

Editorial

Two-Dimensional Gold Islands on Graphene/Ru (0001) Moiré Structure

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Editorial

While bulk gold is largely considered chemically inert, nanostructured Au has demonstrated catalytic activities, under mild conditions, for reactions such as CO oxidation [1], selective hydrocarbon oxidation [2], selective hydrogenation [3], etc. In general, the catalytic activity of nanostructured Au has been explained in terms of synergistic effects between the substrate and Au [4-6] and under-coordinated Au atoms in the nanostructured Au [7]. Nanostructured Au quantized in the vertical direction has also exhibited interesting catalytic properties. Freund and coworkers has demonstrated the exclusive adsorption of CO molecules on the perimeter of two-dimensional (2-D) Au islands on MgO/Ag(111) [8]. Goodman and coworkers have shown that the catalytic CO oxidation activity of the second Au layer is four times higher than the first and thicker Au layers on TiOx/Mo(112) [9].

The formation of 2-D Au islands on graphene/Ru (0001) moiré structure is an intriguing example of nanostructured Au whose formation is assisted by a template surface. Experimental techniques, such as Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES), Low Electron Energy Diffraction (LEED), Polarization Modulated Infrared Reflection Adsorption Spectroscopy (PM-IRAS), and High Resolution Electron Energy Loss Spectroscopy (HREELS), were combined with Density Functional Theory (DFT) simulations to characterize those 2-D Au islands. We found that those 2-D Au islands are structurally flexible and the adsorbed CO molecules can be titrated by O₂ at Liquid Nitrogen (LN₂) temperature.

The Morphology of 2-D Gold Islands and their Structural Model

Single-layer graphene on Ru (0001) was prepared by the carbon surface segregation method [10,11]. I.e. hydrocarbon molecules, such as methane and ethylene, are dissociated on Ru (0001), followed by a high temperature flash. The subsequent cooling process brings the interstitial carbon atoms to the surface, forming the graphene layer [12]. Because of the large lattice mismatch between graphene and Ru (0001) (lateral lattice constants: 0.246 nm for graphene vs. 0.271 nm

for Ru (0001)), single-layer graphene on Ru (0001) forms a moiré structure. Goodman and coworkers first used STM to study the periodicity of this moiré structure on Ru in 1994 [10]. The measured periodicity of ~ 3.0 nm was confirmed by a later paper [13]. DFT calculations revealed that the vertical corrugation of the graphene moiré structure observed by STM originates mainly from the geometric buckling of the single layer sheet, which is determined by the lateral position of the carbon atom relative to the underneath Ru atoms [14,15]. The weak and strong chemical interactions at the high and low regions in the moiré structure cause the splitting of graphene electronic band structure, as revealed by an Angular Resolved Ultraviolet Photoemission Spectroscopy (ARUPS) study [16].

Au was deposited onto the graphene/Ru (0001) moiré structure by physical vapor deposition method in ultrahigh vacuum (UHV) conditions when the sample was kept at room temperature. If the Au dosage is below 1 monolayer (ML) equivalent, it forms 2-D islands with the lateral sizes of approximately 10 nm [17,18]. The Au 2-D islands randomly nucleate on the substrates and are structurally flexible, as evidenced by the fact that the Au islands conform to the periodicity of the underneath graphene moiré structure. The apparent height of those Au islands was measured 0.55 nm by STM, and did not change when the biased voltage varied from -1.0 V to 1.0 V. Therefore, we proposed that the STM apparent height is the actual geometric height of the 2-D Au islands.

DFT calculations were employed to study several possible structures for the 2-D Au islands [18,19], including close-packed Au monolayer and bilayer. The same surface atomic density as Ru (0001) was found to be energetically favored over both lower and higher packing densities. In GGA-PBE, the monolayer is slightly less stable than the bilayer, and both are less stable than bulk Au. On the other hand, in the optB86b van der Waals density functional [20], the monolayer is more stable than the bilayer, and both are more stable than bulk Au. Both the monolayer and the bilayer Au conform to the corrugation of the graphene moiré structure when allowed to fully relax. The calculated height is 0.40 nm for the Au monolayer and 0.73 nm for the bilayer (in GGA-PBE; or 0.35 and 0.66 nm respectively in optB86b). Therefore, we tentatively conclude the 2-D Au islands on graphene/Ru (0001) to be bilayer in height, although further experimental confirmation is necessary.

The CO adsorption on 2-D gold islands

The adsorption of CO on 2-D Au islands was studied by PM-IRAS and HREELS. On graphene/Ru (0001) surface, even at LN₂ temperature, we did not find the any peak at 2063 cm⁻¹, the characteristic CO stretching frequency on clean Ru (0001) [21], which indicated that the whole Ru (0001) surface was covered by graphene. On 2-D Au islands, a CO stretching peak at 2095 cm⁻¹ was observed by both PM-IRAS and HREELS at LN₂ temperature at saturated CO coverage.

The effective charge on Au can significantly affect the bonding of carbon monoxide adsorbed on it, resulting in a change the C-O stretching frequency [22]. While on charge neutral Au the CO stretching frequency is $\sim 2120\text{ cm}^{-1}$ [23], it red-shifts on electron-rich Au and blue-shifts on electron-deficient Au [22]. Hence, the stretching frequency at $\sim 2095\text{ cm}^{-1}$ implied that there is electron transfer from graphene/Ru (0001) into the 2-D Au islands. This experimental observation was supported by our DFT calculations [18].

Both the PM-IRAS and HREELS data showed that the CO peak intensities gradually decreased as the sample temperature increased stepwise, and essentially disappeared after flashing to 140 K. Based on the rate of the intensity decrease, the estimated CO adsorption energy on these 2-D Au islands is 30–40 kJ/mol.

The CO titrated by O₂ on gold islands at cryogenic temperature

Electron-rich gold are more active towards O₂ activation than neutral or electron-deficient gold [24]. On those 2-D Au islands, the reaction of adsorbed CO molecules with O₂ was studied by a O₂ titration experiment [17]. At a temperature of 85 K, O₂ was leaked into the UHV chamber and onto 2-D Au islands covered with CO molecules in saturation. With a continuous increase of O₂ dosage, a continuous decrease of the CO stretching peak intensity and a slight broadening of the peak width was observed by PM-IRAS [17]. This observation was explained by the reaction of O₂ with CO molecules adsorbed on 2-D Au islands, while the co-adsorption of O₂ on the 2-D Au reduces the electron back-donation from the 2-D Au to $2\pi^*$ orbital of CO [17], causing the broadening of the CO stretching peak.

In summary, physical vapor deposition of gold onto the graphene/Ru (0001) moiré structure results in the formation of 2-D Au islands. These Au islands are likely two layers high and conforms to the periodicity of the underneath graphene moiré structure. CO adsorbs on 2-D Au islands with a stretching frequency of $\sim 2095\text{ cm}^{-1}$ and an estimated desorption energy of 30–40 kJ/mol. The red-shift of the CO stretching frequency suggests that those 2-D islands are electron-rich. The O₂ titration experiment suggests that the adsorbed CO can react with O₂ at LN₂ temperature.

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