

Supporting Information

Reactive oxygen species (ROS) formation ability and stability of small Copper (Cu) nanoparticles (NPs)

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1. TEM image of Cu NPs before and after binding of CYS with according particle size distributions

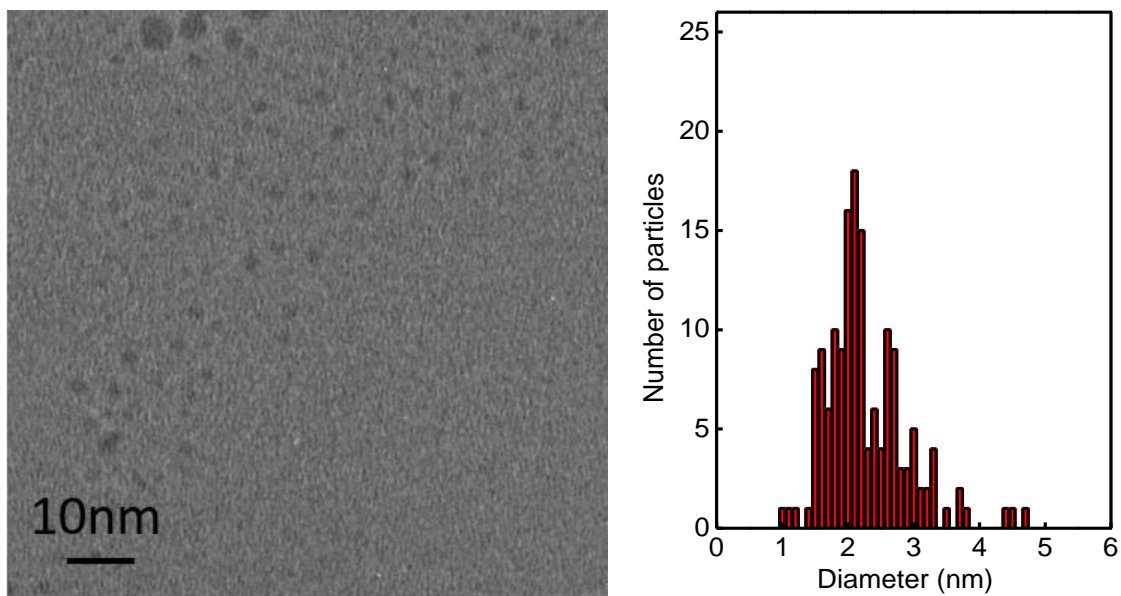


Figure S1. TEM image (left) and size distribution (right) of as prepared Cu NPs. NPs are visible as black spots. The mean diameter of NPs determined from the particle size distribution is 2.3 ± 0.6 nm.

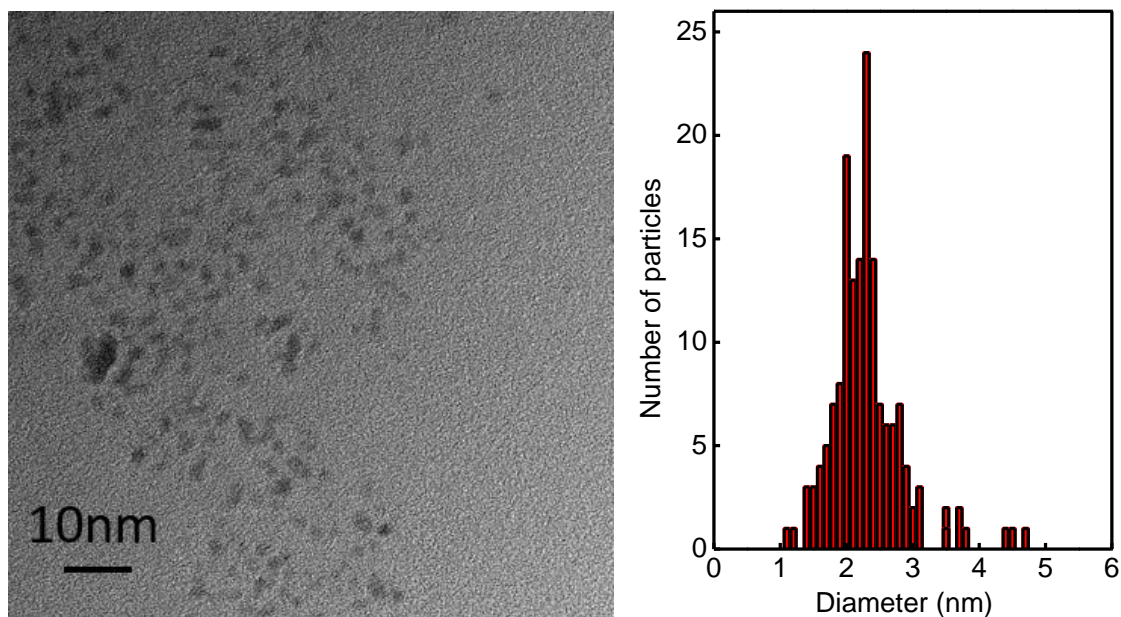


Figure S2. TEM image (left) and size distribution (right) of CYS-Cu NPs. NPs are visible as black spots. The mean diameter of NPs determined from the particle size distribution is 2.2 ± 0.4 nm.

2. Time dependent changes of aqueous CYS-Cu NP dispersion

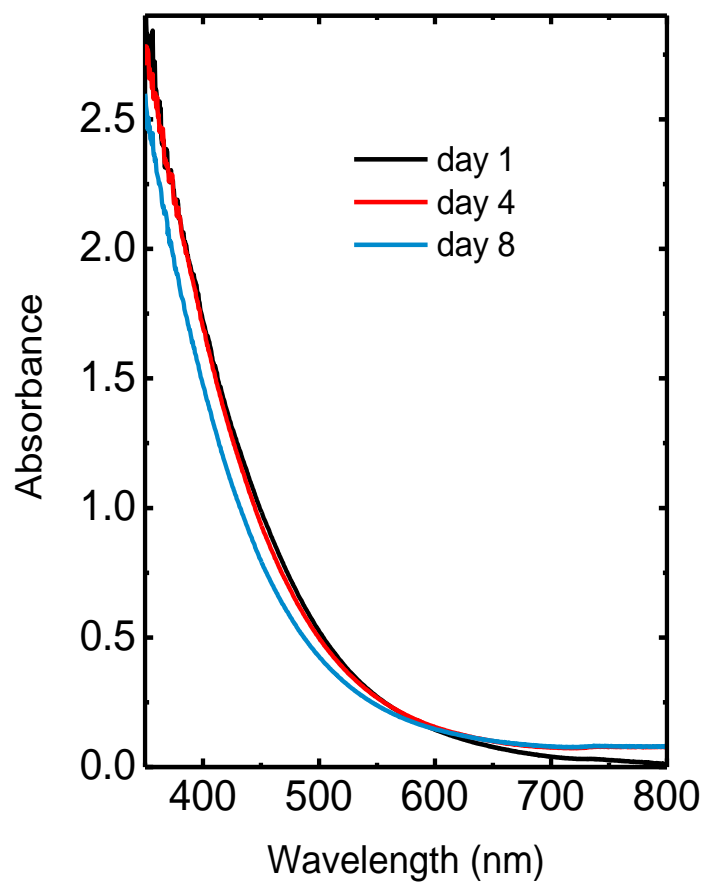


Figure S3. UV-vis spectra of a CYS-Cu NP dispersion after storage. After four days the small changes in the absorption above 600 nm appeared. After eight days a considerable deviation compared to the spectra after one and four days below 600 nm is visible.

3. Additional experimental data of ROS formation test experiments

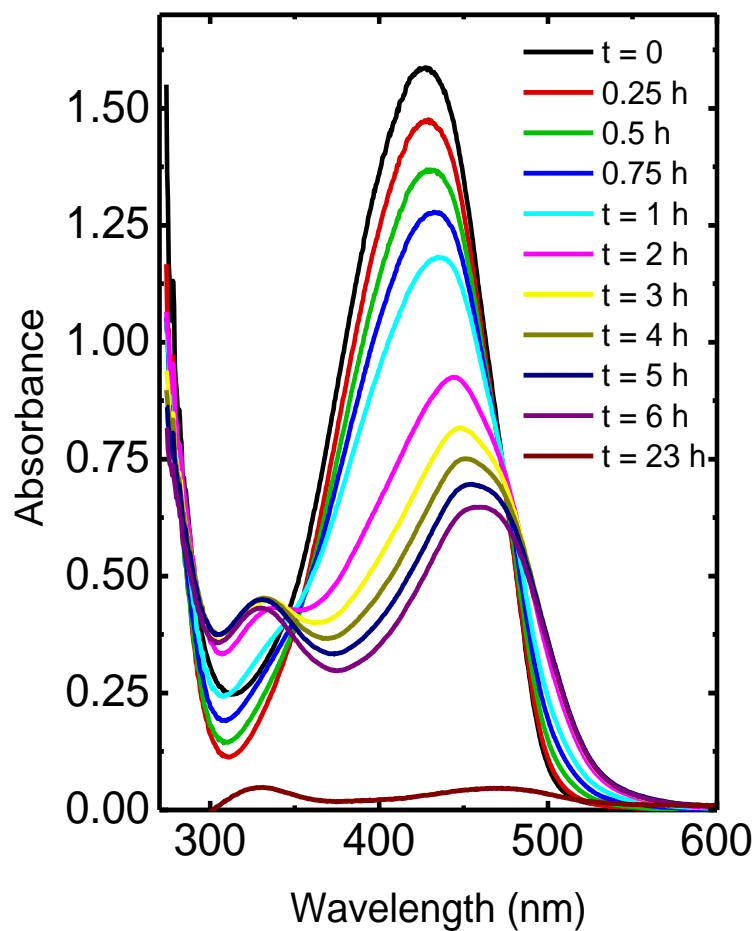


Figure S4. UV-vis spectral change of tartrazine monitored during its degradation in the presence of $7.83 \cdot 10^{-2}$ mM GSH-Cu NPs and 0.22 M H_2O_2 . In the first hour the absorption maximum at 429 nm decreases continuously. After 2 hours the maximum does not merely decrease, but shifts to higher wavelengths indicating that additional degradation reaction steps may take place.

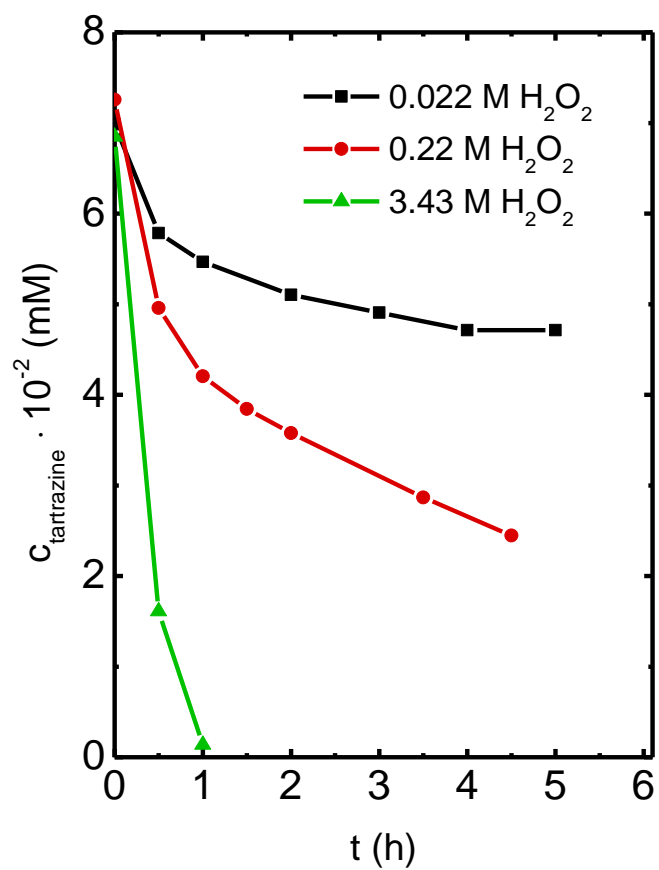


Figure S5. In order to test the effect of the H_2O_2 concentration on the rate of tartrazine degradation, a single experiment was performed with CYS-Cu NPs and the absorption maximum at 429 nm was analyzed. The degradation rate increases as the H_2O_2 concentration is increased.

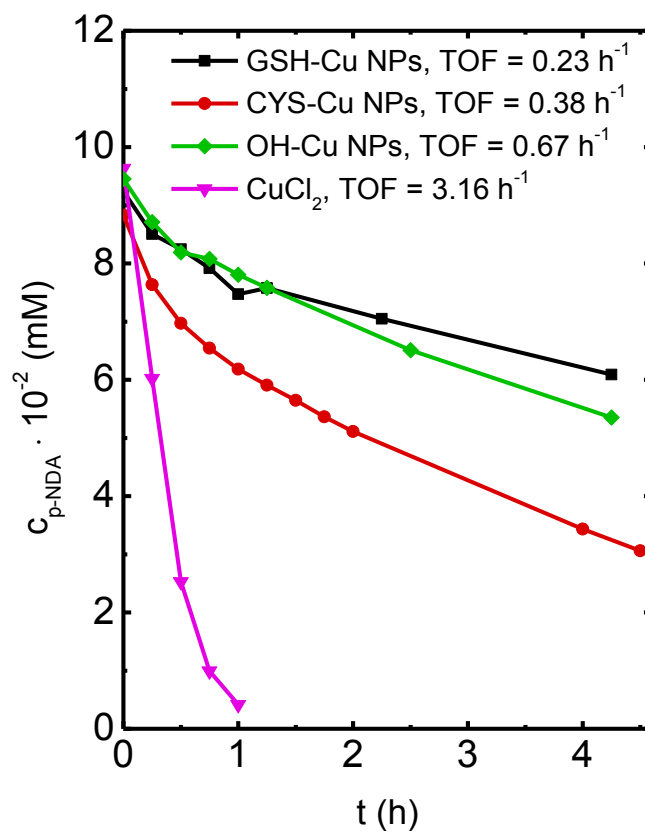
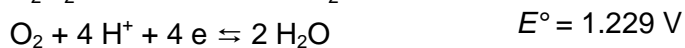
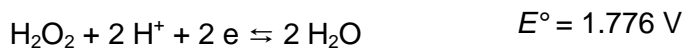


Figure S6. Bleaching of p-NDA by different ligand-functionalized Cu NPs and Cu^{2+} in the presence of 0.11 M hydrogen peroxide. The absorbance maximum of p-NDA at 440 nm was taken as a measure for its degradation. $c(\text{CYS-Cu NPs}) = 3.40 \cdot 10^{-2}$ mM, $c(\text{GSH-Cu NPs}) = 3.28 \cdot 10^{-2}$ mM, $c(\text{CuCl}_2) = 7.83 \cdot 10^{-2}$ mM, $c(\text{OH-Cu NPs}) = 1.44 \cdot 10^{-2}$ mM. GSH-Cu NPs show a lower activity than CYS-Cu NPs. OH-Cu NPs exhibit the highest activity. Cu^{2+} is significantly more active than all Cu NP samples.

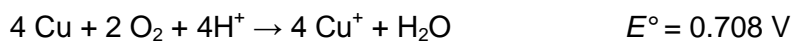
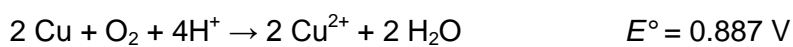
Supplementary data of stability studies

Standard redox potentials:^[1]

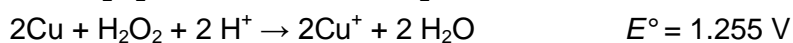
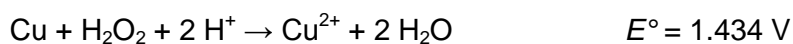


Based on the standard redox potentials the E° values for the oxidation of Cu by O_2 and H_2O_2 can be calculated:

O_2 induced redox reactions of Cu:



H_2O_2 induced redox reactions of Cu:^[2]



In the presence of O_2 or H_2O_2 the oxidation of copper is thermodynamically favored. Furthermore, the oxidation of Cu to Cu^{2+} exhibits a stronger driving force than the oxidation of Cu to Cu^+ .

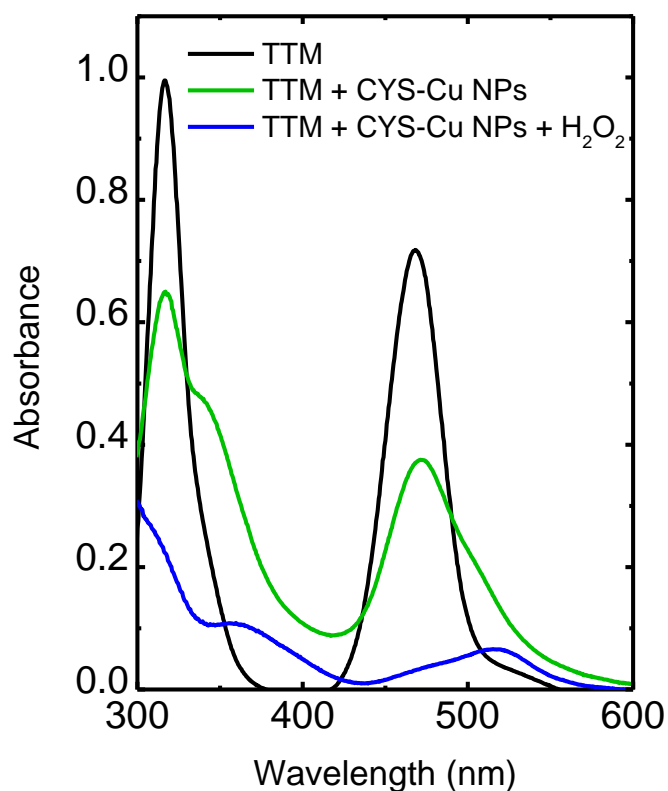


Figure S7. Release of Cu^{2+} ions from CYS-Cu NPs ($3.40 \cdot 10^{-2}$ mM) in phosphate buffer in the presence (blue) and in the absence (green) of H_2O_2 (0.22 M), tested with TTM (black) as a complexing agent. The decrease of the absorbance at 470 nm indicates the consumption of TTM for the formation of Cu^{2+} -TTM-complex. Cu^{2+} ions are present already in the absence of H_2O_2 as evident from comparison of the black and the green spectrum. If hydrogen peroxide is added, additional Cu^{2+} ions are leached (compare green spectrum to blue). The instability of TTM in the presence of H_2O_2 may have an influence on the results. The TTM- Cu^{2+} -complex was however found to be stable for hours, as evident from tartrazine degradation experiments performed in the presence of TTM (see Fig. 5 in the manuscript).

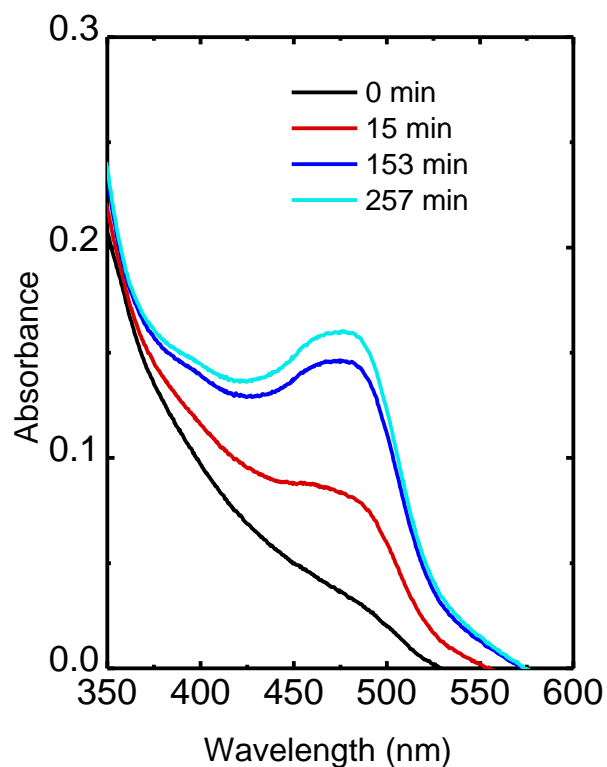


Figure S8. CYS-Cu NPs in phosphate buffer. The absorption band appearing above 470 nm is related to the formation of Cu^+ -BCS-complexes. This process occurs slowly compared to the formation of TTM- Cu^{2+} -complex (see Fig. S7).

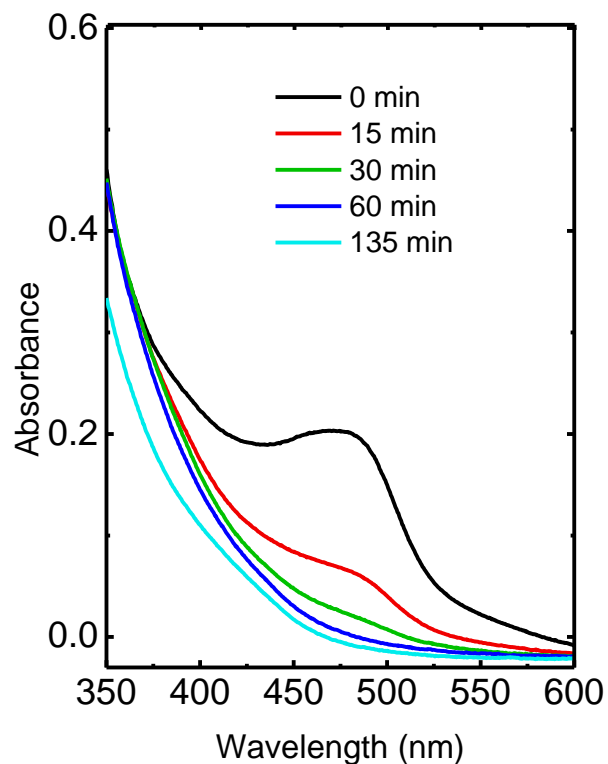


Figure S9. Instability of Cu^+ -BCS-complex (from GSH-Cu NPs) in the presence of 0.11 M H_2O_2 . The rapid decrease of the absorbance indicates the decomposition of the complex.

References

- [1] W. M. Haynes, *Handbook of Chemistry and Physics*, Vol. 9, 1st Edition, **2010-2011**.
- [2] W. He, Y. Liu, W. G. Wamer, J.-J. Yin, Electron spin resonance spectroscopy for the study of nanomaterial-mediated generation of reactive oxygen species, *Journal of food and drug analysis* **2014**, 22, 49–63.