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

Supporting Information

Delamination of MoS_2/SiO_2 interfaces under nanoindentation

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Determination of Young's modulus and hardness from indentation load-depth curves

Based on the indentation load-depth curves extracted from a depth-sensing nanoindentation system, the reduced elastic modulus E_r of the tested system can be determined from[S1]

$$E_r = \frac{\sqrt{\pi}}{2\beta} S \frac{1}{\sqrt{A(h_c)}}, \tag{S1}$$

where β is a constant depending on the geometry of indenter (β = 1.034 for the Berkovich indenter[S2]), $S = \mathrm{d}P/\mathrm{d}h$ is the slope of the load-displacement (P-h) curve at the beginning of the unloading stage, and A is the projected area of the contact with h_c being the contact depth. Specifically, the contact depth h_c can be determined from the following equation:[S3]

$$h_c = h - \varepsilon \frac{P_{\max}}{S}, \tag{S2}$$

where P_{max} is the maximum load and ε is another constant depending on the geometry of indenter (ε = 0.75 for the Berkovich indenter[S3]).

Meanwhile, the reduced contact modulus in Equation S1 has the following expression:[S2]

$$\frac{1}{E_r}=\frac{(1-\nu^2)}{E}+\frac{(1-\nu_i^2)}{E_i}. \tag{S3}$$

Here E and ν are, respectively, the Young's modulus and Poisson's ratio of the indented 2D material/SiO_2 system; and E_i and ν_i are the Young's modulus and Poisson's ratio of the indenter, respectively.

The hardness H usually can be determined from:

$$H=\frac{P}{A}. \tag{S4}$$

After eliminating the contact area based on Equation S1, the composite hardness of the 2D material/SiO_2 system can be further written as

$$H=\frac{4\beta^2}{\pi}\frac{P}{S^2}E_r^2. \tag{S5}$$

From Equation S3 we can see that the Young's modulus estimated from the nanoindentation experiments is dependent on the Poisson's ratio of the tested systems, though the effect of Poisson's ratio is proven to be trivial.[S4,S5] As for the composite MoS_2/SiO_2 or graphene/SiO_2 system considered here, it is very difficult to determine the exact value of its overall Poisson's ratio, which could range between the values of MoS_2 (or graphene) and SiO_2. Under this circumstance, the value range of the Young's modulus of the composite 2D material/SiO_2 systems was estimated here by using the largest and the smallest Poisson's ratios between MoS_2 (or graphene) and SiO_2. It is worth noting that the Poisson's ratios of multilayer MoS_2 and graphene reported in existing theoretical studies have a wide value range,[S6,S7] partially due to their different in-plane and out-of-plane elastic properties. Specifically, the Poisson's ratio of graphene is reported to range between 0.12 and 0.19, while the Poisson's ratio of MoS_2 is between 0.25 and 0.29. Meanwhile, the Poisson's ratio of the SiO_2 substrate is 0.17.[S8] Thus, the upper limit value of the Young's modulus of the MoS_2/SiO_2 system can be obtained by assuming the Poisson's ratio as 0.17 (the value of SiO_2), while the lower limit value can be obtained by assuming the Poisson's ratio as 0.29 (the maximum value of MoS_2). Similarly, the upper limit value of the Young's modulus of the graphene/SiO_2 system can be obtained by assuming the Poisson's ratio as 0.12 (the minimum value of graphene), while the lower limit value can be obtained by assuming the Poisson's ratio as 0.19 (the maximum value of graphene). As for both MoS_2/SiO_2 and graphene/SiO_2 systems, the lower and upper limit values of the Young's modulus are found to be extremely close to each other (see Figure S2), which proves the fact that the Poisson's ratio indeed has a minor effect on the equivalent Young's modulus of the present 2D material/SiO_2 systems estimated from the nanoindentation experiments.

Parameters in the LJ potential

The expression of LJ 12-6 potential is

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{S6}$$

where ϕ is the potential energy between a pair of atoms, r is the separation distance between the pair of atoms, ε is the potential well depth, and σ is the vdW separation distance. Values of ε and σ for some atoms considered in MD simulations are listed in Table S1.[S9] It is noted that the LJ parameters for some other atom types can be further calculated by using the Lorentz-Berthelot mixing rule.

Table S1. LJ potential parameters utilized in the present MD simulations

Atom type	σ (Å)	ε (eV)
C	3.4309	0.0045532
O	3.1181	0.0026018
Si	3.8264	0.017432
Mo	2.719	0.0024284
S	3.5948	0.011882

References

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Supplementary Figures

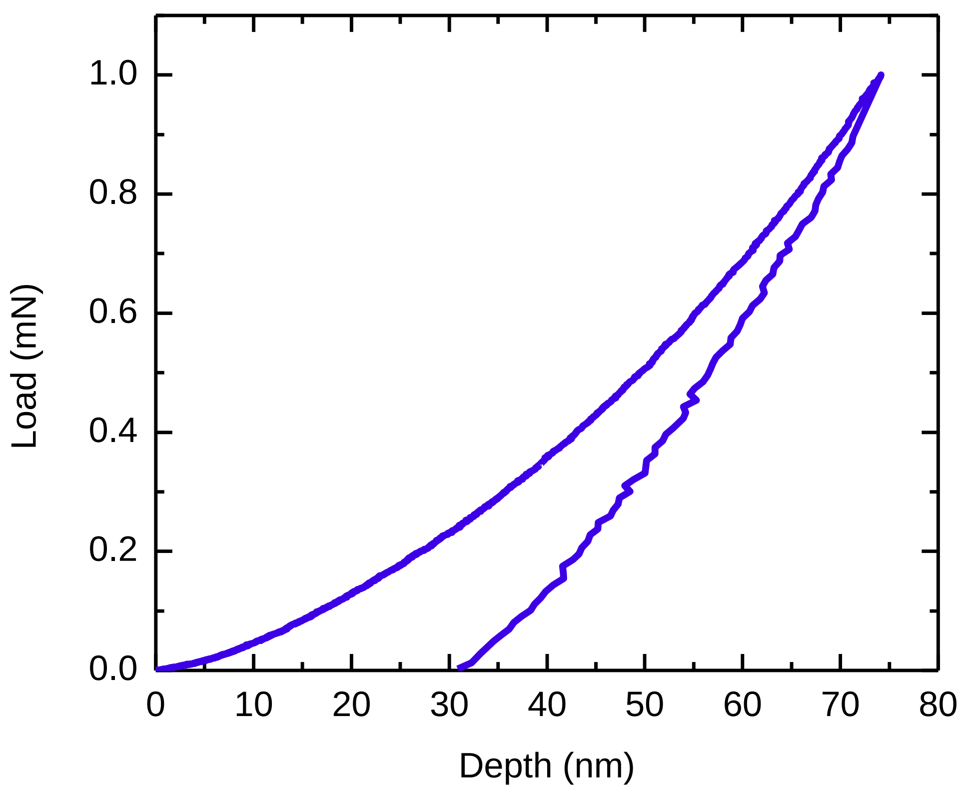

Figure S1. Indentation load-depth curve of the pure SiO_2 substrate. Here, no pop-in events are observed in the loading process.

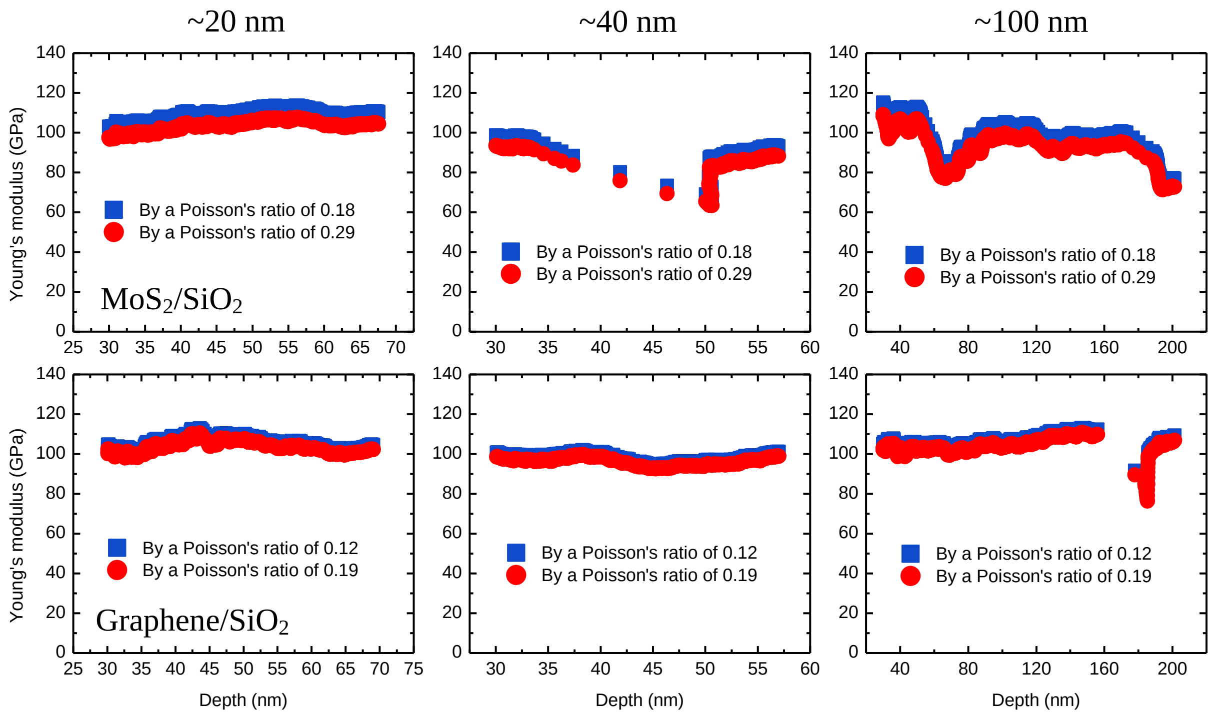

Figure S2. Young's modulus-indentation depth curves of the MoS_2/SiO_2 system (top panel) and the graphene/SiO_2 system (bottom panel) with different MoS_2 and graphene thicknesses (~20, ~40, and ~100 nm).

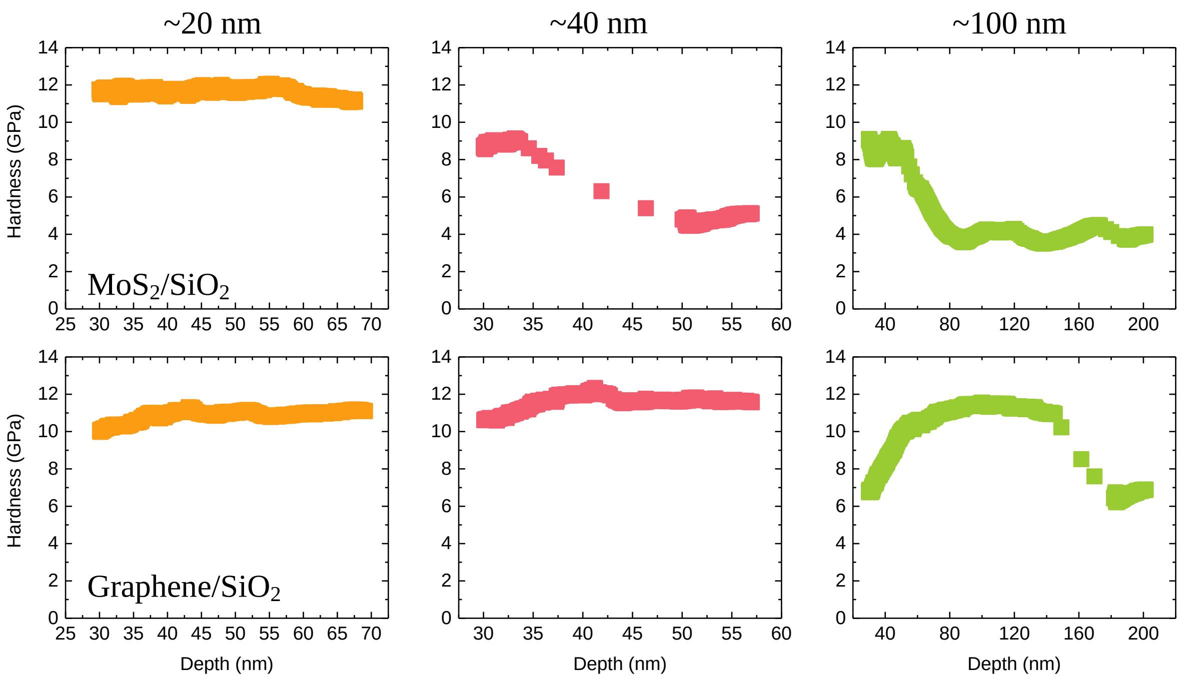

Figure S3. Hardness-indentation depth curves of the MoS_2/SiO_2 system (top panel) and the graphene/SiO_2 system (bottom panel) with different MoS_2 and graphene thicknesses (~20, ~40, and ~100 nm).

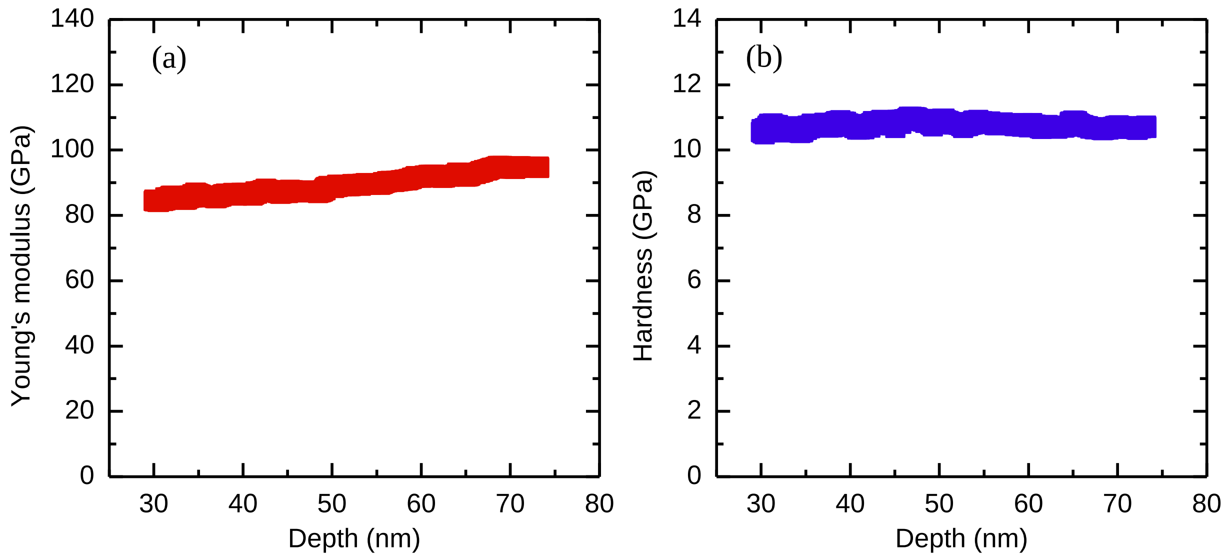

Figure S4. (a) Young's modulus-indentation depth curve and (b) hardness-indentation depth curve of pure SiO_2 substrate.

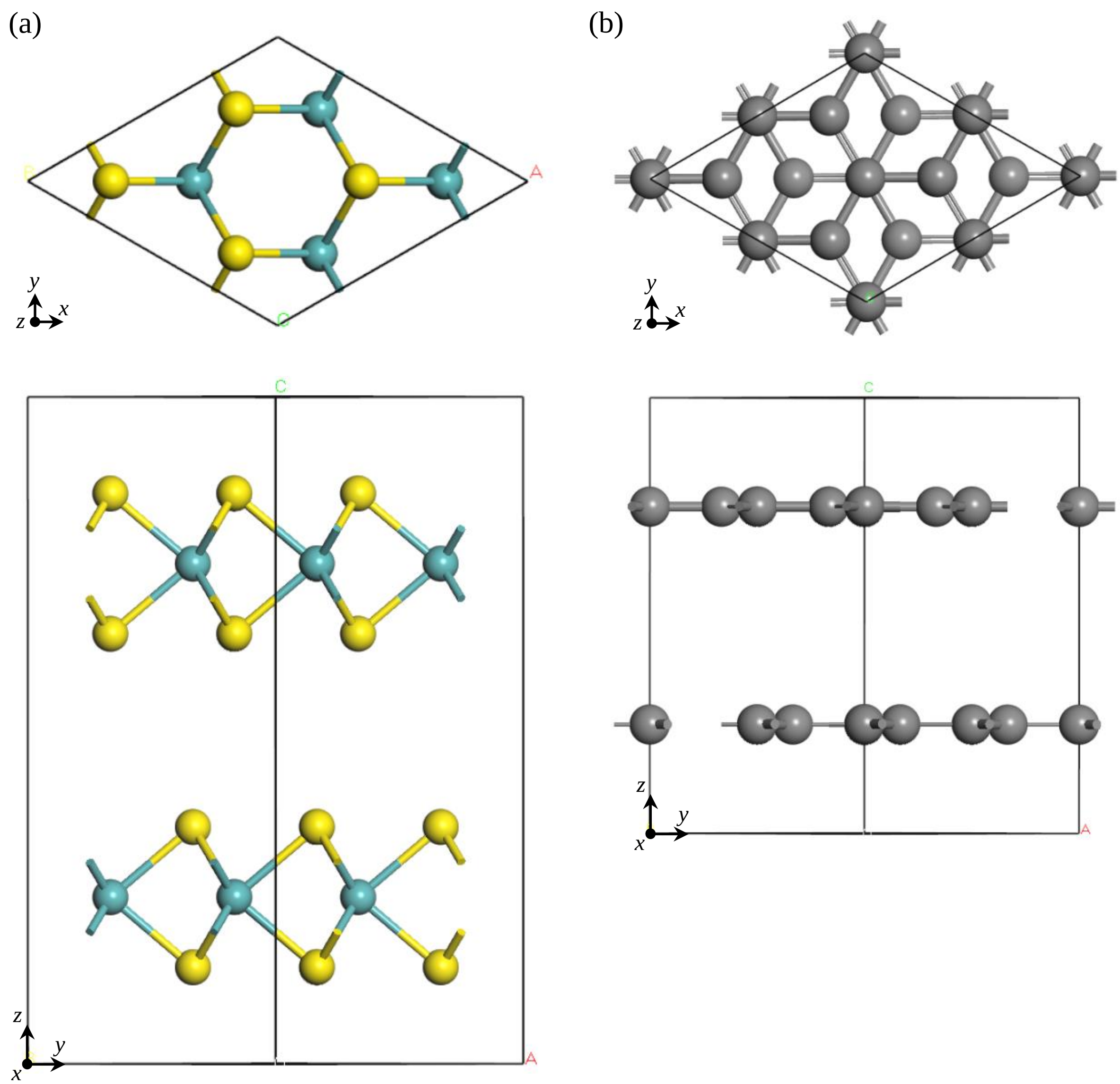

Figure S5. Stacking patterns of multilayer (a) MoS_2 and (b) graphene. Here, cyan, yellow and gray balls respresent Mo, S and C atoms, respectively.

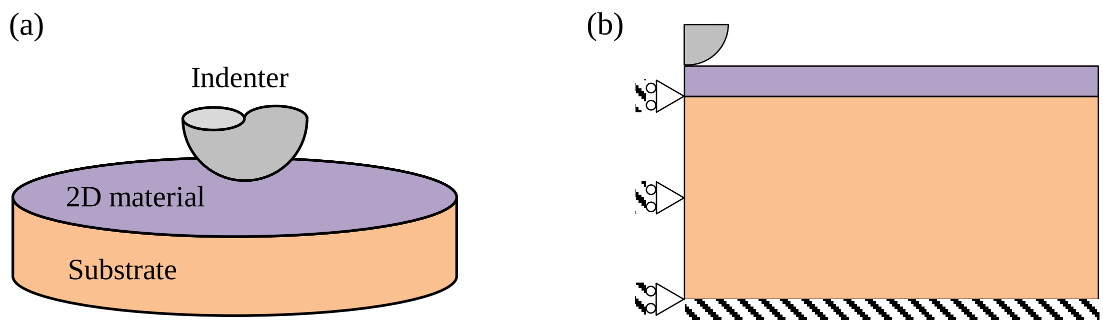

Figure S6. (a) Schematic of the 2D material/substrate model considered in FE simulations of the nanoindentation. (b) FE model of the 2D material/substrate system under the indentation load, in which both 2D material/substrate sample and indenter tip are simplified as the axial symmetric models.