

Polyacrylate Modified Copper Nanoparticles with Controlled Size

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Abstract—The preparation of Cu nanoparticles (NPs) through the reduction of copper ions by sodium borohydride in the presence of sodium polyacrylate with a molecular weight of 1200 is reported. Cu NPs were synthesized at a concentration of copper salt equal to 2.5, 5, and 10 mM, and at a molar ratio of copper ions and monomeric unit of polyacrylate equal to 1:2. The as-prepared Cu NPs have diameters of about 2.5–3 nm for copper concentrations of 2.5 and 5 mM, and 6 nm for copper concentration of 10 mM. Depending on the copper salt concentration and concentration of additionally added polyacrylate to Cu particle dispersion, primarily formed NPs grow through the process of aggregation and/or coalescence into clusters and/or particles with a diameter between 20–100 nm. The amount of additionally added sodium polyacrylate influences the stability of Cu particles against air oxidation. The catalytic efficiency of the prepared Cu particles for the reduction of 4-nitrophenol is discussed.

Keywords—Copper, nanoparticles, sodium polyacrylate, catalyst, 4-nitrophenol.

I. INTRODUCTION

OVER the past few decades, research on the preparation of copper nanoparticles is intensively developed due to their unique optical, electronic, catalytic, and magnetic properties [1]. These extraordinary properties are mainly related to their low particle size and large specific surface area. Copper nanoparticles have thus potential applications in various fields, for example, as catalysts [2], [3], lubricants [4], antibacterial agents [5], [6], electronic and optical nanodevices [7]. A number of techniques have been developed for preparation of copper nanoparticles. They are mainly based on chemical reduction [8], [9], sonochemical reduction [10], radiolysis assisted reduction [11], microwave assisted reduction [12], laser ablation [13], infrared irradiation [14] or electron beam irradiation [15]. Procedures employing chemical reductions of copper ions are one of the most common methods for the preparation of copper nanoparticles because they are fast, simple and the possibility of choosing the suitable reducing agent enables to influence the characteristics of the prepared nanoparticles. Hydrazine [16], ascorbic acid [9] or sodium borohydride [17], [18] are often used as reducing substances. Syntheses can be performed both in non-polar and polar media. The relatively stable Cu NPs have been synthesized in toluene with dodecanthiol, tridecylamine, and lauric acid as the protective agents [19]. Unfortunately, the copper

nanoparticles prepared in polar media are often prone to oxidation which changes their properties [3]. There exist several ways how to prevent the oxidation of the copper nanoparticles. One possibility how to gain stable Cu NPs requires conditions when the reaction medium is previously deoxygenated and the complete synthesis must be kept under an inert atmosphere. Another method how to produce stable Cu NPs exploits inert atmosphere created in-situ by consequent decomposition of reducing substances, e.g. hydrazine [16]. The unwanted oxidation of the prepared Cu NPs, in aqueous solution, can be prevented by high concentrations of a modifier combined with the exploitation of ascorbic acid as a reducing agent which additionally served as the protective agent against the oxidation of Cu NPs [20]. Ascorbic acid can play double role – reducing and antioxidant agent in the reaction system. Wu et al. reported the preparation of copper nanoparticles with particles size less than 5 nm via reduction of copper (II) nitride by ascorbic acid without any other antioxidant agent [8].

In this paper, we report on the synthesis of the copper nanoparticles through reduction of copper (II) salt by sodium borohydride in the presence of a sodium polyacrylate. The prepared Cu particles are protected against oxidation by addition of ascorbic acid to the Cu NP dispersion. The influence of copper salt concentration as well as consequent addition of extra polyacrylate into the dispersion on the size, morphology, stability, and catalytic activity of the prepared Cu particles is demonstrated.

II. EXPERIMENTAL

A. Materials

Following chemicals have been used without further purification: copper sulfate pentahydrate (99%, Sigma-Aldrich), sodium salt of polyacrylic acid (MW 1200, 45% aqueous solution, Sigma-Aldrich), sodium borohydride (98+%, Sigma-Aldrich), ascorbic acid (p.a., Tamda). All solutions were prepared using deionised water (18 M Ω -cm, Millipore).

B. Synthesis of Copper Nanoparticles

Copper NPs were prepared by a rapid injection of NaBH₄ solution (50 ml) to an aqueous solution of CuSO₄·5H₂O (200 ml) in the presence of sodium polyacrylate with a molecular weight of 1200 (NaPA 1200). The syntheses of Cu NPs were carried out for three final concentrations of copper (2.5 mM, 5 mM, and 10 mM). The final molar ratio of sodium borohydride to copper ions and the molar ratio of monomeric unit of used polymer to copper ion were 3:1 and 1:2,

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respectively. All of the performed syntheses of copper NPs were carried out at the laboratory temperature.

C. Characterization of the Copper Nanoparticles

UV-vis absorption measurements were performed using a Specord S 600 instrument (Analytic Jena AG, Germany). All Cu NP samples were diluted by deionised water before UV-vis absorption measurements to concentration equal to 1 mM of Cu. The particle size and morphology were evaluated by the dynamic light scattering method (Zetasizer Nano ZS, Malvern Instruments Ltd., UK) and by the transmission electron microscopy (TEM, Jeol JEM 2010, Japan). For TEM measurements, a drop of the colloidal dispersion of NPs was deposited on copper grids coated with a carbon layer. In order to prevent the oxidation process of the deposited copper NPs, the samples were dried and stored under vacuum. Selected samples were further analyzed by X-ray powder diffraction (XRD) using an X'Pert PRO (PANalytical, The Netherlands) instrument operating in the Bragg-Brentano geometry with Fe-filtered $\text{CoK}\alpha$ radiation (40 kV, 30 mA) and equipped with an X'Celerator detector and programmable divergence and diffracted beam anti-scatter slits. Drops of colloidal dispersion were deposited on a zero-background single-crystal silicon slides and successively scanned prior and after air-drying at a near constant irradiation volume in the 2θ range of $5\text{--}120^\circ$ in steps of 0.017° . The commercial standards SRM640 (Si) and SRM660 (LaB_6) from NIST were used for evaluation of the line positions and instrumental line broadening, respectively. The acquired patterns were processed using X'Pert High Score Plus software (PANalytical, The Netherlands), PDF-4+ and ICSD databases.

D. Catalytic Experiment

The process of catalytic reduction of 4-nitrophenol was studied by UV-visible spectroscopy due to the absorption peak of 4-nitrophenate ions at 400 nm. The spectra were taken every 2s in the spectral range of 250–550 nm.

III. RESULTS AND DISCUSSION

The Cu NPs had been synthesized on the basis of our previous study when the Cu NPs were prepared simply by addition of sodium borohydride to the aqueous mixture of copper ions (final concentration equal to 1mM) and sodium polyacrylate [21]. It was found that the primarily formed Cu NPs with a dimension between 2-3 nm gradually grew by particle aggregation and coalescence mechanism into Cu NPs with a diameter of approximately 14 nm. In this presented study, the influence of copper salt concentration and concentration of additionally added polyacrylate on the essential characteristics (particle size, morphology, stability) of the prepared Cu NPs was investigated with the aim to control the size of the prepared NPs, their air stability and catalytic efficiency. Following the sodium borohydride addition, the blue color of copper ions/NaPA mixture changed to rusty color, indicating the reduction of Cu^{2+} to Cu^0 . With respect to the detailed exploration of stability of the Cu NPs (prepared at molar ratio of copper ions and monomeric unit of

sodium polyacrylate with MW 1200 equal to 2:1), the Cu NP dispersion prepared at each used concentration of copper (i.e., 2.5mM, 5mM, and 10mM) was divided into 4 aliquots and the molar ratio of Cu ions to NaPA 1200 was adjusted to 4:1, 6:1, and 10:1 by addition of extra NaPA 1200. These 12 samples (3 concentrations of copper, 4 different concentrations of NaPA) were stored in closed vessels and periodically monitored by means of DLS measurements, UV-visible absorption, and TEM measurements during 3 weeks. It is well known that the Cu NPs prepared in polar environment at ambient atmosphere are likely to be partially oxidized. In order to prevent oxidation of Cu NPs, the dispersions of Cu NPs must be deoxygenated and the reduction of copper ions must be carried out under protection of inert atmosphere. In our experiments, the oxidation of the prepared nanoparticles is suppressed by addition of ascorbic acid in the final concentration of 20 mM.

The average sizes of the as-prepared copper NPs determined immediately after their preparation by DLS method were 3.6 nm (2.5 mM), 3.8 (5 mM), and 4.7 nm (10 mM), respectively. UV-visible absorption spectra of Cu NPs prepared at a molar ratio of copper ions to monomeric unit of sodium polyacrylate equal to 2:1 are depicted in the Fig. 1. In all used copper concentration, the absorption spectra recorded immediately after preparation and at 3 hours after preparation of Cu NPs exhibit no absorption maximum which is typical for Cu NPs with dimensions below 4 nm. The strong broadening of the plasmon resonance is connected with fact that the dimensions of such tiny Cu NPs copper particles are smaller than the mean free path of the conduction electrons and the collisions of these electrons with the particle surface occur. An increase in the particle size leads to a progressive appearance of plasmon peak about 570 nm [22]. The transmission electron microscopy was used in order to confirm the size of the prepared nanoparticles. TEM images taken 3 hours after the Cu NPs preparation revealed particles with a mean diameter of 3.1 nm (2.5 mM Cu), 3.0 nm (5 mM Cu), and 6.0 nm (10 mM Cu) (Fig. 2) as determined by measuring several tens of particles. Average particle size determined by DLS method and absorption spectra of Cu NP dispersions were then recorded periodically during 3 weeks after their preparations. 24 hours after preparation of Cu NPs, we observed the increase in the absorption at 570 nm. The increase in the absorption was more pronounced for Cu NP dispersion prepared at the final concentration of copper equal to 10 mM (Fig. 1) in comparison to lower concentrations of Cu. In this case, the TEM images revealed larger particles with diameters of about 80 nm (images not shown). However, the Cu NP dispersions prepared at the final concentration of copper equal to 2.5 mM and 5 mM, were still composed of particles with very small dimensions (images not shown) which can be supported by the low values of absorption at 570 nm. The average size of particles gradually grew up during further ageing. The dependences of the average size of the Cu NPs on duration of storage are depicted in Fig. 3. Beside period of aging, the resulting size of the Cu NPs is dependent on the final concentration of both the copper and

sodium polyacrylate. With increasing concentration of copper salt, final Cu NPs are larger. It is caused by the fact that a greater number of primarily generated Cu NPs is present in the dispersion, being thus in a closer contact, and, therefore, bigger Cu particles can be formed upon aging. However, the difference in the sizes of particles gained 2 weeks after Cu NPs preparation at copper concentration of 5 mM and 10 mM are negligible. The growth of the Cu NPs is hindered at a higher concentration of sodium polyacrylate, mainly in the case when the concentration of copper was 5 and 10 mM. The difference in the rate of the particle growth is probably connected to the number of sodium polyacrylate molecules. At a higher concentration of sodium polyacrylate, greater number

of polymer molecules causes larger coverage of particle surface. The consequence of higher electrostatic repulsion of Cu NPs (due to the adsorbed negatively charged polyacrylate molecules) is then reflected in the slower growth of Cu particles. The representative TEM images of Cu particles prepared at a concentration of copper equal to 10 mM and "aged" for 3 weeks at molar ratio of Cu ions and monomeric unit of polyacrylate molecule equal to 1:2 (further referred to as sample A) and 1:10 (further referred to as sample B) are depicted in the Figs. 4 A and B. In both cases, the particles or aggregates with sizes of about 100 nm were observed. However, when a higher concentration of sodium polyacrylate was used, the final Cu particles have a core-shell structure.

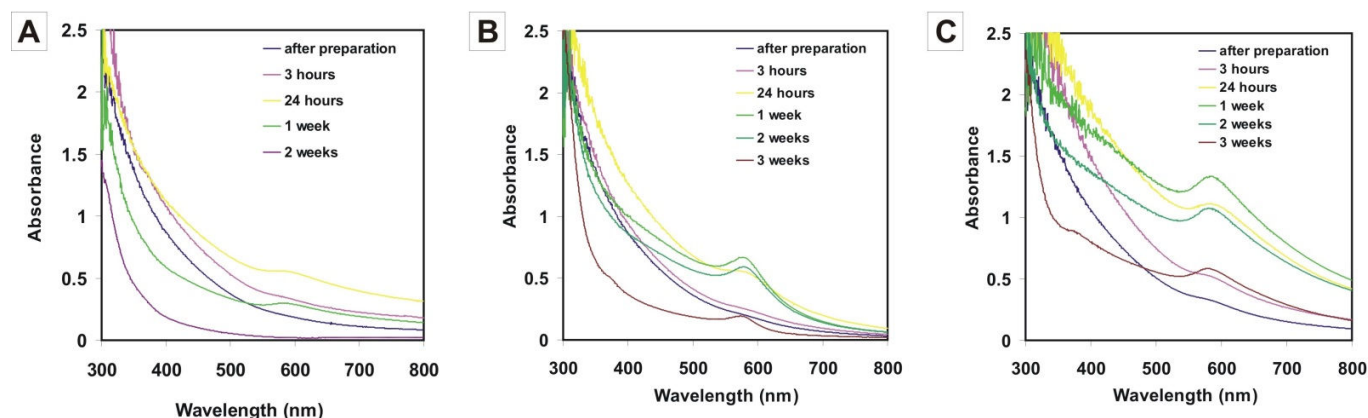


Fig. 1 Time-dependent UV-vis absorption spectra of Cu NPs prepared at the final copper concentration of (A) 2.5 mM, (B) 5 mM, and (C) 10 mM

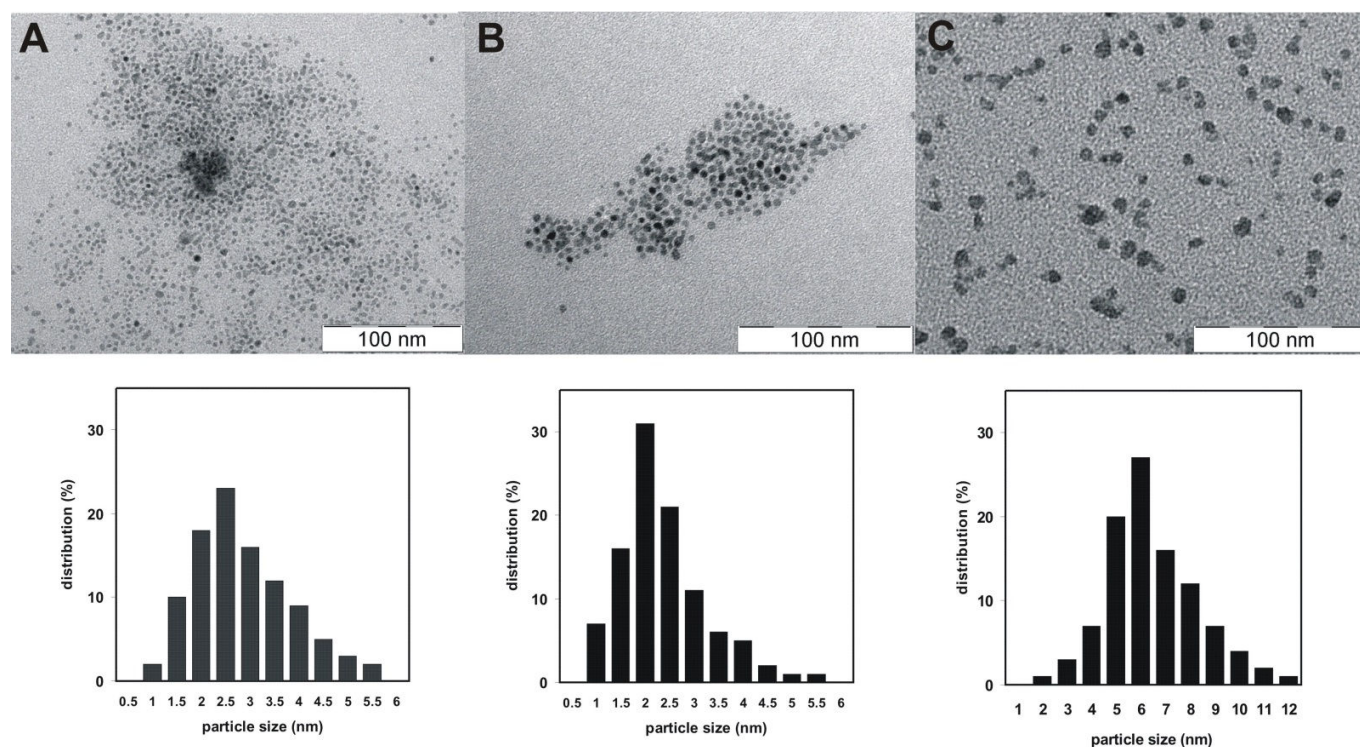


Fig. 2 TEM images of Cu particles prepared at the final copper concentration equal to (A) 2.5 mM, (B) 5 mM, and (C) 10 mM. TEM images were taken 3 hours after the Cu NPs preparation.

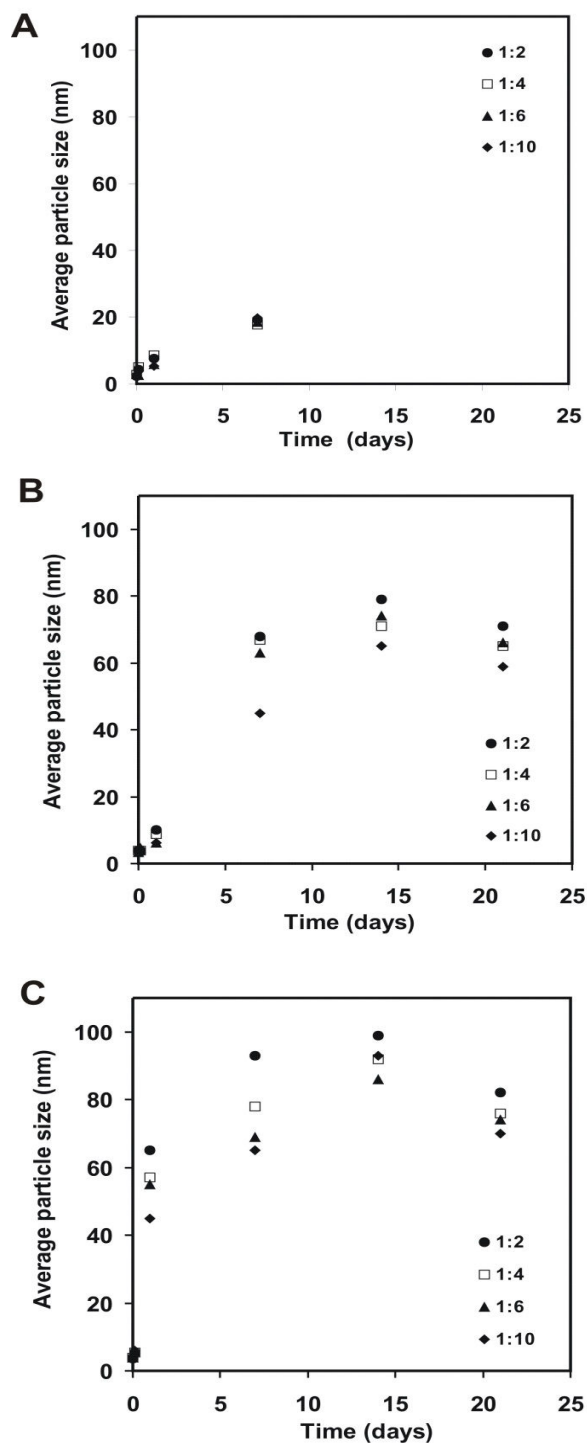


Fig. 3 The time changes in the average particle size (determined by DLS method) of copper particles prepared at the final copper concentration of A 2.5mM, B 5mM, and C 10mM and stored for different molar ratio of copper ions and monomeric unit of polyacrylate

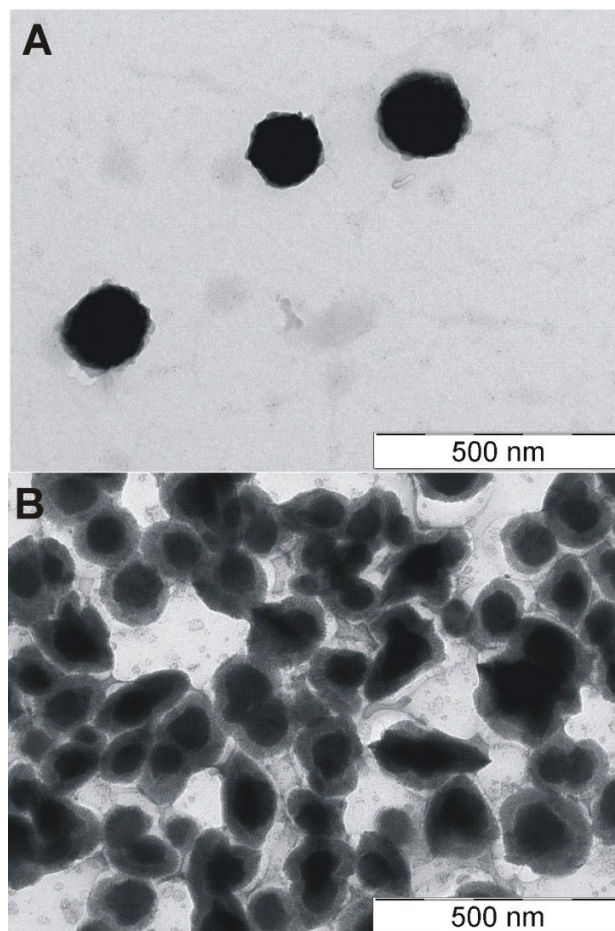


Fig. 4 TEM images of Cu particles prepared at the final copper concentration equal to 10mM and for molar ratio of copper ions and monomeric unit of polyacrylate equal to A 1:2 and B 1:10

The shell exhibits spongy-like character and seems to be consisting of NPs with a diameter of a few nanometers. On the contrary, the Cu particles “aged” with a lower amount of polyacrylate molecules exhibit more compact character in comparison to higher concentrations of polyacrylate.

Samples A and B presented in the Fig. 4 were further characterized by XRD analysis (Fig. 5). Successive scans collected on each sample exposed to ambient-air conditions confirmed the sample stability in terms of their oxidation during drying as no changes in structural properties were observed. The mean particle size, expressed as mean X-ray coherence length - MCL (i.e., dimension of coherently diffracting domains) and determined from broadened diffraction peaks according to Rietveld analysis [23], amounts to ~54nm for the sample A (i.e., with lower concentration of NaPA) and ~24nm for the sample B (i.e., with higher concentration of NaPA). Another important feature calculated from diffraction data is the extent of primary oxidation of Cu nanoparticles to Cu_2O phase (Fig. 5). Approximately 60 ± 5 wt.% of Cu_2O was detected in the sample A, while the sample B contains 68 ± 5 wt.% of Cu_2O . However, the main difference lies in the particle size of the Cu_2O phase (Fig. 5). In the sample A, the mean X-ray coherence length of Cu_2O is well

below 5nm. The formation of small particles of oxides (<5 nm) could indicate a partial surface oxidation of larger metal nanoparticles. The presence of the Cu₂O shell on the Cu particles/aggregates is comparable to the surface oxidation of other metal nanoparticles [24] taking place according to the Cabrera-Mott theory of oxidation of metals [25]. In the sample B, on the other hand, we observed two different size distributions of Cu₂O - one with MCL well below 5 nm (48±5 wt.%) and the second one with MCL ~20 nm (20±5 wt.%). The larger Cu₂O particles (MCL ~20 nm) observed in the sample B could be ascribed to the larger particles of Cu₂O within “spongy-like” structures overgrowing metallic-Cu particles (see Fig. 4). The small Cu₂O particles (MCL <5 nm) could represent (i) a smaller fraction of particles in the spongy-like structure, (ii) thin surface layer on Cu NPs, (iii) small separate particles outside such structures, or combination of all three possibilities. Therefore, we can conclude that Cu particles prepared at the lowest concentration of NaPA have a considerably larger mean particle size compared to Cu particles prepared at 5-times higher excess of NaPA. Moreover, higher polyacrylate concentration prevents Cu NPs from their coalescence as a consequence of electrostatic repulsion of negatively charged polyacrylate anions adsorbed at the Cu NP surface and allowed their more intensive oxidation (sample B). The Cu particles in the sample A prepared at a lower polyacrylate concentration were less susceptible to oxidation in comparison to Cu particles prepared at a higher polyacrylate concentration, which occurred preferentially in marginal parts of larger and more compact aggregates.

Susceptibility of the prepared Cu particles to oxidation can be monitored through the changes in the absorption at 570 nm. When Cu particles gradually oxidize to copper oxide,

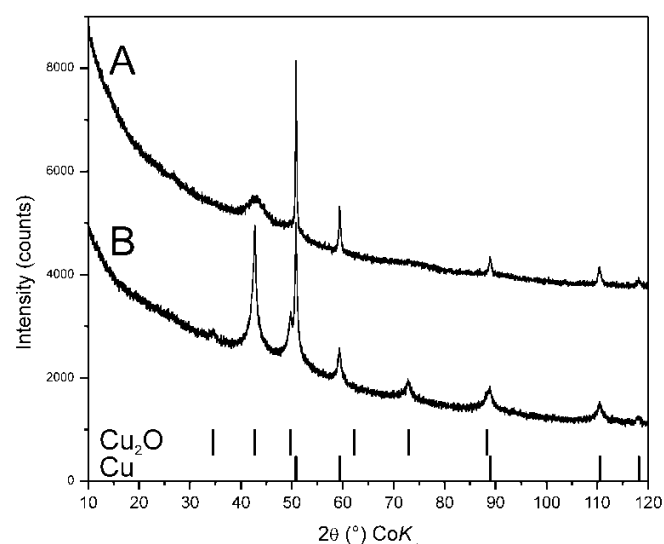


Fig. 5 XRD patterns of Cu particles after 3 weeks of aging. Particles were prepared at the final copper concentration equal to 10mM and for a molar ratio of copper ions and monomeric unit of polyacrylate equal to A 1:2 and B 1:10

absorption at mentioned wavelength decreases. If the

oxidation is completed, the absorption between 550 nm and 800nm is very negligible. As has been already mentioned above, the absorption at this wavelength initially steeply increases for all used final copper concentrations, which is related to changes in the particle sizes (Fig. 1). For a copper concentration equal to 2.5 mM, it can be seen that the absorption at 570nm diminishes after 14 days, which indicates oxidation to copper (I) oxide. On the contrary, particles gained for copper concentrations of 5 mM and 10 mM show a greater resistance against oxidation. Different maximum absorption at 570 nm as well as different susceptibility to air oxidation, for different final copper concentration, is connected with different sizes of the final copper particles. The increasing concentration of sodium polyacrylate has also an impact on the stability of particles against air oxidation. The most pronounced effect of polyacrylate concentration can be observed for the final copper concentration of 10 mM (Fig. 1), for which particles of different morphologies (compact particles vs. core-shell aggregates as proved by TEM and XRD analysis) caused a significant difference in the oxidation rate.

Since metal NPs exhibit a remarkable catalytic efficiency, Cu particles were tested in the reduction of 4-nitrophenol by the excess of sodium borohydride as the model catalytic system. This model reaction [26], [27] is often used for evaluation of the catalytic activity of various metal NPs including silver [28]–[32], gold [33]–[35], palladium [32], [36], [37] and platinum [32], [38], [39]. For this purpose, Cu particles prepared at a concentration of copper equal to 10 mM and “aged” for 3 weeks at a molar ratio of Cu and monomeric unit of polyacrylate equal to 1:2 and 1:10 were employed (i.e., the samples A and B, respectively). After the addition of copper nanoparticles (final concentration of 10⁻⁵ M) to the mixture of 4-nitrophenol (final concentration of 0.1 mM, pH 10) and sodium borohydride (final concentration of 10mM); the peak at 400 nm decreases with time. With a gradual decrease of absorbance at 400 nm, a new peak at 300 nm appears that is due to the formation of reaction product, 4-aminophenol. At the final concentration of Cu NPs equal to 10⁻⁵ M in the above-mentioned catalytic reaction system, the apparent rate constants, calculated from the slope of relation of ln(A/A₀) vs. time, were 0.1056 s⁻¹ and 0.0186 s⁻¹ for Cu particles gained at a molar ratio of Cu and monomeric unit of polyacrylate molecule equal to 1:2 and 1:10, respectively. Although Cu particles with spongy-like Cu₂O shell possess a higher surface area, their catalytic activity is approx. 5.7 times lower than the activity of compact Cu particles. This fact can be attributed to a 5 times higher concentration of polyacrylate which causes greater coverage of particle surface and, therefore, inhibited catalytic action of active sites on particle surface. However, even Cu particles with spongy-like Cu₂O shell (with a lower catalytic activity than compact Cu particles) are sufficiently efficient for the catalytic reduction of 4-nitrophenol. For comparison, the rate constant of the reduction of 4-nitrophenol achieved in the presence of gold spongy-like particles with similar particle size, was determined to be equal to 0.0021 s⁻¹ [40]. This value is

approximately nine times lower than the value determined for our spongy-like particles. These findings indicate that for certain catalytic applications, Cu NPs could potentially replace NPs of the more expensive metals.

IV. CONCLUSION

In summary, the synthesis of copper NPs in aqueous dispersion through the reduction of copper ions in the presence of sodium polyacrylate by sodium borohydride is presented. Morphology, structure, and resistance against air oxidation of final Cu particles is influenced by copper and/or polyacrylate concentrations. The catalytic activity of Cu particles was tested and it was shown that Cu particles are comparable or even more efficient in the reduction of 4-nitrophenol compared to other reported metal, for example, gold NP catalysts.

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