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MULTILAYERS BY SELF-ASSEMBLY

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Nanoparticles, as building blocks, are important for the development of advanced, functional composite materials. Recent developments have shown that self-assembly of nanoparticles is a promising technique for the fabrication of complicate nanostructured materials. Self assembly of the nanoparticles into ordered structures on a substrate can be achieved through chemical treatment of the particle and/or substrate surface. The assembled nanoparticles can have a dramatic effect on the physical properties of the composite. A μ CP technique has been employed to form a SAM of bifunctional silane (APTMS) in the region of contact. The stamps for the μ CP are prepared by polymerization of polydimethylsiloxane (PDMS) on a flat surface. Glass substrates have been used for optical absorption measurements. Oxide or metallic particles have been assembled on the patterned surface after a surface treatment. The self-assembled layer was subsequently treated with bifunctional molecules and multilayers of the same material or composites have been thus obtained.

INTRODUCTION

Chemical synthesis of nanostructures and hybrid organic-inorganic materials represent the fastest growing topics of today's chemistry. Being at the interface of traditional disciplines, these areas of science present rich research grounds with potentially strong fundamental and technological impact. The self-assembly of nanoparticles into useful morphologies is a much anticipated development in the nanotechnology as it offers the promise of creating materials from well-characterized, nanometer-scale constituents with interesting properties [1]. Self-assembled mono- and multilayer films on solid substrates have generated considerable interests recently because of the potential for controlling the molecular architecture and chemical and physical properties of layered assemblies on surfaces. Self-assembly (SA) means spontaneous molecular assemblies on a substrate forming an ultrathin molecular film by the treatment of the substrate with a solution of an active organic molecules. The technique provides an ordered thin film fabricating in molecular level. Self-assembled monolayer (SAM)s are stabilized by various interactions in the monolayer. The first part is the head group that provides the most exothermic process, i.e., chemisorption on the substrate surface. As a result of the exothermic head group-substrate interactions, molecules try to occupy every available binding site on the surface, and in this process they push together molecules that have already adsorbed. The second part is the alkyl chain, and the energies associated with its interchain van der Waals interactions are order of few. The third molecular part is the terminal functionality, which governs surface properties and makes it possible to form multilayer films.

Sarathy et al. prepared heterostructures consisting of alternate layers of semiconductor and metal nanoparticles [2]. Colvin et al. have made use of self-assembly of semiconductor nanocrystals to construct an optoelectronic device [3]. Murray et al. have demonstrated the self-organization of CdSe nanocrystallites into a three dimensional superlattice. Multilayers of semiconductor CdS nanoparticles have also been deposited on a glass substrate using the self-assembly of dithiol molecules [4]. There has been some effort to obtain regular arrangements of metal nanoparticles in different dimensions. Two-dimensional arrays of metal nanoparticles are

readily prepared by using alkanethiols. Whetten et al. have described gold nanocrystals stabilized by thiols [5].

This work is a part of the research on the preparation of thin films from nanoparticles and the investigation of their optical, electrical, thermal and mechanical properties. The self assembly is the thin film preparation technique that is employed in this work. Two examples of multilayer is presented: Au/magnetite (Fe_3O_4) and thermoelectric CoSb_3 -which can be used for heat-electrical energy interconversion- that are prepared by employing the solution synthesis for the nanoparticles and the self assembly method for the film formation.

EXPERIMENTAL DETAILS

Materials:

Mercaptotopyl trimethoxy silane (MPTMS), dodecandithiol, ethanol, HAuCl_4 , NaBH_4 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{OH})_2$, SbCl_3 , HCl , NH_3 and NaOH were obtained from Merck. PDMS Sylgard-184 was obtained from Dow-Corning. Hexane was obtained from Aldrich.

Preparation of Au nanoparticles:

Au nanoparticles are prepared by NaBH_4 reduction of HAuCl_4 in the presence of trisodiumcitrate as the encapsulating reagent.[6]

Preparation of Fe_3O_4 nanoparticles:

Thermodynamic modelling of the reaction conditions has been performed for the synthesis of ferrite with the required composition.[7] Solutions of Fe^{2+} and Fe^{3+} are prepared and mixed with the $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio of 1:2. The modelling results showed that the precipitation of magnetite is possible at a pH above 11. The reaction was performed by the slow addition of a mixture of metal chlorides and NaOH to a continuously mechanically mixed reactor, keeping the pH above 11.

Preparation of CoSb_3 nanoparticles:

A solution chemical method was developed [8] for the synthesis of skutterudite, CoSb_3 , nanoparticles. A thermodynamic modelling of the reaction conditions was performed for the synthesis of a precursor composed of cobalt and antimony oxalates with a ratio of 1:3. The precursor, then, is calcined to oxide, subsequently reduced and alloyed under hydrogen atmosphere. Thus obtained skutterudite nanoparticles are used for the assembly of multilayers.

Functionalizing Surfaces:

Glass substrates were employed in order to perform absorption measurements subsequent to assembly of nanoparticles. The substrates were subject to ultrasound in acetone, boiled in Piranha solution (3:1 H_2SO_4 : H_2O_2) for 1 hr to clean any organic impurity on the surface, and thoroughly rinsed with deionized water prior to use. The substrates were functionalized with APTMS or MPTMS in two ways: *i*) derivating the substrate in ethanolic solution of APTMS, *ii*) using the μCP technique. The structure of functional molecules are shown in Figure 1.

Printing:

PDMS stamps were fabricated by mixing an elastomer with curing agent at a ratio of 10:1. This mixture was poured on Petri dishes to obtain flat stamps. After curing at 60°C for 3 hrs, the

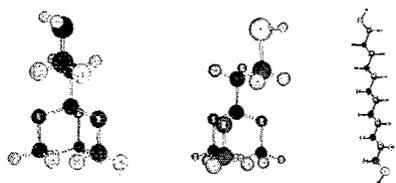


Figure 1: Bifunctional molecules for the functionalization of surfaces, for subsequent self-assembly of nanoparticles. From left to right; APTMS, MPTMS and dodecandithiol.

stamps were peeled away from the master and exposed to liquid ink to transfer silane from solution to the elastomeric stamp. In practical terms, the inker pad is equilibrated for 1 hr with a solution of silane in ethanol, then is withdrawn from solution, dried with a stream of N_2 , to take away excessive silane. The stamp is then transferred to the substrate and contacted for 5 min. The elasticity and surface characteristics of the stamp promote good conformal contact

between the PDMS surface and the substrate, favouring the formation of a continuous interface through which the homogeneous transfer of silane to the substrate surface is possible. All printing work was performed in N_2 atmosphere, since silanes are very sensitive to humidity and can easily polymerize in the presence of water. Figure 2 shows the overall procedure for functionalization of the substrates and formation of multilayers through stepwise functionalization.

Self-Assembly:

MPTMS molecules were transferred to the substrate surface using the μ CP technique with prepared PDMS stamps (Fig. 2). First layer of gold was assembled was attained by dipping the substrate in the colloid solution for 3 hrs. The pH of the colloid solution was adjusted to 5-7 to increase the interaction of nanoparticles and end groups. The derivatizations successfully yielded self-assembly of colloidal Au nanoparticles at MPTMS functionalized surfaces through covalent bonding between the gold surface and $-SH$ groups on the substrate. In the case of $CoSb_3$, the substrate was derivatized in a toluene solution containing skutterudite nanoparticles. The substrates were then ultrasonicated to remove particles adsorbed at unsilanized surfaces.

Depending on the material to be assembled on the second layer, different functional groups can be used to adjust the chemistry for the self assembly process. For the Au/Fe_3O_4 multilayer formation, the assembled Au surface was functionalized with MPTMS. However, the orientation of molecules is reversed, i.e. $-(OCH_3)_3$ groups should point upwards, since they can be attached to oxide surface through the cleavage of $O-CH_3$ bonds. There is no special effort to align the bifunctional molecules, since they will align themselves easily due to the functionality on the substrate surface. Then the substrate was dipped into Fe_3O_4 colloid in toluene and held for another 3 hrs. The assembly of this type of multilayers can be easily performed by the same bifunctional, MPTMS, molecule provided that the target sequence is metal/oxide/metal/oxide etc. Skutterudite multilayer needs a different bifunctional molecule, which is capable of binding the same type of particles in both ends. The commonly used dithiol molecules are very convenient for that purpose. First layer of skutterudite surface was functionalized with dodecandithiol and the substrate was held in $CoSb_3$ dispersed in hexane to self-assemble the second layer.

The characterization of self-assembled surfaces has been performed using Atomic Force Microscope (AFM) in the tapping mode with a Nanoscope IIIa system (Digital Instruments, USA) using a silicon tip.

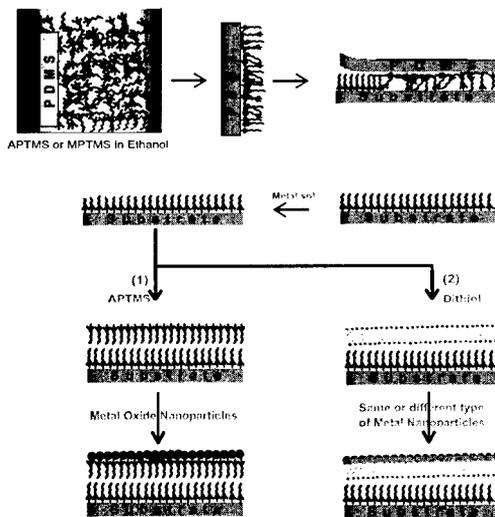


Figure 2: Schema of functionalization of surfaces with contact inking and multilayer formation.

RESULTS AND DISCUSSION

The morphology of self-assembled films was examined by AFM at different processing stages. Figure 3 and 4 shows the AFM images and section analysis of Au/Fe₃O₄ multilayer at first and fourth layers. First layer shows a very high coverage of the substrate surface with highly monodispersed Au nanoparticles. The size of Au nanoparticles is about 200 nm as can be seen from the section analysis of the AFM image. Image analysis of the fourth layer, Fe₃O₄, also shows a very high coverage of the lower surface with highly monodispersed nanoparticles of about 250 nm, as measured from the section analysis of the AFM image.

The assembled multilayer shows interesting optical behaviour as observed from UV-Vis analysis. The absorption spectra for the Au/Fe₃O₄ multilayer -4 layers- is given in Fig. 5. The same slide was used for the same set of measurements after processing stages, in order to

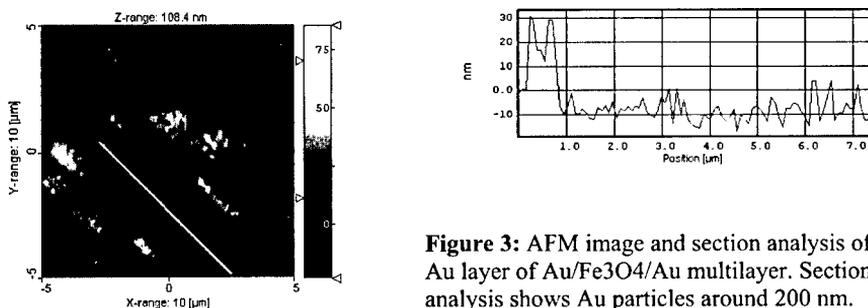


Figure 3: AFM image and section analysis of first Au layer of Au/Fe₃O₄/Au multilayer. Section analysis shows Au particles around 200 nm.

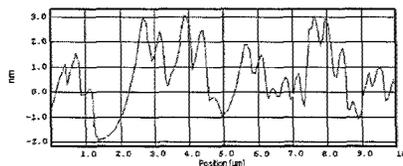
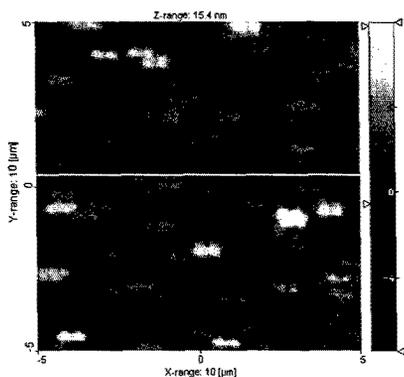


Figure 4: AFM image and section analysis of uppermost layer of Au/Fe₃O₄/Au/Fe₃O₄ multilayer. Section analysis shows Fe₃O₄ particles around 250 nm.

eliminate the experimental errors from different batch of samples. The first layer of gold shows a broad absorption in the 600-800 nm range. Magnetite does not have any absorption band in the measured wavelength range. The first magnetite layer simply enhances the absorption of this wide band. The third layer, Au, shifts the absorption maxima towards 520, where the plasmon absorption of Au takes place. The fourth layer, Fe₃O₄, shifts the absorption band to higher wavelengths and higher order contributions of the scattering give rise to formation of new shoulders at 700 and 850 nm. The plasmon absorption of gold at 520 nm also becomes clearly visible as the layer thickness is increased.

An important part of the work is to study the confinement of phonons in low dimensional structures, making a film of TE for nanoparticles. It has been theoretically suggested[9], and experimentally observed[10] that phonons are highly diffracted when the particle size is comparable to the phonon mean free path. Any reduction in the thermal conductivity of the system, provided that electronic properties negatively affected, will directly enhance the material's TE performance. A two-layer skutterudite film was prepared for this purpose and analyzed microstructure and morphology of the film is examined with AFM. The AFM image, given in Fig. 6, shows an interesting arrangement of particles, which was also observed by the

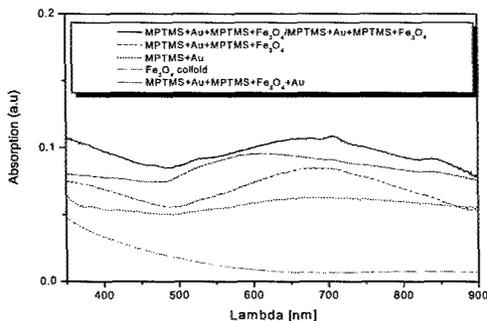


Figure 5: UV-Vis Absorption spectra for Au/Fe₃O₄/Au/Fe₃O₄ multilayer system. As the layer thickness increases interesting features are observed with new absorption satellites.

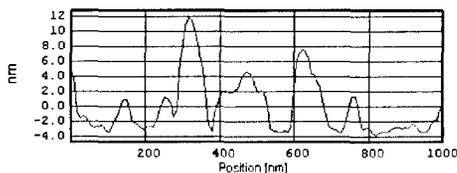
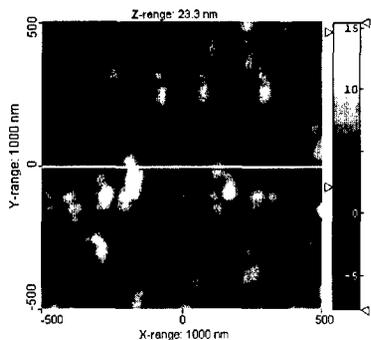


Figure 6: AFM image and section analysis of top layer of two-layer skutterudite film.

TEM analysis. The surface is highly covered but there are still porous regions and there is no registry between the layers. The average particle size of CoSb_3 was measured as 60 nm from the section analysis of the image, which is quite reasonable (TEM analysis $\sim 45\text{-}50$ nm) considering the convolution of AFM tips. Electrical conductivity measurements on the assembled films would give an idea about the porosity of the film, but did not succeed due to contact problems to the nanogranular fragile surface. Mono and multilayer assemblies of TE nanoparticles are currently under detailed investigation and results will be published in future.

CONCLUSION

Self-Assembly was successfully used to prepare metallic and nonmetallic composite multilayer films. The surface chemistry of assembled layers was changed by employing bifunctional molecules and thus the same or different type of nanoparticles were assembled. The thickness of layers can be controlled by using larger nanoparticles and the total thickness by the number of self-assembled layers. Prepared $\text{Au}/\text{Fe}_3\text{O}_4$ multilayer exhibits interesting optical behavior. Thermoelectric film was successfully prepared by, first time to our knowledge, the self-assembly of TE nanoparticles, and the properties are under investigation.

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