Study on Enhancement of Tunnelling-Induced Fluorescence from Porphyrin Film by Substrate Plasmon

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Abstract. We have studied the effect of the plasmon field on the STM-induced luminescence from porphyrin (H₂TBPP) film on Au substrate. We have measured the spectrally resolved photon intensity map for the STM-induced luminescence, and found the similarity of their contrast for the photon maps for different spectral regions with different spectral origins, i.e. molecular fluorescence and the local plasmon induced luminescence from the substrate. This fact indicates that the molecular fluorescence is closely related with the plasmon field of the substrate, and supports that the STM-induced fluorescence from porphyrin film on Au is enhanced by the local plasmon field of the Au substrate.

1. Introduction
Light emission induced by tunnelling electrons from Scanning Tunnelling Microscope (STM) is a feasible technique for the study of the optical properties on a nanometer scale [1-9]. Recently, STM-induced luminescence (STML) from molecules has attracted strong attention because of its potential applications in molecular electronics and optoelectronics [9-15]. The optical properties of H₂TBPP porphyrin (H₂TBPP) have been investigated by means of STM. Dong et al. [12] reported an approach of using molecules as both spacer and emitter and observed well-defined vibrationally resolved fluorescence due to the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) transitions.

STM-induced light emission is explained in terms of the oscillating dipole associated with local plasmon at the STM tunnel junction [3]. The STM induced luminescence from molecules in STM junction can be influenced by the interaction of molecule states with electromagnetic field due to local plasmon. Recently, Liu et al. [14] proposed a model named Surface–plasmon Enhanced Molecular Fluorescence (SEMF) based on the study of STML of spin-cast H₂TBPP film on various substrates and finding that molecular fluorescence was observed for gold and silver substrates but not for HOPG and ITO ones. The rate equation for the kinetics of plasmon enhanced molecular fluorescence has also been proposed to discuss the kinetics of the photon-molecule interaction in a nano cavity at the STM junction [14]. Nishitani et al. [15] have reported a photon intensity map for the H₂TBPP film on Au film, and found a similar contrast to the topography of the underlying Au film: the STM-induced molecular fluorescence of the organic film is most strengthened where the plasmon-mediated light of the Au substrate is most strengthened.

In a previous work [15], we have found the spatial correlation between the topography and the spectrally integrated light intensity H₂TBPP film on Au excited by STM in a UHV system. In this study, we have measured spatially and spectrally resolved molecular fluorescence for H₂TBPP film on Au. We show the correlation between spectrally resolved photon map and the topography of H₂TBPP
film on Au. The spectrally resolved photon intensity which is directly related to molecule fluorescence peak shows a similar contrast to the STM topography image as well as the photon map for the background spectra due to plasmon, and indicates that the stronger tunneling fluorescence comes from the stronger topographies in STM image, and that the molecular fluorescence is well correlated with the plasmon-induced luminescence. This spatial correlation is the same as the previously-reported correlation between the photon map of plasmon-mediated light emission for pure gold and its topography [16]. Present result supports the mechanism of Surface–plasmon Enhanced Molecular Fluorescence (SEMF), i.e. tunneling-electrons-induced molecular fluorescence in organic film is enhanced by the surface plasmons.

2. Experimental setup
The experimental setup of STM-induced light emission measurements is shown in Fig. 1 [6, 7, 15]. The photon mapping measurement was performed in a UHV-STM combined with the photon detection system. Photons emitted from the tip-sample junction were collected using a lens with a solid angle of about 1 str, and then guided to a spectrograph (Kaiser Optical Systems, Inc., HoloSpec f/2.0) through an optical fiber. The spectra were recorded with ICCD detector (intensified charge coupled device, ICCD-1024E, Princeton Instruments, Inc.) with 1024 × 256 pixels. Using these spectrograph and ICCD, this system is capable of covering a wavelength range from 385 to 800 nm. The spectral resolution is about 6.4 nm which is determined by the diameter of the fiber. A spectrum was integrated for around 1.0 s at each point of 64×64 points in the scan region. Spectrally resolved photon map are obtained using these spectra after the 64x64 spectra measurements.

Gold film was deposited on the glass substrate by thermal evaporation in a high vacuum of about \(1\times10^{-7}\) Torr. STM tips used in the experiments were Pt-Ir (10%) tips. The \(\text{H}_2\text{TBPP}\) films were spun-cast from dilute chloroform (CHCl3) solution (\(\text{H}_2\text{TBPP}:\text{CHCl3} = 4\ \text{mg}:\ 10\ \text{ml}\)) at 2000 rpm onto the top of the Au film. The thickness of the organic film was from 4 to 10 nm corresponding to the number of droplet from 4 to 8.

3. Results and Discussion
Figure 2 shows a spectrum of tunneling luminescence for \(\text{H}_2\text{TBPP}\) film on Au, which is averaged by all spectra obtained from 64×64 points in a photon map. In the STML spectrum, there are 0-0 and 0-1
vibronic peaks at around 656 and 722 nm respectively in good agreement with those at 650 and 715 nm in conventional PL spectrum, not shown here.

The spectrally resolved photon intensity map, corresponding to the spectral region indicated in Fig. 2, are shown in Fig. 3, in the spectral range (a) from 600 to 640 nm, (b) from 640 to 700 nm, (c) from 700 to 730 nm and (d) from 730 to 800 nm. The topographic image [Fig. 3(e)] is measured simultaneously with tunneling-induced photon maps [Figs. 3 (a)-(d)] for the H$_2$TBPP covered Au surface at the bias voltage of 2.1 V and tunnelling current 1 nA. The scan size is 255x255 nm$^2$. All spectrally resolved photon maps in Fig.3 (a)-(d) show similar contrast, and correlate with the topography, Fig. 3(e), except for the weak correlation at lower part of Fig.3 (a) possibly due to low intensity signal or due to the microstructure dependent plasmon effect of light emission as discussed in ref 7. The spectral ranges from 640 to 700, and from 700 to 730 nm, correspond to the ranges of luminescence peak due to HOMO-LUMO transitions. The other spectral range is not directly related to the transition of HOMO-LUMO transition, and their intensity may be related with the luminescence due to local plasmon of the substrate Au because the STML spectra for H$_2$TBPP on Au substrates are overlapping of molecular fluorescence peak on the background of plasmon induced light [13,14].
luminescence vs. topographic measurements shows how the luminescence intensity correlates with
topography, which, due to plasmon enhancement, changes with the local topographic features of the
substrate. In Fig. 3(e), we recognize that the surface topography looks similar to the underlying
contour of Au grains and thus consider that the porphyrin film uniformly covers the Au substrate. The
organic film is formed by three droplets and the average thickness is evaluated to be 10 nm. The
similarity in all photon maps [Figs. 3(a)-(d)] indicates that the intensity map for the molecular
fluorescence [Figs. 3(b), (c)] are well correlated with the intensity map for the background due to the
plasmon-induced light emission [Figs. 3(a), (d)]. This fact indicates that the fluorescence from
molecules is related with the STM-induced plasmon field of substrate Au.

Previously, we reported a correlated profile between STM topography and integrated photon
intensity map for the H$_2$TBPP covered Au surface [15]. We have discussed the plasmon enhancement
of the fluorescence from H$_2$TBPP on the basis of the theoretical model of the similar contrast for the
STM topography and the photon map for pristine Au [16], which is explained in terms of the
orientation of the tunneling dipole depending on the tip position over the topography so that the light
emission is nearly proportional to the topographic height of the particle, i.e., the stronger plasmon-
mediated light is emitted from the higher topographies of Au grains.

In addition to the previous result of the comparison between H$_2$TBPP film and pristine Au film [15],
the present results of the similarity of spectrally resolved photon maps in different spectral region
strongly support the plasmon enhancement of the STM-induced fluorescence from H$_2$TBPP film on
noble metal, based on the study of STML of spin-cast H$_2$TBPP film on various substrates (Au, Ag,
HOPG, and ITO) and finding that molecular fluorescence was observed for Au and Ag substrates but
not for HOPG and ITO ones [14]. In this model, the local surface plasmons of the metal substrate are
excited by the tunneling electrons under the electric field caused by the tip, and then the molecular
excitation and molecular fluorescence associated with HOMO-LUMO transitions in H$_2$TBPP film is
well enhanced by electrodynamical coupling between the oscillating dipole associated with the
molecule and local surface plasmons.

4. Summary
We have studied the plasmon enhancement of STM-induced luminescence from H$_2$TBPP film on Au
by means of spectrally and spatially resolved STM light emission. We found the similarity of their
contrast for the spectrally resolved photon maps for different spectral regions with different spectral
origins, i.e. molecular fluorescence and the local plasmon induced luminescence from the substrate.
This fact indicates that the molecular fluorescence is closely related with the plasmon field of the
substrate. The results support that the plasmon enhancement of the STM-induced fluorescence from
H$_2$TBPP film on noble metal. In this model, the molecular excitation and molecular fluorescence
associated with HOMO-LUMO transitions in H$_2$TBPP film is well enhanced by electrodynamical
coupling between the oscillating dipole associated with the molecule and local surface plasmons.

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