

# Mediated Electrosynthesis and Catalytic Activity of Nanocomposites Formed by Metal Nanoparticles with Poly(N-vinylpyrrolidone) and Nanocellulose

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**Abstract**—Nanoparticles (NP) of Au, Ir, Pd, Pt, and Rh are synthesized by benzimidazo[1',2':1,2]quinolino-[4,3-*b*][1,2,5]oxodiazolo[3,4-*f*]quinoxaline (BIQOQ)-mediated electrochemical reduction of AuCl, K<sub>3</sub>[IrCl<sub>6</sub>], PdCl<sub>2</sub>, PtCl<sub>2</sub>, RhCl<sub>3</sub>, respectively, in the presence of poly(N-vinylpyrrolidone) (PVP) and nanocellulose (NC) at the potential controlled in the region of generation of BIQOQ<sup>•-</sup> anion radicals in the DMF/0.1 M Bu<sub>4</sub>NBF<sub>4</sub> medium at room temperature. The efficiency of electrosynthesis is shown to be determined by the nature of the substrate to be reduced. K<sub>3</sub>[IrCl<sub>6</sub>] is virtually unreducible, whereas the other substrates are reduced to form NP–M. As the theoretical charge is passed, the generated metal is formed in the solution volume rather than as the cathodic deposit. NP–Au particles are formed in the quantitative amount, the mediator is retained in the process. In the other cases, the process consumes from ~50 (Ir, Pd, Pt) to 80% (Rh) of the mediator with the corresponding decrease in the NP–M yield. The synthesis produces individual spherical NP–Pd (4 ± 1 nm) and agglomerates of nanoparticles of gold (78 ± 27 nm), platinum (34 ± 14 nm), and rhodium (33 ± 20 nm) all stabilized in PVP shells. In contrast to the earlier described Ag@PVP nanoparticles which decorated NC in the extremely dense way, these particles are bound only partly with NC. The nanocomposites of Pd, Pt, and Au exhibit catalytic activity in the reactions of reduction of nitroaromatic compounds by sodium borohydride in aqueous media.

**Keywords:** electrosynthesis, metal nanoparticles, nanocomposite, mediator, benzimidazo[1',2':1,2]quinolino-[4,3-*b*][1,2,5]oxodiazolo[3,4-*f*]quinoxaline, polyvinylpyrrolidone, nanocellulose, catalysis

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## INTRODUCTION

Several recent decades were characterized by the impressive success in the field of catalysis of chemical and electrochemical reactions by metals [1–5]. As compared with noncatalytic reactions, these reactions consume less energy, are highly selective and highly efficient. This is why the catalytic processes attract attention as the basis for the synthesis of practically useful substances and materials and also for elaboration of energy conversion systems (fuel cells, photocatalytic systems). Under laboratory conditions, the wider use is typical of reactions employing homogeneous metal catalysts, as a rule, metal complexes. However, as regards practice, the heterogeneous catalysts have the wider application, due to several advantages over homogeneous catalysts, i.e., nontoxicity, safety when stored and used, stability in wide intervals of temperature and pressure, long service life, easy

regeneration and extraction from the reaction medium [6]. For this reason, nowadays, special attention is paid to the whole complex of problems associated with the development of highly efficient heterogeneous catalysts, the elaboration of technologies for their synthesis, their application in catalytic reactions, and their subsequent regeneration.

The highly efficient catalysts include those that allow carrying out the target catalytic process at a high rate and with high selectivity, under mild conditions, and with the use of minimum amount of recoverable catalyst. In the liquid phase where the majority of chemical reactions are carried out, the efficient catalysts are the pseudohomogeneous metal nanocatalysts, i.e., mono and bi(poly)metal nanoparticles (NP–M) encapsulated in shells of the stabilizing agent and/or bound to the surface of dispersed or dissolved carriers [7–9]. NP–M have the highly developed surface area; moreover, the smaller the particles, the