

Deposition of gold nanoparticles from colloid on TiO_2 surface

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In this paper, experimental results are presented on the deposition of colloidal gold nanoparticles on the surfaces of TiO_2 prepared on silicon/silicon dioxide. Important procedures, such as titanium dioxide surface hydrophilization as well as functionalization by an organosilane coupling agent (3-aminopropyl) trimethoxysilane and (3-mercaptopropyl) trimethoxysilane were investigated in order to obtain a metal oxide surface with the most convenient properties for immobilization of gold nanoparticles having a dense and uniform distribution. TiO_2 nanotips prepared by reactive ion etching of oxide surface covered with self-mask gold nanoparticles are demonstrated.

Key words: gold nanoparticles, titanium dioxide, hydrophilization, APTMS, MPTMS

1 Introduction

Metallic nanoparticles (NPs) exhibit physical, chemical, catalytic, optical, magnetic and mechanical properties that are different from bulk metals [1, 2]. These properties can be tailored by varying their composition, surface chemistry, shape and size in the range between 1 and 100 nm [1].

Gold nanoparticles are materials with lots of applications in a variety of fields, such as electronic applications, photodynamic therapy, drug delivery and diagnostic in medical applications, probes for imaging, fuel cells applications and various sensors [3, 4]. A number of different syntheses of the spherical gold nanoparticles were described earlier [2, 3, 5–8]. One of the most popular is Turkevich's method based on reducing tetrachloroauric acid in water by sodium citrate. The dimensions of nanoparticles and their properties are controlled by the parameters of synthesis. Since the nanoparticles in the suspensions are thermodynamically unstable, tending to coalescence and agglomerate formation, the suspensions have to be stabilized either sterically or electrostatically [5]. In the first case, the molecules of organic ligands or polymers are adsorbed on the surface of the NPs and form a barrier around the NPs. There are a variety of polymers and other capping agents that are used for stabilization of Au NPs [7]. In the case of electrostatic stabilization, the ionic compounds are adsorbed on the surface of the NPs. The stability of the colloid results from the balance between attractive and repulsive forces acting on the nanoparticles [5]. A simple method is used for deposition of Au NPs from the colloidal solutions onto surface of various substrates (glass, silicon, thin metal oxide films) [9–13]. The substrates are usually immersed in a colloid for a certain time and then rinsed with a proper solvent. However, surfaces of the substrates are usually

not fully compatible for Au NPs deposition. For this reason, the surface of the substrate must be treated properly before applying the nanoparticles. The nanoparticles have to be immobilized to the surface by a proper silane-coupling agent that is able to form a durable bond between gold nanoparticles and inorganics materials. Prior to the functionalization by silane agent, the substrate surface must be sufficiently hydrophilic [9–15]. Subsequent functionalization of the surface by organosilanes can be accomplished in various ways [14]. The deposition from liquid solutions (aqueous alcohol or anhydrous liquid) is the most facile and most frequently used method. Still, the vapour phase deposition is a preferable method at which preferentially the monolayer is formed unlike in liquid methods. Organosilanes MPTMS, APTMS, APTES as well as PEI and cysteamine [9–13] are used for immobilization of Au NPs. MPTMS, the most commonly used linker with a mercapto group ($-\text{SH}$), forming a covalent bond between sulphur and gold. Remarkable physical and chemical properties make gold nanoparticles a versatile platform for chemical and biological sensing of various analytes. Comprehensive surveys of miscellaneous sensing principles and applications of Au NPs are given in [2, 7] and a complex view of the problem of Au NPs used for optimization of metal oxide based conductometric gas sensors is given in [16]. In this paper, detailed knowledge of the methods for modification of metal oxides and responses of the modified sensors to various gases is summarized and generalized. Gold nanoparticles could also be used as an etching mask for nanostructuring [10] the sensitive layer of the sensor structures by dry etching techniques (*eg* reactive ion etching (RIE)) ensuring a significant increase of the active area of the sensor and improving the response of the sensor.

This paper investigates the deposition of gold nanoparticles from a colloid solution on TiO_2 surfaces for improving their properties in sensor applications. Optimized de-

position of nanoparticles involves three steps: surface hydrophilization of metal oxide by deep UV illumination, subsequent functionalization with vapour of MPTMS and deposition of Au NPs from the colloid. All of these three steps are very substantial for achieving a deposit with the desired density and homogeneity of immobilized Au NPs.

2 Experimental

Since the key issue in the fabrication of nanostructured surfaces is the uniformity and density of nanometre-sized objects and the surfaces are usually incompatible with Au NPs deposition, the TiO₂ surface must be treated appropriately prior to applying the nanoparticles. We utilized APTMS (3-amino-propyl-tri-methoxy-silane) or MPTMS (3-mercapto-propyl-tri-methoxy-silane) as a coupling agent for immobilization of Au NPs [10, 12] on the surface of TiO₂. The purities of these organosilane agents were 96.0% (TCI, Japan). Colloidal suspension of gold nanoparticles (5 nm in diameter, NanoComposix, USA) stabilized by dodecanethiol (0.051 mg mL⁻¹) was prepared in toluene. The purity class of other chemicals (IPA, acetone, methanol, toluene) was *pa*. The TiO₂ layer with a thickness of approx. 200 nm was prepared by magnetron sputtering on an oxidized silicon substrate. Then the substrate was annealed in nitrogen atmosphere at 500°C for 1 hour. Before the experiment, the silicon substrate with the TiO₂ thin film having an anatase structure was cleaned ultrasonically in acetone for 5 min, in IPA for 5 min and finally rinsed with deionized water. An essential requirement for formation of a covalent bond between the silane agent and TiO₂ is a hydrophilic surface of the oxide with a suitable concentration of hydroxyl groups. Two methods were studied to increase the wettability of the surface. First, the substrate with titanium dioxide was immersed in NH₄OH:H₂O₂:H₂O (5:1:1) [12] solution for 20 hours. In this case, TiO₂ can be chemically attacked. The other possibility was illumination of the substrate by ultraviolet (UV) light [15]. In the latter method exploiting photoinduced hydrophilic conversion, UV illumination was used with a mercury pressurized lamp (\approx 400 nm, 15 mW/cm², Suss Maskaligner, MJB3) for 1 hour or deep ultraviolet (DUV) light (185 and 254 nm, Samco Ozone cleaner, UV-2) for 10 min. Afterwards, the samples were immersed in APTMS or MPTMS diluted in toluene with different concentrations (1 and 10%), methanol (1 and 10%) or IPA with water (0.5, 2 and 4 parts by volume to 40 parts of IPA and 1 part of water) for 15 hours. In the case of MPTMS (2%), ethanol with water (5%) adjusted with acetic acid to pH 5 was also used as a solvent. Then, the silane layer was cured on a hot plate at 110 °C for 10 min. During this procedure, a covalent linkage is formed with TiO₂. The vapour phase deposition technique was used, besides for liquid phase deposition of silane, also in the case of MPTMS. This procedure was described in detail in [14]. While the formation of self-assembled monolayer of MPTMS molecules in the solutions is difficult and affected by a numerous reaction parameters, in

the case of vapour phase deposition the formation of well-organized monolayer is preferred. After functionalization by the coupling agent, the substrates were immersed in a colloid for a given time, rinsed with a solvent and dried in a centrifuge. In order to get TiO₂ surface covered by Au NPs as densely and uniformly as possible without any agglomerates, a number of parameters were investigated (method and time of surface hydrophilization, type and concentration of silane agent, Au NPs concentration and deposition time). Scanning electron microscopy (SEM) (JEOL 7500) was used to evaluate the metal oxide surfaces. RIE with an ICP source (Vacutec 310/320 reactor) was used for the final fabrication of nanostructured TiO₂ in which the Au nanoparticles were used as the etching mask. TiO₂ was etched in CF₄/Ar plasma at 200 W for ICP power and 100 W of RF chuck power. The total flow rate was adjusted to 14 sccm at process pressure of 0.6 Pa. After etching, the Au NPs were dissolved in gold etchant (KI + I₂).

3 Results and discussion

3.1 Hydrophilization

The surface of as-deposited TiO₂ layer is highly hydrophobic, likewise after annealing at 500 °C in N₂ atmosphere (water contact angle higher than 45°). We have found that in the case of a TiO₂ film the method of photoinduced hydrophilization by UV illumination was a very effective technique to receive sufficient hydrophilicity of the oxide surface. This method is more convenient, faster and easier in comparison with the process of treatment in an alkalic aqueous solution when the sample is immersed in a solution consisting of NH₄OH:H₂O₂:H₂O (5:1:1 in volume) for 20 hours. The dependence of the water contact angle on the time of wet and dry treatment is shown in Fig. 1. It is clear that UV illumination is more effective for conversion of TiO₂ surface to the hydrophilic state and the satisfactory treatment time is 60 min. In addition, if photoinduced hydrophilization is performed, the sample has to be immersed in deionized water immediately after illumination for 10 min to create the hydroxyl groups on the surface of TiO₂. We found that the density of Au NPs on TiO₂ surface, when the sample was immersed before functionalization in water for 10 min, was nearly five times higher than the density at the sample that was functionalized immediately after illumination. Most likely, the ambient relative humidity was not sufficient to create enough hydroxyl groups on the surface. Whereas the method of the photoinduced hydrophilization was proved suitable, the effect of light sources with different wavelengths in combination with higher temperature and/or ozone presence have also been investigated. The results are summarized in Tab. 1. It is obvious that after illumination by the shorter wavelengths, the oxide surface was much more wetted in a markedly shorter time. Conversion of the TiO₂ surface from the hydrophobic nature to hydrophilic was explained in [15]. When used at

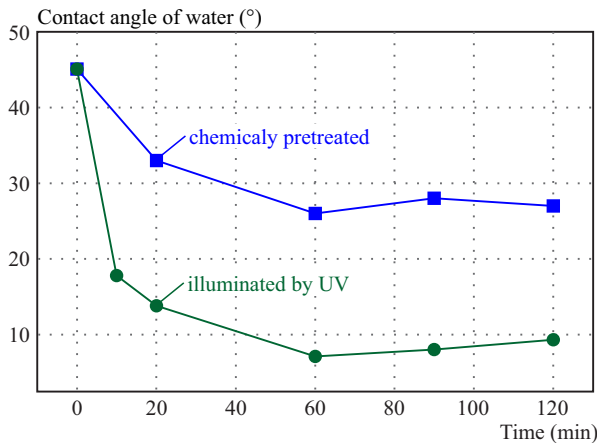


Fig. 1. Time dependence of the water contact angle upon UV illumination and chemical treatment

a temperature of 100 °C, the water contact angle practically could not be measured (<1 deg). The maximum hydrophilicity of TiO_2 surface was achieved after 10 min of DUV exposure at a temperature of 100 °C with assistance of ozone.

Table 1. The influence of various parameters of photoinduced hydrophilization on wettability of TiO_2 surface

Ilumination mode	(min), (°C)	CA (deg)
UV	60, RT	7
DUV	10, RT	5
DUV+Ozone	10, RT	3
DUV	10, 100	1
DUV+Ozone	10, 100	0

CA = contact angle after hydrophilization
RT = room temperature

3.2 Functionalization by aptms and mptms

The results obtained with APTMS and MPTMS as coupling agents are summarized in Tab. 2. In this case hydrophilization was performed only with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (:1 in volume) for 20 hours. After silane functionalization for 15 hours the samples were immersed in

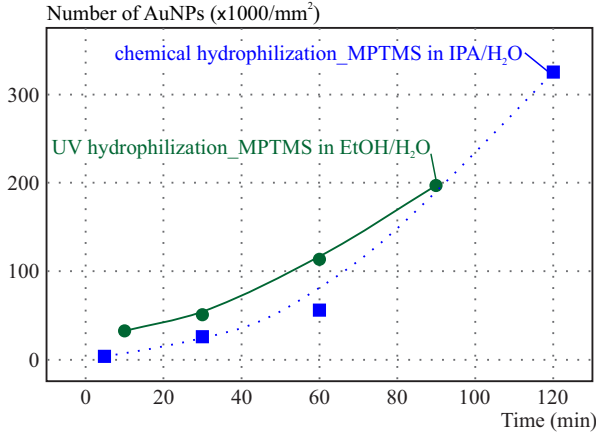


Fig. 2. The dependence of the density of Au NPs on deposition time

colloidal solution of Au NPs for 10 min. For APTMS, the density of Au NPs was rather low and independent of various solvents and their concentrations. On the contrary, the density of particles after using MPTMS was significantly increased when MPTMS was dissolved in IPA and water. We assume that APTMS is not convenient for immobilization of gold nanoparticles. At last the amino group of APTMS does not create covalent bond with gold just mercapto group of MPTMS. Therefore, immobilization of Au NPs based on electrostatic affinity of the amino group to colloidal gold [10] is not reliable.

Later, the hydrophilization procedure of TiO_2 surfaces was carried out by DUV light for 10 min. Afterwards the surfaces of the samples were modified with MPTMS from vapour phase for 3 hours at a temperature of 50 °C. From the contact angle measurements it can be concluded that the more hydrophilized is the surface, the higher quality of the monolayer is reached. In the best case, a contact angle of 68 °C was measured. For a monolayer of the molecules of MPTMS a close value is reported in [18].

3.3 Deposition of Au NPs

The deposition of Au NPs on the surface from a colloid solution is a relatively slow process. The density of

Table 2. The influence of concentration of APTMS, MPTMS and kind of the solvent on deposition of Au NPs

	APTMS		MPTMS	
	Number of Au NPs $\times 1000/\text{mm}^2$	Coverage (%)	Number of Au NPs $\times 1000/\text{mm}^2$	Coverage (%)
0.5:1(H ₂ O):40(IPA)	134	10.5	315	10.3
2: 1(H ₂ O):40(IPA)	133	10.5	348	12.5
4: 1(H ₂ O):40(IPA)	141	7.3	252	14.1
1% in methanol	134	9.0	138	8.1
10% in methanol	110	8.7	127	8.2
1% in toluene	130	7.4	150	8.1
10% in toluene	121	7.2	159	8.5

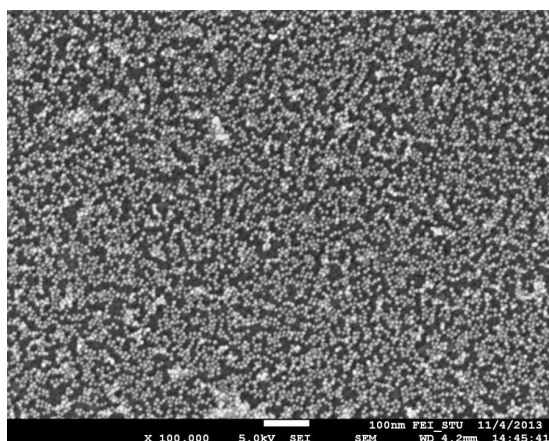


Fig. 3. SEM image of Au NPs immobilized on the TiO₂ surface hydrophilized by DUV and silanized in a vapour of MPTMS

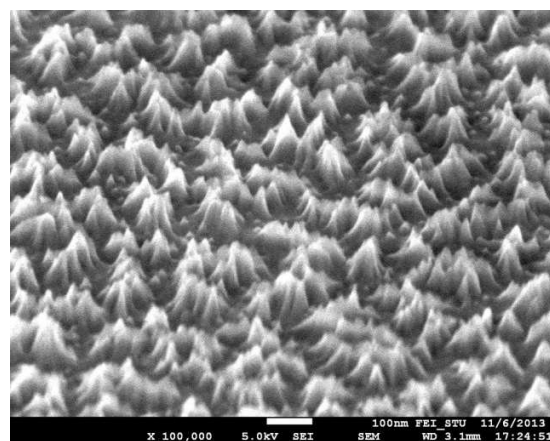


Fig. 4. Sem image of nanostructured TiO₂ surface after removing Au NPs

nanoparticles can be simply controlled by the deposition time. In the case of use of APTMS we observed considerable agglomeration of Au NPs on the surface. This can be explained by the weaker electrostatic affinity of the amino group of APTMS which makes movement of Au nanoparticles on the TiO₂ surface resulting in agglomeration [10]. For MPTMS, the dependence of the density of Au NPs on TiO₂ surface on the deposition time is shown in Fig. 2 for surfaces hydrophilized with different solutions. It was surprising that the aggregation of Au NPs was observed if the TiO₂ surface was functionalized by MPTMS in a solution. On the contrary, the aggregation of Au NPs was not observed if the TiO₂ surface was functionalized by MPTMS from vapour phase and deposition was carried out in toluene gold colloid solution. In the best case when the surface of TiO₂ was hydrophilized by DUV for 10 min and silanized in vapour of MPTMS for 3 hours the deposition of Au NPs was successful. High density of nanoparticles ($\approx 9000 \mu\text{m}^{-2}$) and particularly uniformity was reached (Fig. 3)

3.4 TiO₂ surface nanostructuring

After Au NPs were immobilized on the TiO₂ surface, reactive ion etching was carried out to form titanium dioxide nanotips under optimized etching conditions with etch rate of about 100 nm/min. An example of the surface structure of TiO₂ after etching and after the gold particles were removed from the surface by dissolving in a gold etchant are presented in Fig. 4. Depending on the particle size and deposition parameters, nanostructured surfaces of TiO₂ with different densities of nanotips can be prepared.

4 Conclusion

This paper presents a new method of the deposition of gold nanoparticles with a diameter of 5 nm from a colloidal solution on the surface of TiO₂ films. We can summarize that hydrophilization of the oxide surface by DUV

light and ozone at 100 °C for 10 min as well as subsequent functionalization by MPTMS from the vapour phase at 50 °C for 3 hours were satisfying. In the best case, a close-packed and uniform structure was obtained for TiO₂ with density of Au NPs of $9000 \mu\text{m}^{-2}$. Gold nanoparticles were used as an etching mask for nanostructuring the sensitive layer of TiO₂ by reactive ion etching in order to significantly increase the active area of the layer and hereby to improve its possible response.

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