

Novel Thin Film Deposition of Colloidal Nanoparticles

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Abstract

Process for the fabrication of thin films from nanoparticles has been developed utilizing layer-by-layer assembly by dip coating techniques, using concepts similar to the polyelectrolyte deposition used for preparing multilayer of charged polymers. We have successfully fabricated ~500 nm thin films of gold nanoparticles and manganese doped zinc sulphide nanoparticles by the modified dip coating technique showing surface roughness of ± 2.5 nm. The colloidal films were characterized by UV-Vis spectrophotometer, Scanning Electron Microscopy (SEM) and Surface profilometry.

Introduction

Engineering nanoscale materials utilizing quantum effects, that leads to novel optical, electronic, and nonlinear properties is one of the major motivations for research in nanotechnology today [1]. In order to fabricate novel nanostructured devices, techniques for generating a wide range of nanoparticulate materials with various sizes and properties, and the assembly of these nanoparticles into tailor-made arrangements are necessary. A Self Assembled Monolayer (SAM) of nanoparticles to obtain thin films is one such method that has many promising applications including various functional layers in optoelectronic devices like transparent conducting oxide layers and phosphor layers in flat panel displays, amongst others.

Numerous techniques have been demonstrated by many research groups for obtaining a monolayer of nanoparticles on a substrate. Multilayer films are widely prepared using semiconductor processing techniques [2]. Electrochemical means for obtaining a thin film of nanoparticles have also been reported [3-5]. A solely chemical means to obtain a uniform monolayer of nanoparticles on a substrate is an attractive alternative. In this regard, Huang and Yang [6] demonstrated that a monolayer of colloidal gold nanoparticles could be organized by alternate dip coating of oppositely charged chitosan polymer and citrate stabilized gold nanoparticles. By combining layer-by-layer assembly and Langmuir Schaefer deposition technique, Lowman *et. al.* [7] demonstrated multilayer films of gold quantum dots.

The general strategy for obtaining monolayer assembly of particles involves attaching a functionalized (charged) polymer on a substrate and subsequent exposure of the nanoparticles to oppositely charged polyelectrolyte, facilitating attachment due to electrostatic forces. This process can be repeated to obtain the desired thickness of the films (Figure 1).

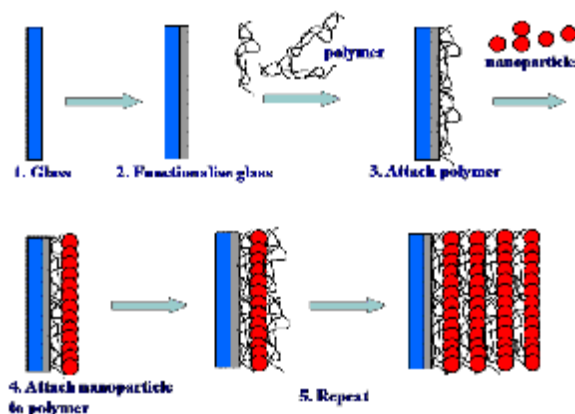


Figure. 1 Common strategy employed for the construction of a self assembled monolayer of particles on a substrate, involving a charged polymer and a nanoparticulate suspension with oppositely polyelectrolyte agent.

Polyelectrolyte deposition techniques have been used for a multitude of film deposition [8]. Dacher has reported on a technique to assemble films based on the attraction between the positive and negative charges of molecules/particles. The multilayer films were formed by

growing subsequent layers of oppositely charged polyelectrolytes. To achieve the multilayer film in a layer-by-layer type of deposition a charge inversion is always essential.

In our work, we have synthesized alternate stacks of monolayers of gold nanoparticles [~ 15 nm particles, figure 2 (a)] and Mn doped ZnS nanoparticles [~ 30 nm particles, figure 2 (b)] by alternate dip coating. By using polycationic chitosan as the first layer on a glass substrate, we assembled a monolayer of gold nanoparticles capped with anionic citrate ions. The subsequent monolayer of ZnS was achieved by capping the ZnS nanoparticles with polycationic chitosan. For this purpose we have constructed a set up that automatically dip coats a substrate that can be programmed to obtain a desired dipping time and number of layers.

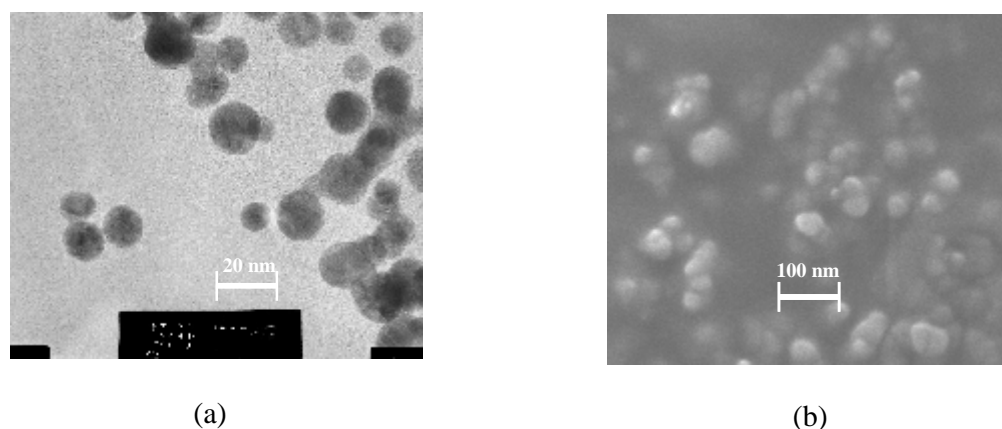


Figure 2 (a) TEM micrograph of AuNP average size of ~ 15 nm and (b) SEM micrograph of ZnS:Mn²⁺ nanoparticle showing an average size ~ 30 nm, used for our experiments

Experimental

Materials and Methods

Preparation of chitosan solution

We have used 80 % deacetylated chitosan with molecular weight of 80,000 (synthesized in-house). Concentrations of 1 % and 0.05 % (g/mL) chitosan solutions in dilute acetic acid (Merck) were used for all the experiments.

Preparation of Gold colloid

5 mM solution of Au(III)Cl₃ (Aldrich Fine Chemicals) and 25 mM trisodium citrate (Merck) solutions in deionised water were prepared and stocked. Gold colloids were prepared by adding 2 mL of the gold solution in 100 mL of deionised water and heated till boiling whereupon 3 mL of trisodium citrate solution was added following the well documented Turkevitch method [9]. It takes about an hour to obtain the bright red color of gold colloids. After cooling to room temperature, size selection was done by centrifuging at 6000 rotations/minute (rpm) for 20 minutes.

Preparation of chitosan capped ZnS:Mn²⁺ colloids

10 ml of 1 M zinc acetate stock solution was added to 10 ml of 0.1 M manganese acetate (Fluka) was added. After proper mixing 70 ml of 0.05 % chitosan solution was added under continuous stirring. Drop-by-drop of 10 ml of 1 M sodium sulphide solution was added to the mixture, with constant stirring. Mn doped ZnS nanoparticles, in the form of white precipitates were formed which were centrifuged at 6000 rpm to sediment agglomerates from the 'mother liquor'. The colloid was then rigorously washed and dialyzed to remove unreacted ions that were used for experiments reported here.

Film preparation

The glass slides were cleaned by sonication in soap for 10 minutes, flooded and sonicated with distilled water for at least 10 mins, followed by sonication in acetone for another 10 mins. The glass slides were then immersed in aminopropyl trimethoxysilane (APTS) in 95 % methanol solution for 24 hrs following which, it was rinsed with distilled water and dried. The glass slides were then treated with 1 M KOH (Merck) for a few minutes prior to any deposition. Thin films investigated in this paper are multilayers of alternate layer stacks of Mn doped ZnS (ZnS:Mn²⁺) nanoparticles capped with chitosan and gold nanoparticles (AuNP). These multilayer thin films were formed by alternating dipping in AuNP colloids and chitosan capped ZnS:Mn²⁺ colloids for

at least 3 mins in each solution. The film growth occurs as gold and ZnS nanoparticles attach to each other due to the opposite charges of chitosan & the electrostatically charged gold nanoparticle. The process was repeated to obtain a desired film thickness. All the dipping process were carried out at rate of 0.15 mm/s.

Film characterization

Scanning Electron Microscopy was carried out in a JEOL JSM-6301F and optical spectroscopy was done with ELICO model SL-164 and surface profilometry was done using DEKTAK Stylus Profiler.

Results and discussion

Once the first layer of nanoparticles (or polymer) is fixed on to the substrate, subsequent layers can be assembled relatively easily. For the first layer, we have attached chitosan capped ZnS:Mn²⁺ following Constantine *et. al.* [10]. This was done by treating the substrate with KOH solution to functionalize it. The basic KOH adsorbed on the glass substrate absorbs a proton from NH₂ to form a negative charge on the glass and thereby facilitating the attachment of polycationic chitosan enrobing ZnS:Mn²⁺ nanoparticle to the glass substrate, thus forming the first layer. Subsequent layers are attached by simple dip coating techniques involving alternate dipping into AuNP colloids and ZnS:Mn²⁺ colloids with intermediate steps of washing. The intermediate washing stage is necessary to remove all unattached excess particles (or polymer) from cross-contaminating the subsequent solution. Figure 3 shows the schematics and mechanism of the KOH treatment of the substrate. Figure 4 shows the schematics of the dipping process and the construction of the multilayer thin film.

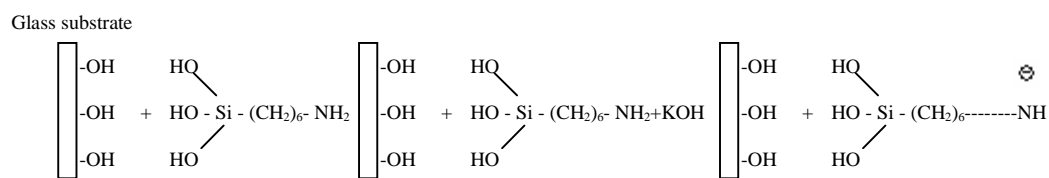


Figure 3. Schematic of APTS to the KOH

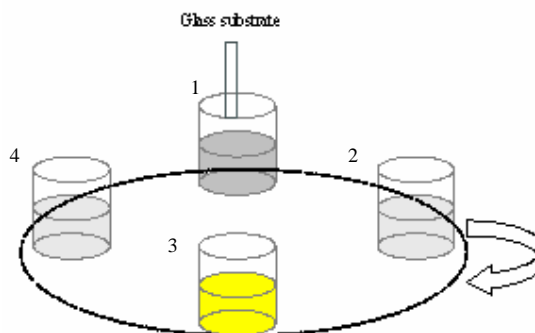
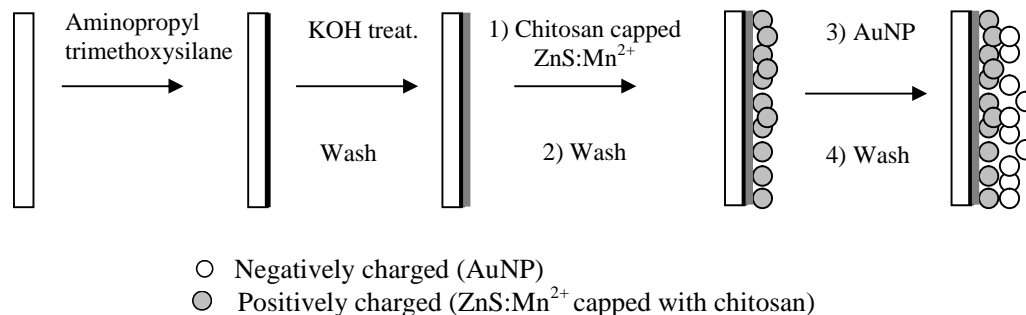


Figure 4. Schematic of dipping process. The glass slide was coated with the APTS and treated with KOH. First layer was formed by dipped into the chitosan capped ZnS:Mn²⁺ solution and washed. Then the glass was dipped in the AuNP solution and washed. The multilayer was formed by repeating the process 1 to 4

Figure 5 (a) shows the optical absorption spectra of colloidal Au nanoparticles, where the absorption due to plasmon resonance is centered at 527 nm. Figure 5 (b) shows the spectra of AuNP/ZnS:Mn²⁺ multilayer on glass slide, showing the evidence of 2 peaks. The first peak centered at 547 nm is believed to arise from the plasmon resonance absorption, red-shifted due to refractive index difference due to the presence of high dielectric constant material like ZnS. This could possibly explained more clearly with Maxwell-Garnett type of modeling, that will be pursued later [11]. The secondary peak at around 665 nm is probably due to gold nanoparticles agglomerating on the glass substrate during the drying process.

Figure 6 shows the nanoscale uniformity of the surface of the Au/ZnS:Mn²⁺ multilayer (with max surface roughness of about ± 2.5 nm). From figure 6 (a) the SEM micrograph of Au/ZnS:Mn²⁺ multilayer coated on the glass slide (cross section). The resolution is not enough to observe individual layers but the total film thickness of about 200 nm is observed. Figure 6 (b)

shows the thickness of the Au/ ZnS:Mn²⁺ multilayer, using a Dektak surface profiler to measure the film thickness. The surface uniformity is evident from the obtained profile.

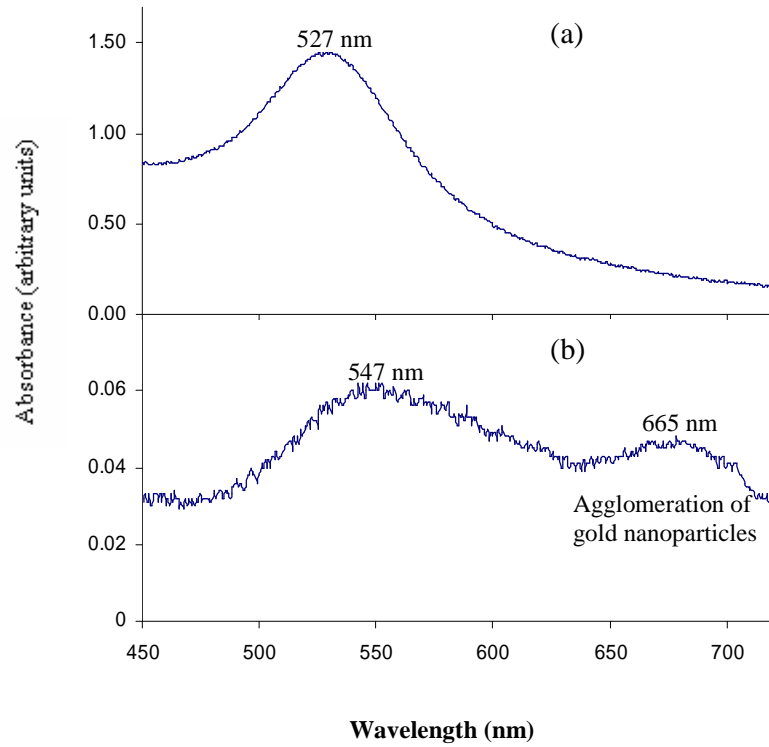


Figure 5 (a) The optical absorption spectra of colloidal Au particle and (b) Optical spectra of AuNP/ZnS:Mn²⁺ multilayer film on glass slide

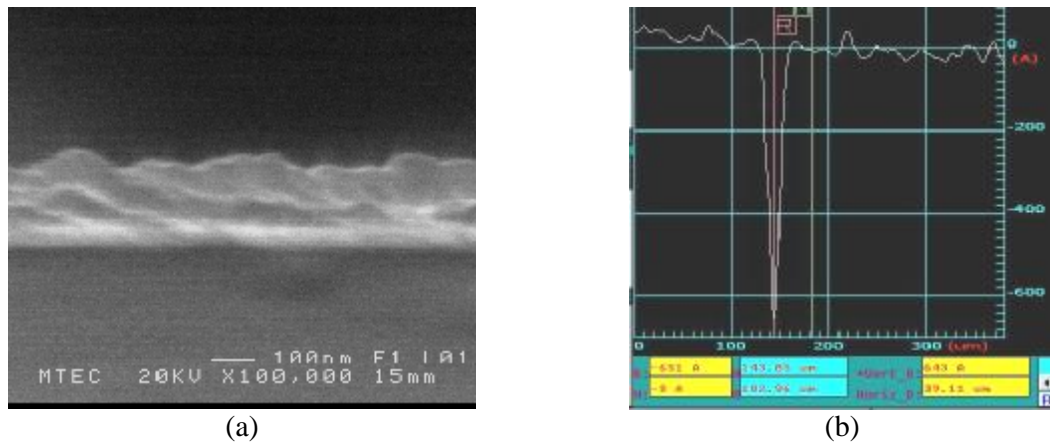


Figure 6 (a) SEM micrograph of cross section of the coating on glass slide with Au/ ZnS:Mn²⁺ alternate layers and (b) surface profile of alternate layers of Au/ ZnS:Mn²⁺ on the glass slide.

Conclusions

Through this work we have demonstrated multilayered thin films comprising of alternate layer stacks of gold nanoparticles (~15 nm) and Mn doped ZnS nanoparticles (~30 nm) by dip coating techniques, combined with layer-by-layer polyelectrolyte deposition. In this process we have circumvented the need for an intermediate layer of a charged polymer by employing specifically charged capping agents for the nanoparticles to provide electrostatic attraction. The films obtained by this process showed high uniformity and very smooth surfaces with maximum surface roughness of about ± 2.5 nm. This simple technique is cost effective compared to conventional methods to obtain thin films, like CVD, sputtering, etc. Alternate layer stacks of ZnS:Mn²⁺(photoluminescent) and gold nanoparticles (metal) have potential applications in optoelectronic devices like FEDs.

Acknowledgment

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