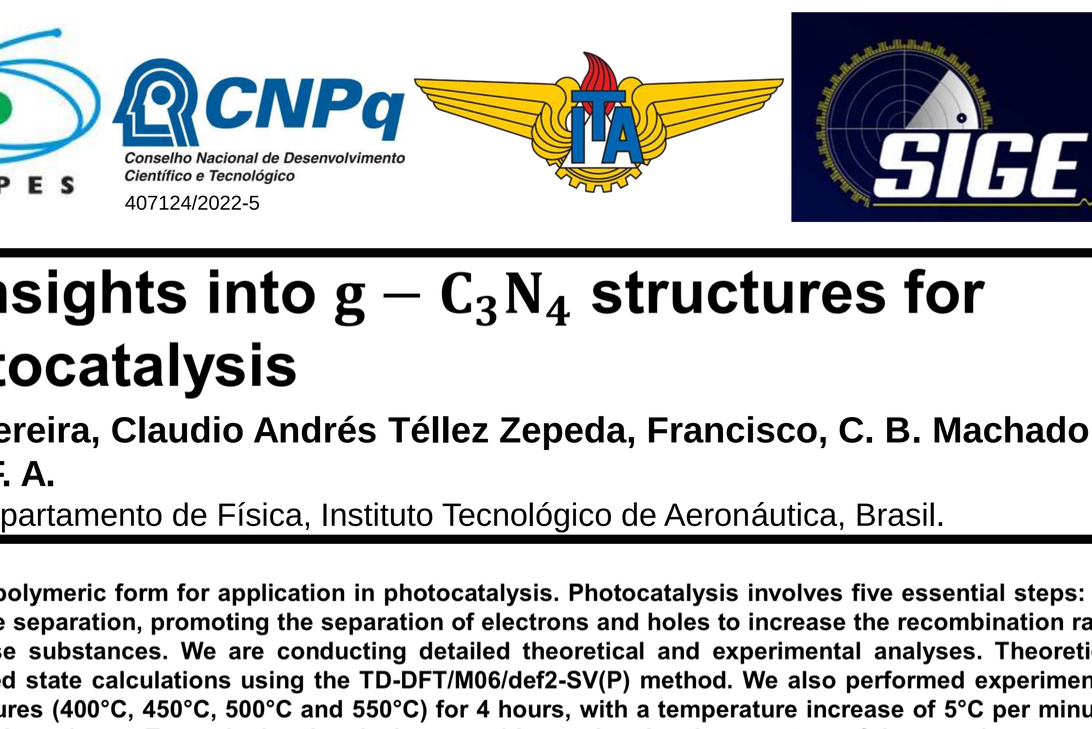
RESULTS:

Ionization Potentials and Excitation Energy

•**Blue Line:** Represents the ionization potential, indicating the energy required to remove an electron from the structure. This value was obtained by the difference between the energies of the neutral and cationic structures.

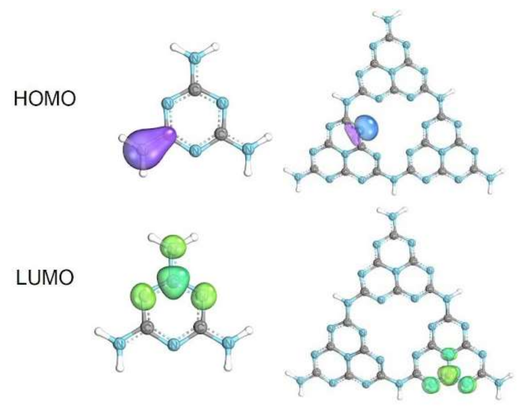
•**Orange Line:** Represents the excitation energy, considering the first singlet excited state. This calculation was performed using TD-DFT (Time-Dependent Density Functional Theory) for excited states.





The graph above represents the FTIR analysis for melamine and the $g-C_3N_4$ polymer. Theoretical and experimental data are compared, with black and blue lines representing computationally calculated data, and green and red lines representing experimentally obtained data.

The HOMO (Highest Energy Molecular Orbital) and LUMO (Lowest Energy Molecular Orbital) were calculated using the PBE functional and the DEF2-SVP basis in the Ibo View program. This computational method offers a robust approach to investigating the electronic properties of the studied molecules, allowing a deeper understanding of their structure and behavior. The values obtained for HOMO and LUMO are crucial for understanding the charge transport properties, chemical reactivity and potential application of these materials in various areas.



CONCLUSION:

- In this work, we focused on a theoretical and experimental investigation of the properties of $g-C_3N_4$.
- We observed that varying the sizes (from melamine to poly-triazine) does little to alter its photocatalytic properties.
- The thermodynamics properties of the structures, ranging from melamine to poly-triazine, showed little variation, fulfilling the essential thermodynamic criteria for photocatalysis in the CO_2 reduction and water oxidation.
- After analyzing melamine at different temperatures, we focused on pure melamine and at 550°C, as it assumes a polymeric form.

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