

Supporting information

Magneto-Plasmonic Nanoparticles Generated by Laser Ablation of Layered Fe/Au and Fe/Au/Fe Composite Films for SERS Application

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Magnetic measurements

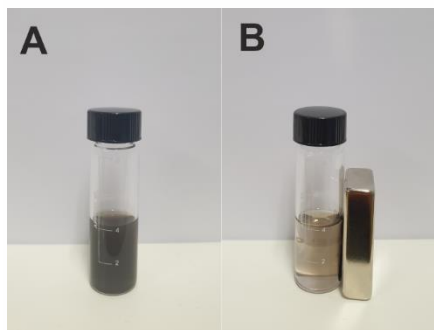


Figure S1. Photographs of ablated magneto-plasmonic nanoparticles in acetone (A) just prepared and (B) 15 minutes after exposure to a permanent magnet.

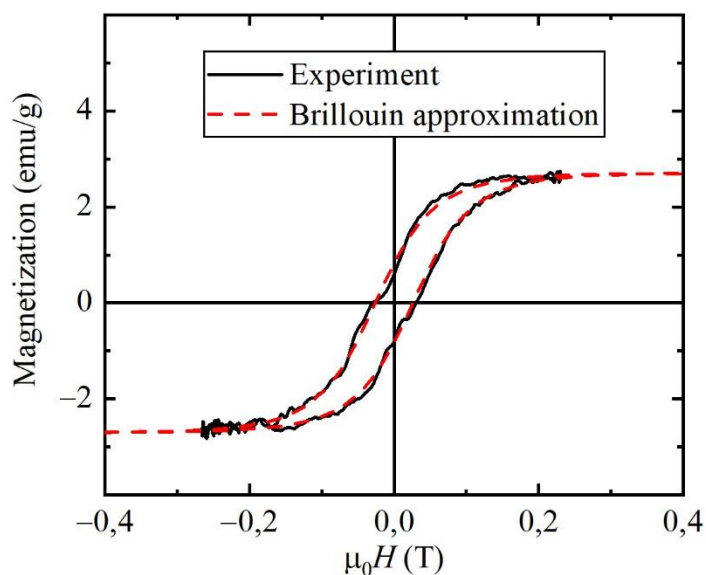


Figure S2. Hysteresis loop of the laser ablated magneto-plasmonic nanoparticles (Fe50/Au150/Fe25) (black), and approximation with Brillouin function (red);

Enhancement Factor Calculations

Enhancement factor (*EF*) calculations for 632.8 nm excitation wavelength were performed for SERS substrate produced from Fe100/Au150 coating for adsorbed 4-mercaptobenzoic acid (4-MBA) molecule as following:

$EF = (I_{SERS} \times N_{Raman}) / (I_{Raman} \times N_{SERS})$, where I_{SERS} and I_{Raman} represent the intensities of SERS and Raman spectral bands at 1588 cm^{-1} , N_{Raman} and N_{SERS} – the average number of excited molecules in Raman and SERS experiments respectively.

SERS and Raman spectra were collected using MonoVista CRS+ spectrometer (S&I, Germany) with 100×/0.8NA objective lens and a laser wavelength of $\lambda = 632.8$ nm (0.8 mW). The diameter D of the focused laser radiation was approximately 1 μm calculated using formula (1):

$$D = \frac{1.22 \times \lambda}{NA} \quad (1),$$

The reported surface density for 4-MBA molecules is about 0.5 nmol/cm² [S1]. Therefore, the number of adsorbed molecules on the hybrid Fe100/Au150 substrate is $N_{SERS} = 2.2 \times 10^6$. For the Raman experiment, the laser volume was considered as a cylinder with the diameter D and length L :

$$L = \frac{16\lambda f^2}{\pi d^2} \quad (2)$$

where, d is the diameter of the unfocused laser beam, f is the focal length of objective lens [S2]. These parameters were as follows: $d = 2$ mm, $f = 6$ mm.

Considering the penetration length of the laser radiation into the bulk 4-MBA sample (about 30 μ m) and the molecular density (1.5 g/cm³), the number of molecules in the irradiated volume is $N_{Raman} = 1.2 \times 10^{11}$. Thus, the SERS enhancement factor for 632.8 nm excitation was calculated to be approximately $\approx 5.8 (\pm 2.8) \times 10^4$. The surface roughness was not accounted for in these calculations.

The enhancement factors for 785 and 830 nm excitation wavelengths were estimated by comparative analysis of SERS spectra from 4-MBA by using three excitation wavelengths (632.8, 785, and 830 nm). The inVia Raman spectrometer (Renishaw, Wotton-under Edge, UK) equipped with a confocal Leica microscope, thermoelectrically cooled (-70 °C) CCD camera, and 633, 785, and 830 nm wavelength laser sources was employed. Laser radiation was focused on a sample using a 50 \times /0.75 NA objective lens; the acquisition time was 100 s, and the final spectra were obtained by averaging 9 spectra from different locations on the sample.

Figure S3 compares SERS spectra of 4-MBA observed at different excitation wavelengths. The enhancement factors for 785 and 830 nm excitations were found to be $2.1 (\pm 0.7) \times 10^3$ and $2.0 (\pm 0.8) \times 10^3$, respectively; considerably lower comparing with 632.8 nm excitation wavelength.

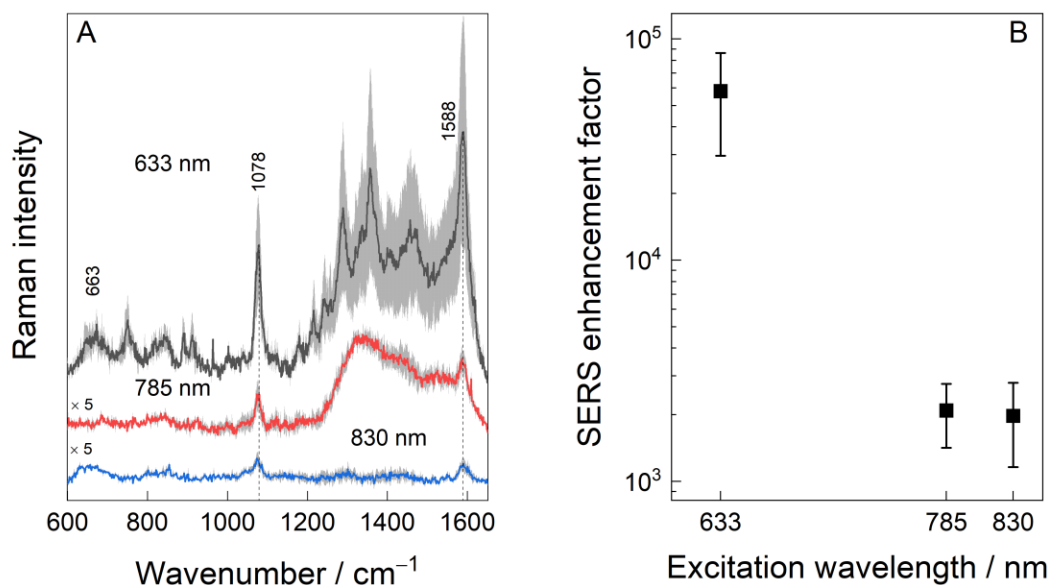


Figure S3. (A) SERS spectra of 4-MBA molecule obtained using magneto-plasmonic nanoparticles at 633, 785, and 830 nm laser radiations. Shaded areas represent the standard deviation from 9 measurements. (B) SERS enhancement factors calculated for different laser excitations.

References

- [S1] Orendorff, C.J.; Gole, A.; Sau, T.K.; Murphy, C. Surface-enhanced Raman spectroscopy of self-assembled monolayers: Sandwich architecture and nanoparticle shape dependence. *Anal. Chem.* **2005**, *77*, 3261–3266.
- [S2] Smith, E.; Dent, G. *Modern Raman spectroscopy: a practical approach*. John Wiley & Sons: Chichester, England, 2005.