

Novel Gold Nanoparticle Organic Composites: Characterization of optical and sensing properties

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Abstract:

Gold nanoparticles with an average sizes of 5 nm were interlinked with 1,4-Benzenedithiol to a thin film. For the film preparation manual layer-by-layer spin-coating was used. The composition of the film was analyzed by X-ray photoelectron spectroscopy (XPS) and Surface Enhanced Raman spectroscopy (SERS). The sensing properties of the sample were determined by measuring of changes of the resistance under the influence of different vapors (toluene, water, 1-propanol and 4-methyl-2-pentanone). The film showed linear I-V characteristics at room temperature.

Key words: Gold, nanoparticles, sensor, X-ray photoelectron spectroscopy (XPS), Surface Enhanced Raman spectroscopy (SERS).

Introduction

The miniaturization of the components for the electronic devices' construction is an essential feature of modern technology. The versatility of physical and chemical properties of noble nanoparticles render them as promising materials in the field ranging from optoelectronics to sensors [1]. The chemical and physical properties of thin films comprised of two- and three-dimensionally cross-linked metal nanoparticles have attracted enormous attention over the past decade [2]. Several research groups demonstrated that these films can be used for numerous applications, such as vapor [3–6] or gas sensors [7], selective coatings for electrochemical sensors [8, 9], strain gauges [10, 11], and substrates for surface enhanced Raman scattering (SERS) [12].

In this work, we report on the assembly, the material conductivity, the chemical composition and the vapor response of nanoparticle networks interlinked with aromatic, conductive organic molecules. As the nanoparticles component, dodecylamine-stabilized gold nanoparticles were used [13], which were interlinked layer-by-layer due to exchange reactions with the organic molecules of 1,4-Benzenedithiol.

Materials and sample preparation

Chemicals were purchased from Sigma Aldrich, Merck, VWR, Technic France and Honeywell and used as received. All chemicals were of technical grade or higher purity. 1,4-Benzenedithiol was utilized as the organic linker molecules (0.5 mmol/L with toluene). 3-Mercaptopropyltriethoxysilane (MPTES) was used as silanization agents for the substrate's surface functionalization. The dodecylamine-protected gold nanoparticles (AuNP) were synthesized as described in [13] at 20° C. Deionized (DI)-water with a resistivity of 1MΩ·cm (Purite HP700 Deioniser) was used throughout the experiments. Silicon wafer with a defined thickness of 625±15 µm obtained from Siltronic AG was cut into small slips with an edge length of about 15 mm and was used as substrates for measurements. Substrate for sensor measurements was equipped with gold finger-electrodes (52 finger pairs, 50 µm width and 5.2 mm length, 100µm gap).

Manually preparation by spin-coating The sample preparation was proposed by *Schlicke et al.*[2] and used in a modified way. The substrate was cleaned for 15 minutes in the ultrasonic bath, filled with acetone, and rinsed with acetone and DI-water.

The next cleaning step included rinsing with DI-water and isopropanol, drying with argon flow and placed for a 20 minutes to the UV/Ozone cleaner (ProCleaner™ Plus). The next stage in the substrate preparation was the silanization. As silanization agent 3-Mercaptopropyltriethoxysilane (MPTES) was used. It was preliminarily heated in an oil bath to 120°C for an hour. We placed the substrate to an attached hermetic glass-tube, where it was functionalized by respective silane vapor for 60 minutes.

After the silanization the film was deposited on the substrate. We used a spin coater (Delta10 BLE Laboratory) with rotation mode of 2500rpm. 12µL NP solution and 2 x 12µL organic linker solution (1,4-Benzenedithiol with toluene) were dropped to the sample layer-by-layer with a pipette. The waiting time between the layers dropping amounts to 20 sec (while the substrate continued rotating). One set of three coatings considered as one cycle. The film's thickness depends on number of cycles. For our goal we used 15 reiterations. The finished film was immersed in a solution of 1,4-Benzenedithiol (0.5 mmol/L in Toluene) over night. Afterwards we repeated cleaning with DI-water, isopropanol and argon-drying. The fabricated sample was stored in the air.

SEM images of the resulting film are shown in Fig. 1. The cross-section (left) reveals a homogenous structure.

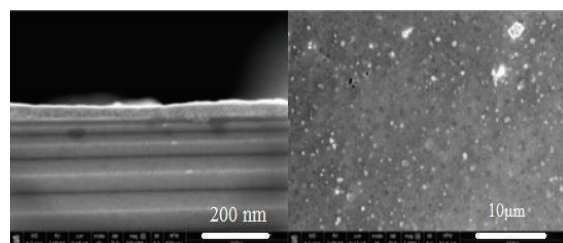


Fig. 1. SEM images of cross-section (left) and surface (right) of gold nanoparticles composites, interlinked with 1,4-Benzenedithiol.

White regions at the surface correspond to gold nanoparticles agglomerations. In order to avoid such agglomerations one can also use lower concentration of AuNP during the deposition process resulting in a more homogeneous surface structure.

X-Ray Photoelectron Spectroscopy (XPS)

These investigations were performed with a ESCALAB250Xi from Thermo Scientific. The spot size of the x-ray source was 650 µm and the power values are 14.8 kV and 13.7 mA. The pass energy of the analyzer was set to 100 eV for the survey spectrum and 20 eV for the element spectra. From all spectra a linear

background was subtracted and the binding energy was calibrated to Au = 84.0 eV. For the film Au, C and S were found. The absence of nitrogen indicates that the stabilizing molecules of dodecylamine of the nanoparticles solution were completely exchanged by the interlinking molecules during the layer-by-layer preparation of the films. The spectra were fitted using Voigt profiles (30% Lorentz, 70% Gauss) with the spin orbit splitting for Au4f and S2p. The intensity ratio was kept at 2:1 (Au4f_{7/2}: Au4f_{5/2}; S2p_{3/2}: S2p_{1/2}). Fig. 2 illustrates the C1s and S2p XPS spectra.

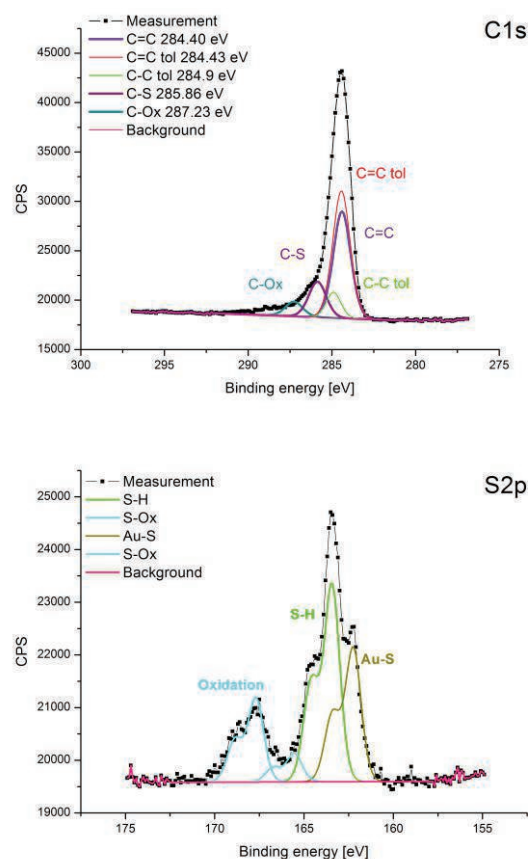


Fig. 2. C1s and S2p XPS spectra

In C1s spectrum one can see five major components i.e two signals near 284.40 eV were attributed to aromatic carbon from the organic molecules and from toluene, aliphatic carbon bonds from toluene at 284.90 eV, carbon bond to sulfur at 285.86 eV and small amount (less than 5%) oxidized carbon at 287.23 eV. The presence of two aromatic and additional aliphatic peaks is caused by residual solvents that may remain inside the film and intercalate between nanoparticles similar to dithiol molecules [14]. Table 1 summarizes and compares ratios between different bonds, obtained from the experimental data and calculated from the molecular stoichiometry.

In S2p spectra two major components and oxidation can be observed. The species at 162.2 eV and 163.4 eV can be attributed to sulfur bond to gold (S-Au), the species at 163.4 eV and 164.6 eV correspond to free thiol groups (S-H), the species at 165.5 eV and 166.7 eV are due to presence of oxidized sulfur in the film, the species at 167.7 eV and 168.9 eV are also caused by oxidation processes but with higher level of oxidation. In the case of common method of preparation the content of it is equal to 25%. From the diagrams shown in Fig. 3 one can easily see that the number of free thiols in film is higher than the sulfur-to-gold bonds.

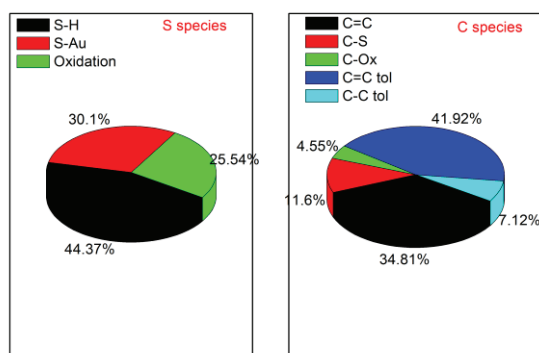


Fig.3. Pie-diagrams of the different sulphur and carbon species

This demonstrates that most of the dithiols are bound only with one end to the gold nanoparticle. A considerable amount of organic molecules seems to be intercalated in the organic matrix instead of being covalent attached to the nanoparticles. Such structure of nanocomposite can be explained by comparative small length of linker molecules and wide distribution of gold nanoparticles. Also we can see that there is a relatively high amount of residual solvent inside the film.

Tab. 1: Ratios between different species and bonds

	Experimental	Stoichiometry
S-Au/S-H	0.85	1
C/S	4.5	3

From Table 1 we can see that all experimentally obtained ratios are comparable to expected values. The difference between the ratios can be explained by oxidation processes, which are not included in the stoichiometric formula and residual toluene. The smaller experimental ratio S-Au/C-H also

confirms observation, that not all sulfur molecules are bound to gold nanoparticles.

Surface enhanced spectroscopy (SERS)

Raman measurements were performed at room temperature using a Raman spectrometer Labram HR 800 (Jobin Yvon). All Raman spectra were excited using the 532 nm (2.33 eV) line of a frequency-doubled Nd:YAG laser at a power level of 0.1 mW. The laser beam was focused on the sample surface by a 50x Olympus microscope objective. The scattered light was collected by the same objective in backscattering geometry. After passing the spectrometer equipped with gratings of 600 grooves/mm, the scattered light was analyzed by a thermoelectrically cooled CCD detector. We performed measurements for two samples, namely for film with AuNP and for pure linker solution. The spectra of the film exhibit sharp peaks at 520 cm^{-1} , 1083 cm^{-1} and 1553 cm^{-1} , which can be assigned to the Si and aromatic/hetero rings (moderate) modes respectively (see Fig.4).

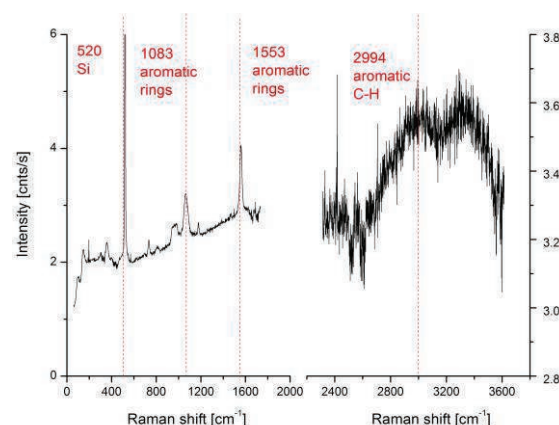


Fig.4. SERS spectrum of film interlinked with 1,4-Benzenedithiol (fingerprint and C-H region).

In the higher frequency region aromatic C-H bonds can be detected, but the peak is very mildly sloping and illegible due to small amount of such bonds.

In the case of pure linker solution just Raman spectra for toluene can be observed because of negligible concentration of 1,4-Benzenedithiol and absence of enhancement effects. Due to presence of AuNP in the film we can use SERS approach and detect evident enhancement of linker signal compared to its solution in organic solvents. However, the intensity of Raman signal still remains low. Moreover we cannot detect a negligible amount of oxidized molecules or residual solvent.

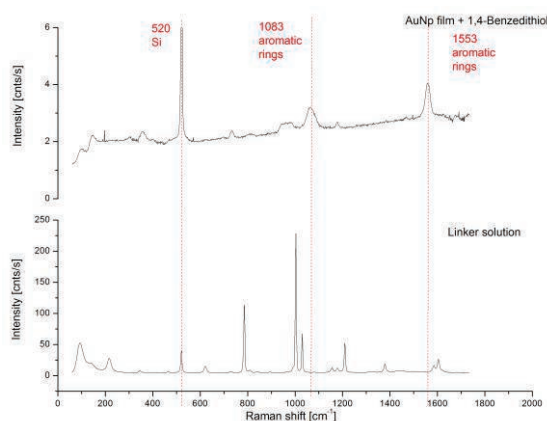


Fig.5. Raman spectra of the film and linker solution.

In Fig. 5 the fingerprint region of Raman spectra of film and linker solution are depicted, respectively. There are no mutual peaks except the one at 520 cm^{-1} , which is attributed to Si just in the spectrum of the film. The peak from aromatic rings in toluene could be shifted to lower frequencies in the film spectrum due to interactions with heavy AuNP.

Sensor results

The sorption of toluene, 1-propanol, 4-methyl-2-pentanone and water in the 1,4 - Benzenedithiol-nanoparticles composites were investigated by coating the material on substrates equipped with interdigitated electrodes. These solvents have similar vapor pressure, which makes them very suitable for studying of chemical selectivity of sensor materials [14]. The response traces toward 5000ppm of the analytes are given in Fig. 6. Relatively high sensitivity can be explained by high sorption capacity of the porosity film with low level of interlinkage. Increasing of resistance during the experiments is connected with phenomena of film's swelling. The selectivity of the analytes uptake in the film are comparable for all materials. The highest response was observed for the hydrophobic toluene, about 20% smaller response was observed for flexible hydrophobic molecule 4-methyl-2-pentanone and polar 1-propanol. The smallest response (three times smaller, than for toluene) was observed for polar water molecules.

The observations revealed right tendency, because conductive molecules cannot increase sharply composites resistance. All water responses are rectangular, all toluene and 1-propanol responses are almost rectangular. Fig. 6 justified, that all measurements are quite fast and fully reversible.

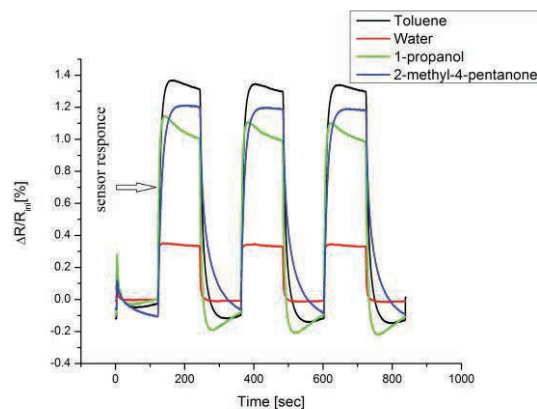


Fig.6. Sensor responses of film interlinked with 1,4-Benzenedithiol.

For all analytes, concentration dependent measurements of the mass in the range 100 – 5000 ppm were performed. The isotherms are shown in Fig. 7.

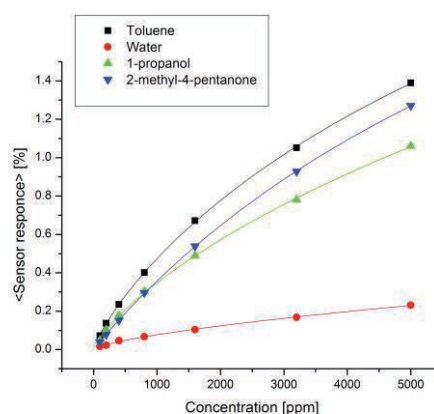


Fig.7. Langmuir fits of resistive response isotherms.

The sorption isotherms of toluene, 1-propanol and 4-methyl-2-pentanone can be better fitted with Langmuir formalism, whereas the sorption of water can be good enough fitted either linearly or with Langmuir fit. That reveals that the interactions of different analytes with film are similar.

Conclusions

Gold nanoparticles film interlinked with 1,4-Benzenedithiol was prepared using spin-coating and characterized by SEM, SERS and XPS. The vapor sensing properties of the film was also investigated. The key results can be summarized as follows:

Dodecylamine-stabilized Au nanoparticles and 1,4-Benzenedithiol linker molecules are well suited for the manually layer-by-layer assembly of interlinked Au nanoparticle films. SEM images indicate that the film has homogeneous, but porous structure. The porosity of composite can be avoided by dint of preparation under vacuum.

XPS analysis of the films revealed that, during the film assembly process, the dodecylamine ligands were completely exchanged by linker molecules. Only about 30% of the 1,4-Benzenedithiol molecules were bound with both ends to the surface of the nanoparticles, the remainder being bound through only one thiol group. About 12% of carbon amount and 26% of sulfur amount were oxidized during the preparation and storage under ambient conditions.

When the films were dosed with vapors of toluene, 1-propanol and 4-methyl-2-pentanone a fast and fully reversible increase of their resistance was measured. During the interaction with water vapors the changes in resistance were also totally reversible but lower, then for other analytes. Our results suggest that swelling could be the dominant component of the sensing mechanism.

The possibility of fast response, reversibility and the high sensitivity to volatile organic compounds (VOCs) make noble metal nanoparticles films promising materials for sensor applications. To further investigate the sensing mechanism, it is necessary to study the dependence of the electrical response on the chain length of the linker molecules. For this organic components with a higher number of aromatic rings could be used.

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