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# On-surface synthesis of size- and shape-controlled two-dimensional Au<sub>n</sub> nanoclusters using a flexible fullerene molecular template†

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Synthesizing nano-clusters with a well-defined size, shape, and composition is an important and challenging goal in nanotechnology. Here we report the application of a single layer C<sub>60</sub> molecule as an effective molecular template for the synthesis of size- and shape-selected two-dimensional gold clusters (Au<sub>n</sub>) on a graphite substrate. This molecular template facilitates the preferential formation of Au<sub>19</sub> clusters with a selectivity as high as 90%. Density-functional-theory (DFT) calculations found an energy minimum associated with C<sub>60</sub>-stabilized two-dimensional Au<sub>19</sub> clusters.

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Gold nanoclusters (NCs), with their interesting size-dependent plasmonic and catalytic properties, have become an important class of materials in modern technology.<sup>1–6</sup> Accurate size-selection of Au NCs has been achieved *via* either wet chemical synthesis of ligand-protected clusters<sup>4</sup> or vacuum-based mass-selected cluster sources.<sup>7</sup> Here we introduce size- and shape-controlled synthesis of planar Au<sub>n</sub> clusters on a graphite substrate. We use a close-packed layer of C<sub>60</sub> on graphite as an active molecular template which is able to organize vacuum-deposited Au atoms into discrete Au<sub>n</sub> clusters. The assembly process is highly efficient with more than 90% of the deposited Au atoms making up the Au<sub>n</sub> clusters, and is highly selective towards the formation of Au<sub>19</sub>.

As the physical dimension of the NCs is reduced, the electron energy levels change from quasi-continuous to discrete. This change of energy structure directly affects the carrier lifetimes.<sup>8</sup> The shape of the NCs has an equally important effect on the electronic structure. When it comes to the application

of metal clusters as building blocks for devices, the clusters are normally required to be resting on a solid substrate for connecting to other components. The cluster–substrate interaction could be an undesirable effect if the intrinsic properties of the cluster are diluted too much *via* a strong cluster–substrate coupling. We recently synthesized magic number 2D Au<sub>n</sub> clusters, with  $n = 19, 35, 49$ , and  $63$ , on the Au(111) substrate<sup>9,10</sup> where a significant energy level mixing between the Au<sub>n</sub> cluster and the Au(111) substrate is expected. Here we replace the Au(111) substrate with highly oriented pyrolytic graphite (HOPG) with a view to further extending the work to insulating substrates such as SiO<sub>2</sub>.

Au atoms interact rather weakly with graphite. Therefore, when Au atoms are deposited onto clean HOPG, they diffuse rapidly to step edges or defect sites where large 3-D Au clusters are formed. To stop Au atoms from moving to steps, we deposit a layer of C<sub>60</sub> on HOPG first. We then add Au atoms by *in situ* physical vapour deposition while the C<sub>60</sub> covered HOPG is kept at 100 K. Some of the deposited Au atoms “sink” to the HOPG substrate whilst others “float” on top of the C<sub>60</sub> layer. The floating Au atoms are mobile at 100 K giving rise to streaks in STM scan lines. There is also evidence that Au atoms are constantly picked up by the STM tip during imaging. By raising the sample temperature to 150 K, we succeed in transporting the floating atoms to the HOPG substrate where Au atoms assemble into single-atomic-layer-high Au<sub>n</sub> clusters. Each cluster has a footprint not greater than the area occupied by a single C<sub>60</sub> molecule, and is stable up to ~475 K.

Fig. 1a shows an STM image of the sample with 0.026 monolayers (ML) of Au deposited. The sample, prepared using the

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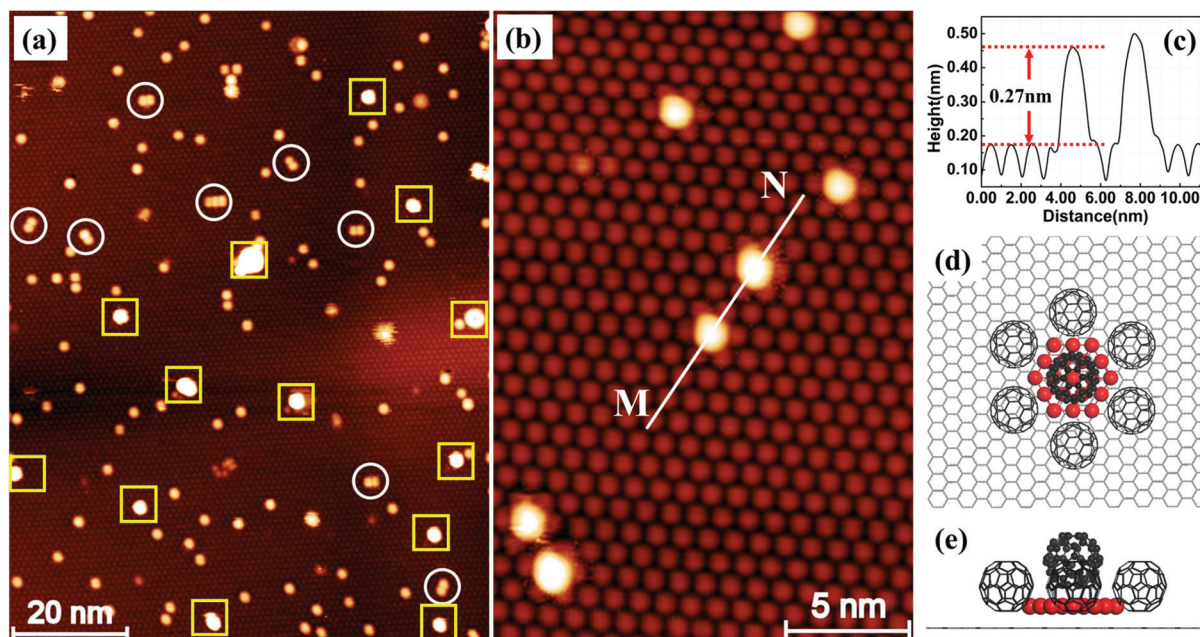
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**Fig. 1** Two-dimensional  $\text{Au}_n$  clusters formed on  $\text{C}_{60}$  covered HOPG. (a) STM image of a single  $\text{C}_{60}$  layer on HOPG following the deposition of 0.026 ML of Au (sample bias voltage: +1.6 V; tunnel current: 0.1 nA). The sample was kept at 100 K during deposition, and was subsequently annealed in steps to 150 K (30 minutes), 200 K (30 minutes) and 375 K (30 minutes). The image is acquired at RT. The spots with the highest brightness, labelled with squares, are multilayer Au clusters floating on top of the  $\text{C}_{60}$  layer. The randomly distributed "bright"  $\text{C}_{60}$  molecules in the image are those sitting on 2D  $\text{Au}_n$  islands. (b) Magnified view showing six raised  $\text{C}_{60}$  molecules. (c) Height profile measured along line M–N in (b) shows that the bright molecules are  $\sim 0.27$  nm taller than the close-packed  $\text{C}_{60}$  layer. (d) Top view of the structural model proposed for a  $(\text{C}_{60})_7\text{Au}_{19}$  cluster. Only  $\text{C}_{60}$  molecules associated with the Au cluster are shown for simplicity. Red spheres represent the gold atoms. The  $\text{C}_{60}$  molecules are shown, arbitrarily, with one of their hexagonal faces parallel to the HOPG surface. The  $\text{C}_{60}$ – $\text{C}_{60}$  nearest neighbour distance is 1.0 nm. There is no well-defined single adsorption site for  $\text{C}_{60}$  on HOPG. (e) Side view of the structural model.

protocol described above, has been annealed at 375 K for 30 minutes before imaging at room temperature (RT). In this image, we can see a uniform layer of close-packed  $\text{C}_{60}$  on HOPG in the background. The bright features in the image appear after the deposition of Au. Most of the bright features are individual spots randomly distributed in the  $\text{C}_{60}$  layer. In the magnified image, Fig. 1b, it can be seen that each bright spot occupies exactly the same position as the  $\text{C}_{60}$  molecule. The height profile along line M–N, Fig. 1c, shows that the bright spot is  $\sim 0.27$  nm taller than the  $\text{C}_{60}$  molecules in the background. A number of relatively large, extra bright spots are observed in Fig. 1a and they are highlighted with squares. These extra bright spots have an apparent height of  $\sim 0.8$  nm, and their positions are not correlated with the position of the  $\text{C}_{60}$  molecules. They can be swept away easily by the STM tip under normal scanning conditions revealing a perfectly organized  $\text{C}_{60}$  array underneath.<sup>11</sup> Therefore, we assign the extra bright spots as Au clusters floating on top of the  $\text{C}_{60}$  layer and will not discuss these clusters any further. Instead, we will focus on the types of bright spots shown in Fig. 1b. These bright spots cannot be moved by the STM tip and they stay in fixed locations without hopping at RT.

Based on our observation in the present study and that in an earlier study of the formation of  $(\text{C}_{60})_7\text{Au}_{19}$  magic number clusters on Au(111),<sup>9</sup> we propose a structural model in Fig. 1d

and e. According to this model, nineteen Au atoms form a 2D hexagonal island which is surrounded by seven  $\text{C}_{60}$  molecules. Six of the seven molecules sit on HOPG next to step edges of the Au island and the seventh molecule sits directly above the Au island. This model provides very good qualitative explanations for the experimental observation. The seven molecules in the  $(\text{C}_{60})_7\text{Au}_{19}$  cluster keep their preferred close-packing configuration with the nearest neighbor distance of  $\sim 1.0$  nm. The  $\text{C}_{60}$  molecule sitting on the  $\text{Au}_{19}$  island is lifted up by a layer of Au atoms. The size of the Au island (19 atoms) matches the footprint of a single  $\text{C}_{60}$  molecule. On the Au(111) surface, each  $\text{C}_{60}$  molecule covers an area occupied by twelve Au atoms.<sup>12</sup> Here, for the nineteen atom Au island, the edge atoms are shared between two molecules and the corner atom is shared among three  $\text{C}_{60}$  molecules, making it 12 atoms per molecule. Analysis of a large number of bright spots shows that the height of the bright spots has a bimodal distribution peaked at 0.27 nm and 0.62 nm (ref. 11) with the majority of the bright spots 0.27 nm tall. We tentatively associate the 0.62 nm height with two-atomic-layer-high Au islands. For example, a two-layer island could be formed with nineteen atoms in the first layer and twelve atoms in the second layer. In Fig. 1a, there are also bright spots appearing in pairs with the distance between the two spots in the pair equal to 1 nm. A number of such pairs are circled in the image. The existence



As shown in Fig. 3a and b, a  $12 \times 12$  graphene/ $3 \times 3$   $C_{60}$  supercell is used in DFT calculations. Neighboring Au clusters are kept apart at about 2 nm, which is large enough to ignore inter-cluster interactions. The structure of the relaxed  $Au_{19}$  cluster, Fig. 3c, shows that the Au atoms on each edge of the

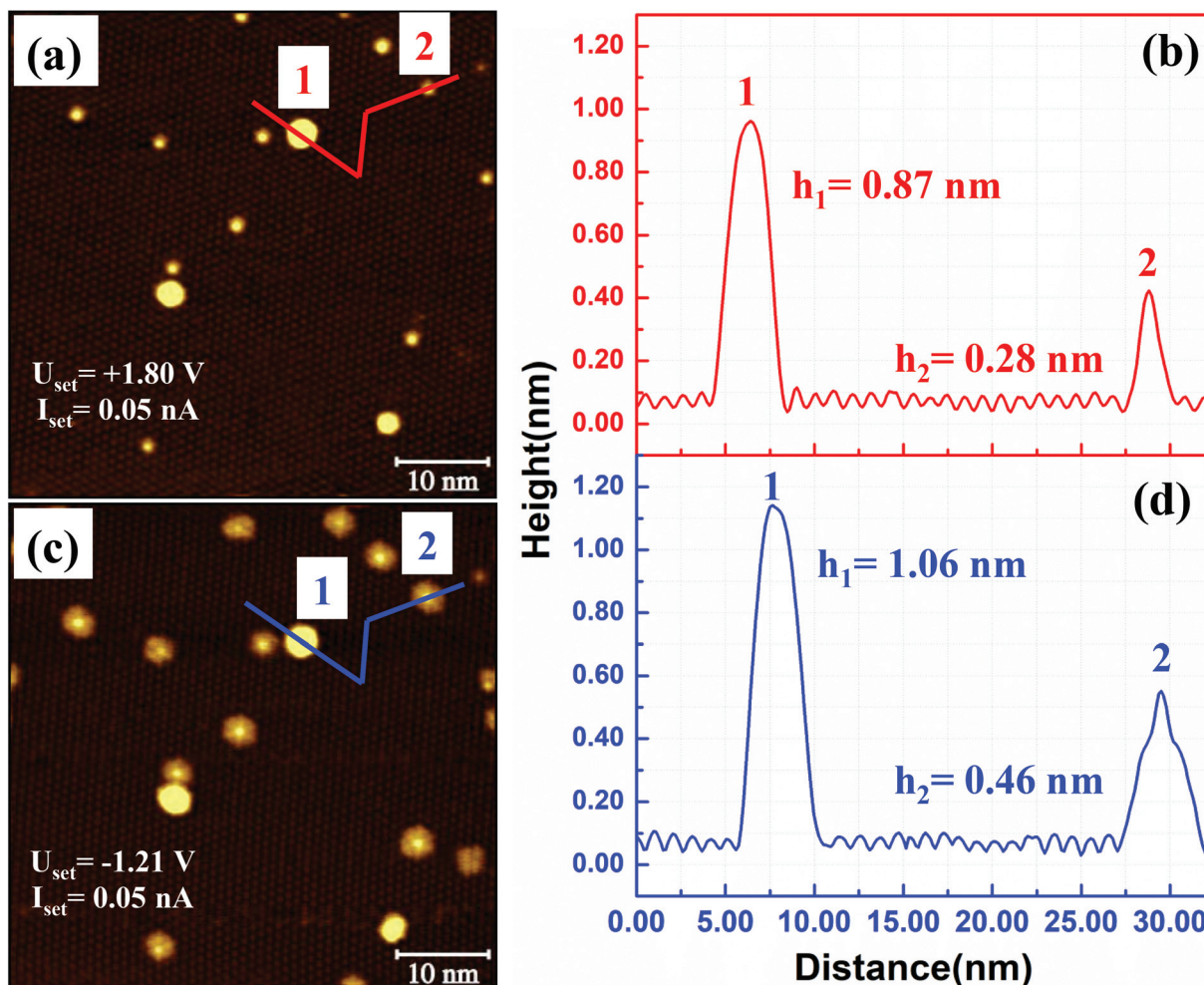
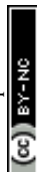


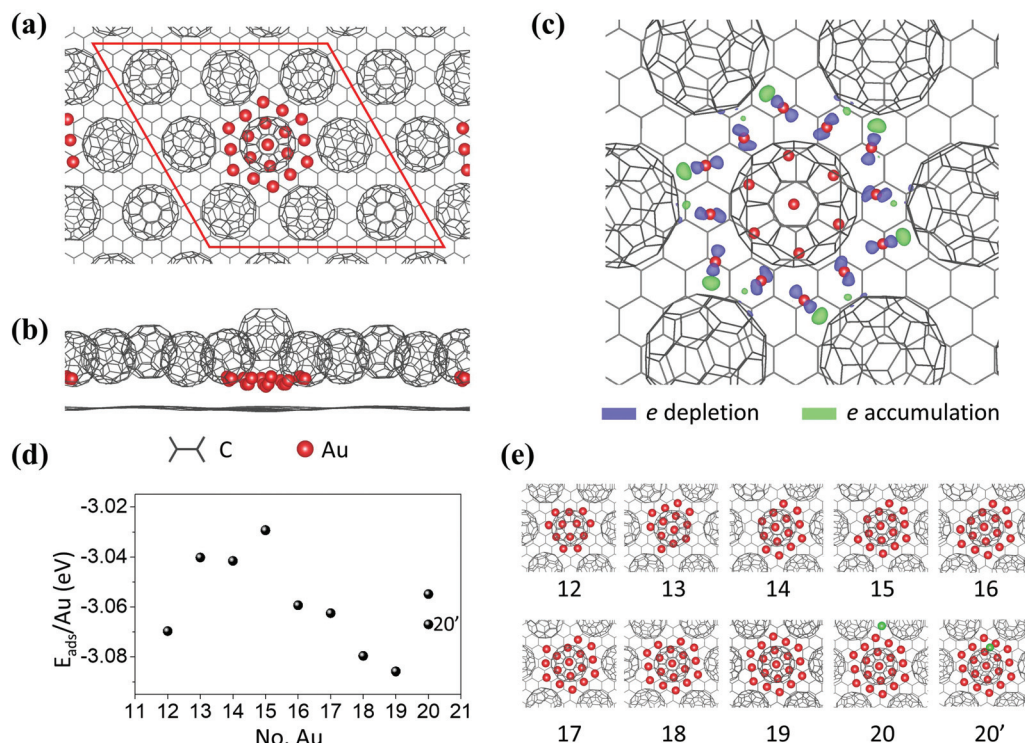
Fig. 2 Bias voltage dependent heights of  $\text{Au}_n$  clusters. (a) STM image acquired with a positive sample bias of +1.80 V. (b) Height profile along the red lines. A  $\sim$  three-layer Au cluster is found at position 1. A 2D  $(\text{C}_{60})_7\text{Au}_{19}$  cluster is located at position 2. (c) The same area imaged with a negative sample bias of -1.21 V. For the  $(\text{C}_{60})_7\text{Au}_{19}$  clusters, in addition to the molecule sitting on the Au island, the surrounding six molecules appear taller than molecules in the background due to charge transfer from the Au island. (d) Height profile along the blue lines in (c).

hexagon interact strongly with  $\text{C}_{60}$  molecules through charge transfer. The charge density difference is obtained by  $\rho(\text{total}) - \rho(\text{Au}_x = 19) - \rho(\text{C}_{60}/\text{graphene})$  ( $\rho$  denotes electron density). From the spatial distribution of the charge density difference shown in Fig. 3c, we find that edge Au atoms donate electrons to the nearest  $\text{C}_{60}$  molecules. Fig. 3d and e show the different-sized clusters studied and the adsorption energy per Au atom as a function of cluster size. The adsorption energy is defined as,  $E_{\text{ads}} = [E(\text{C}_{60}/\text{Au}_x/\text{graphene}) - E(\text{C}_{60}/\text{graphene}) - x \times E(\text{Au})]/x$ , where  $E(\text{C}_{60}/\text{Au}_x/\text{graphene})$  and  $E(\text{C}_{60}/\text{graphene})$  are the total energies of  $\text{C}_{60}/\text{Au}_x/\text{graphene}$  and  $\text{C}_{60}/\text{graphene}$ , respectively.  $E(\text{Au})$  is the total energy of a single Au atom.  $x$  is the number of Au atoms in the cluster. The minimum energy appears for the cluster with 19 Au atoms. The specific binding energy difference is not much greater than thermal energy at RT. For example, the energy difference between  $\text{Au}_{18}$  and  $\text{Au}_{19}$  is 0.01 eV. The energy difference per cluster, however, is 0.18 eV which is high enough to steer the selectivity towards the most

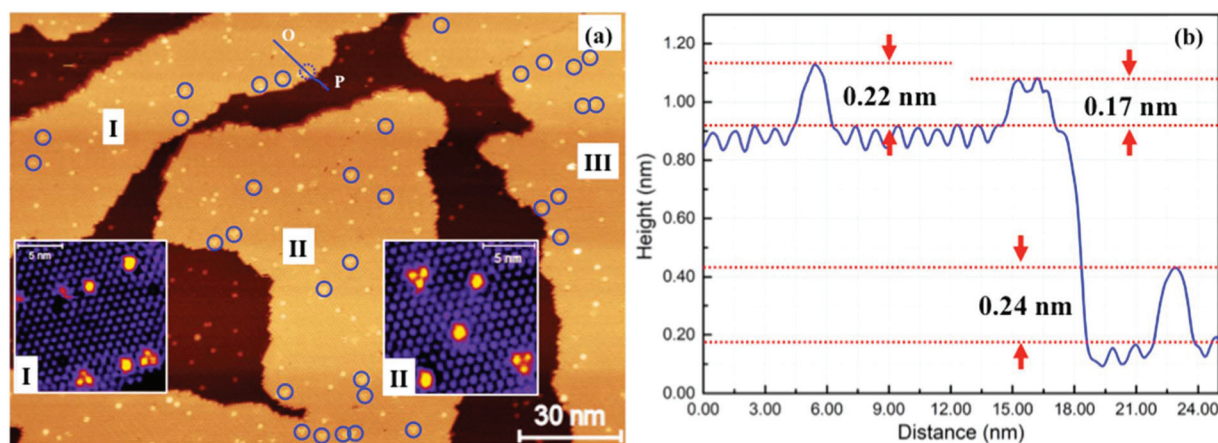
stable cluster. It is worth mentioning that, when an extra Au is introduced, (the green balls in panels 20 and 20' in Fig. 3e), it prefers to go up to the second layer ( $x = 20'$ ) rather than to stay in the first layer ( $x = 20$ ). This finding agrees with the experimental observation that monolayer and bilayer islands coexist. The structural stability of the  $\text{Au}_{19}$  cluster at 300 K is further evaluated using classical-molecular-dynamics (MD) calculations. We find that the  $\text{Au}_{19}$  cluster is stable at 300 K. Details of MD findings can be found in Fig. S4 in the ESI.<sup>†</sup> The CIF file for the  $(\text{C}_{60})_7\text{Au}_{19}$  can be found at the Cambridge Crystallographic Data Centre (CCDC) with deposition number 2034815.<sup>†</sup>

We have also investigated the deposition of Au atoms onto 2 ML  $\text{C}_{60}$  on HOPG. Fig. 4(a) shows an STM image of HOPG which is covered by  $\sim 1.5$  ML of  $\text{C}_{60}$ . In the image, there are three second layer  $\text{C}_{60}$  islands, I, II and III, sitting on a complete 1<sup>st</sup> layer. After 0.026 ML of Au is deposited at 100 K and thermal annealing to 200 K for 30 minutes, we observed bright





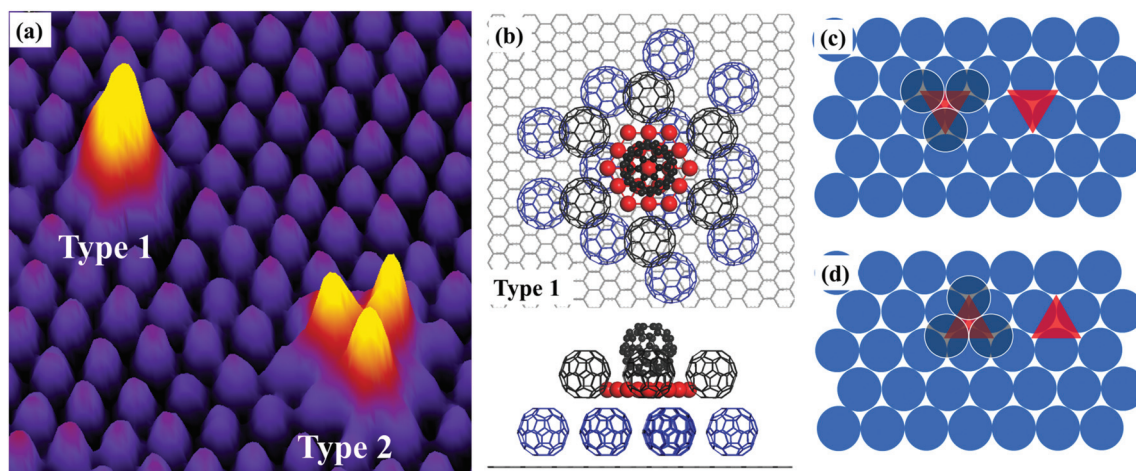
**Fig. 3** DFT calculations on  $\text{Au}_n$  clusters. (a) Top view and (b) side view of the atomic model in DFT calculations. (c) Charge density difference between Au and  $\text{C}_{60}$  molecules. Blue and green shadows represent electron depletion and accumulation, respectively. The isosurface is  $0.053 \text{ e } \text{\AA}^{-3}$ . (d) Adsorption energy per Au atom as a function of the number of Au atoms shows a dip corresponding to 19 Au atoms. (e) Top views of the atomic configurations of the different Au clusters considered in the calculations.



**Fig. 4** Au clusters sandwiched between two layers of  $\text{C}_{60}$ . (a) STM image from an area of HOPG covered by  $\sim 1.5 \text{ ML}$  of  $\text{C}_{60}$ . I, II and III are three second layer  $\text{C}_{60}$  islands. Bright spots in the second layer are due to the trapping of Au atoms. In addition to singly raised  $\text{C}_{60}$  molecules, there are bright  $\text{C}_{60}$  "trimers" as shown in inset I which is a magnified view from part of island I. The trimers have the same azimuthal orientation within the same island. Inset II is a magnified view taken from part of island II. The trimer orientation is flipped upside down in comparison to those in I. (b) Height profile measured along line O-P. The single bright  $\text{C}_{60}$  in the second layer is  $0.22 \text{ nm}$  taller than the normal  $\text{C}_{60}$  molecule in this layer. The  $\text{C}_{60}$  trimer is  $0.17 \text{ nm}$  tall.

(raised) features in both the first and the second  $\text{C}_{60}$  layers. A close examination finds that there are two types of bright spots in the second layer. Type I is singly raised  $\text{C}_{60}$  molecules about  $0.22 \text{ nm}$  taller than the normal molecules. This is similar to

the raised molecules found in the first layer. We also find a number of bright  $\text{C}_{60}$  trimers, type II, standing  $0.17 \text{ nm}$  tall from the background. The trimer/monomer number ratio is  $\sim 1 : 3$ . Inset I in Fig. 4(a) is a magnified view taken from island



**Fig. 5** Structural models of Au clusters trapped between two layers of  $C_{60}$ . (a) STM image showing two types of raised features. Type I: a single raised  $C_{60}$  molecule. Type II: a raised  $C_{60}$  trimer. The  $C_{60}$  molecules in this image are all in the second layer. (b) Structural model for Au clusters trapped at the tetrahedral interstitial site. (c) Structural model for Au clusters trapped at the octahedral site. (d) Alternative arrangement of the octahedral site. The raised  $C_{60}$  trimer in (c) has an opposite orientation to that in (d).

I. The  $C_{60}$  trimer consists of three adjacent  $C_{60}$  molecules and it takes the same azimuthal orientation. Trimers in island II take a uniform orientation which is, however, flipped upside down in comparison to those in island I. Trimers in island III take the same orientation as those in island II.

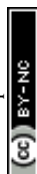
For singly raised  $C_{60}$  in the second layer, we propose a structural model shown in Fig. 5(b). According to this model, there is a Au cluster directly below the raised molecule. The cluster occupies the tetrahedral interstice of the  $C_{60}$  lattice. It is not clear what shape is this cluster. The cluster is larger than the volume of the interstice lifting the  $C_{60}$  above by  $\sim 0.22$  nm. A structural model for the raised  $C_{60}$  trimer is presented in Fig. 5(c). Here a Au cluster is placed in the octahedral interstice. If we shift the position of the second layer  $C_{60}$  from the occupied three-fold hollow site shown in Fig. 5(c) to the nearest neighbour three-fold hollow site, the octahedral interstice moves as a result, Fig. 5(d). Therefore, the orientation of the raised trimer in Fig. 5(d) is opposite to that in Fig. 5(c). The orientation of the trimer within one domain should be the same independent of the location. The number density of raised features (trimer plus monomer) in the second layer is not much different from that of the raised monomers in the first layer. If all the Au atoms landing on top of the second layer form trapped clusters between the two layers, the average size of the clusters trapped between the layers should be similar to that of the Au 2D cluster in the first layer, *i.e.* around 19 Au atoms per cluster. As the sample is annealed progressively to higher temperatures, we find that the number of trimers diminishes whilst the number of singly raised molecules remains relatively constant. This suggests that the Au cluster at the octahedral interstice is less stable. There are nearly three times as many raised  $C_{60}$  monomers as raised trimers. This is probably due to the fact that there are twice as many tetrahedral sites as octahedral sites, assuming an equal probability of nucleation at the two different types of inter-

stice. Nano-structures from the self-assembly of the  $C_{60}$  molecule have been studied previously in the absence of metal atoms.<sup>17,18</sup> What we have demonstrated here is that the flexibility of the  $C_{60}$  layer can be effectively used to regulate the formation of Au nanoclusters.

In summary, a close-packed layer of  $C_{60}$  on HOPG has been used as an effective molecular template for the fabrication of size- and shape-controlled Au clusters. The interaction between Au and the  $C_{60}$  molecules leads to the preferential formation of the planar  $Au_{19}$  cluster which is protected by seven  $C_{60}$  molecules. The on-surface synthesis of size- and shape-controlled clusters thus developed is potentially useful for making regular two-dimensional cluster lattices.  $C_{60}$  double layers are found to be able to trap small Au clusters in between the layers. Such trapped clusters might be three-dimensional with a lateral dimension less than 1 nm. Small metal clusters sandwiched between organic molecular layers are good candidates for solar energy harvesting and energy storage. Further investigation targeting at the electronic structure of the Au clusters would provide more information on the activity of the clusters and their optical response.

## Methods

HOPG (purchased from Goodfellow, 99.99% purity) was used as the substrate. The HOPG sample was prepared by annealing in UHV at 475 K for 30 min to remove surface contamination just before the deposition of the  $C_{60}$  molecules (purchased from MER, 99.5% purity) that were sublimed onto the HOPG substrate using home-built effusion cells. The effusion cells are degassed at 500 K for 5 min before sublimation. Then the  $C_{60}$  molecules were deposited on the surface with a rate of  $0.12 \text{ ML min}^{-1}$  for 10 min. During deposition, the background pressure in the UHV system does not exceed  $10^{-9}$  mbar. After



the C<sub>60</sub> deposition completed, the sample was cooled down to 100 K with L-N<sub>2</sub>. Then gold atoms were deposited using a Createc high-temperature effusion cell with a rate of 0.026 ML min<sup>-1</sup> for 1 min. After the deposition of gold atoms, the sample was annealed at 150 K (30 minutes) and then at 200 K (30 minutes) before finally warming up to RT. STM imaging was performed with an Omicron UHV VT STM. Electrochemically etched tungsten tips were used after high temperature annealing in the UHV chamber. Images were collected using the constant current mode with the tunnelling current set at 0.1 nA and bias voltage varying from -1.70 V to +2.00 V. Gwyddion<sup>19</sup> software was used to analyze the raw data acquired by the Omicron MATRIX 3.3.

Density-functional-theory (DFT) calculations were performed using the Vienna *ab initio* Simulation Package (VASP).<sup>20</sup> Perdew–Burke–Ernzerhof (PBE)<sup>21</sup> general gradient approximation (GGA)<sup>22</sup> and projector augmented wave (PAW)<sup>23</sup> pseudo-potentials were employed to treat the exchange–correlation functions and electron–ion interactions. Grimme's D3 correction<sup>24</sup> was adopted to describe the van der Waals (vdW) interaction. For geometrical optimization, all the atoms were fully relaxed to reach a force tolerance of 0.02 eV Å<sup>-1</sup>. The calculation cell contains one layer of 12 × 12 graphene and one layer of 3 × 3 C<sub>60</sub> on one side, with an Au cluster in between. The neighboring Au clusters are separated by ~2 nm. A 17 Å vacuum gap was added to prevent the interaction between slabs. The cut-off energy was 400 eV and the K-point mesh was gamma only.

Molecular dynamics (MD) simulations were carried out under the NVT ensemble with Gromacs-4.6.7 software.<sup>25</sup> The supercell contains four layers of 64 × 64 graphene and one layer of 8 × 8 C<sub>60</sub> molecules on one side, with two Au<sub>19</sub> clusters in between. The general AMBER force field (GAFF) was used to describe intra- and intermolecular interaction parameters of a C<sub>60</sub> molecule and graphene.<sup>26</sup> Girifalco's parameters are employed to describe vdW interactions for fullerene carbons.<sup>27</sup> The Au atoms interacted with each other (or carbon atoms) *via* the Lennard-Jones (LJ) potential.<sup>28</sup> The Berendsen thermostat is applied to control the temperature. A time step of 1 fs is used in all simulations. A typical of 12 Å cut-off distance is used in the calculation of vdW interactions. The simulation process includes three steps. First, the system undergoes a 5 ns simulation at 100 K to obtain an equilibrium configuration. Second, using the final trajectory at 100 K as the initial structure, the system was heated to 375 K with a heating rate of 1 K ps<sup>-1</sup>, performed a 20 ns simulation at 375 K, and was cooled to 300 K with a cooling rate of 1 K ps<sup>-1</sup>. Finally, using this final trajectory in the previous step, we carried out a 20 ns simulation at 300 K to check its stability.

## Author contributions

Lu'an Guo and Yitao Wang conducted all experiments. De-liang Bao and Hai-hong Jia performed theoretical calculations.

All authors contributed to data analysis and writing of the manuscript.

## Conflicts of interest

The authors declare no competing financial interest.

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