SUPPORTING INFORMATION

EXPERIMENTAL DETAILS:

Film Synthesis: Mesoporous thin films were produced by dip-coating at 1mm s^{-1} on either glass or silicon substrates at a relative humidity (RH) of 40–50 %. The technique was based on the evaporation-induced self-assembly (EISA) strategy using an inorganic precursor and a surfactant template in an ethanol solution. Detailed preparation techniques have been reported elsewhere [S1]. $Si(OEt)_4$ and $TiCl_4$ were used as the inorganic precursors and Pluronics F127 was selected as the polymeric template. For the mesoporous silica films initial solutions were composed of a tetraethyl orthosilicate (TEOS):EtOH:H_2O (0.1M HCl):F127 mixture, with a 1:40:5:0.0075 ratio of the reagents. A prehydrolysis step was carried out by refluxing TEOS for 1 h in a water/ethanol solution, with [H_2O]/[Si]=1 and [EtOH]/[Si]=5. In the case of mesoporous titania films the reagents $TiCl_4$:EtOH:H_2O:F127 were kept in the ratio 1:40:10:0.005. The reagents were continuously stirred at 60 °C for 1 h prior to dip-coating. Silica and titania films are labeled SF and TF, respectively where F represents the surfactant template F127 used to texture the mesoporous films.

After deposition, the films were placed in 50% RH chambers for 24 h, the films were then subjected to a consolidation thermal treatment , which consisted of heating for 24 h at 60 ºC, then 130 °C, and finally 2–10 h at 200 °C. A second layer could then be deposited onto the stabilized film. Several successive deposition–consolidation steps can be carried out to build up multilayered films. Finally, the films were calcined at 350 ºC for 2hs in order to remove the templating agent and the remaining chloride (figure S2).

Film Characterization:

UV-Visible spectroscopy: The surface plasmon resonance of the infiltrated films was conducted with a Hewlett-Packard 8453 spectrophotometer in the absorbance mode. Films on a glass substrate that were not submitted to the infiltration procedure were used as reference.

SEM: The characterization of the films was performed by SEM (Quanta 200, FEI Company) microscopy. In the bilayered films the presence of silver in the bottom layer could not be resolved in the secondary electrons mode because of the low energy of these electrons (10-30 eV) prevented permeation through the upper. Moreover, the secondary electrons are less sensitive to differences in atomic number (Z) than backscattered electrons, making backscattering a better way to detect the contrast between Ti (Z=22) and Ag (Z=47).

EDS: The samples were prepared by depositing scrapings of the films on to carbon tape. In the EDS analysis (EDAX 4®) it was possible to quantify the atomic percentage of Ti and Ag without observing Si.

Conductivity Experiments: Bilayer films were synthesized on glass substrate in the following way: a monolayer of TF was fabricated and stabilized at 200 ºC, before the deposition of the second layer, two drops of polyacrylate 5 mm apart were deposited on the TF film and allowed to dry and polymerize. Then, the second layer, i.e. SF, was dipped and thermally treated as before. Finally, the polyacrylate and the polymeric template were removed in a 2h calcination step at 350 ºC. The presence of the polyacrylate inhibited the formation of the SF layer allowing direct accessibility to the TF bottom layer. Cyano-acryilate removal by calcinations was confirmed by FTIR measurements; the signals from cyano (2250 cm^{-1}) and acrylate (1730 cm^{-1}) groups completely disappeared. After the thermal treatment the film was infiltrated with the Ag^{+} solution and the photodeposition took place with the use of a specific mask that led to a conduction path between the monolayer zones previously filled with the polyacrylate. By exposure of the loaded film with UV light for 60 minutes a nanoparticles path was formed and a confident way to measure conductivity was archived. The proper electrical contacts were performed with silver paint in the exposed areas of the TF film (figure 3).

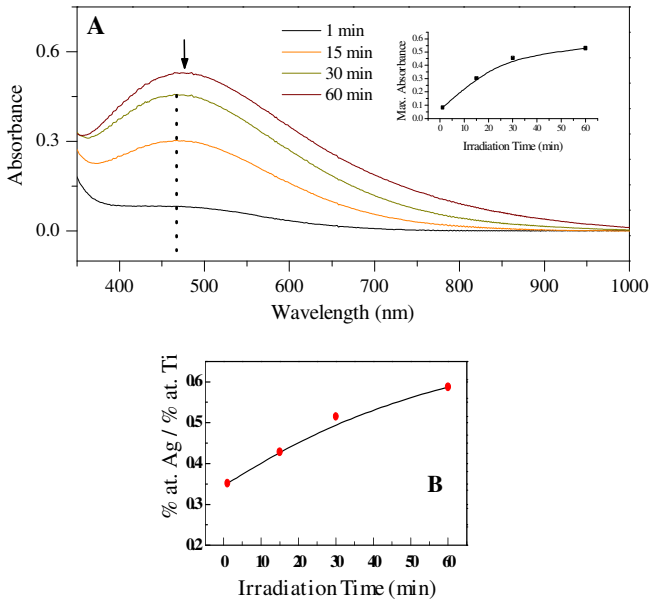

Figure S1: A. UV-Visible absorption spectra of a silver-loaded TF-SF bilayer after progressive UV irradiation times (indicated in the Figure). **B** Ag/Ti ratios obtained from EDS spectra performed in the silver-patterned zone.

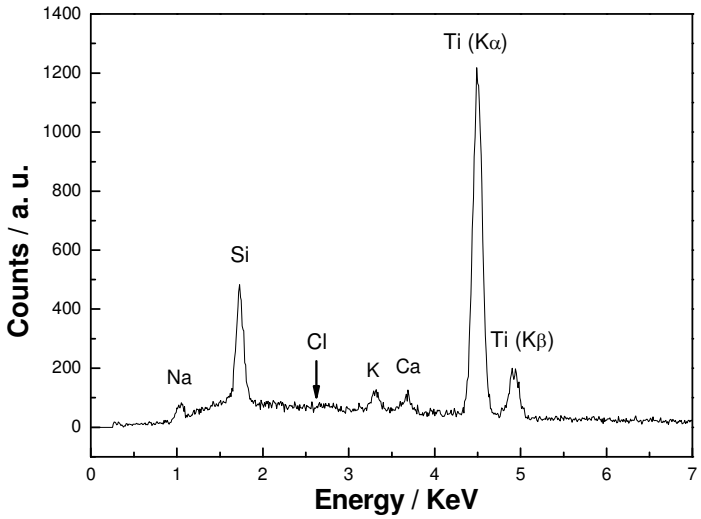

Figure S2: EDS spectra for mesoporous titania films. The arrow depicts the position of the Cl K_α line, showing the absence of chloride. The presence of Si, K, Na and Ca ions is due to substrate fragments.

References:

[S1] a) Angelomé, P. C., Fuertes, M. C., Soler-Illia, G. J. A. A., *Adv. Mater*. **2006**, *18*, 2397. b) Cagnol, F., Grosso, D., Soler-Illia, G. J. A. A., Crepaldi, E. L., Babonneau, F., Amenitsch, H., Sanchez, C., J. *Mater. Chem*. **2003**, *13*, 61. c) Fuertes, M. C., López-Alcaraz, F. J., Marchi, M. C., Troiani, H. E., Luca, V., Míguez, H., Soler-Illia, G. J. A. A., *Adv. Funct. Mater*. **2007**, *17*, 1247.