Electronic Supplementary Information

Magnesium film-over-nanospheres (FONs) for surface-enhanced Raman scattering

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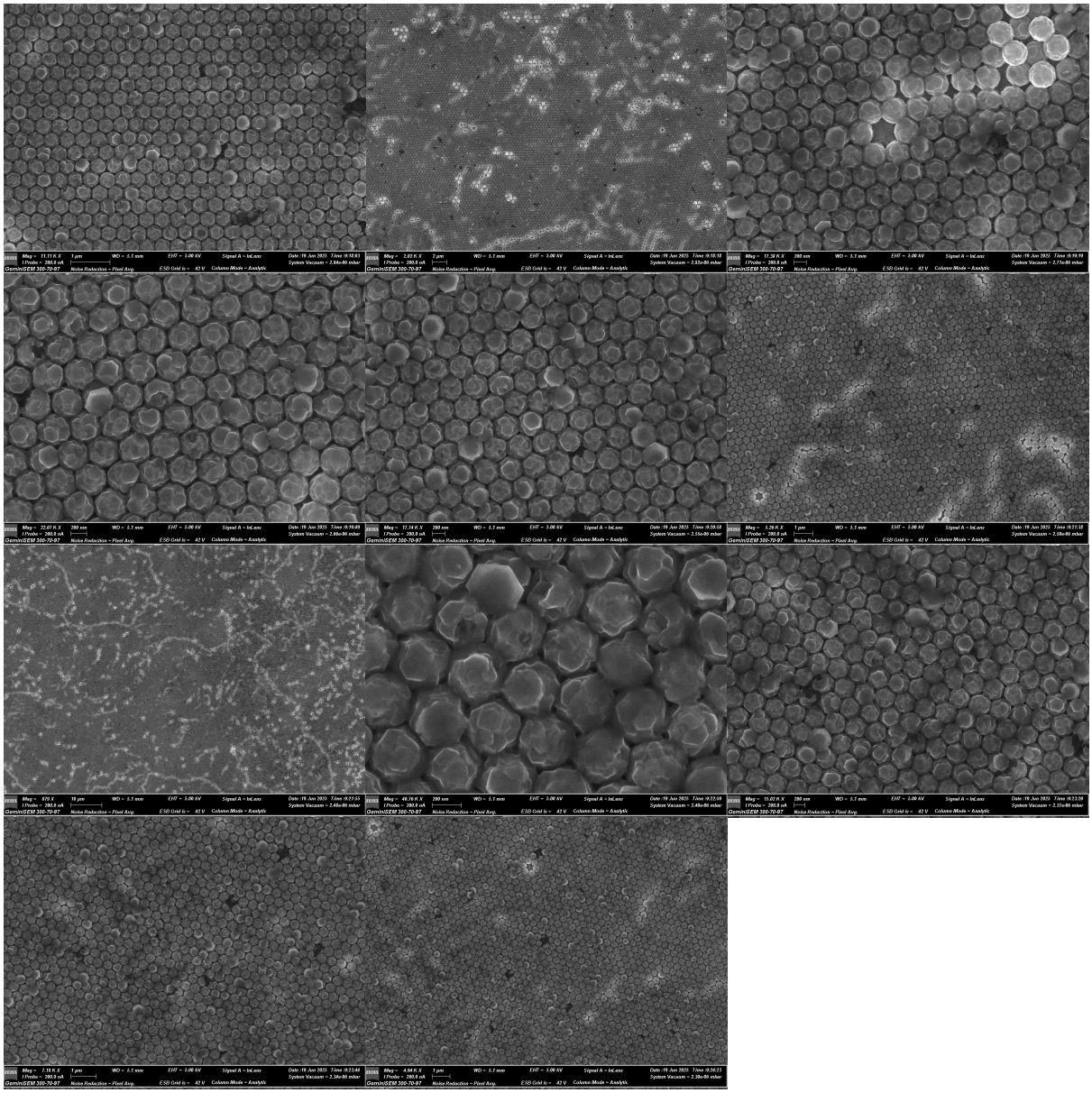

Figure S1. Additional SEM images of Mg FONs.

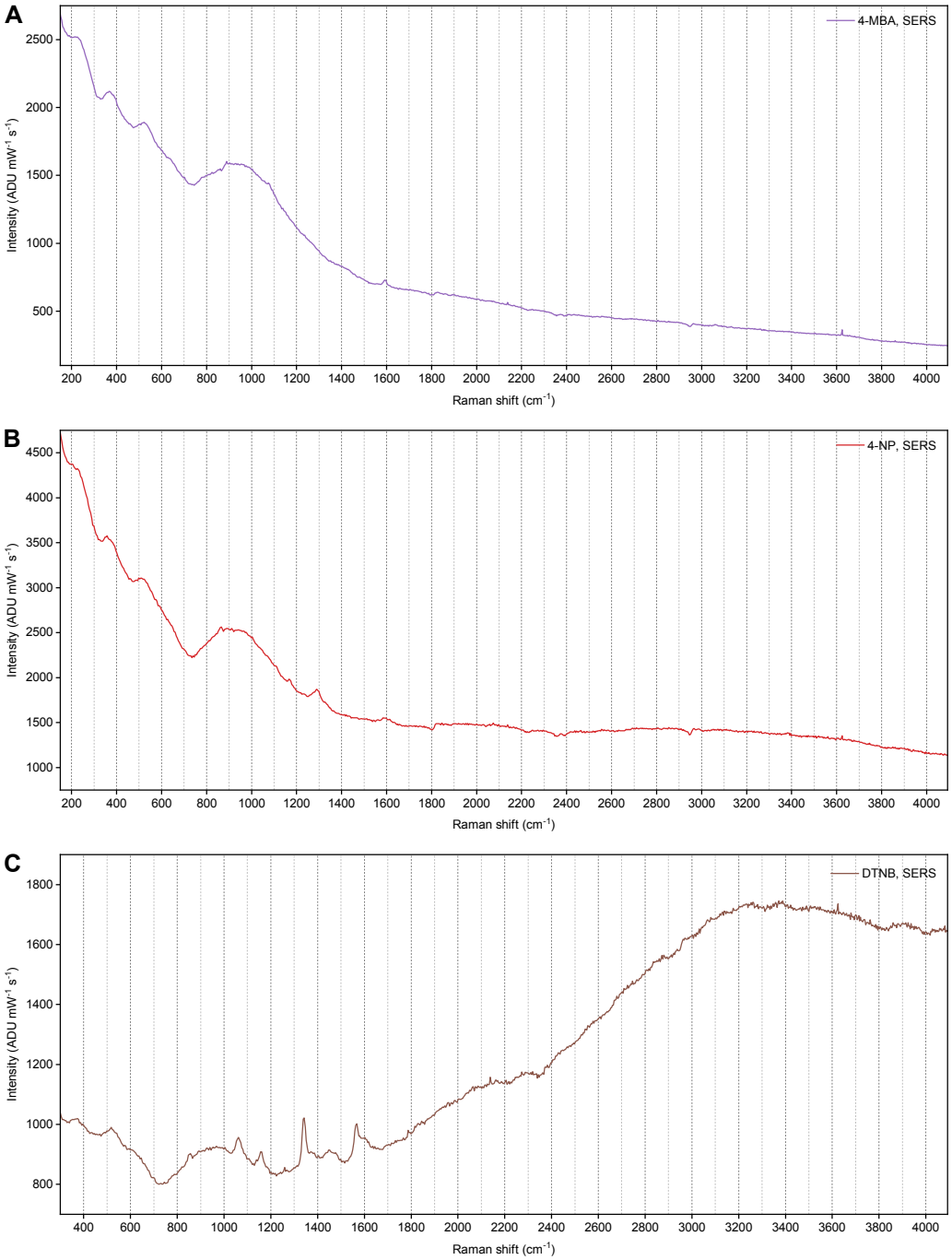

Figure S2. Full SERS spectra of Raman reporter molecules prior to background subtraction, for (A) 4-MBA, (B) 4-NP, and (C) DTNB.

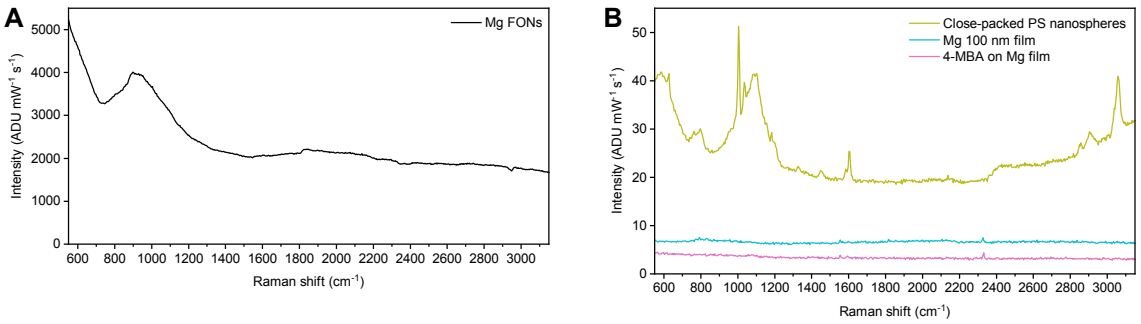

Figure S3. Additional Raman spectra collected as a control. (A) Spectrum of Mg FONs without any molecules deposited. (B) Spectrum of 100 nm (flat) Mg film deposited on glass on top of a 5 nm Ti adhesion layer, of flat Mg film with 4-MBA deposited on top, and of close-packed PS nanospheres on glass.

SERS enhancement factor (EF) calculation

The SERS EF of Mg FON was calculated using the following equation:[1]

$$\mathrm{EF} = \frac{A_{\mathrm{SERS}}}{A_{\mathrm{Raman}}} \frac{N_{\mathrm{Vol}}}{N_{\mathrm{Surf}}}$$

Where A_{SERS} and A_{Raman} are the areas under the peak of the D_3 mode around 1580 cm^{-1}, and N_{Surf} and N_{Vol} are the number of Raman reporter molecules for SERS and Raman, respectively. The D_3 mode was chosen as it did not overlap with any IPA signal in 0.1 M 4-MBA solution in IPA, which was used as a Raman reference. The scattering cross section in solution was estimated to be a sphere with a diameter of 2.5 μm, and was multiplied by the concentration of the solution to give 4.93×10^8 molecules for N_{Vol}. For N_{Surf}, the surface of a FON was estimated to be a collection of hemispheres, which increases the surface area by a factor of 2 compared to a flat surface. Dividing the total FON surface area under a 2.5 μm beam by a thiol footprint[2] of 0.22 nm^2 gives 1.78×10^8 molecules, although this is likely an overestimate. With area under the peak being 731 and 262 ADU mW^{-1} s^{-1} for SERS and Raman, respectively, the final EF is calculated to be 8, a lower bound due to the conservative assumption of coverage density.

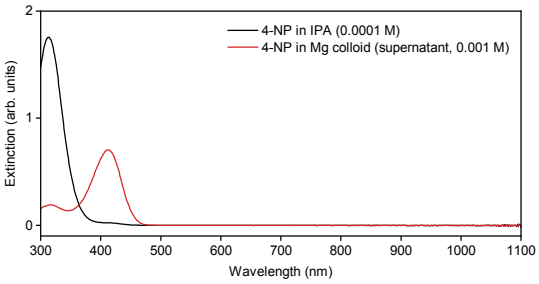

Figure S4. 4-NP dissociates to 4-NP^{-} upon mixture with Mg NPs. UV-vis-NIR spectra of 4-NP (black) before and (red) after mixing with Mg NPs.

References

1. E. C. Le Ru and B. Auguié, *ACS Nano*, 2024, **18**, 9773–9783.

2. C. G. Khoury and T. Vo-Dinh, *J. Phys. Chem. C*, 2008, **112**, 18849–18859.