Supplementary Materials

Theoretical Study of Monolayer Protected Gold Cluster $Au_{317}(SR)_{110}$

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RT-TDDFT Calculation Details:

Except for TD-DFT calculation using the Octopus software, we also carried out real-time TD-DFT calculations to obtain the optical absorption spectra.[1] The CP2K code is adopted to carry out RT-TDDFT calculations.[2] The Perdew–Burke–Ernzerhof (PBE) functional[3] with DZVP-MOLOPT and DZVP-MOLOPT-SR basis set[4] and Goedecker-Teter-Hutter (GTH) pseudopotentials[5] were used to optimize the geometry structure. In the RT-TDDFT calculation, electrical pulses with an intensity of 0.005 a.u. are applied in each of the three Cartesian directions. The time interval is 0.012 fs, and following the electron dynamics for a total of 9 fs. The obtained UV-vis spectra of the three clusters was shown in Figure S1. The $Au_{246}(SR)_{80}$ shows an adsorption peaks located at 622 nm. The $Au_{317}(SH)_{110}$ and $Au_{279}(SR)_{84}$ nanocluster exhibits adsorption peak at 595 and 600 nm, respectively.

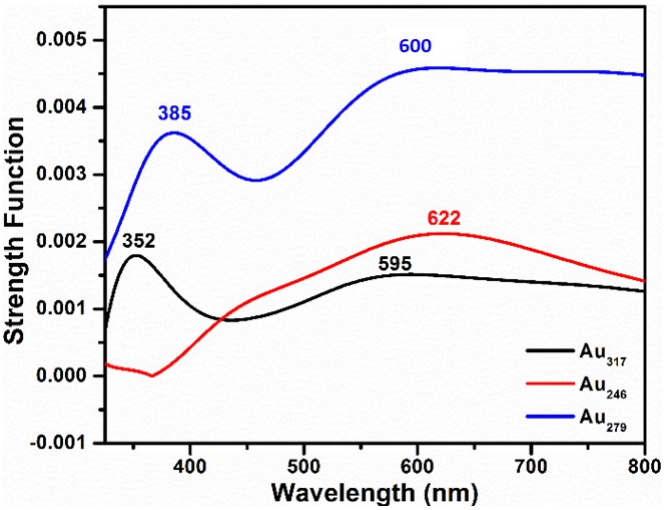

Figure S1. Simulated UV-vis absorption spectra of $Au_{317}(SH)_{110}$, $Au_{246}(SH)_{80}$ and $Au_{279}(SH)_{84}$ clusters by RT-TDDFT approach.

Details of the $Au_{329}(SH)_{84}$ model:

The $Au_{329}(SH)_{84}$ model was constructed based on the Au_{260} core reported previously.[6] The ligand layer consists of 31 monomeric [SR-Au-SR] motifs and 22 SR motifs (Figure S2). The simulated radial distribution functions of $Au_{317}(SH)_{110}$ and $Au_{329}(SH)_{84}$ clusters are compared in Figure S3a. The Au_{317} cluster exhibits split double peaks centered at 2.87 and 2.97 Å, respectively. In contrast, the first dominant g(r) peak of Au_{329} centered at around 2.96 Å, which is similar to the shape and position of Au_{246} and Au_{279}. As shown in Figure S3b**,** the two clusters demonstrated different powder X-ray diffraction curve shapes. The peak of Au_{329} cluster is similar to Au_{279} cluster in Figure 2b.

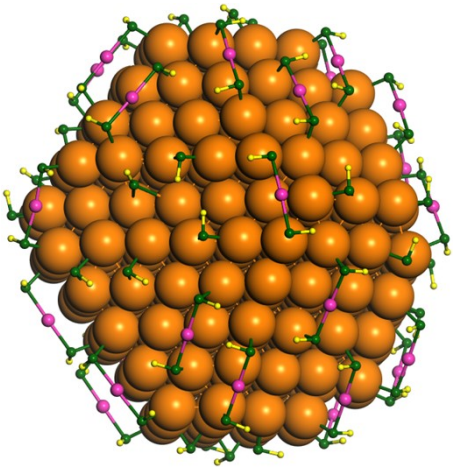

Figure S2. The optimized structure of the $Au_{329}(SH)_{84}$ Orange, pink, green and yellow balls represent Au, Au, S and H atoms, respectively.

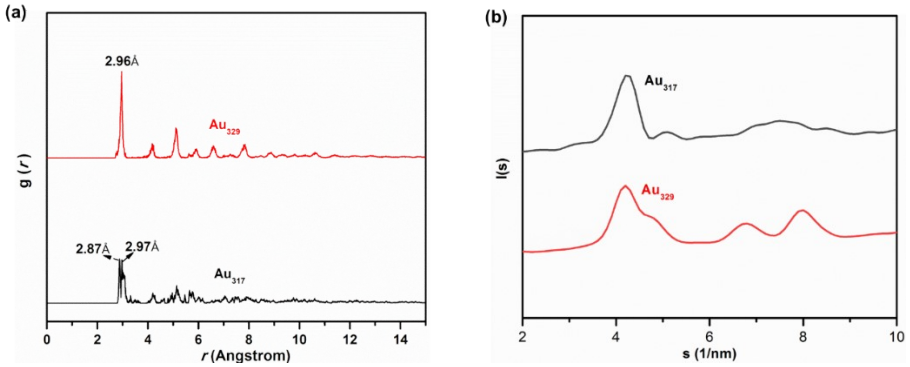

Figure S3. (a) The simulated radial distribution functions of Au_{317} and constructed Au_{329} clusters. (b) The powder X-ray diffraction curve of Au_{317} and constructed Au_{329} clusters simulated based on the Debye formula.

Table S1. The averaged formation energy of gold clusters with number of gold atoms exceeds 100.

Number	Molecular formula	N_{Au}:N_{SR}	$\lvert E_{ave}\rvert$ (eV)
1	$Au_{102}(SCH_3)_{44}$	2.3182	2.7320
2	$Au_{144}(SCH_3)_{60}$	2.4000	2.7653
3	$Au_{133}(SCH_3)_{52}$	2.5577	2.7655
4	$Au_{146}(SCH_3)_{57}$	2.5614	2.7718
5	$Au_{130}(SCH_3)_{50}$	2.6000	2.7831
6	$Au_{191}(SCH_3)_{66}$	2.8939	2.8158
7	$Au_{246}(SCH_3)_{80}$	3.0750	2.8468
8	$Au_{279}(SCH_3)_{84}$	3.3214	2.8727
9	$Au_{317}(SCH_3)_{110}$	2.8818	2.8261

REFERENCE

[1] K. Yabana, G. F. Bertsch, *Phys. Rev. B* 1996, **54**, 4484-4487.

[2] J. Hutter, M. Iannuzzi, F. Schiffmann, J. VandeVondele, *WIREs Comput. Mol. Sci.* 2014, **4**, 15-25.

[3] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.

[4] J. VandeVondele, J. Hutter, *J. Chem. Phys.* 2007, **127**, 114105.

[5] S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* 1996, **54**, 1703-1710.

[6] C. Kumara, X. Zuo, J. Ilavsky, D. Cullen, A. Dass, *J. Phys. Chem. C*, 2015 **119**, 11260-11266.