Biomimetic Synthesis of Polyaniline Catalyzed by Hematine Supported on Graphitic Carbon Nitride

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Outline

1. Polymeric Graphitic Carbon Nitride (g-C_3N_4)
    - Synthesis and Properties of g-C_3N_4
    - Functionalization of g-C_3N_4 (elemental doping)

2. g-C_3N_4 /Hematin hybrids – preparation and characterization

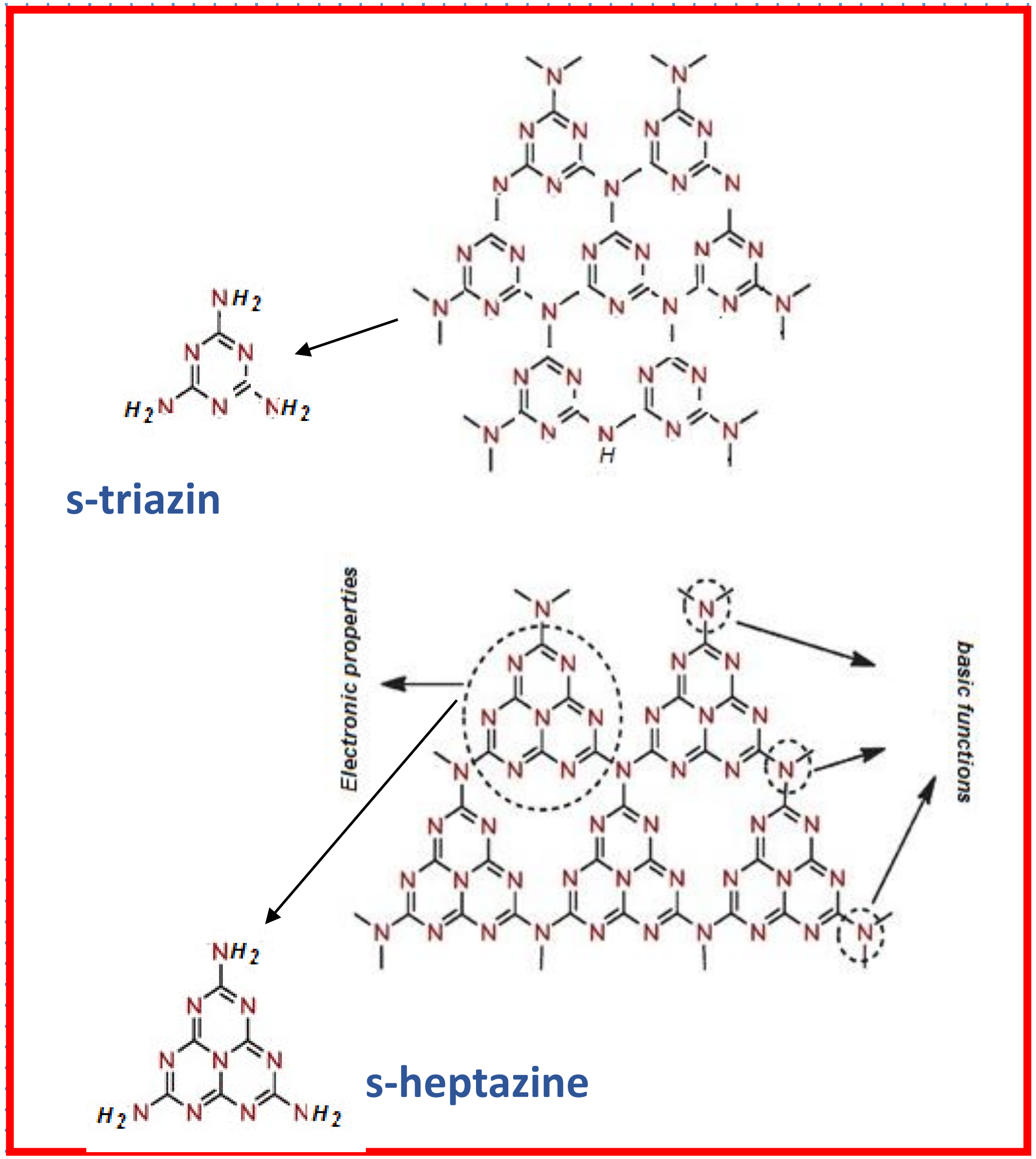
3. g-C_3N_4 /Hematin hybrids, application as catalyst in polyaniline (PANI) Synthesis

4. Properties of PANI.

Polymeric Carbon Nitride ($g\text{-}C_3N_4$)

Main properties

- Semiconductor organic material
- Ultrahard material
- Unique stability (heat endurance and chemical resistance)
- Flake-like structure similar to graphite
- Show electron transition (based in optical and photocatalitic properties)
- As Catalyst:
    - *Friedel-crafts reactions*
    - *Oxygen reduction reaction*
    - *Water splitting*



$g\text{-}C_3N_4$ allotropic form was reported in 1922

Synthesis strategies to prepare ideal g-C_3N_4

Methods

- PVD
- CVD
- Solvothermal Method
- Solid State Reaction
- Thermal Nitridation
- Thermal Condensation

Precursors

- Melamine
- *Cyanamide*
- Thiourea
- Amonium thiocyanate
- Others (S, Metals, P, etc.)

Reactions conditions

- Temperature
- Presence of impurities
- Aerobic/anaerobic
- C/N proportions
- Pressure
- Many more

Applications

A brief history of Polymeric Graphitic Carbon Nitride ($g\text{-}C_3N_4$)

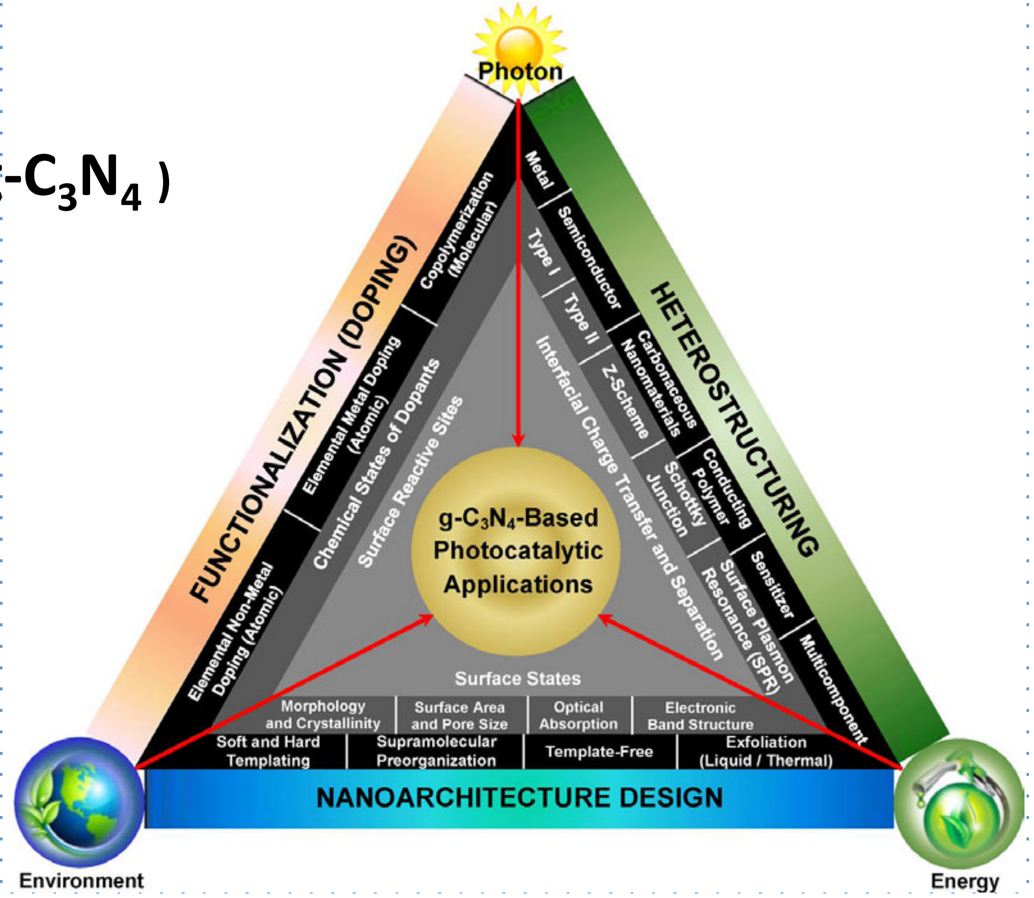
Liebig, J. V. About Some Nitrogen Compounds. Ann. Pharm. 1834, 10, 10

Franklin, E. C. The Ammono Carbonic Acids. J. Am. Chem. Soc. 1922, 44, 486−509

Redemann, C. E.; Lucas, H. J. Some Derivatives of Cyameluric Acid and Probable Structures of Melam, Melem and Melon. J. Am. Chem. Soc. 1940, 62, 842−846.

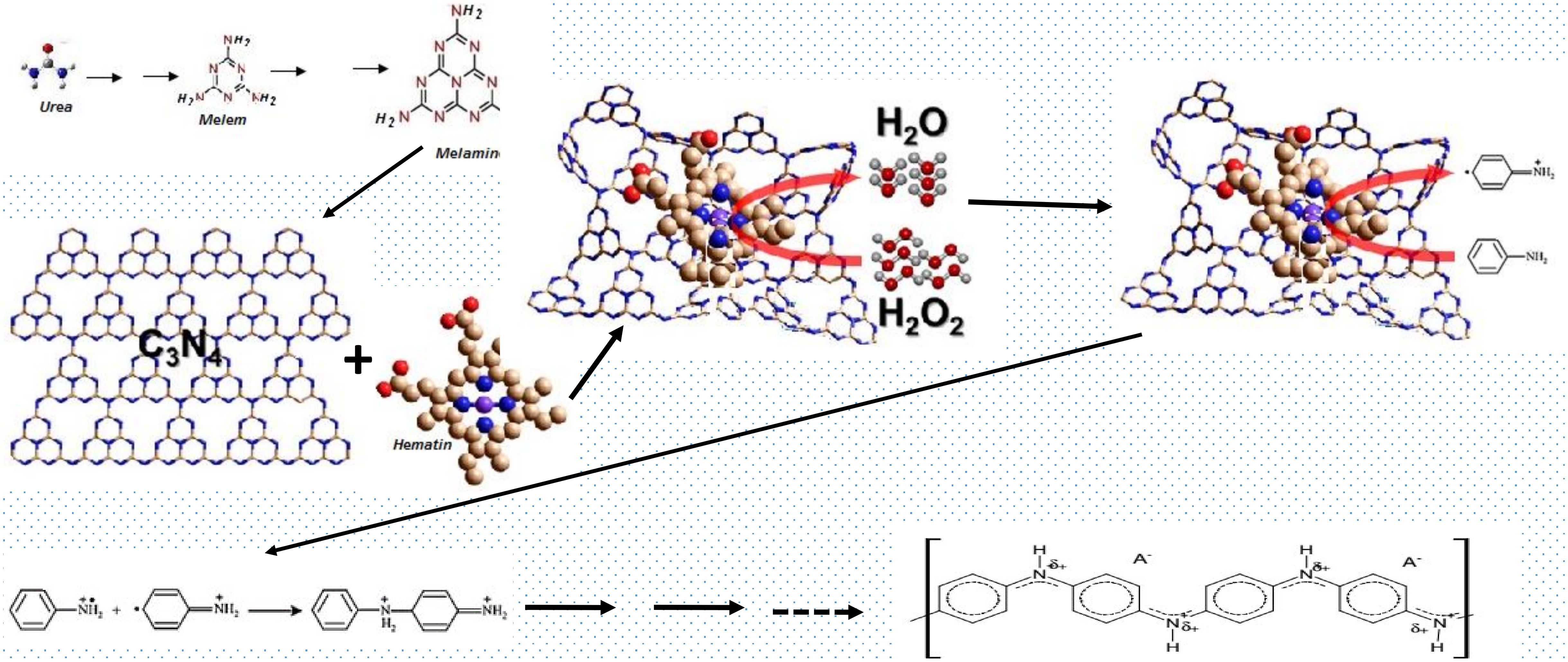
Hosmane, R. S.; Rossman, M. A.; Leonard, N. J. Synthesis and Structure of Tri-s-Triazine. J. Am. Chem. Soc. 1982, 104, 5497−5499

Goettmann, F., *et al* Metal- Free Catalysis of Sustainable Friedel-Crafts Reactions: Direct Activation of Benzene by Carbon Nitrides to Avoid the Use of Metal Chlorides and Halogenated Compounds. Chem. Commun. 2006



Ong, W.-J. *et al.,* Chem. Rev. 2016, 116, 7159−7329

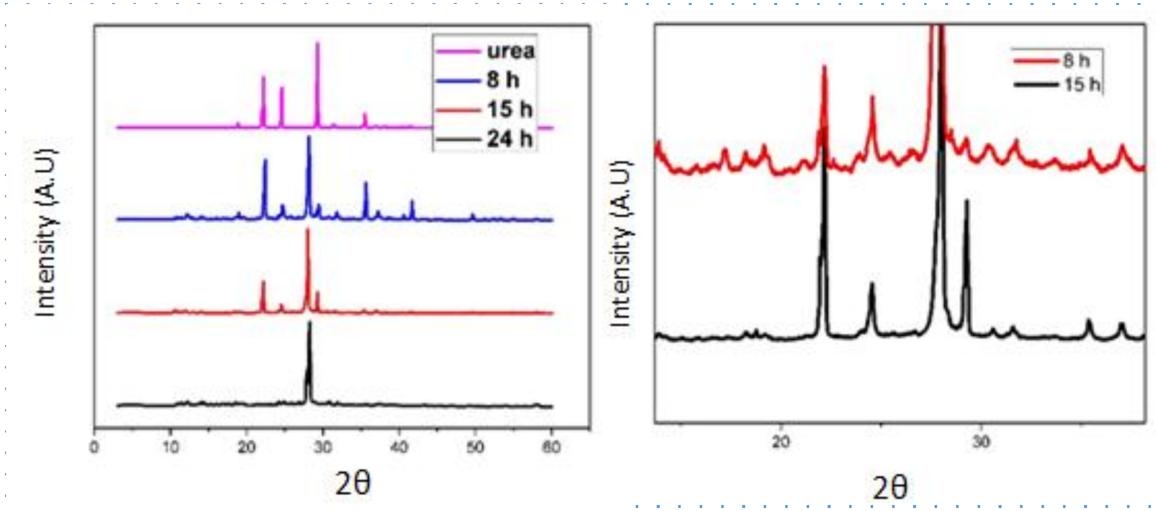
This work



Synthesis of g-OCN oxided phosphate doped

Solvothermal
Urea as a precursor
P_2O_5
230 °C
24 h

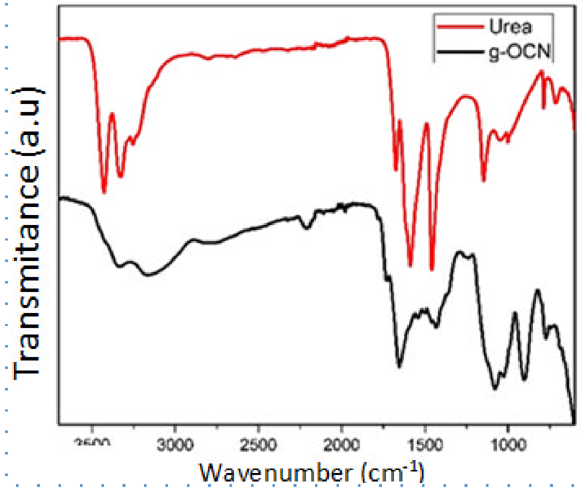
DRX



15h
2θ=22.32 ° y 29.3 °

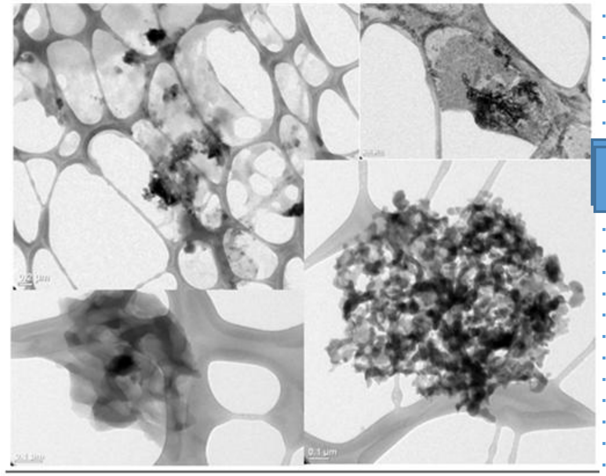
All times
2θ=10.76° and 28.27 typical of gOCN[1]

FTIR



3300 and 3400, NH_2 stretching
3100 and 3100, C=C-H and Ar-H
1200-1650 typical absortion for gCN structures
1545 and 1460 stretching of s-triazine

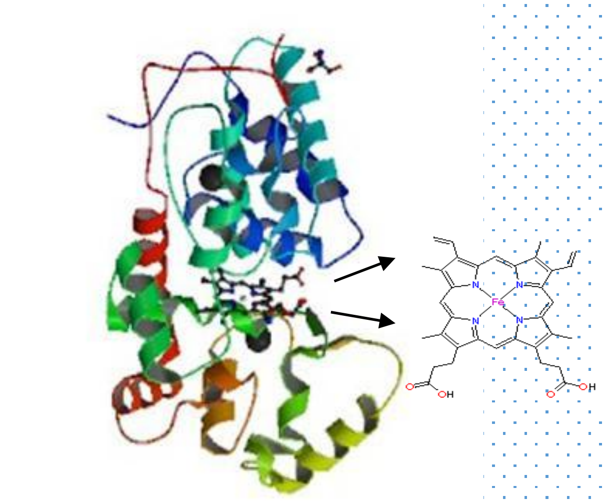
TEM microscopy



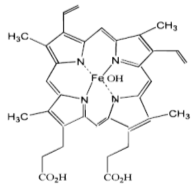
Mesoporous material

1.- Kharlamov, A. I., *et al.*, *Nanomater: Applications &Properties (NAP-2015): Proceeding of International conference V4, No.-01-01NNP.*

Hematin Supported on g-OCN as a Catalyst for Biomimetic Synthesis of Polyaniline

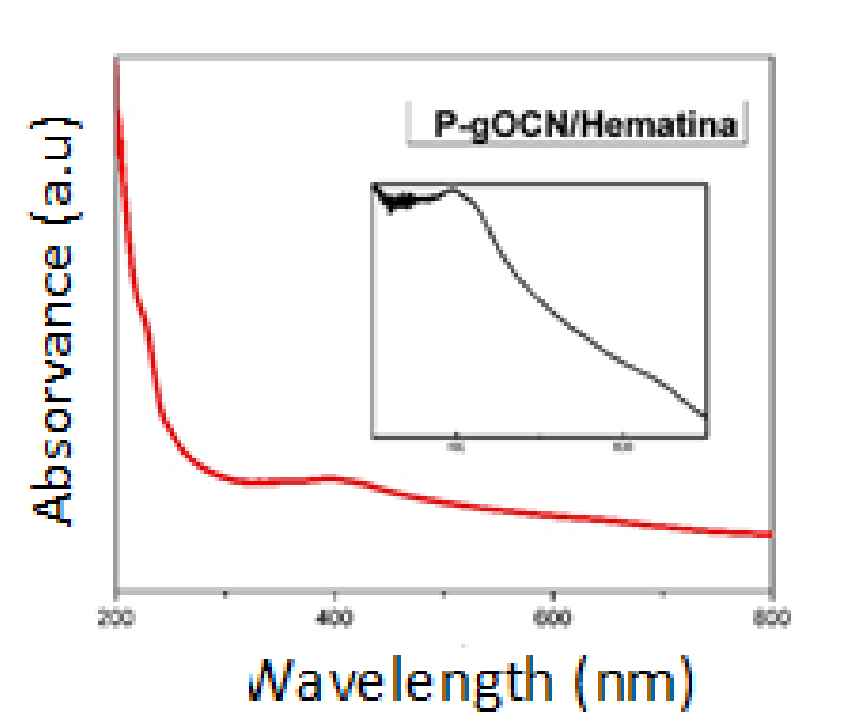


Soybean peroxidase



Hematin

UV-visible spectra



Soret peak of hematin 80 nm

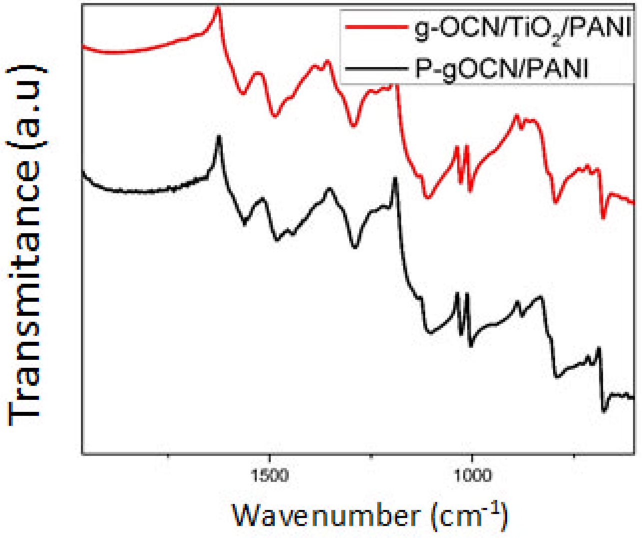
Q band close to 600 nm π–π* transitions.

The hematin peak has shift to the red 398 nm

(Soret peak) interactions with the rings of P-OgCN sheets.

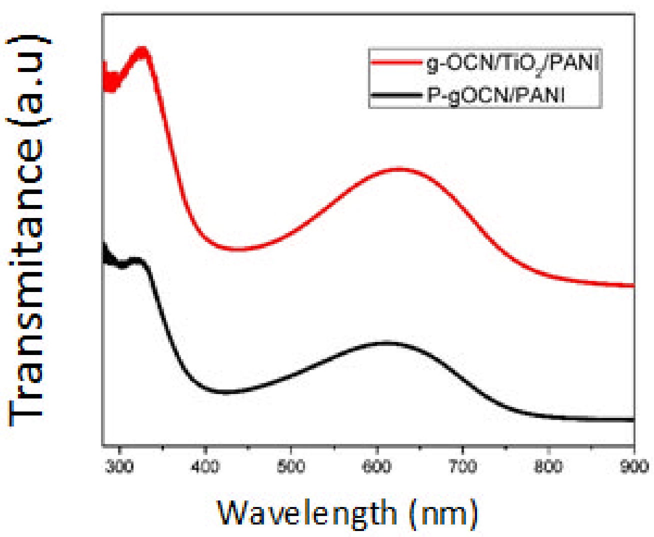
Polyaniline synthesis Catalyzed by hematin supported on g-OCN P doped

FTIR spectra



Stretching
1573, C=C stretching at the quinoid ring
1492, C-C stretching benzenoide ring
1375, stretching of C-N of secondary amines ,
1240, C-C of the BBB units
1103, C-N de aminas
1029, C-O-C
820, indicative of para substitution in the aromatic rings

UV-visible spectra



The signal around 325 nm (327-365 nm), transitions of π-π* of the aniline aromatic ring.

The wide band at 630 nm correspond to the transición n-π* of de grupos quinina-imina groups (exitonic transitions of B-Q rings).

Electrical conductive of PANI was in the order of 0.8 S/cm

Summary

Phosphate doped g-CN were synthesized at high yield (around80 %) , using urea as a precuror.and at relativally low temperature (230 °C). TEM microscopy analysis revealed the presence of a highly porous material and the presence of Single and stacked layers.

Hematin was supported on phophorous doped gOCN materials, apparently a a π-π and other type of interactions are involved in the process.

We demostrate that hematin work as biomimetic biocatalyst in synthesis of the intrisic electrical conductive polyanilinePolymer. The P g-OCN semiconductor material become conductive.

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