Research Article

Uniformly Immobilizing Gold Nanorods on a Glass Substrate

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The goal of this paper is to immobilize gold nanoparticles uniformly on a glass substrate. In order to attach gold-nanorods (GNRs) to an area of a few squared microns surface of glass substrate without preliminary coating of the GNR, 3-(Mercaptopro- pyl)trimethoxysilane molecules were used as linker while using different methods. These methods included placing the glass slide and the GNR (1) inside a tube without any motion; (2) inside a shaker; (3) in a fan setup. The fan setup included a tube containing the GNR solution and the glass slide at a vertical position, when the fan blows above the tube, producing turbulations in the liquid. Each method was evaluated according to the density and the homogeneity of the GNR monolayer on the surface. The uniformity of the monolayer was demonstrated using AFM images of different areas on the slides, and the effectiveness of the protocol was demonstrated by calculating the average density of the GNR on the surface using image processing and analysis software. It was found that while both the shaker and the fan setups improved the monolayer density, the fan setup improved the density by a factor of more than two while the density found using the shaker.

1. Introduction

Nanoparticles play a significant role in an increasing number of researches and variety of applications. Recently, gold nanoparticles (GNPs) have gained popularity, and they serve as promising agents due to their favorable optical properties, such as an enhanced absorption cross-section [1] and scattering properties [2], biocompatibility [3], and well-developed bioconjugation protocols [4]. The increment in the number of applications using GNP has led to an ongoing demand for developing new techniques for immobilization of GNP to the substrate surface. Immobilization of GNP to substrates is required due to their applicability in various fields, among them: optical sensing using effects like surface plasmon resonance (SPR) and surface-enhanced Raman scattering (SERS), using nanoparticles as immobilizers for biomolecules, electron transfer enhancement, and labeling of biomolecules [5, 6].

Immobilization of the particles on the surface can be achieved by using various methods, which may be divided into two groups: physical attachment [7, 8] which is mainly used to obtain a multilayer of particles or a thin film, and chemical attachment [9, 10], which demands plating the substrate with linker molecules and is used to obtain a high-quality monolayer or structure of organized layers. While some of the chemical attachment methods take advantage of the ionic nature of the gold as well as its affinity toward thiol, others require the use of linker molecules [5].

Most of the common methods for chemical attachment between GNP and a substrate use self-assembled monolayers that contain organic groups, especially amine and thiol, while the use of charged polymer as a linker medium serves as an alternative [11].

The principle of using linker molecules is based on the ability of these molecules to self-arrange to what is called a self-assembled monolayer. The linker molecules are in fact bifunctional molecules where one end binds to the substrate, and the other is ready to bind to gold nanoparticles.

Previous studies [12–15] have shown that gold colloids can be self-assembled from solution onto a functionalized glass surface. The self-assembled monolayer is stabilized by attractive electrostatic interactions. Aminopropyltrimethoxy silane (APTMS or APS) has been commonly used to obtain amine-functionalised nonmetal substrate surface for
the attachment of gold colloidal nanoparticles [10, 12, 14, 15]. This utilization has been used for a variance of purposes, mainly for application using SPR [12, 14, 15] and SERS effects [10, 13].

Usually, utilization of this method would be successful with gold nanospheres (GNSs) rather than gold nanorods (GNRs) because GNSs are usually produced in a negatively charged citrate medium, while GNR are usually produced using a positively charged CTAB medium [16].

The positive charge of the top amine group of APTMS is a more suitable instrument in attracting the negatively charged GNS. Although one could stripe the solvent and achieve natural GNP [17], other options like negatively charged coupling agents are preferable due to the difficulty in the total removal of all the remnants of the medium. Among these agents, we can state negatively charged polymer [11] or thiol groups.

Using thiol molecules to link GNP to substrates has been extensively studied not only because of their unique physical and chemical properties but also because of their easy preparation and good performance.

S–H head groups are used on noble metal substrates due to the strong affinity of sulfur in these metals (Figure 1).

The sulfur gold interaction is semicovalent and has a strength of approximately 45 kcal/mol. In addition, gold is an inert and biocompatible material that can withstand harsh chemical cleaning treatments. These traits make thiol molecules attractive candidates for a wide range of applications [18–20]. Among these applications are technologies for the biosensor industry [21] and building of nanostructures for fabrication of nanodevices [9].

In most cases, thiol molecules are used as linkers for metal-metal binding, by using dithiol [22–25], or as a GNP coating in order to prevent self-aggregation [24]. However, thiol molecules could be useful for binding metal to other substrates such as glass. Glass-metal binding is accomplished by using molecules with thiol tail groups and head groups, which are substrate-specific. In case of a glass substrate, an optional functional group is silane [26].

Upon working with GNR, a common problem of aggregation arise as GNR tend to self-aggregate in the solution or on the surface causing a disorder in the layer on the surface. The prevalent solution is an additional step of preliminary coating the GNR by dithiols.

To our knowledge, there are no simple routine methods for coating uniformly a relatively wide area with high-quality, densely packed monolayer of GNR without preliminary coating the GNR. In this work, we used thiosilanes as bifunctional molecules in order to attach the GNR to a glass substrate when silane head groups are attached to the glass substrate and the GNR are chemically bound to the thiol tail groups as shown in Figure 2.

In order to simplify the process and avoid preliminary coating of the GNR, we used a shaker or a central processing unit (CPU) fan to prevent self-aggregation in the solution and on the substrate and to increase the probability of a single GNR to chemically bound to linker molecules on the glass, what improves the quality of the monolayer.

2. Materials and Methods
GNRs were synthesized using the seed-mediated growth method [21]. Their size, shape, and uniformity were characterized using transmission electron microscopy (TEM) and the resultant shape was 25 nm × 65 nm, with a narrow size distribution (10%) [27] (Figure 3).
3-(Mercaptopropyl)trimethoxysilane was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Cover glass slides (2.2 cm × 1.2 cm) with a diameter of 0.13–0.17 mm were cleaned in a piranha solution (3:1 (v/v) H₂SO₄/H₂O₂) that causes vigorous oxidation for 90 min.

A special glass tube was custom produced by us (Figure 4). The tube was composed of a flat part that enables vertical positioning of the slide and a cylindrical part for possible future use of a magnetic stirrer. Vertical positioning of the glass slide is important for obtaining homogeneous binding of the GNR to the slide.
Figure 7: AFM images of the GNR on the glass slides. (a)–(c) are images of different areas of a slide that was coated using a shaker; (d)–(f) are images of different areas of a slide that was coated using a CPU fan.

3. Results and Discussion

Our first goal was to create a monolayer of the GNR.

When rinsing the glass vertically in the GNR solution without any intervention produced no attachment to the glass was seen. In order to improve the results, different manipulations were tried. First, the slides were induced in the GNR colloid for 2 hours in a shaker in order to have maximal contact of the GNR with the surface and try to avoid self-aggregation. Afterwards, the slides were rinsed in ethanol, sonicated for 5 min, and dried at 70°C for 5 minutes. The results can be seen in Figures 7(a)–7(c).

Placing the tube in a shaker improved the attachment of the GNR to the glass, but further improvement was required.

Next, we sought to improve the density, uniformity, and homogeneity of the monolayer without adding steps of preliminary process such as prior coating of the GNR.

In order to improve the quality of the monolayer, the shaker was replaced by a CPU fan. The fan was placed on top of the tube that contained the slides in the GNR solution. The intensity of the blow was controlled by the power supplier as shown in Figure 5.

Both methods, shaker and fan, despite their difference, are based on the assumption that the motion of the GNR...
solution increases the probability of a single GNR to chemically bound to linker molecules on the glass. A scheme of movement of the GNR in the fan setup is shown in Figure 6.

In order to compare the density of the monolayer obtained by using the different methods, AFM images were taken. To confirm the uniformity of the monolayer, images from different areas of the slide were taken for every sample.

While the use of a shaker produced a relatively uniform monolayer (see Figures 7(a)–7(c)), the introduction of the fan to the protocol resulted in a denser layers can be seen in Figures 7(d)–7(f).

In order to quantify the improvement in density between the methods we used a Java image processing program called ImageJ. A particle analysis facility was used on the images, the methods we used a Java image processing program called ImageJ. A particle analysis facility was used on the images, which occupied an area of 2 μm × 2 μm on the glass slide. We converted the images into 8-bit images and adjusted the lower threshold to 90, while the upper threshold was kept at 255. This choice of threshold ensured the exclusion of the surface and the binding layer from the count.

The improvement in the quality of the monolayer is clearly demonstrated where the use of the fan increased the particle density significantly to 180.16 ± 39 particles per frame (2 μm × 2 μm) in comparison to 80.2 ± 32 particles per frame for the shaker.

4. Conclusions

The results reported in this work indicate that using thiolsilane molecules combined with utilization of a fan in the setup applies a uniform high-quality monolayer of GNR on a few micron squared area of glass substrate, which is a relatively wide field.

In order to improve the density and the homogeneous-ness of GNR monolayer and yet avoid preliminary coating of the GNR, two methods were tested. In the first method, the slides were rinsed in the GNR solution and deposited in a shaker. In the second method, the slides were placed in the setup blown with a fan from above. Both methods improved the attachment of the GNR to the glass, but the latter produced significantly better results by increasing the quality of the monolayer. The AFM images clearly demonstrate that the density of the monolayer using the fan is higher than using a shaker. In addition, the monolayer that was obtained was denser than the one that was achieved by Niidome et al. [11] using a negatively charged polymer. Comparison between AFM images of random different areas of the slide indicates the uniformity of the monolayer rather than one image of smaller area.

As was demonstrated, using the fan setup improved the quality of the GNR monolayer on the glass. This suggested that the method enables simplifying the process of attaching GNR to glass substrate. Such a process may serve as a first step towards the development of a novel super resolution method based on GNR attached to an observed object.

References


