Supporting Information

Resonant Mirror Enhanced Raman Spectroscopy

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1. Design principle and method for waveguides used in RMERS

The design principle for the planar optical waveguides used in our experimental demonstration of resonant mirror enhanced Raman spectroscopy (RMERS) is: by properly choosing the thickness of the resonant layer, both excitation laser light (λ_L=532 nm) and Raman scattered light (λ_R=633 nm, corresponding to the Raman shift about 3000 cm^{-1}) must be both supported as fundamental or higher order transverse electric (TE) or transverse magnetic (TM) guided modes in the waveguide, whether in air or water superstrate.

The method is to determine the cutoff thickness for the laser light (λ_L=532 nm) and Raman scattered light (λ_R=633 nm) at first, respectively, by solving the waveguide characteristic equations numerically, and then choose the thickness range that is large enough to support the wavelengths within the range from 532 nm to 633 nm as guided modes. Since the refractive index of PMMA is less than that of the glass slide substrate, there is no upper limit for the PMMA thickness; but for the waveguide using Al_2O_3 (n_3=1.67220 at 532 nm and 1.66587 at 633 nm) or Ta_2O_5 (n_3=2.07638 at 532 nm and 2.06080 at 633 nm) as a resonant layer, there is an upper limit for the thickness of the resonant layer because the effective refractive index of the waveguide cannot be larger than the refractive index of the glass slide substrate. The Al_2O_3 or Ta_2O_5 resonant layer can be deposited onto the MgF_2 buffer layer via RF sputtering.

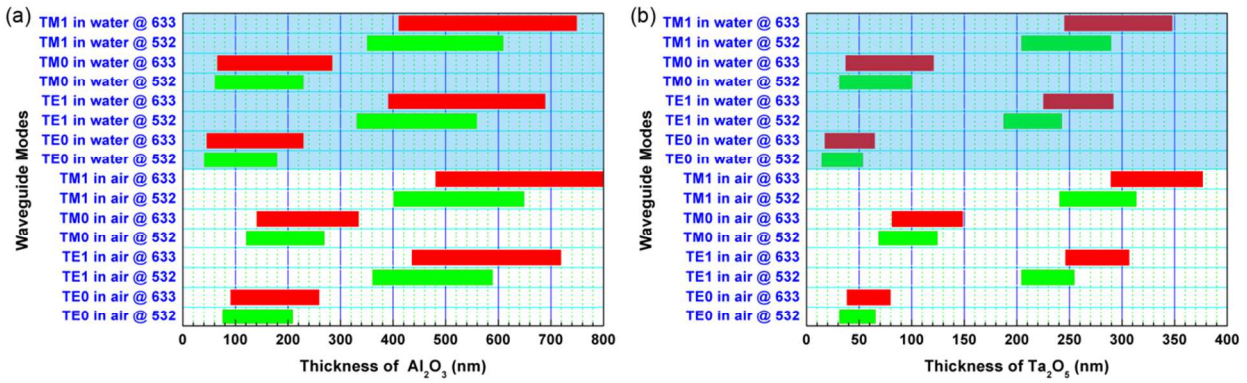

Figure. 1S Design parameters for waveguides using (a) Al_2O_3 and (b) Ta_2O_5 as resonant layers.

2. Optical properties of the materials used in the fabrication of resonant mirrors

Dispersion curves of all the materials used in the fabrication of resonant mirrors are shown in Figure 2S. The dispersion curves of the prism, the glass slide and the thin films (MgF_2, PMMA, Al_2O_3 and Ta_2O_5) were measured by an ellipsometer (J.A. Woollam Co., M-2000), the dispersion curve of the water was from the literature,[1] and the dispersion of air was neglected.

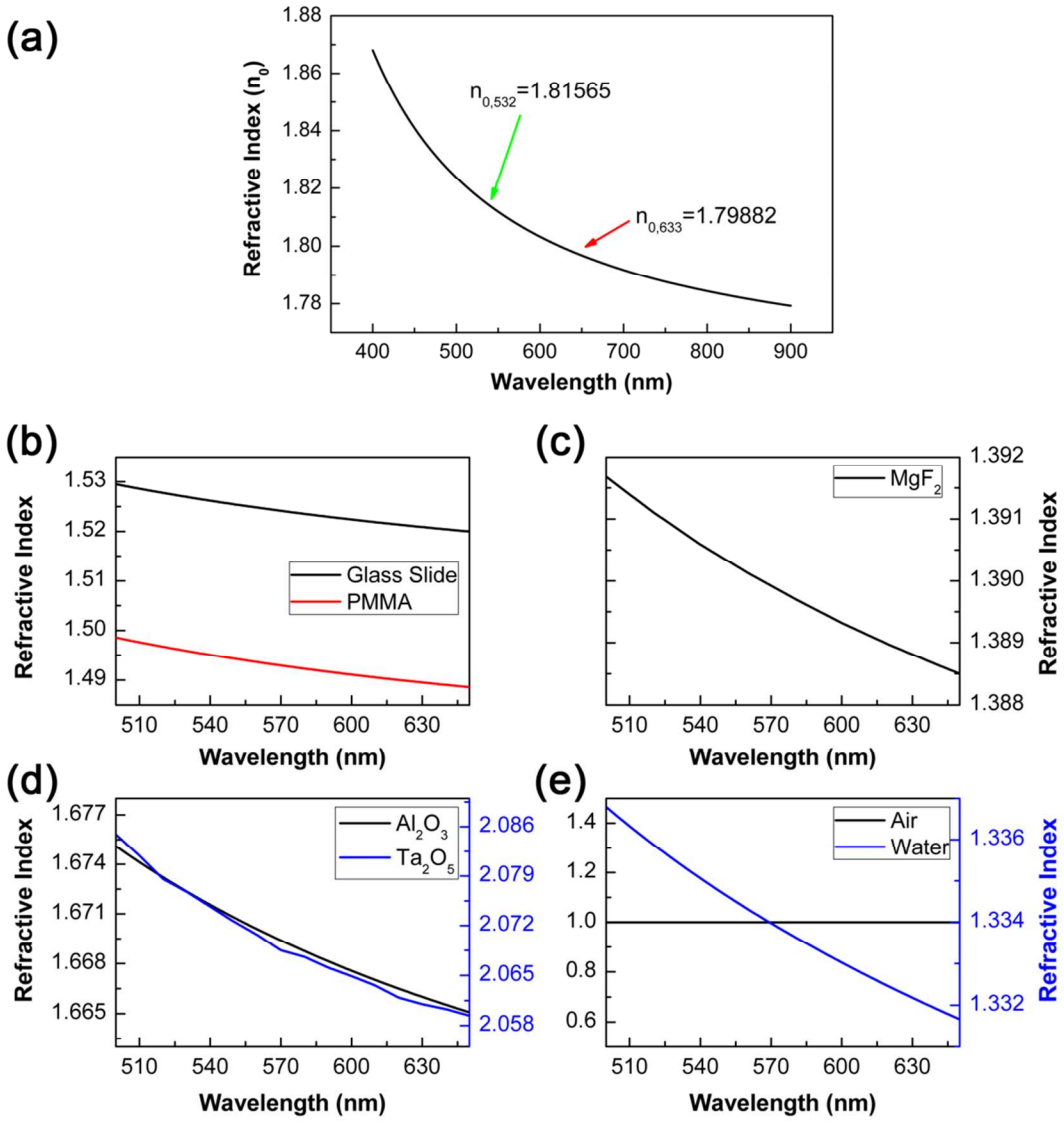

Figure 2S. Dispersion curves of (a) high refractive index coupling prism, (b) glass slide and PMMA, (c) MgF_2, (d) Al_2O_3 and Ta_2O_5, (e) air and water in the 532-633 nm wavelength range.

3. Field enhancement factors of other prism-based configurations

The field enhancement factors (FEFs) of other prism-based configurations (SPR, LRSPR, TIR and PWR) can be calculated via standard transfer-matrix method[2] using the following structural and optical parameters: (1) SPR: 50-nm-thick silver film deposited on glass slide, refractive index of the silver is 0.13+3.19i; (2) LRSPR: 1250-nm-thick MgF_2 buffer layer deposited on glass slide, 20-nm-thick silver resonant layer; (3) TIR: total internal reflection occurs at the glass slide-air/water interface; (4) PWR: 50-nm-thick silver buffer layer deposited on glass slide, 250-nm-thick PMMA resonant layer. The calculation results are illustrated in Figure 3S.

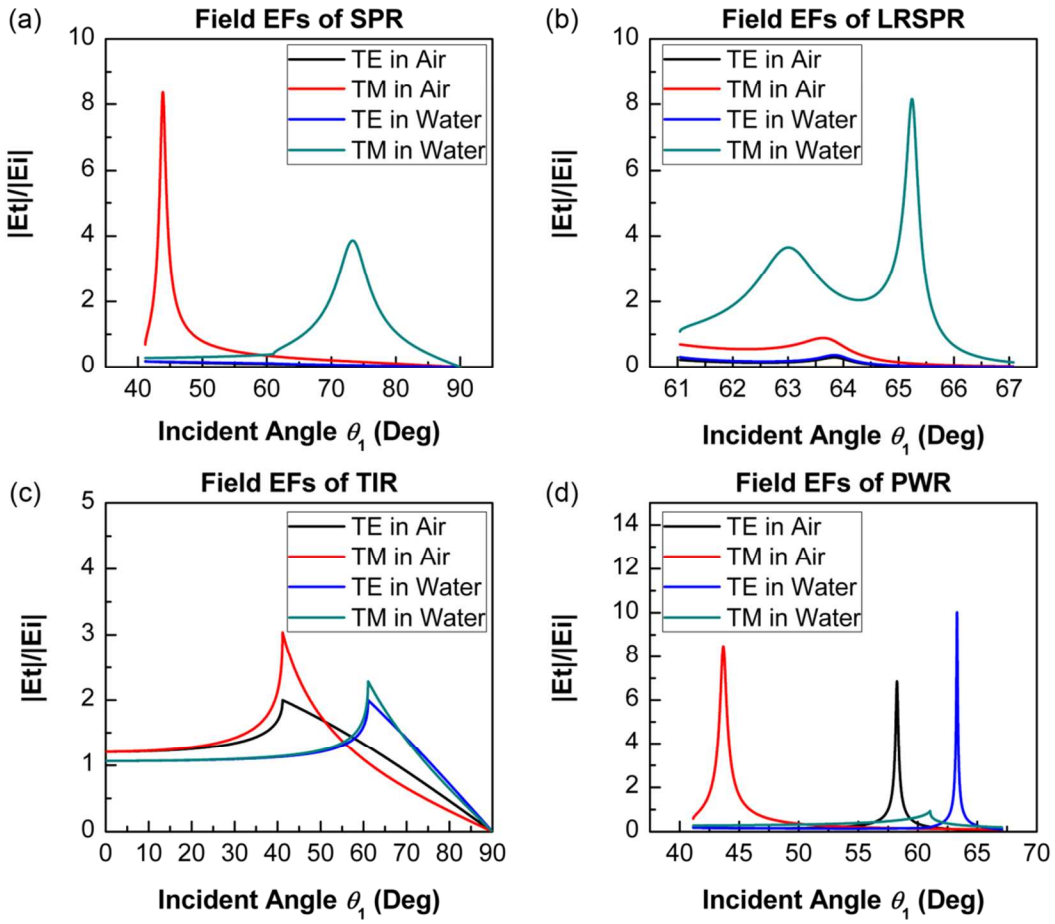

Figure 3S. Field enhancement factors of other prism-based configurations: (a) SPR, (b) LRSPR, (c) TIR and (d) PWR. θ_1 represents the incident angle in the glass slide.

4. Field enhancement mechanism and determination methods of resonant angles for RM#2

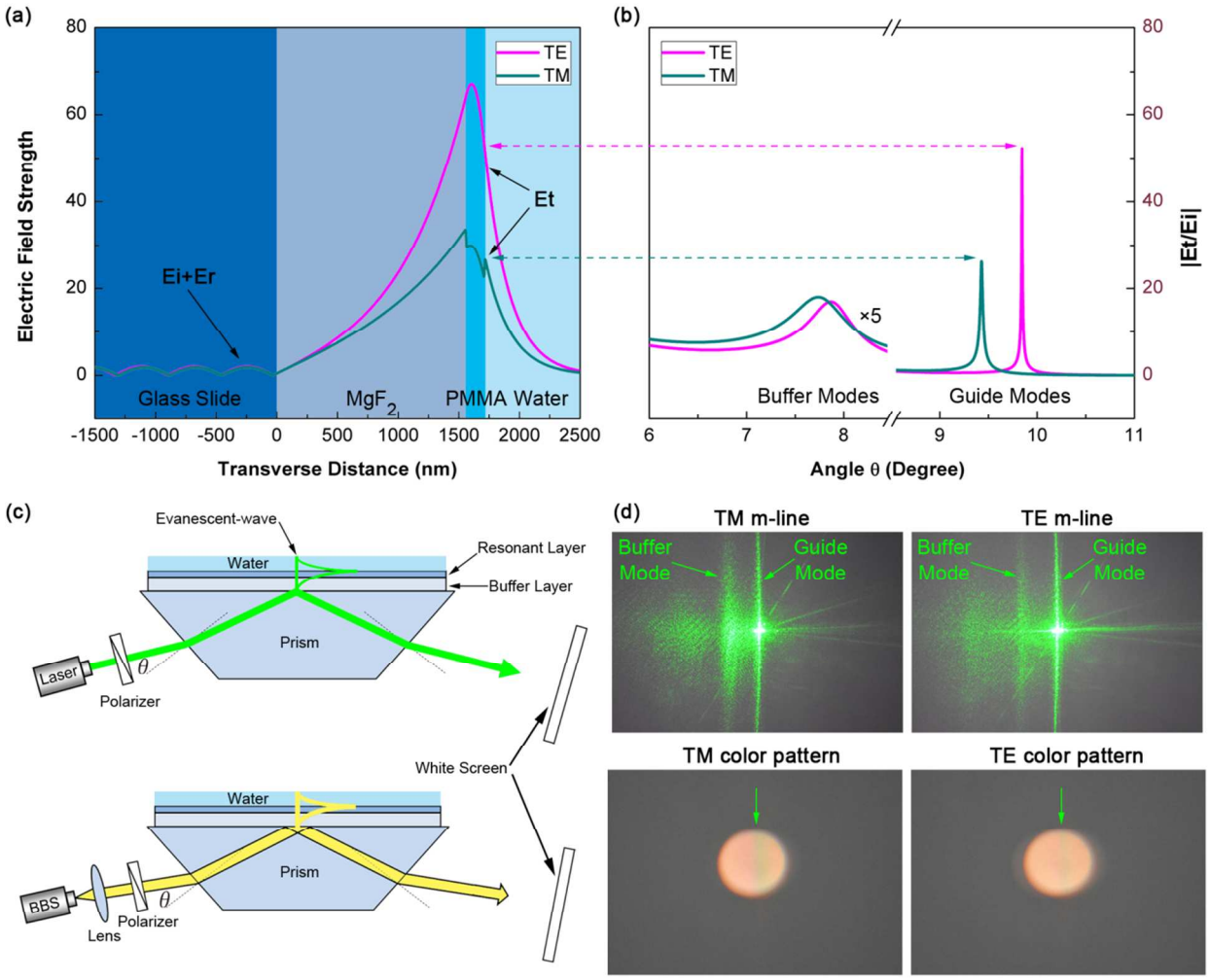

Figure 4S. Field enhancement mechanism and determination methods of resonant angles (θ) for the resonant mirror designed for solid-water interface applications (RM#2). (a) Mode profiles of TE and TM (only the Ex component of the TM mode is shown here, x axis is perpendicular to the waveguide surface) resonant guided modes; (b) Electric field enhancement of the buffer modes, TE and TM guided modes at the waveguide surface. The field enhancement factors on the left of the break are multiplied by five to make the TE and TM buffer modes visible; (c) Experimental setups for the determination of resonant angles of RM#2, m-line method (top) and spectral method (bottom); (d) Experimental phenomena when RM#2 is on resonance. Top: TM

and TE polarized m-lines corresponding to the buffer modes and guided modes, bottom: color patterns corresponding to the TM and TE resonant guided modes.

5. Field and Raman enhancement factors of resonant mirrors off resonance

In the RMERS experiments on CuPc ultrathin film detection, we can switch the resonant mirrors (RM#3 and RM#4) on and off resonance by changing their superstrates either from water to air or vice versa. Using the transfer-matrix method mentioned above we can calculate the field enhancement factors (FEFs) of RM#3 and RM#4 when they are on and off resonance. The calculation results are shown in Figure 5S, from which we can see: (1) the on resonance FEFs of RM#3 are about 40 and 10 for TE and TM polarized incident light, respectively; (2) the off resonance FEFs of RM#3 are about 0.11 and 0.24 for TE and TM polarized incident light, respectively; (3) the on resonance FEFs of RM#4 are about 55 and 28 for TE and TM polarized incident light, respectively; (4) the off resonance FEFs of RM#4 are about 0.08 and 0.10 for TE and TM polarized incident light, respectively. According to equation (1) in the paper: (1) the Raman enhancement factor (REF) of RM#3 off TE resonance for the CuPc Raman peak at 1534 cm^{-1} (corresponding to the wavelength about 579.3 nm) is about 4.6 while the on TE resonance one is about 6.1×10^5; (2) the REF of RM#3 off TM resonance for the CuPc Raman peak at 1534 cm^{-1} is about 2.0 while the on TM resonance one is about 3.5×10^3; (3) the REF of RM#4 off TE resonance for the CuPc Raman peak at 1534 cm^{-1} is about 5.7 while the on TE resonance one is about 2.7×10^6; (4) the REF of RM#4 off TM resonance for the CuPc Raman peak at 1534 cm^{-1} is about 2.8 while the on TM resonance one is about 2.2×10^5.

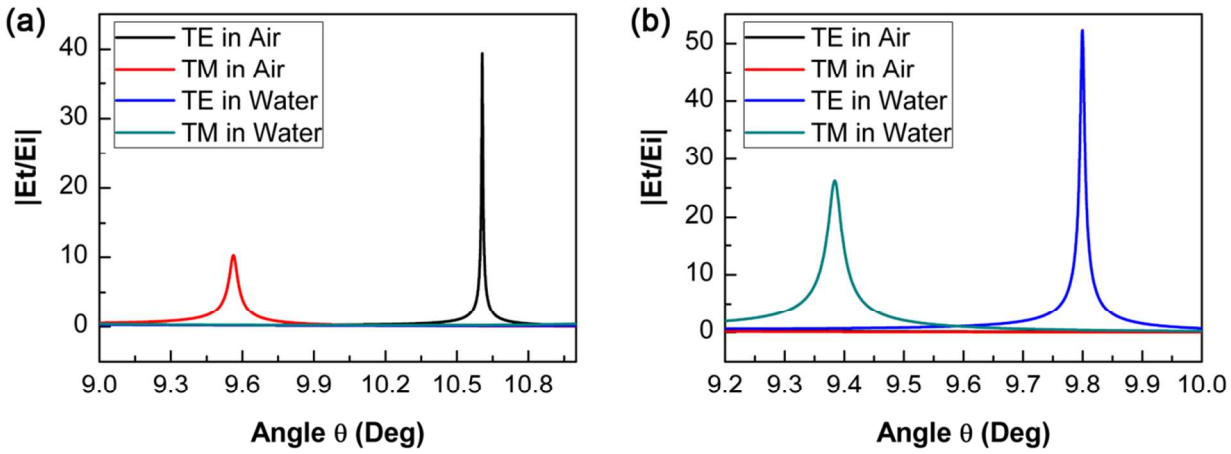

Figure. 5S Field enhancement factors of (a) RM#3 and (b) RM#4 on and off resonance.

6. Transmission absorbance spectrum of the 3.5-nm-thick CuPc ultrathin film

The transmission absorbance spectrum of the 3.5-nm-thick CuPc ultrathin film demonstrated in Figure 6S was measured with an UV-VIS spectrophotometer (SHIMADZU, UV-2700). This spectrum proves that the absorption of CuPc film to the laser light is relatively weak at the excitation wavelength (532 nm, A=0.003).

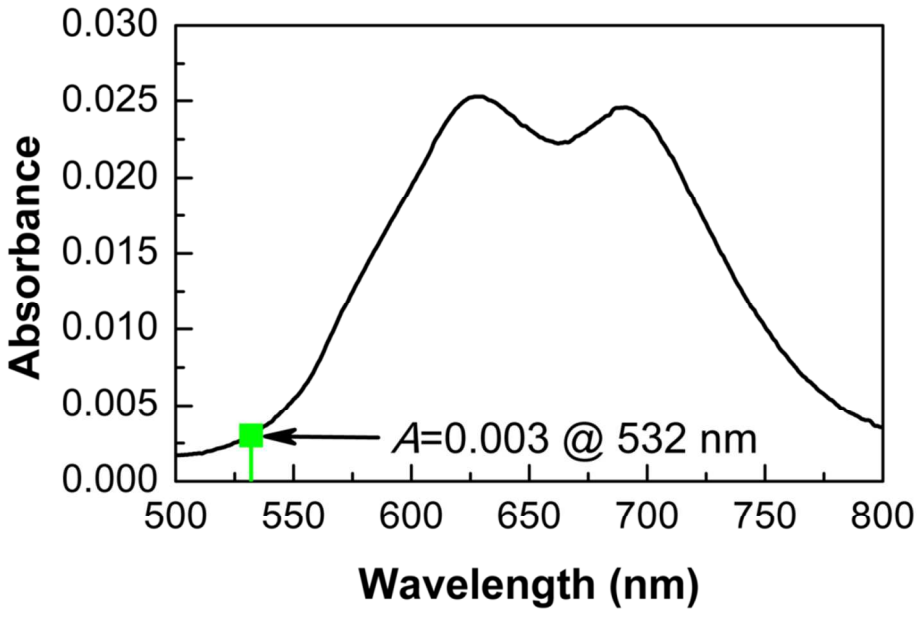

Figure. 6S Transmission absorbance spectrum of the 3.5-nm-thick CuPc ultrathin film.

7. Details about film fabrication and characterization

The MgF_2 buffer layers were vacuum sublimated onto the glass slide substrates at a pressure of 8.0×10^{-4} Pa, and the PMMA resonant layers were dip-coated onto the MgF_2 buffer layers from a PMMA acetone solution of a weight concentration of 5%. PMMA films of different thickness can be obtained by controlling the lifting speed. The CuPc ultrathin films were deposited onto the surface of RM#3 and RM#4 via vacuum sublimation at a pressure of 1×10^{-3} Pa. All the values of refractive indices and thickness related to resonant mirrors and CuPc ultrathin films were evaluated by an ellipsometer (J.A. Woollam Co., M-2000).

REFERENCES

(1) Hale, G. M.; Querry, M. R. Optical Constants of Water in the 200-nm to 200-μm Wavelength Region. *Appl. Optics* 1973, *12*, 555-563.

(2) Born, M.; Wolf, E. *Principles of Optics*; Cambridge University Press: Cambridge, U.K., 1999.