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Morphology of Gold Nanoparticles and Electrocatalysis of Glucose Oxidation

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Abstract

The shape-dependent activity of gold nanoparticles (AuNP) was studied by testing them as electrocatalysts for the notoriously slow non-enzymatic oxidation of glucose in neutral solutions. The AuNP of spherical and irregular (including polyhedral) morphologies were synthesized and attached to glassy carbon electrodes with chitosan. Voltammetric and mass spectrometric studies showed that the irregular AuNP were more catalytically active toward the oxidation of glucose to gluconic acid. No obvious differences between both morphologies were found based on their X-ray diffraction patterns and HRTEM images suggesting that the crystallographic orientation alone did not account for their catalytic properties. While both morphologies contain the (111) crystallographic planes that are catalytic toward glucose oxidation, the better activity of irregular AuNP was ascribed to a higher surface density of incipient gold oxide acting as a fast redox mediator for glucose oxidation. Supporting this, the AuNP of both morphologies oxidized glucose after their anodic activation, although not to the same extent. The amperometric (0.30 V) determination of glucose at electrodes made of irregular AuNP yielded a wide linear calibration plot (0.20–110 mM; R^2 , 0.998), sensitivity of $66 \mu\text{A M}^{-1} \text{cm}^{-2}$, limit of detection of $100 \mu\text{M}$ (S/N, 3), and a response time below 5 s. The advantage of low-cost irregular AuNP over macro gold is that they are catalytic toward glucose oxidation without any need for prior activation.

Graphical abstract

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Keywords

HEPES gold nanoparticles; morphology-dependent electrocatalysis; irregular vs. spherical morphology; oxidation of glucose in neutral solutions

1. Introduction

Recently, there has been an explosion of interest in the dependence of the optical, magnetic, and electronic properties of metal nanoparticles on their morphology (size and shape). Such dependence has been explored in photonic, therapeutic, diagnostic, photovoltaic, and catalytic applications [1,2]. In the present work, we investigate gold nanoparticles (AuNP) with different morphologies as electrocatalysts for the non-enzymatic oxidation of glucose at physiological pH 7.40.

The oxidation of glucose is important in the development of glucose sensors for monitoring diabetes, glucose fuel cells for powering medical implants, and reactors for the synthesis of specialty chemicals (e.g. gluconic acid) [3,4]. However, in contrast to the enzymatic oxidation, the direct oxidation of glucose in neutral solutions is difficult because of the slow kinetics at carbon electrodes. Several transition metal-based electrodes have been designed, including gold, to facilitate the non-enzymatic oxidation of glucose in neutral solutions [5–16]. In this context, the research with single crystals of gold has shown that their low-index crystallographic planes (e.g. (111), (110), (100)) catalyze the oxidation of glucose [17,18].

Here, we test two hypotheses of the shape-dependent catalytic activity of AuNP.

1. the non-spherical morphology of AuNP should promote the presence of diverse crystallographic surface planes including those with low Miller indices that facilitate the adsorption and oxidation of glucose
2. the non-spherical AuNP with corners and edges should support a higher surface density of gold-oxygen sites acting as redox mediators for glucose oxidation

These hypotheses were tested with irregular AuNP_{HEPES} and mostly spherical AuNP_{CIT} that were prepared by using the HEPES and sodium citrate (CIT), respectively, as reducing agents. The nanoparticles and their properties were studied by using the electrochemistry, X-ray powder diffraction, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and electrospray ionization collision-induced dissociation (ESI-CID) mass spectrometry.

2. Experimental

2.1. Reagents and solutions

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES), sodium citrate, polysaccharide chitosan (CHIT, MW $\sim 1 \times 10^6$ Da; ~ 80 % deacetylation), methanol, and ethanol were purchased from Sigma-Aldrich. The chitosan solution (0.10 wt. %) was prepared by dissolving chitosan flakes in a hydrochloric acid solution and following previously established protocol [19]. All solutions were prepared

using 18-M Ω -cm deionized water that was purified with a Synergy Millipore cartridge system.

2.2. Synthesis of gold nanoparticles (AuNP)

The AuNP_{HEPES} were synthesized by mixing 10.0 mL of 100 mM HEPES solution with 1.0 mL of 10.3 mM HAuCl₄•3HO solution at room temperature. In contrast to literature protocols [20, 21], no pH adjustment was done during the present synthesis. Within 3 min, a color of unstirred mixture changed from light yellow to dark brown. The brown precipitate settled down overnight and the supernatant was removed leaving ~1.0 mL of the concentrated colloidal suspension of AuNP_{HEPES}. The centrifugation was avoided because it caused excessive agglomeration of nanoparticles.

The AuNP_{CIT} were synthesized by following a classical citrate method [22]. The 1.0 mL of 10.3 mM HAuCl₄•3H₂O solution was reacted with 10.0 mL of boiling 120 mM sodium citrate. The mixture was stirred and boiled for 10 min while color changed from light yellow to red. After cooling to room temperature, the mixture was centrifuged at 3,000 rpm for 10 min and supernatant was removed leaving ~1.0 mL of the concentrated colloidal suspension of AuNP_{CIT}.

2.3. Preparation of AuNP_{HEPES} and AuNP_{CIT} electrodes

The electrodes were prepared by mixing a 40- μ L aliquot of AuNP_{HEPES} or 120- μ L aliquot of AuNP_{CIT} suspension with a 15- μ L aliquot of chitosan solution on the surface of a glassy carbon electrode, and evaporating water for 2 h at room temperature. This resulted in a uniform film of chitosan holding gold nanoparticles on the electrode surface.

2.4. Electrochemical measurements

The cyclic voltammetry and amperometry experiments were performed by using a CHI 832 workstation (CH Instruments, Inc.). The measurements were performed in the three-electrode system. The working electrode was a 3.0-mm-diameter glassy carbon electrode that was modified with either AuNP_{HEPES} or AuNP_{CIT}. In control experiments, the bare glassy carbon and gold (2.0-mm diameter) disc electrodes served as working electrodes. The auxiliary electrode was made of platinum wire and the reference electrode was the Ag/AgCl/3MNaCl (Bioanalytical Systems, Inc., BAS). Before their use, the glassy carbon and gold electrodes were wet polished on an Alpha A polishing cloth (Mark V Lab) with successively smaller particles (0.30 and 0.05 μ m diameter) of alumina. The alumina slurry was removed from the electrode surface by sonication in deionized water and methanol.

All experiments were performed at room temperature (21 ± 1 °C) using a pH 7.40 phosphate buffer solution (0.10 M) as a background electrolyte. The experiments were repeated minimum three times and the means of measurements are presented with the relative standard deviation.

2.5. Microscopic and X-ray measurements

The microscopic data were collected with a JEOL 2010F and JEOL 1230 (120 kV) using GATAN digital micrograph. The aliquot of water-suspended gold nanoparticles was placed

onto a formvar-coated copper TEM grid (300 mesh, TedPella Inc.) and dried at room temperature prior to analysis. X-ray spectra of gold nanoparticles were recorded by using a PANalytical Empyrean diffractometer (Cu K α radiation; $\lambda = 0.15418$ nm; step size, 0.0001° ; 2θ linearity $\pm 0.01^\circ$ over the whole angular range) with a standard proportional detector and a PIXcel 3D detector.

2.6. Electrospray ionization mass spectrometric analysis

Before analysis, the electrolyzed glucose solution (500 μ M) was diluted 10-fold with an aqueous solution of methanol (50 % v/v). Gluconic acid standard was prepared using the same mixed solvent. The data were collected on an LTQ-Orbitrap Elite mass spectrometer equipped with a nanospray source (Thermo Scientific) and operated in the negative ionization mode (flow rate, $0.50 \mu\text{L min}^{-1}$; source voltage, 2.2 kV; vaporizer temperature, 180°C ; capillary temperature, 200°C , 60K resolution). The calibration was performed externally using Pierce® ESI Negative Ion Calibration Solution (Thermo Scientific). The mass spectra were an average of 2 minutes of scans with an automatic gain control target of 1×10^6 ions or maximum injection time of 100 ms and were processed using Qual Browser Xcalibur™ 2.2 (Thermo Fisher Scientific Inc.). The m/z 195 peak of gluconic acid was isolated and fragmented by collision-induced dissociation (CID) using 20 eV with a 100 ms activation time.

3. Results and discussion

3.1. X-ray and microscopic characterization of AuNP_{HEPES} and AuNP_{CIT}

The AuNP_{HEPES} were synthesized by using Good's zwitterionic buffer HEPES. The piperazine ring of HEPES generated nitrogen-centered free radicals that reduced gold ions to metallic gold [20]. The ring was also responsible for the adsorption of HEPES on different gold facets, with the weakest binding on the (111) plane [21]. Such a reduction and shape-directing abilities of HEPES allowed synthesizing non-spherical nanoparticles quickly without any need for additional reductants or surfactants.

Figure 1A shows that the reduction of HAuCl₄ with HEPES yielded agglomerated AuNP_{HEPES} that displayed a mixture of different shapes and sizes (15–100 nm diameter). In contrast, the reduction of tetrachloroaurate with citrate resulted in mostly spherical AuNP_{CIT} with a narrower size distribution of 10–15 nm diameter (Figure 1B).

The X-ray diffraction patterns were used to characterize the crystalline structures of AuNP_{HEPES} and AuNP_{CIT}. Figure 2 shows that both types of nanoparticles displayed well defined Bragg peaks corresponding to the reflections from (111), (200), (220), (311) and (222) facets that are characteristic for a face-centered cubic structure of gold. The peak corresponding to the (111) plane was the most intense in both AuNP_{HEPES} and AuNP_{CIT}.

The relative peak intensities did not depend on the method of particle preparation. For example, the intensity ratio of (200) and (111) peaks for the AuNP_{HEPES} and AuNP_{CIT} was the same and equal to 0.29. This value is lower than the standard value for macro gold (0.52) indicating that the (111) plane was the dominant orientation with the same highest fraction in both AuNP_{HEPES} and AuNP_{CIT}. This was further confirmed by the similarity of their

HRTEM images (Figure 3) that show that a prevailing lattice spacing was on average equal to 0.235 nm, which is characteristic for the (111) plane of bulk gold. In summary, no obvious differences were found in X-ray diffraction patterns and HRTEM images of AuNP_{HEPES} and AuNP_{CIT} suggesting that they adopt similar crystallographic orientations.

3.2. Characterization of AuNP_{HEPES} and AuNP_{CIT} electrodes

The electrodes were prepared by attaching gold nanoparticles to glassy carbon electrodes with a film of polysaccharide chitosan. Chitosan was used because it (1) strongly adhered to the surface of glassy carbon preventing the loss of nanoparticles from the electrode surface in stirred solutions, (2) protected nanoparticles from deactivating by the adsorption of impurities from a solution, and (3) provided an inert and electrochemically silent matrix that prevented further agglomeration of nanoparticles on the electrode surface.

The nanoparticle load in a chitosan film on the electrode surface was calculated assuming that HAuCl₄ was completely reduced to Au⁰. It was equal to 81 and 120 µg (±20%) in the AuNP_{HEPES} and AuNP_{CIT} electrodes, respectively. The active surface area of each electrode was determined based on the charge necessary to reduce its gold oxide that was formed by cycling the electrode potential to 0.90 V and using a conversion factor of 400 µC cm⁻² [23]. It was equal to 0.12 and 0.051 cm² (±15%) for AuNP_{HEPES} and AuNP_{CIT} electrodes, respectively. The lower active surface area of AuNP_{CIT} electrode, regardless of its larger nanoparticle load, suggested a lower surface coverage of active gold oxide.

The capacitance of each electrode/solution interface was calculated by dividing the background current that was recorded in the double layer region at 0.30 V by the scan rate. The capacitance of AuNP_{CIT} electrode (569 µF cm⁻², ±15%) was larger than that of AuNP_{HEPES} electrode (225 µF cm⁻², ±15%). Apparently, smaller AuNP_{CIT} could store more electrical charge at the interface than the larger agglomerated AuNP_{HEPES}. The capacitance of both AuNP_{CIT} than AuNP_{HEPES} electrodes was much larger than that of the chitosan-coated glassy carbon (56 µF cm⁻², ±10%) or conventional gold (64 µF cm⁻², ±10%) electrodes. The larger capacitance indicated successful modification of glassy carbon electrodes with gold nanoparticles.

3.3. Voltammetric studies of glucose oxidation at AuNP_{HEPES} and AuNP_{CIT} electrodes

The cyclic voltammograms were recorded in two potential windows starting at -0.20 V and going to either 0.50 or 0.90 V in order to minimize or promote, respectively, the formation of surface gold oxide at higher potentials. Figure 4 shows the voltammograms that were recorded at as prepared AuNP_{HEPES} and AuNP_{CIT} electrodes in the narrower potential window. In the presence of glucose in a solution, the AuNP_{HEPES} electrode displayed a distinct anodic current peak at 0.30 V (Figure 4A, red line a) while the AuNP_{CIT} electrode showed only a minimal response to glucose (Figure 4B, red line b). In a control experiment, the conventional macro gold electrode showed no voltammetric response to glucose (Figure 4C, red line c). When adjusted for the difference in the active surface area of the electrodes, the peak current density at 0.30 V was more than five times larger at the AuNP_{HEPES} (51 µA cm⁻², ±15%) than at AuNP_{CIT} (9 µA cm⁻², ±15%) electrode.

The explanation of higher activity of AuNP_{HEPES} in terms of our first hypothesis is rather problematic. The argument of more catalytic crystallographic orientation of AuNP_{HEPES} is not likely because no obvious differences between AuNP_{HEPES} and AuNP_{CIT} were found in X-ray and HRTEM experiments (*vide supra*). The argument of different surface-capping species (HEPES vs. citrate) is perhaps also not adequate because of the stronger competitive adsorption of polymeric chitosan chains. Indeed, a strong adsorption of chitosan on the surface of nanoparticles has been shown to facilitate their solubilization in water [24]. Also, from the purely geometric argument, the smaller AuNP_{CIT} should be more active considering their higher surface-to-volume ratio and, thus, higher content of coordinatively unsaturated surface atoms of gold.

To explain differences in the catalytic activity of AuNP_{HEPES} and AuNP_{CIT}, we formulated a second hypothesis that considered the presence of gold-oxygen surface sites acting as redox mediators of glucose oxidation. The hypothesis was based on the differences in the background voltammograms of AuNP_{HEPES} and AuNP_{CIT} electrodes (Figure 5). Figure 5 shows that, in contrast to AuNP_{CIT}, the AuNP_{HEPES} electrode displays surface activity in the form of two voltammetric peaks in the double layer region at 0.20 and 0.40 V. The position of the first peak (0.20 V) coincides with the onset of glucose oxidation (Figure 4A, red line a). Such a correlation is typically a mark of the redox mediation by active surface species.

For macro gold electrodes, the redox mediation has been explained in terms of the “incipient hydrous oxide adatom mediator” model [25]. The model postulates that the high-energy surface atoms of gold are oxidized to a hydrous oxide, which mediates the anodic electrode processes. In the extension of this model to gold nanoparticles, we hypothesize that the activity of AuNP_{HEPES} is also due to the redox active sites made of incipient hydrous oxide. We postulate further that the surface coverage of such sites is dependent on the nanoparticle morphology. Apparently, the anisotropic morphology of AuNP_{HEPES} with corners and edges favors the formation of higher density of catalytic gold oxide than the more isotropic morphology of AuNP_{CIT}. This is supported by recent studies, which showed that the kinetics at metal nanoparticles increase with the rising number of surface atoms at the corners and edges [26].

The small response of spherical AuNP_{CIT} to glucose (Figure 4B) indicates that the contribution of a catalytic (111) plane to glucose oxidation is limited in the present case. More important seems to be the presence of surface redox active sites, which are scarce on the surface of AuNP_{CIT} as indicated by a featureless background voltammogram of AuNP_{CIT} electrode (Figure 5, blue line b). Indeed, it has been shown that the surface coverage of gold by the incipient oxide can be as low as a sub-monolayer [27], which is below a detection limit of cyclic voltammetry.

To confirm that the observed catalytic activity was due to the gold and not some impurities, the effects of exposing AuNP_{HEPES} and AuNP_{CIT} electrodes to higher potentials were investigated. Figure 6 shows the cyclic voltammograms that were recorded in a glucose solution at electrodes that were previously cycled ten times between -0.20 and 0.90 V in a glucose-free background solution (traces b). Both AuNP_{HEPES} and AuNP_{CIT} electrodes were activated by such a treatment and displayed a glucose current that was six times larger

than that recorded before their exposure to higher potentials (traces a). One can hypothesize that such anodic activation was caused by the formation of a multilayer gold oxide at >0.50 V and its incomplete reduction at <0.50 V leaving the remnants of incipient hydrous oxide with a higher surface coverage than that on as prepared (not activated) nanoparticles. We have shown a similar activation pattern in the case of macro gold [11]. It should be noted that the anodic activation did not bring the catalytic activity of AuNP_{CIT} to that of AuNP_{HEPES} (Figure 6, traces b). This further underlined the importance of morphology-sensitive surface chemistry of gold nanoparticles in determining their catalytic properties.

The mechanism of glucose oxidation at the incipient gold oxide probably involves a removal of labile C1 hemiacetal hydrogen from a glucose molecule as a rate-determining step on a way to gluconolactone, which finally undergoes hydrolysis to gluconic acid. The involvement of slow removal of hemiacetal hydrogen has been confirmed by isotopic studies [18].

3.4. Amperometric determination of glucose at AuNP_{HEPES} and AuNP_{CIT} electrodes

Figure 7 (line a) shows a typical amperometric trace for the determination of glucose at non-activated AuNP_{HEPES} electrodes. The most interesting is the unusually wide range of linear response to glucose (0.20–110 mM; R^2 , 0.998; inset). The sensitivity of electrode to glucose was equal to $66 \mu\text{A M}^{-1} \text{cm}^{-2}$. The limit of detection was equal to $100 \mu\text{M}$ (S/N, 3) and a response time was below 5 s. Consistent with the voltammetric data, the amperometric responses of AuNP_{CIT} (line b) and conventional macro gold (line c) electrodes to glucose were inadequate for analytical purposes.

The gold electrodes are known to deactivate in the presence of chloride ions in a solution. While the AuNP_{HEPES} electrodes showed such sensitivity to chlorides, they could be used in the presence of physiological concentration of NaCl (0.10 M). Under such conditions, the sensitivity of glucose detection decreased by an order of magnitude; however, the glucose signal remained stable at this lower level. The coating of gold electrodes with Nafion and diluting analyzed samples should further decrease the effects of chlorides on their characteristics.

The response of five different AuNP_{HEPES} electrodes to 20 mM glucose was within $\pm 10\%$ documenting a good reproducibility of electrode preparation. The electrodes retained 80% of the initial glucose current even after 2 h of continuous electrolysis in a vigorously stirred solution of 20 mM glucose. If necessary, their activity could be restored by a brief anodic activation. The electrode shelf life was at least a couple of months. In summary, the AuNP_{HEPES} electrodes are a cost-effective addition to the toolbox of electrochemical detectors for chromatographic analyses.

3.5. Mass spectrometry of electrolyzed glucose solutions

Figure 8A shows the ESI mass spectrum of a glucose solution after a 2-h electrolysis at an AuNP_{HEPES} electrode. The substrate glucose and the final product of electrolysis, gluconic acid, were detected as singly deprotonated ions at m/z 179 and 195, respectively. Other peaks in the mass spectrum were due to common contaminants in the methanol/water solvent and were also detected in the blank. The identity of the gluconic acid as the product

of electrolysis was further confirmed by using collision-induced dissociation of the peak at m/z 195. The almost identical tandem mass spectra of the electrolysis product (Figure 8B) and gluconic acid standard (Figure 8C) positively identified the transformation of glucose to gluconic acid at an AuNP_{HEPES} electrode. Fragment peaks at m/z 177, 159, 129, and 99 were due to the successive loss of 1 and 2 $-H_2O$ and then 1 and 2 $-HCHO$ moieties, respectively [28].

4. Conclusions

The zwitterionic buffer HEPES acted as a reducing and shape-directing agent yielding the irregular morphologies of gold nanoparticles (AuNP_{HEPES}) that facilitated the oxidation of glucose in neutral solutions. The regular spherical morphology of nanoparticles was minimally active toward the glucose oxidation under such conditions. A model of catalytic incipient hydrous oxide that was originally developed for conventional macro gold could explain such behavior. In the nanoparticle version of this model, the irregular morphologies of AuNP_{HEPES} with corners and edges supported a higher surface density of incipient gold oxide that acted as a fast redox mediator for the oxidation of glucose. In contrast to photonic applications that typically require uniform nanoparticles, the electrocatalysis was successfully completed with a batch of AuNP_{HEPES} aggregates of different shapes and sizes. The AuNP_{HEPES} are a cost-effective alternative to the expensive single crystals of gold and conventional macro gold for the electrooxidation and determination of glucose. The AuNP_{HEPES} do not require any prior activation for such electrocatalysis, which is important because the anodic activation of gold is not always feasible [11].

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Highlights

- Morphology-sensitive electrocatalysis at gold nanoparticles (AuNP)
- AuNP polyhedral morphologies active toward the oxidation of glucose to gluconate
- Redox-mediation by gold-oxygen sites on the surface of AuNP
- Anodic activation of macro and nano gold toward glucose oxidation

Figure 1. TEM images of (A) AuNP_{HEPES}, and (B) AuNP_{CIT}. Bars represent 20 nm.

Figure 2.
X-ray diffraction patterns for (A) AuNP_{HEPES}, and (B) AuNP_{CIT}.

Figure 3. HRTEM and Fast Fourier Transform images of (A) AuNP_{HEPES}, and (B) AuNP_{CIT}. Bars represent 10 nm.

Figure 4.

Cyclic voltammograms recorded at (A) AuNP_{HEPES}, (B) AuNP_{CIT}, and (C) conventional macro gold electrodes. Traces a, b, and c were recorded in the presence of 50 mM glucose in a solution. Traces a1, b1, and c1 represent the corresponding background voltammograms. Background electrolyte, pH 7.40 phosphate buffer solution (0.050 M). Scan rate, 50 mV s⁻¹.

Figure 5. Background cyclic voltammograms recorded at (a) AuNP_{HEPES}, and (b) AuNP_{CIT} electrodes in a pH 7.40 phosphate buffer solution (0.050 M). Scan rate, 50 mV s⁻¹.

Figure 6.

Cyclic voltammograms recorded in a 50 mM glucose solution at (A) AuNP_{HEPES}, and (B) AuNP_{CIT} electrodes before (blue traces a) and after (red traces b) activation by cycling their potential 10 times between -0.20 and 0.90 V in a background electrolyte solution. Green traces a1 and black traces b1 represent the corresponding background voltammograms. Background electrolyte, pH 7.40 phosphate buffer solution (0.050 M). Scan rate, 50 mV s^{-1} .

Figure 7. Amperometric response of the non-activated (a) AuNP_{HEPES}, (b) AuNP_{CIT}, and (c) conventional macro gold electrodes to the additions of glucose aliquots (1.0, 2.0, 3.0, 8.0, 13.0, 18, 28, 38, 48, 68, 88, 108 mM) to a stirred pH 7.40 phosphate buffer solution. Inset: Calibration plot for a red trace a. Potential, 0.30 V.

Figure 8.

(A) Negative ESI mass spectrum of glucose solution after two-hour electrolysis at AuNP_{HEPES} electrode at 0.30 V. Peaks at m/z 179 and 195 correspond to singly deprotonated species $[M - H^+]^-$ of glucose and gluconic acid, respectively. Other peaks are due to contaminants in the background solvent and were also present in the blank. (B) Tandem mass spectrum of gluconic acid electrolytic product. (C) Tandem mass spectrum of gluconic acid standard.