

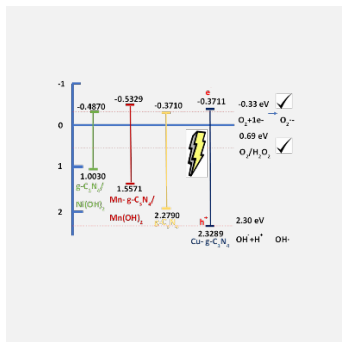
## Small Modifications in g-C<sub>3</sub>N<sub>4</sub> Causing Large Effects in Photocatalytic *E. coli* Disinfection

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**Ricardo A. Torres-Palma**, Elkin Dario C. Castrillon, Angie V. Lasso-Escobar, Jorge Acosta, Sandra Navarro, Estefanía Correa, John Rojas, Yenny Ávila-Torres. Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, A. A. 1226, Medellín, Colombia, [ricardo.torres@udea.edu.co](mailto:ricardo.torres@udea.edu.co), Medellín, Colombia



Carbon nitrides can form coordination compounds or metallic oxides in the presence of transition metals, depending on the reaction conditions. Therefore, composites like g-C<sub>3</sub>N<sub>4</sub>-M(OH)<sub>x</sub> (where M represents metals) were obtained for nickel (II) and manganese (II), while copper (II) yielded coordination compounds such as Cu-g-C<sub>3</sub>N<sub>4</sub>. Notably, the copper coordination compound produced significant hydroxyl radicals. Leveraging this catalytic advantage, with band gap energy in the visible region, all compounds were activated to disinfect *E. coli* bacteria, achieving total disinfection with Cu-g-C<sub>3</sub>N<sub>4</sub>. The determination of radicals generated under light in the presence of dicloxacillin supported the proposed mechanism and highlighted the disinfectant properties of this material.

### Introduction

Carbon nitrides (g-C<sub>3</sub>N<sub>4</sub>) are promising materials in photocatalytic applications. Strategies such as coordination with transition metals or the formation of complexes with metal ions improve photocatalytic efficiency and ROS generation for advanced environmental applications<sup>1</sup>. Therefore, this work explores the coordination of Ni<sup>2+</sup>, Mn<sup>2+</sup>, or Cu<sup>2+</sup> with g-C<sub>3</sub>N<sub>4</sub> in disinfection against *E. coli*.

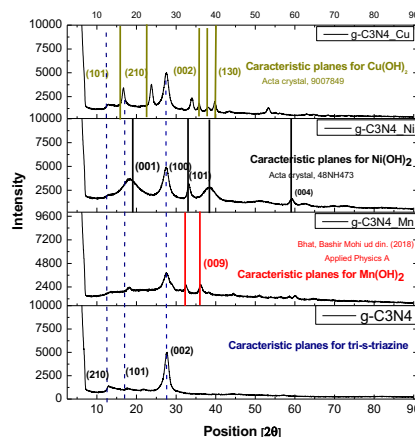
### Material and Methods

g-C<sub>3</sub>N<sub>4</sub> was prepared by pyrolyzing urea at 550°C for 3 h. Then, the synthesized g-C<sub>3</sub>N<sub>4</sub> was stirred at 300 rpm and 25°C during 1 h in presence of Ni, Mn, or Cu hydroxides, and the metal-modified g-C<sub>3</sub>N<sub>4</sub> was obtained. This material was deposited onto a PET surface using a homemade aluminum reflective reactor containing four sunlight lamps (Sylvania FT5T8 8500 K, 40 cm length) that emitted wavelengths between 400 and 700 nm. The photocatalytic processes were conducted at 60 W of light power. The disinfection activity was carried out using a *E. coli* (ATCC 25922) bacterial suspension (1×10<sup>8</sup> UFC) on a PET plate at 250 rpm, with sample collection controlled every 15 minutes for 90 minutes, including a photolysis control for 30 min. The photodegradation of dicloxacillin was tested in the same way using UHPLC at 270 nm as detector. XPS analysis and Electrochemical impedance were used to determine the conduction and the valence bands energy.

### Results and Discussion

XRD showed reflections of (210) at 2θ = 11.5°, (101) at 2θ = 17.54°, and (002) at 2θ = 27.78° for g-C<sub>3</sub>N<sub>4</sub> based on tris-triazine rings. The modifications related to metal ions depended on the ion ability to coexist in its hydroxylated form at the working pH. For nickel, and manganese in a lower extent, the

structure experienced significant modification, evidenced by planes (001)(100)(101) corresponding to Ni(OH)<sub>2</sub> and Mn(OH)<sub>2</sub>. However, copper ion had little effect on the flat structure, likely because it is located in the N-aliphatic fragment on the periphery of the nitride template.



**Figure 1.** XRD patterns high-resolution for g-C<sub>3</sub>N<sub>4</sub> and modified g-C<sub>3</sub>N<sub>4</sub>.

This theory is supported by the XPS results showed in the figure 2. Where in the case of Cu-g-C<sub>3</sub>N<sub>4</sub>, the peaks observed at 400.4, 398.9, and 399.8 eV can be assigned to the bridging N atoms in N(C)<sub>3</sub> groups, and the sp<sup>2</sup>-hybridized nitrogen triazine rings of C=N=C and the Cu-NH bond respectively, indicating that the Cu forms a coordination compound with the final amines of the carbon nitride network. In contrast, in g-C<sub>3</sub>N<sub>4</sub>/Ni and g-C<sub>3</sub>N<sub>4</sub>/Mn, the peak in N1s at 401.1 eV suggests the presence of free

amino groups (C-N-H) on the material periphery, showing the formation of compounds.

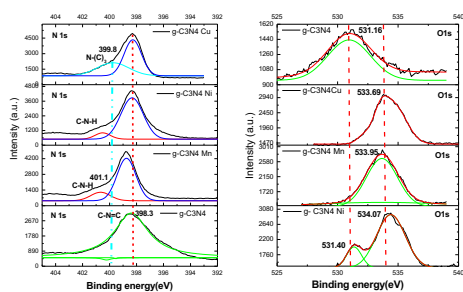


Figure 2. XPS spectra of N1 and O1 for g-C<sub>3</sub>N<sub>4</sub> and modified g-C<sub>3</sub>N<sub>4</sub>

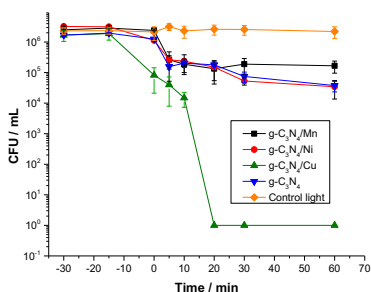


Figure 3. Kinetic of *E. coli* disinfection using g-C<sub>3</sub>N<sub>4</sub> and modified materials with Ni<sup>2+</sup>, Mn<sup>2+</sup> and Cu<sup>2+</sup>.

On the other hand, figure 3 show that g-C<sub>3</sub>N<sub>4</sub>/Cu achieved complete disinfection in 20 minutes, being more effective in the possible generation of ROS than Mn and Ni. However, to rule out that this activity is carried out by the metal hydroxides present in the material, a control experiment to evaluate the disinfecting activity of the hydroxides, which showed some activity in the following order: Cu(OH)<sub>2</sub> > Mn(OH)<sub>2</sub> > Ni(OH)<sub>2</sub>. However, the hydroxides did not surpass the activity of the g-C<sub>3</sub>N<sub>4</sub>. The best activity of the g-C<sub>3</sub>N<sub>4</sub>/Cu is probably due to an improved generation of ROS in the interaction of g-C<sub>3</sub>N<sub>4</sub> with the metal. Copper, in the form of Cu(II), effectively participates in redox reactions and ROS formation, especially hydroxyl radicals, while nickel and manganese can form more stable oxidation states, limiting redox reactions. Cu<sup>2+</sup> ions from carbon nitride act as a catalyst, facilitating electron transfer and generating superoxide species. Carbon atoms from the triazine ring also contribute to electron donation, stabilizing the structure and participating in ROS formation. Therefore, to confirm the presence of ROS in the photoactivated g-C<sub>3</sub>N<sub>4</sub>/Cu, specific scavengers such as methanol and potassium iodide (KI) were used. In this sense dicloxacillin (DCX) was employed

as model pollutant due its sensitivity to these molecules.

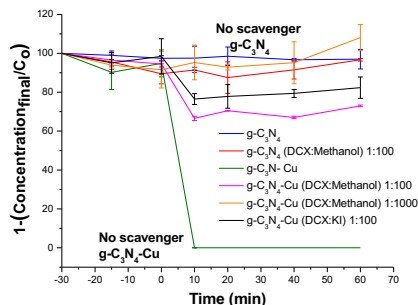


Figure 4. Photodegradation of Dicloxacillin using Cu-g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> with scavengers for ·OH radical and h<sup>+</sup> activation

Poor DCX elimination was observed in the absence of light (from -30 to 0 minutes). However, in presence of light, the degradation occurred in approximately 10 minutes. Scavenger experiments with methanol and KI revealed that methanol, acting as a hydroxyl radical scavenger, significantly inhibited DCX degradation, and KI blocked approximately 15% of the degradation, indicating direct oxidation by h<sup>+</sup>. These findings suggest that both ·OH radicals and h<sup>+</sup> are crucial in the disinfection and degradation processes in the g-C<sub>3</sub>N<sub>4</sub>/Cu material. Determination of the conduction and the valence bands energy, via XPS analysis and electrochemical impedance confirmed the particular ability of the act using these pathways.

### Conclusions

The material g-C<sub>3</sub>N<sub>4</sub> modified with copper (II) was an excellent photocatalyst for disinfecting *E. coli* but also was able to degrade dicloxacillin in the presence of light. It offers another opportunity for this material in the fields of degradation of organic molecules. Definitely, the hydroxides in the structures modified with the transition metals do not make important contributions to the disinfection against this microorganism; their role may be structural. It was concluded that a transition metal coordinated in the N-aliphatic of carbon nitride allows a better electron transfer for the generation of ROS. Conversely, interaction with N-tris triazine can hinder interaction. This soft synthesis opens the opportunity to explore new transition metals by interacting with carbon nitride to degrade organic molecules and enrich disinfection processes.

### Acknowledgments

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### References

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