

## SURFACE MODIFICATION OF GRAPHITIC CARBON NITRIDE WITH COPPER NANOPARTICLES

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### Abstract

Two different synthetic routes were employed to modify surface of graphitic carbon nitride (g-CN) with copper nanoparticles (CuNPs). Structure, morphology and CuNPs distribution on pre-synthesized g-CN surface are characterized by FT-IR, XRD and TEM. Results suggested that the simpler method based on mixing of precursors in inert atmosphere and room temperature, resulted in better CuNPs distribution compared to method which used refluxing as a step in synthesis.

### Introduction

In the pursuit for „green“ semiconductor material with strong spectral response in visible part of the Solar spectrum, g-CN emerged as suitable candidate. This metal-free material can be easily synthesized by simple thermal treatment of nitrogen-rich precursors like urea or melamine. Usually formed as 2D material, it consists of tri-s-triazine units, interconnected by Van der Waals forces, forming layers similar to graphene sheets. With the bulk band gap energy of about 2.7 eV, it is capable for visible light absorption, while high negative potential of conduction band ( $\sim -1.3$  V vs NHE) enables easy formation of reactive oxygen species (ROS). It is used in different photo induced processes like photocatalysts in water splitting [1] or in photoionization in free radical polymerization [1]. Additionally, special interest is given to its antibacterial ability: 2D materials can physically damage cell membrane causing cellular dysfunction and leakage of cytoplasmic components [2] or cell damage can be induced by reaction of photogenerated ROS with phospholipid molecules from cell membrane [2].

However, major drawback for wider usage of g-CN is fast recombination of photogenerated charges. Many different approaches have been probed in order to overcome this issue, including morphology control, surface modification or doping with metal ions and formation of g-CN/metal heterojunctions [2]. In this approach, nitrogen atoms act as anchors and can act as homogeneously distributed sites for adsorption of metal nanoparticles. Different metals (Fe, Zn, Ni, etc.) [2] were used in this approach, but metals like Ag and Cu were of special interest as they alone exhibit also an antimicrobial activity.

Our recent study [3], has shown that copper and its oxide also have significant antimicrobial activity, proven in cases of *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans*. Antimicrobial effect originates from layer of copper oxide formed at the microbial cell wall after CuNPs adsorption, which prevents normal cell function, and subsequently leads to its death [3].

In this study, focus was on finding appropriate route to evenly distribute CuNPs on the surface of the pre-synthesized g-CN. We expect that, comparing to pristine g-CN, Cu-decorated g-CN would exhibit reduced recombination of photogenerated charges, which can be beneficial for its photocatalytic- performance, while, in the same time, antimicrobial efficacy can be improved, comparing to both individual components of heterojunction.

## Experimental

### Synthesis of g-CN

5g of urea powder (p.a. VWR Chemicals) is placed in ceramic crucible and heated at 550°C for 2h with the ramp rate of 10°C/min. After this time, sample is left to cool naturally, grinded and used without any further treatment.

### Synthesis of Cu-gCN nanocomposites

Two synthetic procedures were used for the preparation of Cu-g-CN nanocomposites. Sample labeled as Cu-CN-1 was prepared by “in-beaker” method: under inert atmosphere ( $\text{Ar}_{(g)}$ ), 100 ml of  $\text{Cu}^{2+}$  (0.5 mM; copper(II) chloride dihydrate, Kemika) aqueous acidic solution (pH was adjusted to 3-4 by hydrochloric acid, J.T.Baker) was stirred with g-CN (30 mg). Upon mixing, ascorbic acid (13.2 mM; Sigma-Aldrich) as an antioxidant was added. The color of the reaction mixture changes from milky white to yellowish, indicating some reduction potential of ascorbic acid, as well. Finally, after 30 min, sodium borohydride (13.2 mM; Sigma-Aldrich), as strong reducing agent, was added for complete reduction of  $\text{Cu}^{2+}$ , which is followed by immediate change in coloration of the reaction mixture to dark green/grey. The reaction under  $\text{Ar}_{(g)}$  was left for 48 h, during which there was a gradual change in color towards final, dark yellow. The ultimate suspension was left to rest for 24 h, after which it was rinsed with water several times, dried, powdered, and characterized.

Cu-CN-2 was prepared on reflux, in the round bottom flask. Initially, g-CN (0.05 g) was suspended in 20 ml aqueous solution of sodium hydroxide (0.1 M; Aldrich). L-histidine (1 mM; Ferak, Berlin), as a reducing agent, was added, and the reaction was left stirring at 80°C for 5 h. Finally,  $\text{Cu}^{2+}$  (1 mM) was injected, and the reaction was continued for the next 19 h. There was a change of color from milky white to yellowish. After suspension’s cooling to the room temperature, it was left to rest, and, further prepared for the characterization as described above. Structure and morphology of samples are characterized using X-ray diffraction (XRD, PHILIPS 1050 X-ray diffractometer using Ni-filtered Cu  $K\alpha$  radiation and Bragg-Brentano focusing geometry), Fourier transform infrared spectroscopy (FT-IR, ThermoScientific Nicolet 380) and transmission electron microscopy (TEM, JEOL-JEM-2100, 200 kV) techniques.

## Results and discussion

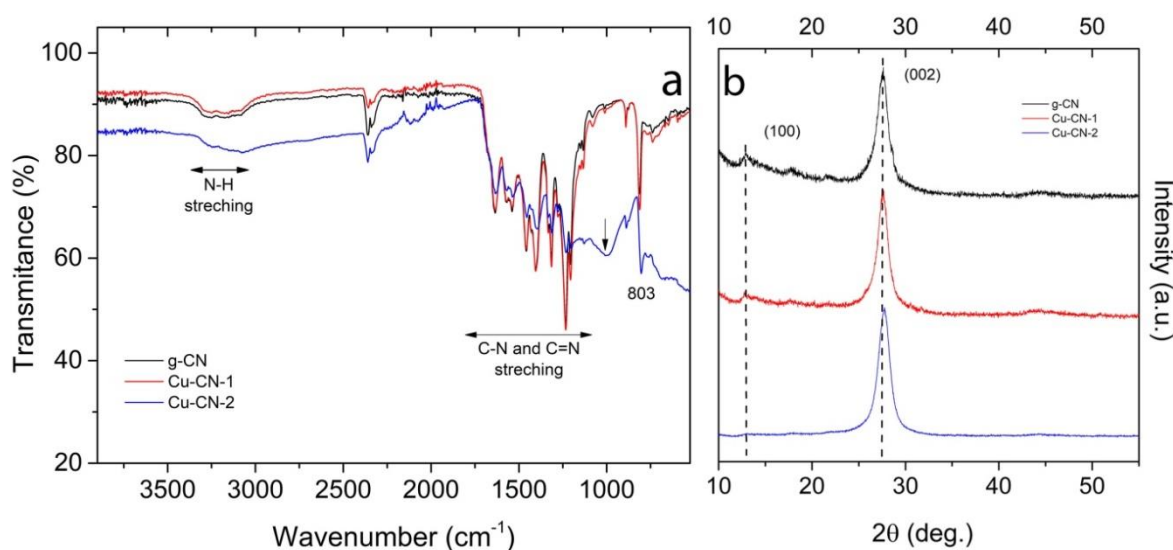


Figure 1. a) FT-IR spectra and b) XRD patterns of synthesized samples

FT-IR spectra of obtained samples are presented in Figure 1a. Three weak bands with maxima at 3277, 3189 and 3080  $\text{cm}^{-1}$  originate from N-H stretching vibrations, while bands with maxima placed between 1632 and 1206  $\text{cm}^{-1}$  originate from C-N and C=N stretching vibrations of heterocycles. Together with band placed at 803  $\text{cm}^{-1}$  that is assigned to breathing mode of triazine rings, all these vibrations are characteristic for g-CN [1]. FT-IR spectrum of Cu-CN-1 sample follows up the same pattern, while in the spectrum of Cu-CN-2 wide band placed at about 1000  $\text{cm}^{-1}$  (pointed by arrow) can be assigned to  $\text{CH}_2$  vibrations of residual L-histidine [4]. No band that can be assigned to Cu – O bond (at about 530  $\text{cm}^{-1}$ ) is detected in Cu decorated samples. However, besides difference in peaks intensity, which in the case of Cu-CN-2 can be assigned to presence of residues of L-histidine, there are no distinguished features in the spectra of Cu-decorated samples that can indicate copper presence in the samples.

XRD patterns of synthesized samples are presented in Figure 1b. Diffraction peak at 27.59° (usually indexed as (002)) corresponds to inter-planar stacking of tri-s-triazine layers, while low-intensity peak at 12.87° resembles in-plane structural packing of tri-s-triazine units (indexed as (100)). XRD patterns of both Cu-decorated samples are characterized by both peaks. No additional copper (at about 43.7 or 50.7° [5]) or copper oxide related peaks can be seen in diffractograms, probably due to detection limit of the instrumental method. However, comparing to XRD pattern of pristine g-CN, main diffraction peak of Cu-CN-2 is shifted towards 27.76° which indicates additional stacking of layers, as interplanar distance is slightly decreased from 0.323 to 0.321 nm. Such a feature is not desirable as it promotes fast recombination of photogenerated charges. In the same time, significant lowering of relative intensity of low-angle peak indicates on some defragmentation in in-plane packing of triazine units.

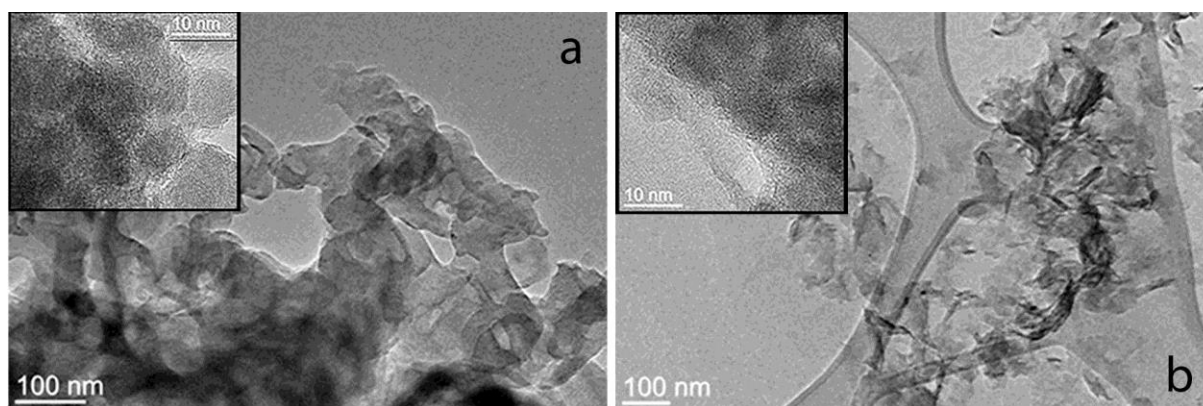


Figure 2. TEM micrographs of a) Cu-CN-1 and b) Cu-CN-2 (insets: higher magnification)

TEM micrographs (Fig. 2) gave final evidence of successful anchoring of copper on g-CN surface. Firstly, synthetic route had obvious influence on g-CN matrix: while Cu-CN-1 consists of inter-connected nanoflakes making one homogeneous structure characteristic for g-CN, g-CN matrix in Cu-CN-2 nanocomposites is partially defragmented in individual sheets. Furthermore, although presences of CuNPs with the sizes in the range from 5 to 10 nm, is obvious in both samples, their distribution is more homogeneous in Cu-CN-1 sample. In Cu-CN-2 sample, CuNPs are partially capped with L-histidine: its terminal carboxyl (hydrophilic) groups can't anchor to hydrophobic g-CN surface, resulting in less homogeneous Cu nanoparticles distribution in Cu-CN-2 sample.

## **Conclusion**

Two different synthetic routes were employed in decorating pre-synthesized g-CN with CuNPs. FT-IR measurements showed no presence of copper related oxides in obtained samples, while XRD measurements pointed on defragmentation of g-CN matrix in Cu-CN-2 sample. TEM micrographs confirmed presence of CuNPs formation in samples obtained by both synthetic routes: however, simpler “in beaker” method of synthesis provides better distribution of CuNPs on the surface of pre-synthesized g-CN, compared to reflux method.

## **Acknowledgements**

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## **References**

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