Electrochemical generation and observation by magnetic resonance of superparamagnetic cobalt nanoparticles

Aliya F. Khusnuriyalova [a, b], Andreas Petr [c, **], Aidar T. Gubaidullin [a], Aleksandr V. Sukhov [b], Vladimir I. Morozov [a], Bernd Büchner [c], Vladislav Kataev [c], Oleg G. Sinyashin [a], Dmitry G. Yakhvarov [a, b, *]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences, Arbuzov Street 8, Kazan 420088, Russian Federation
[b] Kazan Federal University, Kremlyovskaya 18, Kazan 420008, Russian Federation
[c] IFW Dresden, POB 270116, Dresden D-01171, Germany

ARTICLE INFO

ABSTRACT

The electrochemical reduction of cobalt dibromide 2,2′-bipyridine (bpy) complexes (Co/bpy molar ratio 1:1) results in the formation of cobalt nanoparticles (CoNP) formed by the disproportionation reaction of the electrochemically generated cobalt(I) mononuclear complexes. The process of the electrochemical generation of CoNP was monitored by *in situ* EPR-spectroelectrochemistry where the signals of the ferromagnetic resonance (FMR) have been observed for these species. According to small-angle X-ray scattering (SAXS) analysis the average diameter and the average length of the formed cylindrical CoNP is varied from 9 to 10 nm and 30−32 nm, respectively, and correlates to the g-value and the broadness of the FMR signal observed by *in situ* EPR-spectroelectrochemistry during electrochemical process.

1. Introduction

Currently the development of modern chemistry occurs in several priority areas, one of which is the development and the use of technology based on transition metal nanoparticles. These derivatives are widely applied in modern industry. First of all, this is due to specific properties of the nanoparticles and materials modified by them. At the present time possibilities of using metal nanoparticles in creating the new catalysts for a variety of industrial processes grow extensively. These systems obey the principles of self-assembly, which are used in a variety of technologies, applied to the fabrication of the microelectronic elements, sensoric and optical devices, the synthesis of new materials with desired properties. Transition metal nanoparticles, such as iron, cobalt, nickel, are used as catalytic agents, fund applications in magnetic recording devices, composites [1]. The cobalt complexes formed by the chelating imine ligands, including 2,2′-bipyridine, have recently become known as efficient functional materials [2] and solar cell electrolytes [3].

The problem of obtaining nanoparticles is being discussed for a long time [4−7]. The majority of the methods of preparation of nanoparticles, especially physical methods, are energy consuming and require specialized equipment. Constraints of the methods related to the difficulties in controlling the chemical composition of the product, contamination of metal nanoparticles by initial reactants. Therefore, the development of research in this area requires new methods of preparation of nanoparticles.

One perspective direction is an electrochemical process of the preparation of the nanoscale metals. The soft and one-step process conditions, that use a convenient and relatively inexpensive form of energy such as electricity are undoubted advantages of electrochemical methods. Electrochemical process for producing nanoscale metal particles in a solution is discussed in many reviews [8]. In particular, the description of electrochemical synthesis of metal nanoparticles is described in the papers [9]. Reduction of metal ions formed by dissolving the anode in the electrolyte is the basic electrochemical method. Usually the aqueous solutions are used as

* Corresponding author. A.E. Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences, Arbuzov Street 8, Kazan 420088, Russian Federation.
** Corresponding author. IFW Dresden, POB 270116, Dresden D-01171, Germany.
E-mail addresses: yakhvar@iopc.ru (D.G. Yakhvarov), a.petr@ifw-dresden.de (A. Petr).

electrolytes. Many factors such as the nature of the metal and the solvent, the nature and concentration of ions (target metal and impurities), the adhesive properties of the precipitated particles, temperature, the potential of determining the current density, the diffusion conditions affect the texture of the obtained metal-containing precipitate. Very recent examples of the selective preparation of cobalt nanoparticles involve the use of organic mediators for reduction of cobalt (II) complexes in solution [10].

In this work, we present the investigation of the process of the electrochemical generation of nanosized cobalt particles starting from cobalt dibromide and 2,2′-bipyridyl (bpy) by cyclic voltammetry (CV), macroscale electrolysis and *in situ* EPR-spectroelectrochemistry.

2. Experimental section

2.1. General procedures

All manipulations and reactions were carried out under an atmosphere of dry nitrogen. All solvents were purified and dried prior to use. DMF was dried with calcium hydride and purified by distillation. THF and *n*-hexane were distilled from sodium/benzophenone and stored under nitrogen before use. The complexes $[CoBr_2(bpy)]$, $[CoBr_2(bpy)_2]$, $[Co(bpy)_3]Br_2$, $[NiBr_2(bpy)]$, $[NiBr_2(bpy)_2]$, $[Ni(bpy)_3]Br_2$, were prepared *in situ* by dissolving of anhydrous metal dibromide and stoichiometric amount of 2,2′-bipyridine in DMF or using the literature procedures [11]. 2,2′-Bipyridine (99%, Sigma-Aldrich), $CoBr_2$·(99%, Aldrich), $NiBr_2$ (99.9%, Aldrich), $FeBr_2$ (98%, Aldrich), $(NBu_4)BF_4$ (99.0%, Sigma-Aldrich), DMF (99.8%, Sigma-Aldrich), CaH_2 (99.9%, Aldrich) were commercial products. The electrolyte $(NBu_4)BF_4$ was dried by melting in vacuum and stored under nitrogen.

2.2. Electrochemical methods and apparatus

Cyclic voltammograms were recorded with a glassy carbon electrode (working surface $7.0\,mm^2$) in a thermostatically controlled (T $= 20\,°C$) three-electrode electrochemical cell under N_2 in the presence of $(NBu_4)BF_4$ (0.1 M). A silver electrode Ag/$AgNO_3$ ($0.01\,mol·L^{-1}$ solution in CH_3CN) was used as a reference electrode and a platinum wire served as an auxiliary electrode. Curves were recorded at a constant potential scan rate of $50\,mV\,s^{-1}$ using a potentiostat/galvanostat BASi, model EC Epsilon with C3-cell stand.

The electrochemical generation of the CoNP was carried out at room temperature in galvanostatic conditions [the potential of the working electrode was in the region -1.20 to $-1.40\,V$ vs Ag/$AgNO_3$ ($0.01\,mol \times L^{-1}$ solution in CH_3CN)]. The electrolysis was performed in a divided (two compartment) electrochemical cell (three-electrode cell, 30 mL) with separation of anodic and cathodic compartments. A GC electrode with a surface area of $10.8\,cm^2$ was used as cathode and cobalt wire (3.0 cm, d = 1.0 mm) was served as the anode. Nitrogen was continuously bubbled through the stirred electrolyte during the electrolysis.

The glassy flat cell supplied with a platinum cathode (working electrode) and a sacrificial aluminium anode was used for EPR spectroelectrochemical experiments [12]. The silver wire was used as the reference electrode. The EPR measurements were performed with a Bruker EMX spectrometer operational in the X-band. The microwave power used was in the range of $1\,mW-4\,mW$. For the solution spectra we used modulation amplitudes from 0.01 mT up to 0.1 mT. Time constants were chosen properly. For the ESR-spectra at low temperature we used a modulation amplitude of 0.5 mT. The analysis of the size of CoNP was carried out by small-angle X-ray scattering (SAXS) using Nanostar SAXS. The electron

scanning microscope Tabletop 1000 TM has been used for imaging of the CoNP aggregates.

2.3. Electrochemical generation of CoNP in EPR cell

A solution for electrolysis was prepared by dissolving of $CoBr_2$ (5.5 mg, 0.025 mmol) and bpy (3.9 mg, 0.025 mmol for Co/bpy 1:1 M ratio; 7.8 mg, 0.050 mmol for Co/bpy 1:2 M ratio and 11.7 mg, 0.075 mmol for Co/bpy 1:3 M ratio) in DMF (5 mL). Subsequently, this solution was placed in an electrochemical EPR cell, supplied with a Pt cathode and a sacrificial Al anode. A nearly constant current of $5.0\,μA$ was applied by varying the potential of the working electrode in a small range corresponding to the potential of the first reduction peak of the system observed by CV measurements. The formation of CoNP (g $= 2.33$, $1400-2300\,G$) for Co/bpy 1:2$-$3 M ratio was observed after 15 min of the electrolysis time (the potential of the working electrode was in the region -1.60 to $-1.70\,V$ vs Ag/Ag^+) while the EPR signal of CoNP (g $= 2.30$, $800-1400\,G$) derived from the sample with Co/bpy 1:1 M ratio was observed immediately after the electrolysis started (the potential of the working electrode was in the region -1.40 to $-1.50\,V$ vs Ag/Ag^+).

2.4. Electrochemical generation of CoNP for SAXS analysis (macroscale electrolysis)

A solution for electrolysis was prepared by dissolving of $CoBr_2$ (32.8 mg, 0.15 mmol) and bpy (23.4 mg, 0.15 mmol), in DMF (30 mL). A constant current of 16 mA was passed through the solution for 30 min (the potential of the working electrode was in the region -1.20 to $-1.40\,V$ vs Ag/$AgNO_3$, $0.01\,mol \times L^{-1}$ solution in CH_3CN). After the electrolysis was completed, the resulting solution was carefully transferred to the capillary which was sealed by the melted wax. The resulting samples were analyzed by small-angle X-ray scattering analysis.

2.5. Small-angle X-ray scattering experiments

Small-angle X-ray scattering data were collected with the Bruker AXS Nanostar SAXS system using $CuK_α$ (λ 1.5418 Å) radiation from a 2.2 kW X-ray tube (35 kV, 40 mA) coupled with Gobbel mirrors optics and a HiStar 2D area detector. The beam was collimated using three pinholes with apertures of 800, 450 and 700 μm. The instrument was operated with a sample-to-detector distance of 64.4 cm to provide data at angles $0.1° < 2θ < 4.8°$, which correspond to $0.007\,Å^{-1} < q < 0.34\,Å^{-1}$. The value of q is proportional to the inverse of the length scale ($q = (4π/λ)\sin(θ)$ in units of $Å^{-1}$). Scattering patterns were obtained for the samples at $23\,°C$ in an evacuated chamber. The measurements were performed in transition mode with the use of glass capillaries filled by liquid samples. The capillaries (2 mm diameter) were sealed and put into evacuated chamber by means of the holders. For each sample, several experiments were performed, allowing to control the quality of the experiments. The results of the experiments are summarized, so that the total time of each experiment was equal to 30000 s. The 2D scattering patterns were integrated using the SAXS program package [13]. Calculation of structural parameters, simulation, and graphical representation of the results were performed using the SASView [14] and PRIMUS [15] program packages.

3. Results and discussion

3.1. Cyclic voltammetry

The CV-curves obtained for the system $CoBr_2$/bpy are shown in