Surface modification of metal oxide films by gold nanoparticles

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Abstract. The goal of this contribution is to develop a process the most appropriate for the deposition of colloid gold nanoparticles on the surfaces of metal oxides (TiO$_2$, NiO) prepared on silicon and/or alumina substrates. Important procedures such as hydrophilization of metal oxide surface and its subsequent functionalization with a silane coupling agent 3 mercapto propyl trimethoxy silane (MPTMS) were examined so as to reach a metal oxide surface with the most satisfying properties for immobilization of gold nanoparticles having a uniform and dense distribution. TiO$_2$ nanotips prepared by reactive ion etching of oxide surface covered with self-mask gold nanoparticles as well as improved hydrogen gas sensing properties of the NiO film covered by gold nanoparticles are demonstrated.

Keywords: gold nanoparticles, titanium dioxide, nickel oxide, hydrophilization, MPTMS

1. Introduction

Gold nanoparticles (AuNPs) whose properties are comprehensively described in [1] are versatile, making a group of the most widely used nanomaterials in academic research, medical and industrial applications. Various syntheses of the gold nanoparticles have been described earlier [1, 2, 3-6]. The most popular is a method based on reducing tetrachloroauric acid by sodium citrate in water which was discovered by Turkevich. Dimensions, shape and properties of the nanoparticles are adjusted by the parameters of synthesis. The nanoparticles in colloid suspensions are not thermodynamically stable. The colloid solution must be stabilized because the nanoparticles in the colloid have the tendency to coalesce and form agglomerates [3]. A simple technique is used for deposition of AuNPs from the colloid onto surface of different underlay materials (silicon, glass, metal oxide films) [7-11]. Substrates are generally dipped in a colloidal solution for a given time. The NPs need to be immobilized on the surface by an appropriate silane coupling agent which is able to form a permanent linkage between AuNPs and inorganics underlying materials. Before applying of the silane agent, the substrate surface must be sufficiently hydrophilic [12]. For various substrates (glass, silicon, TiO$_2$, ITO), different aqueous solutions are used for hydrophilization (mixtures H$_2$SO$_4$ and H$_2$O$_2$ [7-9] or NH$_4$OH, H$_2$O$_2$ and H$_2$O [10, 12])). The surface of oxides can also be hydrophilized by UV or DUV illumination [12, 13]. Consecutive functional modification of the surfaces by organosilane agents can be accomplished by different methods [12]. Deposition from the vapour phase, at which preferentially the monolayer is formed, is a more preferable way in comparison with the frequently used deposition from a liquid phase. Organosilane agents MPTMS, APTMS, APTES as well as PEI and cysteamine [7-11] are often used for immobilization of AuNPs. MPTMS agent, frequently used linker with mercapto group (-SH), forms a covalent linkage between gold and sulphur. AuNPs are materials with a broad range of applications. Their notable properties make AuNPs a universal platform for sensing of different analytes in chemical and biological areas. A comprehensive overview of miscellaneous sensing principles and applications of
AuNPs is given in [2,5]. A complex view of the problem of AuNPs used for optimization of metal oxides based conductometric gas sensors is in [14]. In this article, knowledge of methods for modification of metal oxides and reactions of the modified sensors to different gases is summarized and generalized. In [15-17] it was discovered that the gas sensing properties of various metal oxide surfaces to different gases were improved significantly after the surface was covered by AuNPs. AuNPs could also be used as an etching mask for nanostructuring the sensitive layer of the sensor structures ensuring a significant increase of the active area of the sensor and improving the response of the sensor. In [8] a possibility to fabricate nanotips on silicon surface by reactive ion etching (RIE) process using a gold nanoparticle monolayer as etch mask is demonstrated. This paper is focused on the research of deposition of AuNPs for potential enhancement of the metal oxide film (MOF) properties for sensors. Gold nanoparticles were used as an etching mask for nanostructuring the sensitive layer of TiO₂ as well as for improvement hydrogen gas sensing properties of the NiO film.

2. Experimental
Deposition of NPs consist of three steps: MOF surface hydrophilization by deep UV illumination (after this step, the undesirable hydrophobic surface of MOF is converted to a hydrophilic surface which is rich in hydroxyl groups), subsequent surface functionalization with vapour of MPTMS (MPTMS molecules join with hydroxil groups on the MOF surface by weak hydrogen bonds which are replaced by covalent linkages after curing) and deposition of AuNPs from the colloid (gold nanoparticles from colloidal solution are immobilized on MOF surface after the covalent bonds are formed between sulphur of mercapto groups (-SH) of MPTMS and gold nanoparticles). Each of these steps is very substantial in terms of achieving a deposit with the required uniformity and density of immobilized AuNPs. A number of parameters (process of photoinduced conversion, concentration of organosilane, functionalization time as well as the time of nanoparticles deposition) had to be optimized. We used deep ultraviolet light with wavelengths of 185 and 254 nm (UV-2 Ozone cleaner, Samco) for 15 min at a sample temperature of 100°C with assistance of ozone for hydrophilic conversion of the MOF surface. Except for the deposition of MPTMS from a liquid solution, a simple vapour phase deposition method was used. For vapour phase deposition, the silane source in a Petri-dish was kept in a vacuum desiccator together with the sample. The desiccator was evacuated using a dry mechanical pump and sealed at this vacuum during deposition. The functionalized layer was thermally treated at 110°C for 10 min. During this procedure a covalent linkage is formed with MOF. The TiO₂ and NiO films with a thickness of approx. 200 and 50 nm, respectively were prepared by magnetron sputtering on an oxidized silicon substrate or alumina substrates. Immediately before the experiment, the substrate was ultrasonically cleaned in acetone and IPA, then rinsed with deionised water and dried at 150°C. For evaluation of a sensing properties of NiO layers with and without AuNPs, platinum interdigitated electrodes (IDEs) on an alumina substrate were used as a support for deposition of the NiO thin film. The IDEs (Pt thickness of 200 nm) with the width and gaps of the electrodes of 150 µm were fabricated by magnetron sputtering on the alumina substrate (50×50 mm²). The chips (3×3 mm²) (figure 1) with gas sensitive NiO film were utilized to demonstrate the improved sensing properties to hydrogen in the case of NiO films covered by AuNPs. The purity of MPTMS organosilane agent (TCI, Japan) was 96.0%. Colloid solution of AuNPs (5 nm in diameter) stabilized by dodecanethiol was prepared with a concentration of 0.051 mg mL⁻¹ in toluene (NanoComposix, USA). The purity class of the other chemicals (acetone, IPA, toluene) was p.a. Scanning electron microscopy (SEM) (JEOL 7500) was used for evaluation of the metal oxide surfaces.
3. Results and discussion

3.1. Hydrophilization of metal oxide film

The surfaces of as-deposited TiO$_2$ and NiO films are hydrophobic, similarly after annealing at 500°C in N$_2$ atmosphere (the water contact angle is higher than 45°). We previously found [12] that in the case of a TiO$_2$ film the method of photoinduced hydrophilization was a very effective technique to receive sufficient hydrophilicity of the oxide surface what is more convenient, faster and easier in comparison with the process of treatment in an alkaline (NH$_4$OH:H$_2$O$_2$:H$_2$O (5 : 1 : 1 in volume)) aqueous solution. It was concluded that applying DUV in combination with a higher temperature and ozone significantly improved the wettability of the TiO$_2$ surface and also reduced the time of hydrophilization. We believe that a similar mechanism could also take place in the case of NiO, since both oxides behave similarly during hydrophilization. Nevertheless, the precise mechanism is still not known. For finding of the best hydrophilizing conditions for the NiO film the following parameters of photoinduced conversion were optimized: DUV exposure time, temperature of NiO film and the effect of ozone. We found optimum conditions to be almost the same as for TiO$_2$. The maximum hydrophilicity of NiO surface has been achieved after 10 min of DUV exposure at a sample temperature of 100°C with assistance of ozone. The water contact angle was virtually non-measurable (<1°). In Table 1, the influence of surface treatment on hydrophilicity of the TiO$_2$ surface is summarized.

| Surface treatment | Water contact angle [°] |
|-------------------|------------------------|
| Chemically        | 60 min, RT             | 26 |
| Chemically        | 120 min, RT            | 24 |
| UV                | 60 min, RT             | 7  |
| DUV               | 10 min, RT             | 5  |
| DUV+Ozone         | 10 min, RT             | 3  |
| DUV               | 10 min, 100°C          | 1  |
| DUV+Ozone         | 10 min, 100°C          | <1 |

3.2. Functionalization of metal oxide film by MPTMS coupling agent

The mechanism of reaction of the MOF and MPTMS is probably analogous to the mechanism which is described in detail for SiO$_2$ and MPTMS [12]. In our experiments the surface of TiO$_2$ and NiO was modified with MPTMS after the sample was immersed in a liquid solution of MPTMS in toluene or placed into the chamber with vapours of MPTMS for 24 hours immediately after hydrophilization. In figure 2, the impact of the different methods of silanization on the deposition of AuNPs is shown. In the
case of the liquid silanization, irregular particles with submicrometer dimensions are observed. We assume that these formations are probably due to the self-polymerization of hydrolyzed molecules of MPTMS which form submicrometer particles condensing onto the surface as irregular polymers. It is likely that the solvent contained the trace quantity of water, which can result in self-polymerization. Moreover, in the case of vapour silanization the particle density was almost three times higher than in the case of liquid silanization.

![Image](image1.png)

**Figure 2.** The influence of the different methods of silanization on deposition of AuNPs on NiO surface: in 5% MPTMS in toluene (left); in vapours of MPTMS (right) silanization time: 24 hours, deposition time: 4 hours.

### 3.3. Deposition of AuNPs

After the surfaces of MOFs were functionalized by MPTMS and subsequently cured at 110°C for 10 min, the samples were immersed in a colloidal solution of AuNPs for a predetermined time. In figure 3, the dependence of the particle density as well as the area covered with AuNPs on deposition time for NiO film is shown. It is obvious that the density of AuNPs is sharply increasing at the beginning and approximately after two hours reaches a saturated state. The highest density (~9800 µm⁻²) and uniformity of immobilized AuNPs were achieved when the deposition time was prolonged for 22 hours. Gold nanoparticles covered nearly 31% of the total area of the NiO surface in this case. When comparing NiO and TiO₂, no differences in nanoparticle distribution and their density were observed.

![Image](image2.png)

**Figure 3.** The dependence of the density of AuNPs and the total area covered by AuNPs on deposition time; silanization in vapours for 24 hours (left) and the structure of densely arranged AuNPs on NiO surface; silanization in vapours for 24 hours, deposition time: 22 hours (right).
The unique properties of the nanoparticles have been shown, when we explored the effect of annealing on the behaviour of the nanoparticles covalently linked to the NiO surface. We observed that any of adjacent gold nanoparticles coalesced to the larger nanoparticles at 200°C, though the melting point of bulk gold is 1068°C. The density of the AuNPs decreases as the annealing temperature increased (figure 4). Surprisingly, with increasing temperature the area increases which is covered with gold. Of course, dodecanethiol (capping agent of AuNPs) as well as MPTMS are decomposed during the annealing. In this figure, the impact of temperature treatment on the changes particle configuration is also demonstrated. Evident contribution was found of the gold nanoparticles (annealed at 400°C for 30 min) to the increased conductivity of the NiO film. The resistance of NiO with AuNPs was lower (30.8 MΩ) than that of the bare NiO film (40.5 MΩ) at room temperature.

3.4. TiO$_2$ surface nanostructuring

After AuNPs were immobilized on the TiO$_2$ 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 TiO$_2$ after etching and after the gold particles have been removed from the surface by dissolving in a gold etchant are presented in figure 5. Depending on the particle size and deposition parameters, nanostructured surfaces of TiO$_2$ with different densities of nanotips can be prepared.

3.5. Gas sensing properties of NiO film with AuNPs

A positive impact of gold nanoparticles on the gas sensing properties of the NiO films to hydrogen is demonstrated in Table 1. Chips with the NiO films (with and without AuNPs) on IDE structure were
inserted into the gas chamber PLV 50 (Cascade Microtech) on a hot plate. Source measuring unit (Agilent B2902B) with an output voltage of 1 V was used to measure the current (for calculating the resistance) using gold-plated probe tips placed on the contact pads of the platinum IDE structures of the chips. The resistance of the NiO films was determined first in clear synthetic air with pressure $8 \times 10^3$ Pa ($R_{\text{air}}$) and then in a mixture of synthetic air and hydrogen (100, 500 and 1000 ppm) ($R_{\text{gas}}$) at 200°C. Formula $S = (R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$ was used to calculate the sensitivity. In the case of the NiO film with AuNPs the sensitivity was found to be more than twice higher for 100 ppm of H$_2$ in comparison with the NiO film.

| Concentration of H$_2$ [ppm] | Sensitivity (NiO) | Sensitivity (NiO with AuNPs) | $S_{\text{NiO with AuNPs}}/S_{\text{NiO}}$ |
|-------------------------------|------------------|---------------------------|-----------------------------|
| 100                           | 0.76             | 1.58                      | 2.08                        |
| 500                           | 2.50             | 3.67                      | 1.47                        |
| 1000                          | 11.76            | 19.50                     | 1.66                        |

Regarding the mechanism for this p-type metal oxide-based gas sensors without and with Au nanoparticles, the most accepted explanation of the improved sensitivity is described in [18]. In the case of the NiO films with AuNPs, the effect of Au nanoparticles on the sensitivity can be described depending on the size of nanoparticles and NiO crystallites. Since the grain size of our NiO films is comparable (~ 10-20 nm) with the size of annealed gold nanoparticles, the mechanism is acceptable in which large gold nanoparticles form new electrical paths between NiO nanocrystallites. This reduced the sensor resistance by 30 to 40% in our case and this reduction results in an increase in the sensor sensitivity.

4. Conclusion

This paper presents a new method of the deposition of gold nanoparticles with a diameter of 5 nm from a colloid on the surface of a titanium dioxide and nickel oxide film. We can summarize that surface hydrophilization of the MOFs 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 24 hours were convenient. In the best case (sample with NiO film held for 24 hours in the colloid solution) the close-packed and uniform structure was obtained with density of AuNPs of 9800 µm$^{-2}$. We also found that the melting temperature of the AuNPs with diameter of 5 nm was approximately 200°C. Gold nanoparticles were used as an etching mask for nanostructuring the sensitive layer of TiO$_2$ by reactive ion etching in order to significantly increase the active area of the layer and hereby to improve its possible response. The influence of the nanoparticles in the sensing properties of the NiO films to hydrogen was demonstrated. In the case of the NiO film with AuNPs we found a more than two times higher sensitivity for 100 ppm of H$_2$ at 200°C in comparison with that of the NiO film.

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