Research article

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Charge transfer and electromagnetic enhancement processes revealed in the SERS and TERS of a CoPc thin film

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Abstract: Phthalocyanines are frequently used as probing molecules in the field of single-molecule surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS). In this work, we systematically compare the SERS and TERS spectra from a thin cobalt phthalocyanine (CoPc) film that is deposited on a Au film. The contributions from electromagnetic (EM), resonance, and charge-transfer enhancements are discussed. Radially and azimuthally polarized vector beams are used to investigate the influences of molecular orientation and the localized surface plasmon resonance (SPR). Furthermore, two different excitation wavelengths (636 and 532 nm) are used to study the resonant excitation

effect as well as the involvement of the charge-transfer processes between CoPc and the Au substrate. It is shown that the Raman peaks of CoPc are mostly enhanced by 636 nm excitation through a combination of resonant excitation, high EM enhancement, and chemical enhancement via charge transfer from the metal to the molecule. At 532 nm excitation, however, the SERS and TERS spectra are dominated by photoluminescence, which originates from a photo-induced charge-transfer process from the optically excited molecule to the metal. The contributions of the different enhancement mechanisms explain the optical contrasts seen in the TERS images of Au nanodisks covered by the CoPc film. The insight achieved in this work will help to understand the optical contrast in sub- or single-molecule TERS imaging and apply SERS or TERS in the field of photocatalysis.

Keywords: TERS; SERS; phthalocyanines; charge transfer; photoluminescence.

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1 Introduction

Surface-enhanced Raman spectroscopy (SERS) has witnessed tremendous development since its discovery in the 1970s [1, 2]. It has been widely applied to the fields of sensing [3, 4], spectroelectrochemistry [5, 6], single-molecule spectroscopy [7], and many others. The physical mechanisms of SERS have been intensively discussed and extended, especially when new types of SERS substrates have been proposed [8, 9].

Electromagnetic (EM) enhancement is believed to contribute dominantly to SERS on metallic substrates, by providing greatly enhanced EM fields both in the excitation and scattering steps. This mechanism is also proposed as the main process to explain the Raman enhancement observed in tip-enhanced Raman spectroscopy (TERS). In TERS, the substrate on which the probing molecules are deposited does not necessarily provide a high EM field;

instead, a sharp noble metal tip (for the visible spectral range) is used. Depending on the type and geometry of the TERS tips [10], be it an electrochemically etched one [11], a specially designed tip shaft (i.e. grating-based) [12], or a tailored tip apex based on a single nanoantenna [13], a strong and localized EM field can be achieved at the tip apex. This EM field can be further localized and intensified via a gap-mode geometry, where the sharp tip is positioned in the proximity of a metallic surface, e.g. a distance of 2–3 nm, for a tip-sample feedback that is based on shear force [14] or 1 nm for one with tunneling current [15, 16]. With this configuration, an optical resolution down to sub-molecular level has been achieved [17].

When the probe molecules adsorb chemically on the metal surface, another Raman enhancing channel through charge-transfer processes, either from the metal to the molecule, or vice versa, can play a role [18]. This kind of mechanism is called chemical enhancement [19]. When the excitation wavelength matches one of the charge-transfer processes, chemical enhancement of specific Raman modes can be observed. For SERS experiments using metallic nanoparticles or roughened metallic surfaces, chemical enhancement has long been regarded as a subsidiary factor [19]. Recently, with the application of two-dimensional materials (i.e. graphene or dichalcogenides) as the SERS substrate, chemical enhancement is often proposed as the main enhancement mechanism [8, 9]. The physical origin of chemical enhancement and its importance have attracted much attention, providing new insights and theories in this regard. Even in TERS, chemical enhancement via charge transfer has been proposed [20]. As reported by Sun et al. in their theoretical work [20], four kinds of charge transfer can be identified: tip to molecule, substrate to molecule, tip and surface to molecule simultaneously, and tunneling charge transfer between the tip and substrate. With the ever-increasing interest in applying TERS to sub-molecular imaging, it is therefore essential to examine the different mechanisms of enhanced Raman spectroscopy and weigh their contributions individually. In particular, both the metal-to-molecule and molecule-to-metal charge transfer could enhance specific Raman modes and are very useful for manipulating chemical reactions at the single-molecule level in photocatalysis.

Transition-metal phthalocyanines (TMPcs) have been intensively studied in optoelectronic devices as electron donors [21]. When it comes to optical spectroscopy, TMPcs are often used as probe molecules because of their large Raman scattering cross-section and their high stability against humidity, oxygen, light, and heat [22]. TMPcs can be deposited onto a variety of substrates using physical

vapor deposition, with well-defined adsorption geometry and controlled surface coverage. This is very beneficial for understanding the influence of molecular orientation on the SERS enhancement. Moreover, at the metallic interface, a variety of interactions with the semiconducting molecules occur [23]. In the case of strong interaction, the electronic structure of both the molecule and the metal can be modified. As revealed by photo-excited electron spectroscopies, local charge transfer from the gold substrate toward the central metal atom of cobalt phthalocyanine (CoPc) affects the charge state of the Co ions. At the same time, enhanced features in the energy region across the d bands of the gold substrate can be observed using photoemission spectroscopy [23]. These characteristics make TMPcs ideal samples to discuss the EM- and the charge-transfer-based chemical enhancement in SERS and TERS.

Here we demonstrate the different enhancement processes in the SERS and TERS measurements on a CoPc thin film that is deposited on a Au surface. Radial and azimuthal polarizations are used for evaluating the contributions from EM enhancement and molecular orientation. Two different excitation laser wavelengths, namely 636 and 532 nm, are applied to investigate the resonance Raman process and to identify the charge-transfer process between the CoPc molecule and the Au substrate. Based on these studies, the optical contrasts observed in the TERS images are analyzed.

2 Results and discussion

2.1 Parabolic-mirror-assisted optical microscopy

For this study, we use a parabolic mirror (PM)-assisted confocal optical microscope, which can also be applied for performing tip-enhanced Raman spectroscopy by combining with shear-force scanning probe microscopy [24–26]. The optical paths of this microscope can be found in Figure S1 (Supporting Information). Different from the conventional setup of using an objective lens for focusing and detection, there are several advantages of using a PM: (1) The PM focuses the incident rays by reflection. Hence, PM is free from chromatic aberration, and it can be easily adapted to work with different laser wavelengths. (2) Opaque substrates can be used since the PM focuses and collects the optical signal both from above the sample. (3) A high numerical aperture (NA) of 0.998 can be achieved in air, which enables a tight focus and large signal

collection efficiency [25, 27–29]. PM is also beneficial for the TERS experiment. In most microscopes used for TERS, the laser beam is incident at the tips from the side, thereby illuminating a large sample area. For a sample with high Raman cross-section or photoluminescence (PL) quantum yield, the optical signal from the far-field excitation could be overwhelmingly stronger than the TERS signal. In addition, a lens system with a long working distance is often required for the configuration with side illumination, which collects only a few percent of photons from one side of the tip. In our case, we insert the tip at the center of the PM, which is able to focus the incident radiation symmetrically onto the tip apex. In this way, the optical signal from the far-field focus is minimized. This is especially advantageous for TERS study of samples with high fluorescence quantum yield or large Raman cross-section.

Besides, in order to excite the oriented adsorbate or plasmonic nanostructure with a defined polarization, we implement higher order laser modes such as radial and azimuthal polarizations in the PM-assisted confocal optical microscope. Radial and azimuthal polarizations are produced by a mode converter, which is composed of four quarters of differently oriented half-wave plates as described in [30, 31]. The schematic of these two modes are shown in Figure 1A. The incoming laser mode is linearly polarized initially. After passing through the mode converter, the polarization is turned into radial or azimuthal. The dashed white arrow denotes the polarization direction, and the black double-ended arrows denote the fast axis of the quarter half-wave plate. Radial or azimuthal polarization could be interchanged by turning the mode converter by 90° . The distributions of the electric field intensity at the focus of the radially and azimuthally polarized beams are shown in Figure 1C and D, respectively. E^2 , E_{xy}^2 , and E_z^2 denote the total field intensity, the field intensity in the xy -plane, and the field intensity in the z -direction (optical axis of the confocal microscope), respectively. λ is the wavelength of the excitation laser. As can be seen in Figure 1C, while the E_z^2 component dominates the electric field intensity in the focus of a radially polarized beam, an exclusive E_{xy}^2 field intensity is present in the focus of an azimuthally polarized beam. These distinctly different electric field distributions allow the determination of the orientation of a dipole moment [32, 33] or the selective excitation of a certain plasmonic mode [34]. Applying higher order laser modes in TERS has been proven advantageous. Thanks to the dominant E_z^2 component in the focus of a radially polarized beam, the long axis of the tip can be effectively excited, giving rise to a strong and localized plasmonic field at the tip apex experimentally [32, 35, 36] and theoretically [37].

2.2 Confocal optical imaging of CoPc on nanostructured Au

For this study, periodic arrays of Au nanodisks with varying diameters and interparticle distances were fabricated lithographically on Au substrates, as sketched in Figure 2A. The nanodisks are 20 nm in height and 80 nm in diameter, with an edge-to-edge interparticle distance of 200 nm. An ultrathin film of CoPc with a nominal thickness of 2 nm was deposited on the sample by organic molecular beam deposition under ultrahigh vacuum conditions. The topographic image of the sample can be seen in Figure S2 (Supporting Information). The chemical structure of CoPc is shown in Figure 2B, which has a planar geometry and is assigned to the D_{4h} point group.

Figure 2C–F is the confocal optical images recorded by scanning the sample through the laser focus. Two excitation wavelengths (532 and 636 nm) were used to excite the different optical processes, namely the molecular resonance of CoPc and the interband transition of gold, independently. The abbreviations “RAD” denotes the radially polarized mode, while “AZI” is the azimuthally polarized mode. The optical images correspond to $40\ \mu\text{m} \times 40\ \mu\text{m}$. In all four pictures, rectangular bright areas can be seen, which are from the Au nanodisk arrays. Because of the diffraction-limited optical resolution, individual Au nanodisks, which have an interparticle distance of 200 nm, are not well resolved. Clear optical contrasts between the Au nanodisk array and the Au film can be seen. Furthermore, it seems that, at the same excitation wavelength, the optical signal excited with radial polarization is stronger than that with azimuthal polarization.

2.3 SERS spectra of CoPc on nanostructured Au

The SERS spectra of CoPc on nanostructured Au are shown in Figure 3A and B. The symbol “ON” denotes the measurements performed at the rectangular bright areas (Au nanodisk array) in Figure 2C–F. “OFF” is used to designate the positions outside the rectangular bright regions. All the spectra were excited with a laser power of 200 μW and an integration time of 60 s. When illuminated by a 636 nm continuous wave laser with radial polarization, CoPc shows well-defined Raman peaks at 1540, 1463, 836, 754, and 684 cm^{-1} [38–40], which are assigned to the in-plane ring symmetric non-metal bond N–C stretch, benzene C–C stretch, macrocycle breathing, in-plane ring symmetric N-metal stretch, and macrocycle breathing, respectively. The most prominent Raman modes (1463, 1540 cm^{-1}) in the

Figure 1: Radial and azimuthal polarization: generation and electric field intensity distribution.

(A) Realization of the radial and azimuthal modes from a linearly polarized laser by a mode converter. The red arrows indicate the polarization of the laser beam, and the black two-side arrows stand for the fast axis of the $\lambda/2$ wave plate. Parabolic mirror (PM, illustrated as a gray block) focuses (B) the radially polarized laser beam, and (C) the azimuthally polarized laser beam onto the sample (orange block). The green arrows indicate the light propagation direction, while the red ones show the polarization directions. The gray-dashed line is the optical axis of the PM. (D, E) Calculated electric field intensity distributions when a radially polarized beam or an azimuthally polarized beam is focused by a PM. $E_{x,y}^2$, E_z^2 , and E^2 are the field intensity of the transverse component, of the longitudinal component, and the total electric field intensity, respectively. The results are calculated using an excitation wavelength of 636 nm and air medium.

spectra are the in-plane modes [41]. One can see that the Raman intensity at the “ON” positions in Figure 3A and B is higher than at the “OFF” positions, which is in agreement with the optical contrasts observed in Figure 2C–F. The Raman peak at 1540 cm^{-1} observed with 636 nm excitation (Figure 3B) from the Au nanodisk array is more than 20 times stronger than that away from the Au nanodisk region.

2.4 TERS spectra and image of CoPc on nanostructured Au

The TERS spectra excited at different wavelengths and locations are shown in Figure 4, which were taken with radially polarized beams. For a better comparison, the SERS spectra are also shown in Figure 4. The index to each

Figure 2: Confocal optical images of CoPc on nanostructured Au.

(A) Schematic diagram of a CoPc thin film deposited on a nanostructured gold substrate. (B) Chemical structure of CoPc. (C–F) Confocal optical images from a Au nanodisk array using 532 nm excitation and 636 nm excitation, respectively. For (C) and (E), a radial incident polarization is used, while for (D) and (F) an azimuthal polarization is used. The abbreviations “RAD” denotes the radially polarized mode, while “AZI” is the azimuthally polarized mode. The excitation power at the sample is $\sim 200 \mu\text{W}$ for the 636 nm excitation and $\sim 50 \mu\text{W}$ for the 532 nm excitation.

Figure 3: SERS spectra of CoPc on nanostructured Au.

SERS spectra taken at different excitation wavelengths, namely (A) 532 nm and (B) 636 nm, incident polarizations, and locations. “ON” stands for spectra recorded from rectangular shaped bright areas, and “OFF” indicates the spectra recorded outside. The abbreviations “RAD” denotes the radially polarized mode, while “AZI” is the azimuthally polarized mode. Excitation power is $200 \mu\text{W}$, and integration time is 60 s. The background of each spectrum is subtracted.

Figure 4: TERS and SERS spectra of CoPc at different excitation wavelengths.

Comparison of the SERS and TERS spectra taken at (A) 636 nm excitation, and (B) 532 nm excitation. The SERS spectra in (A) are integrated for 60 s, while the TERS spectra and the one from the tip alone are taken with only 10 s integration. In (B), all the spectra are taken with 60 s integration time. (C) Comparison of the background-subtracted TERS spectra taken on top of a Au nanodisk at different excitation wavelengths. To highlight the features in the TERS spectrum at 532 nm excitation, the Raman peaks are fitted by Lorentzian functions. The green line is the cumulative fit, and dashed blue curve shows the fitting components. The solid blue line indicates the baseline. The integration time for TERS at 532 nm is 60 s, whilst it is 10 s for the one at 636 nm excitation. (D) Comparison of the intensity ratios between two Raman modes at 754 and 1540 cm^{-1} , which are derived from the SERS and TERS measurements with different excitation wavelengths and locations. Each spectrum is taken by using radially polarized beam. The excitation power at the sample is $\sim 200 \text{ }\mu\text{W}$ for 636 nm and $\sim 150 \text{ }\mu\text{W}$ for 532 nm, respectively. “On” and “Off” stand for positions on the top of or away from a Au nanoparticle, respectively. “BTW” indicates a position at the Au film in between the Au nanoparticles.

spectrum is shown as an inset in the respective picture. Notably, the TERS spectra and the spectrum from the Au tip at 636 nm excitation were collected with an integration time of 10 s. At 636 nm excitation in Figure 4A, the Au tip shows a broad but weak spectral background. Upon approaching the tip to the top of a single Au nanodisk (“ON” position), Raman features from CoPc appear with higher overall intensities than when the tip is in proximity

to the planar Au substrate away from the Au nanodisks (“OFF” position). The peak positions of the main Raman features in TERS are very similar to those in the SERS spectra, though the peak intensity varies in some cases. In Figure 4B, the spectra taken with 532 nm excitation are shown. Notably, all TERS spectra and the tip spectrum at 532 nm excitation were taken with an integration time of 60 s. Interestingly, different from Figure 4A, each

spectrum in Figure 4B has a very strong spectral background. In order to compare the Raman features more clearly, two background-subtracted TERS spectra taken with 636 and 532 nm excitations are shown in Figure 4C. Because of the low Raman intensity with 532 nm excitation, only a few peaks can be seen and the ratios between the individual peaks seem to be different from those with 636 nm excitation. As an example, in Figure 4D, the intensity ratios between the two Raman modes at 754 and 1540 cm^{-1} are compared. The detailed data analysis can be found in Supporting Information. Whereas ratios around 0.4 are derived from the SERS and TERS spectra taken with 532 nm excitation, they are only about 0.2 for the measurements with 636 nm excitation. These phenomena will be further analyzed in Section 2.5.

Additionally, the TERS scattering images are shown in Figure 5A and C, which were recorded with 532 and 636 nm excitation, respectively. The respective topographic images obtained by recording the shear-force feedback signal are shown in Figure 5B and D. The topography in Figure 5B reveals the presence of six neighboring Au nanodisks. The seemingly rough surface for each nanoparticle is shown to be reproducible, which is likely from a slightly worn tip apex. The positions of these nanodisks correlate

well with the bright contrasts seen at the round features in Figure 5A. The TERS images at 636 nm excitation is shown in Figure 5C and D, where a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ sample area is scanned and the optical image is recorded with 128×128 pixels. In the topographic image (Figure 5D), the regular array of the Au nanodisks can be seen clearly resolved. However, in its simultaneously recorded optical images, the positions of the bright spots cannot be directly correlated to the positions of the nanodisks. In detail, optical contrasts of two different sizes are seen, which are highlighted by the white circles in Figure 5C. The mechanisms that could be responsible for the above-mentioned phenomena will be analyzed in the discussion part.

2.5 Discussion

2.5.1 Molecular resonance

The contributions to the SERS signal by resonance, EM, and charge-transfer enhancements are often entangled. Lombardi and Birke have proposed the use of Herzberg-Teller coupling to examine the contributions from all the three processes mentioned above [42]. An analytical

Figure 5: TERS images of CoPc at different excitation wavelengths. TERS images recorded with (A) 532 nm excitation and (C) 636 nm excitation. (B) and (D) are the simultaneously recorded topographic images, respectively. Excitation power at the sample is $\sim 200\text{ }\mu\text{W}$ for both 532 and 636 nm excitations. The incident polarizations for both 532 and 636 nm are radial.

expression for the Raman intensity in the proximity of metal nanoparticle(s) has been introduced. The relationship between the Raman polarizability $\alpha_{IFK}(\omega)$ and the three possible contributions has been proposed as

$$\alpha_{IFK}(\omega) \propto \frac{1}{[(\varepsilon_1(\omega) + 2\varepsilon_0)^2 + (\varepsilon_2(\omega))^2](\omega_{FK}^2 - \omega^2 + \gamma_{FK}^2)(\omega_{IK}^2 - \omega^2 + \gamma_{IK}^2)}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [43] are real and imaginary parts of the dielectric constant of the metal, respectively; ε_0 is the dielectric constant of the environmental medium and is real; and I , K , and F refer to the ground state, excited state, and the charge-transfer state, respectively. Detailed definitions of these states are given in the literature [40]. ω_{FK} and ω_{IK} are the frequencies of the charge-transfer processes between states F and K and between I and K , respectively; γ_{FK} and γ_{IK} are the damping parameters for transitions between states F and K and between I and K , respectively; and ω is the excitation frequency.

We start the discussion from the contribution of the molecular resonance process, which is the third term in the denominator. At $\omega = \omega_{IK}$, the Raman process occurs between the ground state and the electronically excited states of the molecule, giving rise to the so-called surface-enhanced resonant Raman scattering (SERRS). The molecular structure of CoPc contains 18 delocalized π electrons surrounding the central metal atom to form a two-dimensional π -electron conjugated system. The optical absorption spectra of CoPc show two major absorption regions: the Soret band at about 300–400 nm, and the Q band at 600–900 nm, both of which are due to the π - π^* electronic transitions. Particularly, in the Q band regime two peaks appear, with the high-energy one at around 620–635 nm originating from the first π - π^* transition on the phthalocyanine macrocycle [44]. The photon energy of 636 nm laser matches the HOMO-LUMO (highest occupied-lowest unoccupied molecular orbital) separation of CoPc, which is 1.96 eV [45]. Therefore, molecular resonance is one of the reasons for the stronger Raman scattering at 636 nm excitation than at 532 nm excitation, as seen in Figure 3A and B.

2.5.2 Electromagnetic enhancement

Now we turn the discussion to the contribution of EM enhancement, which is described by the first term in the denominator in the equation. First, we discuss the influence of different excitation wavelengths on the EM enhancement of the SERS signal. For a Au thin film, the nanometer-sized surface roughness helps to break the momentum conservation, allowing the coupling

of far-field light to the propagating surface plasmon-polaritons at the interface, which would be otherwise forbidden [19]. SERS enhancement factor in the order of 10^3 – 10^4 due to SPR has been reported [19]. For SERS at Au nanodisks, the excitation of localized surface plasmons (LSPs) needs to be considered, which has been shown to further enhance the local electric field for the optical excitations. This effect is also responsible for the clear optical contrast in intensity from the nanoparticle arrays and the surrounding Au film in Figure 2C–F. In the quasi-static approximation, where the size of a Au nanoparticle is much smaller than the excitation wavelength, the polarizability of the metallic nanoparticle is the largest at the Fröhlich condition, where $\varepsilon_1(\omega) = -2\varepsilon_0$. In the UV-vis spectral range, the dielectric constant of Au has a very small imaginary part and a negative real part. Therefore, the Au nanostructure is often used for producing localized surface plasmon oscillation in the visible range. At shorter wavelengths (less than 600 nm), $\varepsilon_2(\omega)$ of Au is increasing, which damps significantly the LSP resonance that may be present in this region. Moreover, interband absorption of Au also occurs in this spectral range. Therefore, at 636 nm excitation, a more dominant EM enhancement is expected than at 532 nm excitation. A detailed comparison of the TERS spectra is shown in Figure 4C. At 636 nm excitation, the integrated spectral intensities of individual Raman peaks are 2–4.6 times (peak to peak difference) stronger than they are for 532 nm excitation. This observation agrees well with the theoretical prediction that field enhancement at a gold tip using excitation at 636 nm is nearly 5 times higher than that it is with excitation at 532 nm radiation [37].

Additionally, TERS on the Au nanodisk is stronger than that at the Au film, which could be due to the further increase in EM enhancement via a double-tip geometry, where the Au nanodisk acts as the second pointing tip [20, 46]. As predicted by theoretical calculations [47], the local EM field enhancement ratio, $R_{\text{double tip/conventional}}$, from double-tip TERS configuration and from conventional TERS (tip and planar substrate) is about 2 for 632.8 nm excitation. In our TERS measurements, the ratio of integrated Raman intensity of the double tip (tip on Au nanodisk) and conventional TERS (tip on Au film) configuration is 1.6–2.5 (peak-to-peak) at 636 nm excitation, which is in good agreement with theoretical prediction.

Now we discuss the influence of the excitation polarization on the EM enhancement. As can be seen in Figure 3, using a radially polarized incident laser beam, where the dominant electric field is oriented perpendicularly to the substrate plane, the Raman intensity is always higher than that with an azimuthally polarized beam. This

phenomenon is not likely due to the influence of molecular orientation as one might expect according to the surface selection rule. As reported in the literature [41], for a CoPc thin film of about 2 nm thickness on a rough Au surface, the molecular plane at its interface layer tends to be parallel to the substrate surface (“lying”), while it gradually becomes perpendicular (“standing”) with increasing molecular film thickness. The focal depth of our setup is on the order of some hundreds of nanometers. Hence, CoPc molecules of all orientations, from “lying” to “standing”, are probed, giving rise to the minor influence on the polarization-dependent Raman intensity shown in Figure 3. Therefore, the dominant role of LSP resonance at different excitation polarizations needs to be considered. LSP resonances are very sensitive to their surrounding environment. The nearby presence of a conducting surface could induce frequency shifts in the plasmon resonances of a nanostructure [48, 49]. It has been shown experimentally and theoretically that two localized dipolar plasmonic modes can be excited when a Au nanosphere is in close contact with a 45-nm-thick Au film [49]. By varying the incident polarization from 0° (s-polarization) to 90° (p-polarization) with respect to the surface plane, the two peaks in the dark-field scattering

spectrum gradually change their relative intensity, and in the end the red-shifted one dominates the spectrum [49]. This phenomenon has been explained on the basis of the interactions between a dipolar mode in the nanoparticle and its image dipole in the film. When the electric field of the polarized light is parallel to the film, the in-plane (parallel to the film) image dipole moments are opposite to those in the nanoparticle, so that the net scattering from the Au nanoparticle vanishes. The nanoparticle and its image dipole can then be polarized only normal to the surface, which leads to a larger dipole strength [49, 50]. Therefore, independent of the excitation wavelength, the Raman signal is always stronger when a radially polarized laser beam is used, as seen in Figure 3A and B.

2.5.3 Charge-transfer enhancement

Finally we turn our discussion to the second term in the denominator of the equation, which describes the contribution from the charge-transfer process. For $\omega = \omega_{FK}$, the laser can excite the charge-transfer process resonantly. In Figure 6, the energy diagrams of the CoPc thin film on the Au substrate are shown, with the orbital alignments

Figure 6: Energy diagram at the interface between Au and the CoPc molecule.

(A) The different excitation and charge-transfer process occurring at 636 nm excitation. On the left side, only the hot electron population (shown as a blue peak) in Au is excited by the 636 nm laser irradiation. On the right side, the HOMO-LUMO transition in CoPc is resonantly excited by the 636 nm laser. The two blue arrows indicate the possible photo-induced metal-to-molecule charge-transfer processes. The horizontal blue arrow shows the charge transfer from the hot electron population to the LUMO of the CoPc molecule. The diagonal blue arrow indicates the charge-transfer process from the Au Fermi level directly to the LUMO of the CoPc molecule. The downward-pointing brown arrow represents the Raman scattering process. (B) The excitation, emission, and charge-transfer process occurring at 532 nm excitation. The green arrows refer to either the d-sp interband transition in Au or the molecular excitation of CoPc. The downward-pointing dashed green arrow indicates the nonradiative relaxation. The downward-pointing dark-blue arrow indicates the radiative relaxation in Au. The blue arrow indicates the possible photo-induced molecule-to-metal charge transfer. The downward-pointing brown arrow represents the Raman scattering process.

derived from the literature values [23]. On the left side of Figure 6A, the red arrow indicates the excitation of SPR states from the Fermi level of Au with the 636 nm laser. The possible charge-transfer pathways between Au and CoPc are indicated by two blue arrows. The horizontal blue arrow shows the charge transfer from the SPR states to the LUMO of the CoPc molecule. The diagonal blue arrow indicates the charge-transfer process from the Au Fermi level to the LUMO of the CoPc molecule [51]. At 636 nm excitation, both charge-transfer pathways could exist. On the right side, the LUMO and HOMO levels of CoPc are shown. The vacuum level of CoPc ($E_{V, \text{CoPc}}$) is shifted by $\Delta \sim 1.1$ eV downward with respect to that of Au as a result of the formation of an interfacial dipole layer, as reported in [23]. The red arrow between the LUMO and HOMO of CoPc indicates the excitation of the molecular resonance at 636 nm, which matches the absorption of the Q band. The downward-pointing brown arrow represents the Raman scattering process.

It has been reported that for copper phthalocyanine (CuPc) in the spectral region at about 650 nm, the symmetric Raman modes (e.g. B_{1g}) borrow intensity from allowed molecular transitions (Q bands) by charge-transfer resonances [52]. The intensity ratio between the metal-center-related vibrational mode to that of the benzene ring vibrational mode has been used to evaluate the strength of the charge-transfer interaction between CuPc and Au foil or MoS_2 [52]. For the CuPc molecule, the 749 cm^{-1} vibration is assigned to the in-plane N–Cu stretch, while the peak at 1530 cm^{-1} is the in-plane ring symmetric non-metal-related N–C stretch. The lower intensity ratio ($I_{749}/I_{1530} \text{ cm}^{-1}$) observed from the CoPc molecule on the Au surface as compared to that from CuPc on MoS_2 has been attributed to the higher charge transfer between CuPc and Au. Here we follow the same considerations to evaluate the contributions of the charge-transfer process between CoPc and the Au substrate in our experiments. For the CoPc molecule, the vibrational mode involving the metal center appears at 754 cm^{-1} while the non-metal bond N–C stretch is located at 1540 cm^{-1} [52]. The results are shown in Figure 4C. While for SERS and TERS at 636 nm excitation the Raman intensity ratio $I_{754}/I_{1540} \text{ cm}^{-1}$ is ~ 0.2 , it increases to about 0.4 when 532 nm excitation is used. This indicates a higher charge transfer between CoPc and the Au substrate for 636 nm excitation, matching the resonant excitation of the Q band. Notably, this ratio is nearly the same in the SERS and TERS experiments, indicating a similar level of charge-transfer enhancement in both cases. Given the fact that the tip-to-Au substrate distance is about 3 nm larger in our measurements [53–55], extra charge-transfer paths such as between the tip and the

molecule are unlikely to occur as has been predicted for STM-TERS in a theoretical work [20]. Regarding this point, further experiments with a scanning tunneling microscope (STM) feedback are planned.

In addition to the Raman peaks, the intensity of the spectral background is different for the different excitation wavelengths as well. As can be seen in Figure 4, while the Raman peaks dominate all the SERS and TERS spectra at 636 nm excitation, the spectral background is clearly prominent for all measurements at 532 nm excitation. To explain this effect, we start the analysis with the spectrum of the tip taken at 532 nm excitation, shown in the bottom panel of Figure 7A. The photoexcited Au tip by a radially polarized laser beam produces a broad spectrum, which has been assigned to the radiative decay of the localized plasmon oscillation in the form of PL [56–59]. Its spectral profile is shown to be similar to that of the extinction or scattering spectra [56, 60, 61]. The tip shows a strong spectral background with a maximum at about 615 nm at the excitation of 532 nm because the PL is emitted after an interband absorption process. When the tip approaches the Au film or Au nanoparticles (NPs), this PL increases dramatically (Figure 7A and C) and the peak maximum stays at nearly the same position (Figure 7B). To clarify these phenomena, we analyze the different excitation and emission processes occurring at the molecule-metal interface, as shown in Figure 6B. On the left side, the 532 nm green laser excites the interband d-sp transition of Au, shown as an upward-pointing green arrow. On the right side, photons at 532 nm have a much higher energy than the HOMO-LUMO band gap of CoPc, which will therefore excite the molecule in off-resonance condition (upward-pointing green arrow). The excited electron returns to the lowest electronic level of LUMO by a thermal equilibrium (dotted downward-pointing green arrow) step. Here a charge-transfer process may occur from the LUMO of CoPc to the sp band of Au. From there, the electron can further relax energy, for example, by emitting photons (shown as a downward-pointing dark-blue arrow in Figure 6B). Therefore, one observes a stronger PL at 532 nm excitation than at 636 nm. In addition, though the excitation of localized plasmons in Au at 532 nm is much less efficient than at 636 nm excitation due to the interband transition and large damping rate, a weak near-field enhancement induced by the tip is still present. This moderate EM enhancement excites more HOMO-LUMO transitions in TERS than in SERS at 532 nm excitation, enabling more photo-induced charge-transfer processes from the excited LUMO in CoPc to the sp band in Au. Therefore, in all TERS spectra at 532 nm excitation, stronger PL signals are observed than in the SERS measurements, as seen in Figure 7A and C.

Figure 7: Analysis of the TERS spectra.

(A) Analysis of spectral background from the tip alone (bottom), SERS at the Au nanodisks (middle), and TERS at the Au nanodisk (top) at 532 nm excitation. Black curves are the original spectra. The red curves are the sum of the fit. Three Gaussians (blue curves) with the maxima at around 540 nm (a), 580 nm (b), and 613 nm (c) are used to fit the spectral background. (B) Comparisons of the peak positions of a, b, and c, which are derived from the spectra of Au tip alone, SERS on film (SERS OFF), SERS on particle (SERS ON), TERS between the particle (TERS BTW), and TERS on the particle (TERS ON). (C) Comparisons of the peak intensities of a, b, and c. The detailed data analysis can be found in Supporting Information.

Based on the above analysis, now we can clarify the optical contrasts in the TERS images shown in Figure 5 at different excitation wavelengths. For Figure 5A, the optical signal consists mainly of PL signal via a photo-induced molecule-to-metal charge-transfer process. This process is intensified via a stronger EM enhancement thanks to the presence of a double-tip geometry. Therefore, the brighter optical features shown in Figure 5A correlate closely with the individual positions of the Au nanodisks. On the contrary, the optical contrast at 636 nm excitation in Figure 5C is dominated by overlapped Raman signals from both SERS and TERS. The contrast from the TERS signal is highlighted with a smaller dashed white circle, which correlates with the positions of Au nanodisks. The optical contrasts from SERS signal (labeled with a larger dashed

white circle) can be seen at the center of four neighboring Au nanodisks. This can be well understood by considering the diffraction-limited far-field focus in a PM. For a 636 nm laser, the FWHM (full width at half-maximum) of the central Airy disk is about 300 nm [28]. Therefore, when the laser focus is at the center of the four neighboring Au disks, the SERS signals add up, giving rise to intense and diffraction-limited optical signals there.

3 Conclusions

In this article, we systematically discussed the EM enhancement and chemical enhancements in both SERS

and TERS measurements. Using a CoPc thin film on Au as the object, we compared the influences from incident polarizations and excitation wavelengths on the Raman enhancement as well as on the PL signal. As a result of the matching of molecular resonance and effective excitation of plasmon resonance, Raman enhancement at 636 nm is stronger than at 532 nm. Furthermore, it was shown that radial polarization of incident beam leads to a stronger SERS enhancement on the Au nanodisks than on the Au film, which is due to the constructive dipolar interactions in the nanodisk and the underlying Au film. Because of the double-tip effect, the TERS enhancement at the nanodisk is higher than on the Au film. Because of the strong enhancement of the Raman signals in both SERS and TERS measurements at 636 nm excitation, the TERS image from the CoPc/Au nanodisk array shows an overlapping contrast from both processes, where only the enhanced Raman signal from the TERS process correlates with the position and dimension of individual Au nanoparticle. The contribution from the SERS enhancement gives rise to the diffraction-limited optical signal at the center of four neighboring Au nanodisks. Instead, at 532 nm excitation, only a weak Raman enhancement can be seen and the most prominent observation is the largely increased PL intensity. This is likely due to the photo-induced charge-transfer process from the optically excited CoPc to Au, which further relaxes radiatively via an interband transition. This process is stronger thanks to the higher EM enhancement while using the double-tip geometry. Therefore, at 532 nm excitation, the optical contrast in the TERS image is dominated by the PL signal, which correlates directly with the position and dimension of each Au nanodisk.

The findings of this paper can be generalized in several aspects: (1) Though both SERS and TERS benefit from EM enhancement and chemical enhancement, they occur at different levels. At the same excitation wavelength, Raman features appearing in the SERS and TERS spectra are comparable with the regard of peak positions, but with slightly varying relative peak intensities. (2) Both metal-to-molecule and molecule-to-metal charge-transfer processes can happen, which depends sensitively on the energy level alignment at the interface between the semiconducting molecule and metal and the excitation wavelength. In turn, different charge-transfer pathways need to be considered, especially for the rational design of photocatalysis reactions with light of different energies. (3) SERS and TERS spectral background could hint at important photophysical processes occurring in the light-matter interaction. They are important in understanding the contrast of optical

images, especially in the field of single-molecule TERS imaging.

As an outlook, it is known that the Raman scattering signal can be selectively polarized, such as for a single molecule located in the nanocavity of a dimer [62] or randomly oriented molecules on self-organized gold nanowires [63]. As a comparison, for SERS nanostructures without axial symmetry, such as in the cases of trimers and tetramers, the Raman scattering signals are only partially polarized [64, 65]. Therefore further studies on the polarization of the CoPc Raman signals in the SERS and TERS configurations will be performed.

4 Experimental

As the substrate, a 50-nm-thick Au film was evaporated onto a Si wafer coated with a Cr film (2 nm thick). Afterwards, arrays of Au nanodisks were fabricated on top using electron-beam lithography. The edge-to-edge interparticle distance was 200 nm. An ultrathin film of CoPc with a nominal thickness of 2 nm was deposited on the sample by organic molecular beam deposition under ultrahigh vacuum conditions.

Combined optical spectroscopy and topography measurements were conducted using a home-built setup [28]. This is a PM-assisted confocal optical microscope expanded with a shear-force scanning probe microscopy (SPM) function. The setup uses a 636.3 nm diode laser (Picoquant, PDL 800-D, Berlin, Germany) operated in the continuous wave mode, as the excitation source. A 532 nm laser (QIOPTIQ, NANO 250-532 max, UK) is also integrated with the microscope. To reach a diffraction-limited focus, we convert the linearly polarized beam into a radially polarized beam. This is achieved by guiding the beam through an expanding telescope followed by a $\lambda/2$ plate mode converter. Finally, we focus the optical beam on the sample using a PM with a large opening angle (numerical aperture = 0.998). Optical signals were cleared from elastic scattering using two optical notch filters (total optical density = 12) and detected by an avalanche photodiode (single-photon counting module SPCM-AQR-14; Perkin Elmer, MA, USA) for optical imaging. Simultaneously, a liquid-nitrogen-cooled charge-coupled device (CCD) coupled to a spectrometer (Acton Research, SpectraPro 300i, Perkin Elmer, MA, USA) was used to collect spectra. A chemically etched gold tip attached to a tuning fork was used to collect the topogram synchronously with the optical signal. The tuning fork approaches the sample through an opening at the top of the PM and is then placed in the focus to ensure optimal excitation of the tip apex. A constant tip-sample

distance was maintained by monitoring the phase shift using an Ametek 7270 DSP lock-in amplifier and regulating the tip-sample distance with a RHK-SPM100 unit. The optical and topographic images were collected by raster-scanning the sample through the focus.

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