Catalytic oxidation of glucose on gold nanoparticles in neutral pH

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Abstract

We have demonstrated the importance of stabilizing on the catalytic activity towards glucose oxidation of gold nanoparticles which is dependent on the active metal surface. For this purpose we prepare gold nanoparticles stabilized with oleyl amine (AuNPs-OLA) and compare them with phosphomolybdate-capped gold nanoparticles (AuNPs-PMo$_{12}$). The electrochemical oxidation of glucose on glassy carbon electrode modified with these gold nanoparticles has been studied in phosphate buffer (pH=7.4) on glassy carbon electrodes. Under these conditions AuNPs-PMo$_{12}$ are more active in catalytic process than AuNPs-OLA. This is caused by poorly conductive nature of oleyl amine where the amine molecules stabilize the particles nearly covalently and they form densely packed shell on surface of gold nanoparticles blocking metal active sites. The gold nanoparticles will be also subjected to physical characterization, like Spectrophotometry UV-VIS and Transmission Electron Microscopy (TEM) to verify their structure and morphology.

Chemistry, biology and life science
Inorganic and analytical chemistry / electrochemistry / electrocatalysis.

General information

The nanometer size metal nanoparticles exhibit an unique reactivity in comparison to the bulk metal [1]. The functionalization provides nanoparticle stability through preventing their agglomeration [2,3]. The chemical and physical properties of gold nanoparticles are dependent on their size, shape and stabilizing agents [1,3,4,5]. Gold nanoparticles seem to be attractive catalytic material for glucose electrooxidation where during the reaction electrons released [6]. Thus the glucose electrooxidation has been the subject of numerous studies due to their potential application as glucose sensors and biosensors [7,8,9] in the field of medicine and biofuel cells [10,11].

The mechanism of glucose electrooxidation suggested by Hsiao [12,13], Adzic [12,13] and Makovos [14] occurs through different pathways on different gold catalytic surfaces and is not fully unequivocal. If the interaction between glucose and the gold electrode is relatively weak the mechanism can be as follows. The first step of the glucose electrochemical oxidation is formation of $(OH)_{ads}$ species on gold. The second step involves the oxidation of the hydrogen atom from the hydroxyl group bounded to the C_1 carbon atom of the glucose substrate. Free radical species are formed and one electron is transferred to the electrode. The radical species are further oxidized by the removal of residual hydrogen atom. During this process second electron is transferred to the electrode substrate with gluconolactone formation. The last step involves the hydrolysis of gluconolactone to form sodium or potassium gluconate in phosphate buffer [12].

Catalytic properties of small gold nanoparticles are related to the high surface-to-volume ratios and so called quantum-size effects generated by electrons confined within a small volume. Smaller nanoparticles exhibit higher surface area improving the

substrate accessibility to the catalytic active site of Au [1,4]. Influence of the shape is mainly related to different crystallographic facets. From the three low index surfaces of gold Au (110), Au (111) and Au (100) the last surface is more active in the electro-oxidation of glucose than the other two low index planes [12,13].

An important function of organic molecules adsorbed on the (Au) particles is prevention of their agglomeration which is an undesirable effect leading to decrease of their catalytic activity. The impact of the stabilizing agents on catalytic properties of AuNPs is associated with the type of interaction between gold cores and ligands. One of the most important problems related to the application of organic capping layers such as aliphatic amines or alkanothiolates in the electrocatalysis are their insulating (dielectric) properties which decrease the conductivity of the catalytic layers. This usually results in an inhibition of electrocatalytic process. Moreover dense robust organic monolayers are known to be strongly poisoning agents due to their irreversible chemisorption on the active sites of metallic catalysts [1,9,15]. Significant enhancement in the electrocatalytic activity of AuNPs may be achieved by immobilizing them on stable, highly conductive supports such as chemically functionalized carbon nanotubes. The carbon materials will additionally prevent gold nanoparticles agglomeration. The chosen carbon nanotubes provide porosity and high real surface area which will facilitate glucose transport to active sites affecting the kinetics of the electrooxidation process [4,6,16].

Experimental

The oleyl amine-stabilized gold nanoparticles (AuNPs-OLA) were prepared according to single-phase procedure given in the literature [17]. The whole synthesis was carried out in water. The oleyl amine plays a role of reducing and stabilizing agent. By the mixing of proper amount of $HAuCl_4$ (10^{-3} M) and oleyl amine (10^{-3} M) at temperature of 80°C the nanoparticles AuNPs-OLA of desired sizes were produced.

Multiwalled carbon nanotubes (MWCNTs) supported oleyl amine-stabilized gold nanoparticles (MWCNTs/AuNPs-OLA) were prepared according to procedure described by Skunik et al. [18]. Shortly, to purify the MWCNTs were boiled in 12 M HCl solution for 1 h, followed by treatment with 3 M HNO_3 for 8 h at reflux. Then to dry powder of functionalized MWNTs the 2 ml AuNPs-OLA solution was added and the suspension was mixed for 12 h and then left to dry. The resulted MWCNTs/AuNPs-OLA powder was annealed treated at 600°C under the flow of reducing gases (H_2/Ar) for 2 h.

The phosphomolybdate-modified gold nanoparticles were prepared following the procedure reported by Zoladek et al. [19] that involved reaction between partially reduced phosphomolybdate heteropolyblue and the gold precursor ($HAuCl_4$).

Electrochemical experiments were carried out with CH Instruments Model 6016 B (Austin, USA) workstation in conventional three-electrode cell. Glassy carbon electrode (GC) of geometric area 0.071 cm^2 was used as a working electrode. The counter and the reference electrode were graphitic wire and saturated calomel electrode (SCE, Hg/Hg_2Cl_2/KCl (saturated)) respectively. The morphology of AuNPs-OLA, AuNPs-PMo_{12} and MWCNTs/AuNPs-OLA600 were verified by transmission electron

microscopy (Philips CM10 microscope). UV-VIS absorption spectra of the aqueous Au colloidal suspension AuNPs-OLA and AuNPs-PMo$_{12}$ were recorded using Lambda 25 spectrophotometer from Perkin Elmer.

Measurements were performed in phosphate buffer, pH=7.4. The aqueous solutions were prepared using triply distilled deionized (Millipore Milli-Q) water.

Results and discussion

The nanostructural size of prepared gold nanoparticles was confirmed on the UV-VIS spectra. The strong transverse plasmon absorption band with the maximum of the peak located at about 527 nm for AuNPs-OLA (Fig. 1A) and about 529 nm for AuNPs-PMo$_{12}$ (Fig. 1B) may be associated to the collective oscillations of the free electrons at the surface of the nanostructural gold. The slight shift of the maximum of the peak to higher wavelengths for AuNPs-PMo$_{12}$ may be associated to the higher diameter of these nanostructures in comparison to AuNPs-OLA. Moreover, when the nanoparticles concentration is increased 10 times location of the surface plasmon response maximum of AuNPs-OLA was not changing while for AuNPs-PMo$_{12}$ it shifts to higher wavelengths suggesting the decreasing distance beetwen particles (data not shown). Those results indicate that on the surface plasmon response of gold nanoparticles AuNPs-PMo$_{12}$ affect both changes in concentration and as well the local environment. The colloidal suspension AuNPs-OLA was stable for few months.
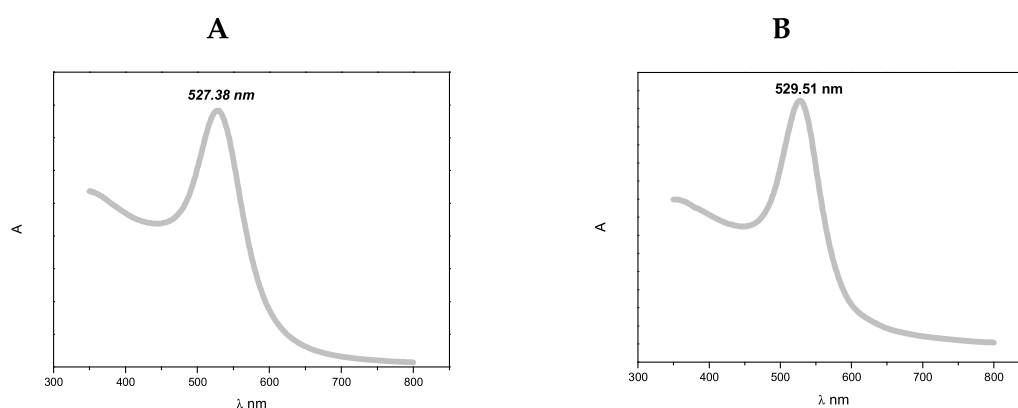

Fig. 1. UV-VIS spectra of (A) AuNPs-OLA, (B) AuNPs-PMo$_{12}$.

Therefore the morphology of resulting nanoparticles was verified with TEM images. The AuNPs-OLA and AuNPs-PMo$_{12}$ nanoparticles were seen on TEM images (Fig. 2 (A) and (B), respectively) as highly dispersed, spherical dark spots of diameters on the level of 30 nm for AuNPs-OLA and well dispersed spherical, hexagonal and subtriangular spots of AuNPs-PMo$_{12}$ of approximate size of 40 nm.
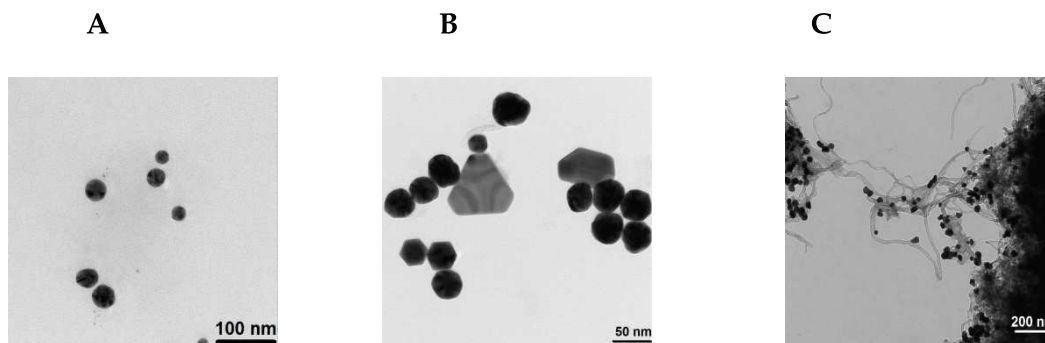
A   B   C

Fig. 2. Representative TEM images of (A) AuNPs-OLA, (B) AuNPs-PMo$_{12}$, (C) MWCNTs/AuNPs-OLA600.

TEM images for MWNTs/AuNPs-OLA600 are consistent with the uniform distribution of gold nanoparticles of the sizes about 40 nm uniformly distributed on the MWNTs surface. Moreover, the material characterise porous structure facilitating mass transfer to the metal active sites that in turn affect on improved catalytic activity.

As the voltammetric response of AuNPs-OLA/GCE registered in the potential range from -0.54 V to 0.8 V in 0.1 M phosphate buffer in presence and absence of 50 mM glucose shows, evidently the oleyl amine stabilized gold nanoparticles have not been active towards glucose electrooxidation (Fig. 3A). Nevertheless, a small characteristic cathodic peak of Au oxides reduction has been observed at potential about 0.5 V. The postulated stabilization of gold surface with oleyl amine trough nearly covalently bond by its amine group [17] may sufficiently block the access to catalytic centers. Even the polarization of AuNPs-OLA/GC electrode to the potential as high as 1.4 V has not cause the modifier desorption. Therefore to remove the deactivating stabilizing shell, the AuNPs-OLA nanostructures were heat treated in the reducing atmosphere (2 h/600°C/(Ar/H$_2$)). To prevent the agglomeration of the AuNPs-OLA centers during annealing the nanostructures were firstly immobilized at the walls of functionalized multi-walled carbon nanotubes.

However, the voltammetry curves of MWCNTs/AuNPs-OLA600 recorded in 0.1 M phosphate buffer in the absence of glucose do not show the typical AuO$_x$ reduction processes at about 0.5 V (Fig. 3B) it show catalytic activity towards glucose electrooxidation (Fig. 3C). The oxidation process starts at considerably low potential of -0.1 V vs. SCE and reaches maximum at 0.2 V. On the reverse potential scan the peak of 1.4 times higher current density in its maximum was registered. In opposite to AuNPs-OLA the active centers of AuNPs-PMo$_{12}$ nanoparticles were not blocked. The polyoxometalates undergoes irreversible chemisorptions at the gold surface where multicenter redox mediator interact through oxygen atoms [19,20]. The strong electrostatic interaction between chemisorbed polyoxometalates prevents nanoparticles agglomeration where only part of their surface is covered with modifier. In neutral aqueous solutions polyoxometalate undergoes decomposition by hydrolysis and can be easily removed without annealing process. The voltammetric response of AuNPs-PMo$_{12}$ layer registered in 0.1 M phosphate buffer shows at potential about 0.5 V the peak which may be associated with reduction of gold oxides. Moreover, at potentials about 0.35 V a pair of peaks was observed which are related of the formation of AuOH layer at the surface of Au(111) [12,13]. In comparison to MWNT/AuNPs-OLA material

the electrooxidation of glucose is shifted negatively (Fig. 3E) but reaches maximum at the same potential. The anodic pre-peak that appear at potential -0.2 V is characteristic for Au(111) [12].

A

B   **C**

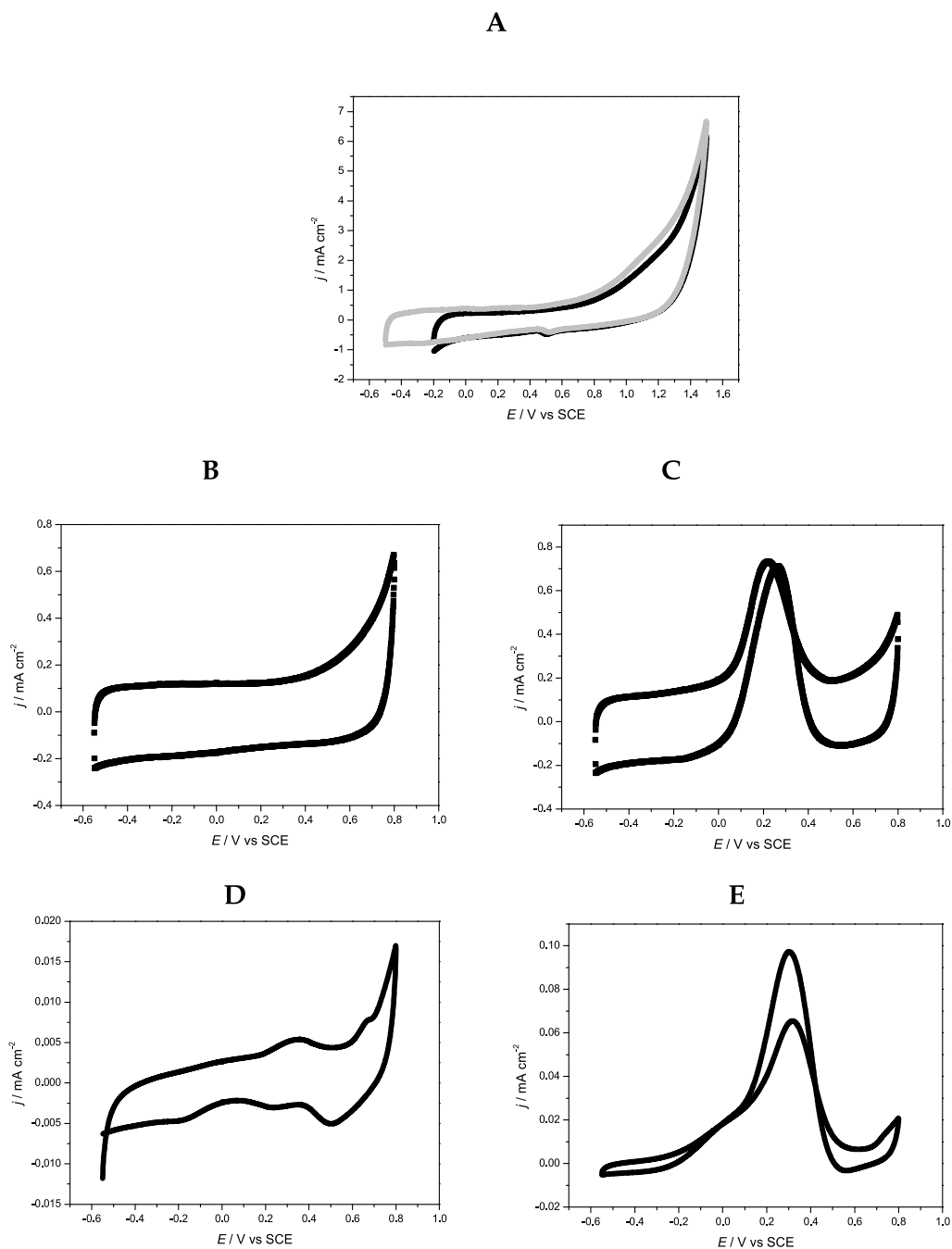**D**   **E**

Fig. 3. Cyclic voltammetry responses in phosphate buffer of (A) AuNPs-OLA in absence of glucose (black curve) and in 50 mM solution of glucose (grey curve), (B) MWNTs/AuNPs-OLA and (D) AuNPs-PMo$_{12}$ in absence of glucose, (C) MWNTs/AuNPs-OLA and (E) AuNPs-PMo$_{12}$ in 50 mM glucose solution.

Partial removal of amine from gold surface resulted in appearance catalytic properties. Removal of organic stabilizing ligands from Au facilitates diffusion to the active centers on gold surfaces.

AuNPs-PMo$_{12}$ show catalytic properties towards glucose electrooxidation. The stabilizing shell is easily removed by hydrolysis in neutral solutions. According to this procedure the catalytic active centers on gold surface are unblocked.

Conclusion

In present work we presented novel materials comprising gold nanoparticles for glucose electrooxidation. Using two different methodologies and stabilizers the gold nanoparticles of diameter in the range 30-40 nm were prepared. Nevertheless the gold modifier has affected greatly their catalytic activity. The Au-PMo$_{12}$ nanostructures were active temselved towards glucose electro-oxidation while the Au-OLA had required the activation procedure.

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