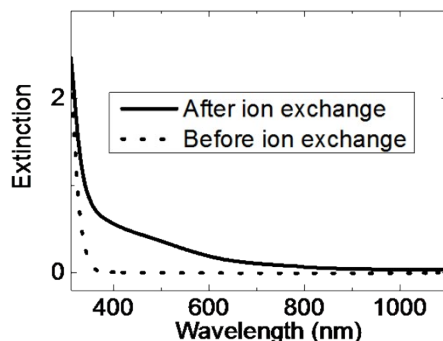
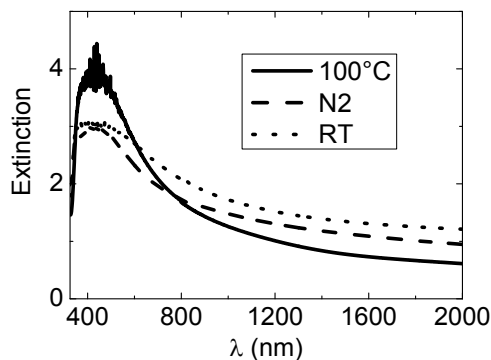


Supporting Information.

S-I.1. Extinction spectra before (shown by dotted line) and after (bold line) silver ion exchange performed on the mesoporous SiO₂/TiO₂ film into which Na ions have been incorporated.



S-I.2. Extinction spectra showing the change in the spectra obtained after photoreduction under various environmental conditions (room temperature in air, 100°C in air, room temperature under nitrogen).

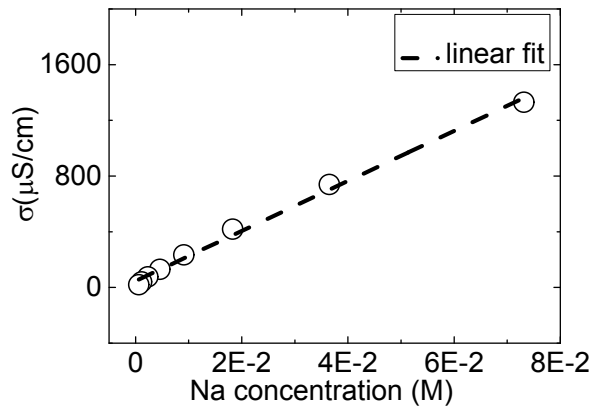


S-I.3. determination of the Ag⁺/Si and Ag⁰/Si molar ratios

Ag⁺/Si molar ratio :

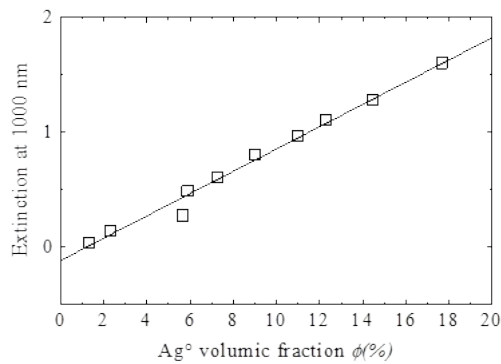
Under our experimental condition, all Na⁺ ions are replaced by Ag⁺ ions after the ion exchange step, so that the amount of Ag⁺ is determined directly by the amount of sodium acetate that was spin coated on the films before the thermal diffusion step. To determine this amount, the substrate after deposition of sodium acetate is put in a given volume of ethanol for dissolution of the sodium salt. Using a calibration curve, measurement of the conductivity allows to determine the concentration of Na⁺ in solution, and thus the amount that was initially on the film. Knowing its surface and the amount of sol-gel silica (1.62 μmole of silica per cm² of substrate*), the relative Na⁺/silica molar ratio can be reduced, thus corresponding the Ag⁺/Si molar ratio in the film before photoreduction.

* calculated considering a volumic fraction of silica of 27% in the film, a thickness of 680 nm and taking a density of 2.65g/cm³ and a molecular weight of 60g/mol.

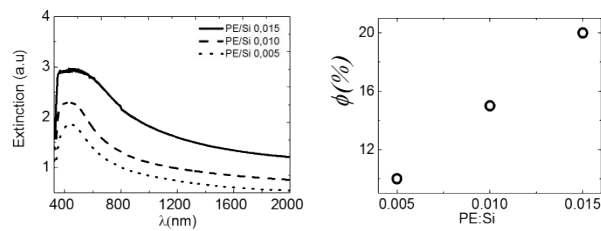


Ag⁰/Si molar ratio:

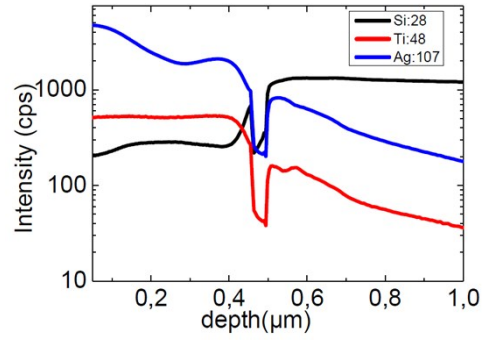
In our previous work,¹⁷ we showed that the silver volumic fraction could be obtained simply by using a calibration curve based on the linear dependence of the extinction at 1000 nm and the silver volumic fraction (determined from chemical analysis). This curve (shown below) has been used in this work to obtain the Ag⁰ volumic fraction, or the Ag⁰/Si molar ratio using a 27% of silica in the films and the appropriate density and molar mass of Ag and SiO₂.



S-I.4. Effect of porosity on the extinction spectra of Ag saturated films and hence on the silver volume fraction. The porosity is changed by playing on the initial PE6800/Si molar ratio in the formulation of the porous silica film. In the 0.005 to 0.015, the volumic fraction of Ag⁰ at saturation is proportional to the PE6800/Si molar ratio that determines the available porosity.



S-I.5. TOF-MS characterization of the Ag/Si/Ti distribution within the film thickness after the ion exchange process (PP-TOF MS equipment from Horiba). For this experiment, the active film has been deposited onto a mesoporous silica layer on a silicon substrate to have a better film/substrate contrast. This experiment evidences a silver concentration about 20% larger at the film/air interface as compared to the film/substrate interface and an average Ag/Ti ration of about 5.



S-I.6. log-log fits of $\epsilon_1(\phi, \lambda=12\mu\text{m})$, $\sigma(\phi, \lambda=12\mu\text{m})$ and $R(\phi)$ near ϕ^* from the insulating side ($\phi < \phi^*$) with a critical law $(\phi^* - \phi)^{-5}$

