CuO NPs obtained by laser ablation for 4-nitrophenol hydrogenation and dye degradation

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Problem: Anthropogenic water pollution by various hazardous chemicals has a strong negative impact on humans and the environment.

→ **Solution:** Use of catalytic technologies for chemical targeted transformations.

→ **By means of what? Heterogeneous CuO_x colloids catalysts*** + cheap and selective + high catalytic activity

→ **How to prepare? PLA of Cu in liquid**** + simplicity + charge stabilization of colloids without the use of surfactants

→ **The aim of the work:** In the present work, features of CuO_x NPs colloids obtained by PLA in water and H_2O_2 water solutions and their catalytic properties towards reduction of p-nitrophenol (NP) and oxidative degradation of methylene blue (MB) were studied.

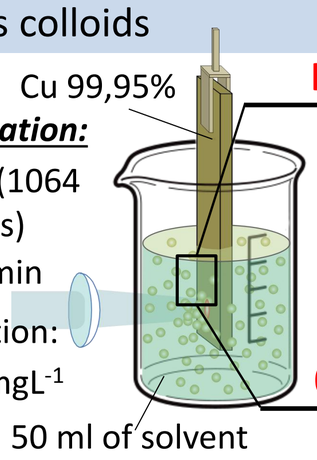
The processes occurring during PLA of Cu in H_2O and H_2O_2 and subsequent aging of the suspension were shown to affect the morphology, phase composition and sedimentation stability of NPs in colloids and as a consequence CuOx NP catalytic activity. MB was selected as a modal organic pollutant for investigation of the oxidative degradation activity. The reduction of NP to p-aminophenol (AP) under mild conditions using $NaBH_4$ is a way to an effective and environmentally friendly method for producing amines as well as a way of neutralization of highly toxic aromatic nitro compounds.

CuOx NPs formed in the initial colloid

The formation of **sedimentation stable, but phase unstable** Cu_2O NPs colloids

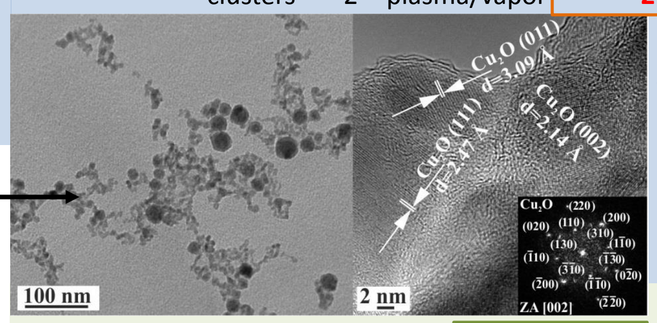
Conditions for colloids preparation:

- Laser Nd:YAG (1064 nm, 20 Hz, 7 ns)
- PLA time: 30 min
- NP concentration: 100 and 160 mgL^{-1}



The formation of **phase and sedimentation stable** CuO NPs colloids

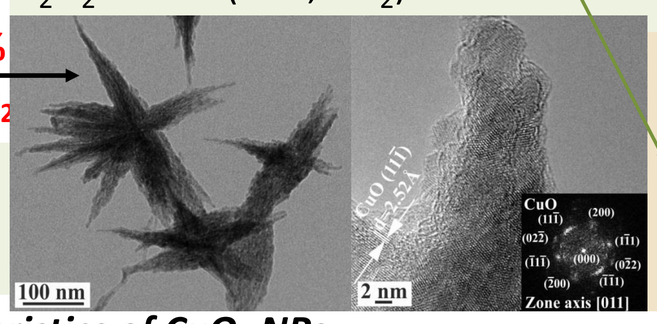
$Cu_{clusters}+H_2O_{plasma/vapor} \rightarrow Cu_2O$ **storage for 30 days** → **CuO**



PLA in H_2O results in the formation the pseudospherical NPs Cu_2O.

$Cu_{cl}+H_2O_{plasma/vapor}+ ROS \rightarrow Cu_2O \rightarrow CuO$

$H_2O_2 \xrightarrow{laser} ROS\ (OH^{\bullet}, O^{-\bullet}_2)$

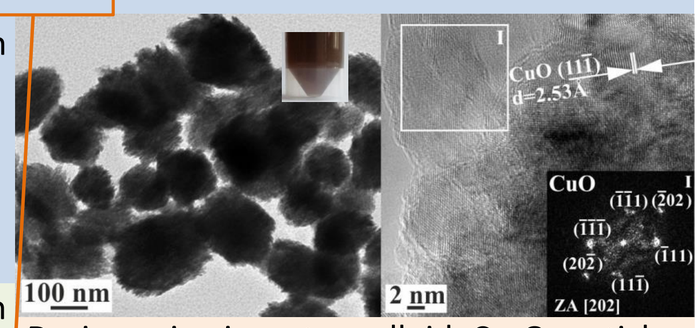


Peroxide provides deeper oxidation of Cu cluster to form CuO phase directly during the PLA synthesis by means of reactions:

1) $Cu^+(s) + 2\,(OH^-)_{(aq)} \rightarrow Cu(OH)_{2(s)}$

2) $Cu(OH)_{2(s)} + 2\,(OH^-)_{(aq)} \rightarrow Cu(OH)_4^{2-}{}_{(aq)} \leftrightarrow$

$\leftrightarrow CuO_{(s)} + 2OH^-_{(aq)} + H_2O$



During aging in water colloid, Cu_2O particles are agglomerated and oxidized through the formation of a copper hydroxide phase to form lenticular-like CuO particles.

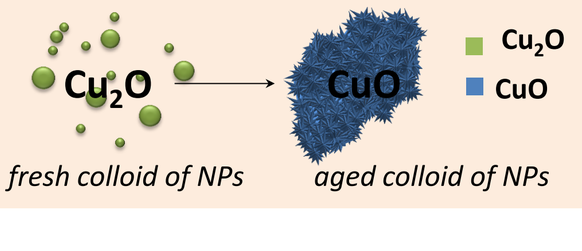


Table. Physical-chemical characteristics of CuO_x NPs

Solvent for PLA	Aging (days)	XRD data, phase(mass%)	ζ-potential
H_2O	0	Cu_2O (97%), Cu (3%)	+35 mV, pH=6.5
	30	CuO (97%), Cu (3%)	+28 mV, pH=6
$H_2O+H_2O_2$ (0.1%)	0	CuO (100%)	+41 mV, pH=6
	30	CuO (100%)	+25 mV, pH=6

Cu_2O phase formation occurs by reacting ejected copper clusters with water. Reactive oxygen species (ROS) are formed in the presence of hydrogen peroxide in the process of PLA, which contribute to the instant transition of the Cu_2O to CuO. PLA in H_2O_2 leading to the formation the sheet-like and flower-like NPs CuO with a polycrystalline (defective) structure.

Catalytic oxidative degradation of MB

The catalytic activity of aged CuO colloid was studied.

2 ml **MB** 2.5×10^{-5} $molL^{-1}$
100 µL **H_2O_2** 0.2 $molL^{-1}$
250 µL **CuO_x** 100 mgL^{-1}

$t_{reactions}$ 0-120 min

30, 40, 50 °C, 300 rpm *λ_{reg}= 450-800 nm*

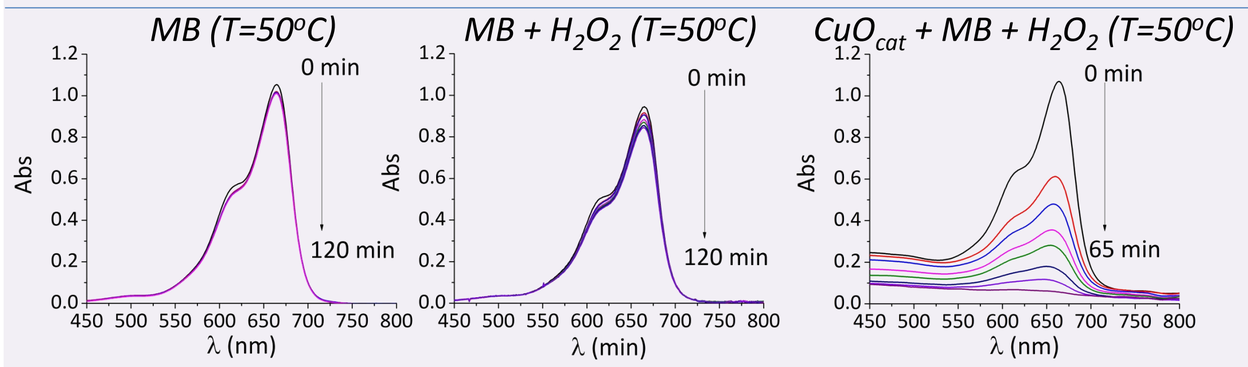
Spectrophotometer Solar CM 2203 with built-in stirrer and thermostat:

Catalytic reduction of p-NP to p-AP

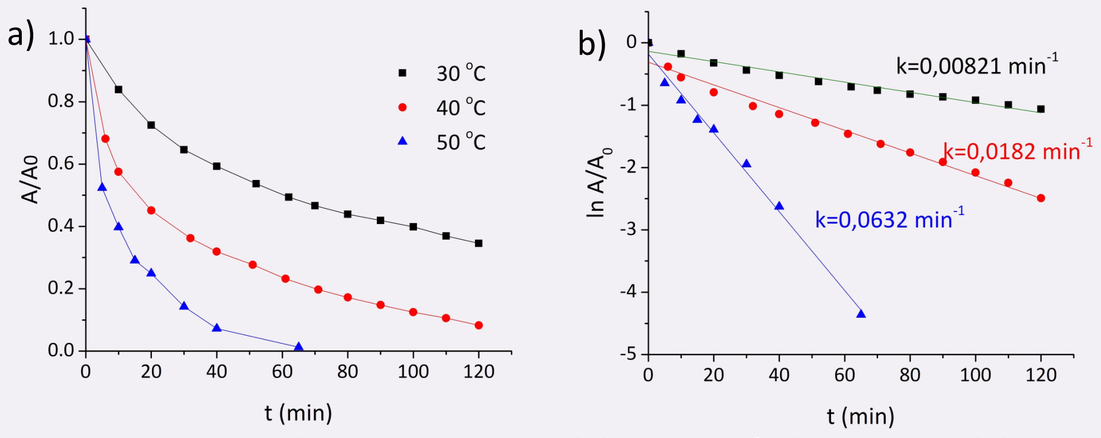
1,7 ml H_2O → + 200 µL **CuO_x** 15 mgL^{-1} + 300 µL **$NaBH_4$** 0,05 $molL^{-1}$ → + 300 µL **p-NP** 2.57×10^{-4} $molL^{-1}$ → $t_{reactions}$ → **p-AP** (product)

19 °C, 300 rpm *recovery of CuOx NPs 2 min* *"Start" λ_{reg}= 400 nm*

Research results:



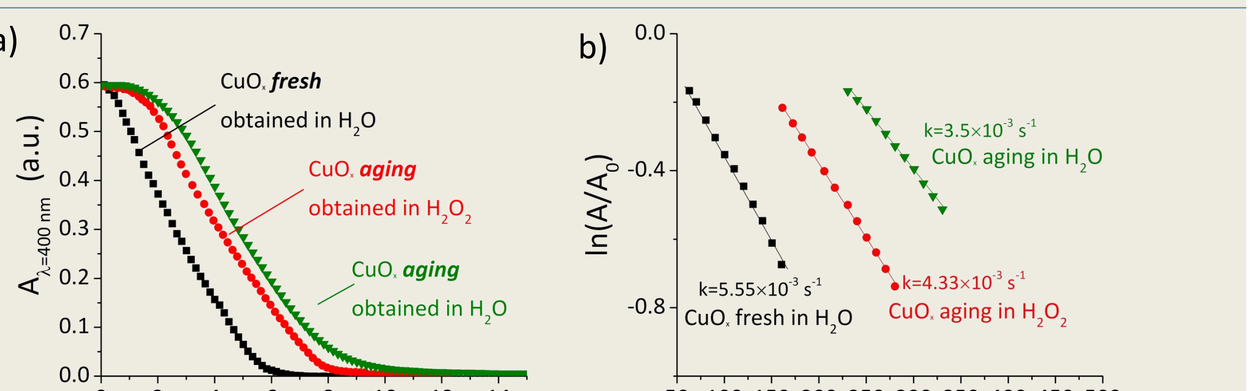
Time dependences of absorption spectra different compositions of reaction mixture



Kinetic dependences of MB consumption (a) and ln(A/A$_0$)-time plots (b) at deferens reaction temperature

The aged CuO colloids obtained by PLA in H_2O_2 was employed for oxidative degradation of dye molecules in the presence of H_2O_2. The as synthesized CuO nanostructure exhibits high catalytic activity for the degradation of MB at 50 °C. The present study provides development of a very effective CuO nanocatalyst for promoting toxic dye degradation in water waste treatment.

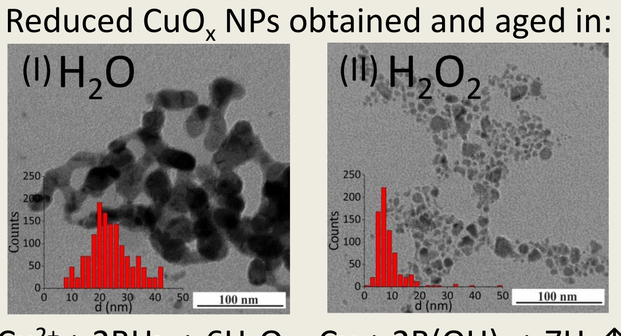
Research results:



Kinetic dependences of NP consumption (a) and ln(A/A$_0$)-time plots (b) for samples obtained in H_2O and H_2O_2

All samples obtained showed high catalytic activity towards NP reduction to AP, with some peculiarities depending on morphology and dispersion of colloid CuO_x NPs. The freshly obtained aqueous Cu_2O colloids showed the highest catalytic activity among the studied samples, but their activity notably decreased with aging. This was associated with the agglomeration and oxidation of the primarely particles, which leads to the formation of dense aggregates of large Cu NPs after the reduction with $NaBH_4$ (TEM (I)). The aged CuO_x colloids obtained in hydrogen peroxide exhibited the catalytic activity lying between, which is due to the production of smaller Cu NPs formed in the result of CuO NPs reduction (TEM (II)).

Reduced CuO_x NPs obtained and aged in:



$Cu^{2+} + 2BH^-_4 + 6H_2O = Cu + 2B(OH)_3 + 7H_2\uparrow$

Catalyst Design
From Molecular to Industrial Level
16-19 May 2021
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* P. Deka, B.J. Borah, H. Saikia, P. Bharali, Chem. Rec. 2019, 19, 462–473; ** D.A. Goncharova, T.S. Kharlamova, I.N. Lapin, V.A. Svetlichyi, Phys. Chem. C 123 (2019) 21731.