

# Galvanic Reaction Based Generation of Electronically Transparent Ag-Au Nanoparticle Thin Films

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## Electronic Supplementary Information

### Experimental Section

**Materials and Substrates.** Chloroauric acid (HAuCl<sub>4</sub>, 17% in HCl) and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich (Germany) and were used as received. CDs and DVDs were purchased from commercial sources. Milli-Q grade water was used for making all the solutions and for washing purposes. Glass cover slips were purchased from Bluestar, India. NaCl was obtained from Merck India Ltd.

**Preparation of the Ag-Au Nanoparticle thin films.** Before performing any chemical reaction, the silver foils from CDs and DVDs were detached from the polycarbonate layer by using an adhesive tape after cutting the CDs and DVDs into small pieces. The details have been discussed elsewhere.<sup>1</sup>

Ag-Au thin films were prepared by reacting approximately 1.55 cm x 2.6 cm pieces of silver foils with different concentrations of HAuCl<sub>4</sub> present in 10.0 mL solutions, which also contained 0.1 M CTAB. The treatment led to change of the color of silver of the CD or DVD into golden in about 10-12 h. The best films were obtained from the reactions of the silver foils with 2.0 x 10<sup>-4</sup> M - 5.0 x 10<sup>-4</sup> M HAuCl<sub>4</sub> solutions. It is worth mentioning here that the time for appearance of golden color depended on the concentration of HAuCl<sub>4</sub>, which was early for high concentration of HAuCl<sub>4</sub>, while it took longer time at low concentrations. On keeping the samples in solution after the appearance of the golden color, the color gradually disappeared leaving behind a blue coloration on the CD or DVD substrate. The samples thus prepared (golden colored ones) were washed carefully with water and air dried. Dried samples were used for further characterizations.

**Scanning Electron Microscopy (SEM).** Leo-VP 1430 scanning electron microscope (SEM) equipped with an Oxford-INCA energy dispersive X-ray (EDX) analyzer was used to characterize all the samples. Images were recorded using the secondary electron detector. Approximately 5.0 mm x 5.0 mm pieces from different samples were taken for analyses. For some of the samples, thin films were transferred to aluminum foils or glass substrates before measurements. This was pursued by first putting the film, prepared on the original CD or DVD substrate, in saturated NaCl solution and then suspending the films in water. By carefully placing the aluminum foil or glass cover slip below the floating films they could then be lifted (and thus be transferred). Except for the samples transferred onto aluminum foil all samples were coated with a thin layer of gold prior to SEM imaging, in order to make them conducting so as to avoid charging of the samples. We have used the EDX studies to show the relative elemental abundance in the films and the substrates on which the films were placed like the substrate from the CD or DVD or the glass cover slips.

**Transmission electron microscopy (TEM) Characterization.** TEM images were recorded for the thin films after transferring the films on to 300 mesh copper grids. The transfer was achieved in a way similar to above where aluminum foil or glass cover slip was replaced by the grid. The

instrument used was a Jeol JEM-2100 transmission electron microscope operating at a maximum voltage of 200 kV.

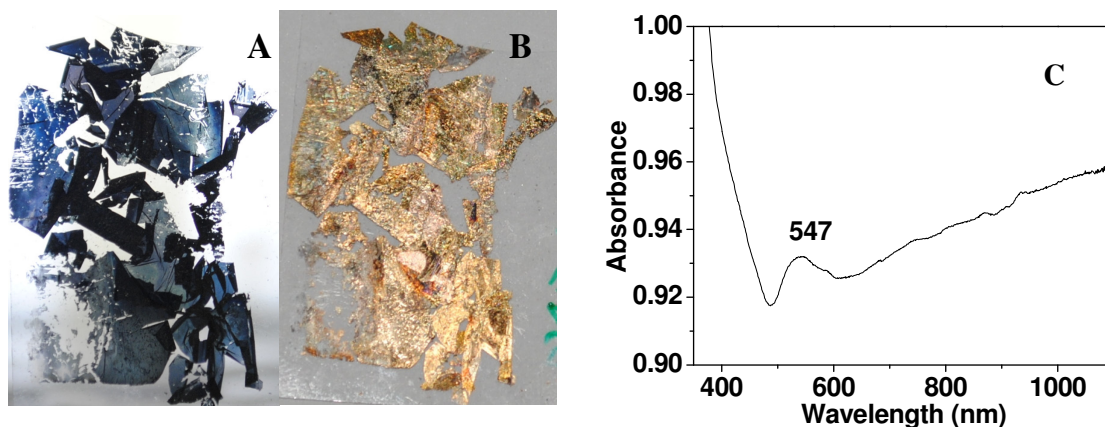
**Atomic Force Microscopy (AFM).** AgAu thin films transferred onto glass cover slips were used for AFM studies. The instrument used was a Veeco Multimode SPM attached with a Nanoscope IV controller (manufactured in USA). Images were recorded in contact mode with silicon nitride tips.

**X-Ray Diffraction (XRD).** A Bruker D8 Advanced powder X-ray diffraction (XRD) instrument was used to characterize the samples. Samples of approximately 3.0 cm x 2.5 cm dimensions were analyzed using XRD. Also, XRD of the thin films after being transferred cover slips were recorded.

**UV-Visible spectroscopy.** The samples were first transferred onto a cover slip by the same method mentioned earlier. Then the UV visible spectra of the samples were recorded in a Perkin Elmer Lambda25 instrument by vertically placing the sample carrying cover slip in the path of the beam, with blank cover slip used as reference.

**Infra Red (IR) Spectroscopy.** For infrared spectroscopic characterization of the samples a Perkin Elmer Spectrum One FTIR spectrophotometer was used. The samples here were prepared by scrapping off the Ag-Au films from the lacquer layer of CD/DVD and then mixed with KBr to make translucent pallet for the measurement. Also the FTIR spectrum of CTAB in KBr pellet was recorded.

**Optical Imaging.** Images of the films transferred to a glass cover slip was taken in both the reflected light and the transmitted light by a Nikon-D3000 SLR camera. Reflected light photographs were taken in the same way as the regular photography while for the transmitted light image a normal fluorescent lamp was placed behind the sample containing cover slip and the camera focussed on the sample.

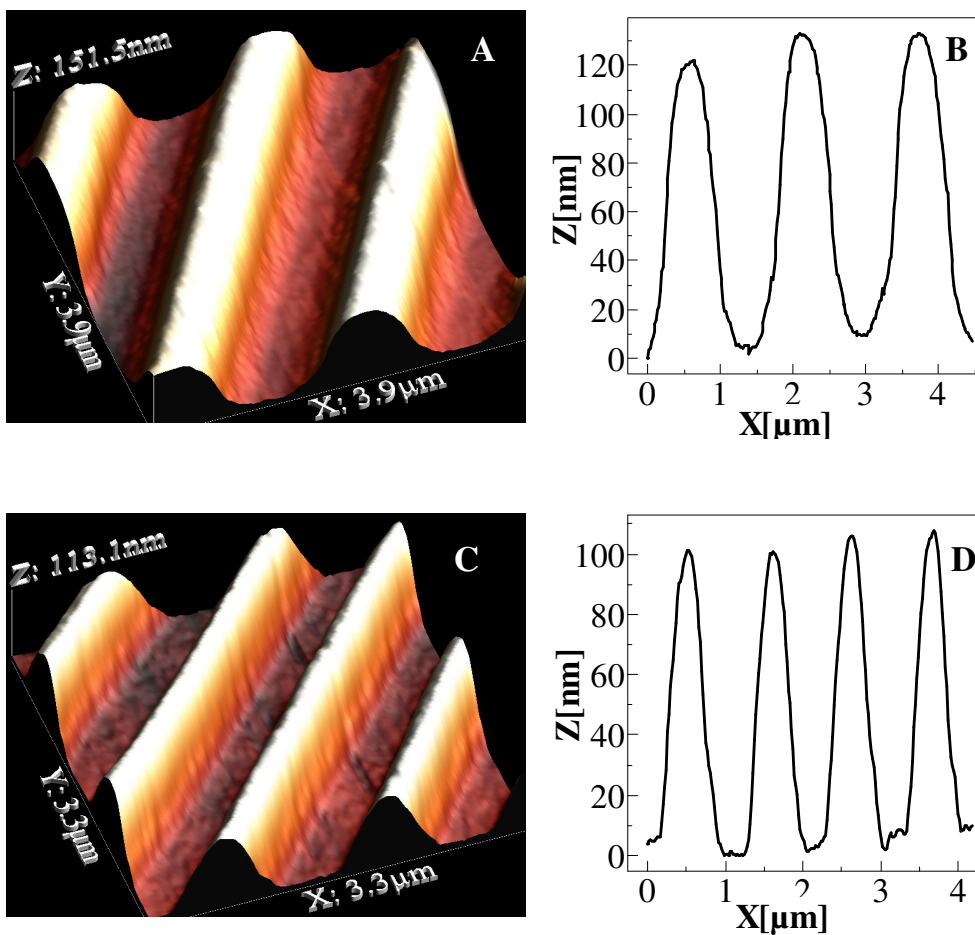


**Figure S1.** Representative photographic images of the thin films generated from DVDs transferred onto a glass cover slip recorded by a digital camera, (A) in the reflected light and (B) in the transmitted light. (C) UV- Visible spectrum of the film from DVD recorded in transmittance mode.

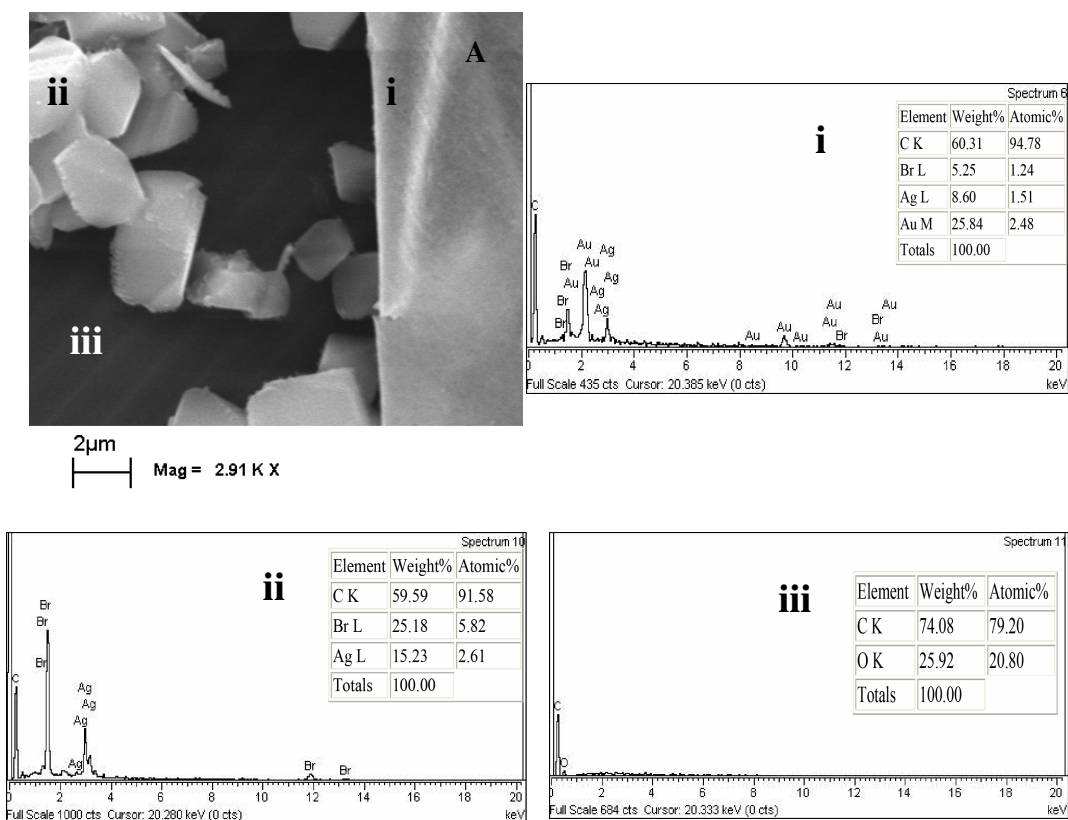
First of all the results presented in the manuscript and in the Electronic Supplementary Information (ESI) are not the product of simple galvanic replacement reaction between  $\text{HAuCl}_4$  and Ag. There is the film (consisting of bulk Ag, a reactant), the dye coating on the film,  $\text{HAuCl}_4$  (reactant) and the CTAB (self-assembler). It can thus be anticipated that the process would be complex and may involve at least diffusion controlled chemical reaction – if not non-linear reaction. Hence one cannot possibly predict a priori the fate of the reaction. There would be difference from sample to sample in this regard. On the other hand, the corrugation present in the product film carries the signature of the height difference in the form of optical interference. This makes the measurement of optical extinction difficult.

In order to alleviate the problem what we have done is to try several samples especially the formation of films at different initial  $\text{HAuCl}_4$  concentrations and report the one where the peak could be clearly observed. The one shown in the manuscript was that of a film generated at lower concentration of  $\text{HAuCl}_4$  (Ag film from CD) and that included in the ESI was from a film which was produced using higher  $\text{HAuCl}_4$  concentration. Thus there was the difference in the peak positions.

Therefore, although the exact compositions of the films in terms of percentage presence of Ag and Au could not be discerned the collections of experimental results presented clearly indicated the presence of Au and Ag NPs in the form of alloy and or core-shell NPs in the films.



**Figure S2.** (A) and (B) are AFM images and the height profiles respectively of the silver foils from CD. (C) and (D) are the same of a foil from DVD. Crest to crest pitch for CD was found to be  $1.8 \pm 0.1 \mu\text{m}$ , while that for DVD was found to be  $1.0 \pm 0.1 \mu\text{m}$ .

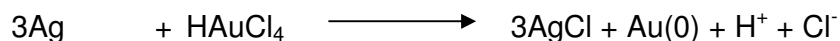


**Figure S3.** (A) SEM image of a part of a sample (generated from CD) directly viewed after initial washing with deionized water followed by drying. In the figure three spots which are marked (i, ii and iii) correspond to the spot EDX spectra recorded (i) on the thin film; (ii) on the bright particles and (iii) on the CD substrate.

The EDX studies carried out along with the SEM images at different points of the film provided us with valuable information about the chemical composition of the films. In order to probe the details of chemical composition as prepared films were observed under SEM along with EDX experiments. Figure S3 shows the SEM image of a thin film generated from an Ag foil of a CD by reacting with  $2.2 \times 10^{-4}$  M  $\text{HAuCl}_4$  in the presence of 0.1 M CTAB and the EDX spectra of different spots in the image are shown in the accompanying figures. In the image (Figure S3A) the spots on which the EDX spectra were recorded are marked by the Roman numerals (i, ii, iii) and the same nomenclatures are used for labeling the spectra. Figure S3(i) shows the spot EDX spectrum with

the elemental percentage in parenthesis, of the thin film at spot (i) in Figure S3A, where it is observed that the weight percentage of Ag and Au were 8.60% and 25.84% respectively. Also observed were Br (5.25%) and C (60.31%). Although EDX spectral analysis does not provide actual quantitative measure of the concentration of the elements the relative abundance could be established for two elements when present together. Thus it is plausible that the film was made of Au and Ag and CTAB was bound to the film (Figure S4). There is the possibility of carbon from the CD substrate (the background Lacquer layer), which adds to the total carbon as the films are considerably transparent to the electron beams, EDX from the substances below the film was recorded simultaneously. The CD substrate contains high percentage of C (74.08%) as observed from Figure S3(iii). Also, one cannot rule out the presence of carbon in the film having been transferred from the lacquer part during formation. On the other hand, the large cuboidal particles (with edge dimensions on the order of 1  $\mu\text{m}$ ) which were present on the surface of the CD consisted of Ag and Br in addition to carbon. This could mean that these particles were made of AgBr crystals and possibly CTAB molecules were attached to the particles providing the source of carbon in the spectrum. It is plausible that the galvanic replacement of Ag by  $\text{HAuCl}_4$  produced Ag and Au composite film, whereas AgBr crystals were generated from the oxidized Ag, in the presence of excess  $\text{Br}^-$  present in the medium (from CTAB) in comparison to the concentration of  $\text{Cl}^-$  (from  $\text{HAuCl}_4$ ). The EDX spectrum of the background consisting of the remainder of the CD indicated the presence of carbon (in addition to oxygen).

The galvanic replacement reaction involved may be as written below..



As it is obvious that the solubility products of silver bromide ( $5.35 \times 10^{-13}$ ) is lower than silver chloride ( $1.77 \times 10^{-10}$ ), silver bromide will be precipitated in preference to silver chloride which is observed in our SEM image and EDX studies as shown in Figure S2A and Figure S2(ii). Also, the grey particles observed with the thin films contained Br and not Cl.

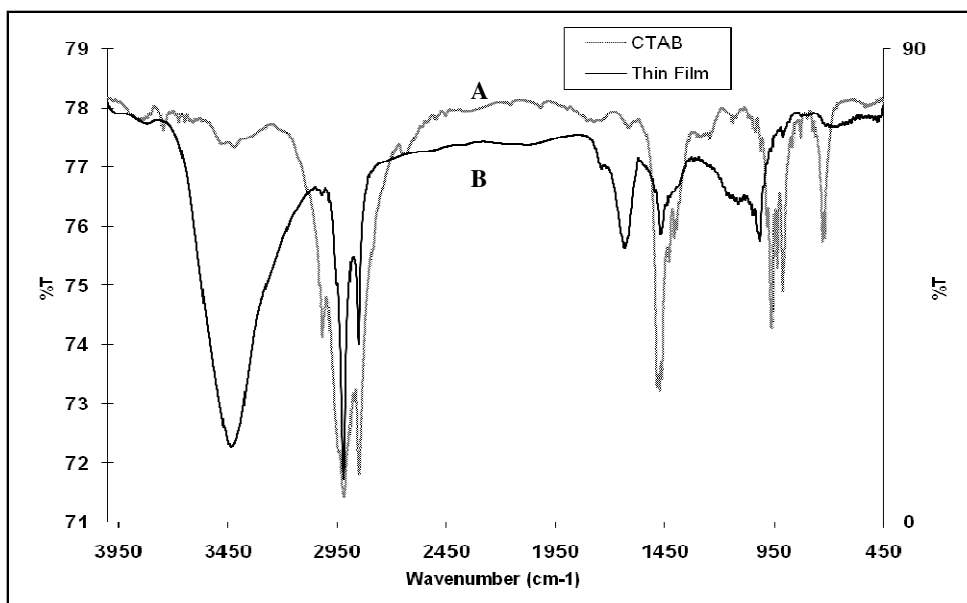
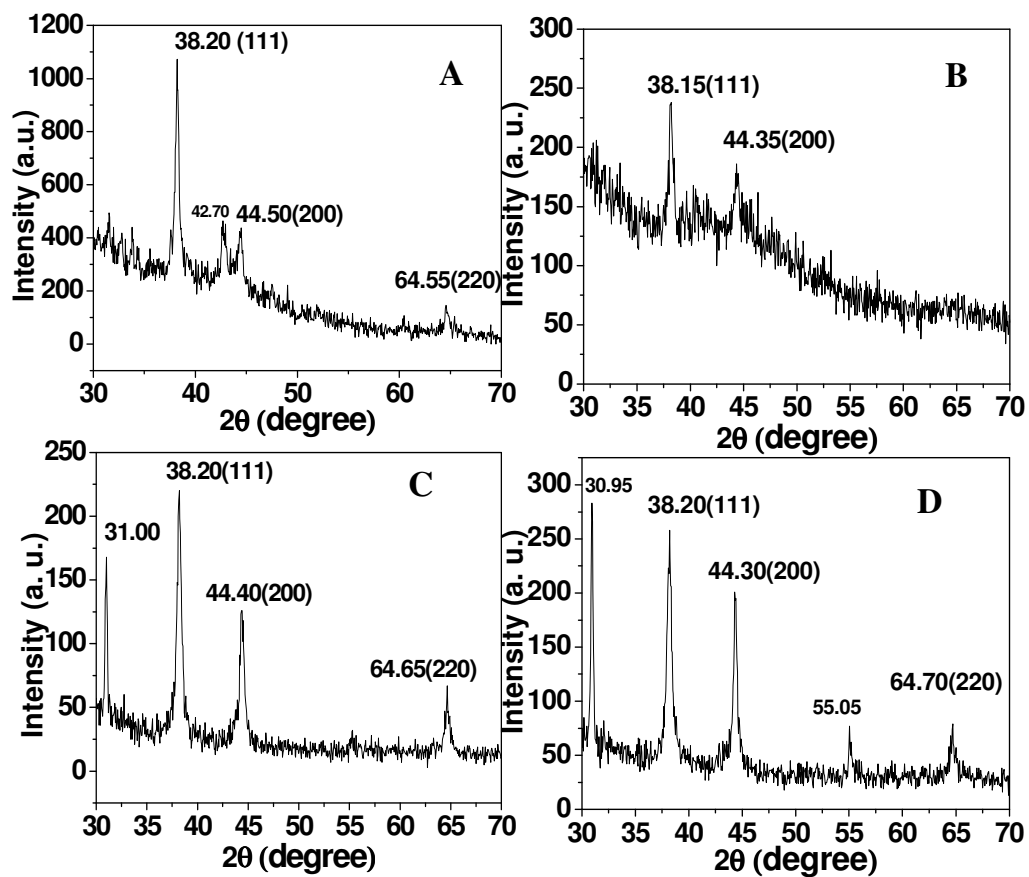
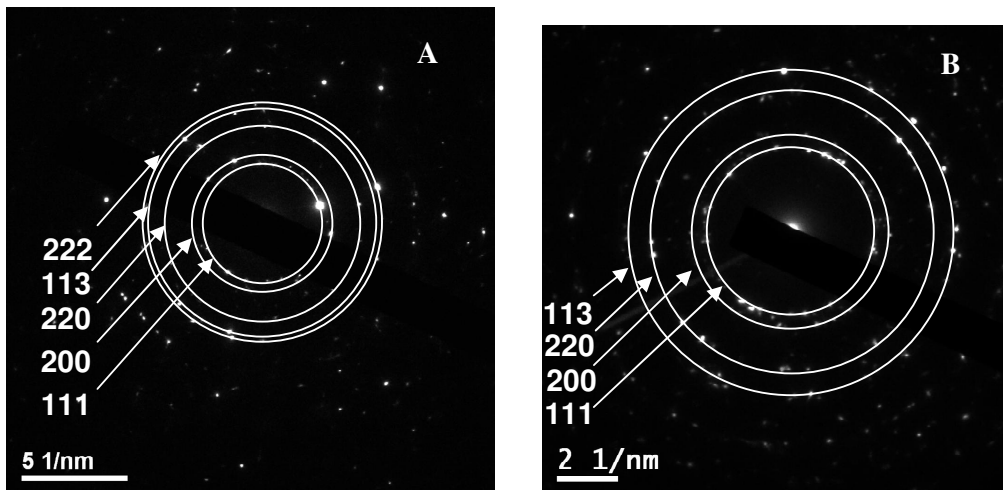


Figure S4. FTIR spectra of (A) CTAB and (B) of thin film generated from DVD.

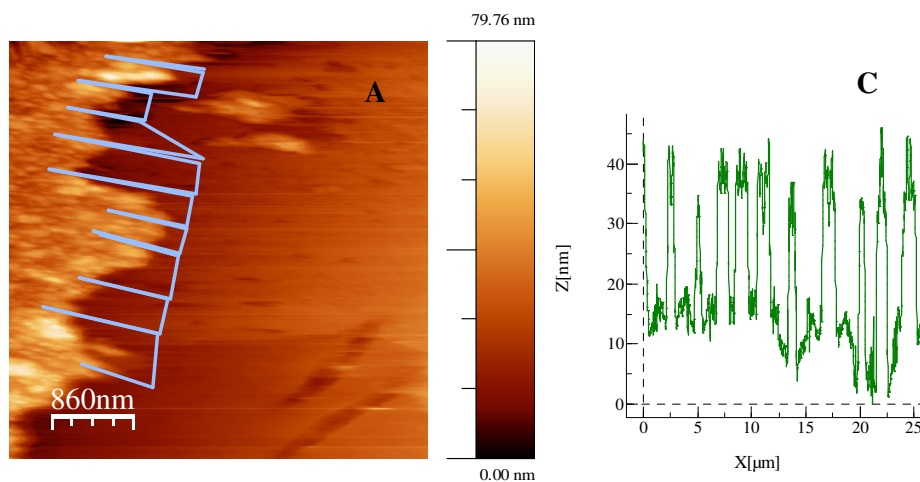


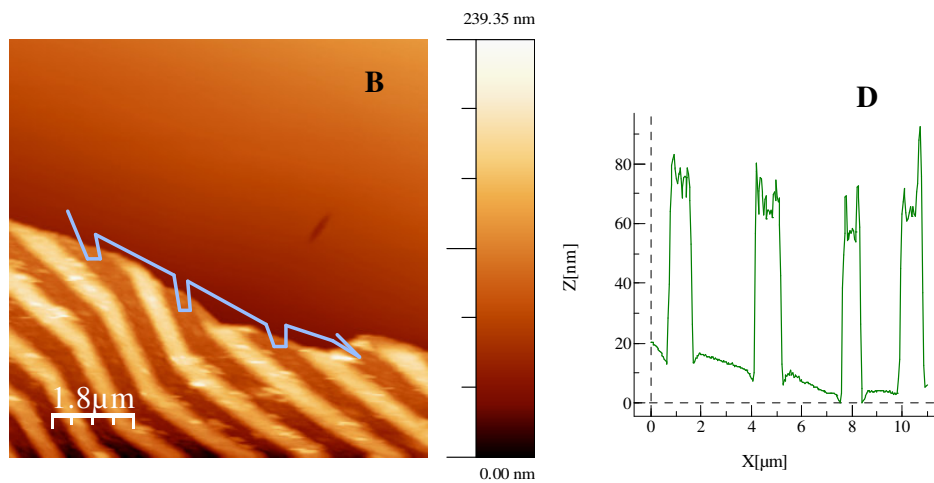


**Figure S5.** X-ray diffraction patterns, of Ag-Au thin films generated from (A) CD and (B) DVD reflective layers, by reacting with  $\text{HAuCl}_4$  followed by washing with deionized water; of Ag-Au thin films from (C) CD and (D) DVD after treating with saturated NaCl solution and then transferring to glass cover slip. Major peaks are identified with the  $2\theta$  values corresponding to places written in parentheses.

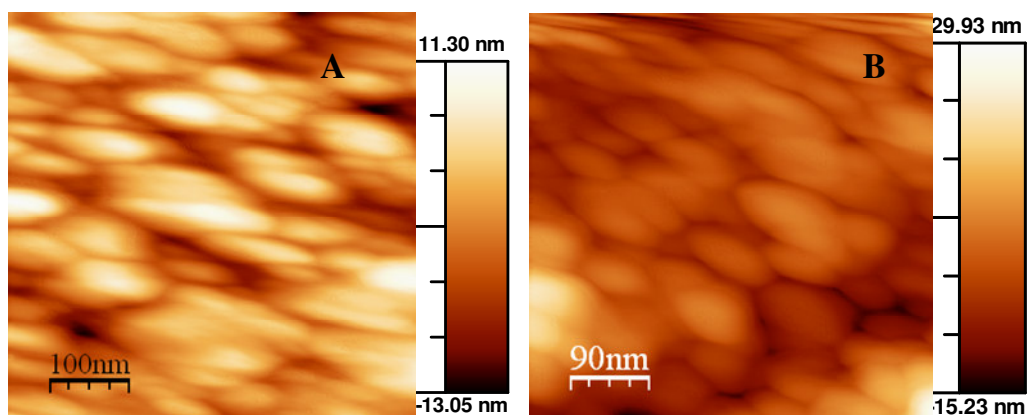


**Figure S6.** (A) SAED pattern of a thin film generated from a CD and (B) SAED pattern of a thin film generated from a DVD.

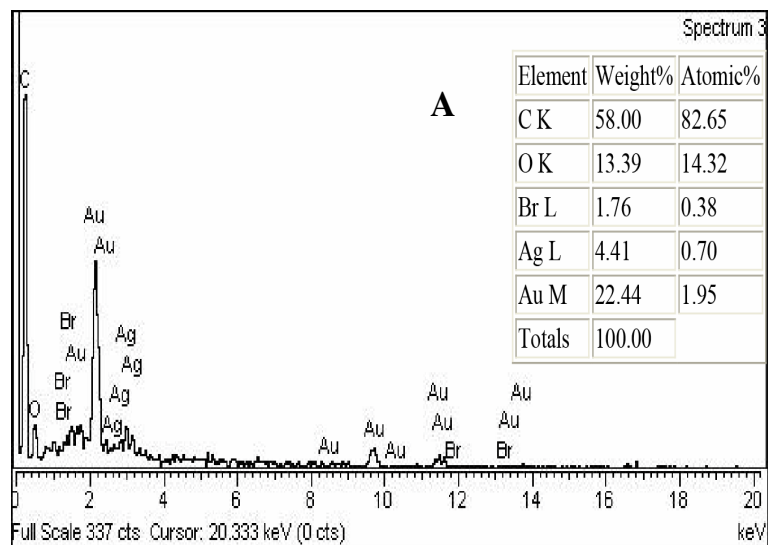




**Figure S7.** AFM topographic images of thin films generated from (A) CD (thickness  $31 \pm 7$  nm) and (B) DVD (thickness  $68 \pm 3$  nm) silver foils, recorded at the glass film boundary, after transfer to glass cover slip. (C) and (D) are corresponding height profiles at the film glass boundary (at the blue lines indicated in A and B).



**Figure S8.** AFM topographic image of a smaller area in the films generated from (A) CD and (B) DVD respectively.



**Figure S9.** (A) EDX spectrum of a thin film generated from silver foil of a written CD with percentage composition shown in the accompanying table.

## Reference

1. Gogoi, S. K.; Borah, S. M.; Dey, K. K.; Paul, A.; Chattopadhyay, A. *Langmuir*, **2011**, 27 (20), 12263–12269.