Supplementary Information (SI) for

Facile deposition and plasmonic resonance of Ag-Au nanoparticles in titania thin film

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[SI-1]. Synthesis of thin film by thermal spray pyrolysis:-

Silver nitrate and gold chloride were purchased from Sigma Aldrich, titanium (IV) oxide bis(2,4,pentanedionate) (M. W= 262.12 gram, Alfa Aesar) and ethanol (Analytical grade) from Merck were obtained.

Step 1: For the synthesis of plasmonic metamaterial based thin film, the microscopic glass slide of Duran group (made in Germany) was used after cleaning. The glass slide were first cleaned in a soap solution, followed by distilled water and then by ultrasonication bath in acetone for an hour at 60°C. Finally the glass slides were dried in an oven at 80°C. The prepared glass slide for use is shown in section (i) of Figure S1. 3 to 4 pieces of glass slides were kept in a hot plate at 400°C for spray coating of thin film. The height of nozzle to substrate was 14cm while the pressure of inlet carrier gas was set at a scale of 2 bars. An airbrush (Richpen 112B, Japan) with a nozzle diameter of 0.2 mm was set in single action mode to fix a ratio for each cycle of deposition. The spray coatings conditions were kept identical for all the deposition of silver nanoparticles, titania thin film and gold nanoparticles.

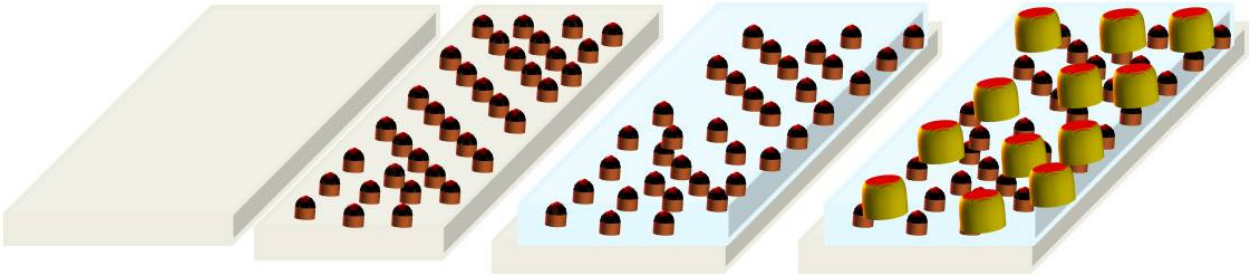

Figure S1: The schematic illustration for thin film grown by spray pyrolysis method.

Step 2: Silver nitrate (1 gram) was dissolved in a beaker containing 100 ml of ethanol and then ultrasonication was done for an hour at 60°C. The solution was ten times sprayed on preheated glass substrate at 400°C by using an airbrush system with N_2 as a carrier gas. Each time 1 ml of solution was used for spray coating with the break of one minute. After spray coatings the glass slides were continuously heated on the hot plate for twelve hours resulting into the change in the color of glass slide which turns into light pink gold color. Few of the glass slides were removed for different characterizations by lowering the temperature of the hot plate. This deposition of glass slide is shown in section (ii) of the Figure S1. At this stage more new glass slides were added to hot plate for further deposition and the temperature of hot plate was again set to 400°C.

Step 3: Then the TiO_2 thin film was prepared by using titanium chloride 1.0 M solution in toluene as a precursor, which was purchased from Sigma Aldrich. 2 ml of this solution was dissolved in a beaker containing a mixture of 20 ml distilled water and 20 ml of toluene. The solution was stirred for 5 minutes in a magnetic stirrer at room temperature and then the ultrasonication was done for an hour at 60°C before using it for spray coating. The solution was then sprayed for 5 times on preheated plane glass substrate (newly added glass substrate) and silver deposited glass substrate at 400°C with N_2 as a carrier gas. After deposition the titania films were continuously heated on the hot plate for thirty minutes resulting into the change in the colour of glass slide. Each time 1 ml of solution was used for spray coating with the break of one minute. Now, newly added glass substrate slides were removed for different characterizations by lowering the temperature of hot plate. The TiO_2 thin film prepared on plane glass substrate (after deposition at 400°C) by spray pyrolysis are levelled as "TiO_2 film" throughout the paper. This deposition on Ag coated glass slide is shown in section (iii) of Figure S1. The new glass slides were added again to hot plate for further deposition and the temperature of hot plate was reset to 400°C. The thin films removed here were characterized by UV-Vis, FTIR, Raman, and FESEM. These "TiO_2 film" samples were further annealed at 600°C for two hour in the presence of N_2 gas atmosphere and these characterizations were done again. The annealed TiO_2 thin film at this stage is named as "TiO_2 annealed film".

Step 4: After this the gold nanoparticles were deposited on these newly added glass substrates and Ag embedded TiO_2 thin films by spraying for 5 times at 400°C. The solution for the deposition of gold nanoparticles was prepared by dissolving gold chloride (0.09 gram) (purchased from Sigma Aldrich of 99.9% purity) in a mixture of water (20 ml) and ethanol (20 ml). The ultrasonication of this solution was also done for homogenous dispersion and uniform coatings for an hour at 60°C. Each time 1 ml of solution was used for spray coating with the break of thirty seconds. After the deposition of the gold nanoparticles the films were kept for constant heating for 4h in the same hot plate at 400°C and then the films were allowed to cool naturally up to room temperature resulting into the mixture of light red-pink-gold colours thin films. The gold coated Ag embedded TiO_2 thin films prepared at this stage (after deposition at 400°C and constant heating for 4h) by spray pyrolysis are levelled as "Ag-Au- TiO_2 film" samples. To promote the formation of Ag and Au nanoclusters in TiO_2 –glass matrix the thermal annealing of the samples in electrical tubular furnace at 600°C for two hour in the presence of N_2 gas atmosphere has been carried out. The gold coated Ag embedded TiO_2 annealed samples at

600°C for 2h in inert atmosphere are levelled as "Ag-Au- TiO_2 annealed film". Beside this, for comparison the role of matrix in growth mechanism the pure gold nanoparticles were deposited on newly added glass substrate and Ag embedded glass substrates but it does not adhere to the surface and show a similar morphology as observed after deposition on gold coated Ag embedded TiO_2 thin films. The whole experiments were also repeated for spray deposition in presence of N_2 gas atmosphere in an especially designed quartz chamber to see the role of deposition in atmospheric conditions. All the experiments and characterizations in atmospheric conditions at different stage were repeated 4-5 times for the reproduction and veracity of the work.

[SI-2]. Raman band observed in Raman spectra:

Table S1. The main peak positions for various Raman bands observed in case of all samples.

Sample name *versus* band position	Band position in cm^{-1}
glass substrate	100, 840, 1030, 2320 cm^{-1}
TiO_2 film	135, 390, 508, 630, 1060 cm^{-1}
TiO_2 annealed film	134, 385, 507, 630, 1060 cm^{-1}
Ag-Au-TiO_2 film	258, 421, 562, 937, 1210, 1430, 1650, 1960, 2230, 2450, 2740, 2970, 3210 cm^{-1}
Ag-Au-TiO_2 annealed film	223, 429, 708, 1190, 1380, 1600, 1800, 2210, 2420 cm^{-1}

[SI-3]. FTIR transmittance spectra:

Table S2: The main peak and dip positions for various bond stretching modes observed in FTIR spectra.

Sample name *versus* bond position	Bond position in cm^{-1}
glass substrate	2270, 2330, 2450 cm^{-1}
TiO_2 film	560, 1910, 2110, 2340 cm^{-1}
TiO_2 annealed film	1870, 2110 cm^{-1}
Ag-Au-TiO_2 film	721, 1350, 1280, 1430, 1500, 1580, 1650, 1740, 1820, 1930, 2110 cm^{-1}
Ag-Au-TiO_2 annealed film	1490, 1650, 1730, 1820, 1930, 1970, 2090 cm^{-1}

[SI- 4]. Basic Information and general scan XPS spectra

XPS measurement has been carried out for "Ag-Au- TiO_2 film" and "Ag-Au- TiO_2 annealed film", by using a Thermo Fisher Scientific model, operating at a base pressure of ~ 3.9×10^{-8} torr

at 300 K with a Al- K_α line source (1486.6 eV), and a hemispherical sector analyzer. Pass energy for general scan and core level spectra kept at 200 eV and 80 eV respectively. Corrections due to charging effects were taken care of by using C-(1s) as an internal reference. The general scan and core level spectra of sample gives an important information about energy variation due to chemical shift, bonding information, presence of oxide layer and many other important features also. The peaks present in the core level spectra are well defined due to the electrons knocked out from the sample as every electron has its particular characteristic binding energies corresponding to each element. The general scan for "Ag-Au- TiO_2 film" and "Ag-Au-TiO_2 annealed film" is shown in Figure S2 while for the annealed film the observations are listed in Table 3. The Auger peaks of Na, and O(KVV) are also observed.

Table S3. The main elements observed in XPS spectra of "Ag-Au-TiO_2 annealed film".

Name of element	*Peak BE*	*FWHM (eV)*	*Area (P) CPS. (eV)*	*Area (N)*	*At. %*
Ti2p	**458.98**	**2.48**	**909619.69**	**1793.25**	**11.78**
O1s	**530.2**	**2.84**	**922856.58**	**5129.81**	**33.71**
Ag3d	**367.68**	**2.38**	**537150.27**	**438.83**	**2.88**
Au4f	**83.78**	**1.63**	**893153.88**	**675.01**	**4.44**
C1s	**285.48**	**2.87**	**356883.82**	**5068.30**	**33.31**
Na1s	**1072.25**	**2.75**	**178811.78**	**564.27**	**3.71**
N1s	**400.11**	**5.86**	**63844.54**	**534.83**	**3.51**
Si2p	**102.18**	**2.72**	**25146.44**	**401.07**	**2.64**
Cl2p	**199.69**	**3.57**	**60364.68**	**359.87**	**2.36**

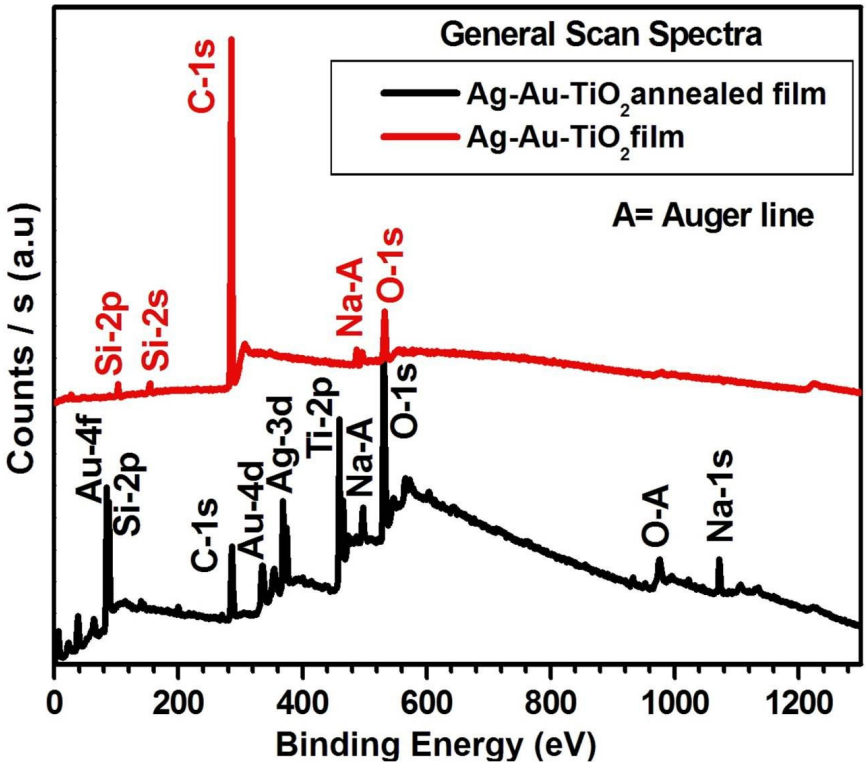

Figure S2: General scan spectra of "Ag-Au- TiO_2 film" and "Ag-Au- TiO_2 annealed film".

[SI-5]. Basic Information about FESEM, EDX Analysis: The film thickness was calculated by taking the micrographs from cross-sectional area of "Ag-Au- TiO_2 annealed film" as shown in Figure S3.

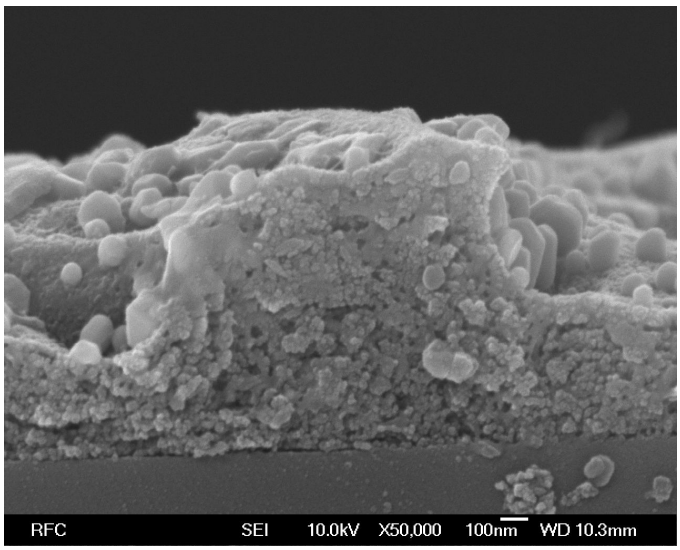

Figure S3: FESEM cross-sectional area of "Ag-Au- TiO_2 annealed film" at 100 nm scale.

The Platinum (Pt) coating was done to make the surface conducting in all the samples. A peak corresponding to Pt was observed in the EDX spectra as shown in the Figure S4. To know about the growth processes and the morphological changes of without annealed and annealed samples during the film formation the thin film were characterized at different stage by FESEM.

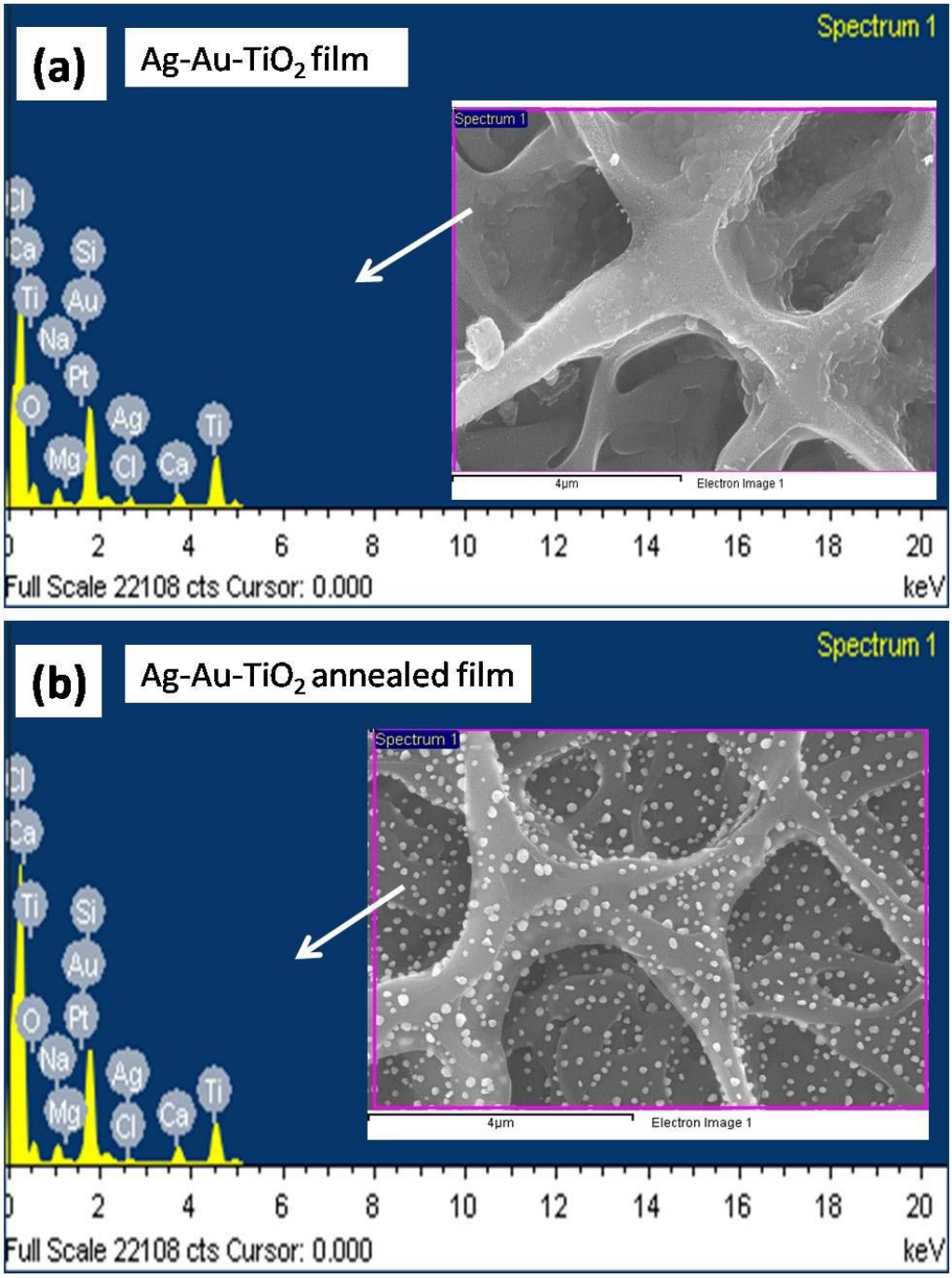

Figure S4: EDX pattern of (a) "Ag-Au- TiO_2 film", and (b) "Ag-Au- TiO_2 annealed film".