

ELECTRICAL MANIPULATION OF GOLD NANOPARTICLES FOR MICROFLUIDIC APPLICATIONS

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ABSTRACT

An electrical method to trap and release gold nanoparticles to and from the surface of alkanethiol-modified gold electrodes is presented. When a positive bias versus a Ag/AgCl reference electrode was applied to gold electrodes, negatively-charged citrate-capped gold nanoparticles (GNPs) were attracted towards and attached to the surface more rapidly than without bias. Partial release was provided by a subsequent negative bias, and varied depending on the alkanethiol used to modify the gold electrode. This work describes the accelerated concentration of GNPs on the surface of the electrodes, their entrapment, and their final release for applications such as nanotoxicity studies.

KEYWORDS: Gold nanoparticles, Impedance, Self-assembled monolayers, Electrical manipulation

INTRODUCTION

The electrical and optical properties of gold nanoparticles have brought about new analytical approaches for applications that span from high-throughput screening to cellular imaging [1]. Currently, there is a need for methods to manipulate nanomaterials (e.g. nanoparticles, nanotubes). The net negative charge observed on gold nanoparticles, due to the citrate stabilizing coating, has been previously used to adsorb gold nanoparticles to group-functionalized silanes, polyelectrolytes, bovine serum albumin, and alkanethiols, among others [2, 3]. In this work we used an applied voltage to move citrate-coated gold nanoparticles onto alkanethiol-modified gold electrodes to demonstrate more rapid trapping and releasing than without the applied voltage.

EXPERIMENTAL

Our device consists of patterned gold electrodes modified with alkanethiols (Figure 1A). The gold electrodes were fabricated on a glass substrate using standard photolithographic methods and thin-film metal deposition techniques. Then, the gold surfaces (15 nm thick) were coated with alkanethiols functionalized with various terminal groups (alcohol, amine, carboxylic acid and methyl) and their interaction with 40 nm GNPs (0.15 nM) were assessed. Bias voltages were applied versus a Ag/AgCl reference electrode and a Pt wire was used as the counter electrode. Characterization of the trapped gold nanoparticles on the surface of the gold electrodes was monitored by UV-Vis, atomic force microscopy (AFM), and impedance measurements before and after the application of positive and negative bias voltages.

AFM images were taken in tapping mode to visually observe the gold nanoparticles adsorbed on the alkanethiol surface. Impedance measurements and UV-Vis spectra were taken after periods of positive and negative bias, but under no applied potential bias.

RESULTS AND DISCUSSION

Our results show an interaction of the gold particles with the alkanethiols. Figure 1B shows the UV-Vis spectrum of GNPs in solution and the spectra of GNP bound to aminoalkanethiol (AAT)-modified gold electrodes after the positive and negative bias. These spectra show a maximum absorption of GNP at about 533 nm in solution as well as on the AAT surface. The absorption of the positively biased sample shows approximately double the absorption of the positively and then negatively biased sample when measured from their baselines suggesting the attraction and anchorage of the GNP onto the surface and later detachment of the GNP.

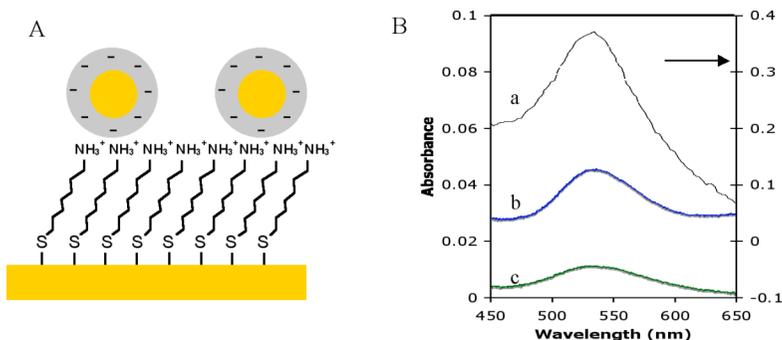


Figure 1. A) Schematic showing a cross-section of the gold pad with bound alkanethiols. The gold nanoparticles (GNPs) are interacting with the functional groups. B) UV-Vis spectra of a) 1.75 nM GNPs in solution (arrow shows the y axis scale that corresponds to this specific absorption), b) GNPs adsorbed on AAT after +0.5V bias for 2 h, c) remaining GNPs adsorbed to AAT after +0.5V bias and then -0.5V bias.

Binding of GNPs to the surface of AAT-modified electrodes via our voltammetric approach shows that after two hours a plateau is reached, suggesting a final coverage of the gold electrodes was attained in about two hours at a concentration of 0.15 nM (data not shown). No absorbance is measurable for a 0.15 nM GNP soln. Comparing this with previously reported binding of GNPs onto charged surfaces without an applied voltage or any other GNP transport method, it is observed that our method requires about the same time (2 to 2.5 hours) but with a much lower concentration (16 times less concentration); while others have shown that takes at least 8 to 12 hours to form a submonolayer at concentrations similar to the previous reports [3]. Figure 2A shows an AFM image of GNPs bound to the surface. Impedance measurements before and after an applied positive bias showed a decrease in impedance, which suggests an increase in conductive material (GNPs) on the surface of the electrode (Figure 2B). All of the modified electrodes showed a change in impedance, however, the largest changes in impedance were observed for methyl- and

alcohol-terminated alkanethiol functionalized substrates (Figure 2B). When a repulsive negative bias was applied (-0.5 V vs. Ag/AgCl) to promote the release of the bound GNPs, the alkanethiol that showed the largest change in impedance was the alcohol-terminated alkanethiol. The largest change in impedance is observed in Figure 2B for the alcohol-terminated alkanethiol which indicates the largest trap and release of GNPs.

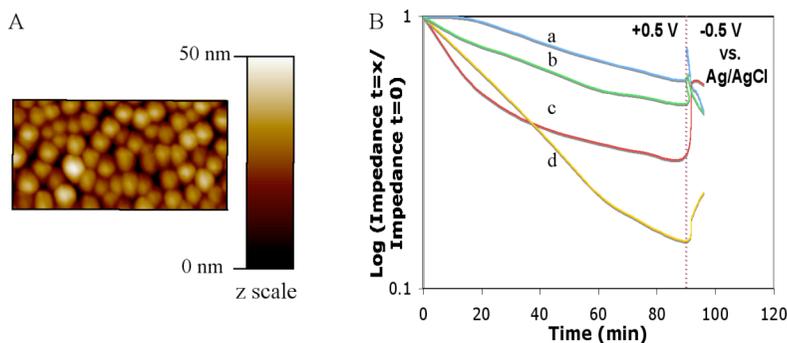


Figure 2. A) Atomic force microscopy image of 40 nm GNPs bound to alkanethiol-modified gold electrodes. The image is 0.5 μm in height and 1 μm in width. The z scale is 50 nm. B) Logarithm of the normalized impedance as a function of time with an applied bias of +0.5 V versus Ag/AgCl. Functional groups: a) COOH, b) NH₃, c) OH and d) CH₃. The vertical gray line denotes the application of a repulsive bias of -0.5 V vs. Ag/AgCl (after 90 minutes of a positive applied bias). A decrease in impedance corresponds an increase in number of GNPs that have absorbed to the substrate.

CONCLUSIONS

These results present a novel electrical method for the on-demand manipulation of gold nanoparticles for the electronically controlled trap-and-release for microfluidic applications. This approach may prove to be beneficial for the instantaneous release of molecules bound to gold nanoparticles in microfluidic devices for future use in clinical diagnostic assays, point-of-care testing, and nanotoxicity studies.

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