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Electrosynthesis of gold nanoparticles mediated by methylviologen using a gold anode in single compartment cell

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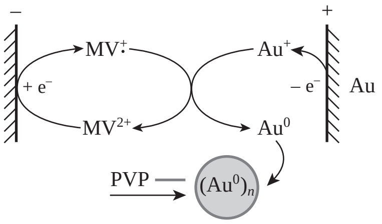
Methylviologen mediated reduction of Au^I ions generated *in situ* by dissolution of a gold anode in single compartment cell has been used for the electrosynthesis of spherical gold nanoparticles (Au-NPs) stabilized by poly(*N*-vinylpyrrolidone). The size of Au-NPs was from 15±6 to 27±9 nm, depending on the electrosynthesis conditions. Au-NPs were characterized by cyclic voltammetry, UV-VIS spectroscopy, dynamic light scattering, scanning and transmission electron microscopy.



The interest in metal nanoparticles (M-NPs) has been increasing lately due to their unique properties and diverse potential applications in catalysis, electronics, biomedicine, optics, analysis, *etc*.[1–7] Currently, chemical reduction of metal ions and metal complexes in solution is the most thoroughly developed and popular method for their synthesis. For example, Au-NPs were prepared using a number of different reducing agents, in particular, hydrogen,[8] sodium citrate, and ascorbic acid.[9] Electroreduction of metal ions and metal complexes is widely used for M-NP preparation on an electrode surface[10] and is rather rarely used for the electrosynthesis of M-NPs in bulk solution. Deposition of metals generated on the electrode surface is the main factor that restricts the use of electrochemistry. Therefore, in all developed methods for M-NP electrosynthesis in bulk solution the deposition problem has to be solved. In the pulse sonoelectrochemistry method,[11–13] the formation of NPs on the electrode surface during short-time electroreduction is combined with their subsequent transfer to the solution by sonication of the electrode. In the method developed by Reetz *et al.*,[14–18] the electroreduction of ions is performed in aprotic organic media using tetraalkylammonium or phosphonium salts as supporting electrolytes. For the same purpose, we have suggested the mediated electrosynthesis method,[19–28] which differs from those mentioned above by moving the step of metal ion reduction from the electrode surface to the bulk solution. In this case, a mediator is reduced on the cathode, then reduced form of the mediator diffuses into the solution and reduces metal ion or metal complex. Thus, metal deposition on the electrode is minimized or completely avoided. The method applicability and efficiency were recently demonstrated by preparing Pd,[19–21] Ag,[22,23] Co,[24] Au,[25–27] and Pt NPs.[28] The following compounds were used as the mediators: methylviologen (MV^{2+}), either free or immobilized on the calix[4]-resorcin platform, anthracene, oxygen, and C_{60} fullerene. Au-NPs were obtained by electroreduction of Au^I in two-compartment cell using MV^{2+}, oxygen, and fullerene as the mediators.

In this paper, we report the electrosynthesis of Au-NPs stabilized with poly(*N*-vinylpyrrolidone) (PVP). The electrosynthesis was performed by *in situ* generation of metal ions from the Au anode in aqueous media and by reduction with methylviologen in single compartment cell. It is known[29] that active anodic dissolution of gold in aqueous media occurs in the presence of chloride ions. Therefore, 0.1 M NaCl was used as supporting electrolyte.

The cyclic voltammetry (CV) curves of the gold electrode in this electrolyte exhibit active dissolution at 0.80–1.30 V *vs.* SCE and an electrode passivation at more positive potentials (Figure 1). The reverse CV curve demonstrates two re-reduction peaks C_1 and C_2 at 0.70 and 0.48 V, respectively. The C_1 peak is considerably weakly expressed, and C_2 is the main peak corresponding to the re-reduction of the generated gold ions. If the scanned potentials are limited to the active dissolution region, the shape of the reverse CV branch remains the same, but the C_2 peak is slightly (by 40 mV) shifted to less anodic potentials.

Reduction of Au^I (AuCl or $[AuCl_2]^-$)[25] and $HAuCl_4$ occurs at similar potentials; the peak potentials on a glassy carbon (GC) electrode are 0.22 and 0.30 V, respectively (Figures S1 and S2, Online Supplementary Materials). Therefore, CV curves show that gold anode is dissolved, but do not provide information about the oxidation product. The nature of the C_1 peak also remains unclear.

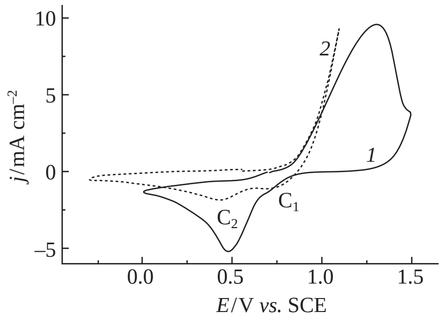


Figure 1 CV curves recorded on an Au electrode in aqueous 0.1 M NaCl solution in the potential region of (*1*) 1.5–0.0 V and (*2*) 1.1 to –0.3 V. υ = 100 mV s^{-1}.