

Effect of Cu₃N and Cu on the photocatalytic activity of Cu₂O nanoparticles

Patricio Paredes^{*1}, David S. Wragg², E. Rauwel¹, P. Rauwel¹

¹Institute of Forestry and Engineering Sciences, Estonian University of Life Sciences, Tartu, Estonia

²Department of Chemistry, University of Oslo, Oslo, Norway

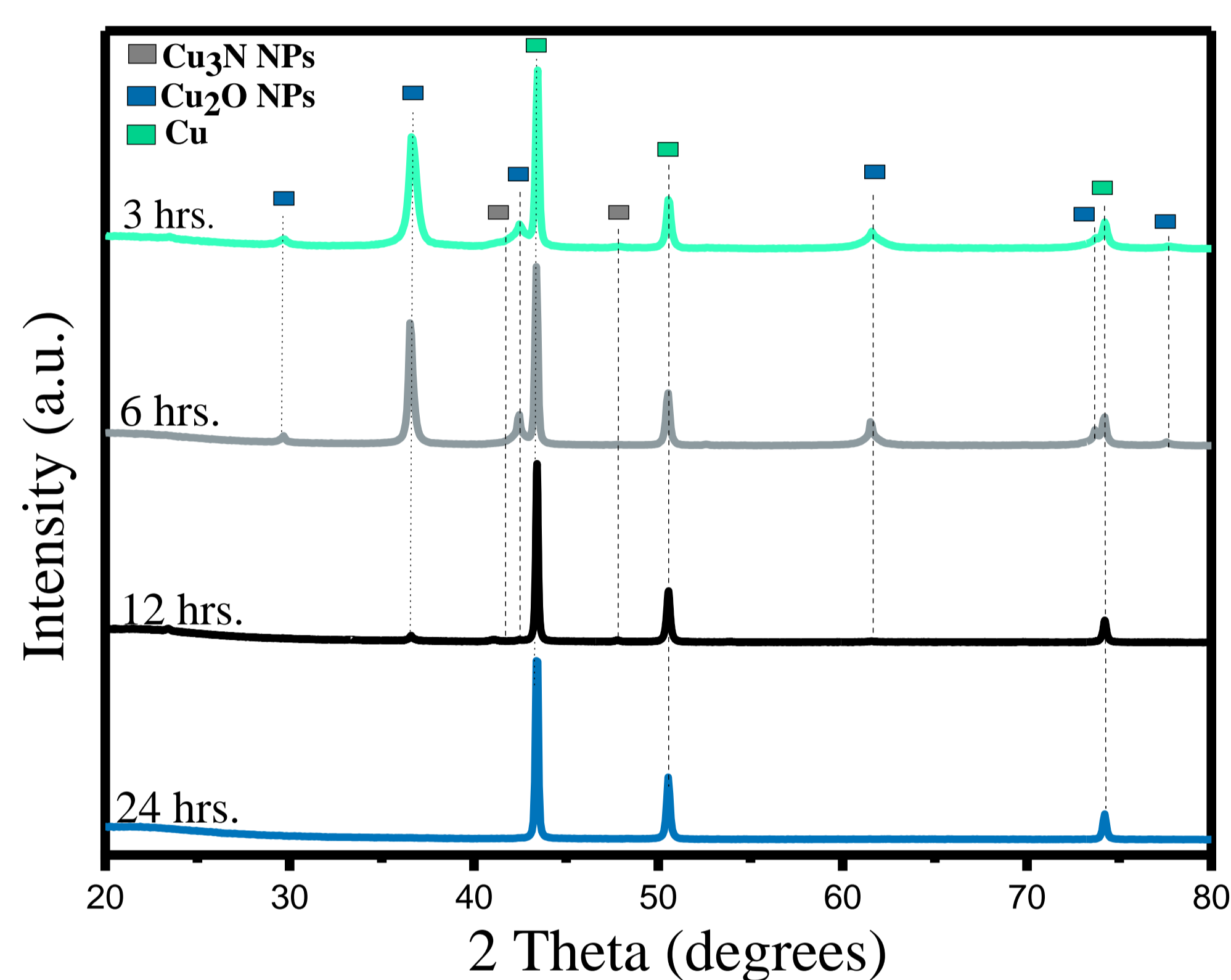
Introduction

In recent years, green photocatalysis has been widely used in environmental remediation using sunlight as an excitation source. Semiconductor-based photocatalysts have attracted much attention in the field because of their low cost and availability. In this work, we synthesized cupric oxide (Cu₂O), copper nitride (Cu₃N) and copper (Cu) nanoparticles using a non-aqueous sol-gel route. We controlled the phase ratios by adjusting the reaction time, and demonstrate that these nanoparticles are efficient catalysts under visible solar radiation.

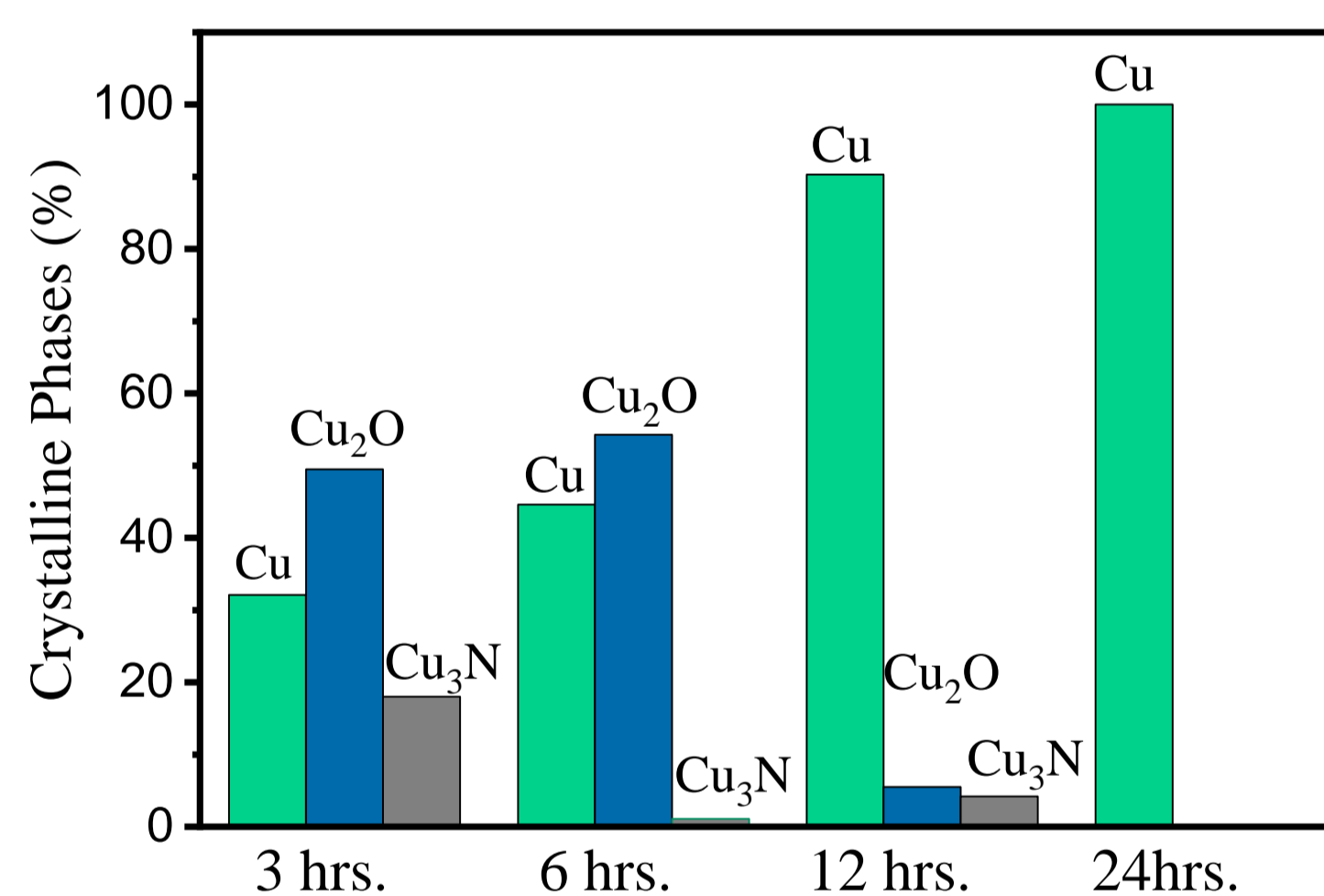
Nanoparticles Synthesis

Cu, Cu₂O and Cu₃N nanoparticles were synthesized using non-aqueous sol-gel methods in a glovebox under controlled N₂ conditions and then transferred into an autoclave. Then the solution was placed in an autoclave and put in an oven at 280°C. The reaction time from 3 to 24 hours in order to optimize the synthesis.

X-ray diffraction (XRD)



Crystalline Phases

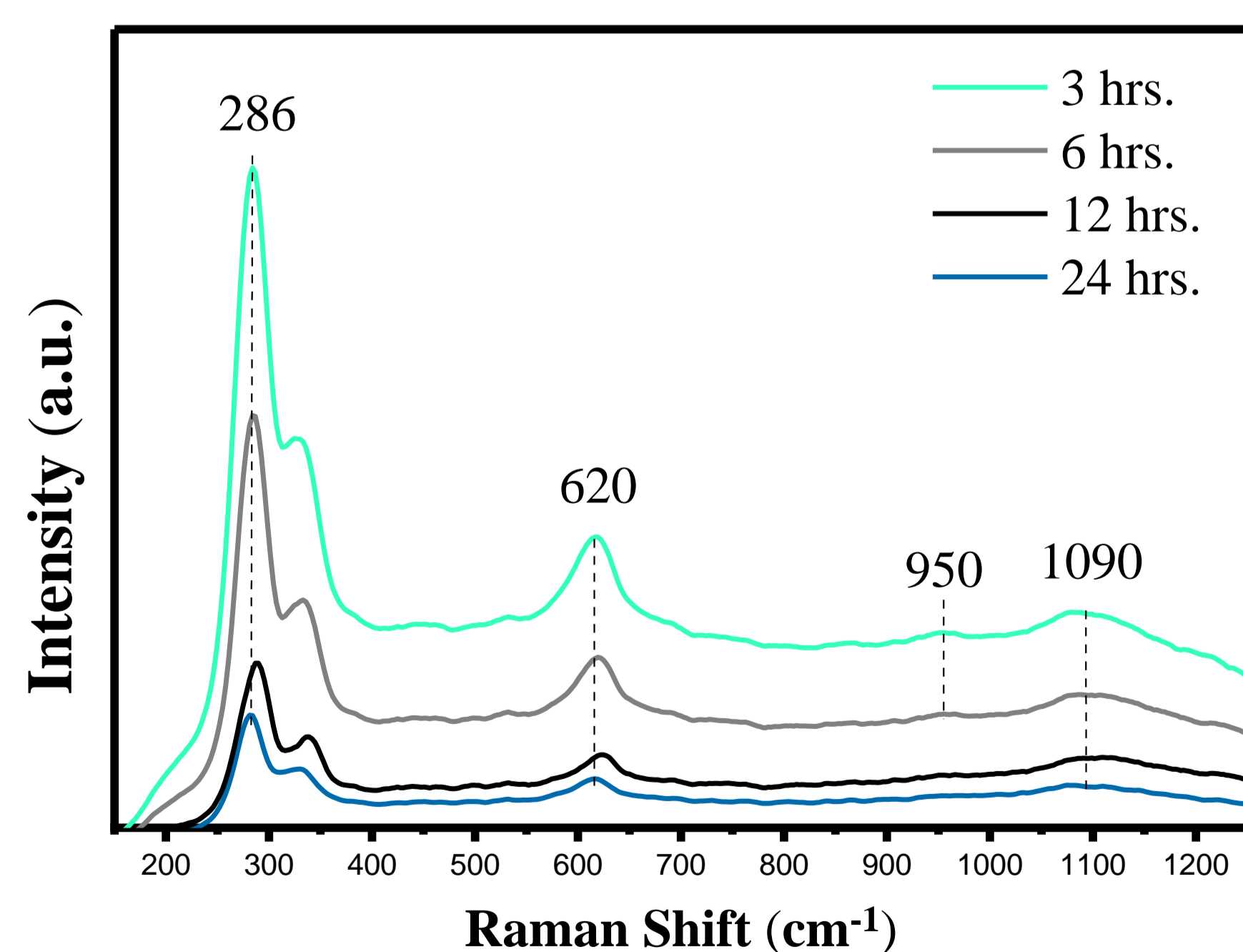


Particle size

| Samples | Cu | Cu ₂ O | Cu ₃ N |
|---------|------|-------------------|-------------------|
| 3 hrs. | 50 | 14.8 | 2.8 |
| 6 hrs. | 51.7 | 26.7 | 27 |
| 12 hrs. | 54 | 30 | 29 |
| 24 hrs. | 71 | - | - |

The XRD patterns show the presence of all 3 phases. The quantity of each phase is provided in the table along with the average size of the nanoparticles obtained from Rietveld refinement.

Raman Spectroscopy



Raman spectra of prepared nanoparticles reveal the characteristic vibrational modes of Cu, Cu₂O and Cu₃N phases. The peak around 620 cm⁻¹ corresponds to the characteristic vibrations modes of the chemical bonds of Cu-N and Cu-O.

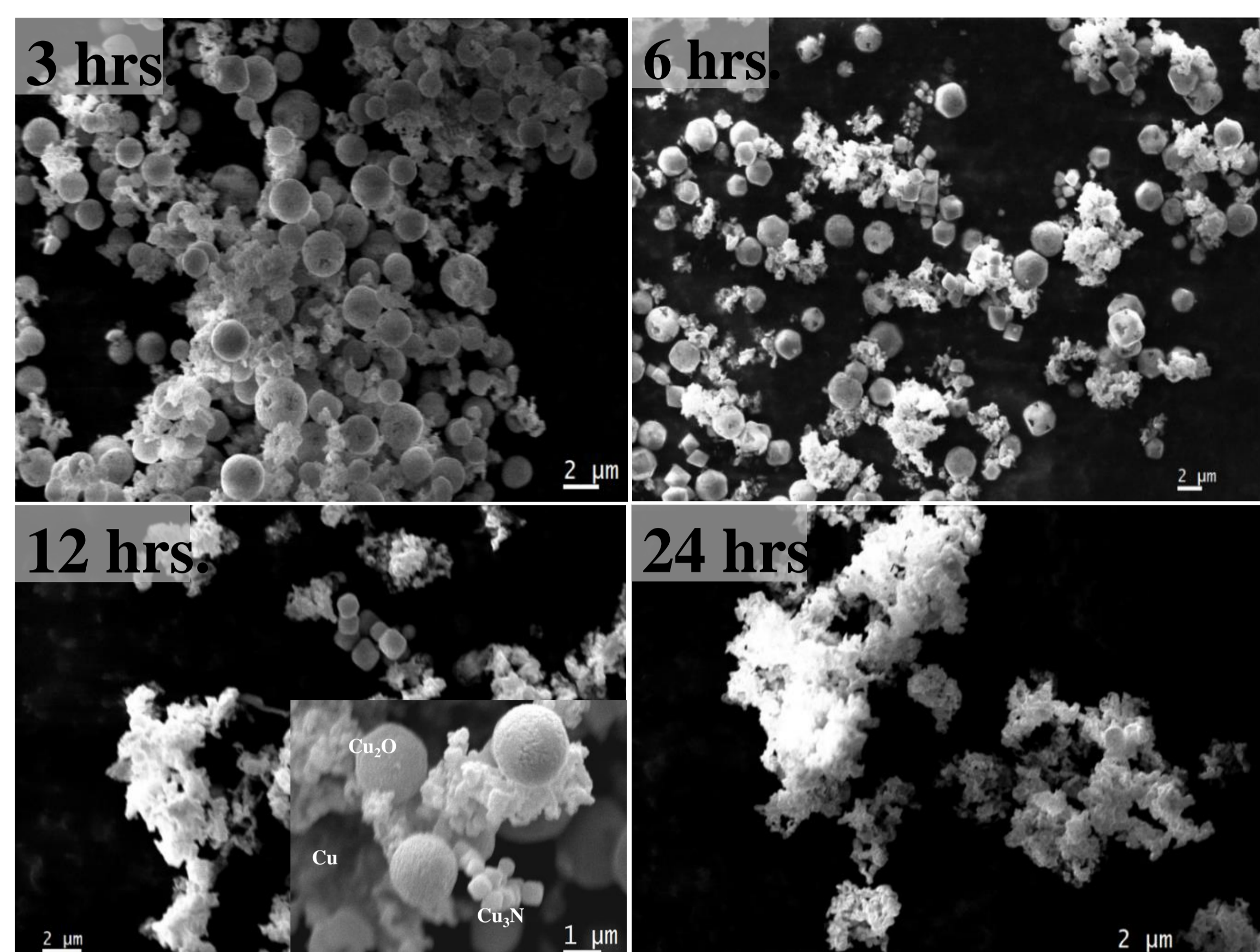
Conclusion

Successful catalytic activity was obtained from the nanoparticles. The samples with 18% of Cu₃N shows the best catalytic performance with a dye degradation rate of 95% after 4 hours.

Acknowledgments

This research has been supported by the European Regional Development Fund project grant TK134 "EQUiTANT" and T210013TIBT "PARROT program". We thank DORA mobility grant for financial support.

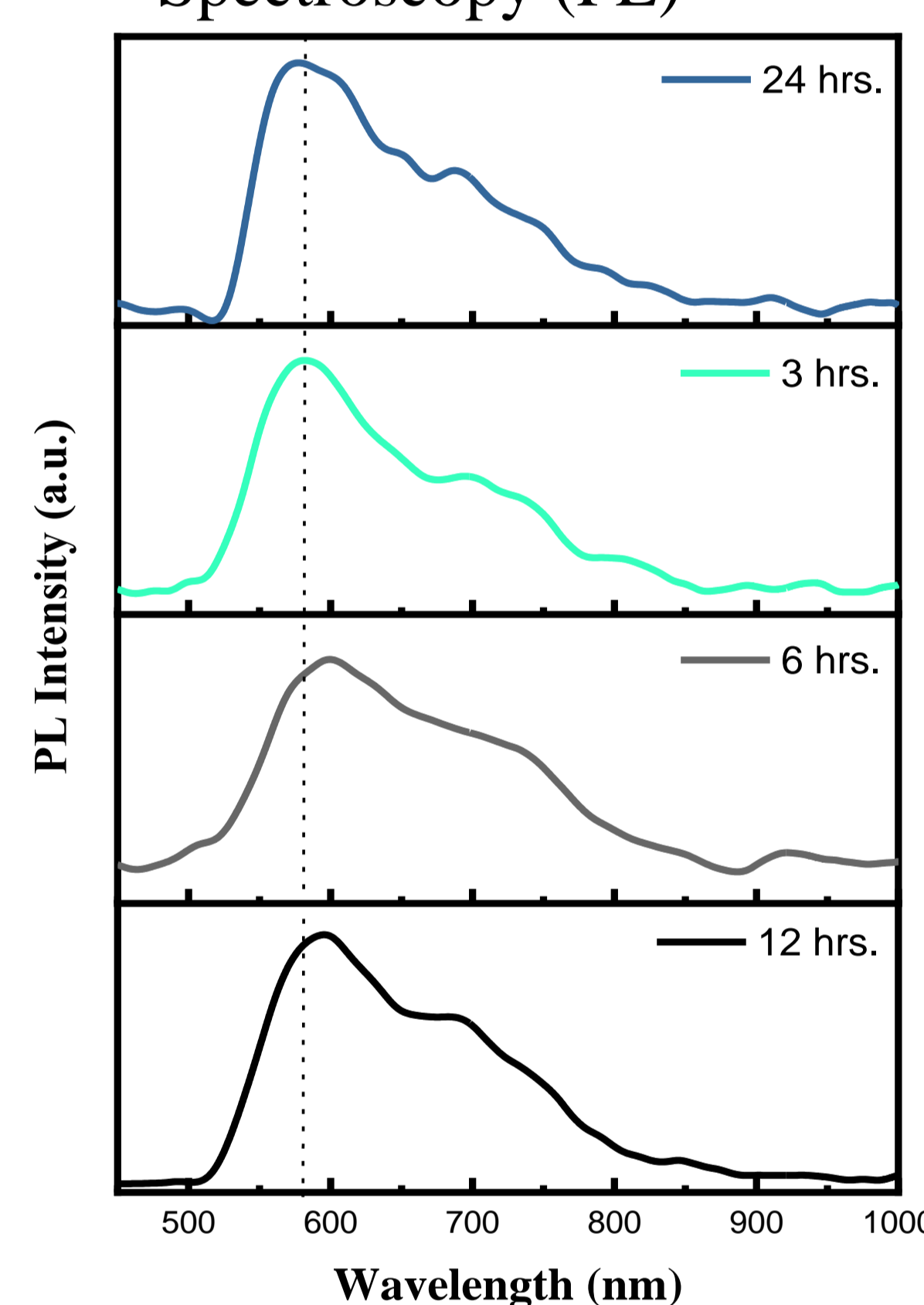
Scanning Electron Microscopy (SEM)



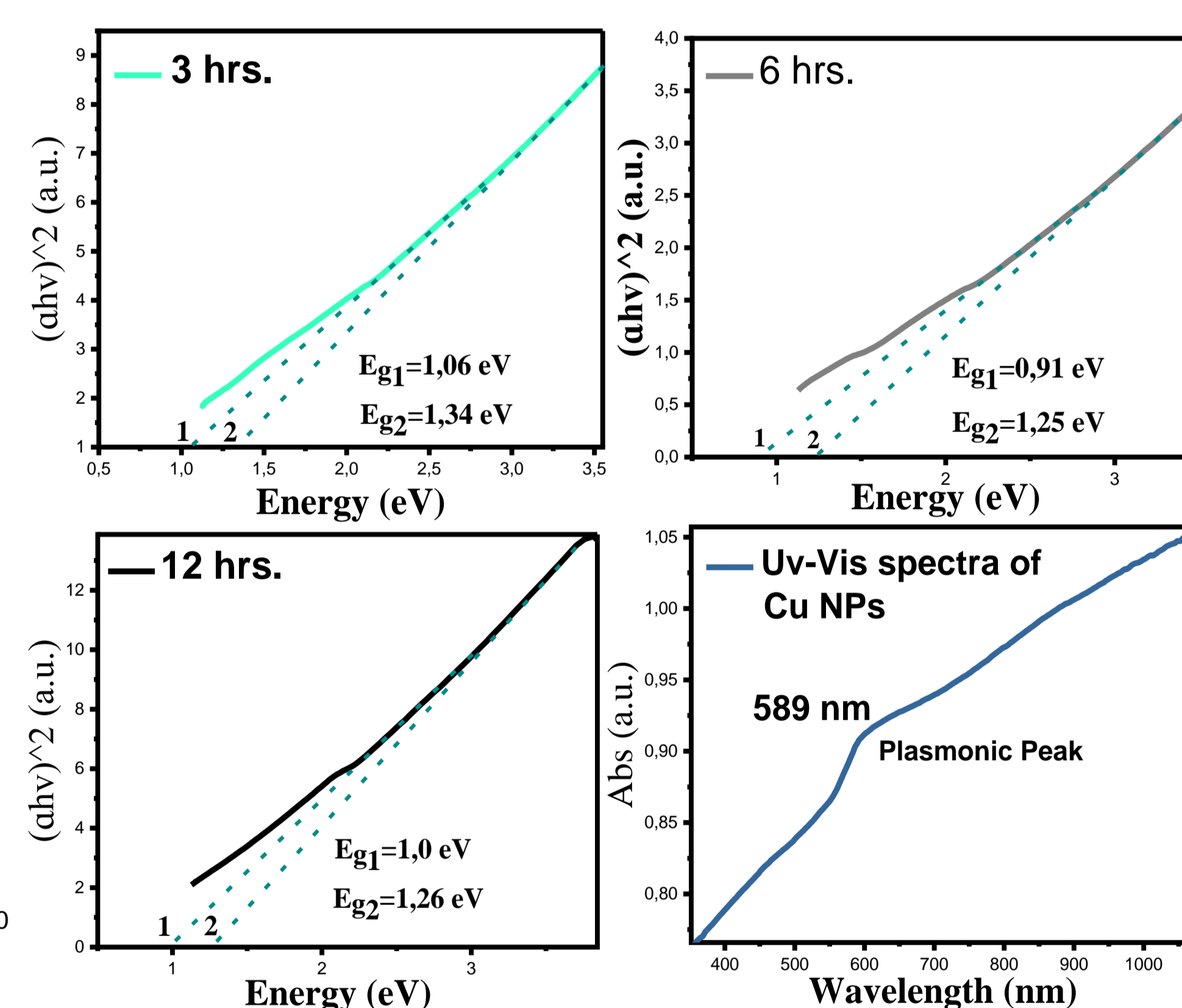
The SEM micrographs reveal the morphology of the various nanoparticle phases. Spherical, cubic and powder features corresponding to Cu₂O, Cu₃N and Cu respectively, were found.

Optical Properties

Photoluminescence Spectroscopy (PL)



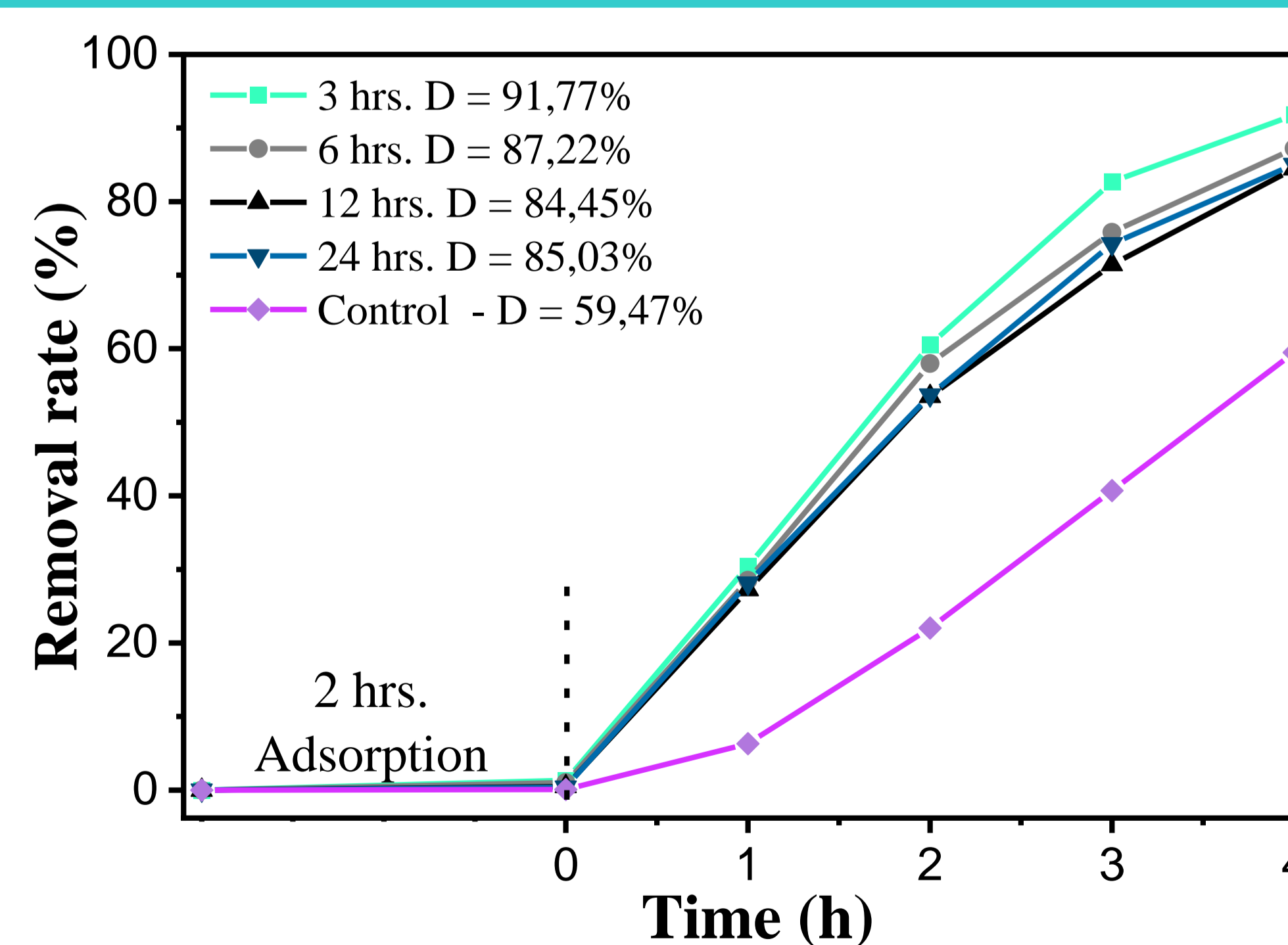
Band Gap Calculations



The emission spectra are dominated by Cu plasmonic nanoparticles. However, emission peaks of Cu₂O at 750 nm are visible. Cu₃N emission is in the infrared and therefore not visible in Room Temperature PL spectra.

Band gaps were calculated from UV-Vis spectra using the Tauc plots. For the mixed phase samples 2 band gaps were obtained. The narrow band gaps correspond to the metallic nature of Cu₃N due to the presence of Cu.

Photocatalysis Experiments



Photocatalytic experiments were performed to degrade 50 ml containing 5 ppm of methylene blue using 5 mg of the synthesized nanoparticles. The study shows that all the nanoparticles have photocatalytic properties. However, the sample synthesized in 3h containing 18% Cu₃N showed the best performance.

