



# The effect of electrocatalytic nanoparticle injection on the electrochemical response at a rotating disc electrode



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## ABSTRACT

A new approach to study electrocatalytic oxidation of glucose is proposed. As opposed to numerous studies on electrodes modified with gold nanoparticles this reaction was studied in their suspension of gold nanoparticles under hydrodynamic conditions on a noncatalytic glassy carbon rotating disc electrode. It has been shown that addition of nanogram amount of positively charged Au nanoparticles results in a clear current response, whereas no clear response is seen for negatively charged ones. This effect results from the electrocatalytic oxidation of glucose on Au nanoparticles mainly adsorbed on glassy carbon electrode. The role of electrode preparation method on reproducibility of the results is emphasized.

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## 1. Introduction

The electrocatalytic properties of nanoparticles (NPs) deposited on the electrode surface are already well recognized [1–3]. Apart of their intrinsic properties, their catalytic action depends very much on the electrode architecture. On the other hand, when they are suspended in solution, the electrocatalytic process occurs only when moving NPs hit the non-catalytic electrode surface allowing for electron transfer [4–7]. Typical experiments were performed in quiescent suspension, when transport of both catalytic NPs and the substrate is governed by diffusion. This results in a low signal to noise ratio, even in concentrated substrate solutions. However, the observation of single electrochemical events in these experiments has already been claimed (see for example [4–7]).

The rotating disc electrode (RDE) is a well established tool for electrode process studies – including catalytic ones [8]. It was frequently applied for the characterization of electrocatalytic activity of nanoparticle modified electrodes [9–11]. Here we will show that addition of nanogram portions of catalytic nanoparticles leads to appearance of catalytic current at inert RDE. RDE experiments in suspension of particles were already reported [12–20]. The effect of inert particles' suspension on electrochemical redox reactions on RDE becomes significant only at their relatively high concentration [12–16]. Metallic and/or metal oxide nanoparticles' suspensions were employed as a source of material in metal electrodeposition at RDE [17–20].

Here we will present the effect of addition of catalytic, namely gold nanoparticles (AuNPs) on the RDE response. As a substrate glucose was selected because of recent numerous studies of its electrocatalytic oxidation on AuNP modified electrode [2,21–23] and it was not yet studied in suspension of nanoparticles. In this study glassy carbon (GC) was selected as inert electrode, whereas suspension electrocatalytic nanoparticles was added to the cell during the experiment.

## 2. Experimental

### 2.1. Chemicals and materials

NaOH and  $\alpha$ -D-glucose (99.5 + %) were obtained from Sigma-Aldrich. HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub> (all p.a.) were from Chempur. Water was filtered and demineralized with an ELIX system (Millipore).

Positively (AuNPs+) and negatively (AuNPs-) charged nanoparticles were synthesized following an earlier described procedure [24]. They are stabilized by 1-(11-mercaptoundecyl)-ammonium and 11-mercapto-1-undecane acetate functionalities. Their diameters estimated by DLS method are  $7.2 \pm 1.4$  nm (AuNPs+) and  $7.4 \pm 2.0$  nm (AuNPs-). They were suspended ( $0.06 \text{ mg dm}^{-3}$  AuNPs+ and  $0.16 \text{ mg dm}^{-3}$  AuNPs-) in methanol.

### 2.2. Instrumentation cell and procedures

Cyclic voltammetry and chronoamperometry were performed with a BioLogic SP-300 (Bio-Logic Science Instruments) electrochemical system with dedicated EC-Lab software v.10.19 in a conventional three electrode cell. GC electrode ( $0.07 \text{ cm}^2$ , ALS) mounted at Rotating

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Ring Disk Electrode Rotator – RRDE-3A (ALS) was used as working electrode. The reported current density was calculated per projected area. Special attention was paid to GC electrode cleaning procedure to remove traces of AuNPs after the experiment. Even after standard polishing with 1, 0.3 and 0.05  $\mu\text{m}$  alumina particles (Buehler) on wet cloth some anodic current at potentials above 0.0 V is seen on voltammogram, perhaps due to glucose oxidation on AuNPs still adsorbed on GC surface. Only cycling of the electrode in diluted aqua regia (0.1 M HCl and 0.32 M HNO<sub>3</sub>) in potential range 0.3–1.05 V [25] with scan rate 0.1 V s<sup>-1</sup> followed by polishing procedure described above provides the absence of this signal. For experiments with AuNP suspension platinum wire ( $d = 0.5$  mm) and Ag|AgCl|KCl<sub>sat.</sub> were used as the counter and reference electrodes, respectively. A suspension of nanoparticles in MeOH was added by micropipette into the solution while the GC electrode was rotating. In some experiments the GC electrode was also deliberately modified with AuNPs + by dropping their suspension on the electrode surface and drying. UV–vis spectroscopy was carried out with UV–vis Spectrophotometer, Thermo Evolution 300.

All experiments were carried out at  $22 \pm 2$  °C. The solution was saturated with argon during the experiments. SEM and EDX analysis was performed with a Nova NanoSEM 450 microscope with EDX detector from Edax.

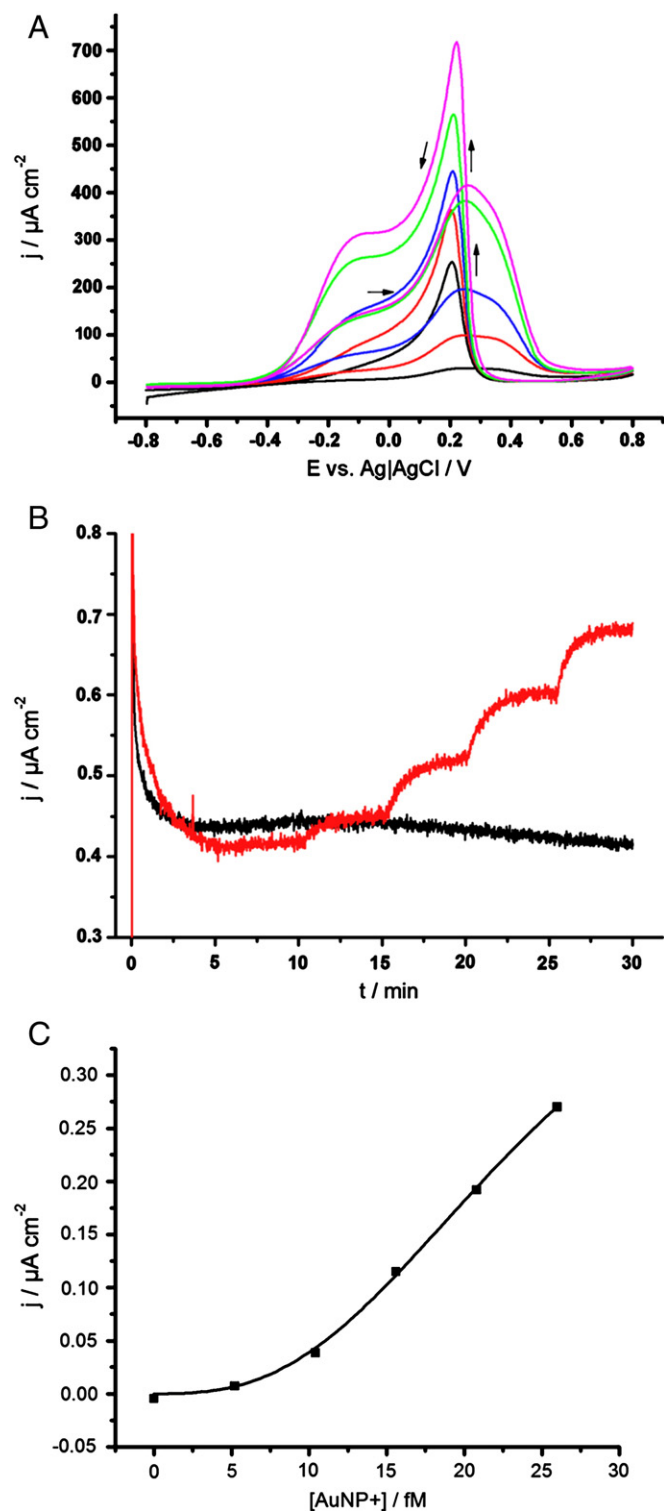
### 3. Results and discussion

#### 3.1. Electrooxidation of glucose in suspension of Au nanoparticles

On the voltammogram recorded in 37.3 ng dm<sup>-3</sup> AuNP + suspension (AuNP concentration is equal to final concentration in experiment described below) in glucose alkaline solution (Fig. 1A) one can find typical features of glucose voltammetry on gold. They include current increase during anodic sweep with onset potential at c.a. -0.45 V followed by oxidation peak with maximum at c.a. 0.22 V. They correspond to oxidation of dehydrogenated adsorbed glucose to gluconolactone and oxidation of gluconolactone respectively [23,26,27]. The most pronounced peak in cathodic sweep was attributed to oxidation of glucose at new active sites formed after reduction of gold oxide [23]. The increase of the current during experiment is especially visible, if one compares voltammograms recorded at the beginning and the end of experiment at the same rotating speed (3000 rpm) (Fig. 1A).

The addition of five 18  $\mu\text{L}$  portions of AuNP + suspension (each portion contained 1.08 ng nanoparticles) to the cell results in stepwise increase of the current recorded at potential 0.2 V corresponding to glucose oxidation, whereas in the case of AuNPs – no current increase is observed (Fig. 1B). This indicates that only positively charged Au nanoparticles exhibit catalytic activity towards glucose oxidation. Interestingly no signal is observed, when potential is set at -0.2 V. This result also shows that 1 ng of AuNPs + can be easily detected. The effect of charge may result from favourable electrochemical adsorption of glucose molecule formed by dehydrogenation reaction due to its delocalized negative charge at positively charged nanoparticles [27]. Importantly, blank experiment – stepwise addition of AuNPs + in the absence of glucose – does not produce any oxidation current indicating no contribution of gold oxide formation. The possible aggregation during the vigorous mixing [30] can be ruled out, because no significant change of position and magnitude of SPR band is observed after 1 h of mixing.

The magnitude of the current steps after the first three additions of AuNPs + suspension is increasing. The last three additions produce similar current steps of c.a.  $0.07 \mu\text{A cm}^{-2}$  (Fig. 1B). The total increase of the current is equal to c.a.  $0.3 \mu\text{A cm}^{-2}$ . This path is always observed even in some experiments the current magnitude is smaller, reaching only c.a.  $0.15\text{--}0.2 \mu\text{A cm}^{-2}$ , what perhaps results from its sensitivity on the electrode surface state. The smaller magnitude of first two current steps is rather not caused by the effect of the background current, because experiments with longer initial delay time (15 min, not shown) bring



**Fig. 1.** (A) Cyclic voltammograms recorded with scan rate  $0.02 \text{ V s}^{-1}$  at GC RDE (3000 rpm) in 0.2 M glucose solution in 0.05 M aqueous NaOH after addition of 56  $\mu\text{L}$  of AuNPs + suspension in MeOH, recorded subsequently with different rotating speeds 3000 (black), 2000 (red), 1000 (blue), 500 (green) and again 3000 (magenta) rpm. For clarity scan direction was marked only at magenta curve. (B) Current–time curve obtained at 0.2 V at GC RDE (3000 rpm), in 0.2 M glucose solution in 0.05 M aqueous NaOH with five stepwise additions of 18  $\mu\text{L}$  AuNP + (red curve) and AuNP – (black curve) suspension. (C) Step plateau current densities (points) normalized to the current density just before first addition together with a fit to a Hill type isotherm (see text).

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