nature portfolio

Peer Review File

Many-body van der Waals interactions in multilayer structures studied by atomic force microscopy

Corresponding Author: Professor Jun Yin

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The study taking into account of many-body effect of 2D materials vdW interactions has a number of flaws. Overall as compared to the literature in this field, the finings are rather incremental and there is a lack of theoretical calculations. I therefore suggest rejection of this manuscript. My detailed comments are as follows.

- The main claim of the paper is to have verified the many-body interaction between graphene and an AFM tip, which is either suspended or supported by various different materials. Additionally they claimed to have amended an overestimation of the graphene interaction by using a many-body DFT model , whilst trying to compare to experimental results. All these points are covered by Chiou et al. (reference [32]), which did equivalent AFM measurements of suspended graphene and graphene supported on Cu and SiO2 with corresponding DFT calculations. Chiou et al. did thus not only show the effective contribution of graphene to the many-body system, they also did it in a more rigorously, by using Lifshitz theory to quantify the Hamaker constant.

- A comparison based on Lifshitz theory allows for a better absolute quantification of the measurement results, compared to the relative comparison between different experimental systems as the authors of the manuscript did. Due to the simplicity of the experiment, calculations based on Lifshitz theory are far more suitable to predict interactions, which makes them paramount for the validation of DFT calculations and evaluation of experimental data. The fact that the authors didn't even attempt to include such calculations, makes it difficult to evaluate the paper in the given field of research.

- The only difference or acclaimed improvement is the increased consistency in measurement results, which also seem to be problematic. The authors compared Cu supported and suspended graphene with respective AFM data on graphite. The resulting ratios were fitted with a Gaussian distribution to extrapolate the mean values, but the corresponding standard deviations of the reported distributions do not match to the reported ones! Fig 1 d) should have an estimated standard derivation of +/- 0.1 and respectively Fig 2 c) one of +/-0.04. These values are up to 2 orders of magnitude larger thant the reported ones of +/- 0.001 and 0.0006 and are actually comparable to the variations found in Chiou et al. Without any explanation as to why they got such small deviations, given that their data is in direct contradiction to their claims, it makes it hard to objectively assess their data.

There are even further problems as for example a non-negligible, linear contribution to the adhesion force due to the elasticity of graphene falsifying the reported results, which is even visible in Fig S7 b), but the sheer fact that the authors reported contradictory data, in which the real data is comparable to past publications. Novelty is rather limited.

Reviewer #2

(Remarks to the Author)
The paper titled "Many-body van der Waals interaction on the surface of supported graphene" provides significant insights into the complex nature of van der Waals (vdW) interactions in a trilayer system comprising an atomic force microscopy (AFM) tip, graphene, and various substrates (metal and graphite). By combining experimental measurements and density functional theory (DFT) simulations, the study investigates the substrate's role in vdW interactions and the many-body effects within these systems. Below is an analysis of the paper, focusing on its strengths, areas for improvement, and potential

enhancements.
Strengths
The research tackles the challenging task of experimentally validating many-body vdW interactions, a topic often theorized but rarely observed. The utilization of supported graphene as a medium for studying these interactions is particularly astute. The paper incorporates a diverse array of experiments, including AFM force measurements on graphene supported by different substrates and freestanding graphene. Employing high vacuum conditions and thermal annealing to minimize external influences enhances the reliability of the results. The integration of DFT simulations alongside experimental data offers a robust understanding of the underlying physics. Comparisons between pairwise vdW theory and many-body dispersion (MBD) theory elucidate the significance of many-body effects in these systems.

Shortcomings and Areas for Improvement
The paper's dense technical language and some of the descriptions may pose challenges for readers unfamiliar with the subject matter. Simplifying the terminology and providing more detailed explanations of concepts and methodologies could improve accessibility. While the experiments are well-designed, the reliance on specific substrates and environmental conditions may limit the generalizability of the findings this needs to be addressed in more details. I find also important to indicate how possible future investigations could explore a broader range of substrates and environmental parameters to validate the observed effects universally. A more extensive comparison with prior research in the field is required to enhance the paper's context.

Highlighting the advancements made by this study in relation to existing literature. Particularly works like the one by Yu-Cheng Chiou et al. titled "Direct Measurement of the Magnitude of van der Waals Interaction of Single and Multilayer Graphene" should be mentioned. Doing so would provide a more comprehensive perspective since Chiou et al. also employ AFM and DFT simulations but concentrate on quantifying the vdW forces across single, double, and multi-layer graphene, examining the impact of supporting surfaces on these interactions. They provide a quantifiable measure of vdW forces across graphene layers and demonstrate how substrates can modulate these forces, thus affecting graphene's physical properties. Both studies showcase innovative approaches and comprehensive analyses in their investigation of vdW interactions, employing robust methodologies that combine experimental and simulation techniques. Each paper elucidates the theoretical and practical implications of their findings, contributing valuable insights into the design and optimization of 2D material-based devices and applications. Both studies rely on DFT simulations, which are subject to assumptions that could affect the generalizability of the results, such as the treatment of charge transfers and the accuracy of models used. Being able to do a better work in creating the context for the work would highlight the work novelty.

Expanding on the experimental methodologies, particularly the AFM experiment is important. At the current stage it would be impossible for an AFM expert to reproduce the results presented in the work. It is imperative to enhance the clarity and depth of the experimental parameters. Specifically, elucidating the operational methodology of the Atomic Force Microscopy (AFM) for force curve acquisition and justifying its selection are crucial aspects. Additionally, addressing the potential underestimation of adhesion force in the chosen operational mode is essential. While the normalization of data is a commendable practice, variations in overestimation across different samples should be acknowledged, as this may impact the range of applicability. While the fundamental essence of the reported outcomes is expected to remain unchanged, such considerations may offer a broader scope of validity. Noteworthy is your mention of maintaining the tip radius constant throughout the experiment, a commendable practice. However, direct measurement of tip radius using the methodology based on critical amplitude could provide further validation and accuracy to your findings. The same is valid for the DFT simulations. More details are necessary to enhance the credibility and reproducibility of the results. Providing more insights into computational parameters, the choice of exchange-correlation functionals, and model validation would strengthen the research's foundation.

While the paper briefly touches on the relevance of its findings to technologies like microelectromechanical systems and sensors, a more extensive discussion on potential applications and future research directions would inspire further studies and technological innovations.

Conclusion
The paper represents a significant advancement in comprehending many-body vdW interactions within supported graphene systems. Its astute experimental setup and comprehensive theoretical analysis offer fresh insights into the non-additive nature of substrate contributions and the significance of many-body effects. Addressing the identified areas for improvement and expanding certain aspects of the research would pave the way for future studies to delve deeper into the complexities of vdW interactions in two-dimensional materials and their technological applications.

Reviewer #3

(Remarks to the Author)
This paper presents combined experimental and theoretical investigations of many body van der Waals (vdW) interactions in multilayer structures.
Atomic force microscopy is exploited to estimate the tip adhesion to substrates characterized by different layer-composition, evidencing the effect of intermediate layers on the overall vdW adhesive force.

From the theoretical side, authors compare pairwise vdW forces with the many-body dispersion (MBD) model, which accounts for screening effects at the RPA level.

While this paper does not introduce new physics or surprising physical effects (see below), the combination of theory and experiment is novel in this specific context. The strength of this work resides in a convincing demonstration of previously predicted screening effects.

In this sense, the content of this paper might be suitable for publication on Nature Communications. However, major revision is needed to improve the manuscript before it meets the required quality standards.

Before further considering this work, the following points should be definitely addressed:

1-Many sentences are hard to interpret due to spelling errors and bad construction. Just a few examples:

line 41: inheriting from the rapid decay of vdW interactions with separation. (maybe "from" should be removed??)
line 52: makes the issue so complex that beyond the scope of pure vdW interaction.
line line 53: let alone the influence of nearly unavoidable contaminates?? (maybe contaminants) in ambient

Such linguistic problems make the article hard to review, and give a bad impression to readers.

2-The authors refer to the AFM tip as a "layer". However, the tip has finite size and this can have an impact on vdW forces.

3-The screening properties of graphene on inert substrates are well known from the theoretical viewpoint [JPCL 10, 2044-2050 (2019); PNAS 115, E10295-E10302 (2018); Carbon 139, 486-491 (2018); Phys. Rev. B 97, 241411(R) (2018)], and qualitatively agree with available experiments [ACS Nano 2014, 8, 12410–12417]. But no discussion is given here in spite of the close relation with this work.

4-While MBD actually accounts for many-body effects in finite-gap systems, it is known that low-dimensional metals or semi-metals can exhibit non-conventional asymptotic decay of the vdW interaction [PRL 96, 073201 (2006); Phys. Rev. X 4, 021040 (2014)]. The exact asymptotic decay is not captured by MBD due to charge confinements at quantum oscillators [JCTC 19, 6434-6451 (2023)]. These aspects deserve remark and justification.

5-It is not clear whether CVD growth eventually leads to high quality graphene or not here. Are there defects which could alter the electronic structure of graphene? Are there interstitial impurities between the layers? These aspect should be addressed in more detail.

6-Maybe the tip-substrate distance is easily estimated by experimentalists, but no detailed discussion is reported here.

7-Authors experimentally consider the maximum adhesion energy, and neglect the dependence of vdW forces on distance. The underlying reasons are understandable but should be discussed and justified.

8-In the case of suspended graphene, no estimate is given for the effect of the supporting graphitic structure, although AFM measurements are conducted close to the edge. What is the expected contribution?

9-What about the hybridization/charge transfer between graphene and the Cu layer? This should be discussed also in view of the available literature mentioned at point 3.

Reviewer #4

(Remarks to the Author)
This manuscript reports a careful experimental study of the vdW interaction of suspended/supported graphene with AFM tips. The main hypothesis is that the AFM tip can sense the substrate beneath graphene. The authors showed by AFM force measurement the small but definitive difference between tip-substrate interaction measured on Cu/graphene, graphite, and suspended graphene. Publication is recommended after the authors addressing the following concerns.

1. Early work has shown that surface contamination by airborne contaminant occurs rapidly on graphene (https://www.nature.com/articles/nmat3709) and such contamination persist under UHV conditions (https://doi.org/10.1016/j.elspec.2019.06.001). While the authors conducted mild thermal annealing in their work, it is not clear if such process actually remove surface contamination on the graphene samples.

2. The experimental procedure of coating the graphite microwell by graphene (Fig 2a) involves polymer assist transfer and it is known that thermal anneal of PMMA leave residues.

3. The theoretical model used H-terminated Si to represent the tip. This is not a realistic model and a -OH termination should be used instead. Given the sensitivity of the surface to the adhesion and the drastic difference in the polarity between -H and -OH termination, it might be meaningful to repeat some of the calculations using -OH terminated Si.

4. Many AFM images do not show the height color scale. AFM image should also be shown with appropriate z-scale to

highlight surface cleanness (or lack thereof).

5. Loading vs unloading. The authors state that the loading curves show no difference between different samples. This is very puzzling because the snap-to-contact is due to vdW attraction (since the authors claim that there is no capillary effect) and should be sensitive to the difference in the substrate. The very different behavior between loading vs unloading raises serious questions since the unloading force could also be impacted by other factors, such as contact area due to mechanical deformation of the substrate.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

Reviewer #3

(Remarks to the Author)
My comments have been addressed. I can recommend publication

Reviewer #4

(Remarks to the Author)
This revision has addressed many of my concerns, however, the following two still remains.

1. Surface cleanness: the FTIR is convincing but I'd suggest not to include the high resolution contact mode AFM image as an evidence. I believe that "atomic" resolution contact mode AFM imaging does not imply absence of molecular adsorbates on graphic surface. The contact mode tip does not have the sharpness to resolve individual carbon atoms, instead it resolves the underneath lattice structure collectively. If I'm not mistaken, such 'atomic' images (Fig R9) can be obtained on graphite substrates in air (where there is abundant water and hydrocarbon adsorbed on the surface), as long as the tip is stiff enough to brush the adsorbates away.
2. Force-distance curve: the authors claim that the difference of the force experienced by tip during the snap-to-contact region is buried within noise. Looking at the data, the force experienced by the tip during the snap-to-contact region is on the order of 1 nN (Fig 1c). The difference in the vdW force during tip snap-off is on the order of 10% (fig 1d). If we assume the same difference (certainly a big assumption) in force is experienced by the tip before snap-to-contact, that translates to 0.1 nN difference in force. With a tip having spring constant of 0.2N/m, this translates to 0.5 nm of difference in z-height, which should be easily resolved by modern AFMs. Maybe I missed something here (maybe force vs force gradient)? Regardless of the validity of my analysis above, this reviewer strongly suggests the authors include a discussion of the noise level of their instrument.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
I am happy with the rebuttal and in my opinion the authors have done the best they could

Reviewer #4

(Remarks to the Author)
Thank you for responding to my comments. My (hopefully the last) comment on the snap-on event: if the force after snap-on event is not reliable, can we learn anything from the z-height of the snap-on event? One would expect a slightly shift in the z-height threshold where is snap-on occurs.

Response to the comments of Reviewers

Changes made in the revision are marked by blue color.

Reply to Reviewer #1:

General remarks: *The study taking into account of many-body effect of 2D materials vdW interactions has a number of flaws. Overall as compared to the literature in this field, the findings are rather incremental and there is a lack of theoretical calculations. I therefore suggest rejection of this manuscript. My detailed comments are as follows.*

Reply: We find it disappointing that the reviewer gave such a negative comment. Indeed, there are several works about the vdW interaction of substrate-supported graphene. While the theoretical researches (PRB 97, 241411, 2018; PNAS 115, E10295, 2018; Carbon 139, 486, 2018) have predicted that graphene can partly screen the vdW interaction between an object located above graphene and the underlying substrate, the quantitative experimental studies of the many-body effect are still scarce. Chiou et al. (Langmuir 34, 12335 2018) have investigated the substrate contribution to the measured force on AFM tip, but they did not consider the many-body effect (refer to response to ***Comment 1*** for details). We have now provided a more extensive discussion on the related works in the revised manuscript to highlight the advancements of our work.

The work presented herein provides a comprehensive study that not only examines the substrate contribution but also delves deeper into the many-body effect of vdW interaction in the tip-graphene-substrate tri-layer, through a combination of experimental measurements and theoretical calculations. Experimentally, in contrast to previous experiments conducted in gaseous environments, the rigorous sample preparation, the atomically smooth sample surface, the absence of contaminants on graphene surface, the absence of impurities at graphene-substrate interface and the vacuum environment guarantee the robustness of our findings.

Theoretically, the underlying physics is elucidated by applying the many-body dispersion (MBD) theory, an advanced vdW method suitable for describing collective effects in systems with atomic scale feature sizes/separations. The MBD not only obtains a good consistency with the experiment findings, but also provide a picture on how collective quantum fluctuations give rise to the many-body effect. The pairwise method assuming additivity of vdW interaction is found to overestimate the substrate contribution. In the revision, we show that the Lifshitz theory can reflect the screening effect by graphene (refer to response to ***Comment 2*** for details). However, because of the assumption of continuum dielectric media, the Lifshitz theory is more suitable for a qualitative understanding instead of a quantitative description of systems with atomic scale feature sizes/separations.

Thus, this work is of significant advances compared to the previous ones and represents a solid verification of the many-body effect in such a unique system through combined experimental measurements and theoretical calculations.

Comment 1: *The main claim of the paper is to have verified the many-body interaction between graphene and an AFM tip, which is either suspended or supported by various different materials. Additionally, they claimed to have amended an overestimation of the graphene interaction by using a many-body DFT model, whilst trying to compare to experimental results. All these points are*

covered by Chiou et al. (reference [32]), which did equivalent AFM measurements of suspended graphene and graphene supported on Cu and SiO2 with corresponding DFT calculations. Chiou et al. did thus not only show the effective contribution of graphene to the many-body system, they also did it in a more rigorously, by using Lifshitz theory to quantify the Hamaker constant.

Reply: Chiou *et al.* (Langmuir 34, 12335, 2018) have made a pioneering contribution to understanding the substrate contribution to the vdW interaction between an AFM tip and graphene. However, no investigation has been made on the many-body effect (namely, because of collective effects, the total vdW energy of tip-graphene/substrate is not a summation of tip-graphene and tip-substrate vdW energies). For instance, Eq. 2($F \cong -\frac{A_{402}R}{6L^2} - \frac{A_{102}R}{6(L+b)^2}$) and Eq. 3 ($F \cong -\frac{A_{402}R}{6L^2} - \frac{A_{102}R}{6(L+b)^2}\left(\frac{n_1^2-n_4^2}{n_1^2+n_4^2}/\frac{n_1^2-n_0^2}{n_1^2+n_0^2}\right)$) of the Langmuir paper consider the force as a summation of the tip-graphene force and the tip-substrate force, neglecting the non-additivity. Evidently, the main findings presented in the current work cannot be encompassed by the Langmuir paper.

Comment 2: *A comparison based on Lifshitz theory allows for a better absolute quantification of the measurement results, compared to the relative comparison between different experimental systems as the authors of the manuscript did. Due to the simplicity of the experiment, calculations based on Lifshitz theory are far more suitable to predict interactions, which makes them paramount for the validation of DFT calculations and evaluation of experimental data. The fact that the authors didn't even attempt to include such calculations, makes it difficult to evaluate the paper in the given field of research.*

Reply: To address the concerns of the reviewer, we now try to qualitatively understand the many-body effect in the tip-graphene-substrate tri-layer via the Lifshitz theory. To properly apply the Lifshitz theory, it's crucial to carefully define the electromagnetic boundaries. As illustrated in **Fig. R1** (Supplementary Fig. 12 of the revised SI), graphene is considered as a continuum slab with a thickness of 3.3 Å and a semi-infinite Cu substrate is adopted. Then, the separation between the bottom surface of graphene slab and the Cu substrate is 1.65 Å, since the separation between the carbon plane and Cu surface is ~3.3 Å (PRB 79, 195425, 2009). Dielectric functions taken from previous literatures are applied.

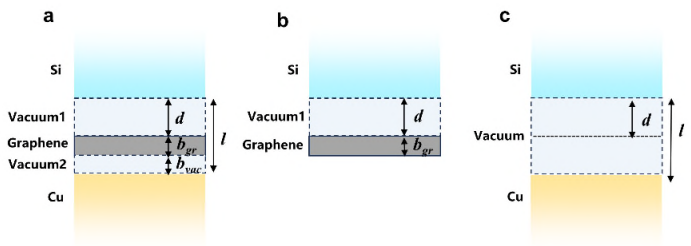

Figure R1. Illustration of models used in the Lifshitz theory for a qualitative understanding of vdW screening effect. Models used to calculate the vdW energy **a,** between semi-infinite silicon and graphene supported by semi-infinite Cu substrate, **b,** between silicon and graphene and **c,** between silicon and Cu substrate.

According to the Lifshitz theory calculations, the vdW energy between the tip and Cu-supported graphene is lower than a direct summation of tip-graphene and tip-Cu vdW energies, verifying the many-body character in the tri-layer (see the ratio of screening shown in **Fig. R2**).

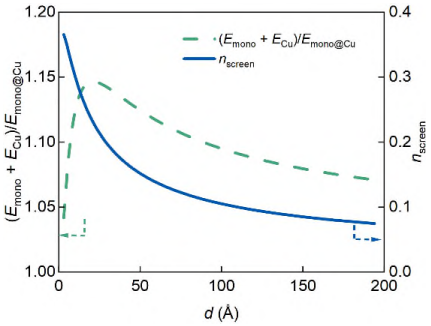

Figure R2. Ratio of vdW screening n_{screen} and ratio of energy. The green dashed line represents the energy ratio $(E_{mono}+E_{Cu})/E_{mono@Cu}$. The blue solid line is vdW screening ratio, expressed as $n_{screen} = 1 - (E_{mono@Cu} - E_{mono})/E_{Cu}$.

However, because of the assumption of continuum dielectric media, the Lifshitz theory is more suitable for providing a qualitative understanding instead of a quantitative description of systems with atomic scale feature sizes/separations. In contrast, the many-body dispersion (MBD) theory developed by Tkatchenko *et al.* is more suitable for considering the many-body effects in atomic scale systems and has been applied to reveal a series of novel vdW phenomena (Science 351, 1171 2016; Nat. Commun. 11,1651, 2020; Nat. Commun. 12, 137, 2021; Nat. Commun. 14, 8218, 2023; etc).

Comment 3: *The only difference or acclaimed improvement is the increased consistency in measurement results, which also seem to be problematic. The authors compared Cu supported and suspended graphene with respective AFM data on graphite. The resulting ratios were fitted with a Gaussian distribution to extrapolate the mean values, but the corresponding standard deviations of the reported distributions do not match to the reported ones! Fig 1 d) should have an estimated standard derivation of +/- 0.1 and respectively Fig 2 c) one of +/-0.04. These values are up to 2 orders of magnitude larger than the reported ones of +/- 0.001 and 0.0006 and are actually comparable to the variations found in Chiou et al. Without any explanation as to why they got such small deviations, given that their data is in direct contradiction to their claims, it makes it hard to objectively assess their data.*

Reply: We apologize for the lack of explanation about the deviation value. The reported ± 0.001 and ± 0.0006 are the fitting error of mathematical expectation value (x_c), not the standard deviations (σ), as illustrated in **Fig. R3**. As pointed out by the reviewer, the standard deviations obtained from the Gaussian fits in Fig. 1d and Fig. 2c are 0.113 and 0.028, respectively. We now show the standard deviation value in the revision with clear statements to prevent further misleading.

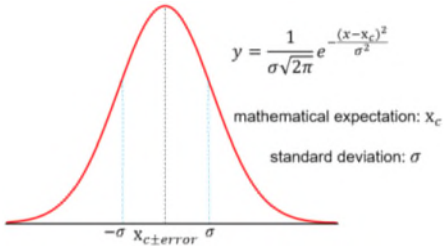

Figure R3. Illustration of the Gaussian function used to fit the distribution of ratio of critical adhesion forces.

Comment 4: *There are even further problems as for example a non-negligible, linear contribution to the adhesion force due to the elasticity of graphene falsifying the reported results, which is even visible in Fig S7 b), but the sheer fact that the authors reported contradictory data, in which the real data is comparable to past publications. Novelty is rather limited.*

Reply: To minimize the influence of elastic deformation of suspended monolayer graphene, we have taken the critical adhesion force measured at the suspended edge regions as a reference for comparison with that measured on bulk graphite. As shown in **Fig. R4,** the critical adhesion force measured at the suspended edge regions is lower relative to that measured at the hole center, indicating that the effect of elasticity has been significantly reduced.

Moreover, the main conclusion discussed in the manuscript is based on the ratio of critical adhesion forces measured on top of mono@Cu to that measured on top of bulk graphite, for which the effect of elasticity shall be limited.

Thus, the reported experimental data show a good consistency, being well interpreted by the many-body effect as revealed by the MBD theory and qualitatively confirmed by the Lifshitz theory.

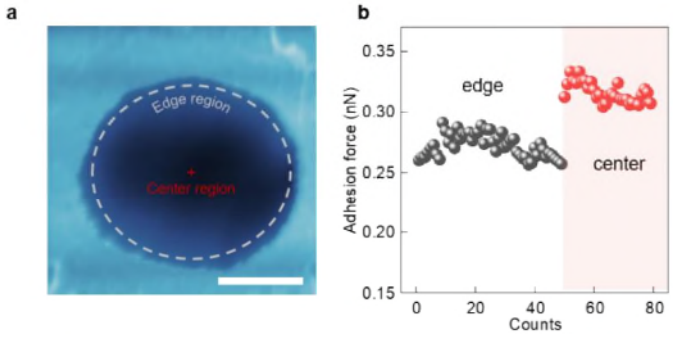

Figure R4. Dependence of critical adhesion force on the measuring position for suspended graphene. **a,** AFM topography of graphene suspended over a graphite hole with a diameter of 2.5 μm. Scale bar, 1 μm. **b,** Critical adhesion force measured on suspended graphene at the hole center and ~100 nm away from the hole edge.

Reply to Reviewer #2:

General remarks: *The paper titled "Many-body van der Waals interaction on the surface of supported graphene" provides significant insights into the complex nature of van der Waals (vdW) interactions in a trilayer system comprising an atomic force microscopy (AFM) tip, graphene, and various substrates (metal and graphite). By combining experimental measurements and density functional theory (DFT) simulations, the study investigates the substrate's role in vdW interactions and the many-body effects within these systems. Below is an analysis of the paper, focusing on its strengths, areas for improvement, and potential enhancements.*

The research tackles the challenging task of experimentally validating many-body vdW interactions, a topic often theorized but rarely observed. The utilization of supported graphene as a medium for studying these interactions is particularly astute.

The paper incorporates a diverse array of experiments, including AFM force measurements on graphene supported by different substrates and freestanding graphene. Employing high vacuum conditions and thermal annealing to minimize external influences enhances the reliability of the results. The integration of DFT simulations alongside experimental data offers a robust understanding of the underlying physics. Comparisons between pairwise vdW theory and many-body dispersion (MBD) theory elucidate the significance of many-body effects in these systems.

Conclusion

The paper represents a significant advancement in comprehending many-body vdW interactions within supported graphene systems. Its astute experimental setup and comprehensive theoretical analysis offer fresh insights into the non-additive nature of substrate contributions and the significance of many-body effects. Addressing the identified areas for improvement and expanding certain aspects of the research would pave the way for future studies to delve deeper into the complexities of vdW interactions in two-dimensional materials and their technological applications.

Reply: We thank the reviewer for fully confirming the experimental and theoretical advancements of this work.

Comment 1: *The paper's dense technical language and some of the descriptions may pose challenges for readers unfamiliar with the subject matter. Simplifying the terminology and providing more detailed explanations of concepts and methodologies could improve accessibility. While the experiments are well-designed, the reliance on specific substrates and environmental conditions may limit the generalizability of the findings this needs to be addressed in more details. I find also important to indicate how possible future investigations could explore a broader range of substrates and environmental parameters to validate the observed effects universally. A more extensive comparison with prior research in the field is required to enhance the paper's context.*

Reply: We thank the reviewer for providing useful suggestions, based on which the quality of our work has been further improved.

The accessibility of the manuscript has been improved through simplifying the terminology and providing more detailed explanations of concepts and methodologies. The advancement of our study is also highlighted through extensive comparative analysis with prior researches.

To show the generalizability of our findings, we have measured the critical adhesive forces exerted on the AFM tip by Ni-supported monolayer graphene (mono@Ni) and Cu-supported

monolayer BN (BN@Cu), as illustrated in **Fig. R5**. The preliminary results verify that the Ni substrate also contributes to the adhesive force on the graphene surface, and the adhesive forces measured on the surface of monolayer BN are also influenced by the substrates. However, we note that other factors, such as charge transfer, interface spacing may play an important role therein, especially in the case of mono@Ni. Further study is required to clarify the influence of these factors, which is beyond the scope of this work.

Regarding to the environment, to reveal the intrinsic contribution by the substrates, the experiments was strictly conducted in a vacuum environment, since the results obtained in gaseous environments can be easily distorted due to the adsorption of hydrocarbons and water (Nat. Mater. 12, 925, 2013; Langmuir 18, 8045, 2002). Investigation of the interface interaction of tri-layer systems in other environments is crucial for practical applications, but it would be influenced by combined effects.

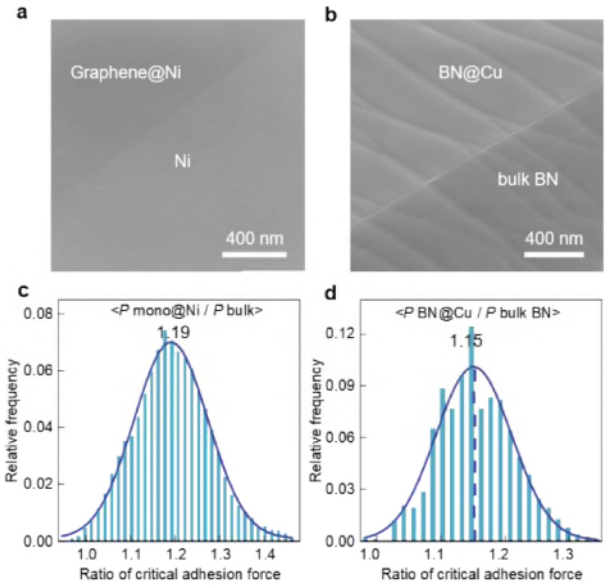

Figure R5. Critical adhesive force measured in other tri-layer systems. a, b, Scanning Electron Microscope images of monolayer graphene on Ni substrate (a) and monolayer BN on Cu substrate (b). **c,** Histogram distribution of the ratio of critical adhesion forces measured on mono@Ni to that on bulk graphite. The standard deviation is 0.195. **d,** Histogram distribution of the ratio of critical adhesion forces measured on BN@Cu to that on bulk BN. The standard deviation is 0.059.

Comment 2: *Highlighting the advancements made by this study in relation to existing literature. Particularly works like the one by Yu-Cheng Chiou et al. titled "Direct Measurement of the Magnitude of van der Waals Interaction of Single and Multilayer Graphene" should be mentioned. Doing so would provide a more comprehensive perspective since Chiou et al. also employ AFM and DFT simulations but concentrate on quantifying the vdW forces across single, double, and multi-layer graphene, examining the impact of supporting surfaces on these interactions. They provide a quantifiable measure of vdW forces across graphene layers and demonstrate how substrates can modulate these forces, thus affecting graphene's physical properties. Both studies showcase innovative approaches and comprehensive analyses in their investigation of vdW interactions, employing robust methodologies that combine experimental and simulation techniques. Each paper elucidates the theoretical and practical implications of their findings, contributing valuable*

insights into the design and optimization of 2D material-based devices and applications. Both studies rely on DFT simulations, which are subject to assumptions that could affect the generalizability of the results, such as the treatment of charge transfers and the accuracy of models used. Being able to do a better work in creating the context for the work would highlight the work novelty.

Reply: Thanks for this suggestion. In the revised manuscript, we have situated the current study within the broader context of existing literatures, with a particular emphasis on highlighting the pioneering work conducted by *Chiou et al*. (Langmuir 34, 12335 2018), in order to establish the advancements made by the present investigation.

Chiou *et al.* have quantified the vdW forces across single, double, and multi-layer graphene and examined the impact of supporting substrates on these interactions. However, they did not investigate the many-body effect as revealed here. Both the DFT-D2 simulations and Eqs. 2 and 3 ($F \cong -\frac{A_{402}R}{6L^2} - \frac{A_{102}R}{6(L+b)^2}$, $F \cong -\frac{A_{402}R}{6L^2} - \frac{A_{102}R}{6(L+b)^2}\left(\frac{n_1^2-n_4^2}{n_1^2+n_4^2}/\frac{n_1^2-n_0^2}{n_1^2+n_0^2}\right)$) in the Langmuir paper fully neglect the non-additivity of vdW interactions.

Experimentally, to overcome the limitations of previous experiments, such as the unavoidable surface contamination and adsorbed water in gaseous environments, here we have achieved the atomically smooth sample surfaces, the absence of contaminants on graphene surface and the absence of impurities at graphene-substrate interface, while also conducting the force measurements under vacuum condition. Moreover, the MBD simulation is performed to rationalize the measured ratio of critical adhesion forces and to highlight the many-body effect neglected by *Chiou et al.*

Comment 3: *Expanding on the experimental methodologies, particularly the AFM experiment is important. At the current stage it would be impossible for an AFM expert to reproduce the results presented in the work. It is imperative to enhance the clarity and depth of the experimental parameters. Specifically, elucidating the operational methodology of the Atomic Force Microscopy (AFM) for force curve acquisition and justifying its selection are crucial aspects. Additionally, addressing the potential underestimation of adhesion force in the chosen operational mode is essential. While the normalization of data is a commendable practice, variations in overestimation across different samples should be acknowledged, as this may impact the range of applicability. While the fundamental essence of the reported outcomes is expected to remain unchanged, such considerations may offer a broader scope of validity. Noteworthy is your mention of maintaining the tip radius constant throughout the experiment, a commendable practice. However, direct measurement of tip radius using the methodology based on critical amplitude could provide further validation and accuracy to your findings. The same is valid for the DFT simulations. More details are necessary to enhance the credibility and reproducibility of the results. Providing more insights into computational parameters, the choice of exchange-correlation functionals, and model validation would strengthen the research's foundation.*

Reply: As suggested by the reviewer, more details of experimental methodologies and DFT simulations are provided in the Methods and Supplementary Information.

The tip-sample adhesion was evaluated through static force curves, which is the most

established and direct way to access the tip-surface force interactions. In static force curves, the tip remains in a quasi-equilibrium state, allowing for the reliable determination of critical adhesion forces. Compared to dynamic methods, such as frequency modulation and amplitude modulation, the process of associating frequency or amplitude information with the tip-sample force inevitably introduces a plethora of assumptions and approximations (Appl. Phys. Lett. 84, 1801, 2004; Rev. Sci. Instrum. 91, 103702, 2020), which could be fully avoided in interrupting the data acquired through the static mode.

Surface roughness is a common and major source of underestimation in adhesion force measurements (Langmuir, 18, 8045, 2002). To eliminate the influence of surface roughness, rigorous sample preparation was conducted, which guarantees atomically flat surfaces for both graphene/copper and graphite (Supplementary Fig. 1).

As suggested by the reviewer, the tip radii of the two AFM tips were evaluated through critical amplitude method (Rev. Sci. Instrum. 83, 043707, 2012). As summarized in **Fig. R6**, there was no significant change in the tip radii for both tips during hundreds of force curve tests, in line with the SEM imaging results.

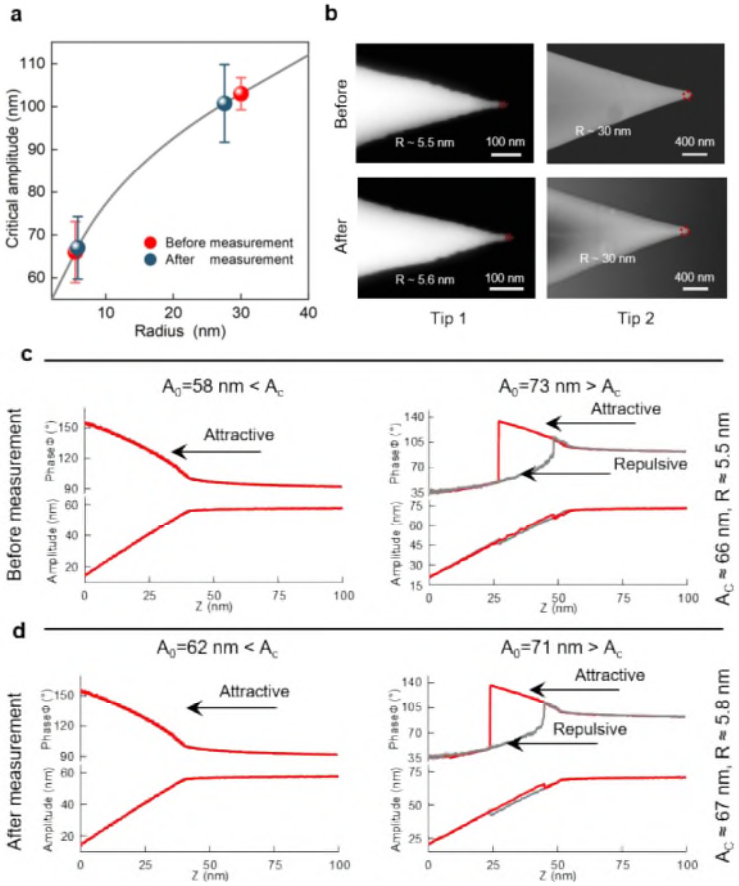

Figure R6. In situ determination of tip radius by the critical amplitude method. a, The change in tip critical amplitude (A_c) and the corresponding tips radius (AN-CSG01) after performing 300 force curves. **b,** SEM images of the two tips used for the tests. **c, d** Typical amplitude and phase versus distance curves recorded at different free amplitudes (A_0). When A_0 is smaller than A_c, the tip remains in the attractive regime with phase always above 90°. When A_0 is set to be above A_c, the tip exhibits a transition from the attractive to the repulsive regime. The Red and gray curves represent the loading and unloading stage, respectively.

Comment 4: *While the paper briefly touches on the relevance of its findings to technologies like microelectromechanical systems and sensors, a more extensive discussion on potential applications and future research directions would inspire further studies and technological innovations.*

Reply: Extensive discussion on potential applications and further research directions have been made in the revision.

Surface adhesion plays an important role in the stacking of vdW heterostructures and the controlled exfoliation of two-dimensional materials, as manifested by recent works (Nat. Nanotech. 14, 567, 2019; Nat. Electron. 7, 17, 2024; Sci. Adv. 6, eabc6601, 2020). The way reported here for modulating the surface adhesion of 2D materials could inspire novel approaches to guide surface molecular assembly and construct hybrid vdW structures.

As suggested by the reviewer, further investigations on a broader range of substrates and 2D materials would extend the generalizability of our findings. It would also be interesting to reveal the influence of other factors, such as interfacial spacing and interface intercalation, on the surface vdW interaction of 2D materials.

Comment 5: *Conclusion*

The paper represents a significant advancement in comprehending many-body vdW interactions within supported graphene systems. Its astute experimental setup and comprehensive theoretical analysis offer fresh insights into the non-additive nature of substrate contributions and the significance of many-body effects. Addressing the identified areas for improvement and expanding certain aspects of the research would pave the way for future studies to delve deeper into the complexities of vdW interactions in two-dimensional materials and their technological applications.

Reply: We thank the reviewer for this positive assessment and insightful suggestions.

Reply to Reviewer #3:

General remarks: *This paper presents combined experimental and theoretical investigations of many body van der Waals (vdW) interactions in multilayer structures. Atomic force microscopy is exploited to estimate the tip adhesion to substrates characterized by different layer-composition, evidencing the effect of intermediate layers on the overall vdW adhesive force. From the theoretical side, authors compare pairwise vdW forces with the many-body dispersion (MBD) model, which accounts for screening effects at the RPA level. While this paper does not introduce new physics or surprising physical effects (see below), the combination of theory and experiment is novel in this specific context. The strength of this work resides in a convincing demonstration of previously predicted screening effects.*
In this sense, the content of this paper might be suitable for publication on Nature Communications. However, major revision is needed to improve the manuscript before it meets the required quality standards.

Reply: We thank the reviewer for the positive assessment and helpful suggestions. We have improved the quality of this work according to the insightful comments/suggestions.

Comment 1: *Many sentences are hard to interpret due to spelling errors and bad construction. Just a few examples:*
line 41: inheriting from the rapid decay of vdW interactions with separation. (maybe "from" should be removed??)
line 52: makes the issue so complex that beyond the scope of pure vdW interaction.
line 53: let alone the influence of nearly unavoidable contaminates?? (maybe contaminants) in ambient
Such linguistic problems make the article hard to review, and give a bad impression to readers.

Reply: Thanks for pointing out those language issues. We have revised the manuscript thoroughly.

Comment 2: *The authors refer to the AFM tip as a "layer". However, the tip has finite size and this can have an impact on vdW forces.*

Reply: Thank the reviewer for the insightful suggestion.

It is true that the finite size of the tip affects the measured vdW forces. To eliminate the impact of tip size on the reported results, the normalization of data with respect to the bulk graphite (P_{bulk}) is found to be an effective approach. For instance, although the data presented in Supplementary Figs. S6 and S8 were acquired by different tips with distinct inert materials (silicon or diamond-like-carbon) and radii (ranging from 10 nm to 40 nm), the obtained ratios of $P_{mono@Cu}/P_{bulk}$ are all close to 1.10.

Theoretically, we have revealed that the tip-sample interaction is dominated by the neighboring layers in contact, for example, the predicted P_{mono}/P_{bulk} is around 0.93. Considering that thickness of H-passivated silicon layer is significantly larger than that of the monolayer graphene, it is reasonable to expect the tip-sample interaction to be dominated by the H-passivated silicon layer in contact with graphene, and validity of the simulation model in investigating the ratios of critical adhesion force. Another practical reason for considering a “layer” rather than a sphere with a comparable size to the AFM tips in the DFT simulation is due to the

limitation of amount of computation. We deeply appreciate the reviewer's understanding.

Comment 3: *The screening properties of graphene on inert substrates are well known from the theoretical viewpoint [JPCL 10, 2044-2050 (2019); PNAS 115, E10295-E10302 (2018); Carbon 139, 486-491 (2018); Phys. Rev. B 97, 241411(R) (2018)], and qualitatively agree with available experiments [ACS Nano 2014, 8, 12410–12417]. But no discussion is given here in spite of the close relation with this work.*

Reply: As suggested by the reviewer, the revised manuscript has been put better into context with existing work in the literatures.

We have now highlighted the theoretical contributions by (PRB 97, 241411, 2018; PNAS 115, E10295, 2018; Carbon 139, 486, 2018; JPCL 10, 2044, 2019; JPCL 12, 4993, 2021) in the main text. The pioneering experimental work on vdW screening (ACS Nano 2014, 8, 12410) is also highlighted now. We note that the measurement of critical adhesive forces at short separations reported here, combined with the measurements in a longer distance range (23 ~ 20 nm) by (ACS Nano 2014, 8, 12410), jointly provide convincing evidences on the many-body effect.

Comment 4: *While MBD actually accounts for many-body effects in finite-gap systems, it is known that low-dimensional metals or semi-metals can exhibit non-conventional asymptotic decay of the vdW interaction [PRL 96, 073201 (2006); Phys. Rev. X 4, 021040 (2014)]. The exact asymptotic decay is not captured by MBD due to charge confinements at quantum oscillators [JCTC 19, 6434-6451 (2023)]. These aspects deserve remark and justification.*

Reply: Thanks for pointing out these novel asymptotic behaviors of vdW interaction. The related works have been discussed in the revised manuscript. We think that the recent development of the many-body dispersion (MBD) method incorporating the effect of electrical conductivity (JCTC 19, 6434, 2023) represents a significant milestone achievement in this field. We are hopeful that we will be able to gain access to this new version of the MBD method in the near future.

Comment 5: *It is not clear whether CVD growth eventually leads to high quality graphene or not here. Are there defects which could alter the electronic structure of graphene? Are there interstitial impurities between the layers? These aspects should be addressed in more detail.*

Reply: The quality of the graphene sample was characterized by Raman spectrum. As shown in **Fig. R7**, the absence of D peak (≈1350 cm^{-1}), which corresponding to the defects, indicates the high quality of graphene samples. Moreover, spherical aberration corrected transmission electron microscope image with perfect hexagonal carbon lattice further confirms its high quality.

As has been commonly observed (Carbon 77, 1082, 2014; Adv. Mater. 27, 1376, 2015; JACS 133, 12536, 2011), the as-prepared Cu-supported graphene is free of interstitial impurities, since the interference between the copper lattice and graphene lattice were clearly discerned.

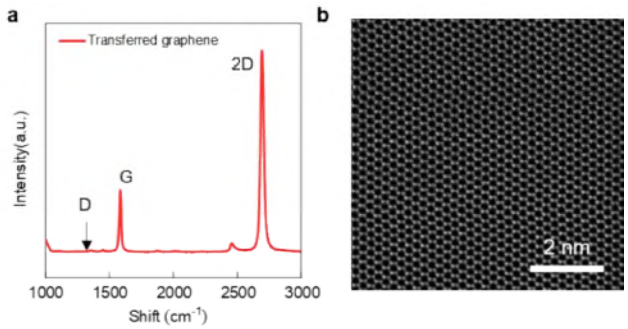

Figure R7. Characterization of CVD grown graphene. a, Raman spectrum of CVD grown monolayer graphene transferred onto SiO_2/Si substrate**. b,** Spherical aberration corrected transmission electron microscope (AC-TEM) image of CVD grown monolayer graphene**.**

Comments 6: *Maybe the tip-substrate distance is easily estimated by experimentalists, but no detailed discussion is reported here.*
Authors experimentally consider the maximum adhesion energy, and neglect the dependence of vdW forces on distance. The underlying reasons are understandable but should be discussed and justified.

Reply: In fact, it is difficult to determine the actual tip-sample distance from the AFM measurement. The displacement presented in the force curves does not reflect the actual tip-sample distance but reflects the change of the distance between the fixed end of AFM cantilever and the sample surface.

To determine the adhesion force with a high accuracy, soft AFM cantilevers with an elastic constant close to 0.2 N/m was adapted in our tests. During loading, once the surface force gradient exceeds the elastic constant of the cantilever, 'snap-to-contact' due to the instability of the cantilever happens (**Fig. R8a**) and the force-distance information is lost in this region. At even large tip-sample distances, the vdW force is too weak to be detected in our measurements, as shown in Fig. R8c.

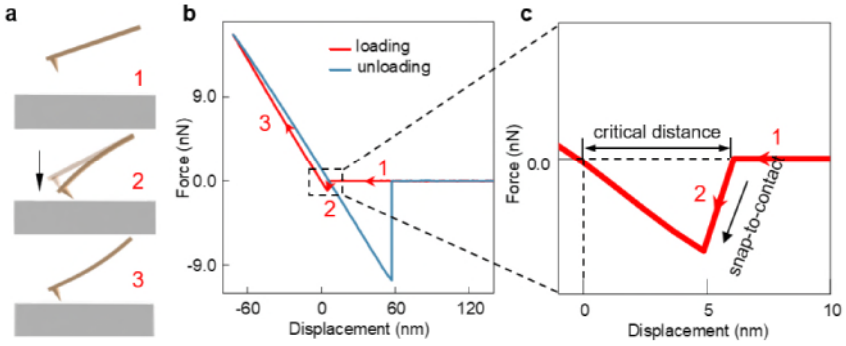

Figure R8. Force versus displacement curve measured on graphene-Cu system.

Comment 7: *In the case of suspended graphene, no estimate is given for the effect of the supporting graphitic structure, although AFM measurements are conducted close to the edge. What is the expected contribution?*

Reply: For the suspended graphene, AFM measurements were performed on suspended regions nearly 100 nm away from the graphite edge, where the vdW force from the graphite is expected to be greatly attenuated due to its rapid decay with distance. Thus, we can safely ignore its

influence here.

Comment 8: *What about the hybridization/charge transfer between graphene and the Cu layer? This should be discussed also in view of the available literature mentioned at point 3.*

Reply: As graphene is physically adsorbed on Cu substrate, the charge transfer between graphene and Cu is not significant, as confirmed by the limited change in plane-average charge density upon the formation tip-mono@Cu complex from isolated tip, monolayer graphene, and Cu, as shown in Figs. 3a and 3b. It is in consistence with the weak bonding between graphene and Cu reported previously (PRL, 101, 026803, 2008).

As discussed in the manuscript, such a weak bonding between graphene and Cu does not result in notable difference in the energies and pressures contributed by PBE interactions (see Fig. 3c, d). These results are consistent with the fact reported in Carbon 139, 486, 2018, that the screening capability of physically adsorbed graphene is not significantly modified by the weak graphene-substrate charge transfer. The relevant discussion has been supplemented in the revised manuscript.

Reply to Reviewer #4:

General remarks: *This manuscript reports a careful experimental study of the vdW interaction of suspended/supported graphene with AFM tips. The main hypothesis is that the AFM tip can sense the substrate beneath graphene. The authors showed by AFM force measurement the small but definitive difference between tip-substrate interaction measured on Cu/graphene, graphite, and suspended graphene. Publication is recommended after the authors addressing the following concerns.*

Reply: We thank the reviewer for the positive assessment and providing helpful comments/suggestions.

Comment 1: *Early work has shown that surface contamination by airborne contaminant occurs rapidly on graphene (https://www.nature.com/articles/nmat3709) and such contamination persist under UHV conditions (https://doi.org/10.1016/j.elspec.2019.06.001). While the authors conducted mild thermal annealing in their work, it is not clear if such process actually remove surface contamination on the graphene samples.*

Reply: To verify the efficiency of mild thermal annealing in removing the airborne contaminants, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was conducted before and after the vacuum thermal annealing. The results confirm that annealing at 200°C for 1h can efficiently remove hydrocarbon contaminants. The remaining, but notably weakened, peaks corresponding to -CH_2 and -CH_3 group maybe contributed to the unavoidable re-adsorption of the hydrocarbon due to the re-exposure to air during ATR-FTIR tests.

In addition to the thermal annealing, contact mode imaging of the targeted region at large normal loads was also performed to further remove the hydrocarbon residuals, if there is any (Appl. Phys. Lett., 100, 073110, 2012). As shown in **Fig. R9**, lattices of graphene can be readily got, indicating the absence of surface contaminants. More details on treatments taken to remove surface contaminants have now been provided in the revised manuscript.

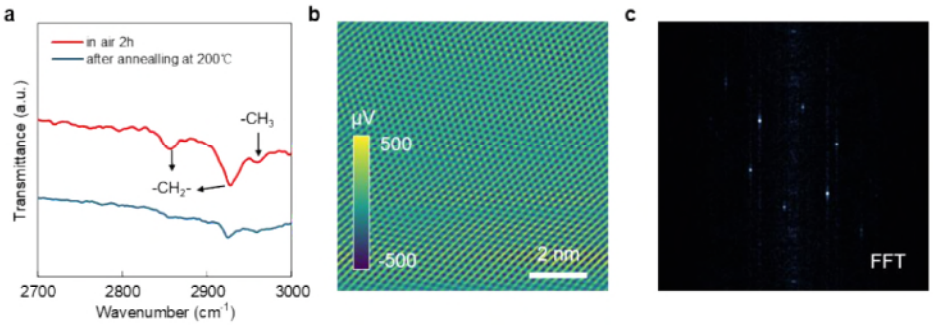

Figure R9. Surface cleanness of graphene samples. a, ATR-FTIR spectrum of graphene on Cu sample. The peaks at 2850 cm^{-1}, 2930 cm^{-1} and 2950^{-1} are assigned to the symmetric and asymmetry stretching of the -CH_2- group and asymmetric stretching of -CH_3 group, respectively. **b,** The AFM lattice image of graphene surface. **c,** Corresponding FFT pattern, indicating a lattice constant of 0.249 nm.

Comment 2: *The experimental procedure of coating the graphite microwell by graphene (Fig 2a) involves polymer assist transfer and it is known that thermal anneal of PMMA leave residues*

Reply: As mentioned above, the residual PMMA can also be efficiently removed by scraping the

sample surface using contact mode at large normal loads (see **Fig. R10**). This is a well-established method (Appl. Phys. Lett., 100, 073110, 2012). The lattice image of graphene supported on graphite shown in **Fig. R10c** confirms the atomically cleanness of the surface.

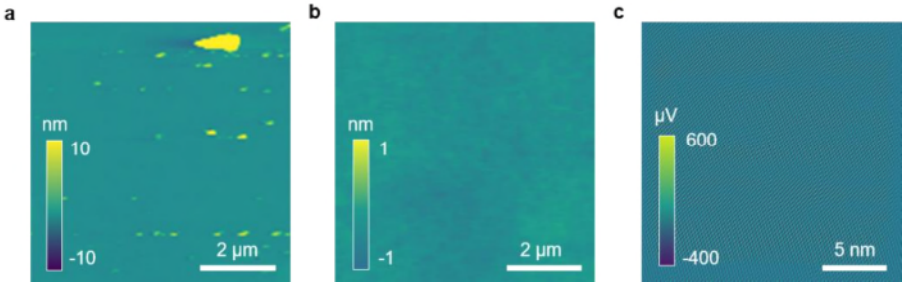

Figure R10. Removing PMMA residue on graphite. a, Residuals left on graphite surface after annealing at 400℃. **b,** Topography image of graphite surface after in-situ scraping. **c,** Lattice image of the sample.

Comment 3: *The theoretical model used H-terminated Si to represent the tip. This is not a realistic model and a -OH termination should be used instead. Given the sensitivity of the surface to the adhesion and the drastic difference in the polarity between -H and -OH termination, it might be meaningful to repeat some of the calculations using -OH terminated Si.*

Reply: Thanks for this suggestion. We have conducted DFT-MBD simulations considering an OH-terminated silicon layer. As shown in **Fig. R11**, the ratio of binding energy $E_{mono@Cu}/E_{bulk}$ (1.128) calculated with OH-terminated Si layer is comparable to that calculated with H-terminated Si layer (1.121), verifying that H-terminated Si or OH-terminated Si has limited effect on the calculation results.

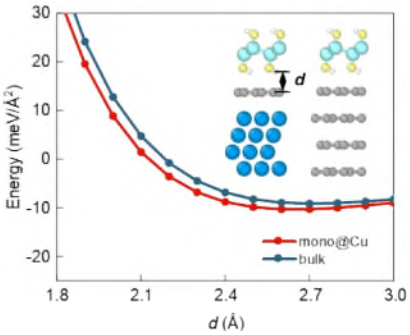

Figure R11. The interlayer binding energies of the SiOH-mono@Cu and SiOH-bulk graphite interfaces, as a function of distance.

Comment 4: *Many AFM images do not show the height color scale. AFM image should also be shown with appropriate z-scale to highlight surface cleanness (or lack thereof).*

Reply: We thank the reviewer for the careful review of the manuscript. We have added the height color bar with z-scale for all the AFM images.

Comment 5: *Loading vs unloading. The authors state that the loading curves show no difference between different samples. This is very puzzling because the snap-to-contact is due to vdW attraction (since the authors claim that there is no capillary effect) and should be sensitive to the difference in the substrate. The very different behavior between loading vs unloading raises serious questions since the unloading force could also be impacted by other factors, such as contact area*

due to mechanical deformation of the substrate.

Reply: It is true that, in principle, there should be a difference during the loading process as well. However, to determine the adhesion force with a high accuracy, soft AFM cantilevers with an elastic constant only around 0.2 N/m was adapted. Such a low elastic constant leads to a large tip-sample distance of ~6 nm corresponding to the 'snap-to-contact' (**Fig. R12c**), which happens when the surface force gradient exceeds the elastic constant of the cantilever. At such large tip-sample distances, the vdW force between the tip and the sample is hard to be detected, submerged in the noise of the measurements, as shown in Fig. **R12c**.

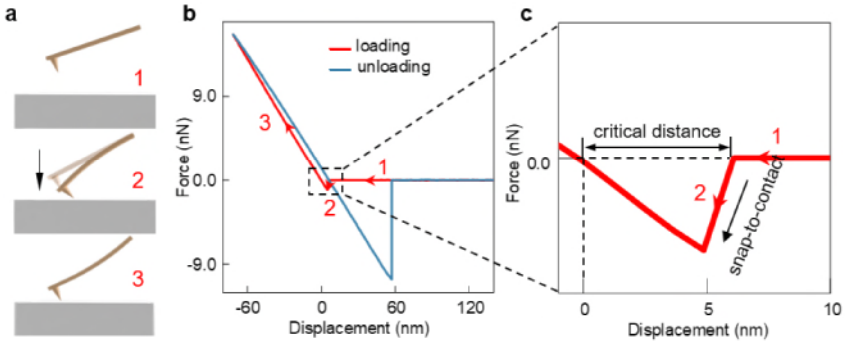

Figure R12. Force versus displacement curve measured on graphene-Cu system.

Response to the comments of Reviewers

Changes made in the revision are marked by blue color.

Reply to Reviewer #2:

Note: Reviewer #2 provided confidential remarks. The following comments are the summary shared by the editor.

Comment 1: *In their confidential comments, reviewer #2 let us know that several of their original comments have not been fully addressed. In particular, while relevant literature has been added in the revision, reviewer #2 comments that the discussion of Ref. [38] (Chiou et al., Langmuir 34, 12335 (2018)) mentioned by both reviewer #1 and #2 is lacking in depth in the current rebuttal, as while multibody effects were not explicitly discussed in [38], the experimental samples and data contained the same effects showing the same phenomena as the present work.*

Reply: Ref. [38] is now discussed in depth with more details in the revision. We note that Chiou's work pioneers the investigation on the substrate contribution to the surface vdW adhesion of atomically thin materials. Especially, the dynamic bimodal AFM and amplitude modulation AFM allows for the high throughput mapping of Hamaker coefficient, a coefficient proposed by Hamaker for quantifying the strength of the vdW interactions between two homogenous bodies.

Besides the substrate contributions, we moved forward to reveal the many-body effect therein. To achieve such a goal, careful sample preparation and astute experimental setup were adapted to eliminate distortion from surface/interface contamination, which is inevitable in ambient tests demonstrated by Chiou's work. The distortion induced by the contamination could prevent reliable investigation of the intrinsic interface vdW interface and consequently the many-body effect. It is confirmed by our experiment during the revision. We compared the surface adhesion of a sample under ambient and vacuum conditions, and found a significant increase in adhesion and a decrease in the ratio of $P_{mono@Cu}/P_{bulk}$ due to exposure to air, as shown in **Figure R1.**

In the theoretical aspect, Chiou *et al.* had understood the substrate contribution using the DFT-D2 and the Lifshitz theory. Nevertheless, the many-body effect cannot be considered by the D2 method that assumes pairwise additivity. To describe the substrate contribution via the Lifshitz theory, Chiou *et al.* derived a simplified Hamaker-like equation assuming a summation of tip-graphene force and tip-substrate force. Such treatment is very concise and straightforward, however, at the expense of neglecting the non-additivity. To theoretically understand the many-body effect, we here resort to the many-body dispersion theory, obtaining an agreement with the experimental measurement and showing a consistency with the full Lifshitz theory.

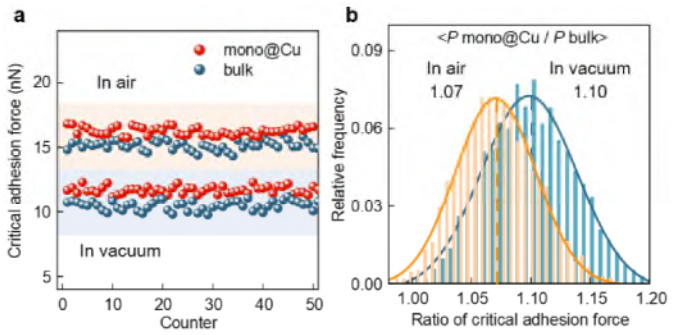

Figure R1. Surface adhesion of sample measured in vacuum and ambient. a, Critical adhesive force detected on mono@Cu and bulk graphite in air (orange shaded region) and vacuum (blue shaded region). **b,** Histograms distribution of $P_{mono@Cu}/P_{bulk}$ measured in air (orange) and vacuum (blue). The solid lines are Gaussian fits. The standard deviations are 0.034 and 0.040, respectively.

Comment 2: *In addition, reviewer #2 finds that the statement of tip-sample adhesion evaluation through static force curves being the most established and direct method to assess tip-surface-force interactions is not properly acknowledging extensive AFM literature that establishes and validates frequency and amplitude modulation techniques. In this regard, comparative analysis is needed to establish the performance of the approach.*

Furthermore, reviewer #2 comments that several comments about theoretical and experimental methodologies lacks detail and justification, such as the underestimation of adhesion force and selection criteria for specific methodologies which require more thorough explanation to ensure reproducibility and robustness of results.

Reply: Indeed, dynamic force spectroscopy techniques, including bimodal, frequency and amplitude modulation techniques, have showed great advantages in reconstructing the tip-sample force and force-spectra mapping (*J. Appl. Phys.* 129, 134302, 2021; *Nat. Nanotechnol.* 7, 217, 2012; *Nanoscale* 13, 17428, 2021; *ACS Nano* 18, 18683, 2024). Especially, compared to the quasi-static force curves, dynamic AFM compensates for the limitation that cantilever instability leads to loss of information within a few nanometres of tip-sample distance, and shows a great ability to quantitatively characterize and map the Hamaker coefficient between two homogeneous bodies.

However, the force field of the multilayer system investigated here is expected to varies from that well established for two homogeneous bodies. As shown in **Figure R2**, we acquired the force spectrum between an AFM tip and graphene/Cu by frequency modulation (FM) AFM. The deduced force curve (**Figure R2b**) cannot be well described by $F = RH/6d^2$, which is commonly adapted for describing the sphere-plane vdW interaction.

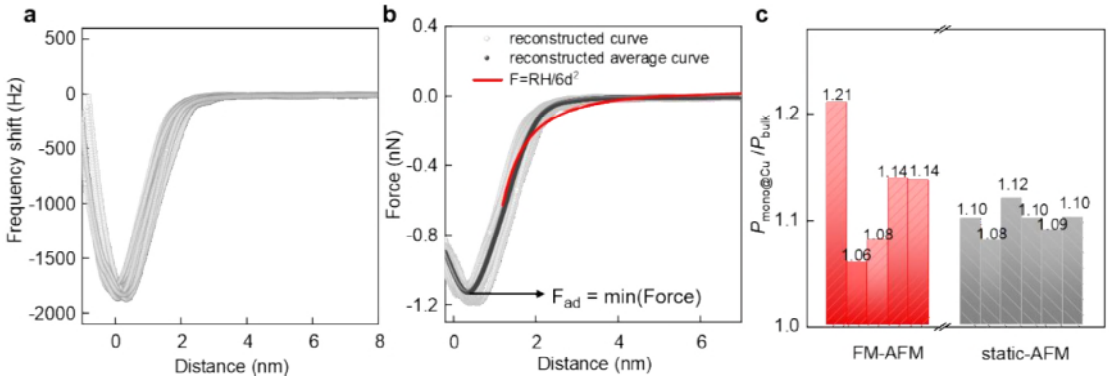

Figure R2. Force curves obtained from frequency modulation AFM. a, Frequency shift versus distance curves obtained from the FM-AFM. **b,** Reconstructed force versus distance curves using Sader-Jarvis method (*Appl. Phys. Lett.* 84, 1801, 2004). **c,** Ratios of critical adhesion force of the mono@Cu to that of the bulk graphite measured through FM-AFM (red bars) and static-AFM (gray bars). Each value is obtained through Gaussian fitting of more than 400 data of $P_{mono@Cu}/P_{bulk}$.

Due to the challenge in quantitative interpretation of the force-distance relationship for such multilayer systems, we focus on investigating the critical adhesion force in this work. Another reason is that the substrate contrition to the critical adhesion force is more notable, as the vdW interaction decays rapidly with distance. In this regards, quasi-static force curve is more appropriate to determine the critical adhesion force, which can be directly assessed from the force curve following Hooke's law. In contrast, obtaining the critical adhesion force from dynamic force spectrum require a full-range integration of the force spectrum before the contact between tip and sample, following implicit functions with a critical approximation (*Appl. Phys. Lett.* 84, 1801, 2004; *Nanotechnology* 20, 165703, 2009). Such integration process may lead to accumulation of the test

errors and large variation of the deduced adhesion force. We also determined the critical adhesion force through FM-AFM, and the results are summarized in **Figure R2c.** The deduced $P_{mono@Cu}/P_{bulk}$ ratio through FM-AFM ranges from 1.06 to 1.21, showing a significant larger variation compared with that determined by the quasi-static force curves.

The underestimation of adhesion force due to surface roughness has been verified experimentally (*Langmuir* 27, 9972, 2011; *Nanoscale,* 7, 10760, 2015; *Appl. Surf. Sci.* 562, 149976, 2021). The Rabinovich model (*J. Colloid Interf. Sci.* 232, 10, 2000), You's model (*Langmuir* 29, 9104, 2013) and Sun's model (*Appl. Surf. Sci.* 562, 149976, 2021) have also theoretically derived the effect of sample surface roughness on tip-sample adhesion. We plotted the normalized adhesion force vs. surface roughness of mono@Au samples predicted by these models in **Figure R3.** It is common in all these models that ~ 0.4 nm surface roughness of the mono@Au sample leads to a reduction in the tip-sample adhesion force, although the reduction ratio varies greatly between models. Thus, we focused on the CVD grown mono@Cu samples in the manuscript, which are of atomically flat surface similar to that of graphite (**Figure R4).**

Besides the above discussions, more details regarding to the theoretical and experimental methodologies have also been provided in the revised manuscript and Supplementary information to ensure reproducibility and robustness of results. To further justify the performance of the MBD, we cite the literatures those have investigated the interlayer interactions of vdW crystals using the MBD (*Proc. Natl. Acad. Sc.* 115, E10295, 2018; *Phys. Rev. Lett.* 114, 096101, 2015), in the Methods section.

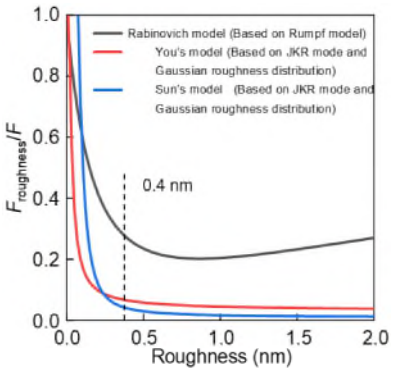

Figure R3. Roughness adhesion model. $F_{roughness}/F$ is the ratio of adhesion on tip-sample (rough) and tip-sample (smooth).

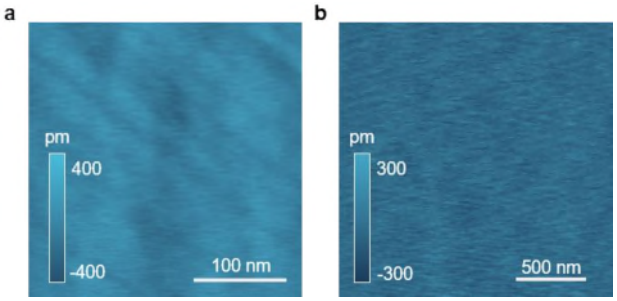

Figure R4. Surface roughness of the samples. a, b, Topography image of graphene on Cu **(a)** and bulk graphite (**b**). The roughness is around 70-80 pm for both the samples.

Reply to Reviewer #4:

General remarks: *This revision has addressed many of my concerns, however, the following two still remains.*

Reply: We thank the reviewer for the suggestions, which have been incorporated into the revision.

Comment 1: *Surface cleanness: the FTIR is convincing but I'd suggest not to include the high-resolution contact mode AFM image as an evidence. I believe that "atomic" resolution contact mode AFM imaging does not imply absence of molecular adsorbates on graphic surface. The contact mode tip does not have the sharpness to resolve individual carbon atoms, instead it resolves the underneath lattice structure collectively. If I'm not mistaken, such 'atomic' images (Fig R9) can be obtained on graphite substrates in air (where there is abundant water and hydrocarbon adsorbed on the surface), as long as the tip is stiff enough to brush the adsorbates away.*

Reply: Indeed, such 'atomic' images can be obtained on graphite substrates in air if the tip is stiff enough. Thus, the atomic resolution image alone is not sufficient to support the absence of adsorbates, although we supposed that the high vacuum environment prevents the re-adsorb of the adsorbates onto the sample surface. To prevent possible misleading, we have removed the high-resolution AFM image as the reviewer suggested.

Comment 2: *Force-distance curve: the authors claim that the difference of the force experienced by tip during the snap-to-contact region is buried within noise. Looking at the data, the force experienced by the tip during the snap-to-contact region is on the order of 1 nN (Fig 1c). The difference in the vdW force during tip snap-off is on the order of 10% (fig 1d). If we assume the same difference (certainly a big assumption) in force is experienced by the tip before snap-to-contact, that translates to 0.1 nN difference in force. With a tip having spring constant of 0.2N/m, this translates to 0.5 nm of difference in z-height, which should be easily resolved by modern AFMs. Maybe I missed something here (maybe force vs force gradient)? Regardless of the validity of my analysis above, this reviewer strongly suggests the authors include a discussion of the noise level of their instrument.*

Reply: We are sorry for the lack of clarity in discussing the snap-to-contact process. The snap-to-contact represents the instability of the cantilever as the surface force gradient exceeds its spring constant, and only the force before and after the snap-to-contact can be detected. The ~1 nN force is the force experienced by the tip AFTER the snap-to-contact and forming contact with the sample. A more detailed explanation of the snap-to-contact is illustrated in **Figure R6**.

The noise level of the force curve can be extracted from the region with tip far away from the sample, and is found to be around ± 0.03 nN, as illustrated in **Figures R5c**. Major sources of the noise include cantilever Brownian motion due to thermal fluctuations, mechanical noise from the environment and optical shot noise. The force signal detected BEFORE the snap-to-contact is comparable to the noise level (**Figures R5b**), thus the potential difference contributed by the substrate is easily lost.

The force experienced by tip during the snap-to-contact undergoes a sudden increase from point B to point C, as illustrated in **Figure R6a**, corresponding to point 1 to point 2 in **Figure R5**. Ideally, the Z positions of point 1 and 2 in **Figure R5** should be the same. However, they are different due to continuous changing of the piezo displacement during the measurement and limited data-acquiring speed. Given the large slop of the F(D) curve at point C in **Figure R6a**, such

a variation in Z would lead to a large uncertainty of the measured F_c. Thus, the detected 1 nN force AFTER the snap-to-contact cannot be used to investigate the substrate contribution as well.

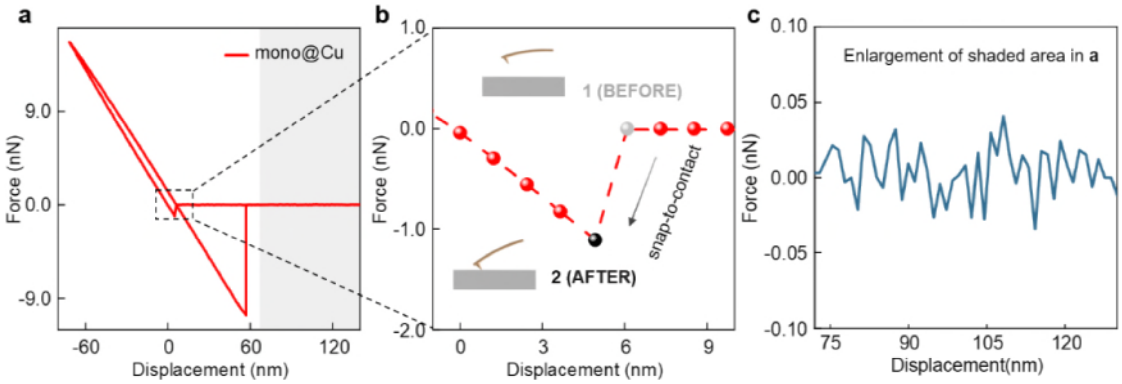

Figure R5. Force versus displacement curve measured on graphene-Cu system. a, Typical force versus displacement curve**. b,** Enlarged view to highlight the 'snap-to-contact' process at the loading stage. **c,** Enlarged view of the shaded region in **a** to show the measurement noise.

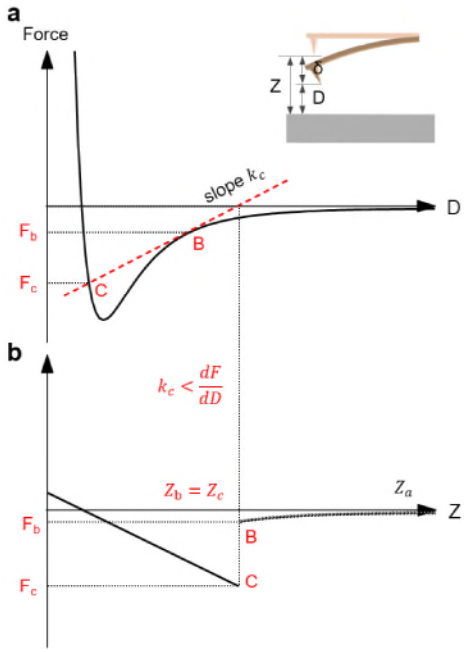

Figure R6. a, Schematic of the tip-sample interaction F(D), D is the tip-sample distance. The slope of dotted line is equal to the cantilever spring constant. The force values F_b and F_c are the ordinates of the intersections B and C between F(D) and the dashed line**. b,** Graphical construction of the force–displacement curve measured by AFM. It is assigned to the Z, Z = D+δ, where Z is the distance between the sample surface and the rest position of the cantilever, δ is the cantilever deflection. The distances Z_b and Z_c are given by the intersection between the dotted line and the horizontal axis. Copyright © 2016, Springer Nature. With permission of Springer. (B. Cappella, *Mechanical properties of polymers measured through AFM force-distance curves,* Springer International Publishing, 2016, Springer Nature).

Response to the comments of Reviewer

Reply to Reviewer #4:

Comment: *My (hopefully the last) comment on the snap-on event: if the force after snap-on event is not reliable, can we learn anything from the z-height of the snap-on event? One would expect a slightly shift in the z-height threshold where is snap-on occurs.*

Reply: We thank the reviewer for careful consideration. Ideally, the z-height threshold corresponding to the snap-on event is expected to different for varied substrates. However, during the force curve measurement, the tip approaches the sample continuously and the exact z-height threshold cannot be acquired precisely due to the limited data acquiring speed. As shown in Fig. R1b, the distance between adjacent data-points of the force curve is more than 1 nm. Thus the expected shift in z-height threshold cannot be distinguished.

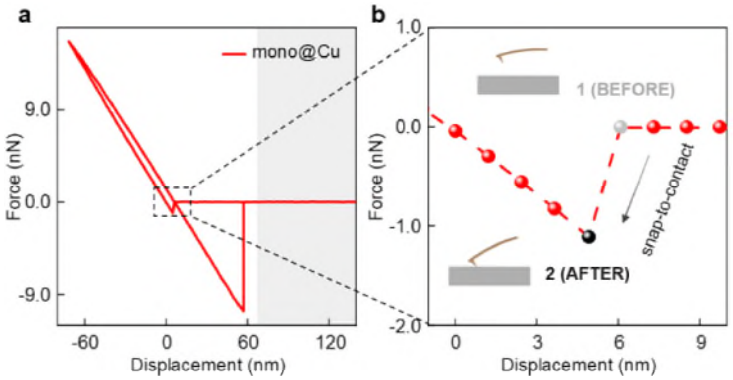

Figure R1. Force versus displacement curve measured on graphene-Cu system. a, Typical force versus displacement curve**. b,** Enlarged view to highlight the 'snap-to-contact' process at the loading stage.