Applied Surface Science 258 (2012) 8991–8995

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Gold nanoparticles grafting on glass surface

Ondřej Kvítek*, Marek Bot, Václav Švorčík

*Department of Solid State Engineering, Institute of Chemical Technology, 166 28 Prague, Czech Republic*

ARTICLE INFO

*Article history:*
Received 5 April 2012
Received in revised form 23 May 2012
Accepted 25 May 2012
Available online 1 June 2012

*Keywords:*
Glass
Plasma
Gold nanoparticle
Grafting
Atomic force microscopy
X-ray photoelectron spectroscopy

ABSTRACT

New method of grafting of gold nanoparticles (AuNPs) to glass surface was developed and investigated. The method based on glass activation by plasma discharge use dithiols for AuNP binding as an alternative to silane chemistry currently used for binding AuNPs onto glass surface. XPS measurements confirmed the presence of sulfur and gold on the modified glass surface. The presence of AuNPs on modified glass surface was then directly proven with AFM method. UV–vis spectra of samples with grafted AuNPs show a peak of SPR absorbance. With increasing modification time, more AuNPs are bound to the glass surface, which can aggregate.



## 1. Introduction

Deposition of Au nanoparticles (AuNPs) on solid surface is a critical step of a process to form a functional material that could be used in certain analytical methods such as surface-enhanced Raman scattering (SERS) or surface plasmon resonance (SPR) sensing. AuNPs, forming a rough metal surface, function in SERS method as a signal amplifier which can amplify Raman signal by a factors up to $10^6$ [1,2]. Metal colloid solutions are used in SERS mostly due to their cheap and simple preparation, but a big drawback is their instability leading to possible aggregation, which causes measurement irreproducibility. Attaching AuNPs to solid surfaces would improve stability of the SERS substrate, retaining its great sensitivity. Recently, surface plasmon resonance in AuNPs has been used in sensing of biomolecules especially. Aggregation assays use colloid solutions for this purpose, but such systems are not suitable for certain applications. Binding AuNPs to a solid surface enables miniaturization, multiplexing and compatibility with inflow assays [3]. AuNP interlayer is also useful in various applications to improve adhesion of subsequently deposited metal films since adhesion is crucial in determining the lifetime of a coated component [4,5].

Many approaches were employed to bind AuNPs onto glass surfaces. Borosilicate glass was modified with various organic compounds on silane basis [6] (e.g. aminopropyltrimethoxysilane [7]). Highly organized structures were fabricated on Au surface using decane-1,10-dithiol forming a self-assembled monolayer [8,9]. Films of AuNPs were prepared on $Al_2O_3$ and glass using instrumentally complicated method of laser ablation of gold target and subsequent deposition of evaporated Au particles [10]. A structure similar to AuNPs bound to surface was obtained by annealing of sputtered Au thin films. This structure shows the same UV–vis absorption properties as Au colloid, but adhesion of the Au to the glass surface is rather poor [11,12].

In this work a new approach to bind AuNPs on glass surface was investigated. Previous methods of AuNP grafting on glass surfaces use either complicated instrumentation or delicate chemical substances. We investigated combination of these approaches by using common instrumental method and simpler chemicals. Plasma treatment was used to increase reactivity of glass surface which in the next step is grafted with dithiol whose thiol (—SH) groups are known to form strong bonds with Au. Then the samples were immersed in AuNP colloid to bind AuNPs to the second —SH of the dithiol. To determine the outcome of this process, element concentration was measured by XPS, surface morphology and surface roughness by AFM method. UV–vis spectra were measured to investigate optical properties of modified glass.

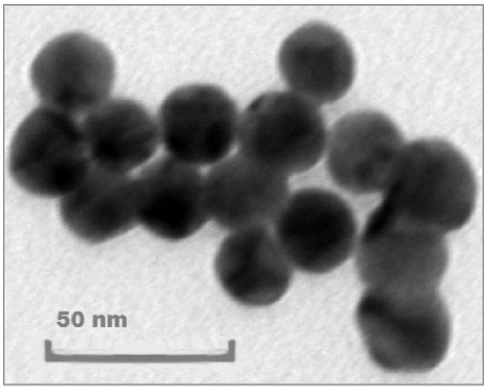
## 2. Materials and methods

### 2.1. Materials, plasma treatment and Au nanoparticles (AuNPs) grafting

Borosilicate microscopic cover glass 15 mm × 15 mm supplied by Menzel–Gläser was used as a substrate for deposition. Glass

* Corresponding author at: VŠCHT Praha, Technická 5, Praha 6–Dejvice, 166 28, Czech Republic. Tel.: +420 220445159; fax: +420 224310337.
*E-mail address:* kviteko@vscht.cz (O. Kvítek).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.05.136



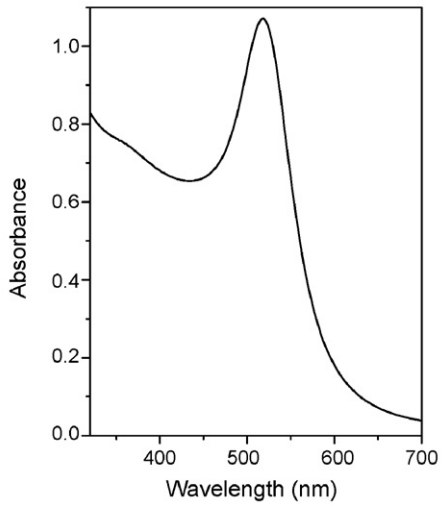




**Fig. 1.** Image of citrate capped AuNPs from transmission electron microscope (TEM). For structural characterization TEM (JEOL JEM-1010, Japan) operated at 80 kV was used (top). UV–vis spectrum of AuNP colloid (bottom).

was cleaned with methanol (p.a.) and dried in a stream of $N_2$. Plasma treatment was carried out in Balzers sputter-coater SCD 050 device in etching mode. Chamber was evacuated to a pressure lower than 2 Pa, then Ar gas was introduced at a pressure of 10 Pa. High voltage was brought to electrodes and at 630 V electric current was 15 mA. $Ar^+$ ions interacted with samples placed on anode. The exposition times 120, 240 and 360 s were chosen.

Plasma treated samples were immersed in $4 \times 10^{-4}$ mol $l^{-1}$ solution of ethane-1,2-dithiol (EDT) for 24 h. Glass with grafted EDT was cleaned with methanol to wash off adherent dithiol molecules that did not form covalent bond with the surface. To coat the glass with AuNPs the samples were immersed for 24 h into freshly prepared gold colloid solution (concentration of 0.05 g $l^{-1}$, citrate reduction [13,14]). Position of SPR band in measured UV–vis spectrum of Au colloid suggests AuNPs size of about 20 nm [15], which was confirmed by transmission electron microscopy too (Fig. 1). Finally, samples were cleaned with methanol again to wash off adherent AuNPs.

### 2.2. Methods of analysis

AFM measurements were carried out to examine surface morphology and roughness of plasma treated and AuNPs grafted samples. Digital instrument CP II Veeco was used in non-contact mode with silicon P-doped probes RTESPA-CP with a spring constant of 20–80 N/m. Images of 1 μm × 1 μm area of surface were taken in topographic and phase mode.

Elemental composition of the modified surface layer was measured by X-ray photoelectron spectroscopy (XPS) 24 h after the grafting with AuNPs. Omicron Nanotechnology ESCAProbeP spectrometer was used to measure photoelectron spectra (error of 10%). Exposed and analyzed area had dimension of 2 mm × 3 mm, spectra were measured in two regions to check for the data homogenity. X-ray source was monochromated at 1486.7 eV with step size 0.05 eV, the take off angle was 0° according to surface normal. The O (1s), C (1s), Si (2p), S (2p) and Au (4f) peaks were evaluated using CasaXPS program [13], elemental surface composition was calculated on the base of peak area of respective elements.

UV–vis absorption spectra were measured by Varian's Cary 50 spectrophotometer. Absorbance values were obtained for wavelength range of 300–900 nm with a step of 1 nm. Xe lamp was used as radiation source. Absorption spectrum of clean, pristine glass slide was used as a background standard for all measured spectra.

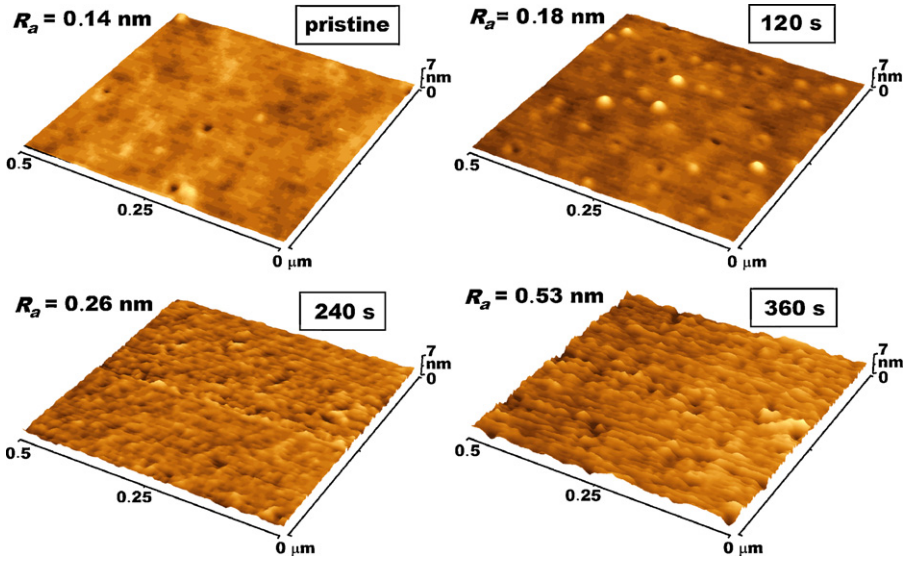



**Fig. 2.** AFM images of glass (pristine) and glass samples treated with Ar plasma for 120, 240 and 360 s.