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# Influence of Modified Nano Metal Oxide Particles on the Reaction between Nitrocobalamin and Ascorbic Acid

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## Abstract

Since nanoparticles of CuO were demonstrated to have a significant effect on the kinetics of the formation of nitrosylcobalamin (CblNO) in the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid (Asc), further studies remained to be interesting aspects for such investigations. Nanoparticles of CuO were modified by coating with a poly-dopamine layer and addition of functional ligands (o-(aminoethyl) polyethylene). It was demonstrated that the introduction of modifications improved the stability of the suspension and partially eliminated the aggregation of the nanoparticles. Kinetic measurements showed the influence of the modified nanoparticles of CuO on the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid (Asc) under weakly acidic conditions. The presented research is part of the project 'Air Pollution versus Autoimmunity: Role of multiphase aqueous Inorganic Chemistry' that aims at studying the effect of inorganic compounds as a part of particulate matter (PM) on representative bioinorganic reaction systems.

## Keywords

nitrocobalamin, nitrosylcobalamin, ascorbic acid, redox reactions, nanochemistry, nanoparticles, nano metal oxides, particulate matter, air pollution

## Introduction

Particulate matter (PM) is defined as a mixture of solid particles and liquid droplets in the air, varying in size and composition [1–4]. The formation of PM resulted in both natural and anthropogenic aspects [3–5]. The main sources connected with human activity are power plants, vehicles, industry and fires [5,6]. Detailed analysis of Standard Reference Material (SRM) 1648a, i.e. dust samples collected in an urban area of St. Louis, MO over a 12 month period during 1976 and 1977. This SRM was certified by the National Institute of Standards and Technology (NIST) in the US, and showed that PM contained both organic and inorganic species, including metals and metal compounds [7]. Especially worth to mention is a substantial content of transition metals, e.g. 610 ± 70 mg/kg of Cu, 790 ± 44 mg/kg of Mn, or 3.92 ± 0.21 % of Fe [7] that could be involved in different physiological redox processes [8,9]. However, the specific influence of these species, as a part of particulate matter towards living organisms, is still under investigation. Earlier reports that formed part of the project 'Air Pollution versus Autoimmunity: Role of multiphase aqueous Inorganic Chemistry' (APARIC) showed that PM has an impact on representative bioinorganic reaction systems [10–14]. It was demonstrated that nanoparticles of CuO, $Fe_3O_4$ or $Mn_3O_4$ have an influence on the redox reaction of Vitamin B12 derivatives [12]. Among them, special attention is required to be given for the nanoparticles of CuO. The studies showed that addition of nCuO causes the most significant changes in the observed rate constant for the formation of nitrosylcobalamin (CblNO) in the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid Asc (pH = 4.3, T = 25° C). The mentioned reaction was ca. 2–3 times faster than the reaction in the absence of nCuO particles [12]. Even stronger effects ($k_{obs}$ increase by 1.5 – 6 times) were observed when nanoparticles were added to the solution of Asc followed by mixing with nitrocobalamin (delay- time experiments, for details see [12]). This interesting observation lead to the following series of experiments that focused on nCuO, modification of mentioned nanoparticles and the effect caused by nanoparticles during redox reactions of Vitamin B12 derivatives.

In this report, our goal was to show if modification on the nanoparticles' surface may cause any changes in the activity of nCuO towards the reaction between $CblNO_2$ and Asc under weakly acidic conditions (pH = 4.3) [12,15]. For this purpose the nanoparticles of nCuO were modified by coating with a poly-dopamine layer [16] and addition of functional ligands (o-(aminoethyl) polyethylene) [17]. The synthesis was carried out based on the methods described by Liu M. et al. and Park J. et al. [16,17]. The optimization of the synthesis, characterization of the obtained materials, as well as the kinetic tests, are described in detail in the following paragraphs.

## Materials and General Methods

### Materials

All chemicals used throughout this study were of analytical reagent grade or better. Hydroxocobalamin hydrochloride (CblOH·HCl, ≥ 98%) was obtained from Sigma-Aldrich. Copper oxide nanopowder (CuO, 99.95+%, 25-55 nm) was obtained from US Research Nanomaterials Inc. Sodium nitrate, ascorbic acid, acetic acid ($CH_3COOH$, ≥ 99.5-99.9%), hydrochloric acid (35-38%), sodium hydroxide (NaOH, ≥ 98.8%)), Tris base, polyvinylpyrrolidone, dopamine hydrochloride, o-(aminoethyl) polyethylene glycol, ethanol (98%) and ammonium hydroxide (25%) were obtained from a range of suppliers (Sigma-Aldrich, Merck, Fisher Scientific, POCH CHEMPUR).

### General Methods

All solutions were prepared in de-ionized water purified using a water purification system (Hydrolab HPL10 UV). Strictly anaerobic solutions were prepared using appropriate air-free techniques and handling the solutions in appropriate glassware. Oxygen free argon was used to deoxygenate the reactant solutions.

### Synthesis of nCuO-pDP-polymer

Modification of nCuO by coating with poly-dopamine layer and addition of o-(aminoethyl) polyethylene as functional ligand was carried out based on methods described by Liu M. et al. and Park J. et al. [16,17]. The method of the synthesis was modified and optimized to obtain the materials with the best properties and parameters.

### Preparation of the nCuO suspension

10 mg of polyvinylpyrrolidone were dissolved in 773 µL of ethanol (98%) and 58 µL of ammonia solution. Then 1 mg of nCuO was added to the mixture. The mixture was treated by ultrasonication at room temperature for 30 min (program: total time 30 min, 6 x 5 min of ultrasonication, 30 s of break, power 25%). Sample was kept in the ice bath to avoid heating up during sonication.

### nCuO coating by poly-dopamine

125 µL of dopamine solution (40 mg/mL) dissolved in ethanol was added to the nCuO suspension prepared as was described above and stirred at room temperature for 3 h. The pD-

coated nCuO were collected by centrifugation (10.000, 4 min, room temperature) and washed with ethanol three times.

### Modification of nCuO-pDP by o-(aminoethyl) polyethylene:

The nCuO-pDP nanoparticles were re-suspended in Tris buffer (0.01 M, pH = 8.5). 2 mg of o-(aminoethyl) polyethylene was added to the solution (the final concentrations of particles and ligand were 1 and 2 mg/mL, respectively). The mixture was stirred at room temperature for 24 h and after this time were collected by centrifugation (10000, 4 min, room temperature) and washed with de-ionized water three times.

### Preparation of poly-dopamine modified by o-(aminoethyl) polyethylene

80 g of dopamine was incubated in 16 mL of ethanol (98%) and 1.2 mL of ammonia solution by stirring at room temperature for 3 h. The pD was collected by centrifugation (10000, 4 min, room temperature) and washed with ethanol three times. 40 mg of pDP was re-suspended in 40 mL of Tris buffer (0.01 M, pH = 8.5) and 80 mg of o-(aminoethyl) polyethylene was added (the final concentrations of particles and ligand were 1 and 2 mg/mL, respectively). The mixture was stirred at room temperature for 48 h. pDP-polymer sample was collected by centrifugation (10000, 4 min, room temperature) and washed with de-ionized water three times.

### Experimental procedures

Nitrocobalamin solutions ($8.6 \times 10^{-5}$ M) were prepared by mixing solutions of aquacobalamin with sodium nitrite in the concentration ratio 1:5 at pH 4.3 (acetate buffer). Appropriate amounts of nanoparticle suspension were added to the nitrocobalamin solution, followed by addition of ascorbic acid (concentration ratio $CblNO_2$:Asc = 1:20). The measurements were started just after addition of ascorbic acid to the reaction mixture. All of the operations were done under argon atmosphere.

### UV-Vis spectral measurements

UV-Vis spectral measurements under anaerobic conditions were performed in screw-cap cuvettes equipped with a silicone septum. UV-Vis spectra and kinetic data for the reactions were recorded on a Perkin Elmer Lambda 25 spectrophotometer equipped with a thermostated (25.0 ± 0.1 °C) cell holder (Perkin Elmer PTP-6 Peltier System). All kinetic data were collected under pseudo-first-order conditions at 25.0 ± 0.1 °C. The data were analyzed using Origin Lab software.

## pH measurements

Acetate (0.10 M) and Tris (0.01 M) buffers were used to control the pH. The pH measurements were carried out at room temperature using a HI 221 (Hanna Instruments) pH meter equipped with an AmpHel glass electrode filled with a 3.0 M KCl solution.

## Zeta Potential measurements

In order to study zeta potential of the nanomaterials, proper measurements were performed. Appropriate amounts of the aqueous suspension prepared as described above, were added to the water. The measurements were performed immediately after addition of the suspension. All data were collected using Malvern Zetasizer Nano ZS.

## TEM measurements

TEM analyses were performed in order to check the size of the nanoparticles in suspensions prepared as described above. Appropriate amounts of the aqueous suspension were added to ethanol. Samples of the suspensions were dropped on the Lacey Carbon film (300 Mesh Cu) (Agar Scientific). All data were collected using Tecnai Osiris microscope (Thermo Fisher Scientific Inc., Carlsbad, CA, USA) operating at 200 kV or FEI Tecnai G2 F20 HR(S)TEM microscope operating at 200 kV with field emission gun (FEG) high resolution and analytical TEM/STEM.(FEI Company, Tecnai F20-G2 Hillsboro, OR, USA).

## ATR IR measurements

ATR measurements were performed to confirm the coating and functionalization of the nCuO. The materials obtained as a result of the synthesis described above, were left to dry at least 48 h and used for ATR IR measurements. All data were collected using Bruker Tensor 27/PMA50FTIR Spectrometer (Bruker Optics GmbH, Ettlingen, Germany) in a range of 4000–400 cm$^{-1}$.

# Results and Discussion

## Synthesis and characterization of CuO-pDP-polymer nanoparticles

The first aim of the study was to introduce the modification of CuO nanoparticles that allow to improve the stability of the material suspensions with appropriate diameter. Based on the literature [16,17], it was decided to perform the synthesis that provided the coating of nCuO by polydopamine, followed by functionalization of the nanoparticles' surface by functional ligands. The method and conditions of the synthesis were modified and optimized to obtain the materials with the best properties and parameters, as described in detail in the previous section (see Materials and General Methods).

The obtained material: nanoparticles of CuO coated by polydopamine and functionalized by o-(aminoethyl) polyethylene was characterized by TEM, IR spectroscopy and Zeta Potential measurements. In addition, similar tests were performed for the semi-product of the synthesis: nCuO coated by polydopamine (nCuO-pDP). TEM studies provided detailed analysis of the obtained materials and clearly showed that the CuO nanoparticles in quite regular shape with a mean size 20-50 nm were coated by very thin layer of pDP or pDP + polymer. After the modifications of the nanoparticles, they aggregated to form the units with the mean diameter 300-400 nm (Figure 1 and Figure S1). In addition, the formation of pDP or pDP-polymer layer on the nCuO surface was confirmed by IR spectroscopy since the IR spectra of the nanoparticles fit well with those of pure pDP and pDP-polymer (Figure S2). In the spectrum of nCuO-pDP, we can observe peaks at 1570 and 1445 $cm^{-1}$ that are attributed to C=C, and a peak at 1500 $cm^{-1}$ to C=N. The broad band with maximum at 3240 $cm^{-1}$ is assigned to -NH and –OH groups [16,18]. Zeta Potential measurements indicated that the introduced modification led to obtain the material that is characterized by better stability of the suspension compared with unmodified nanoparticles (see Supporting Information).

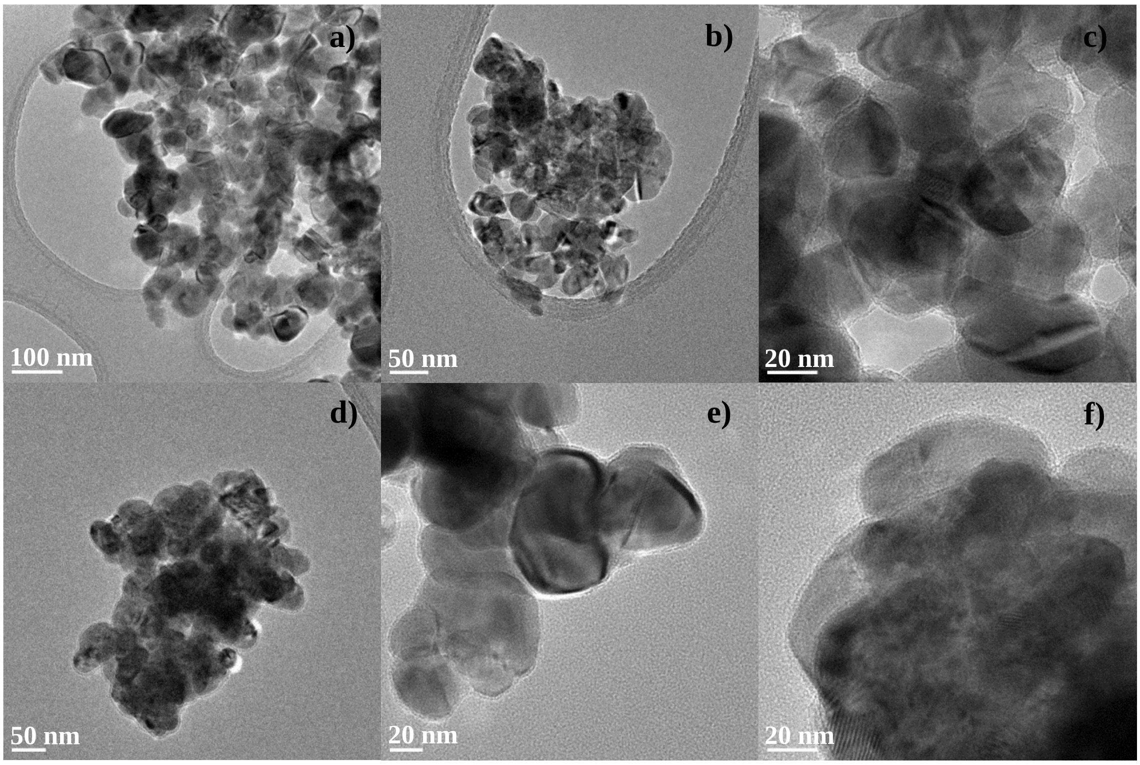
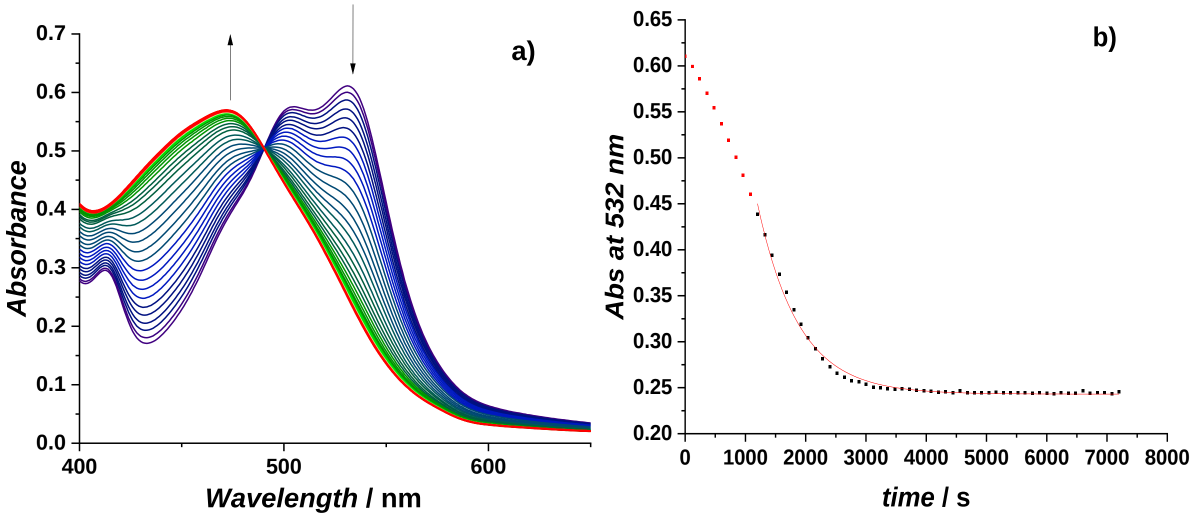


**Figure 1.** TEM images of nCuO-pDP (**a**,**b**,**c**), and nCuO-pDP-polymer (**d**,**e**,**f**), in which the coating with the polymeric material can be observed.

## Influence of CuO-pDP-polymer nanoparticles on the reaction between Nitrocobalamin and Ascorbic acid at pH = 4.3

The reaction between nitrocobalamin (CblNO$_2$) and ascorbic acid under weakly acidic conditions, leads to the formation of the reduced compound nitrosylcobalamin (CblNO) – a Vitamin B12 derivative in which the nitrosyl ligand (NO$^-$) is coordinated to the Co$^{3+}$ ion [15,19]. The mentioned reaction was the subject of detailed investigations that showed the formation of CblNO to be a rather complex process [15]. Clear evidence for the formation of CblNO are the characteristic bands at 316, 344 and 476 nm [15,19] in the UV-Vis spectra. Appearance of these UV-Vis bands are connected with the disappearance of the bands at 354, 413 and 532 nm that are characteristic for CblNO$_2$ [20–22]. These clear changes in UV-Vis spectra make the reaction a good system for monitoring how the addition of different nCuO species affect the observed process [12]. The analysis and discussion concerning the effect of the addition of CuO-pDP-polymer nanoparticles on the reaction between CblNO$_2$ and Asc is detailed above

In order to study the possible influence of nCuO-pDP-polymer on CblNO formation, an appropriate amount of the nanoparticles suspension was added to the solution of CblNO$_2$ (8.6 × 10$^{-5}$ M), followed by addition of Asc (1.7 × 10$^{-3}$ M) at pH 4.3 (0.10 M acetate buffer) that initiated the studied reaction. The UV-Vis spectra recorded during the described reaction are shown in Figure 2a and c. Note, that the change in absorbance at 532 nm shows a typical sigmoid behavior that is ascribed to redox cycling of traces of dioxygen. After some time good pseudo-first-order kinetic traces were observed.



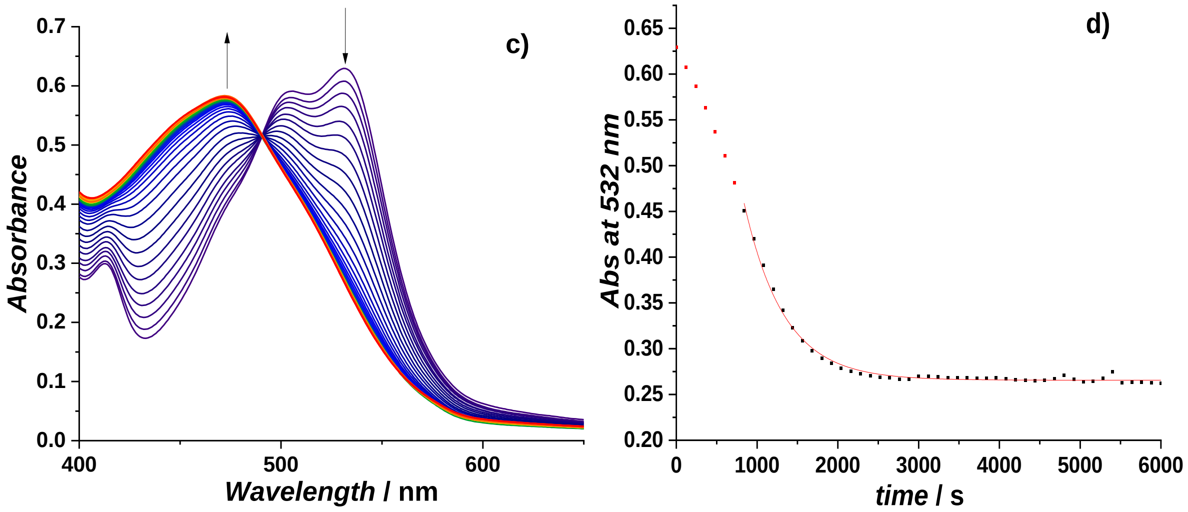


**Figure 2.** UV-Vis spectra recorded during the reaction between $CblNO_2$ ($8.6 \times 10^{-5}$ M) and Asc ($1.7 \times 10^{-3}$ M) at pH 4.3 (25.0 C, acetate buffer) in the presence of 0.004 mg/mL **(a)** and 0.040 mg/mL **(c)** of the nCuO-pDP-polymer. Spectra were recorded every 2 minutes. Plots of absorbance at 532 nm versus time with first-order fits (**b** and **d**) for reactions observed in **a)** and **c)**, respectively.

The observed spectral changes (appearance of the bands at 476 nm and disappearance of the bands at 413 and 532 nm) provide clear evidence for the formation of CblNO, accompanied by clean isosbestic points at 490 nm. Thus, the presented results suggest that in the presence of modified CuO nanoparticles do not have any influence on the observed reaction, considering the type and nature of the formed product. However, it can be easily noticed that depending on the concentration of the added nanoparticles, the observed reaction becomes faster (Figure 2b and d). The obtained data fits resulted in first-order kinetics with rate constants of $k_{obs} = (1.47 \pm 0.3) \times 10^{-3}$ $s^{-1}$ and $k_{obs} = (2.02 \pm 0.05) \times 10^{-3}$ $s^{-1}$ for reactions with addition of 0.004 mg/mL and 0.040 mg/mL nCuO-pDP-polymer, respectively.

These interesting observations were the motivation for systematic studies with different concentrations of nCuO-pDP-polymer nanoparticles. The results of the measurements are given in Figure 3. The reported data clearly show a significant acceleration of the formation of CblNO when modified nanoparticles of the nCuO-pDP-polymer are added to the reaction mixture. The observed rate constant ($k_{obs}$) is even 2.5 - 3.5 times faster when compared to the reaction in the absence of the nanoparticles and increases with nCuO-pDP-polymer concentration. The effect that was observed is very similar when unmodified nanoparticles of CuO were used instead, which was demonstrated and described in earlier studies [12].

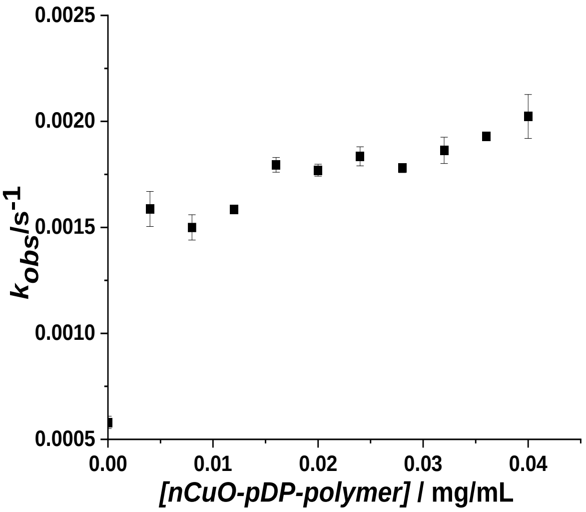


**Figure 3.** Plot of observed rate constant ($k_{obs}$) versus concentration of CuO-pDP-polymer nanoparticles for the reaction between $CblNO_2$ ($8.6 \times 10^{-5}$ M) and Asc ($1.7 \times 10^{-3}$ M) at pH 4.3 (25.0 °C, acetate buffer). The data point at zero concentration is the reference value in the absence of any nanoparticles.

To obtain more information on the observed influence, additional studies were performed. In the mentioned experiments, semi-products of the CuO-pDP-polymer synthesis were used, i.e. nCuO coated by polydopamine without addition of polymer (nCuO-pDP), polydopamine (pDP) and polydopamine with addition of the polymer on the surface (pDP-polymer). As before, an appropriate amount of the nanoparticles suspension was added to the reaction mixture and the UV-Vis spectra were recorded. In all cases the observed spectral changes were very similar to those shown in Figure 2. The data of the absorbance changes at 532 nm with time were fitted using first-order kinetics to obtain the $k_{obs}$ values. The obtained results are summarized in Table 1.

The analysis of the obtained results allow the following conclusions to be made. First of all, the data clearly demonstrated that both nCuO coated only with polydopamine layer (nCuO-pDP) and nCuO modified by pDP with addition of a functional ligand (o-(aminoethyl) polyethylene) (nCuO-pDP-polymer), affected the observed interaction between $CblNO_2$ and Asc at pH 4.3. Both materials cause the acceleration of the observed reaction when they are present in the reaction mixture. The increase of $k_{obs}$ is stronger when larger concentrations of nanoparticles were added during the reaction. When comparing the mentioned results for both modified materials (nCuO-pDP and nCuO-pDP-polymer) with the results for unmodified CuO nanoparticles [12], we can see that the trend is very similar and the obtained $k_{obs}$ values are in reasonable agreement. Another important observation is that the calculated observed rate constants ($k_{obs}$) for the reaction with no nanoparticles and with addition of 0.004, 0.02 or 0.04 mg/mL pDP or pDP-polymer, have very similar values (close to (5.90 - 6.00) × $10^{-4}$ $s^{-1}$). Thus, it could be concluded that the presence of both pDP and pDP-polymer nanoparticles in the reaction mixture do not have any influence (both kinetic and considering the type of the formed product) on the formation reaction of CblNO. All in all, the most important feedback of the study is that the implemented modifications on the nCuO surface do not have an influence on the catalytic properties towards the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid (Asc) at pH 4.3.

**Table 1.** Summary of the observed rate constants $k_{obs}$ for the experiments with addition of nanoparticles. Presented values are average values from 3 measurements.

| **Concentration of the nanoparticles mg/mL** | **Observed rate constant ($k_{obs}$ / $s^{-1}$) for different type of nanoparticles:** | | | | | |
|---|---|---|---|---|---|---|
| | **pDP** | **pDP-polymer** | **nCuO-pDP** | **nCuO-pDP-polymer** | **nCuO [12]** | **No nanoparticle [12]** |
| **0.000** | - | - | - | - | - | (5.80 ± 0.30) × $10^{-4}$ |
| **0.004** | (5.89 ± 0.17) × $10^{-4}$ | (5.97 ± 0.03) × $10^{-4}$ | (1.61 ± 0.02) × $10^{-3}$ | (1.59 ± 0.08) × $10^{-3}$ | (1.30 ± 0.07) × $10^{-3}$ | - |
| **0.02** | (6.09 ± 0.04) × $10^{-4}$ | (6.11 ± 0.08) × $10^{-4}$ | (1.76 ± 0.03) × $10^{-3}$ | (1.77 ± 0.03) × $10^{-3}$ | (2.02 ± 0.10) × $10^{-3}$ | - |
| **0.04** | (6.18 ± 0.06) × $10^{-4}$ | (5.79 ± 0.08) × $10^{-4}$ | (2.08 ± 0.02) × $10^{-3}$ | (2.02 ± 0.10) × $10^{-3}$ | (2.07 ± 0.10) × $10^{-3}$ | - |

## Conclusions

The reported studies focused on the modification of the surface of CuO nanoparticles and demonstrated the role of this modification on the catalytic properties of nCuO towards the reaction between $CblNO_2$ and Asc at pH 4.3. The performed synthesis provides a coating of nCuO by polydopamine and a functionalization by o-(aminoethyl) polyethylene (a functional ligand of the nCuO-pDP-polymer). The nCuO-pDP-polymer was characterized by a better stability of the suspension compared to the unmodified nanoparticles. Studies on the possible influence of the nCuO-pDP-polymer on CblNO formation supports the conclusion that addition of the material to the reaction mixture strongly accelerates (2.5 -3.5 times) the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid (Asc) at pH 4.3. However, the observed changes in

$k_{obs}$ values are similar when both modified and unmodified nanoparticles are present during the reaction. Thus, it can be concluded that modifications on the nCuO surface do not have an influence on the catalytic properties towards CblNO formation.

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