

# Anthracene mediated electrochemical synthesis of metallic cobalt nanoparticles in solution



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## ABSTRACT

The metallic cobalt nanoparticles in the bulk solution were obtained by anthracene mediated reduction of [CoCl<sub>4</sub>]<sup>2-</sup> in the potentiostatic electrolysis in an undivided cell at the potential of the anthracene reduction to radical anion at room temperature in DMF/0.1 M Bu<sub>4</sub>NCl media. [CoCl<sub>4</sub>]<sup>2-</sup> ions are generated by the sacrificial cobalt anode dissolution during the electrolysis. The metal particles are oxidized upon contact with the air to form the oxidized cobalt nanoparticles with a low dispersity (20–30 nm).

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## 1. Introduction

In recent years, the metal nanoparticles are of great scientific interest due to their unique physical and chemical properties different from those of bulk metals, and a wide variety of potential applications in the field of catalysis, biomedicine, optics, electronics and other [1–7]. Methods of preparation of metal nanoparticles are quite diverse. They are conventionally divided into physical, chemical and sometimes into biochemical ones. The electrochemical methods of obtaining of metal nanoparticles in solution have found only limited application [6–14], although the electrochemical reduction of the metal ions and complexes is the classical method of producing metals, metal plating, metal black on the electrode surface on an industrial scale [15]. This is primarily because the direct reduction of metal ions results in metal deposition on the electrode surface. For example, when using this method of producing silver nanoparticles in solution, up to 80 percent of the metal is deposited on the electrode surface [11]. The problem of deposition is partially solved by a combination of the metals accumulation process during a short current impulse followed by the metal transfer from the surface into the solution by means of sonification of the working electrode (pulse sono-electrochemistry) [12–14].

It seems that another more efficient approach to implementation of the electrochemical process for production of metal and

metal-alloy nanoparticles in solution can be a transfer of electro-reduction reaction of ions or their complexes from the electrode surface into the solution using mediators. In the process of chemical synthesis of a finely-dispersed metal using alkali metals to reduce metal salts in ethereal or hydrocarbon solvents according to Rieke process, organic electron carriers (naphthalene, biphenyl, anthracene, etc.) are widely used as mediators [16–19]. The idea of using organic electron carriers for generating highly reactive metal (0) in solution by mediated electrochemical reduction of metal ions and metal complexes have been used by us to create highly efficient electrocatalytic systems for reduction of various organic substrates [20]. Based on this idea [20] recently an efficient electrosynthesis of palladium and silver nanoparticles have been carried out by the mediated reduction of [PdCl<sub>4</sub>]<sup>2-</sup> in 60% aqueous DMF [21,22] and DMSO [23], anode-generated silver ions Ag<sup>+</sup> in DMF [24] using methylviologen MV<sup>2+</sup> and/or tetraviologen calix[4]resorcine MVCA-C<sub>n</sub><sup>8+</sup> (n = 1,5,10) with n-alkyl substituents in the resorcinol cycles as a mediator at potential of redox couples MV<sup>2+</sup>/MV<sup>•+</sup>, MVCA-C<sub>n</sub><sup>8+</sup>/MVCA-C<sub>n</sub><sup>4•+</sup>. Tetraviologen calix[4]resorcines also stabilized nanoparticles both in the solution and/or on the electrode surface. In this article, the electrochemical synthesis of cobalt nanoparticles in DMF/0.1 M Bu<sub>4</sub>NCl using anthracene as a mediator is reported. Nanoparticles of cobalt and its alloys are of interest as catalysts [16,18] and magnetic materials [19,25]. Co<sup>2+</sup> ions are reduced harder than the above-mentioned ions, so a reducing agent more effective than methylviologen radical cation is required to reduce them. Therefore, the choice of a medium and a mediator is made on the basis of earlier [20] findings of the reduction of cobalt ions by anthracene radical anion.

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## 2. Experimental section

The investigation was carried out using the methods of cyclic voltammetry (CV), electrolysis, dynamic light scattering (DLS) and scanning electron microscopy (SEM).

The CV recordings were done with a P-30S potentiostat (without IR-compensation) in argon atmosphere. The working electrode was a glassy carbon disk electrode ( $\varnothing=2$  mm) brazed in glass. The electrode was cleaned by mechanical polishing with diamond paste before each measurement. Platinum wire was a counter electrode. The potentials were measured relative to the aqueous saturated calomel electrode (SCE),  $E_0'(Fc/Fc^+)=+0.41$  V. Aqueous SCE was connected by a bridge filled with supporting solution. The temperature was 295 K. The diffusion nature of the peak currents  $i_p$  was proven using the theoretical shape of the voltammogram and the linear dependence  $i_p - \nu^{1/2}$  by varying the potential scan rate  $\nu$  from 10 to 200 mV/s, and the adsorption nature was substantiated by the presence of an adsorption maximum.

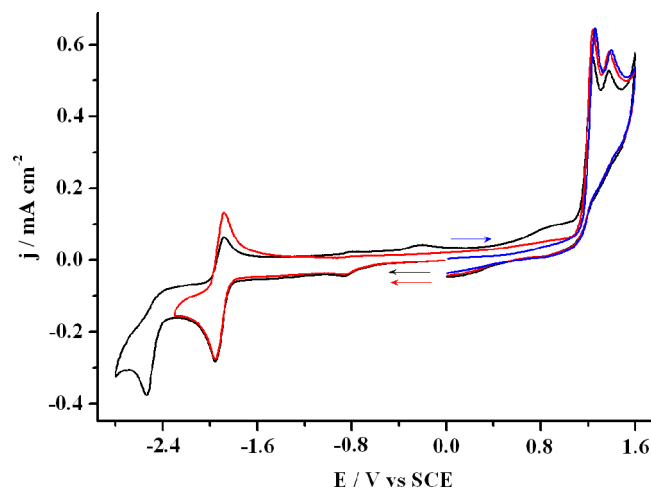
Anthracene,  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ , the supporting electrolytes  $\text{Bu}_4\text{NBF}_4$  (Aldrich),  $\text{Bu}_4\text{NCl}$  (Fluka) and the solvent *N,N*-dimethylformamide (DMF) (Alfa Aesar) were used as purchased without additional purification.

The microelectrolysis was carried out in a three electrode undivided glass cell in a potentiostatic mode in argon atmosphere at room temperature ( $T=295$  K) using a P-30S potentiostat. During the electrolysis, the solution (DMF, 0.1 M  $\text{Bu}_4\text{NCl}$ , 2 mM Anthracene,  $V=20$  ml) was stirred with a magnetic stirrer. Glassy carbon tissue was the cathode ( $S=10$  cm<sup>2</sup>); a cobalt plate ( $S=4.2$  cm<sup>2</sup>) was the anode; and SCE was the reference electrode. SCE was connected by a bridge filled with supporting solution.

When the electrolysis was over the solution was controlled by CV on the indicator glassy carbon disk electrode ( $\varnothing=2$  mm) directly in the electrolyzer, and then, the metal particles formed in the process of electrolysis were analyzed with DLS and SEM.

The DLS measurements were performed using Malvern Instrument Zetasizer Nano. The measured autocorrelation functions were analyzed with Malvern DTS software.

For carrying out the electron microscopic analysis the solution was applied to the surface of the titanium foil was previously cleared by sonification in acetone. Then the sample was exsiccated at low heat (not above 40 °C). The morphology of the SAMPLE surfaces was characterized in plan-view with SEM using a high-resolution microscope Merlin of Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for energy-dispersive X-ray spectroscopy (EDX) analysis with AZTEC X-MAX energy-dispersion spectrometer from Oxford Instruments.



**Fig. 1.** CV curves of anthracene (1 mM) in DMF/0.1 M  $\text{Bu}_4\text{NBF}_4$  media using a glassy carbon electrode.  $\nu=100$  mV/s.

## 3. Results and discussions

### 3.1. DMF/0.1 M $\text{Bu}_4\text{NBF}_4$ media

The cyclic voltammogram (CV) of anthracene recorded using a glassy carbon electrode exhibits two diffusion one-electron reduction peaks in the cathodic potential region, the first one is reversible while the second is not (Fig. 1, Table 1). According to the literature [20,26], a stable radical anion forms at the first peak potential, while a dianion forms at the potentials of the second peak which undergoes rapid irreversible chemical transformations. Two poorly separated irreversible oxidation peaks are recorded on the anode region. The first peak ( $E_{p,ox}=1.27$  V) is dominant and the second is faint.

$\text{Co}^{2+}$  ions are reduced significantly easier than anthracene, the reduction peak is sharp, irreversible and diffusion-controlled (Fig. 2, Table 1). Two re-oxidation peaks are observed at potentials near zero and 1.48 V on the reverse part of the CV curve, the first peak is the adsorption. With the increase of  $\text{Co}^{2+}$  ions concentration the reduction peak and the first reoxidation peak increase proportionally, while the second reoxidation peak somewhat decreases. The rise of the oxidation current of bulk metallic cobalt to form  $\text{Co}^{2+}$  starts from almost zero volts in this medium (Fig. 3). Evidently, the recorded reduction peak of  $\text{Co}^{2+}$  corresponds to its two-electron reduction to  $(\text{Co}^0)_n$ , which is deposited on the electrode and is oxidized at the first reoxidation peak potential. The high steepness of the  $\text{Co}^{2+}$  reduction peak (Table 1) is due to the easier  $\text{Co}^{2+}$  ions reduction on the as-deposited cobalt particles,

**Table 1**

The characteristics of the reduction and reoxidation peaks of anthracene (1.0 mM),  $\text{Co}(\text{II})$  (2.0 mM), obtained by CV using a glassy carbon electrode in DMF/0.1 M  $\text{Bu}_4\text{N}^+\text{X}^-$  media.

Substrate	$\text{X}^-$	$E_{p,red}^1, \text{V}$	$E_{p,red}^1 - E_{p/2,red}^1, \text{mV}$	$j_{p,red}^1, \text{mA cm}^{-2}$	$E_{p,red}^2, \text{V}$	$E_{p,red}^3, \text{V}$	$E_{p,red}^4, \text{V}$	$E_{p,red}^5, \text{V}$
anthracene	$\text{BF}_4$	-1.95	62	0.26	-1.89	-2.53	-	-
+ $\text{Co}^{2+}$		-1.15	26	0.74	0.01	-	1.48	-
anthracene + $\text{Co}^{2+}$		-1.21	50	0.70	-1.87	-1.97	-0.05	-
anthracene	$\text{Cl}$	-1.92	65	0.26	-1.85	-2.51	-	-
$\text{Co}^{2+}$		-2.22	137	0.55	-0.44	-	0.72	-
anthracene + $\text{Co}^{2+}$		-1.97	98	0.76	-0.54	-	-0.02	0.68

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