



Electrocatalytic glucose oxidation at gold and gold-carbon nanoparticulate film prepared from oppositely charged nanoparticles



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ABSTRACT

Electrocatalytic oxidation of glucose was studied at nanoparticulate gold and gold-carbon film electrodes. These electrodes were prepared by a layer-by-layer method without application of any linker molecules. Gold nanoparticles were stabilized by undecane thiols functionalized by trimethyl ammonium or carboxylate groups, whereas the carbon nanoparticles were covered by phenylsulfonate functionalities. The gold nanoparticulate electrodes were characterized by UV-vis and XPS spectroscopy, atomic force microscopy and voltammetry, before and after heat-treatment. Heat-treatment facilitates the aggregation of the nanoparticles and affects the structure of the film. The comparison of the results obtained with film electrodes prepared from gold nanoparticles with the same charge and with gold-carbon nanoparticulate electrodes, proved that positively charged nanoparticles are responsible for the high electrocatalytic activity, whereas negatively charged ones act rather as a linker of the film.

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1. Introduction

There is an increasing popularity of metallic nanoparticulate films as electrode materials for electrocatalysis [1]. Among them are electrodes modified with gold nanoparticles (AuNPs) [2] or nanoporous gold [3], utilizing the catalytic properties of gold [4]. These electrodes exhibit large electrochemically active surface, good electronic communication with enzymes and relatively easy functionalization [1,5,6].

There are two main strategies of preparation of Au nanoparticulate films. One involves direct preparation of the nanoparticles on the electrode surface by electrodeposition [7], seed mediated growth [8] or dealloying [9]. An alternative strategy involves immobilization of already synthesized nanoparticles. In this bottom up approach [10] they are employed as a building blocks of three dimensional structures prepared by layer-by-layer method [10–12]. If the nanoparticles are stabilized by charged functional groups, polymers bearing oppositely charged functionalities can be used as a linker. However, this strategy generates matrix effect, restricting substrate access to the electroactive surface. In another approach the polymeric linker can be replaced by nanoparticles stabilized by functionalities with the opposite charge [13–15]. Following this strategy, one [16,17] and two [18–21] components

nanoparticulate film electrodes were prepared, for example consisting gold nanoparticles [16] or gold and carbon nanoparticles [18]. The superiority of this approach was recently demonstrated for bioelectrocatalysis at silicate-carbon nanoparticulate film electrode [21].

Here we report the preparation and spectroscopic and electrochemical characterization of nanoparticulate film electrodes prepared from oppositely charged AuNPs stabilized by thiols undecane alkyl chains capped by trimethylammonium (AuNPs⁺) or carboxylic (AuNPs⁻) groups. Electrocatalytic glucose oxidation was selected as a model reaction, because is catalysed by AuNPs [16,22–24]. Moreover, its importance for gluconic acid production [25,26], energy generation in glucose biofuel cells [27,28] or sensing [29,30] cannot be overestimated. We will show that high electrocatalytic activity of the film results from the presence of trimethylammonium functionalized gold nanoparticles, whereas oppositely charged carboxyl functionalized nanoparticles act as linkers. Therefore, the negatively charged gold nanoparticles can be replaced by negatively charged carbon nanoparticles (CNPs⁻) without considerable loss of electrocatalytic activity.

2. Experimental

2.1. Chemicals and materials

KOH and α -D-glucose were purchased from Sigma-Aldrich. H₂SO₄ was obtained from Chempur. Ru(NH₃)₆Cl₃ was from Strem

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Chemicals Inc. $K_3Fe(CN)_6$ and NaOH were from POCH and $NaClO_4$ was from Fluka. Indium tin dioxide (ITO) coated glass plates (surface resistivity 15–30 Ω) were obtained from Delta Technologies Ltd., USA. Water was filtered and demineralized with ELIX system (Millipore). Argon (99.99%) was supplied by Multax.

AuNPs+ and AuNPs- were synthesized following the procedure described earlier [31]. They are stabilized by N,N,N trimethyl(11-mercaptoundecyl)ammonium chloride or 11-mercaptoundecanoic acid respectively. Their diameters, estimated by dynamic light scattering, are 7.24 ± 1.39 nm and 7.35 ± 1.96 nm for AuNPs+ and AuNPs- respectively. For electrode modification they were suspended (0.06 mg dm^{-3} AuNPs+ and 0.16 mg dm^{-3} AuNPs-) in methanol.

CNPs- (ca. 7.8 nm mean diameter, Emperor 2000) with phenyl sulphonate functionalities were supplied by Cabot Corporation (Dunkinfield, United Kingdom). They were also used for preparation of positively charged carbon nanoparticles (CNPs+) [32]. CNPs- or CNPs+ suspensions were obtained by mixing 3 mg of nanoparticles with 1 ml of water followed by 30 min of sonication [33].

2.2. Film electrode preparation

ITO substrates were cleaned with ethanol, deionized water and heated in tube furnace (Barnstead International) at 500°C for 30 min to remove impurities. Next, they were alternately immersed into AuNPs+ and AuNPs- suspensions for 5 s. After each withdrawal from suspension the substrate was dried in air and immersed for 5 s in methanol to remove weakly bonded AuNPs. For simplicity, the whole described procedure will be called one immersion step. These immersions were repeated three, six, nine and twelve times and the obtained electrodes and named as AuNPs+/AuNPs-(3), AuNPs+/AuNPs-(6), AuNPs+/AuNPs-(9) and AuNPs+/AuNPs-(12), respectively. Other electrodes were prepared by consecutive immersions in AuNPs+ or AuNPs- suspensions to obtain films consisting of nanoparticles with the same charge and they will be marked as AuNPs+(n) or AuNPs-(n), where n denotes number of immersion steps. Some of these electrodes were heated at 300°C in a tube furnace for 30 min under air atmosphere. Another class of electrodes were prepared by alternate immersions in AuNPs+ and CNPs- suspensions or AuNPs- and CNPs+ suspensions for 5 s. These electrodes are marked as AuNPs+/CNPs-(n) or AuNPs-/CNPs+(n), where $n = 3, 6, 9$ or 12. For electrochemical experiments each electrode surface (0.2 cm^2) was defined by masking with scotch tape. A piece of copper tape assured good electrical contact.

2.3. Instrumentation and cell

UV-Vis spectroscopy of the nanoparticulate films was carried out with Thermo Evolution 300 UV-Vis Spectrophotometer. Spectra were collected over the range of 400–800 nm. X-Ray photoelectron spectroscopy (XPS) measurements were carried out using ESCALAB-210 Spectrometer (VG Scientific). The instrument uses a focused monochromatic Al K_{α} X-ray (1486.6 eV) source for excitation. Scanning electron microscopy (SEM) was performed with a Zeiss Ultra Plus Field Emission microscope. Atomic force microscopy (AFM) was done with a MultiMode Scanning Probe Microscope (Veeco) in ScanAsyst mode using tips from Bruker. For determination of the film thickness part of the film was scratched with the tip of a needle in order to remove a part of a film and uncover bare ITO surface [16,33].

Cyclic voltammetry (CV) with film electrodes was done with an Autolab (Metrohm Autolab) electrochemical system with dedicated software in a conventional three electrode cell. Modified ITO, platinum wire ($d = 0.5$ mm) and $Ag|AgCl|KCl_{\text{sat}}$ were used as the working, counter and reference electrodes, respectively.

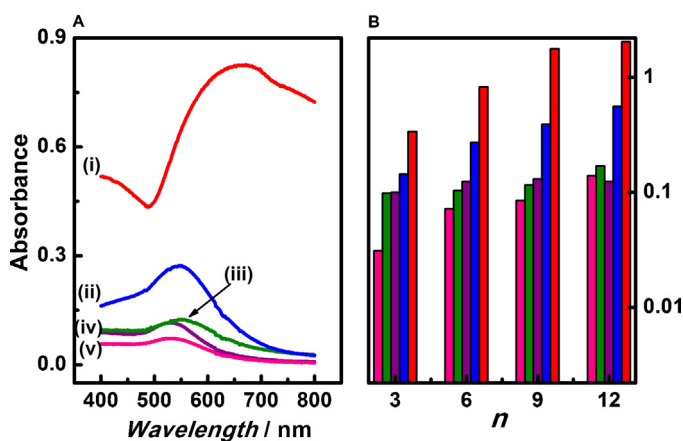


Fig. 1. (A) UV-Vis absorption spectra of AuNP+/AuNPs-(6) electrodes after (i) and before (ii) heat-treatment and of AuNP-(6) (iii) and AuNPs+(6) (iv) electrodes and of AuNP+/AuNPs-(6) electrodes prepared from diluted suspension. The staple diagram (B) shows dependence of the maximum absorbance and the number of immersions (n) for AuNPs+/AuNPs-(n) electrodes after heat-treatment (red) and before heat-treatment (blue) and of AuNPs+(n) (violet), AuNPs-(n) (green) and of AuNP+/AuNPs-(n) electrodes prepared from diluted suspension (pink).

All electrochemical experiments were carried out at $22 \pm 2^\circ\text{C}$. Before measurements solutions were deaerated with argon (5.0 N) from Multax.

3. Results and discussion

3.1. UV-Vis spectroscopy and XPS analysis

The obtained Au nanoparticulate films have pink-violet colour, which is typical for Au nanoparticles. For larger number of immersions the colour intensity increases. After heat-treatment the colour changes to blue with a faint golden shine. The intensity of the colour increases with the number of immersions into the AuNP suspensions. On the spectra of the AuNPs+/AuNPs-(n) films one can see the surface plasmon resonance (SPR) band signaling the nanoparticulate structure. For example a strong SPR band at 545 nm is seen on the spectrum of AuNPs+/AuNPs-(6) film (Fig. 1A). It is shifted towards longer wavelength as compared to the value expected for the size of AuNPs used for film preparation. For AuNPs with diameter below 15 nm SPR band is found around 517–520 nm [2]. This indicates some AuNPs aggregation due to electrostatic attraction [2,9]. After heat-treatment of the AuNPs+/AuNPs-(6) film SPR band shifts to 613 nm and its magnitude increases indicating further aggregation of the AuNPs and perhaps removal of functional groups. The increase of the band width may result from broader distribution of the size of the AuNPs after heat-treatment.

The comparison of XPS spectra before and after heat-treatment indicates changes in the AuNPs functionalities. Typically the S 2p band is described by the doublet arising from spin-orbit coupling $2p_{3/2}$ and $2p_{1/2}$ [22]. The energy difference between the larger and the smaller peak and their ratio is expected to be 1.18 eV and 2:1 respectively [34]. Here (Fig. 2) bands are observed at 161.56 eV and 163.85 eV are the lower peaks assigned to the S^{2-} form of sulfur and thiolate species, respectively. After heat-treatment the formation of a new band is seen at 168.98 eV (Fig. 2B). It is connected with the oxidation of thiolate and generation of sulfonate species [22].

A tenfold dilution of the AuNPs suspensions used for preparation of the AuNPs+/AuNPs-(6) film causes a shift of the SPR band to 525 nm (Fig. 1A) and a decrease of its magnitude (Fig. 1B). This points to smaller degree of nanoparticle aggregation and a smaller amount of deposited material. The maxima of SPR bands of the films obtained from only positively

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