Zinc oxide doped with copper and nitrogen exhibits photocatalytic antibacterial activity under light from common fluorescent tubes

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Introduction

Zinc oxide nanoparticles (ZNPs) have been subjected to increasing interest in previous years. As a semiconductor and photocatalyst, they have shown remarkable antimicrobial properties [1] as well as relatively low toxicity to humans [2]. Their photocatalytic activity is however only achieved under UV light, which limits their use as indoor biocidal agents. In this work, we used a sol-gel method [3] to synthetize and dope ZNPs with copper and nitrogen in an effort to improve their photocatalytic antibacterial activity under light of common fluorescent tubes.

Synthesis

Pure and doped ZNPs were synthetized via a previously reported sol-gel technique with modifications [3]. Briefly, zinc acetate dihydrate (0.37M) was dissolved in diethylene glycol and reacted at 180°C for 2 hours.

Polyol synthesis was doped with either only 2% copper (w/w_{ZnO}) or 2% copper (w/w_{ZnO}) and 3% nitrogen (w/w_{ZnO}) by addition of copper acetate monohydrate and ammonium acetate during the dissolution process. This process results in three ZNPs powder called Polyol, Polyol 2%Cu and Polyol 2%Cu 3%N.

X-Ray Diffraction (XRD)

As shown by characteristic XRD patterns in Figure 1, all syntheses successfully produced a wurtzite zinc oxide. Using Scherrer equation, crystallite sizes were estimated to 16±3nm, 20±5nm and 21±4nm for Polyol, Polyol 2%Cu and Polyol 2%Cu 3%N, respectively. No significant difference could be observed between pure zinc oxide and doped ones.

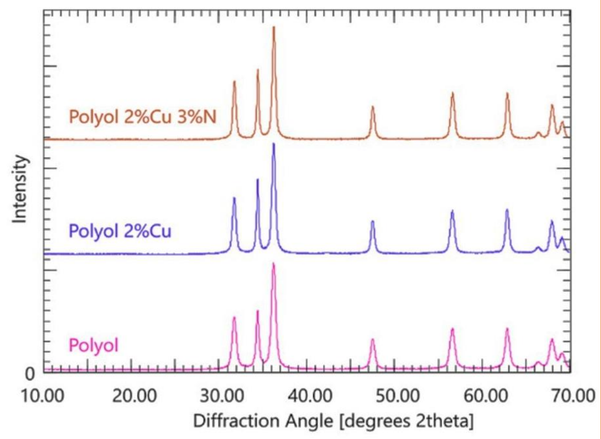

Fig. 1 – X-ray diffraction patterns of pure and doped ZNPs.

Scanning Electron Microscopy (SEM)

Figure 2 shows important differences in size and aggregation behavior of the ZNPs. Indeed, while Polyol and Polyol 2%Cu 3%N seem quite similar, Polyol 2%Cu forms smaller and more spherical aggregates with smaller grains. These observations demonstrate that copper has a significant effect on the morphology of the particles. On the other hand, nitrogen doping seem to hamper the effect of copper.

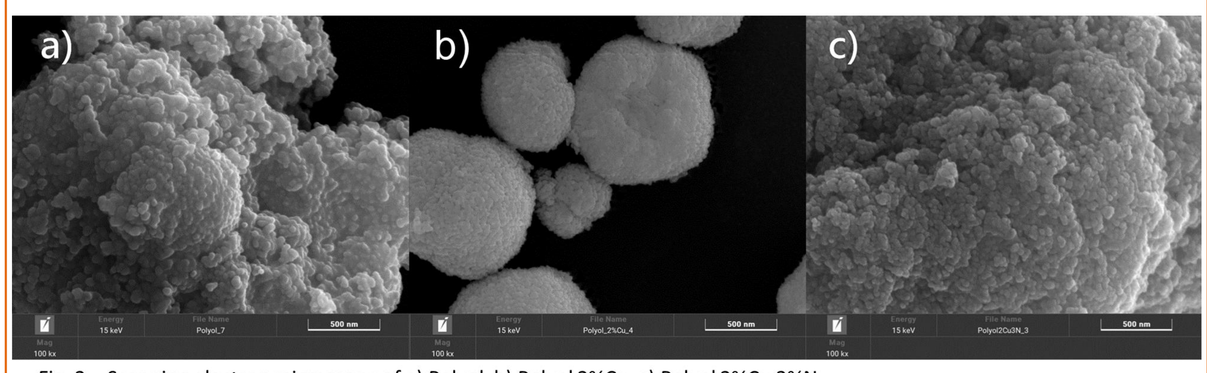

Fig. 2 – Scanning electron microscopy of a) Polyol, b) Polyol 2%Cu, c) Polyol 2%Cu 3%N.

Photocatalysis

To assess their photocatalytic activity, ZNPs were coated in 6-well plates which were then filled with methylene blue (MB) solutions. The discoloration of methylene blue solutions were then measured in the dark and under the light of common fluorescent tubes. As shown in Figure 3, a similar kinetic between Polyol and Polyol 2%Cu 3%N can be observed. However, Polyol 2%Cu exhibits a lower photocatalytic efficiency. As suggested by the results obtained in the dark, discoloration of the MB only solutions can be mostly attributed to the adsorption of the MB on the container walls.

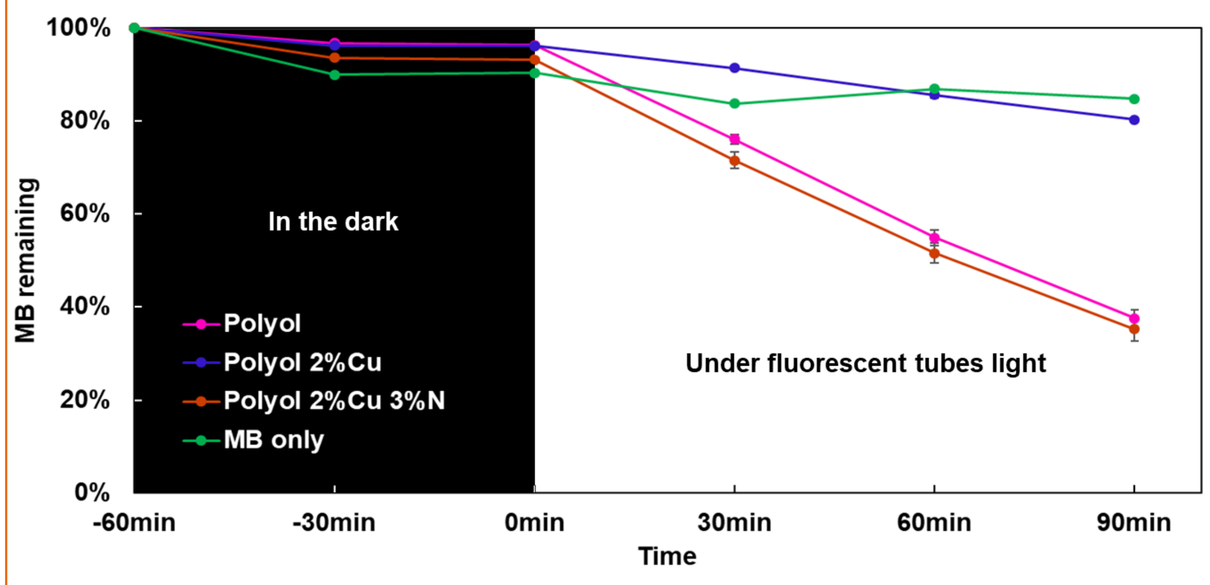

Fig. 3 – Discoloration of methylene blue under light from fluorescent tubes in presence of pure and doped ZNPs

Antibacterial effect

Antibacterial effects of the ZNPs under light from fluorescent tubes was measured placing *Staphylococcus aureus* in suspension with ZNPs for 3h. In Figure 4, Polyol 2%Cu 3%N demonstrates a higher antibacterial activity under visible light compared to pure Polyol with a log reduction of 3.9 and 1.0, respectively. Polyol 2%Cu exhibits strong antimicrobial effects even in the dark with a log reduction of 5.4. These effects in absence of light are believed to arise from Cu^{2+} ions leaking from the materials, as it is a well-known antibacterial agent.

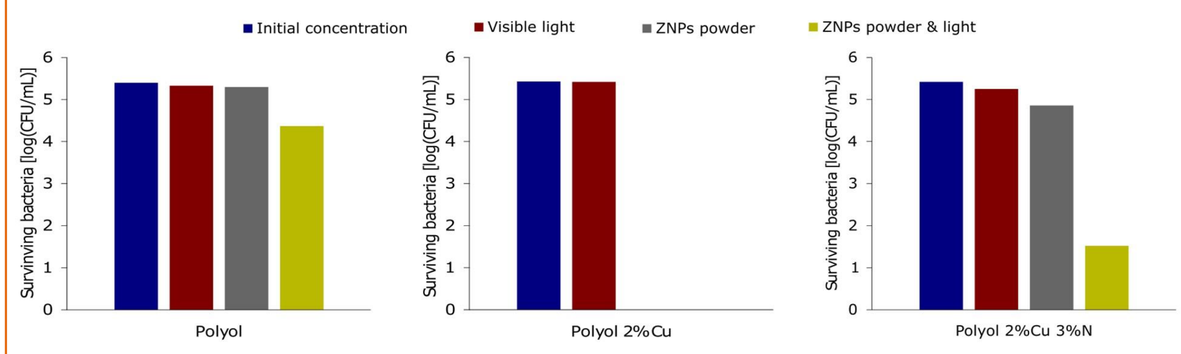

Fig. 4 – Surviving bacteria under light from fluorescent tubes in presence of pure and doped ZNPs.

Conclusion

Wurtzite zinc oxide produced by a polyol sol-gel technique was doped with copper and nitrogen to improve its photocatalytic antibacterial effect. Although showing a slow discoloration of MB, copper doped-only ZNPs demonstrate high antibacterial efficiency believed to be due to Cu^{2+} and/or Zn^{2+} ions leakage. On the contrary, ZNPs doped simultaneously with copper and nitrogen exhibit a faster discoloration of MB and biocidal properties only under light, which we attribute to photocatalytic antibacterial activity.

Further investigations are needed to assess the influence of ions leakage, zeta potential and specific surface area on the antibacterial effect of the ZNPs.

References

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