

Catalytic Activity of Nanodiamonds in Azocoupling Reaction

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Received 4 June 2014; revised 3 July 2014; accepted 14 July 2014

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Abstract

The catalytic efficiency of modified nanodiamonds (MND) in reactions of interaction between organic compounds was demonstrated on the example of azocoupling reaction (hydrogen peroxide-4-aminoantipyrine-phenol). It was found that catalytic action of MND was caused by redox active metal ions of Fe and Cu located on the MND surface. The neutralization of the ions significantly decreased catalytic properties of MND.

Keywords

Diamond Nanoparticles, Catalytic Activity, Metal Ions, Organic Reaction

1. Introduction

Unique surface properties of nanodiamonds synthesized by the detonation technique [1] [2], especially the abundance of different chemically active groups and high surface area, allow us to predict the prospects for application of this nanomaterial as a catalyst. Application of the nanodiamonds modified using thermal and electrochemical treatment followed by deposition of metallized palladium in catalytic oxidation reactions (gas-phase CO oxidation to CO₂ and electrochemical hydrogen oxidation) has been reported [3] [4]. Nanodiamonds themselves have shown catalytic activity (dehydrogenation of ethylbenzene under steam-free conditions) [5].

In this work, we have experimentally demonstrated the applicability of nanodiamonds as catalysts for reaction of interaction between organic compounds on example azocoupling reaction: H₂O₂-4-aminoantipyrine-phenol. It is known that the reaction of oxidative diazotization is stimulated by the biocatalysts peroxidases [6] and accompanied by the formation of a stained reaction product (quinoneimine). Nowadays, this reaction is widely used in medical diagnostics for determination of physiologically important substances (for example, glucose,

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cholesterol and triglycerides) as well as in ecological analysis for determination of phenol and phenolic compounds [7] [8].

In this work, we have studied MND-catalyzed azocoupling reaction (H_2O_2 -4-aminoantipyrine-phenol) at the different conditions and reagent concentrations as well as the rationale of catalytic efficiency of the MND particles in the reaction.

2. Materials and Methods

2.1. Materials

MNDs (RUDDM grade 0 - 125, $d_{50} = 49.6$ nm and RUDDM Grade 200 - 500, $d_{50} = 270$ nm) exhibiting a high colloidal stability in hydrosols were produced by "Real-Dzerzhinsk" Ltd. (Russia) using a known technology [9] [10] and used in the experiments. The hydrosols with a concentration of nanoparticles up to 5 wt% were obtained by adding deionized water (Milli-Q system, Millipore, USA) to a portion of MND powder.

2.2. Reagents

The following reagents of high purity grades were used in the study: 4-aminoantipyrine (1-phenyl-2,3-dimethyl-4-aminopyrazolone) (4-AAP), phenol (Fluka, Germany), 3% hydrogen peroxide (GalenoPharm™, Russia), EDTA (Serva, Germany), salts (NaCl, MnCl_2 , FeSO_4 , CoCl_2 , NiCl_2 , CuSO_4 , MgSO_4 , CaCl_2 , CdCl_2 , ZnCl_2 , AlCl_3). Reagents solutions were prepared in situ with DI water.

2.3. Azocoupling Reaction

The reaction mixture contained: 0.03% H_2O_2 , 0.10 mg/ml 4-AAP, 0.56 mg/ml phenol. The reaction was initiated by metal ions (in salt form) at concentration 5×10^{-4} mg/ml or MND in a concentration range of 0 - 0.5 wt%. After adding all reagents the samples were intensively agitated for 3 - 5 seconds on Vortex-Genie 2 g-560E (Scientific Industries, Inc., USA) and incubated at temperature 20°C or 40°C.

2.4. Measurement of the Reaction Product Yield

To estimate the reaction product formation the spectral analysis of the stained product was carried out at a wavelength 506 nm (UV/VIS spectrophotometer UVIKON 943, Kontron Instruments, Italy). The samples containing MND were centrifuged at 16,000 g (Centrifuge 5415R, Eppendorf, Germany) for 10 min at 10°C to remove MND particles from the reaction mixture.

2.5. Quantitative Elemental Analysis of MND Samples

For quantitative determination of metal ions in different-sized MND clusters the elemental analysis of the nanoparticles was carried out using an electron microscope TM-1000 (Hitachi, Japan).

3. Results and Discussion

It was experimentally shown that the MND particles are able to catalyze the interaction between organic compounds in azocoupling reaction (H_2O_2 -4-AAP-phenol). The reaction was accompanied by the formation of quinoneimine. Under chosen experimental conditions the reaction rate had a linear dependence within the range of 5 to 20 min (Figure 1). Under the same reaction conditions but without the catalyst the reaction was practically unobservable and the product was formed at neither 20°C nor 40°C. The absorbance of the reaction without MND did not exceed 0.2% - 0.3% of the absorbance of the MND-catalyzed reaction.

It has been found that the increase of reaction absorbance due to product formation was linear at phenol concentrations in the range of 0 - 10 mkg/ml (Figure 2). Such linear trend was observed at both 20°C and 40°C but the absorbance values at 40°C (Figure 2) were approximately fourfold higher than those at 20°C.

It is evident from the dependence of optical density on the amount of catalysts (Figure 3) that the product formation at the MND concentrations up to 0.1 wt% has a nearly linear trend. A further increase in the concentration of nanoparticles drives the reaction to a plateau. It indicates that the reaction system is saturated with the catalysts under the experimental conditions used.

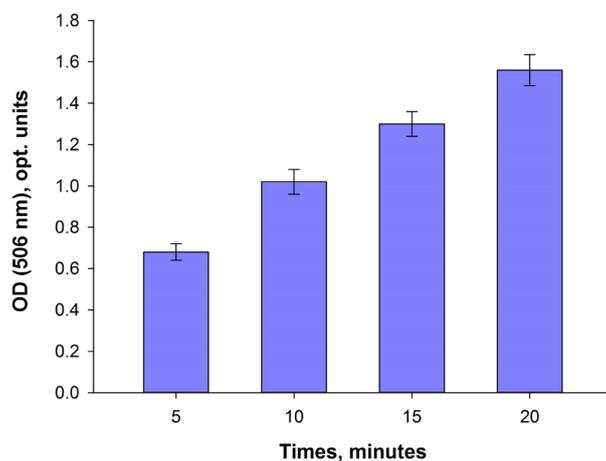


Figure 1. The time dependence of product yield in the azo-coupling reaction catalyzed by MND (nanoparticles concentration was 0.5 wt%) at 20°C.

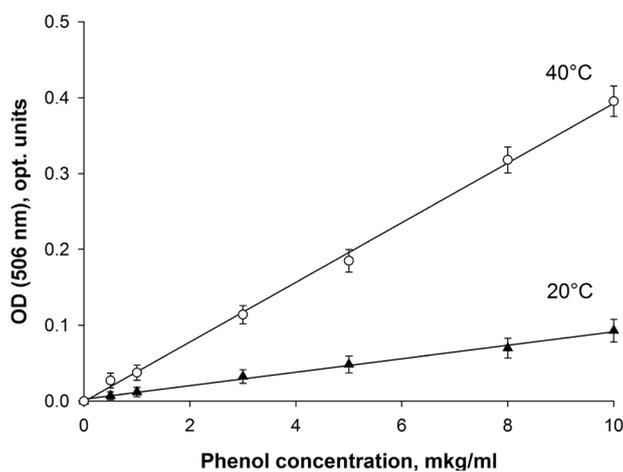


Figure 2. The product yield in the MND-catalyzed reaction vs. phenol concentration (10 min incubation at 20°C and 40°C).

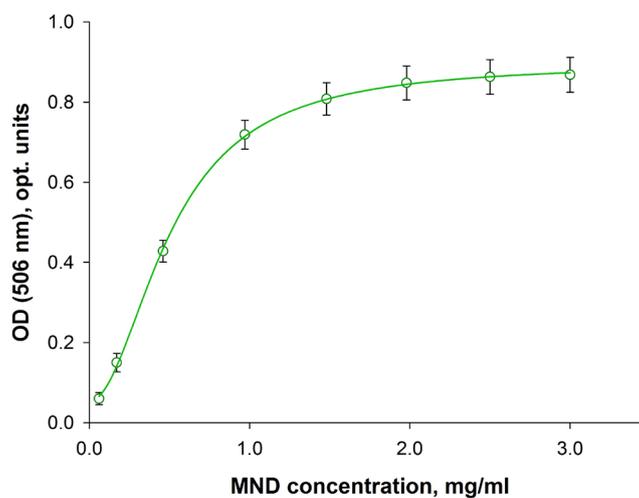


Figure 3. The product yield in the MND-catalyzed reaction vs. concentration of the nanoparticles (10 min incubation at 40°C).

The dependence of optical density on H_2O_2 concentration has a hyperbolic shape (Figure 4). In this process, the addition of hydrogen peroxide to the reaction system in the concentration range of 0% - 0.003% is accompanied by a virtually linear increase in the yield of reaction product.

We had supposed that the MND-catalyzed azocoupling reaction was initiated by metal ions found on the MND surface [9] [11]. In order to understand a principle of MND catalytic action in the reaction, it was investigated which metal ions are able to catalyze the reaction H_2O_2 -4-AAP-phenol. For this purpose the metal salt containing the metal ions found on the MND surface were examined: monovalent Na ions; bivalent ions of first transition series Mn, Fe, Co, Ni, Cu; bivalent Mg, Ca, Cd, Zn ions and trivalent Al ions.

It was experimentally shown (Figure 5) that among the first transition series only Fe and Cu ions were able to catalyze the azocoupling reaction in aqueous media. The other ions of the first transition series (Mn, Co and Ni ions) did not catalyze the reaction—the reaction dynamics with these ions was practically the same as the control reaction dynamics (reaction without catalyst) (Figure 5).

As is shown in Figure 5, kinetics of the reactions catalyzed by Fe ions and Cu ions are different. Within the range of 0 - 50 min, the reaction with Fe ions carried more intensive than the reaction with Cu ions. In the range of 50 - 100 min, formation of the product was more intensive in the presence of Cu ions, after then the reaction stopped and the product yield did not increase. At the same time, the Fe-catalyzed reaction did not stop—product formation grew practically linearly in the range of 50 - 140 min.

Under the chosen experimental conditions (aqueous media, concentrations of reagents and catalysts) monovalent Na ions; bivalent Mg, Ca, Cd, Zn ions and trivalent Al ions did not catalyze the azocoupling reaction. The reaction dynamics with these ions was practically the same as the control reaction dynamics.

The addition of EDTA (chelant of bivalent metal ions) in the reaction almost completely neutralized catalytic properties of Fe and Cu ions. The product yield of the reaction catalyzed Fe and Cu ions in the presence of EDTA (at equimolar ion-chelant ratio) was 15% and 2% respectively of the EDTA-absent reaction. This result is in agreement with known binding constants of Fe and Cu ions with EDTA [12].

In the MND-catalyzed reactions, it was shown (Figure 6) that product formation was twofold higher in the present of small-sized MND clusters ($d_{50} = 49.6$ nm) in comparison with the product formation observed in the reaction catalyzed by large-sized MND clusters ($d_{50} = 270$ nm). Bearing in mind the obtained data: 1) only Fe and Cu ions were able to catalyze the azocoupling reaction and 2) both ions were found on MND surface [9] [11], the quantitative elemental analysis of these nanodiamond samples was carried out.

This analysis showed (Table 1) that contents of Fe and Cu ions in small-sized MND clusters were significantly higher (2 and 1.5 fold respectively) than their contents in large-sized MND clusters. Thus, it is arguable that the differences of catalytic activity of different-sized MND clusters in the azocoupling reaction are associated with different amount of Fe and Cu ions on the surface of nanodiamonds.

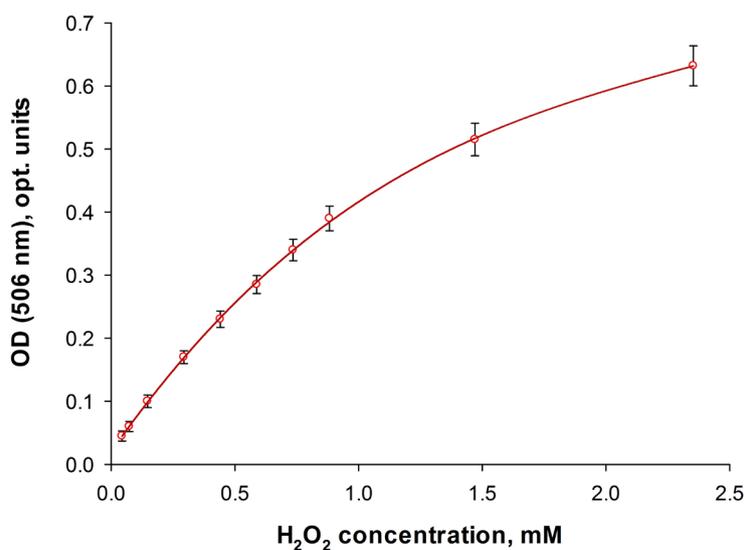


Figure 4. The product yield in the MND-catalyzed reaction vs. hydrogen peroxide concentration (10 min incubation at 40°C).

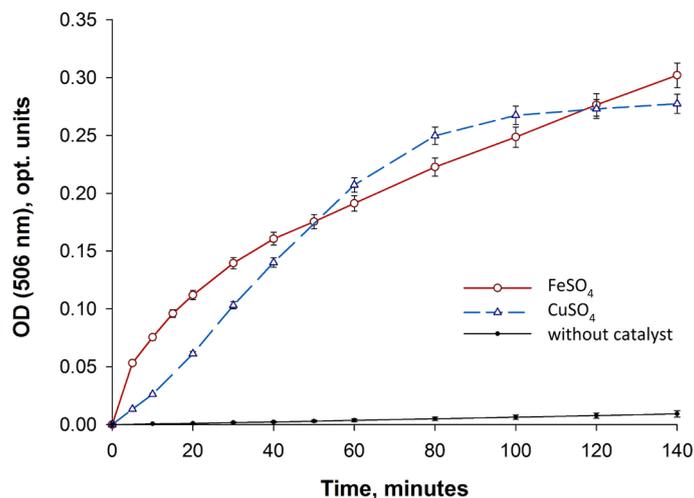


Figure 5. The time dependence of product formation in H_2O_2 -4-AAP-phenol reaction catalyzed by different metal ions and without catalyst.

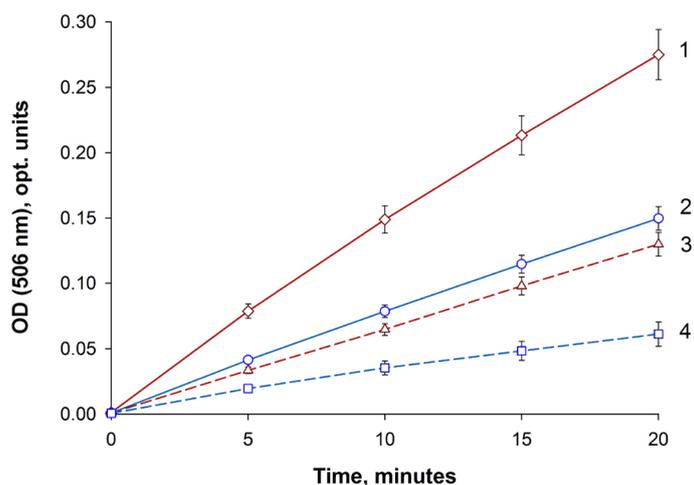


Figure 6. The time dependence of product formation in H_2O_2 -4-AAP-phenol reaction catalyzed by small-sized MND clusters ($d_{50} = 49.6$ nm) and large-sized MND clusters ($d_{50} = 270$ nm): original MNDs (1,2) and EDTA-treated MNDs (3,4).

Table 1. Contents of iron and copper impurities on the surface of different-sized MND clusters.

Element impurities	Samples of MND	
	RUDDM 0 - 125 ($d_{50} = 49.6$ nm)	RUDDM 200 - 500 ($d_{50} = 270$ nm)
Fe, mkg/mg	4.6 ± 0.3	3.1 ± 0.3
Cu, mkg/mg	1.3 ± 0.2	0.6 ± 0.2

Additionally, it was shown that pretreatment of the MND particles with EDTA resulted in significant reduction of their catalytic properties. In the reaction with small-sized and large-sized MND clusters pretreated by EDTA, the product formation was decreased by 2 and 2.5 times, respectively (Figure 6). It is an additional indication on the role of Fe and Cu surface ions in mechanism of MND catalytic action in the azocoupling reaction. At the same time, this result allows making an important suggestion. As EDTA pretreatment of the MND did not lead to the total loss of their catalytic properties, it should not be ruled out additional catalytic action, for example, with the participation of chemically active oxygen-containing functional groups existing on MND sur-

face [11].

4. Conclusions

1) In the work, we have demonstrated the catalytic efficiency of the MND particles in reactions of interaction between organic compounds on the example of the azocoupling reaction (H_2O_2 -4-AAP-phenol). It was found that catalytic action of MND was due to Fe and Cu ions located on the MND surface. These results increase our knowledge about MND catalytic function in the reactions and can be used for designing new MND-based indicating systems for application, for example, in ecological monitoring.

2) The catalytic efficiency of different-sized MND clusters in the azocoupling reaction depends on the amount of surface Fe and Cu ions, which neutralization leads to significant reduction of MND catalytic properties.

3) We do not exclude that the catalytic mechanism of the MND-catalyzed reaction can include, along with Fe and Cu ions, other chemically active oxygen-containing groups located on the MND surface [11].

Acknowledgements

The study was supported by the Presidium of RAS (Program No. 24, Project No. 57). The authors are grateful to Mr. Kargin (ICCT SB RAS, Krasnoyarsk) for elemental analysis of MND samples.

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