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# Effect of synthesis temperature on the formation of nickel-copper composite nanoparticles

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The influence of temperature on the process of synthesis of catalytic nanoparticles is studied. The microstructure of nanoparticles and copper to nickel ratio were investigated by transmission electron microscopy, scanning transmission electron microscopy, energy dispersive X-ray microanalysis and X-ray diffraction. It was found that even minor temperature variations led to the drastic microstructure changes in the nanoparticles.

**Keywords:** Cu-Ni nanoparticles, polymer, bimetallic composition, microstructure, bimetallic particle.

## 1. Introduction

The synthesis of nanoparticles with desired and controlled properties is one of the most promising research areas of modern materials science. The development of new nanoparticles with catalytic properties fits perfectly this concept. One of the most promising routes of the formation of such nanoparticles is the chemical synthesis of copper nanoparticles. Recently, high catalytic properties of the particles obtained by this method have been demonstrated [1–3]. If so, copper nanoparticles could replace more expensive catalysts based on noble metals. Moreover, composite nanoparticles based on two metals, namely Cu and Ni, allow expanding their application area. Apart from the use in the catalysis such bimetallic systems exhibit peculiar thermal, electrical, magnetic, mechanical properties and even cytotoxicity and antifungal effects [4–7]. Undoubtedly, these properties largely depend on the size, shape and composition of particles in the nanocomposites [8,9]. A number of new methods for synthesis of nanoparticles with required size, composition and shape have been discovered [10–12]. For example, Romanovsky et al [12] demonstrated a new modified method of synthesis of metal nanopowders based on the combustion of a solution using citric acid. The analysis of the nanopowders obtained by this method revealed pure bimetallic nature of all samples wherein the crystal structure of each metal adopted a distorted face centered cubic lattice.

One of the simplest and cheapest methods of Cu (Ni) nanoparticle synthesis is chemical reduction. This method does not require special conditions and highly specialized equipment. During chemical reduction, metal nanoparticles are formed in the zero valence state. Two processes take place in this method, namely, reduction and interaction between metal and polymer particles [13].

Therefore, one task is to find the route to influence the synthesis conditions, which allow one to gain desired composite microstructure. It was found that in the low-temperature range poly (N-vinylpyrrolidone) (PVP) can be used as a stabilizer of metal particles, which permits to obtain stable sols with a sufficiently small particle size. This is due to a change in the thermodynamic quality of the solvent in relation to the polymer [14–16].

Lately, Bonet et al [17] and Niu et al [18] found a noticeable influence of extremal temperatures on the composition, morphology and properties of Cu-Ni nanoparticles. It was found that the mechanism of bimetallic particles formation is controlled by the solubility of the reagents and on precision control of reduction temperature. It is worth to note that the synthesis in these studies was carried out at a temperature range between 95°C and 200°C. However, such extremal temperatures require special equipment, which could be expensive. Thus, we concentrate our study on the synthesis at relatively low temperature, which is unsophisticated and cheap method. However, the effect of temperature on the process of formation of a nanocomposite consisting of a polymer (PVP) and Cu-Ni nanoparticles, and, ultimately, on its microstructure and composition should be carefully studied.

The present work is devoted to the study of the microstructure and composition of PVP-Cu-Ni nanoparticles composite formed by chemical reduction at +25°C and +5°C.

## 2. Experimental

The copper-nickel composite nanoparticles were obtained by chemical synthesis from an aqueous solution of salts. Copper (II) sulfate pentahydrate and Nickel (II) sulfate heptahydrate. Cu and Ni ions were reduced by tert-butylamineborane in aqueous solutions of poly (N-vinylpyrrolidone) at different temperature. The prepared reducing agent solution

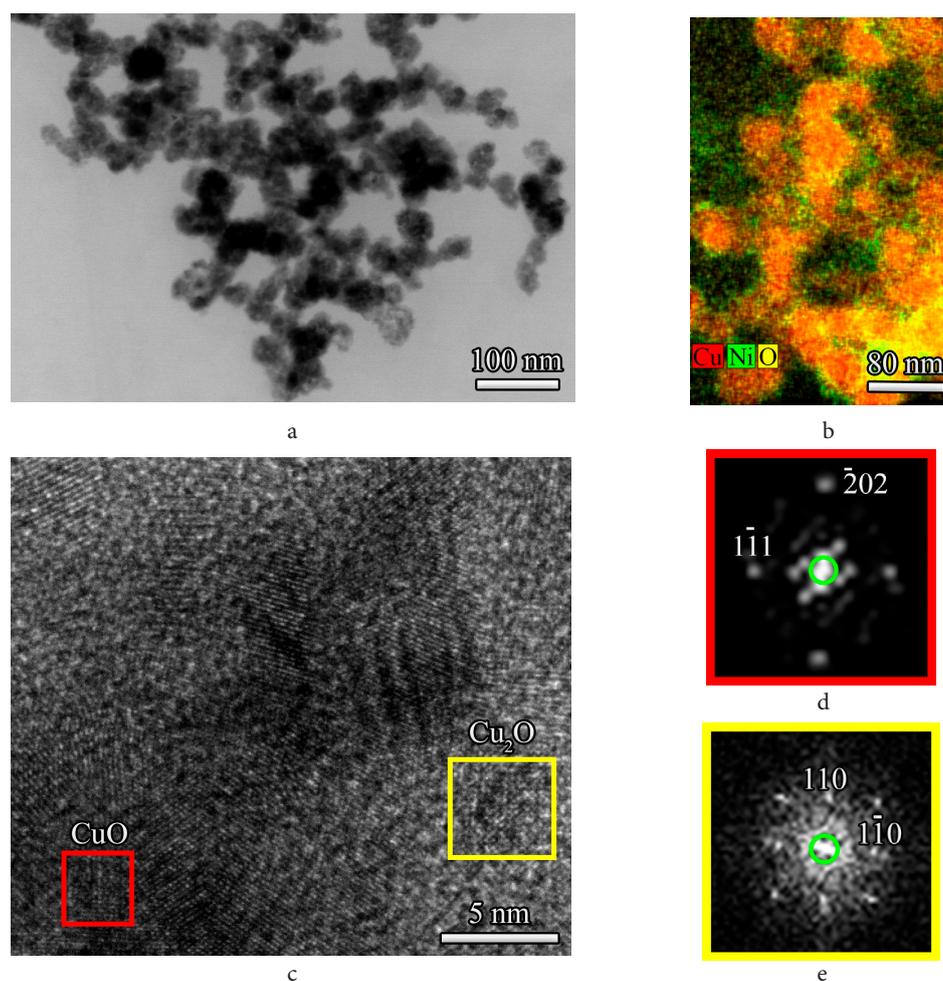
(0.02 mol/L) was added to an aqueous solution containing copper salt (0.02 mol/L), nickel salt (0.02 mol/L) and PVP (0.02 basemol/L). Each component was brought to a specified temperature. In the first experiment it was equal to +5°C, and in the second to +25°C. After the end of the reaction, sols were separated by centrifugation (3400 rpm, 45 min) and then they were dried in air at room temperature.

The study of the morphology and structure of the solid products was carried out by scanning/transmission electron microscopy (S/TEM), electron diffraction (ED), energy dispersive X-ray (EDX) microanalysis, and X-ray diffraction (XRD). Specimens for TEM, STEM, and EDXS studies were prepared by dipping the Lacey carbon film on the Cu grid into a vial with the powder. The samples were studied in an Osiris TEM/STEM system (Thermo Fisher Scientific, USA) equipped with HAADF detector (Fischione, USA) and a Super-X EDXS (Bruker, USA), at an accelerating voltage of 200 kV. The XRD patterns of the samples were recorded using a powder X-ray diffractometer Rigaku MiniFlex 600 (Rigaku, Japan) with CuK $\alpha$  radiation (40 kV, 15 mA, Ni-K $\beta$  filter) in the angle range  $2\theta = 7 - 55^\circ$  with a scanning step of  $0.02^\circ$  and a rate of  $0.6^\circ \text{ min}^{-1}$ . The size of the beam incident on the sample was set by horizontal and vertical slits — 10 mm and  $1.25^\circ$ , respectively. The phases were identified in the PXDRL program (Rigaku, Japan) using ICDD PDF-2 datasets (release 2020).

### 3. Results and discussion

The bright field (BF) STEM image of the samples synthesized at a temperature of +25°C (Fig. 1a) demonstrated that the particles are connected in chains forming dendrite-like microstructure. The sizes of the particles are in the range between 20 and 80 nm. EDX elemental mapping (one example is presented in Fig. 1b) indicated that the particles contain mainly Cu and O. The O content is higher in areas close to the surface of the particles. Ni (NiO) was found in the peripheral areas. High resolution (HR) TEM images (see Fig. 1c) indicated that particles are polycrystalline with the grain size less than 5 nm. Close inspection of the images and Fast Fourier Transform (FFT) analysis (Fig. 1d, e) revealed two crystal phases, namely cubic Cu<sub>2</sub>O (Space group Pn $\bar{3}$ m,  $a = 0.426 \text{ nm}$  [19]) and monoclinic CuO (Space group C<sub>2</sub>/c,  $a = 0.46837(5) \text{ nm}$ ,  $b = 0.34226(5) \text{ nm}$ ,  $c = 0.51288(6) \text{ nm}$ ,  $\beta = 99.54(1)$  [20]). Few NiO crystals (images are not presented here) were found by HRTEM in the specimen, however, Cu crystals were not observed. That could be due to the core-shell structure of the particles with Cu crystals in the core. The overlapping of thick CuO<sub>2</sub>/CuO shell with Cu core could conceal the Cu lattice image.

The images of the samples obtained at a temperature of +5°C demonstrate completely different morphology. Typical



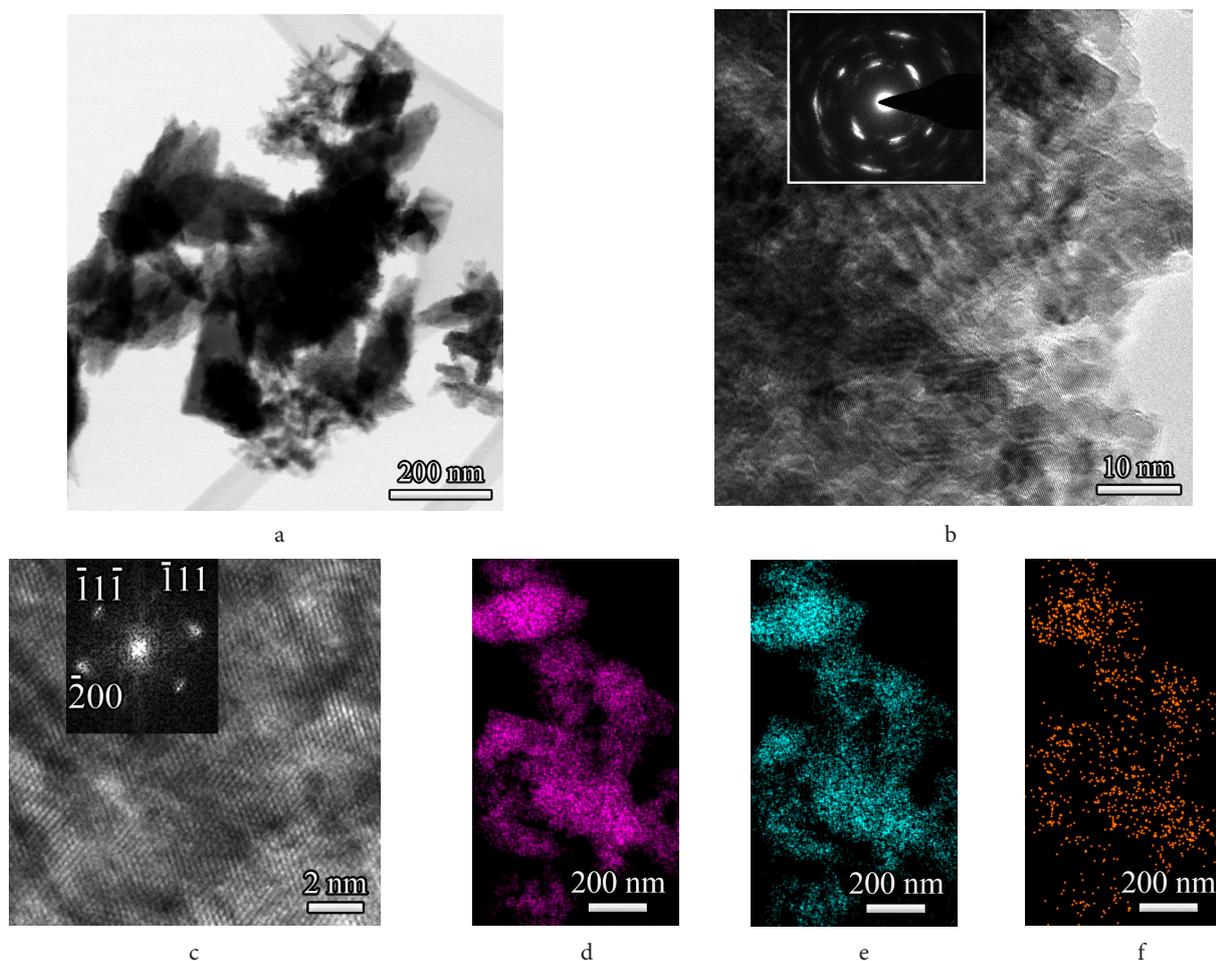
**Fig. 1.** (Color online) BF STEM image of the sample, obtained at temperature +25°C (a); complex elemental EDX map of the specimen (b); HRTEM image with Cu<sub>2</sub>O nanocrystal highlighted by yellow square and CuO by red square (c); FFT pattern obtained from red square area (CuO) (d); FFT pattern obtained from yellow square area (Cu<sub>2</sub>O) (e).

BF STEM image is presented in Fig. 2a. The particles exhibit an irregular shape with the sizes up to 300 nm. There are also smaller needle-like particles 10–20 nm in length. Selected area electron diffraction pattern (inset in Fig. 2a) from larger particle and HRTEM images (see Fig. 2b) indicated that these larger particles are highly textured polycrystals. The FFT pattern (inset in Fig. 2c) unambiguously showed that the crystal structure of the larger particles corresponds to monoclinic CuO, similar to the one, observed in the previous sample. The FFT pattern corresponds to the CuO crystal observed in the [011] zone axis. We failed to find other crystal phases like Cu<sub>2</sub>O in that specimen. The absence of Cu<sub>2</sub>O particles might be explained by large size of the crystals, which prevented them from attaching to the supporting carbon film.

The results of XRD study of two samples are presented in Fig. 3. One can see that the angular positions of the main reflections coincide, although the intensities differ. Three phases were identified as: fcc-Cu — PDF 01-085-1326 ( $a=0.3615$  nm), cubic cuprite (Cu<sub>2</sub>O) — PDF 01-078-2076 ( $a=0.4267$  nm), monoclinic copper oxide (CuO) — PDF 01-089-2530 ( $a=0.46839$  nm,  $b=0.34734$  nm,  $c=0.51226$  nm,  $\beta=99.73$ ). Comparing the ratio of reflection intensities, one can estimate the mass ratio of phases in the samples. However, due to the overlapping of reflections only a semi-quantitative assessment was performed by RIR method. For the sample formed at room temperature (+25°C) the ratio

is: Cu — 45%, Cu<sub>2</sub>O — 36%, CuO — 19%. For sample formed at +5°C: Cu — 3%, Cu<sub>2</sub>O — 83%, CuO — 14%.

The results of the present study show that the minor temperature changes affect drastically on the content and microstructure of the composite nanoparticles. A similar relationship between the high temperature changes and microstructures of the nanocomposite was found in the work of Bonet et al [17]. It was shown in this study that the microstructure and composition of Ni-Cu particles depend both on the reaction conditions and on the chemical reagents used as metal sources. The sizes of the particles obtained by reduction within 4 hours at 190°C from a solution of nickel carbonate and copper carbonate was in the range between 0.3 and 1.0 μm. When using nickel nitrate and copper nitrate as metal sources, the bimetallic Ni-Cu powder obtained at 196°C contains particles with a narrow size distribution and an average size of 140 nm. In the present study, we managed to obtain particles with an average size of 80 nm despite the low synthesis temperatures. Thus, it was shown that using the proposed relatively cheap method, it is possible to obtain particles of a predictable size. In the work of Romanovsky et al [12], the solutions prepared from copper and nickel nitrates were quickly dried in a microwave oven until foam was formed. Then it was placed in a preheated muffle furnace. The sizes of Ni particles in the composite, which were distributed over the surface of copper crystals,



**Fig. 2.** (Color online) Sample obtained at +5°C: BF STEM image (a); HRTEM image, selected area diffraction pattern is in the inset (b); enlarged part of HRTEM image and corresponded FFT pattern in the inset (c); EDX elemental maps: Cu (d), O (e) and Ni (f).

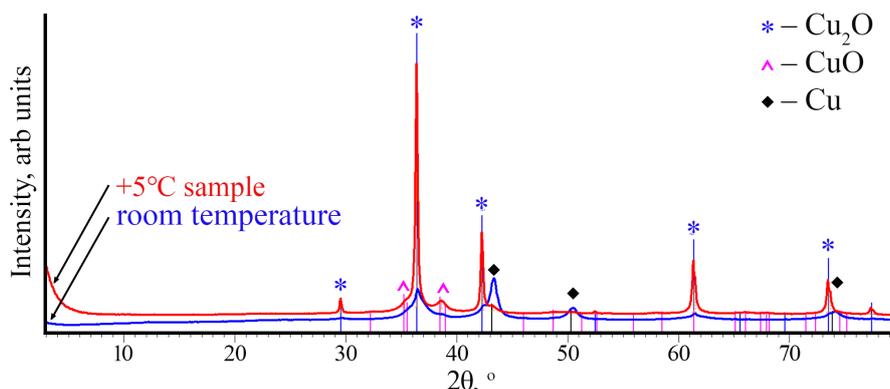


Fig. 3. (Color online) XRD patterns from both samples at 25°C to 5°C.

varied over a wide range between 2 and 90 nm (individual large aggregates reached a size of 90 nm). The actual sizes of aggregates of Cu-Ni nanoparticles were in a relatively large range of 20–200 nm. The main disadvantages of the methods are high cost and strict requirements for the application and manufacture. In our work, the process of obtaining nanoparticles does not require strict synthesis conditions and complicated equipment. At the same time, the sizes of the resulting particles are in the range from 20 to 80 nm at 25°C and up to 300 nm at 5°C. That might be very promising for the use as a catalyst.

#### 4. Conclusion

The study revealed that chemical reduction is a very useable and cheap method for the synthesis of the composite nanoparticles based on the polymer with embedded  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{Cu}$  and  $\text{NiO}$  nanoparticles. Two samples of the composite nanoparticles obtained at +25°C and +5°C demonstrated completely different morphology and size of nanoparticles. The core-shell ( $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu} + \text{NiO}$ ) structure of the nanoparticles are typical for the reduction at +25°C. Larger and uniform  $\text{Cu}(\text{Ni})\text{O}$  particles with monoclinic crystal structure were found in the sample prepared at +5°C. The study of both samples showed that the  $\text{Ni}/\text{NiO}$  part was mostly located between  $\text{Cu}$  ( $\text{CuO}$ ) particles. The rest was identified as clusters of  $\text{Ni}$  atoms or  $\text{NiO}$  molecules connected with  $\text{Cu}$  ( $\text{CuO}$ ) particles. This result proves that minor temperature changes can drastically affect the composition and microstructure of the nanocomposite, which, in turn, leads to a change in the properties of the resulting product.

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