



Molecular oxygen as a mediator in the electrosynthesis of gold nanoparticles in DMF



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ABSTRACT

The possibility of using of molecular oxygen as a mediator in electrosynthesis of metal nanoparticles by reduction of their ions and complexes in aprotic media was demonstrated by the example of electrosynthesis of gold nanoparticles by reduction of Au(I) in DMF.

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1. Introduction

Electroreduction of metal ions and complexes is quite rarely used for electrosynthesis of in-demand [1–7] metal nanoparticles (MNP) in solution bulk. The main factor limiting the use of electrochemistry is precipitation of generated metal on an electrode surface. Therefore, in all the methods developed for MNP electrosynthesis in solution bulk, the deposition problem is solved in some way. In the pulse sonoelectrochemistry method [8–10], this problem is solved by combining the process of MNP generation on an electrode surface during electroreduction for a short time with its subsequent transfer into the solution by sonication of the working electrode. In the method by Reetz et al. [11–15], electroreduction of ions is carried out in aprotic organic media using salts of surfactant cations, such as tetraalkylammonium or phosphonium, as a supporting electrolyte. For these purposes we have proposed a method of mediated electrosynthesis [16–25] which differs from the above-mentioned electrochemical methods in such a way that the step of metal ion reduction is moved from the electrode surface into the solution bulk. In this case, a mediator is reduced on the cathode and the reduced form of the mediator diffuses into solution bulk where it reduces the metal ion or complex. Thus, deposition of the metal on the electrode is completely prevented or minimized. The feasibility of the method and its efficiency have been recently demonstrated by the examples of preparation of Pd [16–20], Ag [21–23], Co [24], Au [25] NP in the absence and presence of stabilizers in aqueous, aqueous-organic and non-aqueous media from

metal salts and complexes, or from metal ions generated in situ in solution upon dissolution of a metal anode during electrolysis. The method is equally efficient with soluble ions and complexes ($[\text{PdCl}_4]^{2-}$, Ag^+ , AuCl , $[\text{CoCl}_4]^{2-}$) and insoluble metal salts (AgCl , spherical $\text{AgCl}@CTAC$ NP), irrespective of whether reduction of the mediator on the electrode is easier or harder than reduction of the metal substrate. Methylviologen, free or fixed on calix[4]resorcin platform, and anthracene were used as a mediator.

In this paper, we report on the possibility of using of molecular oxygen as a mediator in electrosynthesis of MNP by reduction of metal salts and complexes in aprotic media by the example of electrosynthesis of AuNP in DMF. Oxygen is a non-polluting gas that is dissolved from the air in organic media under normal conditions at concentrations sufficient for a mediator [26]. Thus, the need of using of other mediators and subsequent removal of them from MNP are eliminated.

2. Experimental Section

Chemicals. AuCl (Alfa Aesar), polyvinylpyrrolidone (PVP) 40,000 (Alfa Aesar), the supporting electrolyte Bu_4NCl (Fluka), DMF (Alfa Aesar) were used as purchased without additional purification.

The CV recordings were done with a P-30J potentiostat in DMF/0.1 M Bu_4NCl . The working electrode was a glassy carbon (GC) disk electrode ($\varnothing = 2.0$ mm) pressed into glass. The electrode was cleaned by mechanical polishing before each measurement. Platinum wire was a counter electrode. The potentials were measured relative to the aqueous saturated calomel electrode (SCE). The aqueous SCE was

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