Supporting Information for

Preserving Plasmonic Nanostructures from Laser-Induced Deactivation by a Protective Dielectric Shell

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S1. Supplementary Figures

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**Figure S5.** Intensities of the TERS peaks and the temperature increase in the hot spot do not correlate for most of the measured nanostructures. Apparent correlations (A) are coincidental rather than typical. For most shell-isolated Ag tips the signal intensity grows linearly with the laser power (B), but the temperature does not follow the linear trend. For some shell-isolated tips, the signal intensity drops suddenly at a certain threshold laser power (not every shell-isolated tip is perfect), but the temperature continues to rise (C). This lack of correlation is even more evident for bare tips (D).
Figure S6. TEM images of shell-isolated Ag tips. Most tips are covered with a thin conformal coating. The thickness of the SiO$_2$ layer varies from batch to batch, however all of the tips reach proper STM feedback, and most of them give stable TERS signal at high laser power.

S2. Removal of the silica shell

In order to verify the removal of the silica shell from the surface of the Ag tips during STM scanning, we performed TEM and TERS measurements of shell-isolated tips before and after the STM scans. The TEM (Fig. S7) and TERS (Fig. S8) experiments did not provide consistent results: the silica shell was preserved in the TEM experiments, but it was partially removed in the TERS trials. This
suggests that the survival of the SiO$_2$ shell may depend on the exact operating conditions of the STM: ideally, very low set point current and low scan rate should be used.

Figure S7. TEM images of a shell-isolated Ag tip before (A, B) and after STM scanning (E, F). All images obtained show a conformal coating, which indicates that no pinholes are formed during the STM scan (C). Proper tunneling conditions are confirmed by the STM scan of HOPG (D).
**Figure S8.** Pinhole tests of a shell-isolated Ag tip before and after STM scanning. (A) Firstly, the tip was dipped in a solution of PhSH (5mM in EtOH, 10 s) and rinsed with EtOH. Thanks to the conformal coating, PhSH did not bind to the tip. (B) Next, TERS was performed on a 4-PBT sample. The spectrum showed only the peaks of 4-PBT. (C) During the STM experiment, a pinhole was created in the silica shell. (D) The presence of the pinhole was verified by dipping the tip in the PhSH solution and rinsing it again. This time, PhSH did bind to the exposed Ag surface. (E) The corresponding TER spectrum shows peaks of both 4-PBT and PhSH, which confirms the formation of a pinhole.