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Activation of gold nanostructures with Meerwein's salt

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A new method based on surface treatment with triethyloxonium tetrafluoroborate is proposed for the activation of a gold electrode modified by gold nanoparticles using an oleylamine technique in order to improve the electrochemical signals of a gold surface.

Nanostructures obtained from colloid gold particles are widely applied in optoelectronics and the development of chemical sensors.[1,2] Various physical (*e.g.*, photolithography)[3] and chemical methods are used to produce the nanostructures. The oleylamine method of obtaining nanostructures is based on the slow oxidation of oleylamine and the reduction of Au^{I} particles with the formation of Au^{0} nanoparticles.[4] The interaction of the nanoparticles with each other leads to the formation of nanowires of various diameters and lengths.[5,6] The oleylamine method affords gold nanoparticles 5–15 nm in diameter and nanowires 1 μm in length.[4] The above modification provides an enlargement of the electrode surface and an increase in the catalytic activity of biosensors based on these electrodes. The disadvantages of the oleylamine method include the limited use of gold nanostructures due to the fact that the stabilizing organic oleylamine shell prevents electron conductivity and blocks and deactivates the electrode surface. The aim of this work was to develop methods of oleylamine shell destruction and produce more active gold nanostructures.

Gold nanostructures were synthesized from gold(I) chloride[5] or gold(III) chloride (with heating a reaction mixture to 120 °C for the reduction of Au^{I} to Au^{0})[7] solutions and oleylamine.

The nanostructures were gradually deposited on the surface of a gold electrode using 50 μl of a solution of nanostructures in hexane or toluene and left to dry. Further, the electrode was washed with hexane or toluene and distilled water. Modified electrodes and solutions of nanostructures were stored in a refrigerator at 4 °C.

Figures 1 and 2 show the SEM images† of the gold electrode surface before and after the modification of gold nanostuctures, respectively.

The formation of nanostructures (a mixture of nanoparticles 5–15 nm in diameter and nanowires 1 μm in length) is evident. The electrochemical measurements of the gold electrode modified with nanostructures in water solutions showed no signal because the hydrophobic shell of oleylamine blocked the electrode surface.

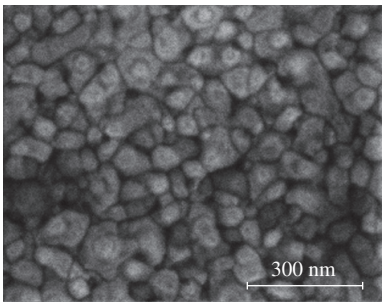


Figure 1 SEM image of the gold electrode surface before modification with nanostructures.

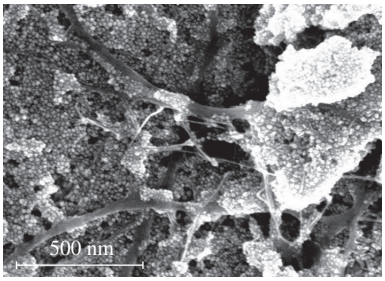


Figure 2 SEM image of the gold electrode surface modified with nanostructures obtained using a published method.[7]

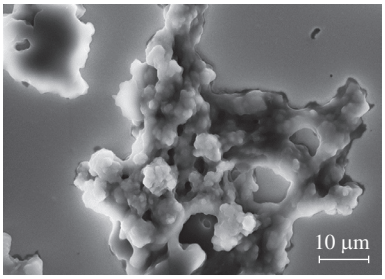


Figure 3 SEM image of the gold electrode modified with gold nanostructures after treatment with oxygen plasma.

Earlier,[8] oxygen plasma was used for the activation and hydrophilization of an electrode surface with polydimethylsiloxane (PDMS) (as a cross link reagent). In our case, oxygen plasma treatment (200 W, 1–3 min) for surface activation did not cause a positive effect (Figure 3).

The decrease in the surface area of the modified gold electrode after oxygen plasma treatment in comparison with the unmodified

† A Magellan XHR scanning electron microscope was used for studying the obtained nanostructures; the oxygen plasma treatment was performed on a FEMTO Plasma system; the electrochemical measurements were carried out on an AUTOLAB PGSTAT302 potentsiostat galvanostat with an electrochemical cell with a silver chloride electrode as a reference electrode, a platinum electrode as an auxiliary electrode, a silicon dioxide substrate (1 μm) with a layer of titanium (10 nm) and an upper layer of gold (300 nm) as a working electrode. The reagents from Sigma Aldrich of 99.9% purity were used for the synthesis and electrochemical measurements. All solutions were prepared using deionized water from Merck Millipore: Milli-Q Advantage A10 Ultrapure Water Purification System.

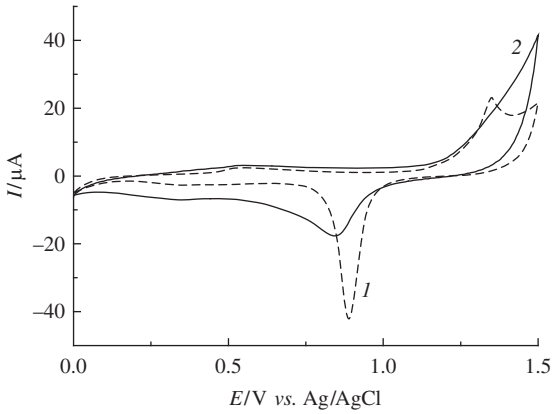


Figure 4 Cyclic voltammograms in a 0.1 M solution of sulfuric acid for (*1*) a gold electrode and (*2*) the gold electrode modified with gold nanostructures after treatment by oxygen plasma.

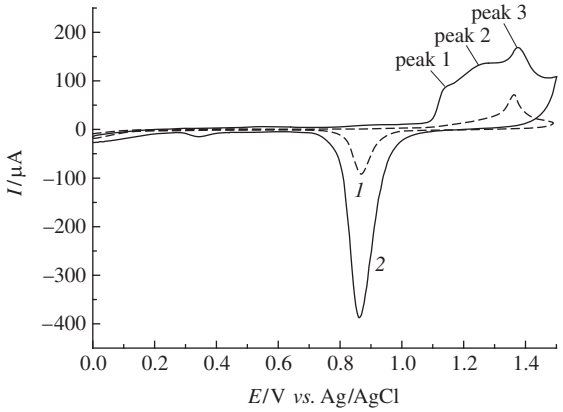
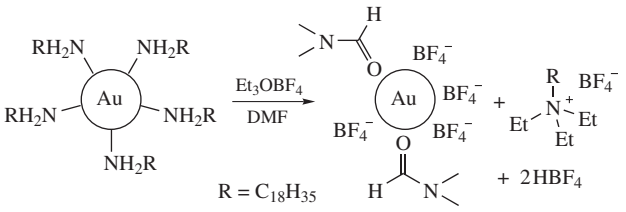


Figure 6 Cyclic voltammograms in a 0.1 M sulfuric acid solution for (*1*) a gold electrode and (*2*) the gold electrode modified with gold nanostructures after treatment by Meerwein's reagent.

gold electrode can be seen in cyclic voltammograms (Figure 4). The area of electrodes in Figure 4 was evaluated by the reduction peak of gold(I) at 0.75 V. All peaks stayed upon after scanning the third cycle.

Recently,[9] it was shown that the treatment of nanocrystals by Meerwein's reagent led to the cleaning and activation of their surface. To solve the problem of electrochemical measurements in aqueous solutions with electrodes modified with nanostructures obtained by the oleylamine method[5,7] the treatment of the electrode surface with Meerwein's reagent (triethyloxonium tetrafluoroborate) was proposed (Scheme 1).



Scheme 1 Interaction of gold nanostructures with Meerwein's reagent.

Meerwein's reagent[9] acts as an oxidizing agent for stabilizing a shell of oleylamine.[9,10] The activation of the electrode surface was carried out with a 0.01 M solution of Meerwein's reagent in acetonitrile; the modified electrode was washed with acetonitrile, toluene[7] and hexane.[5]

The SEM images obtained after the treatment of a modified gold electrode with Meerwein's reagent demonstrate (Figure 5) that the nanostructured surface remained intact.

The cyclic voltammograms of an unmodified gold electrode and a gold electrode modified with gold nanostructures after treatment with Meerwein's reagent are presented in Figure 6.

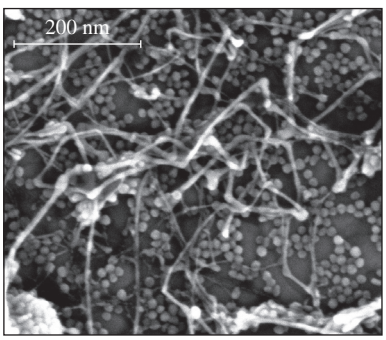


Figure 5 SEM image of the surface of a gold modified electrode after treatment with Meerwein's reagent.

The presence of several oxidizing peaks in Figure 6 (curve *2*) means that nanostructures[11,12] on the electrode surface exist in higher energetic level [oxidizing peaks 1 (1.137 V) and 2 (1.357 V)] than the atoms of gold on the electrode surface without modification [peak 3 (1.374 V)]. Therefore, the oxidation potential of the nanostructured surface is lower than that of the unmodified surface. Potentials of gold ionization from gold surface are similar for modified and unmodified electrodes; hence, oleylamine does not act as an inhibitor. Therefore, increase in the effective surface of the modified electrode is caused by the treatment with Meerwein's reagent.

Thus, a treatment method with the use of Meerwein's reagent has been developed for the activation of surfaces modified with nanostructures obtained by an oleylamine method. These nanostructures can be used for electrochemical measurements in aqueous solutions.

References

1 *Problemy analiticheskoi khimii (Problems of Analytical Chemistry), Vol. 14. Khimicheskie sensory (Chemical Sensors)*, ed. Yu. G. Vlasov, Nauka, Moscow, 2011 (in Russian).
2 E. B. Namdas, M. H. Tong, P. Ledochowitsch, S. R. Mednick, J. D. Yuen, D. Moses and A. J. Heeger, *Adv. Mater*., 2009, **21**, 799.
3 Zh. Gao, J. C. Yang, J. Ji, J. M. Hogle, D. N. Larson, H. Liu and X. Zhang, *Photonics and Nanostructures – Fundamentals and Applications*, 2010, **8**, 131.
4 A. Kisner, M. Heggen, E. Fernández, S. Lenk, D. Mayer, U. Simon, A. Offenhäusser and Yu. Mourzina, *Chem. Eur. J*., 2011, **17**, 34.
5 A. Kisner, S. Lenk, D. Mayer, Yu. Mourzina and A. Offenhausser, *J. Phys. Chem. C*, 2009, **113**, 20143.
6 C. Wang, Y. Hu, C. M. Lieber and S. Sun, *J. Am. Chem. Soc*., 2008, **130**, 8902.
7 A. Halder and N. Ravishankar, *Adv. Mater*., 2007, **19**, 1854.
8 R. Nickerson, *Plasma Surface Modification for Cleaning and Adhesion,* AST Products, Inc., Billerica, MA.
9 E. L. Rosen, R. Buonsanti, A. Llordes, A. M. Sawvel, D. J. Milliron and B. A. Helms, *Angew. Chem. Int. Ed.*, 2012, **51**, 684.
10 S. Pud, A. Kisner, M. Heggen, D. Belaineh, R. Temirov, U. Simon, A. Offenhäusser, Yu. Mourzina and S. Vitusevich, *Small*, 2013, **9**, 846.
11 M. Yu. Ziangirova, M. S. Kotelev, G. S. Skorikova, E. V. Ivanov, L. T. Perelman and V. A. Vinokurov, *Mendeleev Commun.*, 2014, **24**, 53.
12 E. K. Beloglazkina, A. G. Majouga, R. B. Romashkina, N. V. Zyk and N. S. Zefirov, *Russ. Chem. Rev*., 2012, **81**, 65.

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