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# 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.

## 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 ($[PdCl_4]^{2-}$, $Ag^+$, AuCl, $[CoCl_4]^{2-}$) and insoluble metal salts (AgCl, spherical 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]resorcine 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 (Ø = 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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connected by a bridge filled with supporting solution. The temperature was 295 K.

**The preparative reduction** of the solution (10 ml) containing 1.5 mM AuCl (3.5 mg), ~2.9 mM $O_2$, 8.33 g/l PVP (83.3 mg), 0.1 M $Bu_4NCl$ (417 mg) was carried out in a cell separated with a porous glass diaphragm in potentiostatic mode (−1.10 V) at room temperature (T = 295 K). During the electrolysis, the solution was stirred with a magnetic stirrer. A GC plate ($S = 5.6$ $cm^2$) was used as the working electrode. The reference and auxiliary electrodes were used as in CV experiments. After the electrolysis (Q = 1.0 F with respect to AuCl) solid AuCl (poorly soluble in DMF) disappeared. When the electrolysis was over, the solution was studied by CV on the indicator GC disk electrode (Ø = 2.0 mm) directly in the electrolysis cell.

**TEM** analysis of NP was carried out using a Hitachi HT7700 Excellence transmission electron microscope. Sample preparation: 10 μl of the suspension was placed on a Formvar™/carbon coated 3 mm copper grid, which was then dried at room temperature. After complete drying, the grid was placed into a transmission electron microscope using special holder for microanalysis. Analysis was held at an accelerating voltage of 80 kV in TEM mode.

**SEM** analysis and **DLS** measurements were performed as described in [25].

**UV–visible spectra** were recorded on a Perkin-Elmer Lambda 25 spectrometer.

## 3. Results and Discussions

The CV curves of molecular oxygen (C ~ 2.9 mM) dissolved in DMF/0.1 M $Bu_4NCl$ medium under ordinary conditions in contact with air contain two reduction peaks in full accordance with the literature data [27]. The first of them is chemically reversible and the second is irreversible (Fig. 1A). The first peak is due to one-electron reduction of oxygen to the radical anion (superoxide ion). Reversibility of the peak indicates sufficient stability of generated $O_2{\bullet}^-$ under these conditions. When PVP widely used as a MNP stabilizer is added to the solution, the reversibility of the peak remains (Fig. 1A). One-step reduction of Au(I) (AuCl or $[AuCl_2]^-$ [25]) is irreversible in the absence of oxygen, is significantly easier than reduction of oxygen and does not depend on the presence of PVP in the solution (Fig. 1A). Unlike aqueous media [25], metallic gold generated and deposited on the electrode is not oxidized in the available region of potentials. The morphology of the CV curve of $O_2$ and Au(I) mixture corresponds to the additive curve of individual components. The sum of current of the one-step reduction peaks of Au(I) and $O_2$ is also equal to the additive value. This means that quantitative reduction of Au(I) to $Au^0$ and of $O_2$ to $O_2{\bullet}^-$ occurs at the potentials of the first peak of oxygen reduction. However, CV curves do not answer the question: how is Au(I) reduced — by mediated process or directly on the electrode.

Preparative electroreduction of Au(I) (1.5 mM AuCl, ~2.9 mM $O_2$, 8.33 g/l PVP) was performed in DMF/0.1 M $Bu_4NCl$ medium in a diaphragm cell at controlled potential of the first stage of oxygen reduction to $O_2{\bullet}^-$ (E = −1.10 V). Currents are gradually decreased from 6.1 to 2.5 mA during the electrolysis (7 min 15 s). The initially yellow solution became colorless, it remained homogeneous, and formation of a precipitate was not observed visually. Such change of the solution color is not typical of the formation of AuNP in solution. The AuNP solutions are usually colored [6,25].

After passing 1.0 F with respect to Au(I), the peak of Au(I) reduction is absent and only the initial intensity peaks of oxygen reduction and reoxidation (Fig. 1B) are present on the CV curves. The cathode weight is kept constant. Therefore, after passing the theoretical amount of electricity, quantitative transformation of Au(I) to very soluble $Au^0$ occurs. The generated $Au^0$ is not deposited on the electrode and is electrochemically inactive in the available potential range. Because the electrolysis is carried out at the potentials of reduction of $O_2$ the reduction currents of which are significantly higher than for Au(I), and only reduction of Au(I) takes place as the result, it is evident that oxygen mediated electroreduction of Au(I) occurs in the solution bulk (Scheme 1).

In the resulting electrolyte (*solution 1*), NP with a mean hydrodynamic diameter of 10 and 69 nm are recorded by DLS, and the largest number of particles has a size of 7 nm (PdI = 0.479 ± 0.017), while UV–visible spectrum shows the very weak absorption band of AuNP at 550 nm (Fig. 2). However, an attempt to precipitate NP by centrifugation (15,000 rpm for 2 h) failed. Because of this, DMF was removed from part of *solution 1* by water-jet pump vacuum, and dry residue was dispersed in ethanol (*solution 2*) and water (*solution 3*) by sonication. The *solution 1* remained colorless for a long time upon storage in the dark at room temperature, but then slowly began to become violet (color of AuNP) and after 15 days was intense violet. In this case in the *solution 1*, NP with a mean hydrodynamic diameter of 30 and 121 nm are recorded by DLS, and the largest number of particles has a size of 24 nm (PdI = 0.269 ± 0.003). The UV–visible spectrum contains the intense absorption band of AuNP with $\lambda_{max} = 585$ nm (Fig. 2). Similar conversions of the *solutions 2* and *3* occurred more rapidly for 48 and 8 h, respectively. After precipitation from all three solutions of AuNP by centrifugation (15,000 rpm for 2 h), twice ethanol washing and subsequent precipitation, NP was dispersed in ethanol (*solutions 1′*, *2′* and *3′* respectively) and was investigated by complex of methods.

In the resulting *solution 1′*, *2′* and *3′*, NP with a mean hydrodynamic diameter of 26 and 121 nm, 104 and 330 nm, 58 and 216 nm respectively are recorded by DLS (Fig. 2B), the largest number of particles has a

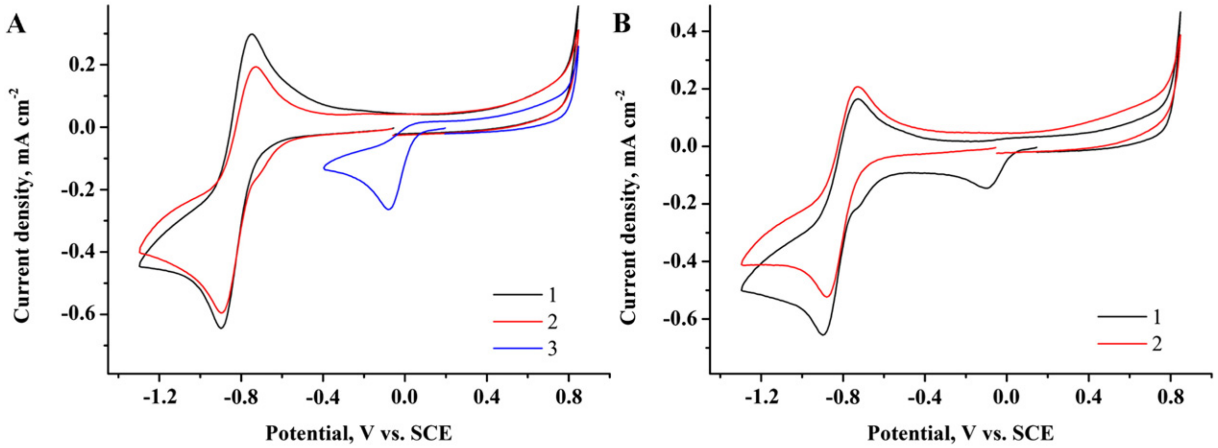

**Fig. 1.** (A) CV curves of (1) $O_2$ (~2.9 mM) (2) the PVP (8.33 g/l) + $O_2$ (~2.9 mM) system and (3) the AuCl (1.5 mM) + PVP (8.33 g/l) system; (B) CV curves of the AuCl (1.5 mM) + PVP (8.33 g/l) + $O_2$ (~2.9 mM) system (1) before and (2) after reduction at −1.10 V (Q = 1.0 F with respect to AuCl). DMF/0.1 M $Bu_4NCl$. $\nu = 100$ mV/s.