

Chemiresistors Based on Bisdithiocarbamate Interlinked Gold Nanoparticles [†]

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Abstract: The assembly, structure, composition and sensing properties of novel bisdithiocarbamate based gold nanoparticle networks have been investigated. The sensing properties have been studied with vapors of toluene, 1-propanol, water, and 4-methyl-2-pentanone. We demonstrated that bisdithiocarbamates based chemiresistive sensors show sensing properties versus volatile organic compounds (VOC) comparable to thiol based composites but that they are superior in their long term stability.

Keywords: chemiresistor; gold; nanoparticle; bisdithiocarbamate; volatile organic compounds; ozone; oxidation; long term stability; aging

1. Introduction

Over the past few years, one effort of materials research was the development of composite materials which can be tailor-made for certain applications on the molecular level. Especially nanocomposites based on metal nanoparticles and organic molecules show attractive possibilities in chemiresistive sensing [1]. Nearly all composites use thiol based molecules to stabilize or link gold nanoparticles even if they are known to be prone to oxidation of the thiols by ozone from ambient air. This degrades the material and limits their long term stability and thus their application in sensing [2].

2. Materials and Methods

4 nm dodecylamine stabilized Au nanoparticles were synthesized based on a previously reported method [1]. Chemicals with reagent grade or higher purity were purchased from Sigma Aldrich, VWR and Acros Organics and are used as received. For the layer-by-layer self-assembly, N,N-dimethyl-1,8-octanebisdithiocarbamate (BDTC) had to be synthesized in-situ by a base catalysis induced addition of carbon disulfide in 2-propanol from N,N-dimethyl-1,8-octanediamine as described previously [3]. For the sensing measurements, oxidized silicon substrates equipped with gold interdigitated electrodes characterized by a finger length of 5.2 mm, a height of 100 nm, and a spacing of the fingers of 50 μm (providing 52 finger pairs in total) were used. The electrode substrates were cleaned by an oxygen plasma followed by a gas phase silanisation procedure with 3-aminopropyldimethylethoxysilane [1].

As shown in Figure 1a, the preparation of the sensitive material has been performed in an automated layer-by-layer self-assembly procedure using two microfluidic cells [3] where solutions of Au nanoparticles and BDTC were pumped through, alternating with pure solvents with 14 assembly cycles. While coating of the sensor substrate took place in the custom-made cell, the coating progress was monitored in the QCM cell.

The composite has been investigated by Scanning Electron Microscopy (SEM) with an FEI Helios NanoLab 600i and by X-ray photoelectron spectroscopy (XPS) with an ESCALAB250Xi from Thermo Scientific. The setup describing the chemiresistive sensor measurements have been described previously [1]. The chemiresistive behavior at room temperature vs. 100–5000 ppm of vapors of toluene, 4-methyl-2-pentanone, 1-propanol, and water has been investigated. To investigate the oxidation stability the chemiresistor samples were treated with ozone in the UV/Ozone cleaner (ProCleaner™ Plus).

3. Results and Discussion

3.1. Layer-by-Layer Self-Assembly

The layer-by-layer self-assembly revealed a stepwise assembly of the gold particles and the linking bisdithiocarbamate molecules with major mass increase during the gold nanoparticle exposure as shown in Figure 1b as known from thiol based composites [3].

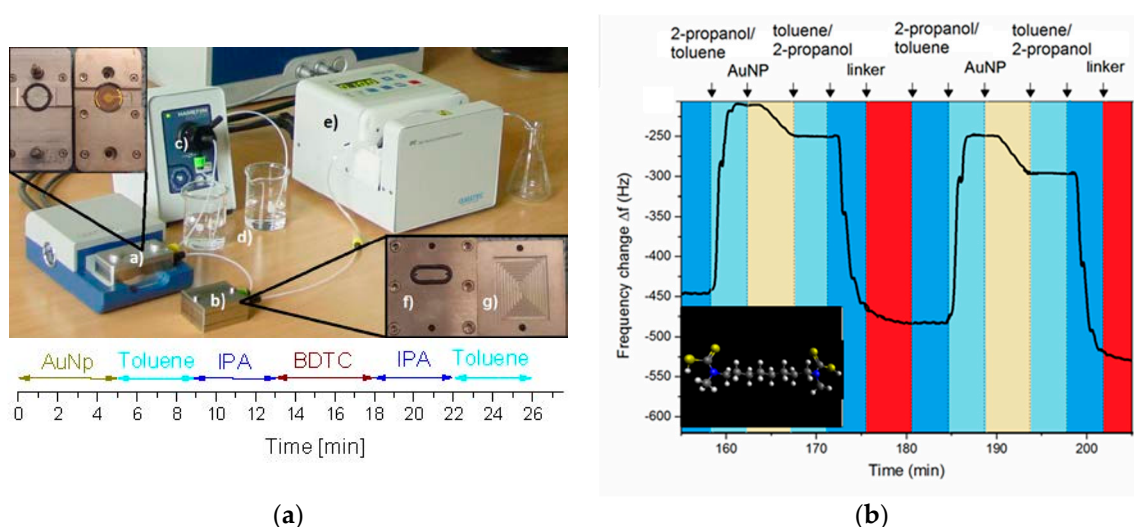


Figure 1. Layer-by-Layer self-assembly process: (a) automated setup for the nanocomposite preparation as described previously [3]. It includes also the used assembly cycle at the bottom; (b) detailed view of the frequency shift over time during two deposition cycles for the composite. The respective injection steps for the nanoparticles, the BDTC solution, and the solvent rinses are colored (light blue, toluene; dark blue, 2-propanol; yellow, gold nanoparticles in toluene; red, linker in 2-propanol). The inset shows the used bisdithiocarbamate.

3.2. Composite Characterisation

The structure of the composite has been investigated by Scanning Electron Microscopy (SEM) and reveals intact particles and unchanged sizes.

The materials composition was studied with X-Ray Photoelectron Spectroscopy (XPS). The C1s and S2p XP spectra are given in Figure 2. The spectra of the fresh composites reveal the incorporation of bisdithiocarbamates in the composites. During the oxidation procedure the C1s spectra remain nearly unchanged while the S2p spectra show a change in composition from mainly thiols in the fresh film to fully oxidized sulfur in the 10 min treated sample. In contrast to thiol based systems [2] there is no tremendous loss of sulfur in the oxidized systems.

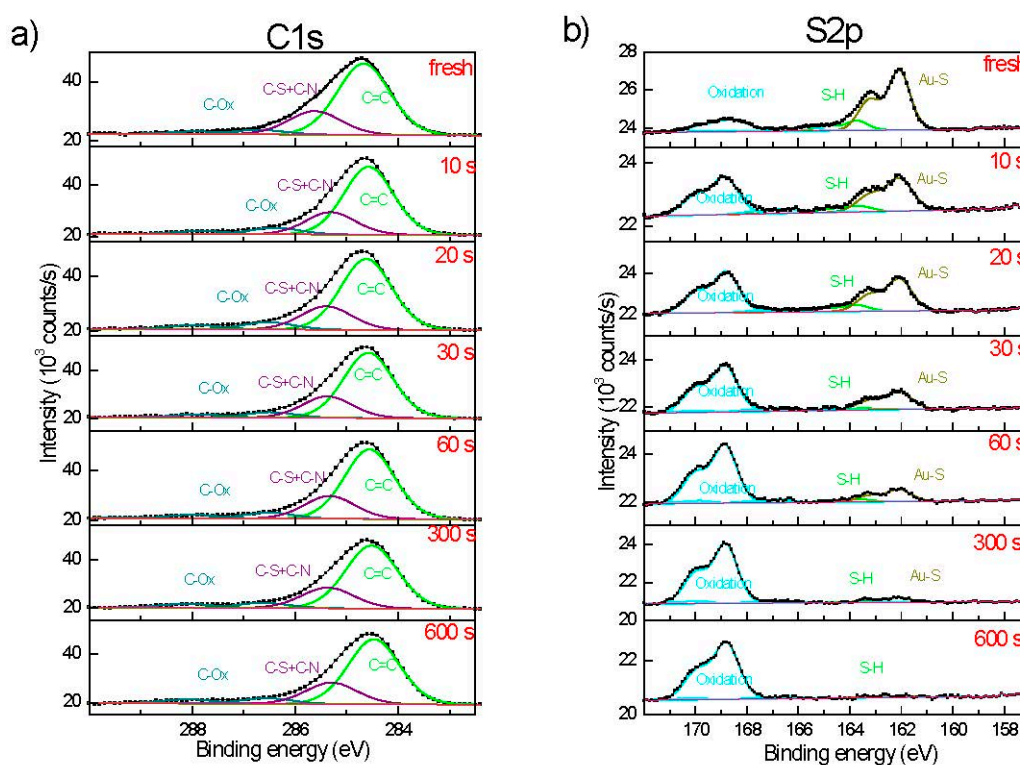


Figure 2. X-Ray Photoelectron spectra of freshly prepared and oxidized films. The treatment time in the ozone generator is indicated. (a) C1s spectra, (b) S2p spectra.

3.3. VOC Sensing

The sensing properties towards 5000 ppm of the respective vapor are shown in Figure 3. The black curve is the fresh sample, while the other curves indicate samples that are treated for the indicated time in the ozone generator.

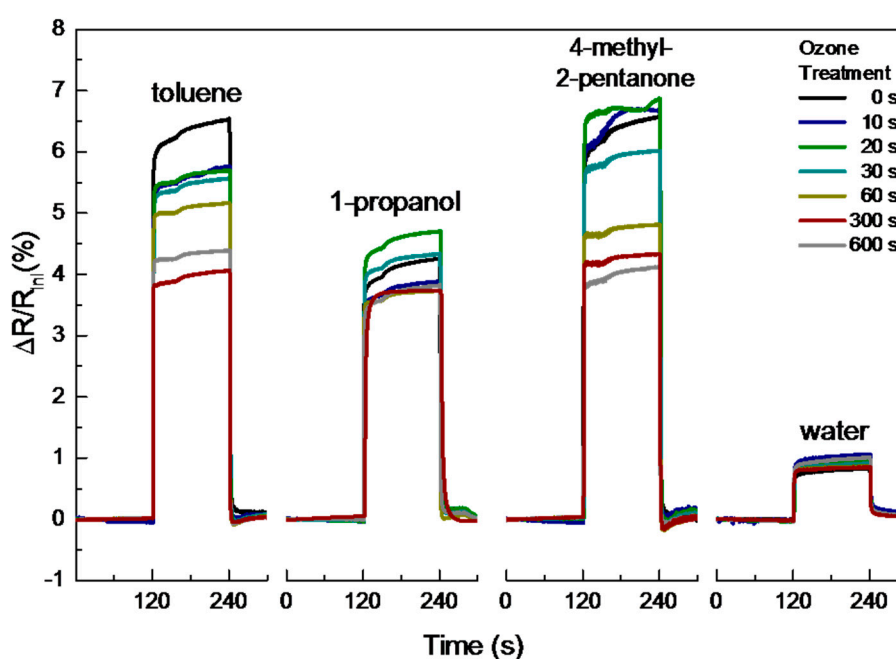


Figure 3. Sensor responses for 5000 ppm of the indicated analyte of the bisdithiocarbamate composites: The black curve is the freshly prepared composite, while the other curves indicate the response of the sensor material after ozone treatment for the indicated time.

The freshly prepared film showed fast and reversible responses to all investigated analytes. The responses to the three organic vapors are in the same order of magnitude, while the response to water is considerably lower. It is clearly visible, that the sensor responses are changing slightly with oxidation, but even after 10 min of ozone treatment, the sensor is still responding. This could not be achieved by dithiol interlinked composites in parallel experiments.

4. Conclusions and Outlook

The assembly of a novel bisdithiocarbamate based gold nanoparticle network has been demonstrated. The composite was oxidized with an ozone generator to investigate the oxidation stability of the novel composite and reveal only minor sulfur loss during oxidation. The sensing properties have been investigated with vapors of toluene, 1-propanol, water, and 4-methyl-2-pentanone. The bisdithiocarbamates based chemiresistors show sensing properties versus volatile organic compounds comparable to thiol based composites but that they are superior in their long term stability.

In the future other bisdithiocarbamate based composites have to be studied and the reason for the increased stability during sensor measurements on a molecular scale has to be clarified.

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Conflicts of Interest: The authors declare no conflict of interest.

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