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CO Adsorption on Au Nanoparticles Grown on Hexagonal Boron Nitride/Rh(111)

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S Supporting Information

ABSTRACT: CO adsorption on size-controlled Au nanoparticles grown on an *h*-BN/Rh(111) nanomesh surface has been examined to probe their potential catalytic properties. A combination of high-resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and density functional theory (DFT) calculations demonstrate that the CO adsorption strength depends heavily on the Au deposition coverage and particle morphology. Particles resulting from low Au coverages deposited at the liquid nitrogen temperature exhibit significantly enhanced CO binding relative to bulk crystalline Au. The resulting CO TPD spectra, and the significantly red-shifted C–O stretching frequency and negative charging of the Au nanoparticles as evidenced by HREELS and DFT, all correspond to those reported for catalytically active Au nanoparticles grown on reactive metal oxides, even though the *h*-BN/Rh(111) surface is free of carbon, oxygen, or defects. DFT modeling further suggests that the enhanced CO adsorption occurs at highly undercoordinated Au atoms on the perimeters of the nanoparticles. As the Au coverage is increased, the CO adsorption energy and C–O stretching frequency converge toward values associated with bulk Au. Annealing to 600 K results in bulk-like CO adsorption characteristics at any Au coverage. These results suggest that the *h*-BN/Rh(111) surface represents a potential platform for evaluating the role of Au vs support in low-temperature CO oxidation.

1. INTRODUCTION

The remarkable activity of Au nanoparticles (NPs) toward low-temperature CO oxidation has been known for over three decades now,¹ but parsing the various effects responsible for their catalytic properties remains challenging. Size is apparently critical: Au NPs which are monolayer and bilayer in height and 2–3 nm in diameter exhibit the highest catalytic activity, while those >5 nm are essentially inert.^{2–6} Similarly, negative charging of Au NPs by electron transfer from transition metal (TM) oxide supports is widely thought to be responsible for their catalytic activity for CO oxidation.^{4,5,7–11} The role of the support in catalyzing CO oxidation is not yet completely understood. Though the morphologies of Au NPs undoubtedly result from their interactions with the support, whether TM oxides are directly involved in CO oxidation by assisting in the activation of one of the reactants or by functioning as an oxygen or CO reservoir, or not at all, is still an active topic of catalysis research.^{12–16}

It is therefore of fundamental interest to probe the properties of Au NPs that exhibit similar size, morphology, and charge distribution to those supported on TM oxides that have been found to be catalytically active but exist on an inert and defect-free surface. Recently the preparation of dense arrays of size-controlled, well-ordered NPs by deposition onto patterned

substrates has received increased attention.¹⁷ Monolayer graphene and hexagonal boron nitride (*h*-BN) films grown epitaxially on TM surfaces show unique promise in this regard.^{18–23} The lattice mismatch between graphene or *h*-BN and TM surfaces yields an undulating corrugated superstructure, which provides large arrays of identical, regularly spaced trapping sites for cluster nucleation. Both 2D films are easily prepared, contain no oxygen, and are chemically inert to well above room temperature. In particular, BN/Rh(111) has been demonstrated to be stable following exposure to ambient air, water, and perchloric acid.^{24,25} Graphene moiré-supported TM clusters are already being explored for potentially unique catalytic properties.^{26,27}

We have recently demonstrated that Au NPs of size and height that are thought to be active for low-temperature CO oxidation can be prepared via deposition onto *h*-BN/Rh(111).²⁸ The *h*-BN/Rh(111) nanomesh consists of high-lying “wire” regions as well as low-lying “pore” regions that are essentially flat,^{25,29–31} the latter of which can trap Au clusters and limit their diameters to <3 nm for up to 5 ML equivalent of

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Au coverage. With 5 ML of Au deposited at 115 K and annealed to room temperature, the resulting NPs are densely packed (~ 0.08 clusters/nm²), the density of which rivals Au NP samples obtained on alumina and iron oxide thin films,³² and exhibit long-range monodispersity on micron scales (Figure 1).²⁸ STM measurements indicate primarily an “upward” as

Figure 1. $2000 \times 2000 \text{ \AA}^2$ scanning tunneling microscopy (STM) image of 5 ML of Au deposited on *h*-BN/Rh(111) at 115 K and imaged at 300 K. Reproduced with permission from ref 28. Copyright 2014 American Physical Society.

opposed to “outward” growth mode, as the resulting particles exhibited diameters clustered around 2.9 nm and heights of 10–25 Å.²⁸ The height of the NPs can be limited by the deposition temperature. For example, 0.16 ML of Au deposited at 115 K yields Au NPs that are primarily one layer high and occupy $\sim 80\%$ of the pores. Conversely, at the same Au coverage, NPs formed at room temperature fill $\sim 40\%$ of the pores and exhibit a nearly equal number of mono- and bilayer clusters but are still confined to the pore regions. This difference is presumably due to a high diffusion barrier for an Au adatom on this surface.³³ In comparison, Au deposited on graphene/Ru(0001) forms exclusively large flat bilayers that span multiple moiré cells^{20,21,34} because of low diffusion barriers for Au adatoms³⁵ and for small Au clusters.³⁶ Annealing of Au on *h*-BN/Rh(111) up 500 °C would eventually cause Au to alloy into the Rh surface.³⁷

Despite their promising size and diameter, whether Au NPs on *h*-BN/Rh(111) exhibit other properties associated with catalytically active Au supported on TM oxides has yet to be established. Herein we use CO as a probe molecule to further examine the properties of Au NPs grown on *h*-BN/Rh(111), by means of high resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and density functional theory (DFT) calculations. Notably, significantly enhanced CO binding and red-shifted C–O frequency compared to bulk Au surfaces are observed for Au NPs grown on *h*-BN/Rh(111) under certain conditions, indicating that highly undercoordinated sites and negative charging are the features key to the reactivity of Au NPs, at least as far as CO adsorption is concerned. Since these features are also exhibited by Au NPs supported on TM oxides,^{11,38} these results suggest that Au NPs supported on *h*-BN/Rh(111) are potential model catalysts for low-temperature CO oxidation and possibly other reactions requiring activation by electron

transfer (such as CO₂ reduction³⁹) and furthermore that *h*-BN/Rh(111) may be an ideal platform for evaluating the roles of metal vs support in reactions catalyzed by metal NPs in general, by offering an oxygen-free surface that can nonetheless stabilize NPs at appropriate temperature. Moreover, the carbon-free nature of the *h*-BN film may avoid further complicating the spectroscopic characterization of carbon species in potential organic reactants on nanoparticles formed on the pore-wire structure as opposed to nanoparticles formed on graphene.

2. METHODS

TPD and HREELS experiments were performed in two different ultrahigh vacuum (UHV) surface science chambers, where the same recipes were followed for the *h*-BN/Rh(111) surface preparation and Au deposition to ensure the consistency between the two sets of experimental measurements.

2.1. Sample Preparation. An Rh(111) single crystal was cleaned by repeated cycles of Ne⁺ or Ar⁺ sputtering and flashing by an e-beam heater to 1200 K. Upon obtaining a clean Rh(111) surface, a monolayer *h*-BN nanomesh was synthesized by exposure to 80–120 langmuirs of borazine vapor (gas exposures are herein given in langmuirs; 1 langmuir = 1×10^{-6} Torr·s) with the sample held at 1000 K. This procedure routinely results in a well-ordered, extended-size *h*-BN monolayer as monitored by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), EELS, and STM, with no elemental impurities present within the sensitivity of Auger.^{25,28,29} Prior to Au dosing, full coverage of the Rh(111) surface by the *h*-BN film was verified via EELS and TPD measurements by dosing CO on the bare nanomesh. The lack of an EELS peak ~ 248 meV, corresponding to CO adsorbed on Rh,⁴⁰ and the lack of any CO TPD feature at 470–490 K, corresponding to CO desorption from Rh,⁴¹ confirmed complete coverage of Rh(111) by *h*-BN. Au was then deposited on the *h*-BN covered Rh(111) substrate from home-built thermal evaporators. Au coverage was calibrated via the Auger break point method by evaporating Au on the clean Rh(111) substrate, and each sample was checked for cleanliness by ensuring that Auger spectra showed no adventitious carbon or other species. All deposition amounts here are defined as ML equivalents, where 1 ML corresponds to the number density of Rh atoms in the Rh(111) surface.

2.2. TPD. TPD experiments were carried out in an UHV chamber with a base pressure of 5.0×10^{-10} Torr. The chamber is equipped with a quadrupole mass spectrometer (QMS) (UTI 100C Precision mass analyzer), AES (PerkinElmer 15-155 cylindrical mirror analyzer), LEED (PRI 11-020), and a sputter ion gun (PerkinElmer 04-161 2 kV). The sample temperature was measured by a C-type thermocouple spot-welded to the back of the Rh(111) sample. High purity CO was dosed on the Au clusters supported on *h*-BN/Rh(111) at liquid nitrogen temperature (77 K), designated herein as LN₂, through a leak valve. 30 langmuir CO exposure was employed to ensure saturation coverage on the Au clusters. Following CO exposure, the sample was accurately positioned in front of the aperture of the shield that surrounds the QMS,⁴² and the thermal desorption products were monitored while the temperature was ramped at a rate of 3.0 K/s.

2.3. HREELS. HREELS experiments were performed in a UHV chamber with a base pressure of 1.0×10^{-10} Torr consisting of two chambers connected by a gate valve. The preparation chamber contains a sputter gun, leak valves to dose

Figure 2. CO TPD on Au/*h*-BN/Rh(111) for various Au depositions at saturation CO coverage. (a) Au deposited at LN₂. (b) Au deposited at room temperature and then annealed to 600 K.

various gases, LEED, and a single-pass cylindrical mirror analyzer with coaxial electron gun for Auger electron spectroscopy. The EELS chamber contained an LK Technologies LK2000 electron energy loss spectrometer. All vibrational EELS measurements were taken with a primary beam energy of 7 eV in the specular geometry (with respect to the surface normal, incident beam angle = exiting beam angle = 60°) with energy resolution of order 8–10 meV measured by the fwhm of the elastically scattered beam. The sample manipulator was cooled to 90 K using a liquid nitrogen flow cryostat, with sample temperatures measured by a type K thermocouple in contact with the sample stage. Measurements of adsorbed CO were done by first preparing the *h*-BN nanomesh and evaporating Au on the sample preparation manipulator and then transferring the sample into the EELS system, cooling the manipulator to 90 K, and holding the sample at LN₂ throughout gas dosing and EELS measurements. Unless otherwise noted, EELS spectra reported below were normalized to the height of the elastic peak, with offsets added for clarity.

2.4. DFT Calculations. Periodic density functional theory (DFT) calculations were performed using the Vienna *Ab Initio* Simulations Package (VASP)⁴³ in the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof⁴⁴ and using the vdW-corrected Bayesian error estimation functional (BEEF) of Wellendorff et al.⁴⁵ As will be shown below, BEEF yields a better description of ΔE_{CO} on Au than PBE when compared to experimental measurements, although the calculated lattice constants are slightly worse. The core electrons were described by the projector augmented wave method⁴⁶ and the Kohn–Sham valence electrons (including Rh(4d5s), 229 eV cutoff; Au(5d6s), 230 eV cutoff; B(2s2p), 319 eV cutoff; C(2s2p), 400 eV cutoff; N(2s2p), 400 eV cutoff; and O(2s2p), 400 eV cutoff) were expanded in a plane wave basis set up to a cutoff energy of 400 eV. The electronic states were smeared using a first-order Methfessel–Paxton scheme⁴⁷ with a width of 0.1 eV. All total energies were extrapolated back to 0 K.

The *h*-BN pore-wire structure on Rh(111) was modeled as a (13 × 13)-*h*-BN monolayer on (12 × 12)-Rh(111) surface unit cell (“13-on-12”, see Figure S1 in Supporting Information),

consisting of a total of 169 B, 169 N, and 432 Rh atoms. The calculated lattice constant for Rh is 3.824 Å (PBE) and 3.848 Å (BEEF), in close agreement with experiment (3.80 Å).⁴⁸ The Rh(111) surface was modeled as a semi-infinite three metal layer slab. Prior to geometry optimization, an initially flat *h*-BN monolayer was placed on one side of the Rh slab and fully relaxed. The entire *h*-BN monolayer, the top layer of Rh atoms, and any Au and CO adsorbed thereon were fully relaxed while the bottom two layers of Rh were fixed at their bulk positions. Approximately 16 Å of vacuum space (measured from the top of the *h*-BN film) and electrostatic decoupling⁴⁹ were applied in the *z* direction to accommodate the presence of the Au cluster and any adsorbed CO and minimize electronic interactions between neighboring slab images. Because of the large size of the surface unit cell, the surface Brillouin zone was sampled at the Γ point only. Further structural details of the optimized *h*-BN/Rh(111) nanomesh model have been reported previously.^{28,50}

CO adsorption on bulk Au crystalline surfaces was also considered for comparison. The calculated Au lattice constant is 4.157 Å (PBE) and 4.208 Å (BEEF) compared to the experimental value of 4.08 Å.⁴⁸ An Au(111) surface was modeled by a four-layer slab with a (3 × 3) surface unit cell. The Au(211) surface was modeled by a three-layer (in the direction normal to the terrace) slab with the terrace being four atoms wide and three atomic rows deep. Finally, the Au(563) surface was modeled by a three-layer (again in the direction normal to the terrace) slab with the terrace being three atoms wide and four atomic rows deep. The choice of the Au structures is explained later. Electrostatic decoupling and at least 12 Å of vacuum space were applied in the *z* direction to minimize interactions of neighboring slab images. During geometry optimization the top two layers of the Au(111) slab and the top layers of the Au(211) and (563) slabs (which includes also the row of atoms directly beneath the step edge) along with any adsorbed CO were fully relaxed, while the bottom layers of the Au slabs were held fixed at their bulk positions. The Brillouin zone was sampled using a 5 × 5 × 1 Monkhorst–Pack *k*-point grid for all three surfaces. The convergence criterion for all geometry optimizations in this study was set to 0.05 eV/Å for each relaxed degree of freedom.

The adsorption energy (ΔE) of a CO molecule was calculated as $\Delta E_{\text{CO}} = E_{\text{total}} - E_{\text{surf}} - E_{\text{CO}}$, where E_{total} is the energy of the overall system, E_{surf} is the energy of the surface without any adsorbate, and E_{CO} is the energy of a gas-phase CO molecule. A more negative adsorption energy corresponds to stronger adsorption. The CO vibrational modes were computed from a two-sided finite difference approximation of the dynamical matrix, with the magnitude of the displacement being 0.01 Å in each degree of freedom. Zero point energies for free and adsorbed CO were calculated from their respective vibrational frequencies as $\frac{1}{2} \sum h\nu_i$. Atomic charges were evaluated using the Bader method⁵¹ as implemented in the code of Henkelman and co-workers,⁵² which partitions the total electron density into nonoverlapping atomic volumes whose surfaces are defined as regions of zero flux in the electron density gradient.

3. RESULTS

3.1. CO TPD. For Au NPs deposited at LN₂ (referred to hereafter as the LN₂ samples, Figure 2a), and those then annealed to 600 K (referred to hereafter as the annealed samples, Figure 2b), CO thermal desorption started at 80 K with the first peak appearing at 87 K. It is assigned to the CO desorption from the sample holder. The small 174 K peak seen for all the annealed samples (Figure 2b) and the low-coverage (≤ 1.0 ML) LN₂ samples (Figure 2a) also appeared on the bare *h*-BN/Rh(111) surface and became significantly more intense when a small amount of H₂O was first deposited at LN₂ before CO exposure (Figure S2). It is assigned to CO molecules trapped in amorphous ice, which were released with the desorption of the ice during the heating process.⁵³ This assignment is supported by a single sharp H₂O desorption peak at 174 K concomitant with CO desorption at 174 K (Figure S2). Previous STM and DFT works have shown that water at low exposures is exclusively trapped in the pores of the *h*-BN/Rh(111) nanomesh,⁵⁴ which is likely where ice formed in our systems, too. At high Au coverages, Au NPs occupy nearly all of the nanomesh pores on *h*-BN/Rh(111),²⁸ which explains why the 174 K desorption feature appeared only on samples with less than 1.0 ML Au coverage, and why its intensity decreased with increasing Au coverage (Figure 2a). Prior STM of Au NPs supported on *h*-BN/Ru(0001),⁵⁵ for which both the pore-wire structure and the morphology of deposited Au NPs are similar to *h*-BN/Rh(111),²⁸ showed that annealing to 850 K leads to Au NP ripening. We postulate that annealing to 600 K likewise caused Au NPs to aggregate, thereby freeing up some portion of the pores that become available for ice formation (Figure 2b).

A low-temperature CO desorption peak (LTP) and a high-temperature CO desorption peak (HTP) from Au nanoparticles were observed for all samples in Figure 2. In general, the positional shifts of the LTPs and the HTPs as a function of the Au coverage, as well as the change in their relative intensities after the thermal annealing, reflect the morphology and charge state of the supported Au NPs. Both the annealed samples and the high-coverage (≥ 1.0 ML) LN₂ samples exhibit the LTP at ~ 115 K and the HTP at ~ 185 K. Note that the HTP for the annealed samples largely overlaps with the 174 K peak in Figure 2b. The positions of the LTP and HTP features (~ 115 and ~ 185 K) are reminiscent of CO desorption features from bulk Au crystalline surfaces. Indeed, the presence of an LTP in the range of 110–150 K and an HTP at ~ 185 K have been characterized as a “universal phenomenon” for CO

adsorption on bulk Au surfaces, with examples including Au(332),⁵⁶ Au(211),⁵⁷ Au(111),⁵⁸ and Au(110)-(1 $\times$ 2)⁵⁹ surfaces. For bulk Au crystals there is some ambiguity in the literature regarding whether these two features should be assigned to desorption from terrace and step sites^{57,59,60} or from step and kink/corner sites, respectively.^{56,58} However, two pieces of evidence favor the latter explanation. First, both peaks are absent for CO TPD measurements on pristine Au(111),⁵⁸ indicating CO binding to Au terrace sites is too weak to produce these desorption features. Second, previous DFT calculations of CO adsorption energies on Au terrace sites fall between -0.2 and -0.3 eV,^{61–63} which, when coupled with Redhead analysis assuming first-order desorption kinetics and a pre-exponential factor of 10^{13} – 10^{15} , indicates that CO desorption from terrace sites should occur below ~ 115 K. Hence, we attribute the LTP (~ 115 K) and HTP (~ 185 K) for both the annealed samples and the high-coverage LN₂ samples to CO desorption from Au step edge and kink/corner sites, respectively.

A notable difference between the CO TPD for the high-coverage LN₂ samples and the annealed samples is that the HTP dominates in the former, while the LTP dominates in the latter. In this regard, the high-coverage LN₂ samples more closely resemble Au NPs grown on reactive oxide supports in terms of CO desorption properties. For example, Au NPs supported on Al₂O₃, FeO(111), and Fe₃O₄(111) films all exhibit dominance of the HTP over the LTP at high Au deposition amounts, and the position of the HTP approaches 185 K as seen here when the Au coverage is increased.^{32,64} The dominance of the HTP in the high-coverage LN₂ samples is likely due to a greater number of highly undercoordinated Au atoms compared to faceted Au NPs resulting from annealing. We postulate that the combination of the support and low-temperature conditions prevented the Au NPs from agglomerating and faceting to become bulk-like particles even at high Au coverages. On the other hand, thermal annealing (cf. the annealed samples) evidently resulted in the faceting of the Au NPs and a concomitant decrease of the concentration of undercoordinated sites because the edge to kink/corner site ratios of our annealed Au samples match those of bulk-like Au crystals.

In contrast to the high-coverage LN₂ samples as well as the annealed samples, the positions of the LTP and HTP for the low-coverage LN₂ samples (< 1.0 ML, see Figure 2a) are coverage-dependent. Most dramatic is the shift in the HTP, which first appeared at 228 K for the lowest Au coverage, and gradually downshifted to 212 K at 1.0 ML of Au. These values exceed those observed for crystalline Au surfaces and fall within the 210–250 K range observed for low-coverage Au NPs grown on Al₂O₃, FeO(111), and Fe₃O₄(111) films.³² Hence, the HTP positions highlight a strong dependence of ΔE_{CO} on Au NP size. Our previous STM and DFT analysis indicates that for Au coverage amounts up to 0.25 ML on *h*-BN/Rh(111) the Au NPs are mostly monolayer and bilayer in height.²⁸ Such Au NPs possess a significant number of highly undercoordinated sites (with a coordination number (CN) even lower than kink/corner sites on bulk Au) than thicker Au NPs.⁶³ Multimonomolayer coverage of Au deposition results in multilayer-high Au NPs,²⁸ for which the number of such highly undercoordinated sites is expected to decrease significantly, causing a downshift of the CO desorption temperature. Notably, the enhanced efficacy of oxide-supported Au NPs in binding CO relative to bulk Au is often attributed to similar size effects and

Figure 3. HREELS vibrational spectra of 100 langmuirs of CO dosed on bare *h*-BN/Rh(111), and on 0.1 and 1 ML of Au deposited on *h*-BN/Rh(111) at room temperature. CO dosing and measurement were done at 90 K. (a) Survey spectra showing all recorded vibrational peaks from 0 to 500 meV (0–4000 cm^{−1}). (b) Close-up of the C–O stretching region. Data points are open circles, and fits to the data are solid lines. Each spectrum is fit with a single Gaussian peak using a linear background subtraction. The peak energies are indicated in bold text.

Table 1. DFT Calculated CO Adsorption Energy (ΔE_{CO} , in eV) and C–O Vibrational Frequency ($\nu_{\text{C–O}}$, in cm^{−1}) on Several Au Crystal Surfaces and the Au₃₀/*h*-BN/Rh(111) Model Cluster

	PBE		BEEF		$\Delta E_{\text{CO}}/\text{ZPE}$	peak desorption temp ^a (K)
	ΔE_{CO}	$\nu_{\text{C–O}}$	ΔE_{CO}	$\nu_{\text{C–O}}$		
Au(111)	−0.39	2054	−0.20	2050	−0.16	63
Au(211)	−0.57	2056	−0.32	2053	−0.28	108
Au(563)	−0.83	2058	−0.53	2052	−0.49	186
Au ₃₀ I	−1.39	2033	−0.69	2032	−0.64	241
Au ₃₀ II	−1.42	2035	−0.66	2029	−0.61	230
Au ₃₀ III	−1.12	2047	−0.39	2037	−0.35	134
Au ₃₀ IV	−0.40	2100	desorbed			

^aPeak desorption temperatures were estimated using Redhead analysis assuming first-order desorption kinetics, a prefactor of 10¹³ s^{−1}, and a temperature ramp rate of 3 K/s.

is regarded as a key component of their catalytic activity.^{5,32,61} Here, however, the highly undercoordinated sites are available on Au NPs in the absence of a reactive oxide support.

3.2. HREELS. The HREELS measurements were performed by dosing 100 langmuirs of CO at 90 K on a clean *h*-BN/Rh(111) surface and on *h*-BN/Rh(111) with 0.1 and 1.0 ML of Au deposited at room temperature. The results are presented in Figure 3. On the clean *h*-BN/Rh(111) surface, we identify only the transverse optical phonon peak with out-of-plane polarization (TO_⊥) at 97 meV and the overlapping longitudinal optical (LO) and TO_∥ peaks at 188 meV (782 and 1516 cm^{−1}; the TO_∥ is a shoulder on the low-energy side of the LO peak), which are indicated by labeled arrows in Figure 3a. These features agree well with prior results for *h*-BN nanomeshes on Rh(111) and Ru(0001).^{65,66} Notably the lack of any vibrational mode that may be ascribed to CO precludes any significant interaction between CO and *h*-BN, which confirms that the *h*-BN nanomesh is inert to CO at low temperatures under UHV conditions. Additionally, we observed no peaks in the region of the O–H stretching vibration (400–450 meV or 3200–3600 cm^{−1}) that would indicate water or hydroxyl-containing species coadsorbed during gas exposure at any temperature. Because

EELS shows no evidence of water on the surface at low temperature, we attribute the presence of water ice inferred from the TPD spectra in Figure 2 to originate from background gas in the TPD chamber that became adsorbed while cooling to LN₂. The better base pressure in the EELS system (<1.0 × 10^{−10} Torr) leads to a substantially lower level of sample contamination.

Following deposition of Au at room temperature, a coverage-dependent peak appeared in the CO stretching region signifying CO adsorbed onto Au. In agreement with our TPD results, this peak disappeared for both Au coverages following warming to room temperature, indicating that CO desorption occurred. In light of the fact that our TPD measurements clearly indicate the existence of two distinct CO adsorption states, it is interesting to note that only one CO stretching feature is evident in the HREELS spectra. This characteristic is common to CO adsorption on both bulk Au crystals and supported Au NPs and indicates that the value of the CO stretching frequency is rather insensitive to ΔE_{CO} and hence the CN of the Au adsorption site. Examples where CO adsorption onto Au leads to two distinct TPD peaks but only one CO stretching frequency include Au(211),⁵⁷ Au(332),⁵⁶

Figure 4. Models for Au sites of different structures: (a) Au(111) terrace site (CN = 9); (b) Au(211) step site (CN = 7); (c) Au(563) kink site (CN = 6); (d) top and (e) side views of Au₃₀ formed in the pore region of *h*-BN/Rh(111). In (a–c), the CO molecule indicates the sites for which ΔE_{CO} is reported in Table 1; C = black; O = red; top layer Au = golden. In (d), the CN values for Au sites I–IV are 3, 3, 4, and 6, respectively. In (d, e), Au = golden; Rh = silver; B = green; N = blue.

and roughened Au(111) bulk crystals⁵⁸ and Au NPs grown on HPOG⁵⁸ and FeO thin films.⁶⁰ That the CO stretching frequency is independent of the Au CN (which does correlate with ΔE_{CO}) is supported by DFT calculations. Yim and co-workers have reported that CO binding energies on a defective Au(332) surface increase by -0.10 eV on going from an Au site with CN = 7 to CN = 6 and by -0.13 eV on going from CN = 6 to CN = 5. However, the calculated CO stretching frequency ($\nu_{\text{C-O}}$) at all three sites agree within 1 cm^{-1} .⁵⁸ Similarly, Mehmood et al. computed a -0.14 eV increase in ΔE_{CO} on going from step to kink sites (represented by Au(211) vs Au(532), respectively), while the $\nu_{\text{C-O}}$ remained unchanged.⁶² Our DFT calculated $\nu_{\text{C-O}}$ (see Table 1 and section 3.3) for CO adsorbed on the terrace, step, and kink sites are all nearly the same, which agrees with the previous studies.

In the present study, $\nu_{\text{C-O}}$ appears at 2066 cm^{-1} (256.1 meV , see Figure 3b) at 0.1 ML of Au coverage, a dramatic red-shift relative to the gas-phase CO molecule⁵⁸ at 2143 cm^{-1} . On charge-neutral Au, the CO stretching frequency generally lies in the $2100\text{--}2120 \text{ cm}^{-1}$ range³⁸ or a red-shift of less than 45 cm^{-1} relative to gas-phase CO. In contrast, the red-shift of 77 cm^{-1} observed here for 0.1 ML Au NPs supported on *h*-BN/Rh(111), which is 32 cm^{-1} more red-shifted than on neutral Au, closely resembles the $\nu_{\text{C-O}}$ of $\sim 2070 \text{ cm}^{-1}$ for CO adsorbed on highly negatively charged Au NPs supported on an MgO/Mo(001) thin film at comparable Au coverages.⁶⁷ The well-known “back-donation” mechanism for explaining the red-shift of the $\nu_{\text{C-O}}$ following CO adsorption on d-block metals was first proposed by Blyholder on the basis of simple Hückel MO theoretical arguments⁶⁸ and posits that the TM d orbitals of the appropriate symmetry hybridize with the formerly unoccupied CO $2\pi^*$ orbital to yield the partial occupancy of antibonding CO states, which weaken the C–O bond (but not necessarily the Au–CO bond). Since the degree to which such states are occupied increases with the amount of negative

charge on the metal atom, Chen and Goodman have suggested that the magnitude of the red-shift of $\nu_{\text{C-O}}$ can serve as an experimental measure of the degree of negative charging on Au NPs.⁵ Our previous STM measurements suggest that <0.2 ML Au deposition on *h*-BN/Rh(111) followed by warming to room temperature yields a mixture of mono- and bilayer Au NPs,²⁸ with almost no particles exceeding two layers in height. Hence, the present red-shift is indicative of negative charging of 2D Au NPs grown on *h*-BN/Rh(111), which is also characteristic of many Au NP formed on TM oxides.

Increasing the Au coverage from 0.1 to 1.0 ML resulted in a blue-shift of the $\nu_{\text{C-O}}$ from 2066 to 2078 cm^{-1} (257.7 meV , Figure 3b). As the coverage increase causes a transition from Au NPs that are one or two layers high, to clusters that are several layers high, it is reasonable to attribute the 12 cm^{-1} blue-shift to a decrease in the average negative charge of Au atoms in larger clusters. This is consistent with our previous DFT-based finding that the average negative charge density per Au atom strongly decreases with increasing cluster size for Au NPs supported on *h*-BN/Rh(111).²⁸ Similar blue-shifts resulting from increased cluster size have also been demonstrated by Freund and co-workers for Au NPs supported on FeO⁶⁰ and MgO⁶⁷ thin films and were also attributed to weakened back-donation due to a decrease in the excess charge density on Au adsorption sites.⁶⁷

3.3. DFT. We have performed DFT-based modeling of CO adsorption on several Au structures chosen to represent probable adsorption sites on Au NPs supported on *h*-BN/Rh(111). We hypothesize that Au dosed on *h*-BN/Rh(111) gains sufficient thermal energy during annealing to 600 K to agglomerate and restructure into NPs with bulk-like exterior surfaces. Therefore, CO adsorption sites on the annealed samples were represented by the Au(111), (211), and (563) surfaces (Figure 4a–c), which correspond to close-packed terraces, step edges, and kinks, respectively. These models are

also used to interpret the high-coverage LN_2 samples, as the LTP and HTP positions in our CO TPD on 5.0 ML of Au coverage indicate a convergence of ΔE_{CO} to bulk surface values and hence a transition to bulk-like properties at high Au coverages.

Conversely, we hypothesize that Au dosed at LN_2 lacks the thermal energy necessary to escape the energy traps of the pore region or to even diffuse sufficiently within the pores to fully minimize the energy of individual Au nanoparticles. Thus, the low-coverage LN_2 samples are expected to present numerous sites with an average CN lower than those prevalent on bulk-like Au crystals. We model these potential low-coordination sites using a monolayer Au_{30} cluster located in the pore region of $h\text{-BN/Rh(111)}$ (Figure 4d,e), which presents several highly undercoordinated Au sites for CO adsorption. In our previous study we have found Au_{30} to be approximately the size where monolayer to bilayer transition occurs for Au clusters on $h\text{-BN/Rh(111)}$.²⁸ The general validity of 2D structure models for small Au clusters is supported by the fact that they tend to prefer flat geometries on reactive supports^{32,64,67} and that negative charging of supported Au clusters increases their preference for 2D over 3D structures.^{69–72} Furthermore, the present model is also consistent with the size and shape of Au NPs on $h\text{-BN/Rh(111)}$ at low Au coverage and deposition temperature, as observed in our previous STM study.²⁸

Consistent with the chemical inertness of bulk Au,⁷³ ΔE_{CO} on the close-packed Au(111) surface is calculated to be -0.16 eV (ZPE-corrected BEEF result, same below; see Table 1). This corresponds to a peak desorption temperature of ~ 60 K, which is lower than the CO dosing temperature of 77 K in our TPD experiment. Thus, bulk Au(111) surfaces are unlikely to adsorb any CO in our experiments, consistent with prior studies,⁵⁸ and neither the LTP in our TPD experiment nor the observed $\nu_{\text{C-O}}$ in HREELS can be attributed to CO adsorption onto terrace sites. Adsorption onto step edge sites (CN = 7), represented here by an Au(211) step edge (Figure 4b), strengthens ΔE_{CO} to -0.28 eV, which is consistent with a peak desorption temperature near 110 K. This value agrees well with the LTP feature in our TPD, supporting the assignment of this peak to CO desorption from step-like Au sites (CN ~ 7). The strongest adsorption for CO on a bulk Au surface occurs on the kink site (CN = 6)^{63,74} on the Au(563) model (Figure 4c), -0.49 eV, which corresponds to a peak desorption temperature of ~ 185 K, closely matching the HTP position for our high-coverage LN_2 samples, as well as the HTP desorption feature observed on a variety of Au bulk crystal surfaces. Hence, our DFT results support the assignment of Yim et al. of the two CO desorption peaks on bulk-like Au particles to step and kink sites, rather than to terrace and step sites.⁵⁸

While the CO binding energies on bulk-like Au particles closely correlate with the CN of the adsorption site,⁶³ the calculated CO stretching frequencies do not. Instead, $\nu_{\text{C-O}}$ is essentially identical (~ 2050 cm^{-1}) on all three bulk surfaces, which lends support to the notion that the value of $\nu_{\text{C-O}}$ depends mainly on the charge of the Au adsorption site rather than its CN.^{5,58,67} Given that the experimental values of $\nu_{\text{C-O}}$ on charge-neutral Au fall within the range of 2100–2120 cm^{-1} , clearly DFT produces values that are too low. This phenomenon is well documented and arises from the underestimation of the energy of the CO $2\pi^*$ orbital by DFT, which yields unphysically enhanced back-donation from the metal d orbitals and produces CO stretching frequencies that are too low.^{38,75} Additionally, DFT is also found to

underestimate the value of the gas phase CO stretch relative to experiment (2123 vs 2143 cm^{-1} , respectively).⁵⁸

Markedly different CO adsorption characteristics are apparent for the model Au_{30} cluster supported on $h\text{-BN/Rh(111)}$ compared to bulk Au surfaces. CO is found to desorb from the 6-fold coordinate terrace sites (site IV, Figure 4e), indicating CO does not adsorb on the interior of 2D Au NPs supported on $h\text{-BN/Rh(111)}$. Notably Nørskov and co-workers have reported that a freestanding monolayer of Au(111) terrace atoms are also unable to bind CO.⁶¹ On the other hand, strong CO binding is found on the highly undercoordinated perimeter edge and corner sites, including 4- and 3-fold coordinate Au atoms (sites I, II, and III in Figure 4e). The calculated ΔE_{CO} at the edge site (site III, Figure 4e) is -0.35 eV, which is more exothermic than a bulk step edge site (i.e., Au(211), -0.28 eV; see Table 1). The calculated ΔE_{CO} at the corner sites (sites I and II, Figure 4e) is ~ -0.60 eV, which is lower than that on a bulk kink site (i.e., Au(563), -0.49 eV). As indicated in Table 1, the expected desorption temperature associated with CO bound to these corner Au sites is ~ 230 K, which is very near the position of the HTP for the low-coverage LN_2 samples. The preferential binding of CO to perimeter sites has also been reported for small Au NPs supported on MgO films in DFT³⁸ and STM⁶⁷ studies. Perimeter-adsorbed CO molecules have been imaged directly with STM, which appear as dark depressions at the oxide film–Au NP interface.

CO adsorption on the edge and corner sites of the supported Au_{30} nanoparticle results in a red-shift of ~ 20 cm^{-1} in $\nu_{\text{C-O}}$ relative to the values calculated for the bulk Au(111), (211), and (563) surfaces. This DFT calculated red-shift vs charge-neutral Au is in agreement with the ~ 32 cm^{-1} red-shift based on our HREELS experiments mentioned above. Bader charge analysis revealed that the Au_{30} cluster receives a net charge of $-2.23|e|$ from the Rh support, consistent with our XPS findings.²⁸ While an equal distribution of this excess charge over the entire particle would result in a meager average charge per Au atom, this is in fact not the case. Instead, $>95\%$ of the excess charge density is calculated to localize on the perimeter atoms, with the average charges for the corner, edge, and interior sites of the Au_{30} being $-0.16|e|$, $-0.12|e|$, and $-0.01|e|$, respectively. The propensity for excess charge on Au NPs to localize on perimeter sites rather than to be evenly distributed throughout the cluster has previously been explained to result from the fact that the former charge distribution minimizes interelectronic repulsions.¹¹

Negative charging of Au NPs on a variety of supports has been either deduced or observed by a number of authors.^{5,34} For example, STM imaging of Au NPs supported on an MgO/Ag surface revealed that perimeter Au atoms appeared as a bright rim in contrast with the darker interior atoms.⁶⁷ This was attributed to the localization of additional electronic states near the Fermi level on perimeter atoms, which contain the negative charge received from the support. This interpretation is supported by differential conductance maps, where high dI/dV intensity about E_{Fermi} is observed only for the Au NP's perimeter atoms.¹¹ DFT-based charge analysis suggests a $-0.2|e|$ average charge per perimeter Au atom on MgO/Ag supported Au NPs,¹¹ which is only slightly higher than that found here for the Au_{30} clusters supported on $h\text{-BN/Rh(111)}$. This is consistent with the fact that the CO stretching frequency for adsorbed CO on MgO film-supported Au NPs are more red-shifted than is the present case.^{38,67}

On the other hand, there is evidence that negative charging of Au actually impedes its ability to bind CO. Pacchioni and co-workers reported that ΔE_{CO} on an Au adatom supported on MgO weakened by 0.6 eV as the charge state of Au was changed from neutral to $-1e$.⁷⁵ Similarly, ΔE_{CO} on the corner of an Au_{12} cluster was found to weaken by 0.17 eV on going from a neutral to negative charge state.³⁸ Freund and co-workers have advanced the explanation that dative CO–Au bonding is partially interrupted by negative Au charging due to impeded electron donation from the CO 5σ orbital to the metal center.⁶⁷ Taken together, these findings indicate that the very low coordination of the perimeter Au atoms is predominantly responsible for the enhanced adsorption of CO, while the excess negative charge serves mainly to enhance back-donation to the $2\pi^*$ orbital, thereby weakening the C–O bond and increasing the red-shift in the C–O vibrational frequency. The repulsive effect of the negative charging on the Au–CO bonding, however, is outweighed by the very low coordination of the perimeter sites.

Finally, we note that the PBE CO adsorption energies are substantially larger than those given by the BEEF functional, though both functionals give nearly identical CO stretching frequencies. Yim et al. recently argued that the PBE functional produces CO–Au adsorption energies that are too high to be compatible with experimental CO TPD measurements,⁵⁸ which is also found to be the case here. For example, a ΔE_{CO} of -0.39 eV on Au(111) (Table 1) is suggestive of a CO desorption peak at ~ 150 K, which is clearly inconsistent with the fact that Au(111) is unable to adsorb CO at low-temperature UHV conditions. Similarly, a ΔE_{CO} of -0.57 eV on the step edge (Au(211), Table 1) should produce a peak desorption feature at ~ 215 K in CO TPD, which is significantly higher than the ~ 185 K HTP frequently observed on bulk Au crystalline surfaces. That the PW91 functional overbinds CO to metal surfaces while nonetheless producing reasonable CO stretching frequencies has been known.⁴⁰ Specifically regarding CO–Au bonding, Pacchioni and co-workers reported PW91 to overbind CO up to 200% relative to the highly accurate CCSD(T) wave function approach that can be expected to approach chemical accuracy (i.e., bond energies with an error bar of ~ 0.04 eV).^{38,75} The relevance of this finding is that CO–Au adsorption energies produced by the PBE functional are nearly the same as those given by PW91 when comparing similar adsorption sites. For instance, the ΔE_{CO} on Au(111) and Au(211) computed by PW91⁶² and PBE⁶³ agree to within 0.03 eV, while CO adsorption on kink sites given by PW91⁵⁸ and PBE⁶³ agree to within 0.02 eV, despite using different surface models. Insofar as these results suggest that PBE may also overbind CO to Au significantly, the discrepancies between the BEEF and PBE CO adsorption energies seen in Table 1 are therefore not unreasonable.

4. CONCLUSIONS

The *h*-BN/Rh(111) nanomesh provides an immense array of regularly spaced trapping sites that allow deposited Au to self-assemble into dispersed Au nanoparticles (NPs). Depending on the amount of Au deposited, two distinct types of CO adsorption characteristics have been observed for Au NPs self-assembled at low temperatures.

4.1. Low Au Dosages. These NPs exhibit narrowly varied diameters and are single- to bilayer in height at the lower Au coverages studied. In TPD, the high-temperature CO desorption peak appears at 210–230 K for these Au NPs,

whereas it occurs at ~ 185 K for bulk Au crystals. DFT calculations (GGA-BEEF) for a model 2D Au_{30} cluster supported on *h*-BN/Rh(111) indicates that the highly undercoordinated perimeter edge and corner sites bind CO more strongly than bulk Au surfaces and that the Au cluster also contains a sizable negative charge, which is localized on the perimeter atoms. Consistent with the negative charging, CO stretching frequencies measured by HREELS following CO adsorption on Au NPs formed at low Au coverages (e.g., 2066 cm^{-1} at 0.1 ML of Au) are significantly red-shifted relative to the 2100–2120 cm^{-1} values observed for charge-neutral Au. Importantly, the thickness, diameter, negative charging, and CO adsorption characteristics of these Au NPs are all similar to catalytically active Au NPs supported on reactive metal oxides reported in the literature.

4.2. High Au Dosages. These Au NPs still exhibit tightly controlled diameters but grow in height with increasing Au coverage. TPD shows that both the low- and high-temperature CO desorption peaks occur at essentially the same temperatures as those found on bulk Au. DFT calculations indicate that for bulk-like surfaces, undercoordinated step and kink sites are most likely to bind CO, with the adsorption energies in close agreement with the low and high peak desorption temperatures (~ 115 and ~ 185 K). The negative charge density per Au atom decreases with increasing cluster size, and the HREELS measured C–O stretching frequency blue-shifts with increasing Au coverage, presumably due to decreased back-donation.

4.3. Annealing to 600 K. For both the low and high Au coverage samples, the high-temperature CO desorption peak is severely diminished after annealing to 600 K, suggesting that elevated temperature results in Au diffusion and cluster agglomeration, along with faceting to diminish the concentration of highly undercoordinated Au sites. This yields essentially bulk-like Au particles.

In short, the *h*-BN/Rh(111) nanomesh provides a carbon-, oxygen-, and defect-free and inert support that allows the self-assembly of size-limited Au NPs, with morphological, charging, and CO adsorption characteristics similar to those associated with catalytically active Au NPs supported on reactive TM oxides. The Au NPs supported on *h*-BN/Rh(111) are therefore potential model catalysts for low-temperature CO oxidation and can provide valuable mechanistic insights into the role of Au vs support in this reaction. Furthermore, the *h*-BN/Rh(111) nanomesh may prove to be a useful model support surface capable of providing similar insights for reactions catalyzed by NPs of transition metals in the 2–3 nm size range in general.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b01645.

An illustration of the “13-on-12” *h*-BN/Rh(111) nanomesh structure used for DFT modeling and experimental CO and H_2O TPD curves on a clean *h*-BN/Rh(111) nanomesh without Au (PDF)

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Notes

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