INSIGHTS INTO THE PHOTOCATALYTIC ACTIVITY OF g-C_3N_4-TiO_2:Cu NANOCOMPOSITES

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1. INTRODUCTION

In modern society, nanomaterials are showing great potential for enabling and improving technologies for water treatment by photocatalysis. In photocatalytic processes reactive oxygen species (ROS) play crucial roles in the degradation of most organic compounds (dyes, antibiotics, etc) in the solution. g-C_3N_4-TiO_2 nanocomposites has attracted much attention due to its functionalities combining the properties of TiO_2 and graphitic carbon nitride (g-C_3N_4) in one single entity. The present work is focused on the photocatalytic properties of g-C_3N_4-TiO_2:Cu nanocomposites obtained by deposition of TiO_2:Cu nanoparticles obtained through a sol-gel process onto the g-C_3N_4 resulted from decomposition of urea. The preparation conditions of these composites are correlated with the need to obtain electron-hole recombination rates as low as possible, thus increasing the efficiency of the photocatalytic process.

2. EXPERIMENTAL PART

Preparation methods:

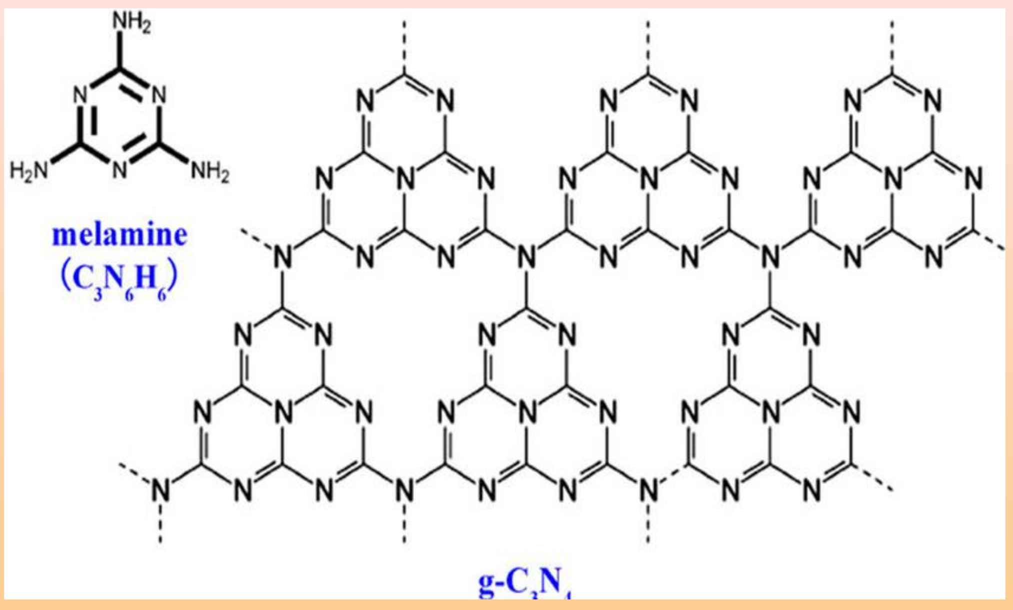
g-C_3N_4- TiO_2:CuX% composite nanoparticles were prepared in two stages:

g-C_3N_4 nanosheets –thermal decomposition of urea

TiO_2 nanoparticles-sol-gel, alcoxidic route

Finally, the g-C_3N_4-TiO_2 composite nanoparticles were thermally treated for 2h at 550ºC

Different samples with different Cu ions concentrations: g-C_3N_4-TiO_2:CuX% (x= 0- 5mol%)



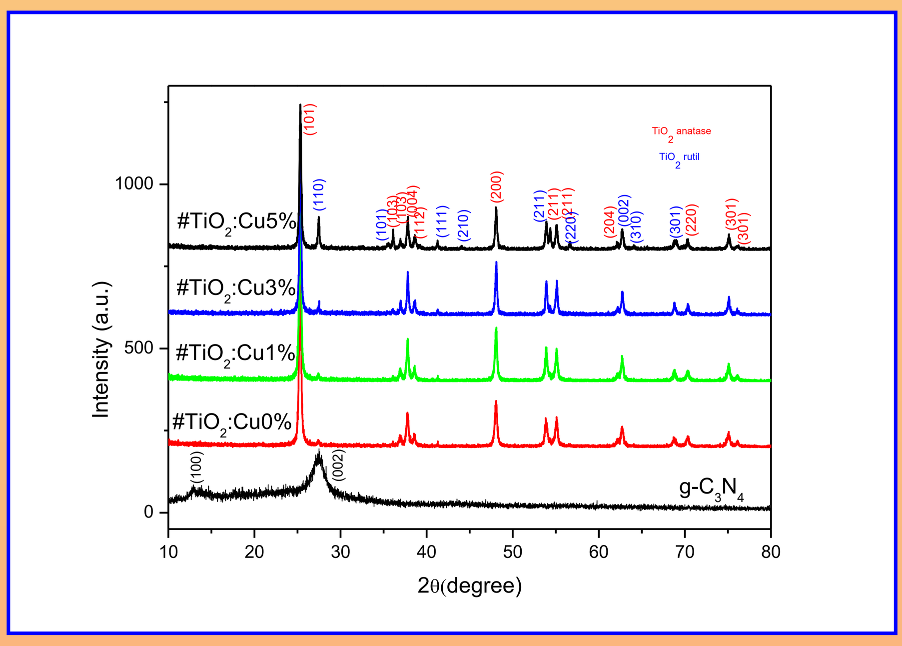
g-C_3N_4 structure

Samples characterization:

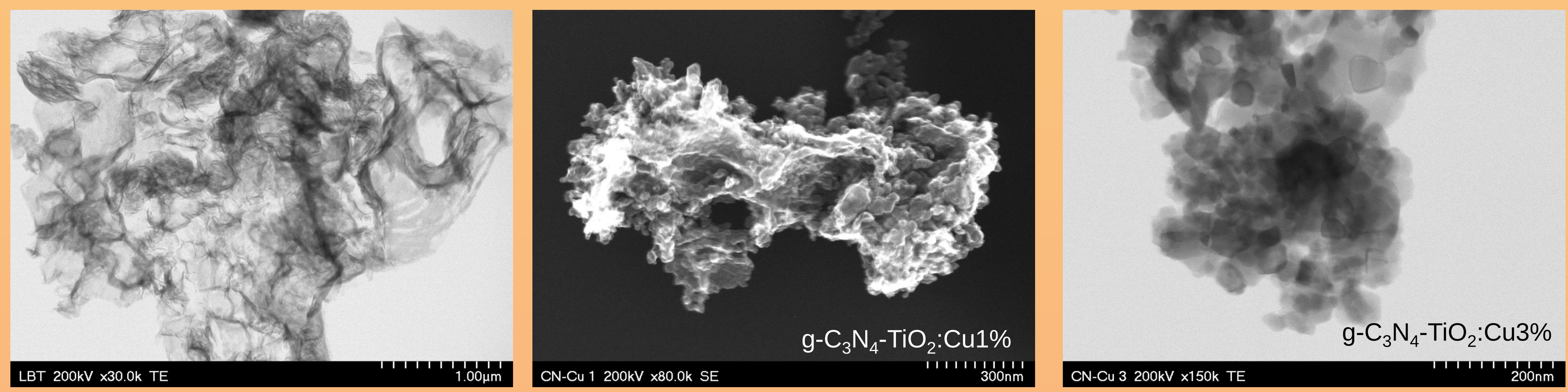
- X-Ray Scattering patterns ⇔ Rigaku - SmartLab automated Multipurpose X-ray Diffractometer
- *TEM images* ⇔ Hitachi H9000NAR transmission electron microscope
- UV–VIS absorption spectra ⇔ JASCO V570UV– VIS-NIR Spectrophotometeequipped with absolute reflectivity measurement JASCO ARN-475 accessory
- FT-IR spectra ⇔ JASCO 610 Spectrometer (KBr pellets technique).
- ROS generation ⇔ EPR spin trapping technique
- XPS spectra ⇔ SPECS custom built system

3. RESULTS AND DISCUSSION

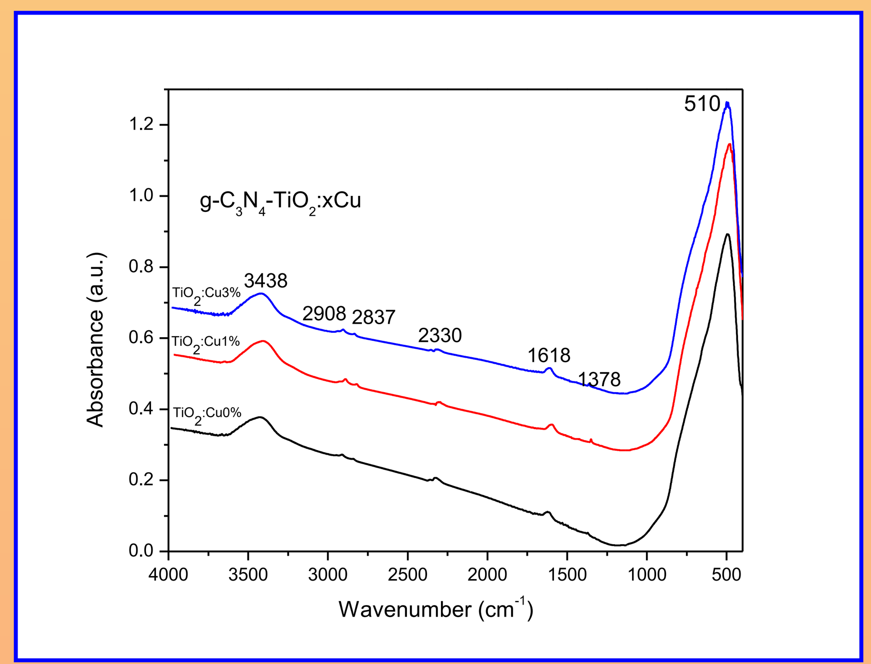
3.1 Structure, morphology and composition



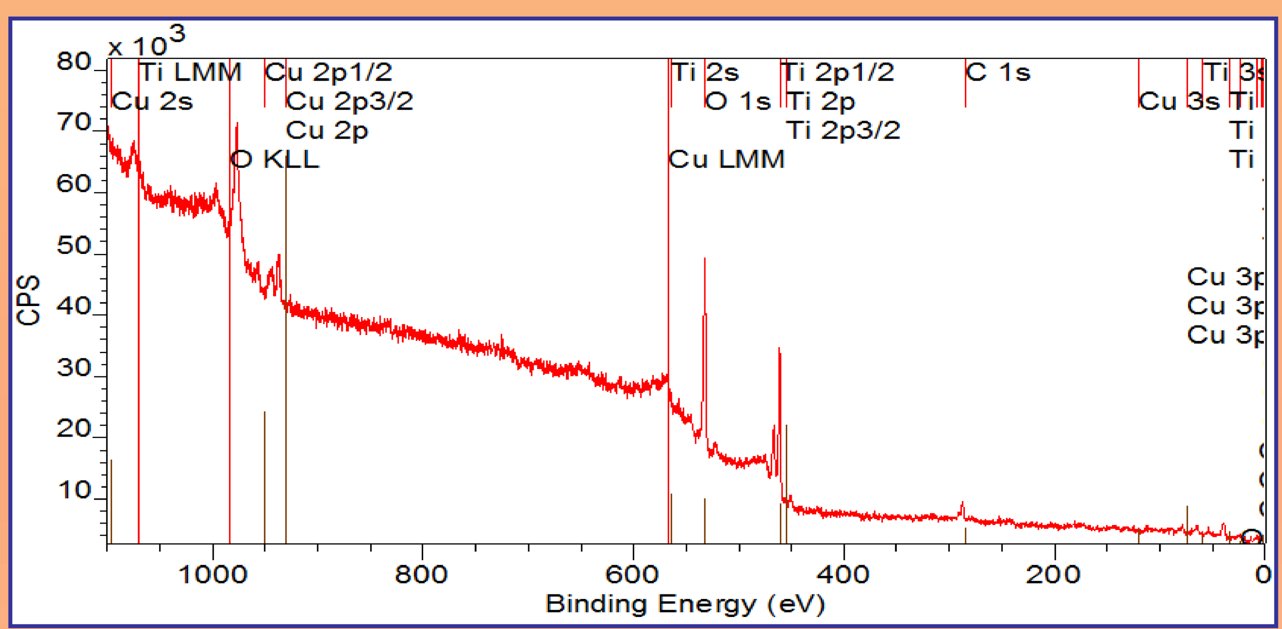
XRD patterns of g-C_3N_4 and g-C_3N_4- TiO_2:CuX% based nanocomposites



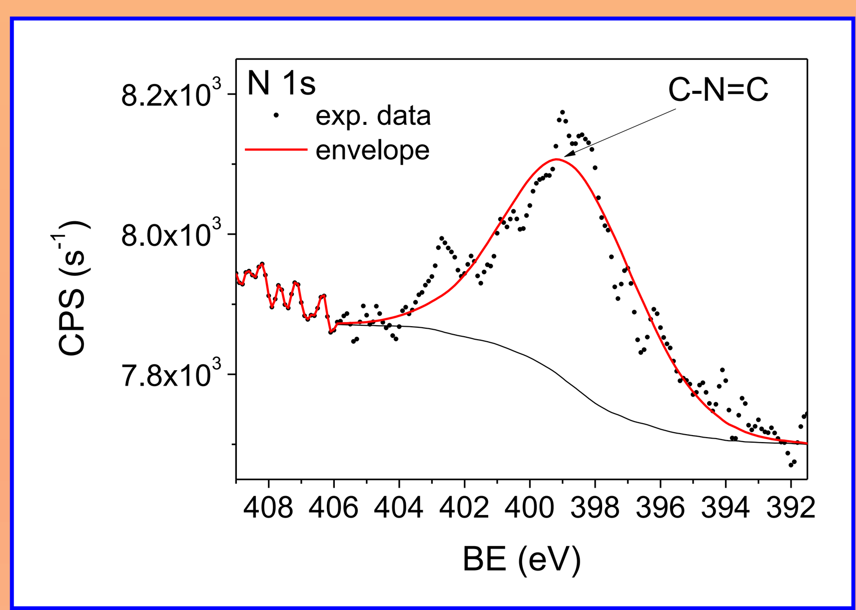
TEM image of g-C_3N_4- TiO_2:CuX% based nanocomposites



FT-IR spectra of g-C_3N_4- TiO_2:CuX% based nanocomposites



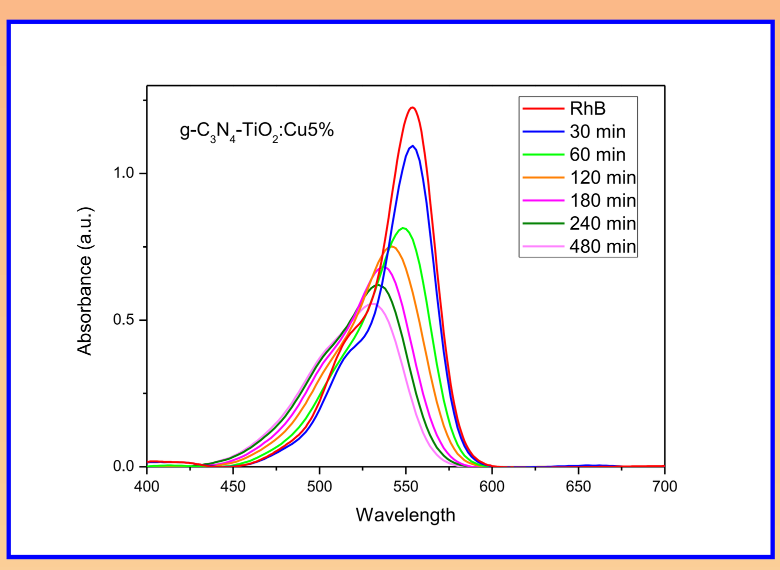
XPS survey spectrum of g-C_3N_4 TiO_2:Cu5% sample.
Cu, Ti, O, C are identified in the spectrum.



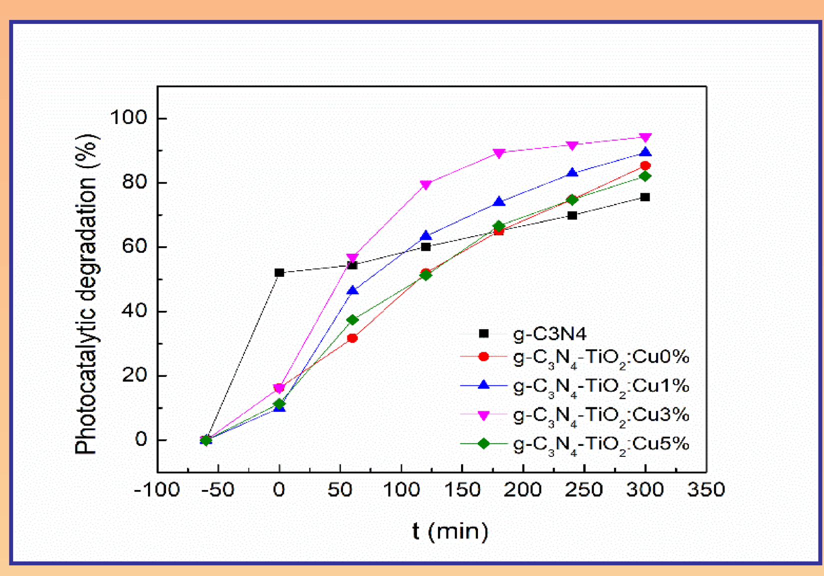
XPS spectrum of N1s recorded after Ar ion etching corresponding to 3.9nm depth. The observed peak at 397.5 eV is assigned to sp2 bonded N atom in C-N=C triazine rings

	Wavenumber [cm^{-1}]	Bands Assignment
g-C_3N_4-TiO_2:CuX%	3438	stretching vibrations of O-H and N-H
	2908	symmetric and asymmetric vibrations of C-H groups
	2837	aromatic C -N stretching
	2330	C=O streching vibrations
	1618	stretching or bending vibration of aromatic CN heterocycles including C- NH and C-N
	1378	bending vibrations of C-H group from titanium acetylacetone complex.
	510	Ti-O stretching mode

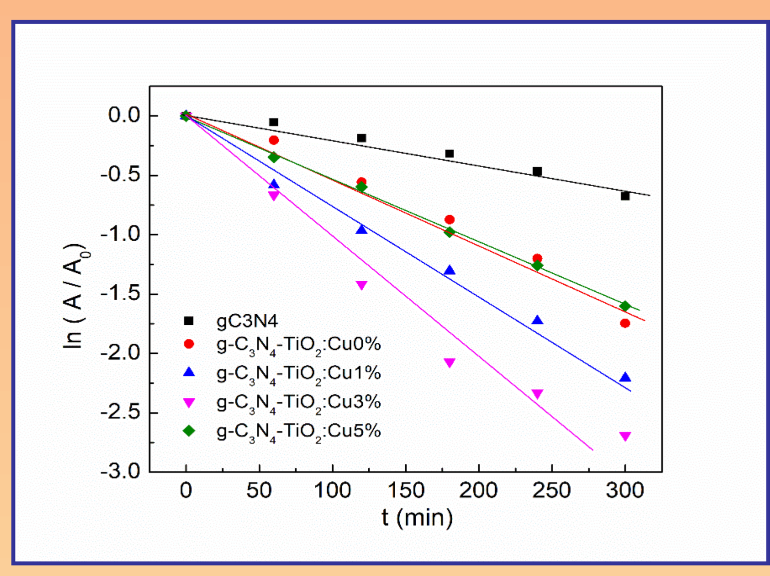
3.1 Photocatalytic properties



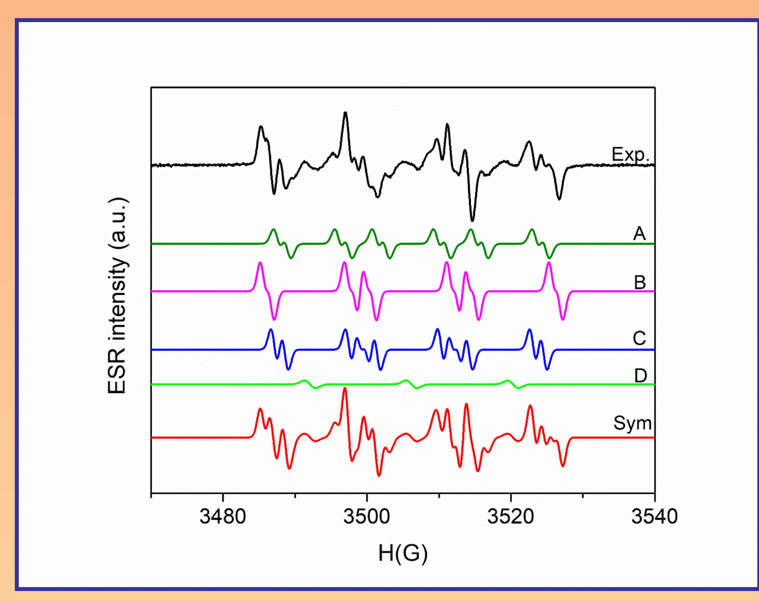
UV–Vis absorption spectra of RhB aqueous solution with g-C_3N_4-TiO_2:CuX% nanocomposites at different irradiation time intervals



Degradation curves of RhB in the presence of g-C_3N_4-TiO_2:CuX% samples



Evaluation of photodegradation kinetic



Experimental spectra and simulated spectra of DMPO spin adducts generated by g-C_3N_4-TiO_2:Cu3% sample. The simulated spectrum represents a linear combination of following spin adducts: ·DMPO-OCH_3 (a), ·DMPO-OOH (b), ·DMPO-O_2^- (c) and ·DMPO-N_2

4. CONCLUSIONS

- g-C_3N_4 was synthesized by thermal degradation of urea, 2h at 550⁰C. After that Cu doped TiO_2 nanoparticles were growth on g-C_3N_4 by sol -gel alcoxidic route;
- XRD pattern illustrates the diffraction peaks corresponding to g-C_3N_4 nanoparticles and TiO_2, respectivelly.
- FT-IR spectra evidenced the specific stretching or bending vibration of aromatic CN heterocycles including C- N and C- NH. Also the specific vibrations corresponding to TiO_2 were observed.
- TEM images shows the morphology of samples. Compared to the pure g-C_3N_4 sample, TiO_2 agglomerates seem to be dispersed on the external surface of g-C_3N_4 in the case of composite samples.
- XPS spectra evidence qualitative composition of the samples. Cu, Ti, O, C and N are identified in the spectrum.
- All the samples show photocatalytic activity against RhB and the best performance was obtained using 3% Cu – doped TiO_2 based nanocomposites. The evidencing of Reactive oxygen species(ROS) were highlighted.
- From the simulation results that g-C_3N_4-TiO_2:Cu3% sample generates ROS species in almost equal quantity which are able to degrade the dye molecules.

ACKNOWLEDGEMENTS

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