Supporting Information for

Au_6S_2 Monolayer Sheets: Metallic and Semiconducting Polymorphs

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Table S1. The calculated relative energies and the lowest frequencies of octahedral $Au_6(2e)$ and triangular prism $Au_6(2e)$.

	octahedral $Au_6(2e)$	triangular prism $Au_6(2e)$
Relative energy/eV	0	0.45
The lowest frequency/cm^{-1}	43.5	-34.9

Table S2. Test on reliability of our methods. Computed average Au-Au bond lengths, Au-S bond lengths and Au-S-Au angles for two thiolate-protected gold clusters are compared with experiment.

Au-S system	Parameters	our calculations	experiment	error
$Au_{108}S_{24}(PPh_3)_{16}$ [ref 1]	Au-Au length (Å)	2.856	2.833	0.81%
	Au-S length (Å)	2.495	2.478	0.69%
	Au-S-Au angle (°)	97.456	96.866	0.61%
Au-S system	Parameters	our calculations	experiment	error
$Au_{28}(SR)_{20}$ [ref 2]	Au-Au length (Å)	2.903	2.885	0.62%
	Au-S length (Å)	2.329	2.323	0.26%
	Au-S-Au angle (°)	96.75	96.53	0.23%

References:

(1) Kenzler, S.; Schrenk, C.; Schnepf, A. $Au_{108}S_{24}(PPh)_{16}$: A Highly Symmetric Nanoscale Gold Cluster Confirms the General Concept of Metalloid Clusters. *Angew. Chem. Int. Ed.* **2016**, *55*, 1-5.
(2) Chen, Y.; Liu, C.; Tang, Q.; Zeng, C.; Higaki, T.; Das, A.; Jiang, D. E.; Rosi, N. L.; Jin, R. Isomerism in $Au_{28}(SR)_{20}$ Nanocluster and Stable Structures. *J. Am. Chem. Soc.* **2016**, *138*, 1482-1485.

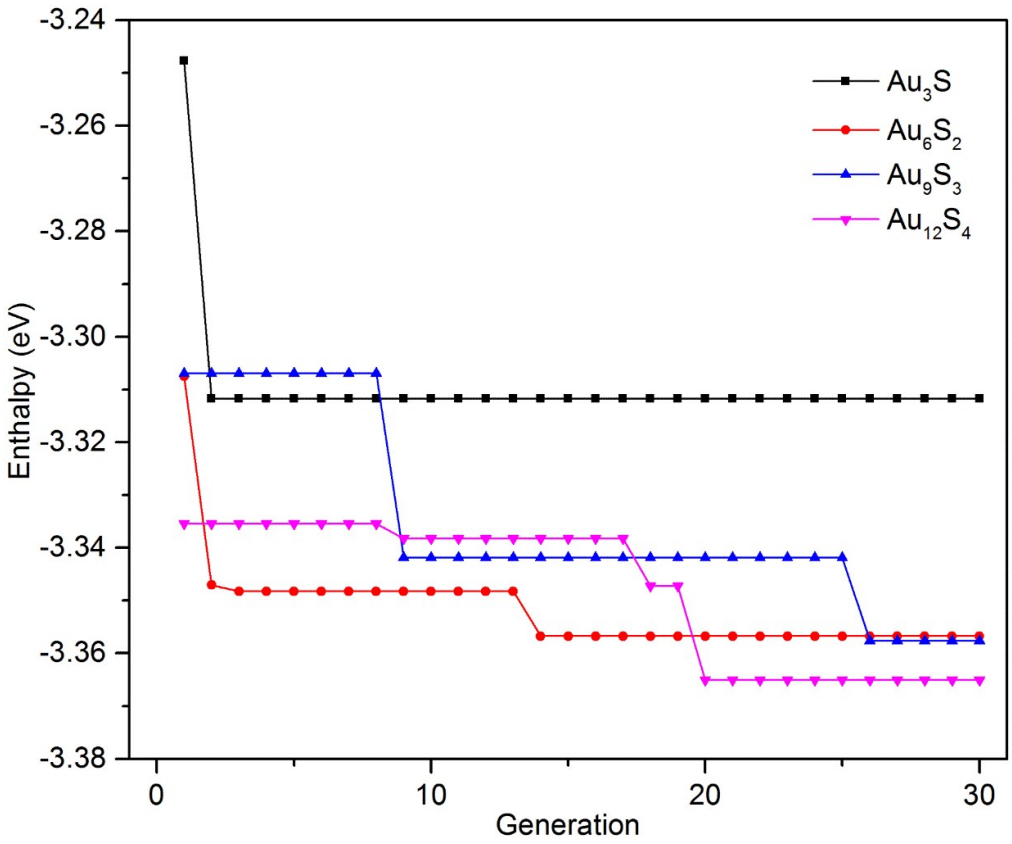

Figure S1. A history of CALYPSO search performed on $(Au_3S)_x$ (x=1-4) monolayers.

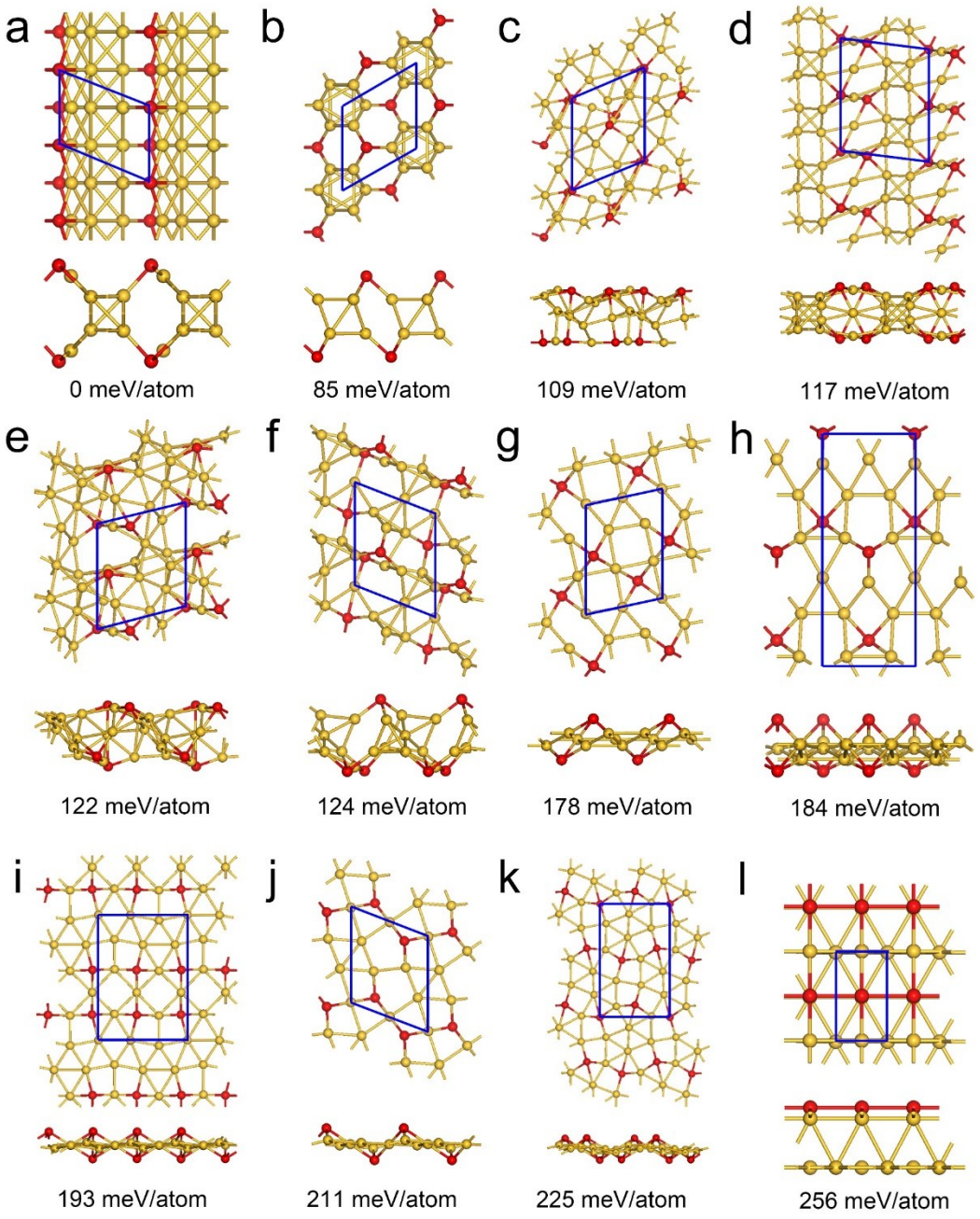

Figure S2. Some typical low-energy freestanding $(Au_3S)_x$ (x =1-4) monolayers searched based on the CALYPSO program. Their relative energies compared to monolayer with the lowest energy are computed at PBE+SOC level. Au and S atoms are marked with gold and red spheres, respectively. Solid blue frames indicate boundaries of primitive cells.

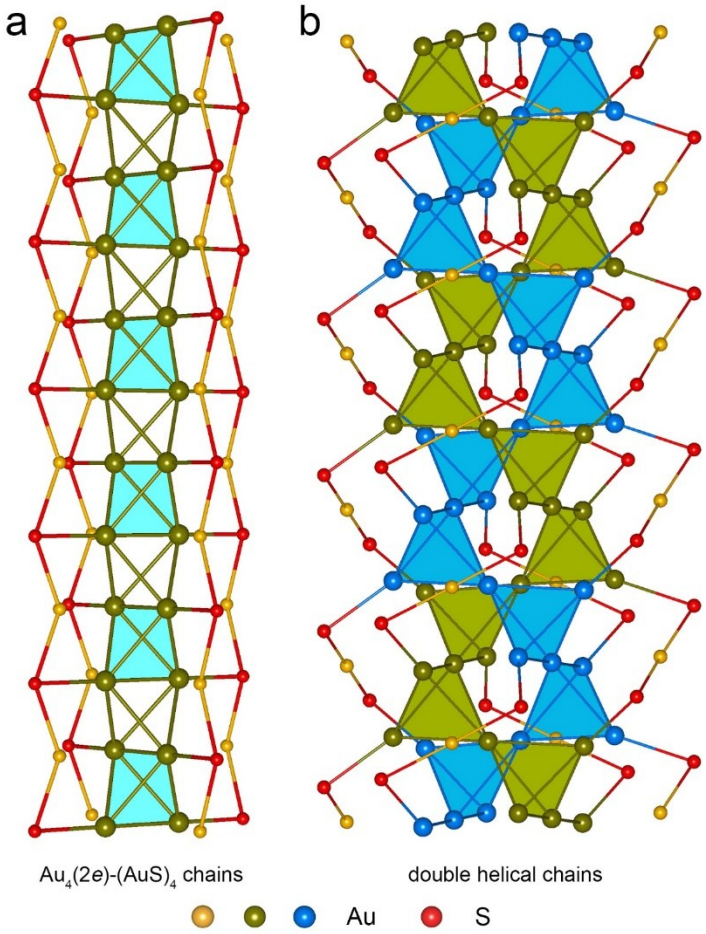

Figure S3. (a) $Au_4(2e)$-$(AuS)_4$ chain in G-Au_6S_2 monolayer. (b) Double helical chains composed of tetrahedral $Au_4(2e)$ elementary blocks are protected by staple motifs [Taken from the reference "Xu, W. W.; Li, Y.; Gao, Y.; Zeng, X. C. Unraveling a generic growth pattern in structure evolution of thiolate-protected gold nanoclusters. *Nanoscale*, **2016**, 8, 7396–7401"].

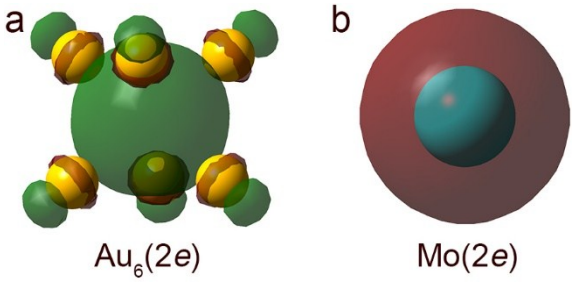

Figure S4. The delocalized 1S orbitals of $Au_6(2e)$ in T-Au_6S_2 monolayer (a) and Mo(2*e*) in T-MoS_2 monolayer (b).

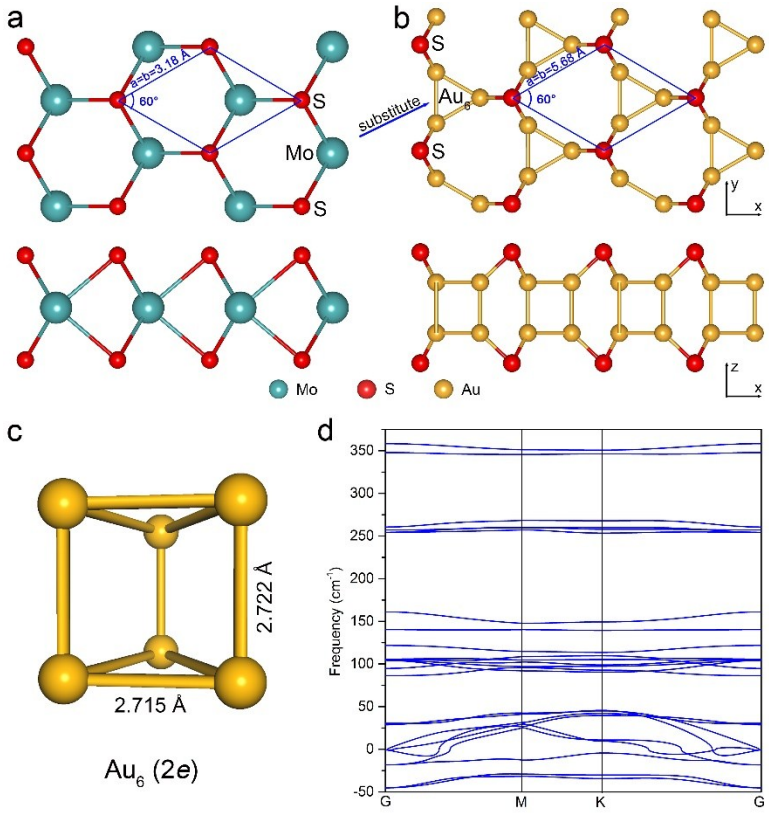

Figure S5. (a, b) Top views (top panels) and side views (bottom panels) for atomic structures of H-MoS_2 (a) and H-Au_6S_2 monolayer (b). (c) Perspective view of triangular prism Au_6(2*e*) cluster. (d) Phonon dispersion of H-Au_6S_2 monolayer. Unit cells are denoted with blue lines, and lattice constants are also noted. Mo, S and Au atoms are marked with cyan, red and gold spheres, respectively. H-Au_6S_2 monolayer can be derived from corresponding H-MoS_2 monolayer by substituting Mo atom with triangular prism Au_6 clusters.

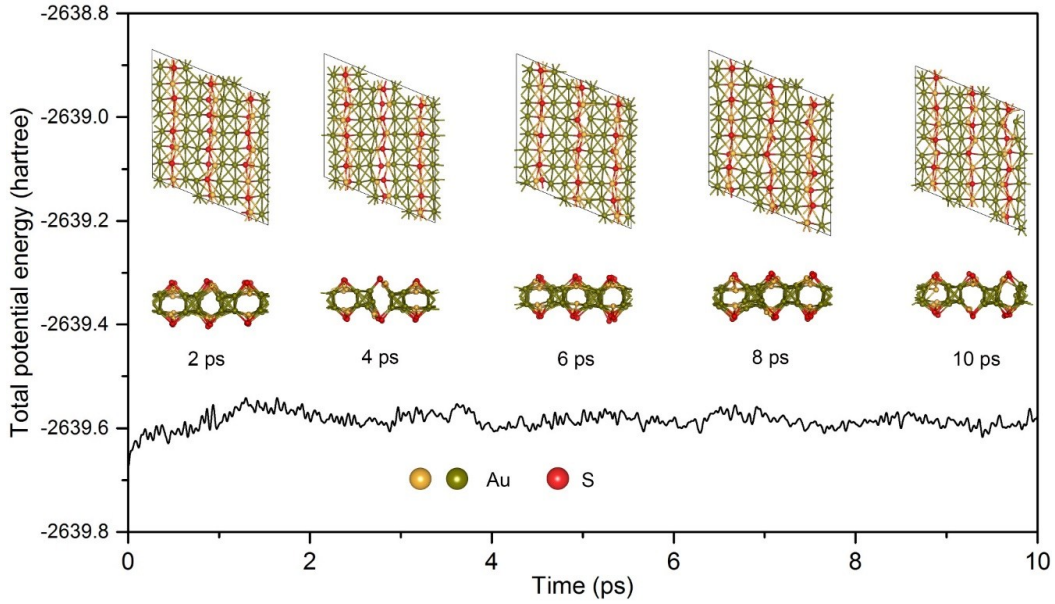

Figure S6. *Ab initio* MD results for G-Au_6S_2 monolayer. Total potential energy as function of MD time were plotted. Snapshot at 2 ps, 4 ps, 6 ps, 8 ps and 10 ps are inserted inside.

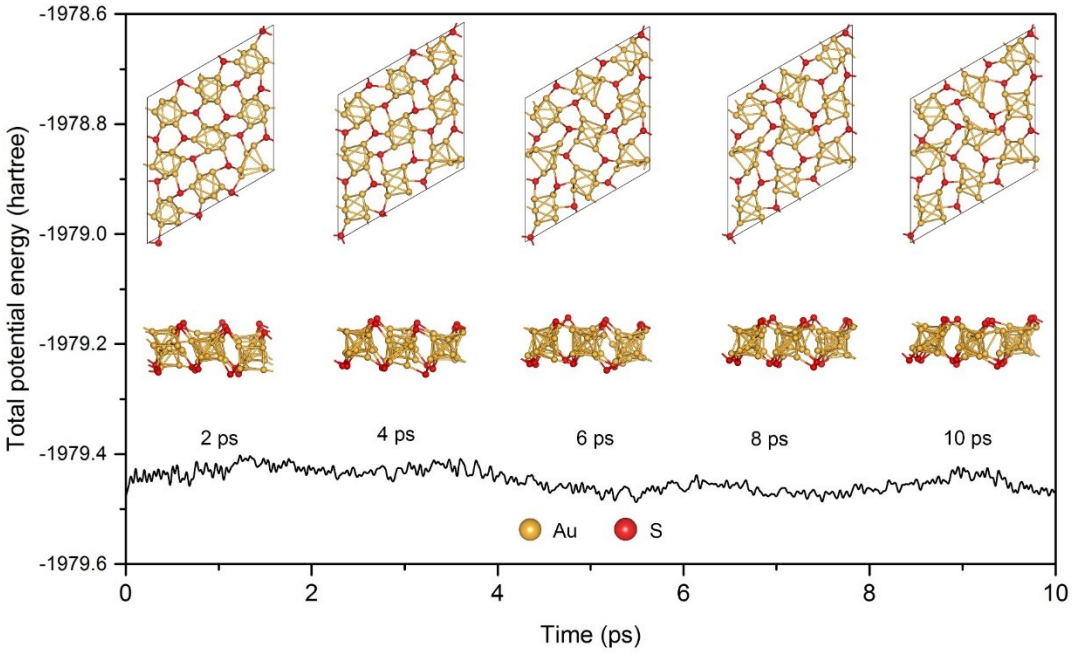

Figure S7. Ab initio MD results or T-Au_6S_2 monolayer. Total potential energy as function of MD time were plotted. Snapshot at 2 ps, 4 ps, 6 ps, 8 ps and 10 ps are inserted inside.

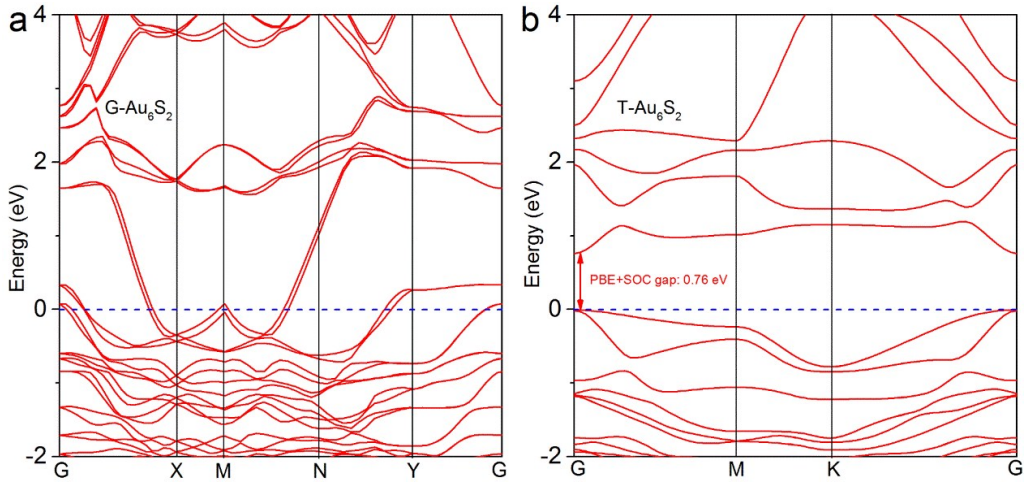

Figure S8. Computed band structures of G-Au_6S_2 (a) and T-Au_6S_2 (b) at PBE level. Spin-orbit coupling (SOC) was considered.

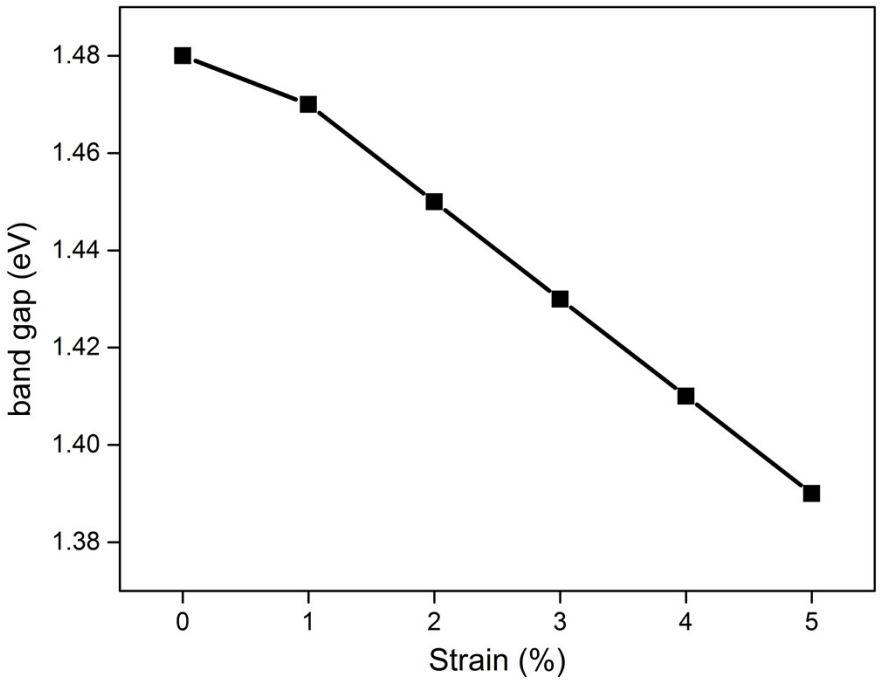

Figure S9. Strain effect on the band gap of T-Au_6S_2 monolayer.

Substrate effects on electronic band structure. Graphene is selected as a substrate to form vertical heterostructures with G-Au_6S_2 and T-Au_6S_2, respectively (Figure S10a and S10b). Projected band structures for heterostructures were plotted in Figure S10c and S10d, demonstrating that the intrinsic electronic structures of predicted Au_6S_2 monolayers are well preserved on substrate. Of course, Fermi levels are shifted due to the possible charge transfer from graphene to G- and T-Au_6S_2.

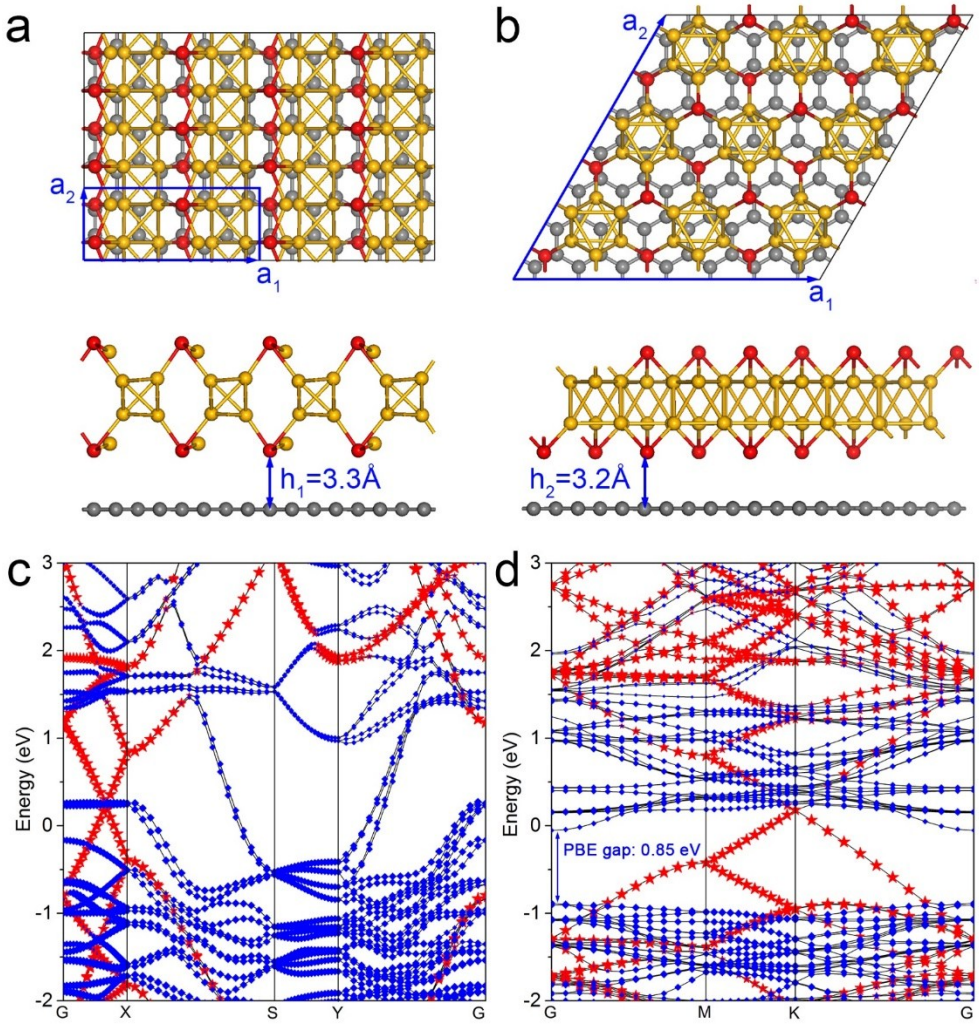

Figure S10. (a, b) Atomic structures (top and side views) for G-Au_6S_2 and T-Au_6S_2 monolayer adsorbed on graphene substrate. Gold, red and grey spheres in (a, b) stand for Au, S and C atoms, respectively. $\mathbf{a_1}$ and $\mathbf{a_2}$ indicate unit cells for heterostructures. (c, d) Projected band structures at PBE level for G-Au_6S_2-graphene (c) and T-Au_6S_2-graphene (d) Heterostructure systems. Red and blue dots in (c, d) represent the weight of Au_6S_2 and graphene, respectively. Fermi levels are set to 0. SOC was not considered here in order to reduce the huge computational cost.

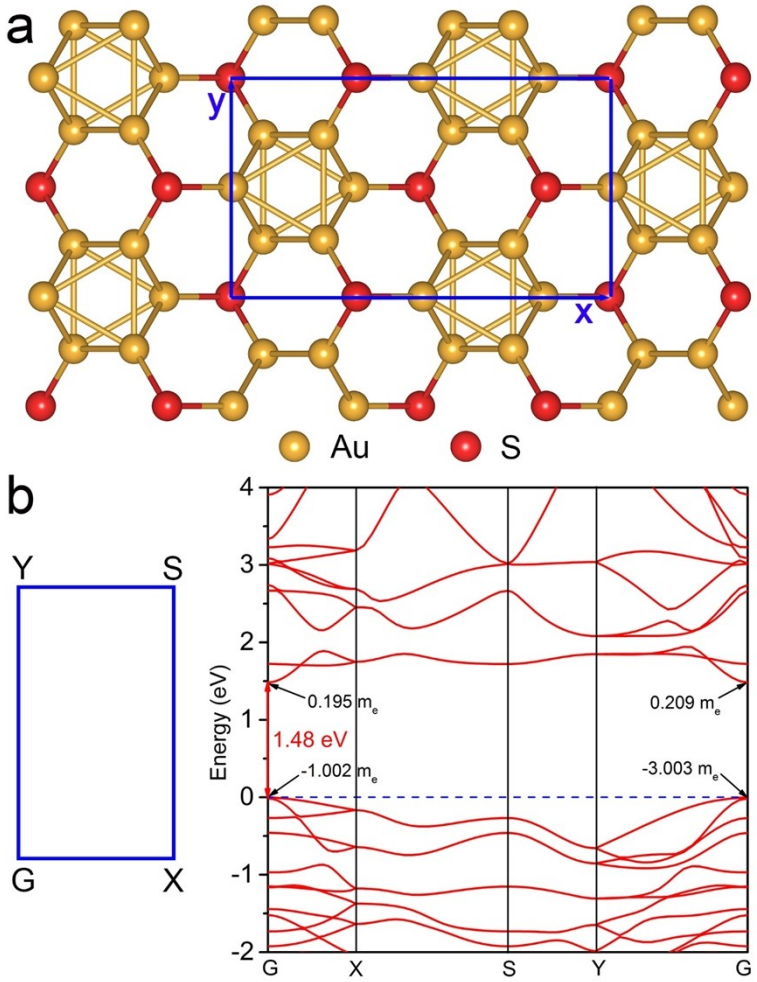

Figure S11. (a) Representative structure of rectangle cell of T-Au_6S_2 monolayer as indicated with blue lines and texts. (b) Sketch for brillouin zone and band structures calculated based on HSE06 functional. Band gap and effective electron/hole masses are noted inside.

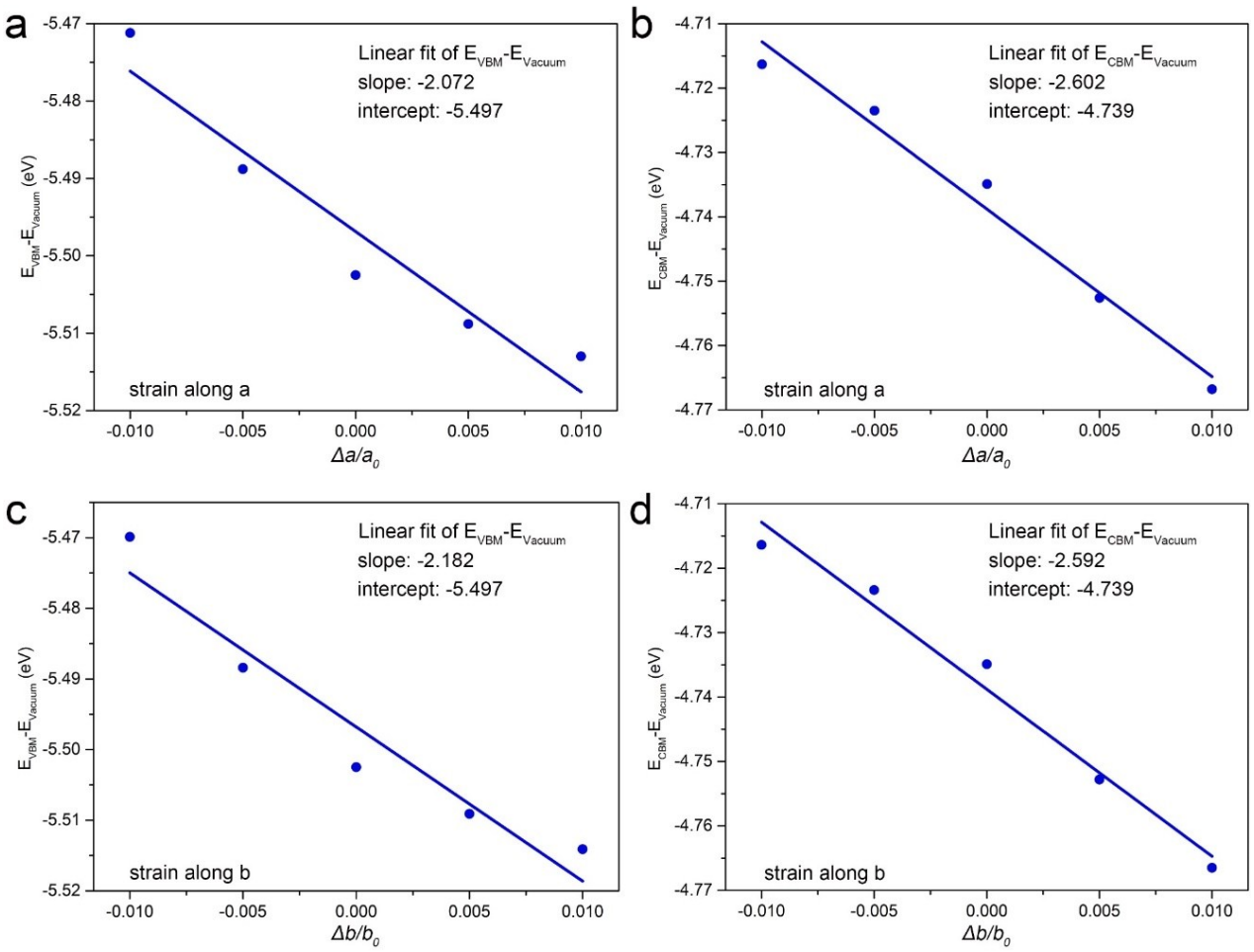

Figure S12. Linear fitting of deformation potential. Band energy of the VBMs (a, c) and CBMs (b, d) of Au_6S_2 monolayer with respect to the vacuum energy as a function of lattice dilation. PBE-GGA functional with SOC considered was adopted to compute deformation potential constant for reducing the huge computational cost.

Lattice parameters (a, b, c and α, β, γ; units are Å and degree) and Cartesian coordinates for structures in Figure S2 and H-Au_6S_2.

G-Au_6S_2 monolayer in Figure S2.

4.4088	5.7457	20.0000	90.0000	90.0000	67.3840
Au001	3.883675960	0.153038005	9.859762800		
Au002	1.685229084	3.587876227	7.914511800		
Au003	1.678524279	1.291930506	11.057992200		
Au004	1.680909399	0.151738114	7.967035800		
Au005	3.887618438	3.588919405	9.914360400		
Au006	3.885791950	1.295235549	6.772689000		
S001	3.882461370	1.991957299	11.670505200		
S002	1.681507183	1.993502573	6.156082800		

T-Au_6S_2 monolayer in Figure S2.

5.7451	5.7451	20.0000	90.0000	90.0000	60.0000
Au1	4.187833194	0.705910113	9.026880000		
Au2	5.578549551	1.508940085	6.718720000		
Au3	2.805131252	1.508790822	6.712320000		
Au4	2.801224584	3.107586677	9.027040000		
Au5	4.191883490	3.910616648	6.718720000		
Au6	5.574585432	3.107735939	9.033440000		
S7	1.316173685	0.649240278	5.116480000		
S8	7.063542999	3.967385991	10.629280000		

H-Au_6S_2 monolayer

5.6752	5.6752	20.0000	90.0000	90.0000	60.0000
Au1	3.095685616	1.801158137	8.120350800		
Au2	5.811253081	1.801516920	8.120215800		
Au3	4.453158510	4.153064419	8.120268000		
Au4	3.095672373	1.801117726	10.842823800		
Au5	5.811271619	1.801473560	10.842962400		
Au6	4.453158320	4.153052514	10.842910200		
S1	1.615761399	0.946507843	12.459234600		
S2	1.615711022	0.946511524	6.503954400		

Strcuture (c) in Figure S2.

7.2748 8.5624 20.0000 90.0000 90.00000 67.0606

Au001	6.980157596	5.315556830	11.397117600
Au002	2.585092485	2.780052374	7.598397600
Au003	4.442672433	6.656655868	12.327129000
Au004	6.230022813	2.855970924	7.458804000
Au005	8.564771656	7.458383946	11.135755800
Au006	6.013763651	7.571446079	10.116460800
Au007	4.662101673	4.359086859	9.874006200
Au008	4.700482234	1.232620282	9.051957000
Au009	2.642060194	2.464805652	10.409166000
Au010	7.829674222	2.887210553	12.095913600
Au011	2.369391591	4.909612325	11.781003600
Au012	7.511441433	0.970769519	9.755899200
S001	0.732654638	1.346292759	7.472775600
S002	7.083520230	0.686070332	12.190116600
S003	4.389996364	4.304023372	7.537213800
S004	4.837324253	4.315699654	12.259983600

Strcuture (d) in Figure S2.

7.3009 9.3323 20.0000 90.0000 90.0000 97.0059

Au001	4.619304180	3.149842567	8.987598000
Au002	1.599090353	6.489223204	8.388307800
Au003	4.050703130	7.780885501	8.989974000
Au004	0.233618770	1.729598473	7.654033800
Au005	-0.339538868	6.359618602	10.324960200
Au006	-0.231256555	4.441424374	8.386021800
Au007	2.169558320	1.857424345	9.592792200
Au008	1.139843595	9.201029769	7.655014800
Au009	-0.798698731	9.072072625	9.591768000
Au010	4.906987069	0.832071821	7.104891600
Au011	4.331985317	5.467306720	10.873274400
Au012	1.704728168	4.568478670	10.325205000
S001	5.137451612	7.739189643	11.125416600
S002	5.707880701	3.105286748	6.852938400
S003	3.533228460	3.193523068	11.123562600
S004	2.964189920	7.822330342	6.854682600

Strcuture (e) in Figure S2.

7.1955 8.2625 20.0000 90.0000 90.0000 76.2718

Au001 5.403364434 3.679702355 6.944031000

Au002 3.960898756 6.154047406 7.448385600

Au003 3.195397950 3.399008101 8.777374200

Au004 6.307480500 5.999273883 9.044541000

Au005 2.240400361 0.758201493 8.067088800

Au006 5.545324071 1.130423716 9.313540200

Au007 1.561652829 2.039054302 10.437697800

Au008 1.364304036 4.810513270 10.337211000

Au009 8.539455831 6.065988314 7.279507800

Au010 2.464989113 7.278097708 9.484363800

Au011 4.011795220 5.090367835 10.733092200

Au012 6.237210565 3.240495004 11.200721400

S001 6.866032432 0.850292912 11.279590200

S002 6.249554122 5.631614505 11.404913400

S003 6.311139585 5.794344034 6.555664800

S004 4.373414660 1.612496253 7.350438600

Strcuture (f) in Figure S2.

6.3247 7.6519 20.0000 90.0000 90.0000 111.4882

Au001 5.228807482 1.082311904 9.976032449

Au002 1.836229640 3.364237196 6.562151208

Au003 3.945399360 1.826434581 7.695755340

Au004 0.328958166 1.256877708 7.669737134

Au005 -0.232021291 6.108165007 7.696121029

Au006 3.349027739 5.577808906 7.951438710

Au007 -1.705538868 5.681773343 10.319564378

Au008 1.040909225 5.476036271 10.042931753

Au009 -0.632304608 3.599502290 8.850540450

S001 2.689935373 6.389462428 11.466869163

S002 2.206763409 0.998386246 6.237158971

S003 1.729576995 5.628975816 6.283458416

Strcuture (g) in Figure S2.

5.6591 8.0220 20.0000 90.0000 90.0000 78.6486

Au001 5.713393155 2.868720492 8.160331200

Au002 4.465781225 5.054574237 7.250646400
Au003 4.402361544 7.859234114 7.715185600
Au004 2.763380472 2.799305677 8.174851200
Au005 1.515471721 4.983559665 7.262448000
Au006 7.231966496 7.858518392 7.713444800
S001 4.248002735 1.207494937 9.221854400
S002 2.980277496 6.646707445 6.205238400

Strcuture (h) in Figure S2.

5.7800 14.8896 20.0000 90.0000 90.0000 90.0000
Au001 4.431906182 10.315083082 7.289450170
Au002 1.337279154 10.313893403 7.288336787
Au003 2.882064936 12.284539407 8.399056541
Au004 -0.006354831 12.561293892 7.966042323
Au005 4.371825524 0.167299546 8.248526083
Au006 1.393959698 0.166820100 8.249545491
Au007 1.545324415 2.872719020 7.305609292
Au008 4.231274809 2.874691892 7.306628304
Au009 0.001343512 4.842720305 8.418756462
Au010 2.888800871 5.118663306 7.986890641
Au011 1.487787652 7.614724582 8.250170565
Au012 4.290215450 7.614630778 8.249727169
S001 2.883164739 14.161215658 9.805315610
S002 2.886610584 8.616842309 6.543848797
S003 -0.001451828 6.728747224 9.812053930
S004 -0.004564548 1.181126454 6.550111918

Strcuture (i) in Figure S2.

8.1161 11.4544 20.0000 90.0000 90.0000 90.0000
Au001 -0.000353050 -0.011102750 8.317873601
Au002 4.055491805 11.448053979 8.325946118
Au003 3.489936797 4.360806671 8.576372252
Au004 7.552479059 7.068920926 8.562341379
Au005 2.029831740 1.964842962 8.318673321
Au006 2.021993211 9.331732305 8.296514407
Au007 4.621526475 7.081910420 8.003320783
Au008 6.078357497 4.848521097 8.266428037
Au009 2.029729477 6.586856015 8.281912998

Au010 0.559382714 4.360869875 8.016313257
Au011 6.091162268 2.103696352 8.318788228
Au012 6.082828656 9.473658910 8.305922114
S001 4.076747871 2.046198841 9.567466773
S002 0.010808210 9.383658677 9.548256944
S003 -0.012778799 2.037825960 7.069881459
S004 4.037556847 9.411866001 7.056141461

Strcuture (j) in Figure S2.

6.6657 7.6109 20.0000 90.0000 90.0000 110.4530
Au001 5.333558698 3.557770862 8.288390400
Au002 2.000588658 3.558133835 8.289275200
Au003 2.844269499 6.533326619 7.956968000
Au004 1.156040589 0.582778463 8.621542400
Au005 3.755897160 1.334054347 8.393390400
Au006 0.244815472 5.781982989 8.188121600
S001 0.307060273 2.546648923 9.581712000
S002 3.693765801 4.569661534 6.996438400

Strcuture (k) in Figure S2.

7.5376 12.2533 20.0000 90.0000 90.0000 90.0000
Au001 1.303759828 2.569674987 9.130761330
Au002 6.236200948 9.706348232 9.048338087
Au003 2.468414002 8.672187130 9.098444022
Au004 5.063531291 3.556290835 9.115834598
Au005 7.464184530 4.883815640 8.906568738
Au006 0.057762890 7.416458086 9.535618678
Au007 3.824179501 10.962542012 8.619840568
Au008 3.701927920 1.233627676 9.289724455
Au009 6.213112526 0.234321873 8.692927550
Au010 1.354258733 11.993506664 9.355624668
Au011 2.441981900 5.894009901 9.507461818
Au012 5.114602300 6.385468747 8.822719197
S001 6.825391774 2.425960547 7.937018554
S002 0.703501544 9.855835202 10.262672863
S003 4.471988734 8.513718737 7.887677493
S004 3.056228461 3.722752055 10.306516327

Strcuture (l) in Figure S2.

2.8321 4.8758 20.0000 90.0000 90.0000 90.0000

Au001 2.528224450 1.226827166 6.415988538

Au002 1.118157261 1.288652408 9.106479832

Au003 1.111680248 3.666747309 6.411346866

S001 1.118687147 3.729006399 9.703943662