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MODIFICATION OF HEAVY METAL SURFACES WITH THIOLS

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Self-assembled thiol monolayers on gold have been studied extensively and various interesting nanotechnological applications have been demonstrated [1]. Thiols also interact strongly with other metal surfaces. However, it was found that treating of the bismuth surface with 1-octadecanethiol solution in ethanol produces a thick layer of tris(1-octadecylthio)-bismuthine [2], but not a self-assembled thiol monolayer.

In this work, the surfaces of Bi, Pb, Sn, Cd, Hg, and Sb were modified with thiol solution in ethanol in order to study the thickness and structure of formed layers. The contact angle of a drop of water changes noticeably after metal modification with thiols, indicating to the more hydrophobic nature of thiol modified metal surfaces. However, electrochemical measurements indicate much larger amount of thiolate on the electrode surface than expected for a monolayer.

In order to study the structure of metal thiolates more thoroughly, these were also synthesized from the corresponding metal oxide and thiol. Differential scanning calorimetry, infrared spectroscopy and X-ray diffraction methods were used to characterize the structural properties and composition of formed thiolates. Prepared metal thiolates have interesting crystal structure (Fig. 1), which decomposes irreversibly during melting.

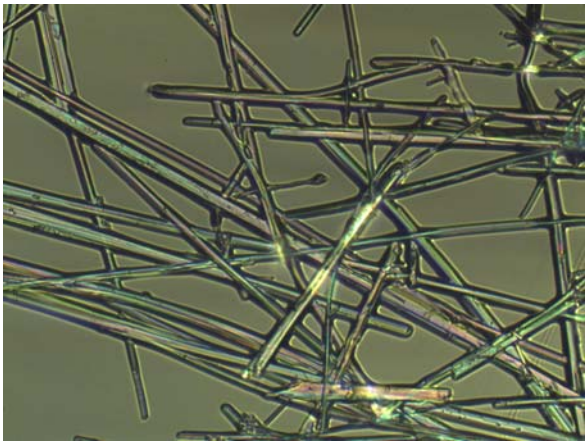

Fig.1. 0.16 x 0.12 mm optical microscopy image of $Bi(SC_{18}H_{37})_3$ *crystals.*

Still, the most interesting metal under study is bismuth because of giant magnetoresistance of bismuth nano-structures and thermoelectric properties of porous bismuth and some bismuth compounds (Bi_2Te_3). Thus, the possibility of the formation of stable thiol monolayers on bismuth surface was further studied by using thiols with different functional groups at the other end of hydrocarbon chain. Nevertheless, experiments with 1-octadecanethiol, 1-decanethiol, 16-mercaptohexadecanoic acid, 1,8-octanedithiol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hepta-decafluoro-1-decanethiol, and 1-adamantanethiol show that reaction with thiols does not stop at a monolayer stadium. Synthesis of bismuth thiolates from bismuth chloride, instead of bismuth oxide, gave red compounds, instead of yellow.

Thiolate films under study can protect the underlying metals against corrosion or change the surface properties according to the chosen functional groups in thiols.

References

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