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Tunneling electron induced luminescence from porphyrin molecules on monolayer graphene



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ABSTRACT

Using epitaxially grown graphene on Ru(0001) as a decoupling layer, we investigate the evolution of tunneling electron induced luminescence from different number of layers of porphyrin molecules. Light emission spectra and photon maps, acquired via a combined optical setup with scanning tunneling microscopy (STM), indicate that the electronic decoupling effect of a monolayer (ML) graphene alone is still insufficient for generating molecule-specific emission from both the 1st- and 2nd-layer porphyrin molecules. Nevertheless, interestingly, the plasmonic emission is enhanced for the 1st-layer but suppressed for the 2nd-layer in comparison with the plasmonic emission on the monolayer graphene. Intrinsic intramolecular molecular fluorescence occurs at the 3rd-layer porphyrin. Such molecular thickness is about two MLs thinner than previous reports where molecules were adsorbed directly on metals. These observations suggest that the monolayer graphene does weaken the interaction between molecule and metal substrate and contribute to the reduction of nonradiative decay rates.

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1. Introduction

The tip of a scanning tunneling microscope (STM) can be used as an atomic-size source of tunneling electrons to excite nanoscale objects and generate photon emission [1], beyond high-resolution imaging and manipulation. This technique is called STM induced luminescence (STML) and has been used to study fluorescence from organic molecules at the single molecule level [2,3]. For molecules adsorbed directly on metal substrates, the photon emission from the molecular junction is believed to be plasmonic in nature and molecule-specific emission is quenched due to strong interaction between molecules and metal substrates [4–7]. In order to obtain molecule-specific emission through tunneling electron excitation in STM, a decoupling layer between molecules and metal substrate is crucial to avoid fluorescence quenching caused by metals [8]. Such strategy has produced intrinsic molecular luminescence from molecules supported on thin oxide [3,9,10], chloride [11–13] and molecular multi-layers [14,15]. Recently, such decoupling concept has also been adopted in a multi-functionalized molecule of tripodal porphyrin that has a built-in spacer unit and shows molecule-specific electroluminescence [16].

Graphene, a single-layer carbon sheet, has recently attracted considerable attention due to its unique properties and potential applications in electronics [17]. Organic molecules adsorbed on epitaxially grown graphene on metal substrates have also been investigated by STM to explore the possibility of graphene based organic devices [18–21]. According to the occurrence of intrinsic molecular electronic states on graphene for molecules such as perylene, pentacene and fullerene [20], graphene appears to act as a buffer layer to reduce the interaction between molecules and metal substrates. But the question is: can the monatomic thick graphene be used as a decoupling layer to obtain molecule-specific emission in STML experiments? This issue is believed to be important for the potential application of graphene on molecular optoelectronics. In this work, we explore this issue by using an established molecule, the meso-tetrakis-(3,5-di-tertiarybutylphenyl) porphyrin (H₂TBPP), that has proven to produce molecule-specific emission in the STM configuration upon efficient decoupling [14]. Starting from the investigation of STML on graphene itself, we study the evolution of the STML along with the increase of H₂TBPP-layer thickness from one monolayer (ML) to three MLs on the monolayer graphene (MG) epitaxially grown on Ru(0001). Our results indicate that, the nature of photons emitted from the STM junction is found to change from plasmonic in the first monolayer to molecule-specific at the third layer. These observations suggest that the electronic decoupling of a monolayer graphene alone is still not sufficient to generate intrinsic molecular fluorescence from the first-two monolayers of H₂TBPP. However,

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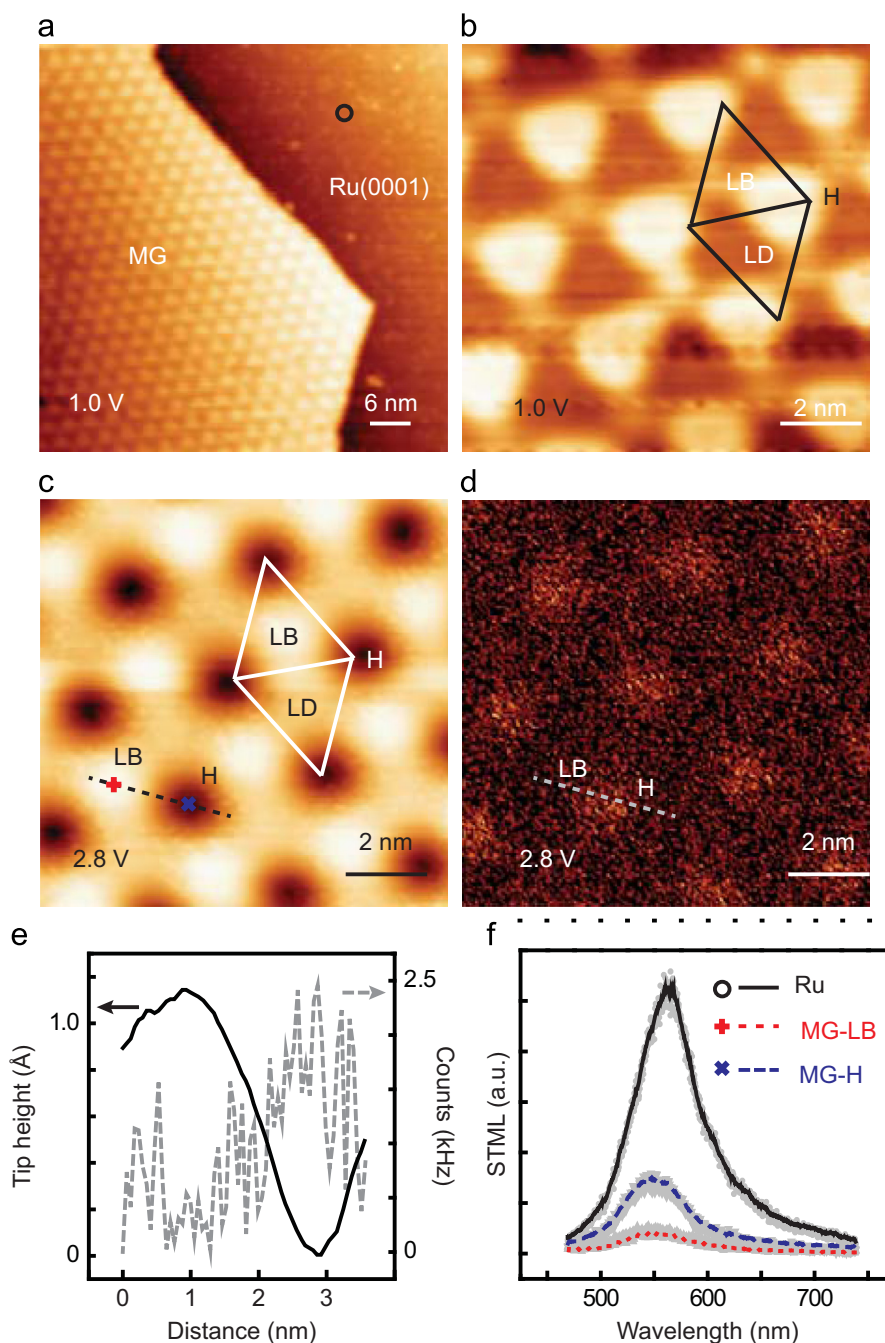


Fig. 1. (a) STM image of partially covered MG on Ru(0001) (1.0 V, 10 pA, $60 \times 60 \text{ nm}^2$). (b) Moiré pattern of a small area of MG on Ru(0001). The repeating unit cell is indicated as a black rhombus with three different regions: “H”, “LB” and “LD” (1.0 V, 10 pA, $10 \times 10 \text{ nm}^2$). (c) and (d) show STM topograph and simultaneously acquired photon map for the same area as in (b) (2.8 V, 500 pA, $10 \times 10 \text{ nm}^2$, 2 ms/pixel). (e) Height profile (solid) of the line trace indicated in (c) and photon count profile (dashed) for the same line trace in (d). (f) STML spectra (2.8 V, 500 pA, 1 min) on Ru (solid) marked as “o” in (a), “LB” site (dotted) marked as “+” and “H” sites (dashed) marked as “x” in (c) on MG, respectively.

the monolayer graphene does weaken the interaction between molecule and metal substrate, enabling the occurrence of molecule-specific emission from the third ML, which is two MLs thinner than what observed in previous molecular multilayers adsorbed directly on metals [14,15].

2. Experiment

The experiments were conducted with a low-temperature ultrahigh-vacuum (UHV) STM (Unisoku) at a base pressure of $\sim 1 \times 10^{-10}$ Torr at ~ 80 K, operated in the constant-current-

topographic mode with the sample biased. The Ru(0001) substrate was cleaned in UHV by cycles of Ar^+ sputtering (800 V) and annealing (~ 1100 K). High quality MG was prepared by thermal decomposition of ethylene on Ru(0001) as reported [22]. The H_2TBPP molecules, purchased from J&K Scientific and further purified by column chromatography on silica gel, were thermally deposited onto the MG on Ru(0001) from an evaporation cell at ~ 600 K with the substrate kept at room temperature. Electrochemically etched silver (Ag) tips were used for STM imaging and STML experiments, taking advantage of Ag in producing strong plasmonic field [23]. The dI/dV spectra were measured with a lock-in technique under the open-loop conditions. The

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