Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPORTING INFORMATION

Structure, stability, electronic and optical properties of TMDC/coinage metal composites: Vertical atomically thin Self-assembly of Au_6 cluster

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S1: Initial geometry taken for metal clusters adsorbed on TMDCs monolayer

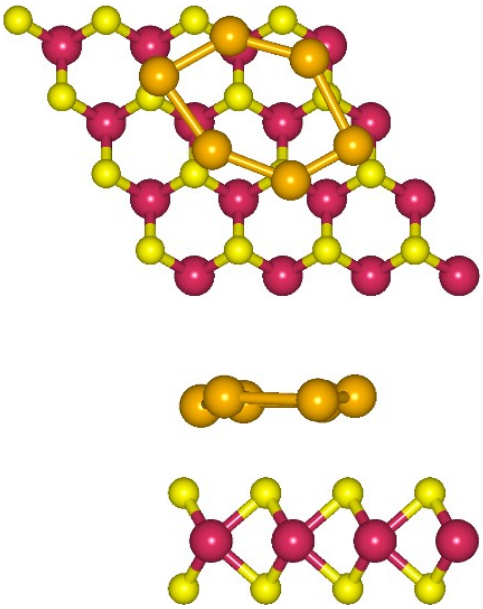


Figure S1. Top and side view of the initial geometry metal clusters adsorbed on TMDCs monolayer.

S2: Optimized geometry of TMDCs/M_6 composites, important geometrical parameters.

The six Ag atoms tends to get clustered on MoS_2 monolayer to give a cone like cluster where five Ag atoms are in plane forming the base of the cone. The sixth Ag atom is present at the vertex of the cone. The minimum Ag–Ag distance for the basal Ag atoms is 2.82 Å, while the distance between basal Ag and vertex Ag is 2.76 Å which is marginally low in comparison with the Ag–Ag distance observed for the basal Ag atoms. The base of the cone is found to adsorb on the surface of MoS_2 monolayer, whereas its apex faces upwards. The optimized geometry is shown in Figure S2. The basal Ag atoms strongly adhere on the surface *via* the S atoms. The minimum distance between the Ag and S atoms is 2.67 Å. The distance between

apical Ag and S is found to be 3.94 Å. In the optimised geometries, it has been observed that the Ag_6 cluster adsorbs on the surface is a manner that the Ag atoms mostly occupies the atop site of the S. The Ag–S distance ranges from 2.67–3.03 Å.

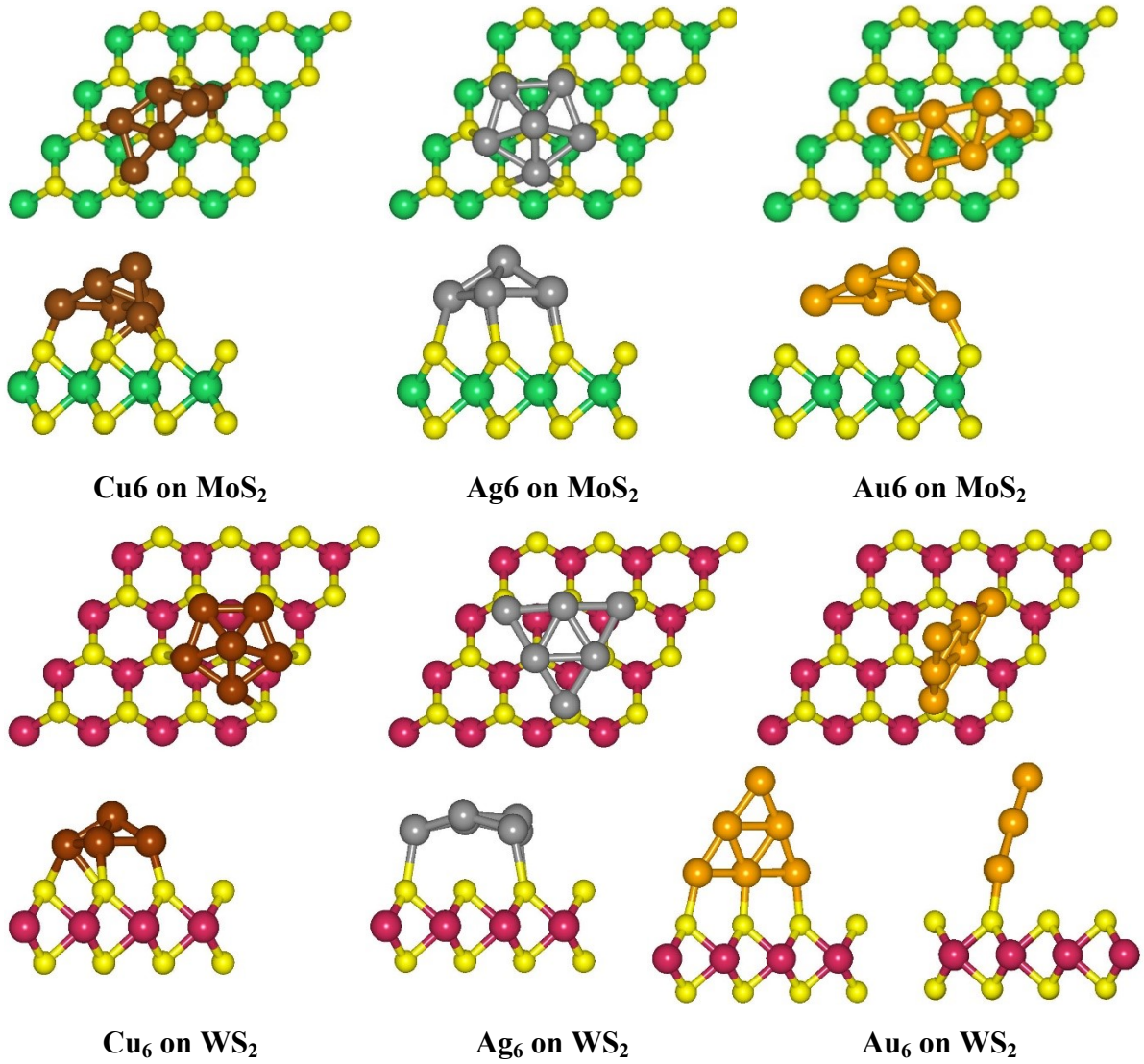


Figure S2. Top and side view of the optimized geometries of TMDCs/M_6 composites obtained without inclusion of the dispersion correction. (Color code: Yellow: S, Green: Mo, Brown: Cu, Grey: Ag, and Orange: Au).

Furthermore, Au_6 and Cu_6 cluster was found to adsorb on the MoS_2 surface in an irregular shape. In Au_6 cluster, the five atoms are in plane and one Au is out of plane tilted towards the surface at a distance of 2.44 Å from the S. The Au–Au distances in the Au_6 cluster lies within the range of 2.66–2.89 Å. The Cu_6 clusters adsorbs on the MoS_2 monolayer analogous to the Au_6 cluster. The distance between the Cu and S atom vary from 2.32 to 2.53 Å. This clearly suggests that the Cu_6 cluster is more closely bound to the S atoms on the MoS_2 layer. The Cu–Cu distance in Cu_6 cluster on MoS_2 ranges from 2.38 to 2.62 Å. It should be

noted that there is no significant variation in the geometry of TMDCs monolayer is observed after the adsorption of coinage metal cluster.

The distance between the terminal Ag atoms to the closest S ranges from 2.82 to 2.85 Å, while the internal Ag atoms are 3.27 to 3.44 Å. This solely indicates that the terminal Ag atoms are more closely bound to the surface than the internal Ag atoms. The Ag–Ag distance in 2D Ag_6 cluster adsorbed on WS_2 surface varies from 2.74–2.83 Å and the Au–Au distances in 2D Au_6 cluster on WS_2 ranges from 2.65 to 2.87 Å. The minimum S–Au distance in WS_2/Au_6 composite is 2.52 Å. The distance between the apical Au atom with the closest S of WS_2 is 6.88 Å. Therefore, it is apparent from the geometry that both the Ag_6 and Au_6 clusters preferably achieve the 2D triangular morphology on WS_2 monolayer. The calculated angle on inclination of the planar 2D Au_6 cluster is 75.79 degrees from the WS_2 surface.

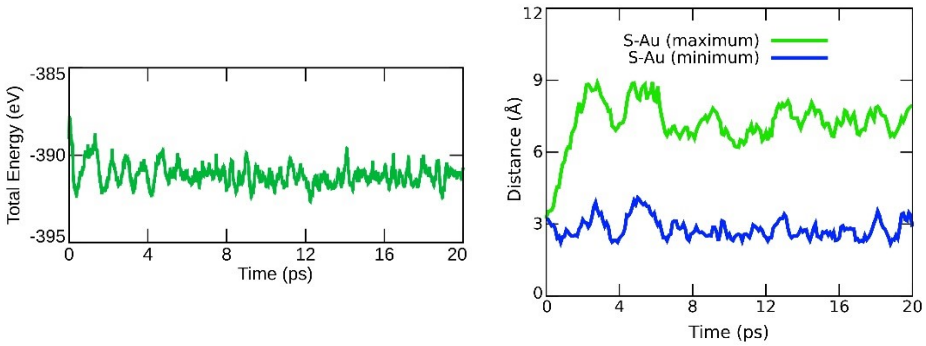
S3: Interaction Energy (IE) and its Various Components for TMDCs/M_6 composite (GGA-PBE).

Table S1. Interaction Energy (IE) and its Various Components for TMDCs/M_6 composite (GGA-PBE).

System	Pauli	Electrostatic	Steric	Orbital	IE
Cu_6 on MoS_2	21.00	-13.65	7.35	-10.09	-2.74
Ag_6 on MoS_2	8.66	-5.76	2.90	-4.07	-1.17
Au_6 on MoS_2	8.66	-5.68	2.98	-4.82	-1.84
Cu_6 on WS_2	15.94	-10.52	5.43	-7.32	-1.90
Ag_6 on WS_2	4.43	-2.96	1.47	-2.10	-0.63
Au_6 on WS_2	9.16	-6.20	2.96	-3.87	-0.91
* All the energy values are given in eV					

S4: *Ab initio* molecular dynamics (AIMD) simulation.

(a) AIMD simulation of WS_2/Au_6 composite for 20 ps

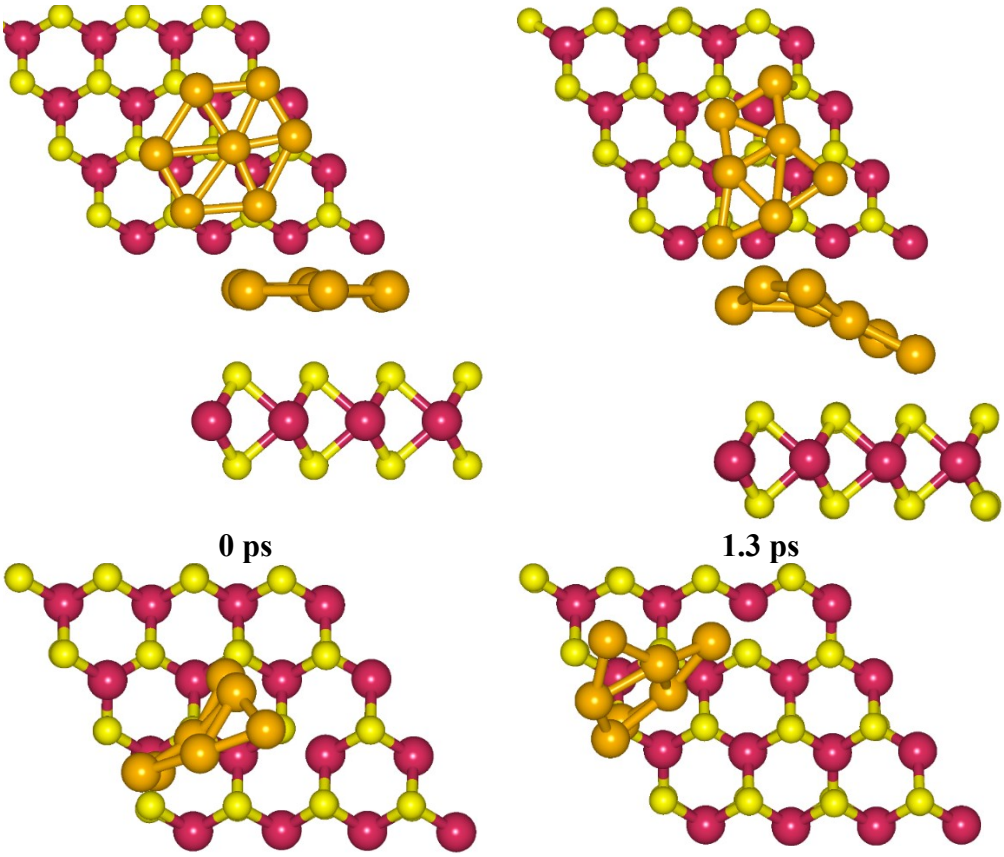


(a) **(b)**

Figure S3. Variation in (a) energy and (b) Au–S distances during the AIMD simulation (20 ps) of Au_6 cluster on the surface on WS_2 monolayer.

There are no significantly larger fluctuations in energy can be observed during the simulation and the energy of the system seems to attain the equilibrium. Moreover, the distance between the S with the closest Au mostly lies between 2.5 to 3.5 Å which indicates that the contact of Au_6 cluster is maintained on the WS_2 monolayer. The distance between the S and the farthest Au atom increases gradually up to 3.5 ps due to the upward motion of the Au atoms during its vertical assembly. After 6.5 ps, the minimum distance between the S and the farthest Au mostly fluctuates within the range of 6.5 to 8.2 Å. These fluctuations are in agreement with the calculated distance between the closest S and the apical Au (6.88 Å) in the optimized geometry of the WS_2/Au_6 composite.

(b) AIMD simulation of WS_2/Au_7 composite for 10 ps.



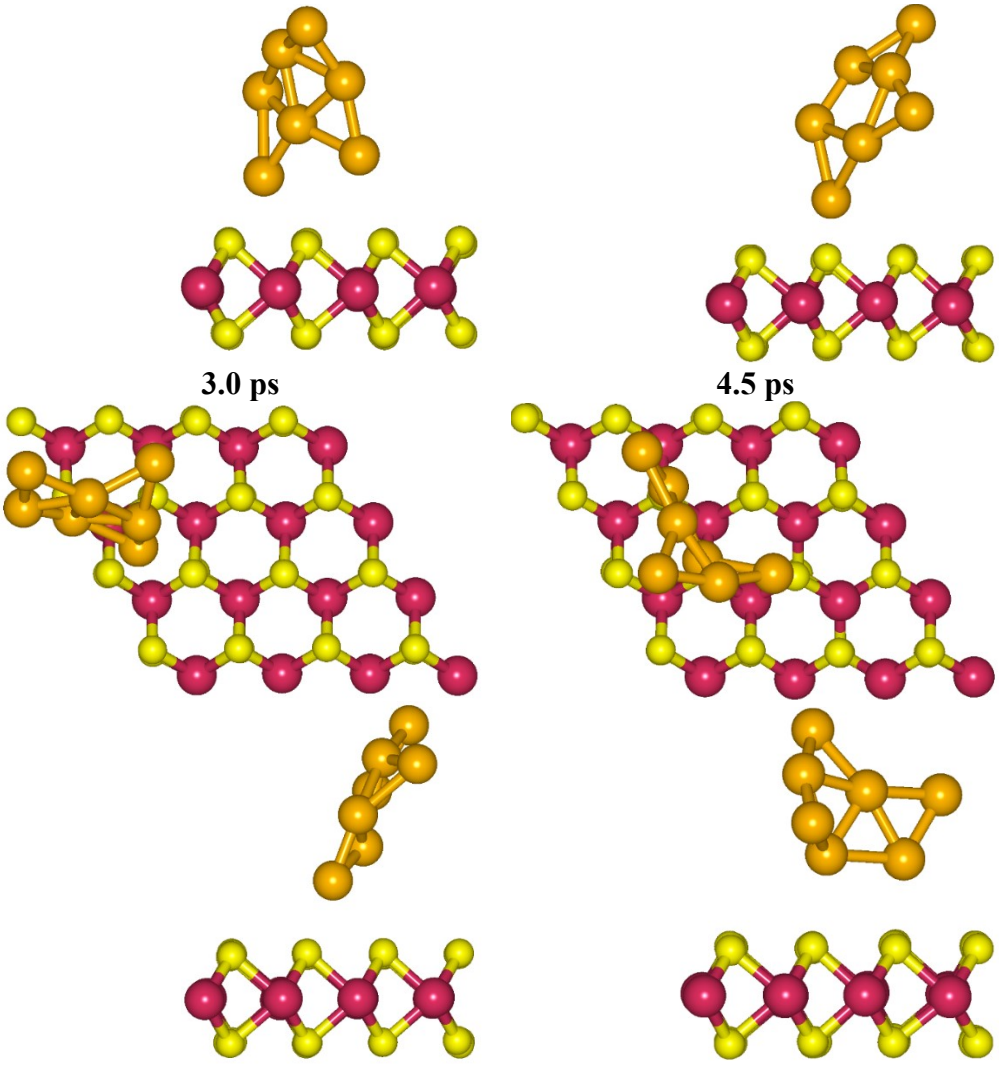
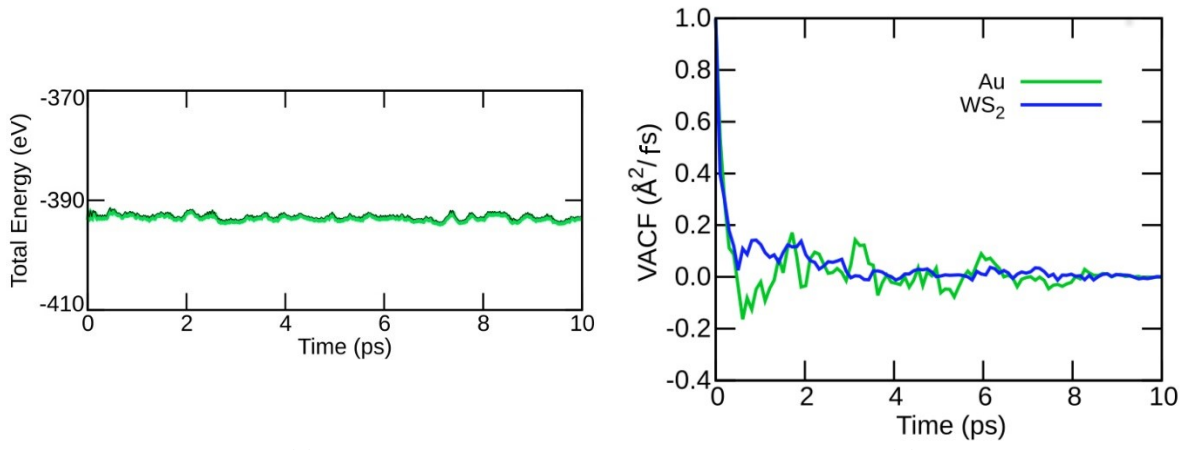
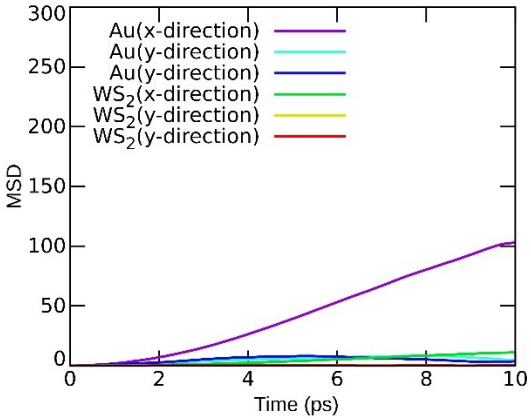


Figure S4. Top and side view of some important geometries of WS_2/Au_7 obtained during the AIMD simulation. (Color code: Yellow: S, Pink: W, and Orange: Au)



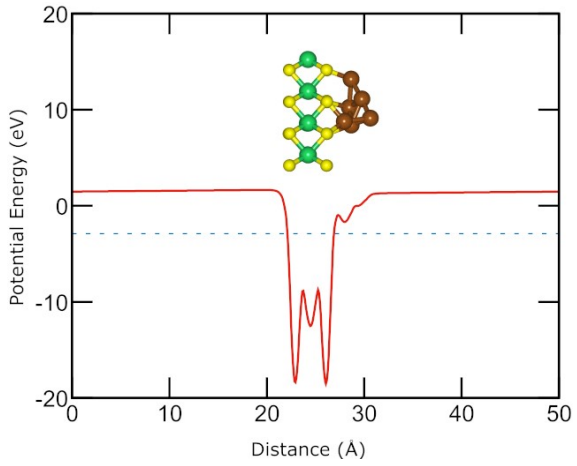
(a) **(b)**



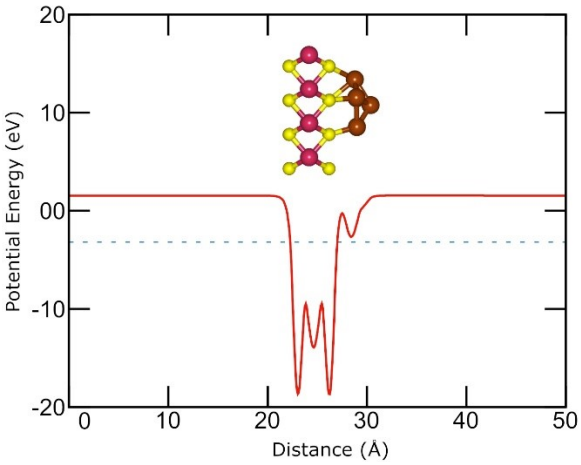
(c)

Figure S5. (a) Variation in the total energy with time and (b) Velocity average autocorrelation function. (c) Mean square displacement of Au_7 on WS_2 monolayer.

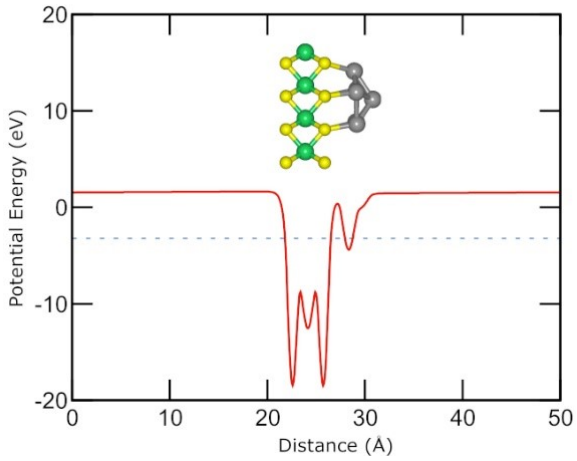
S5: The variation in the potential energy of the system in TMDCs/M_6 composites



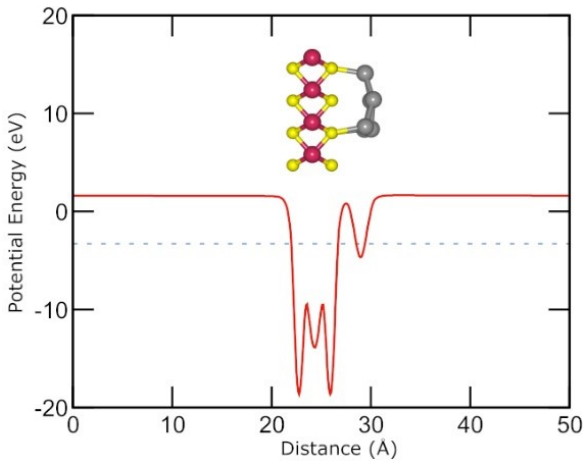
MoS_2/Cu_6



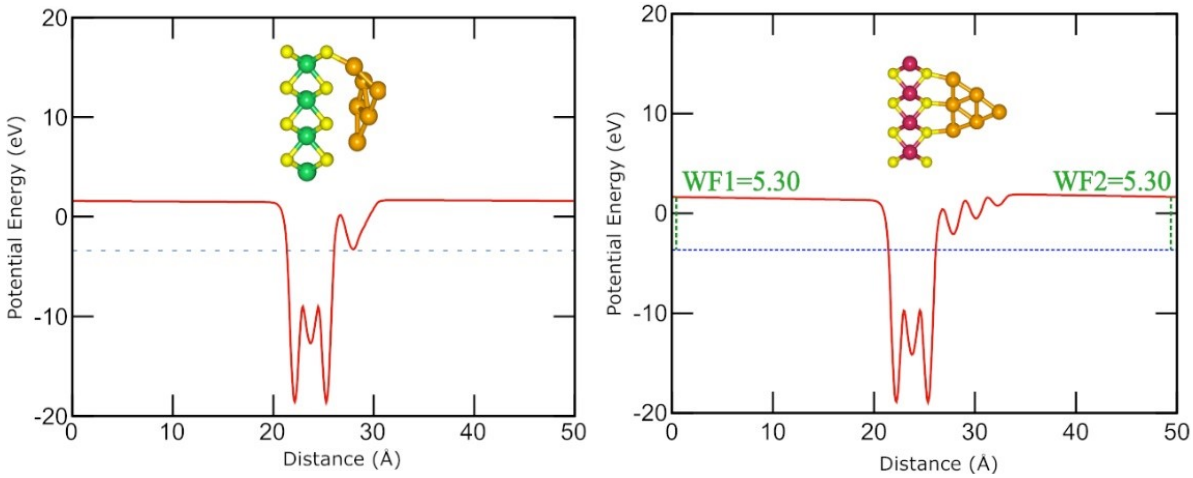
WS_2/Cu_6



MoS_2/Ag_6



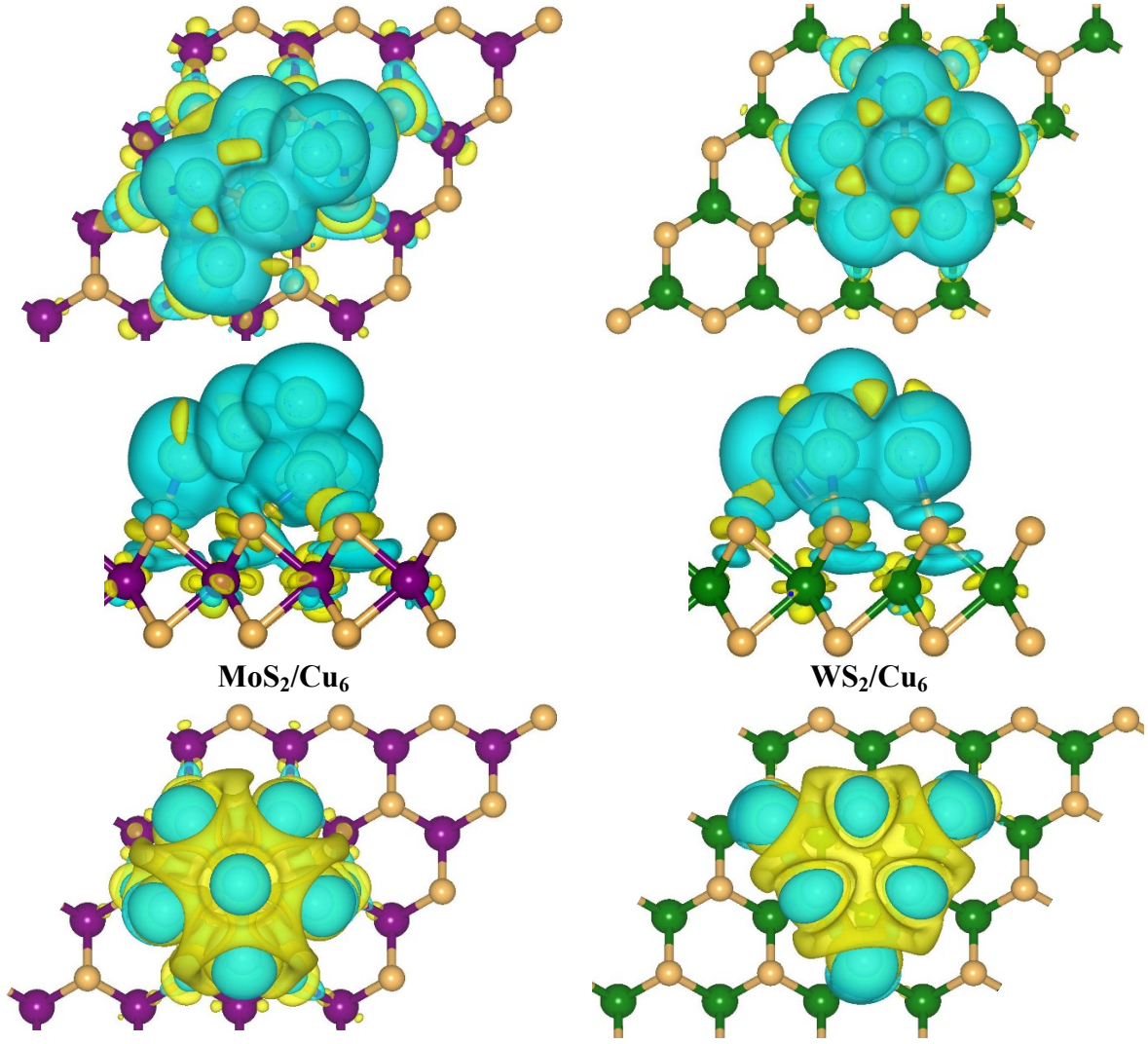
WS_2/Ag_6



MoS_2/Au_6 **WS_2/Au_6**

Figure S6. The variation in the potential energy of the TMDCs/M_6 composites along the z-direction.

S6: Differential charge density plots of TMDCs/M_6 composites



MoS_2/Cu_6 **WS_2/Cu_6**

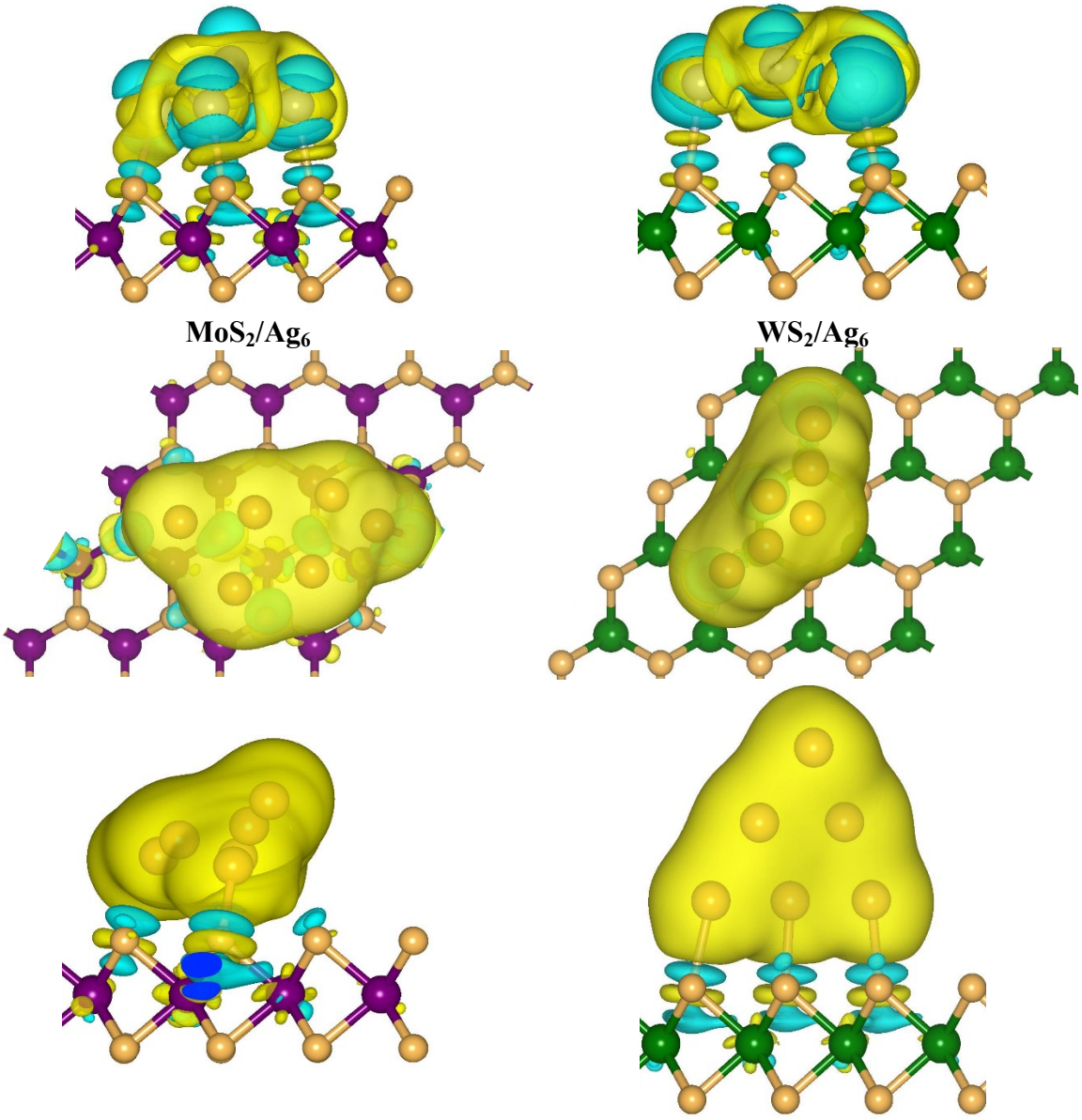


Figure S7. Top and side view of the differential charge density plots for TMDCs/M_6 composites. (Colour code for isosurface: Cyan=Electron depleted region; Yellow=Electron enhanced region; Colour code for balls: Purple=Mo; Green=W; Orange=S)

S7: Optical properties

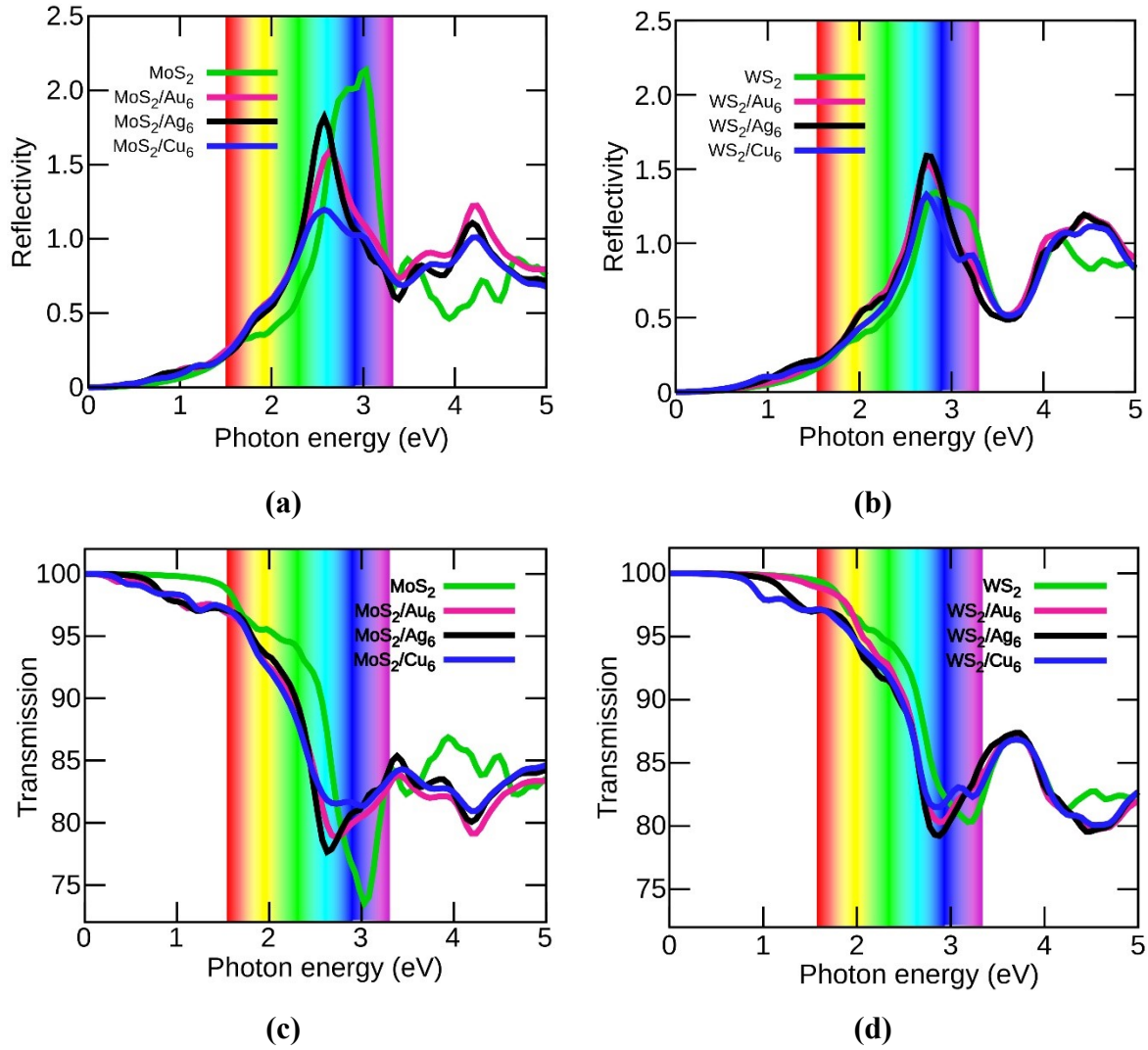


Figure S8. Optical properties of pristine TMDCs and TMDCs/M_6 composites (a) Reflectivity spectra for pristine MoS_2 and MoS_2/M_6 composites, (b) Reflectivity spectra for pristine WS_2 and WS_2/M_6 composites, (c) transmission spectra for pristine MoS_2 and MoS_2/M_6 composites, (d) Transmission spectra for pristine WS_2 and WS_2/M_6 composites.