Unfolding the Origin of Superlubricity at Macroscale with Graphene-Nanodiamond Ensembles

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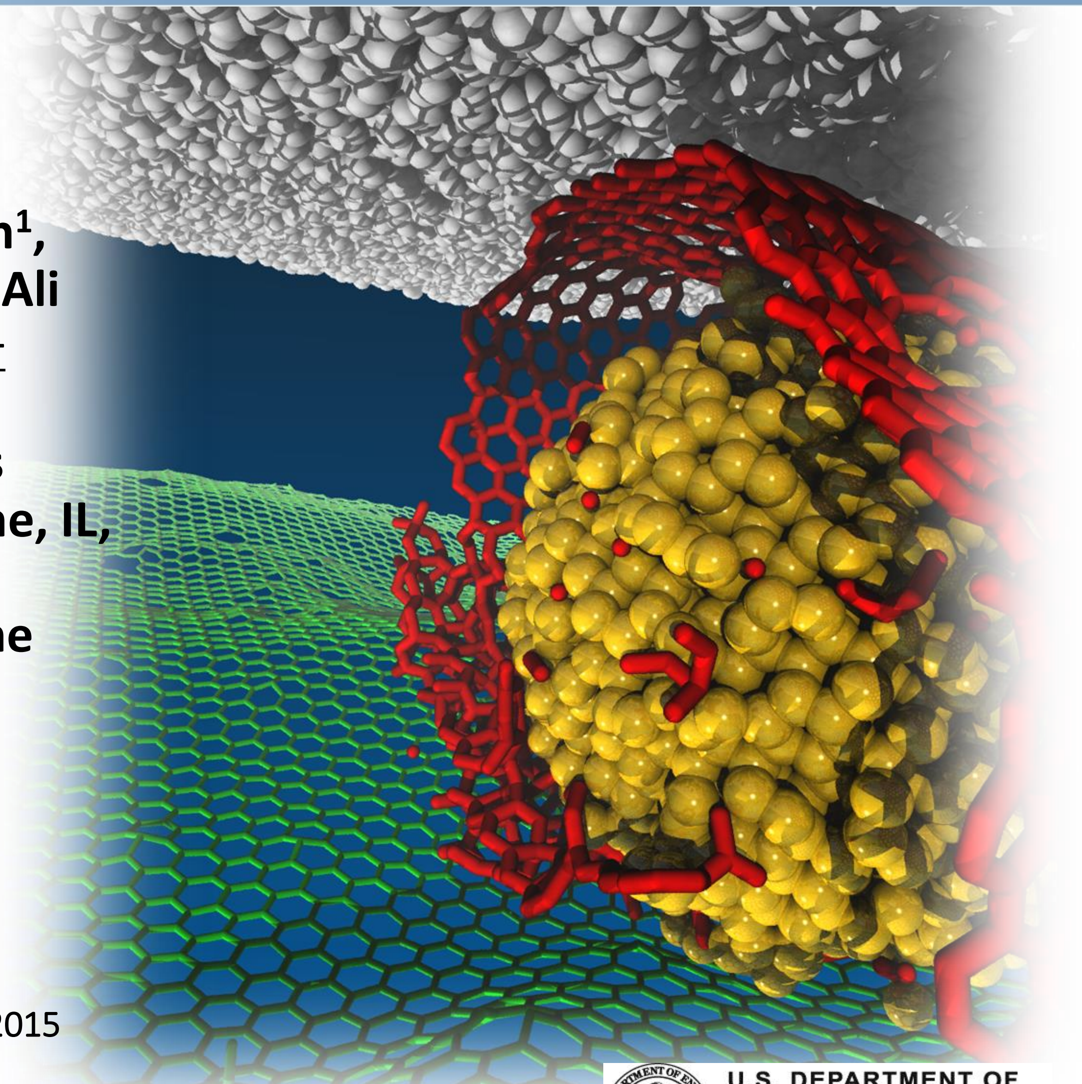
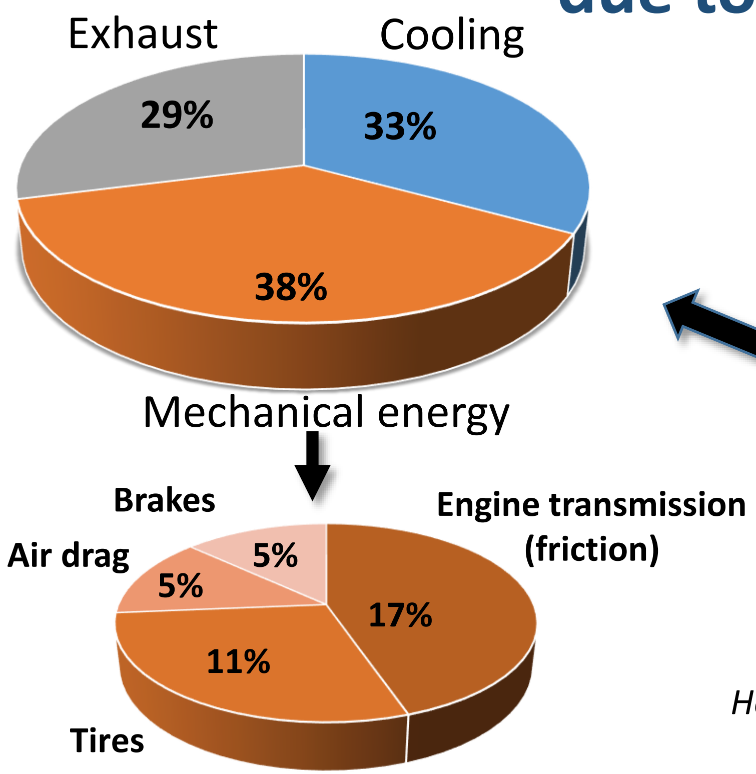
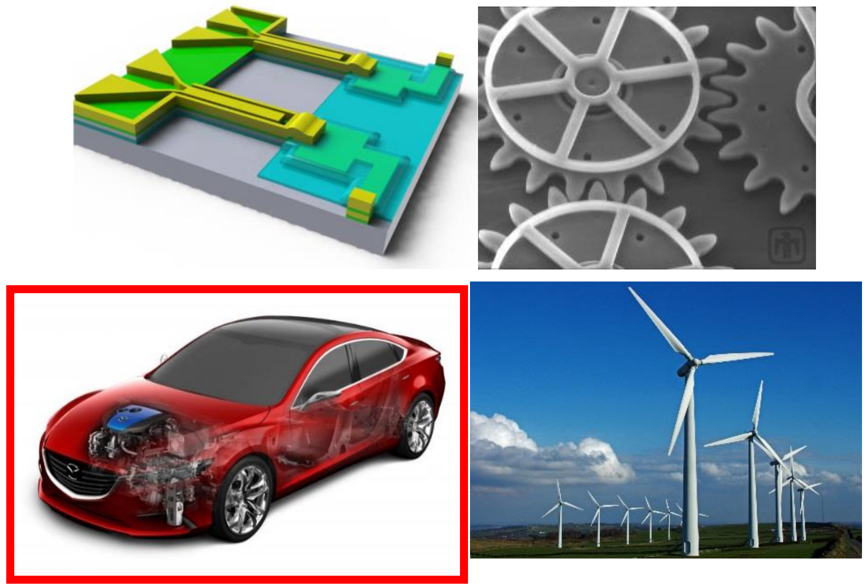


PSE Open Mic Talk, Argonne, July 21, 2015

Superlubricity core team at Argonne

Grand challenges of 21st century: Reducing energy loss due to the friction





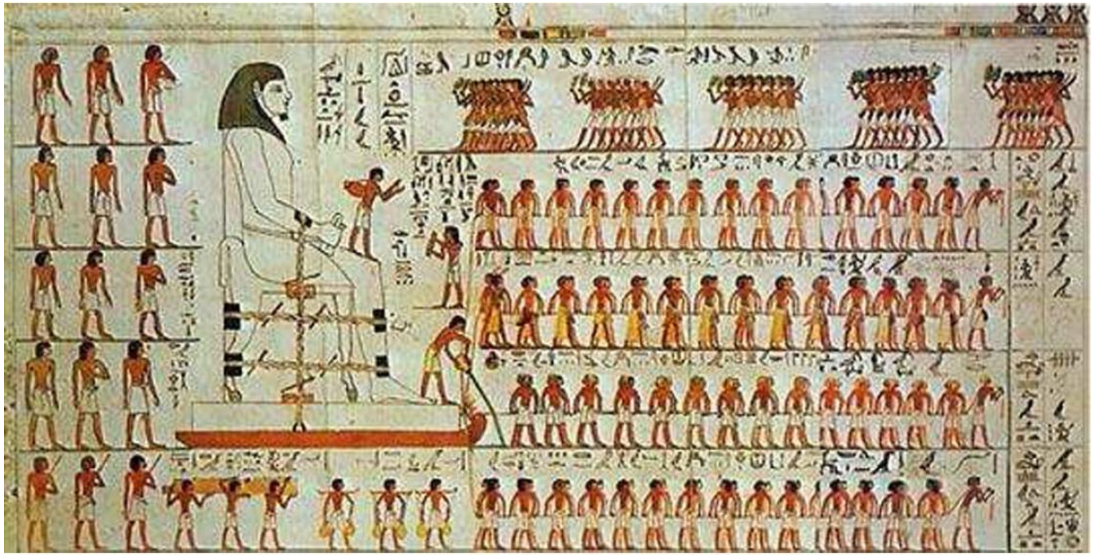
Holmberg, Anderson, Erdemir, Tribology International, 47, 221 (2012)

New innovations are needed not only to save energy by reducing the frictional loss but also to reduce emission of hazardous industrial waste into the environment

Fundamental research in materials is the key to solve problems at atomistic level that will enable new innovations

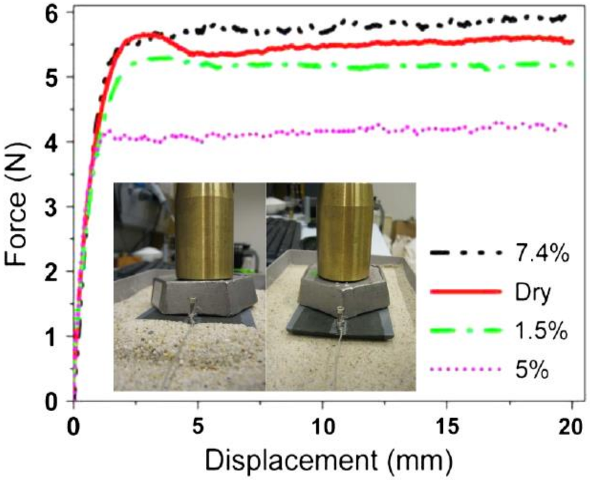
First documented use of lubricant

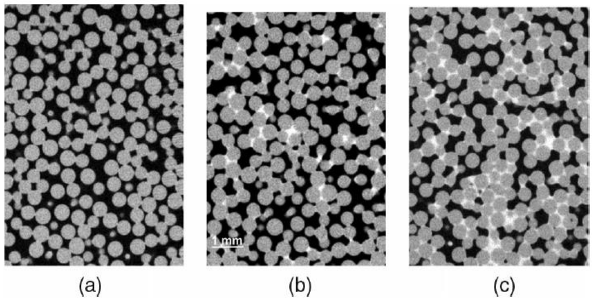
Transportation of an Egyptian colossus c. 1880 B.C.



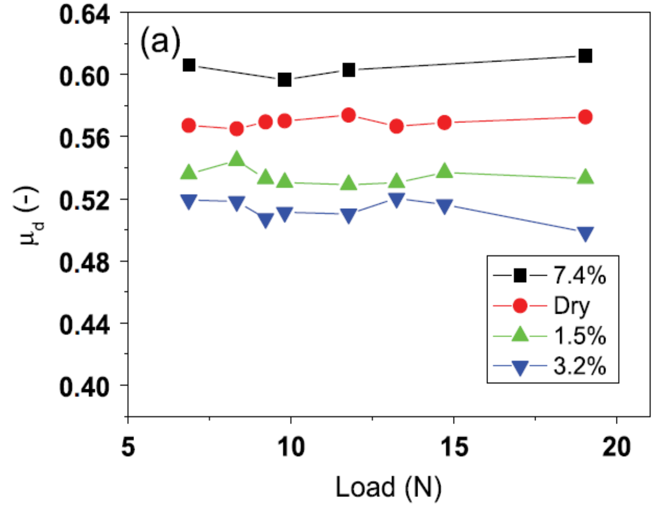
Sliding friction on wet and dry sand

Fall et al., PRL 112, 175502 (2014)





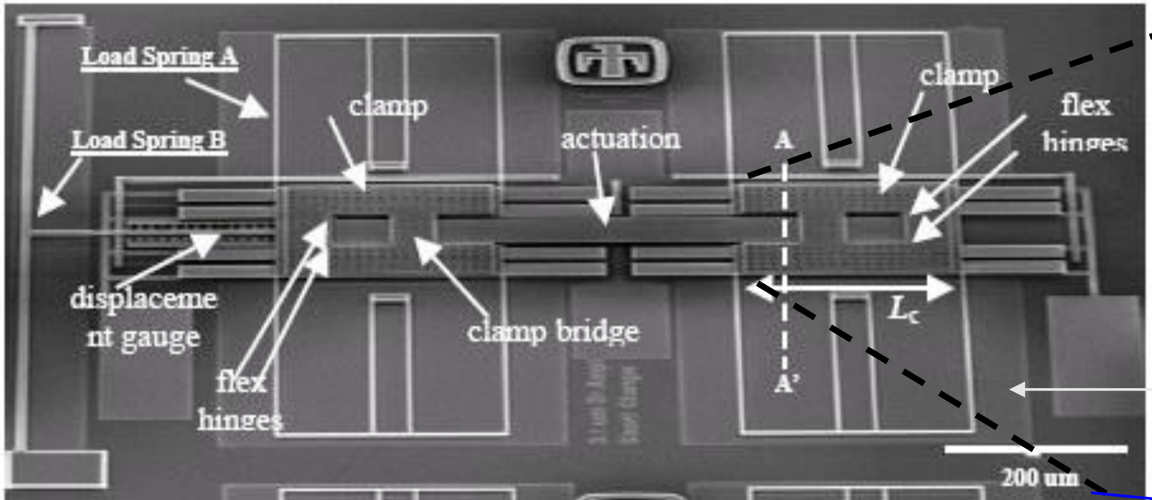
1% 5% 10%



The force necessary to move the sled on the sand can be reduced by 40% by pouring small amount of water

Reducing adhesion/friction in micromachines using SAMs

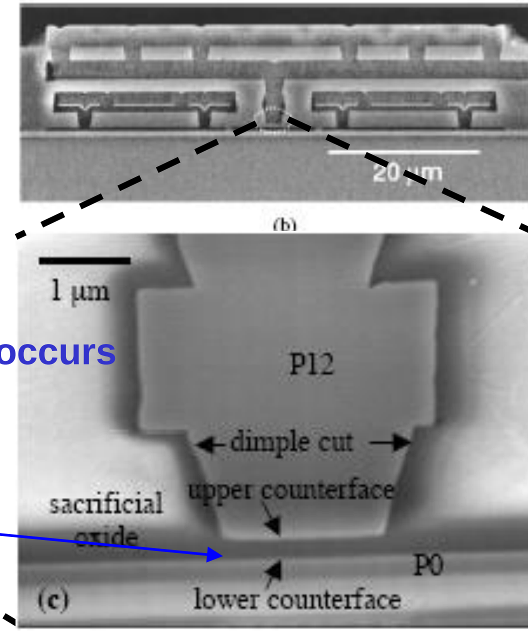
SEM image of the Sandia's Nanotractor (Top view)



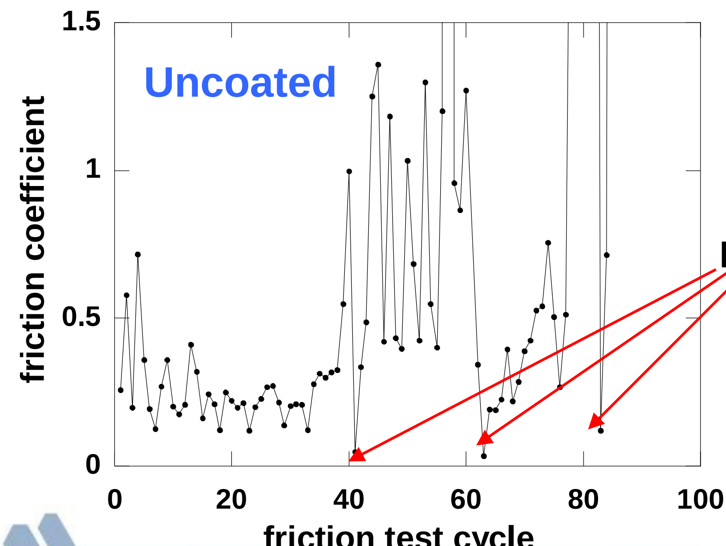
Wear occurs here

M.P. de Boer, D.L.Luck, W.R.Ashurst, R.Maboudian J.MEMS 13(1) 2004

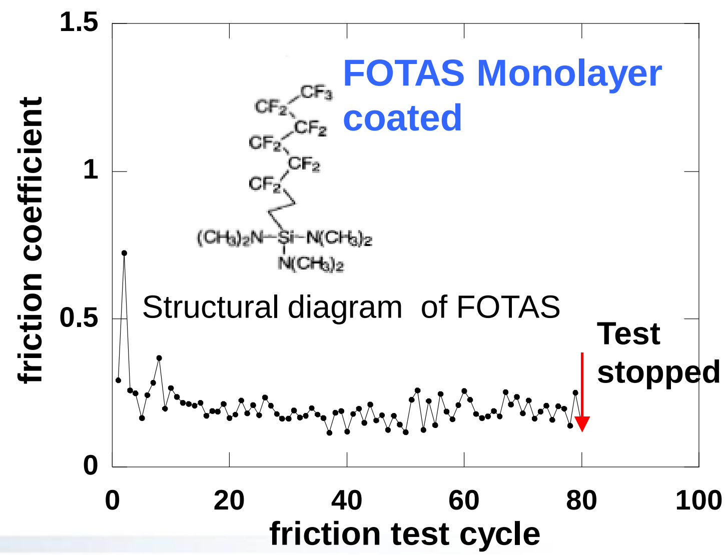
Surface coated with FOTAS monolayer



Cross section



Device stuck

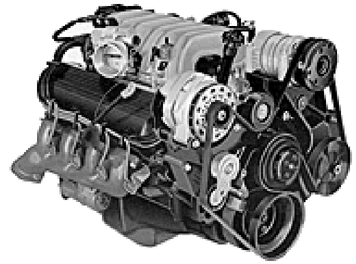


E. Flater, A.D.Corwin, M.P.de Boer, R.W.Carpick Wear, 260(6),580 (2006)

Surface Forces (Adhesion, Friction) are Increasingly Important at Small Scales

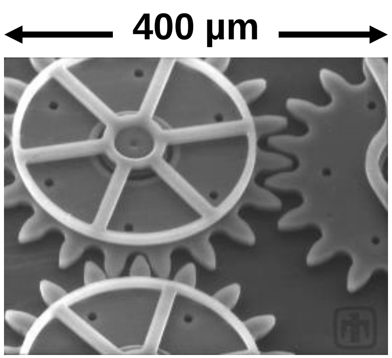
$$\frac{\text{surface}}{\textbf{VOLUME}}$$

macro



$$\frac{\textbf{surface}}{\textbf{volume}}$$

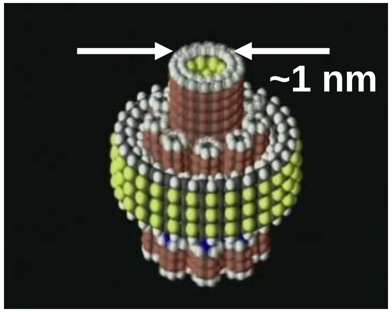
micr



Micromachine image (c) Sandia National Laboratories

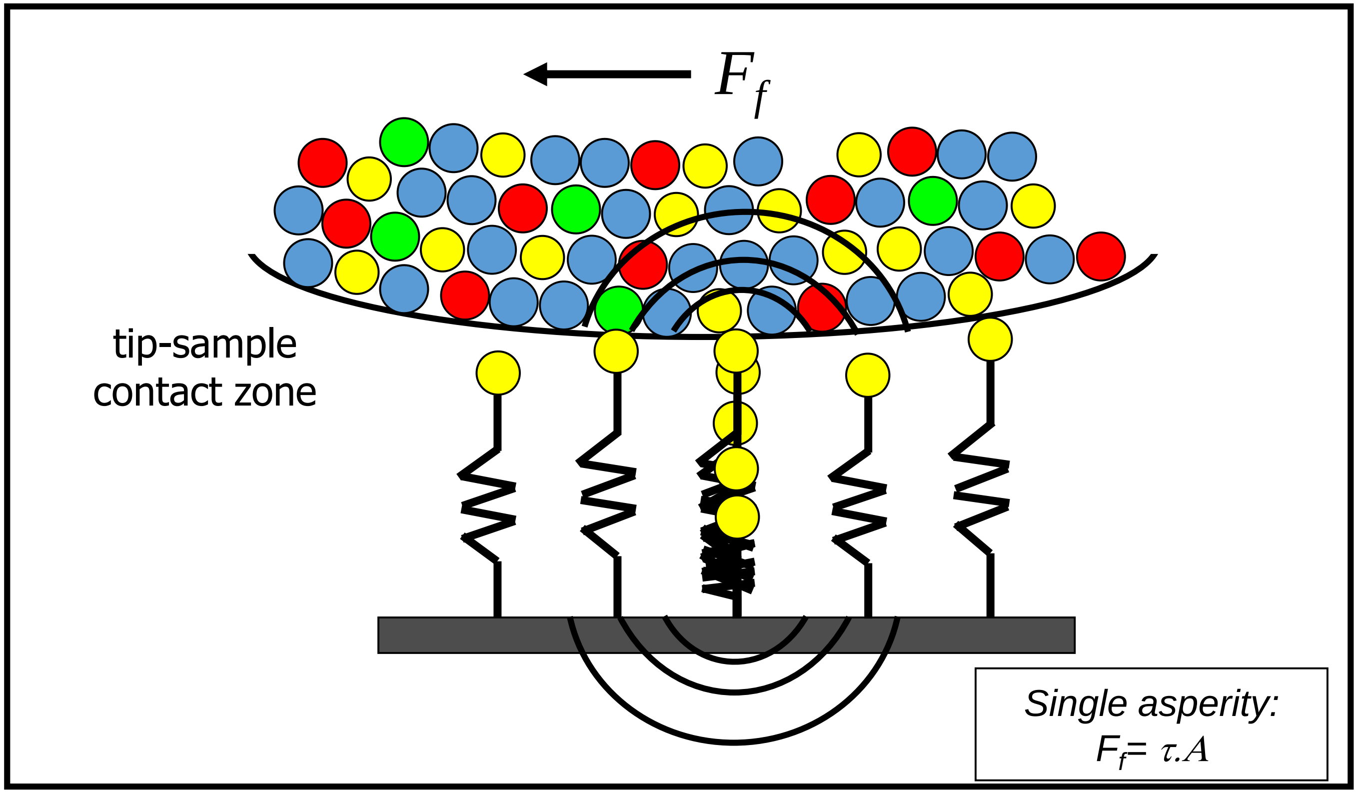
$$\frac{\textbf{SURFACE}}{\text{volume}}$$

nano

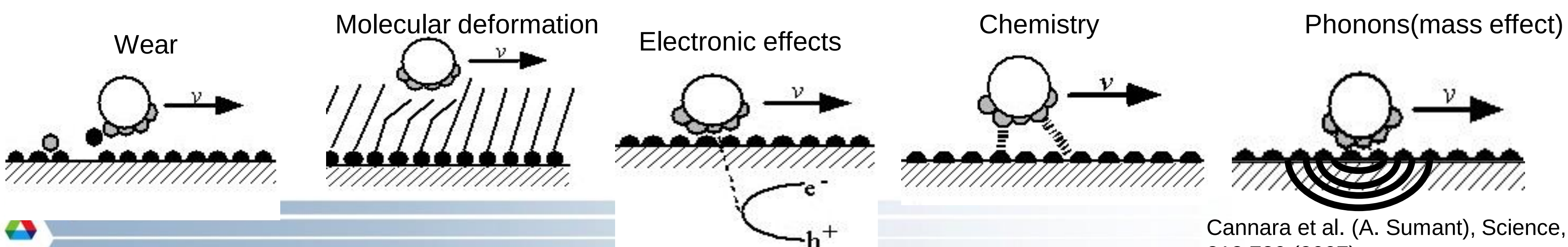


Nanomachine image (c) Foresight Institute

Understanding Friction at Atomic Scale

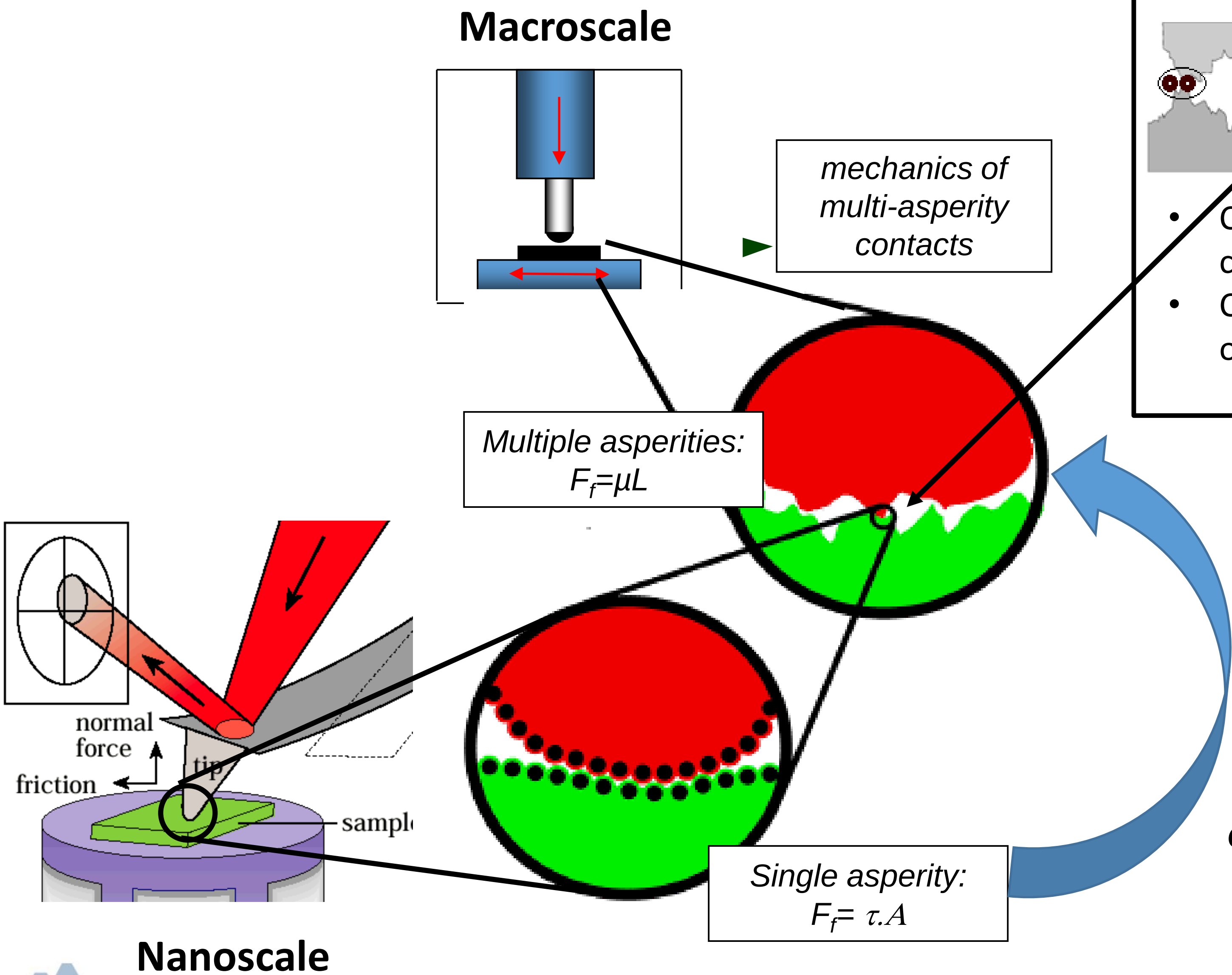


What are the possible mechanism of frictional energy dissipation?

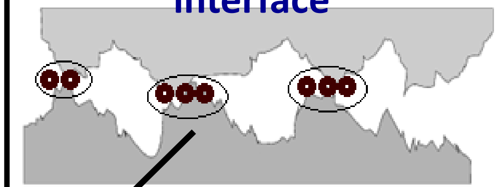


Cannara et al. (A. Sumant), Science, 318 780 (2007)

Friction laws differ at different length scales



Introduce 3rd body at the interface



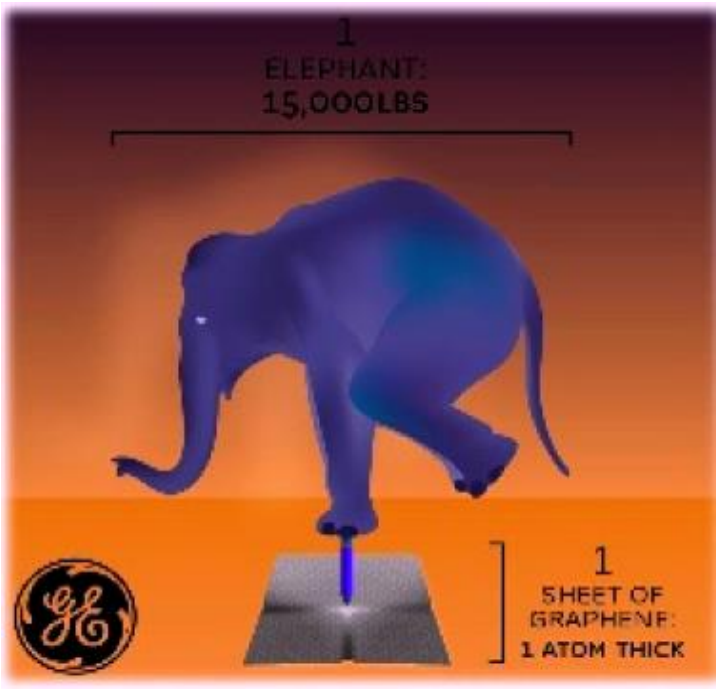
- Changing the surface chemistry
- Changing the dynamics of the interface

Mesoscopic link combining two is still missing

There is greater need to come up with unifying mechanism that will enable us to predict and design systems with expected outcome

Graphene: A miracle material

Akinwande et al., Nature Communications, 5, 5678 (2014)



Graphene:

- 200 times stronger than steel
- highest Young's modulus 1 TPa
- can be stretched 20% more than its original size
- what about tribological properties?

The new solution

Conventional lubricants

- Require large amount
- Produces hazardous waste
- Dangerous exhaust
- Needs vacuum for coating

→

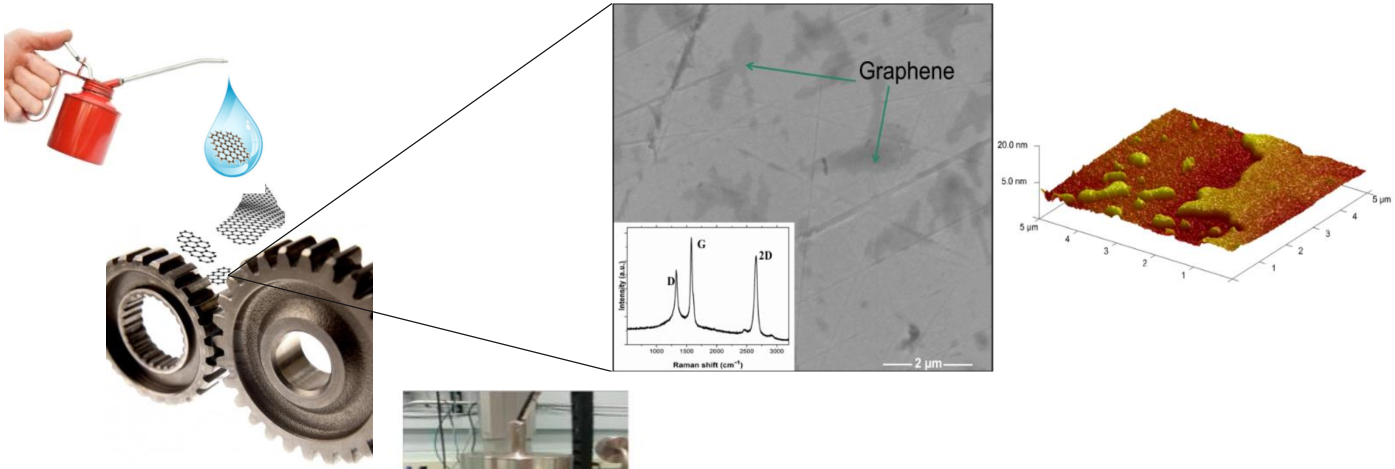
Graphene lubricants

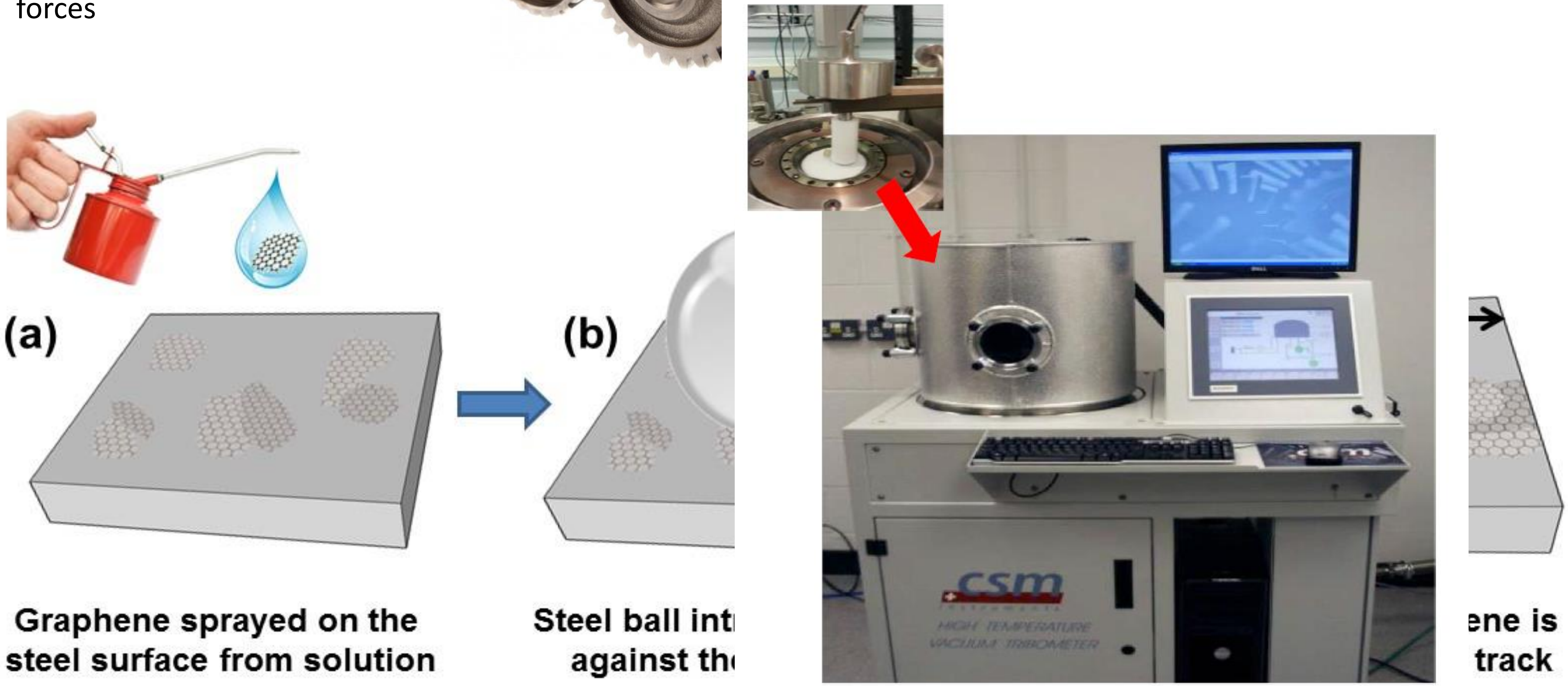
- Require small amount
- Non-hazardous
- Superior strength
- Atomically thin
- Easy to apply
- Scalable to large area

Coating Materials	Coating Method	Performance	Test Conditions	Cost
Graphite powder	In air but requires in large quantity	Wear reduced by 2 orders of magnitude in air	Only in humid air	\$~0.05/cm^{2}
TiN	Physical vapor deposition(in vacuum)	Wear reduced by 32 times, friction by 2-3 times	Humid and dry	\$0.5/cm^{2}
TiCN	Physical vapor deposition(in vacuum)	Wear reduced by ~100 times	Humid and dry	\$1/cm^{2}
MoS_2	Physical vapor deposition (in vacuum)	Wear reduced by 3 orders of magnitude in dry environment	Only in dry environment	NA
Graphene	In air by dripping through liquid or by spraying	Wear reduced by **10,000** times, friction by 6 times	Humid and dry	\$ 0.1/cm^{2}

The new solution: How does it work?

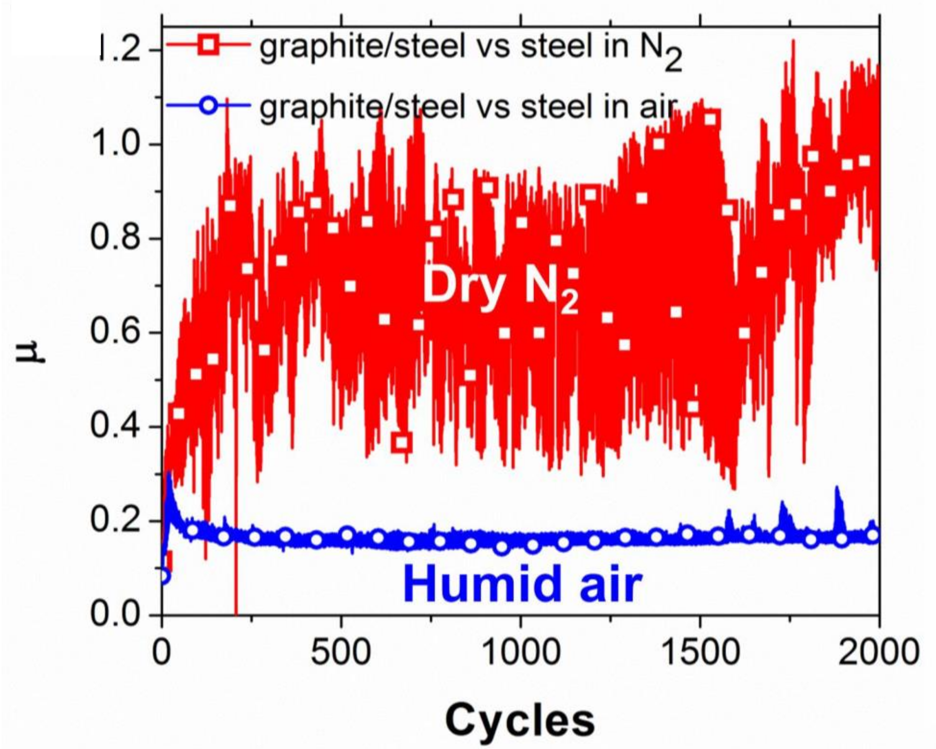
- Graphene coating can be applied simply by dripping through liquid medium or by spraying
- Graphene adhere strongly to the coating surface due to van der Waals attractive forces



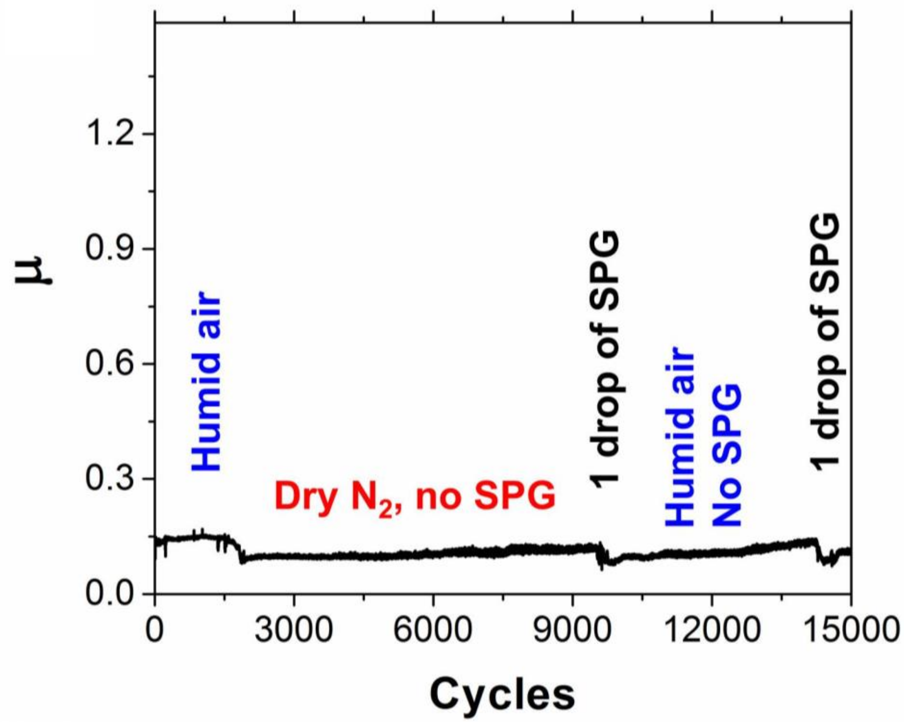


Graphene: A next emerging lubricant

Graphite



Graphene

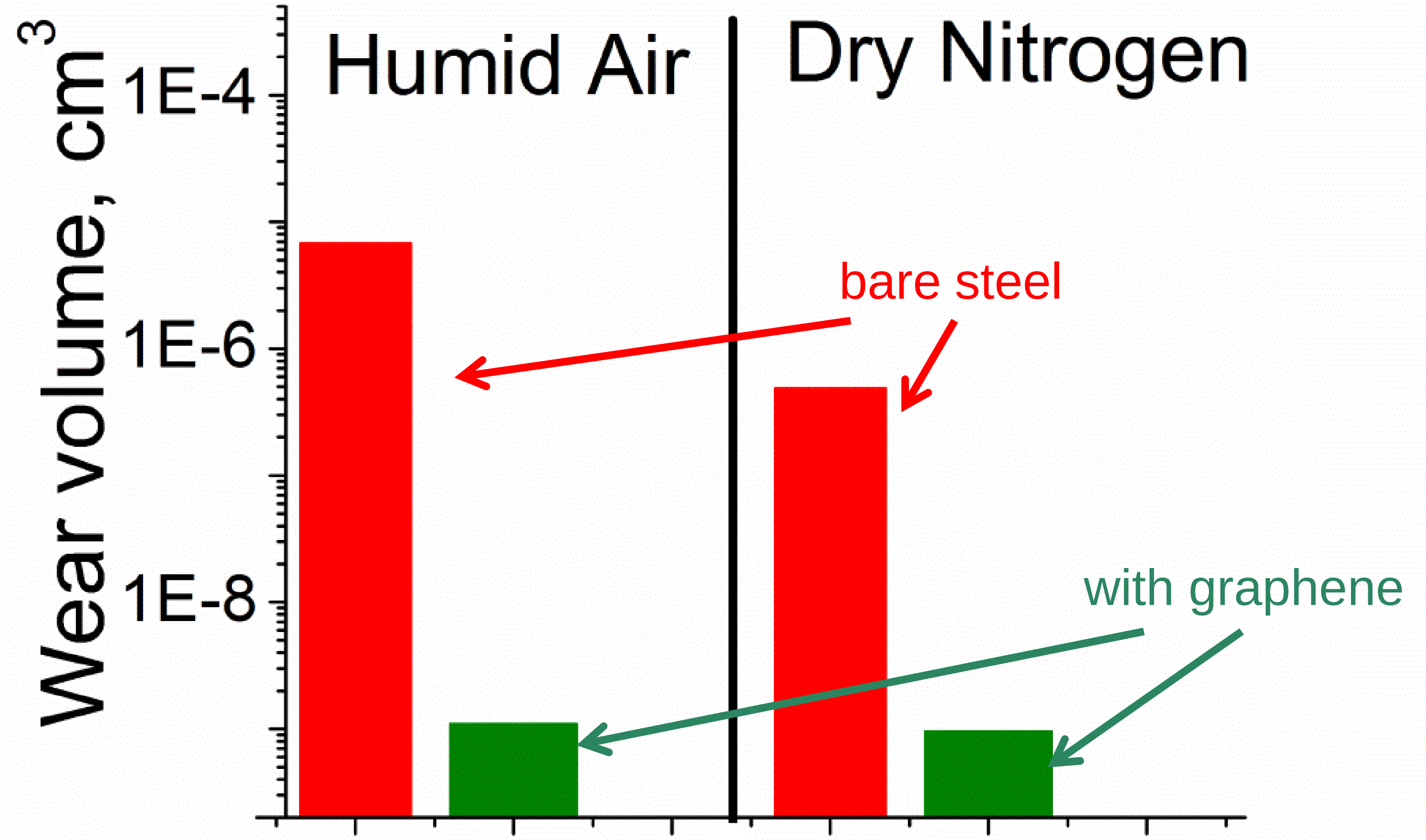


Graphite shows poor performance in dry environment
<u>Graphene works equally good in dry or humid environments</u>!

D. Berman, A. Erdemir, and A.V. Sumant. Materials Today, 17(1), 31 (2014) invited review article
D. Berman, A. Erdemir, and A.V. Sumant. Carbon, 59, 167 (2013)
D. Berman, A. Erdemir, and A.V. Sumant. Carbon, 54, 454 (2013)
D. Berman, A. Erdemir, and A.V. Sumant. Appl. Phys. Letts. 105(23), 231907 (2014)

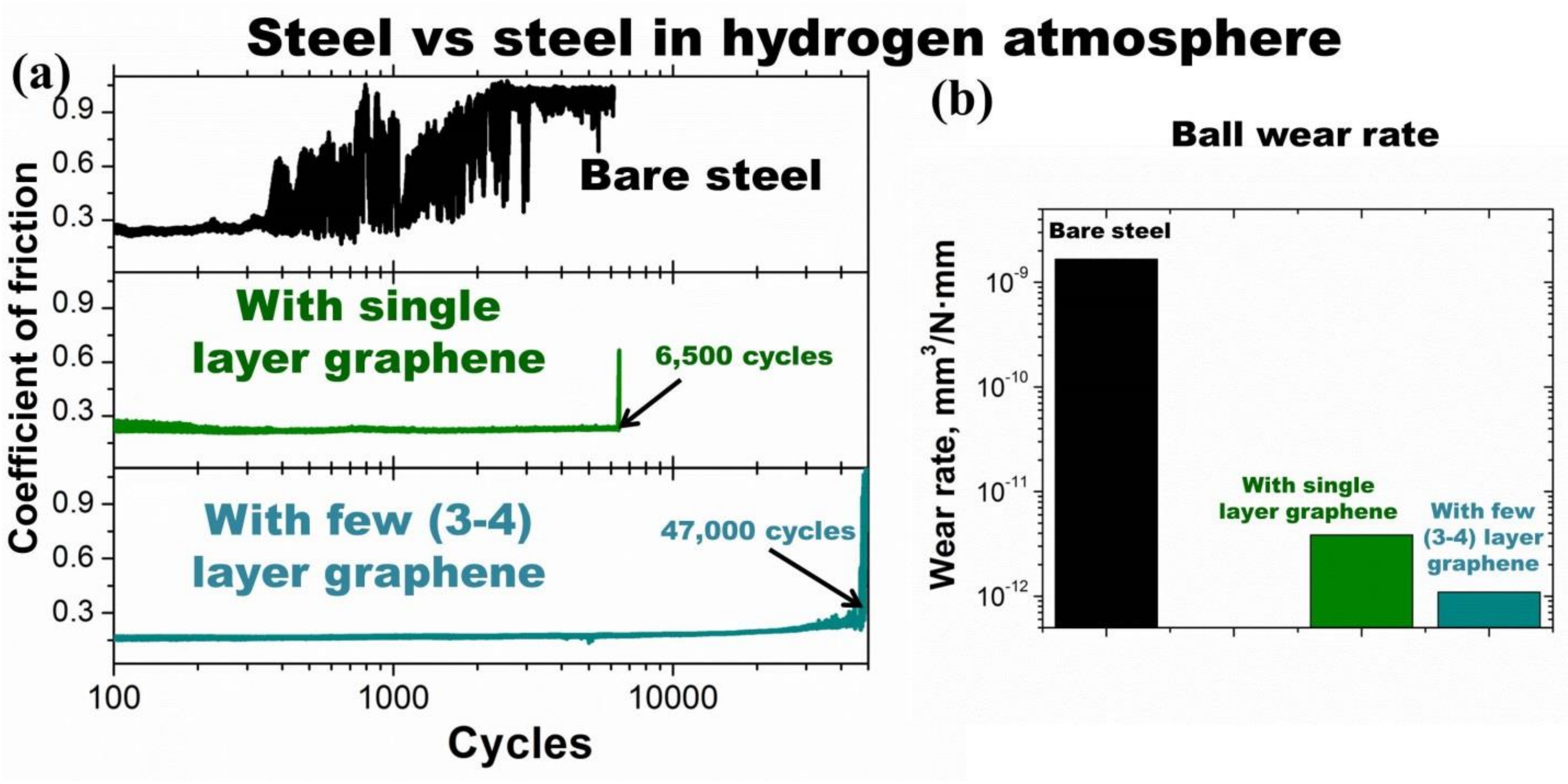
Wear rate measurements

Wear rate is dramatically reduced in both dry and humid environments



- Graphene reduces friction coefficient of steel by 6 times and wear rate by 10,000 times
- Graphene works equally well in humid and dry environments
- Graphene drastically slow down the tribo-corrosion process in steel

The wear life of a single and few layer graphene in hydrogen

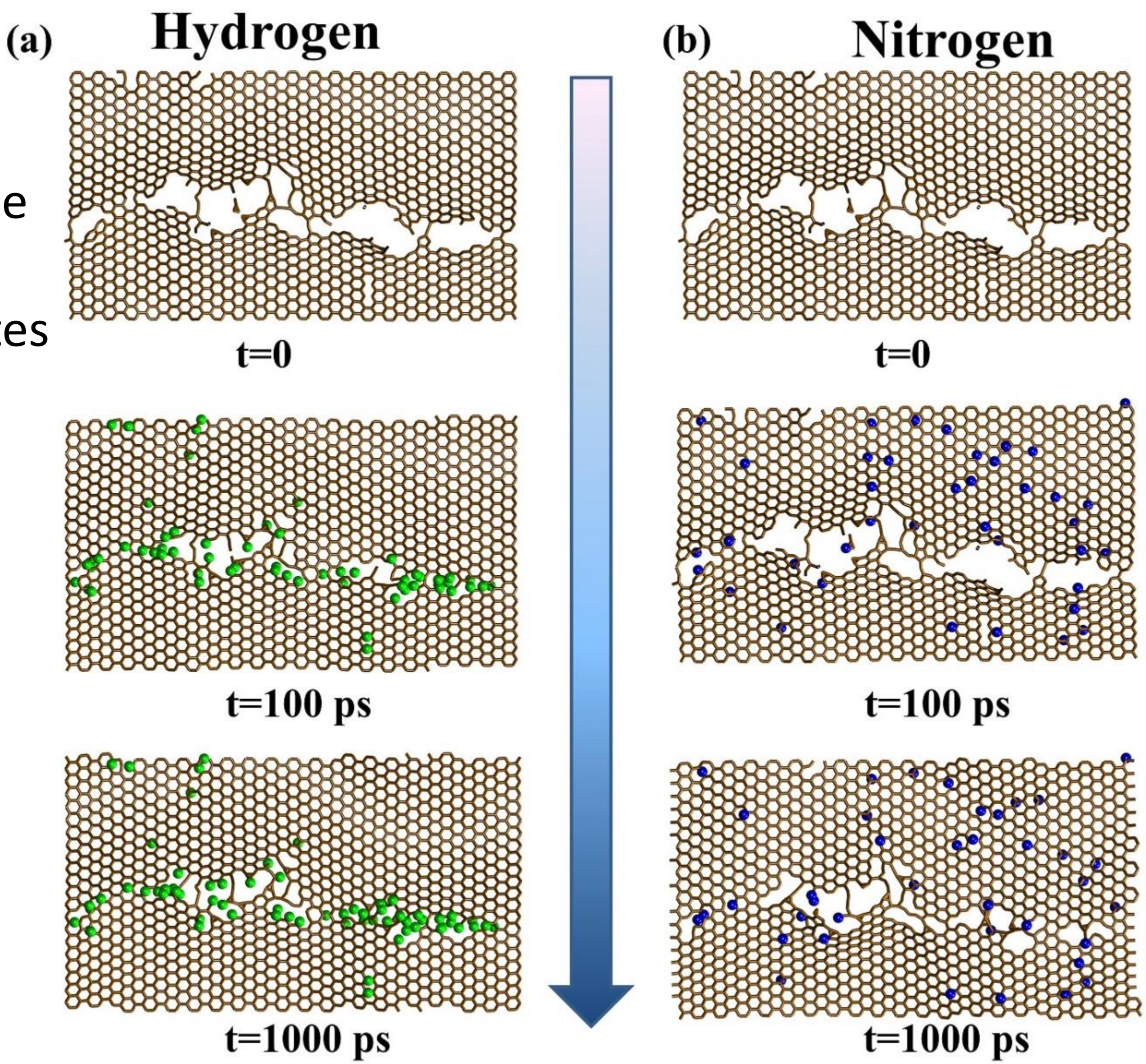


The single layer of graphene in hydrogen is extremely wear resistant!
Few layer graphene last 4.3 kms of continuous sliding without replenishment!

Comparison of hydrogen and nitrogen interaction with graphene

MD simulation using reactive force field:

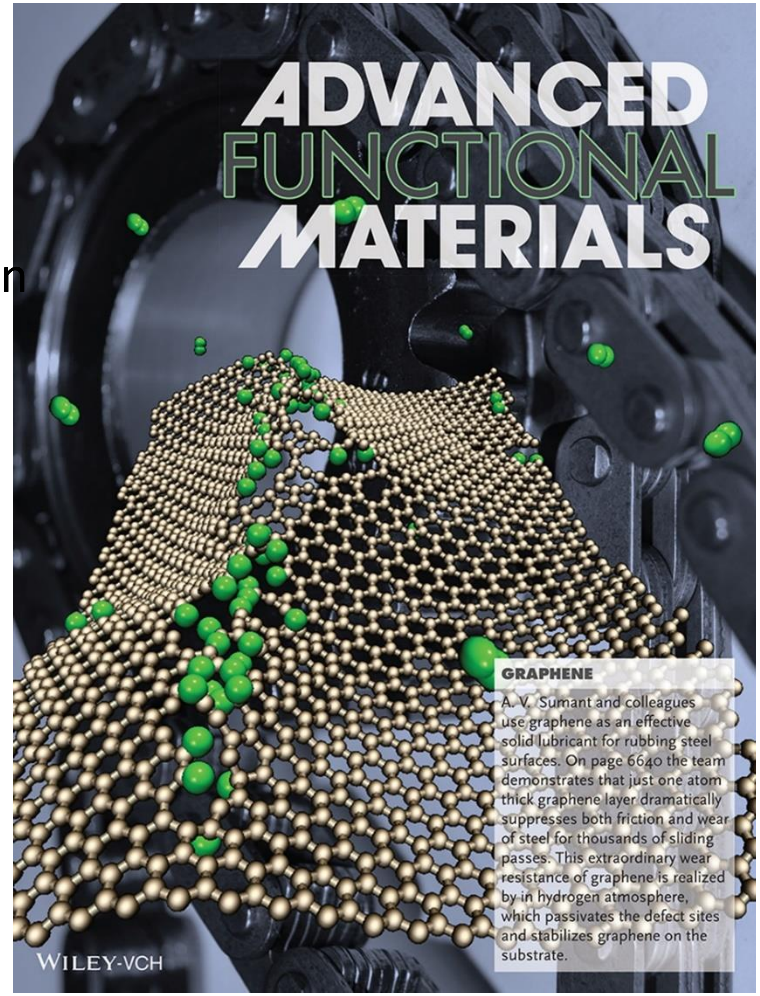
- Hydrogen passivates defect sites through
  chemical bonding
- Hydrogen “stiches” graphene quilt and
  prevent it from disintegration



New paradigm shift in understanding friction in 2D materials

- **Characteristically different tribological behavior of 2D material from their 3D counterpart**
- New insight into the fundamental origin for such behavior
- Strong vdW interaction leads to excellent adhesion
- Excellent passivation=>corrosion protection
- Potentially game changing
- Sensitive to surface chemistry
- Can we make hybrid 2D materials, which are environmentally adoptive?
- Can we build 2D materials genome? database
- that can help design complete tribosystems?

Opens completely new area to harness extraordinary properties of 2D materials



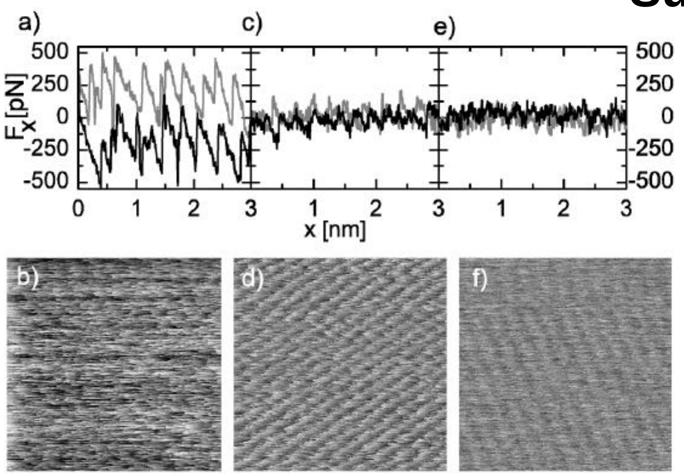
Adv. Funct. Mater. 24(42), 6640 (2014)

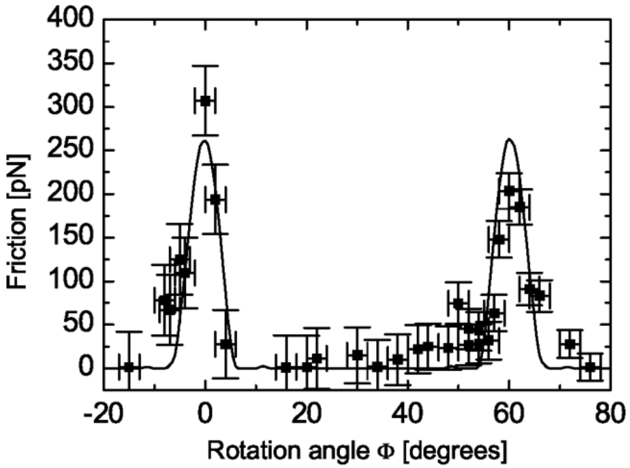
Can we achieve superlubricity at macroscale using graphene?

Structural superlubricity (Graphite)

The term “superlubricity” was introduced by Hirano et al. in 90s describing near zero friction when two incommensurate solid surfaces sliding against each other at atomic scale

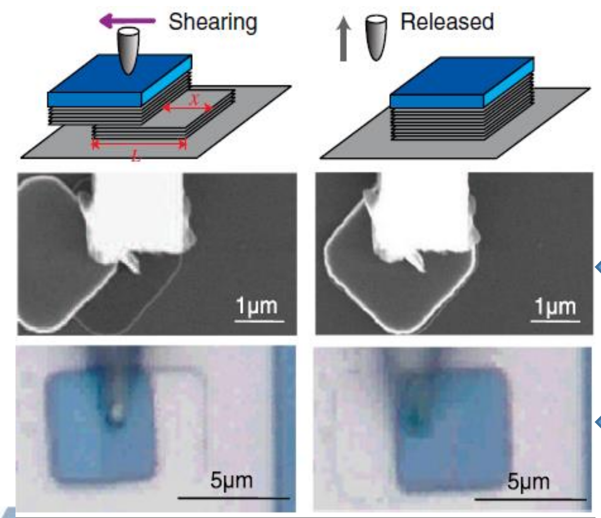
Superlubricity in graphite at atomic level





- **Perfectly aligned defect free structures**
- **Restricted to materials interactions at nanoscale**

Dienwiebel et al. PRL 92(12), 126101 (2004).



Superlubricity in graphite at microscale (contact area 10 x 10 μm²)

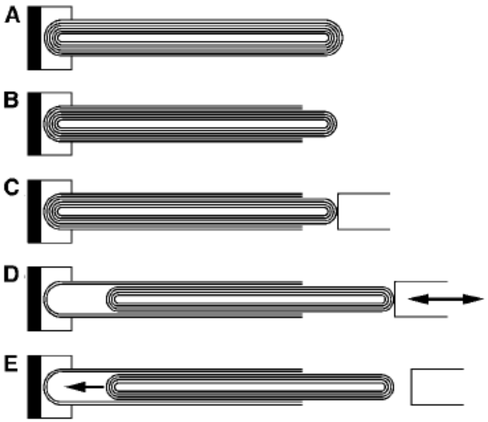
In vacuum

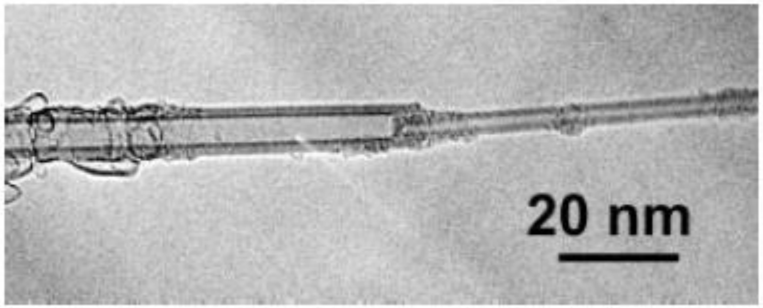
In air

Ze Liu et al. PRL 108 205503((2012).

Structural superlubricity (Carbon Nanotube)

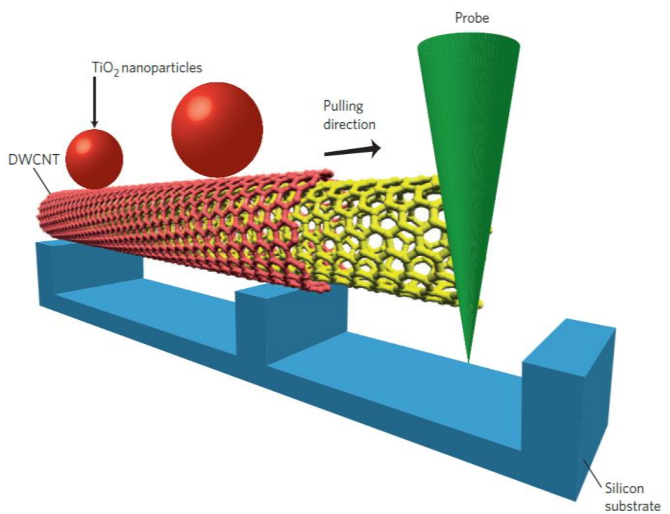
➢**Linear bearing from sliding MWCNTs (nanoscale):**

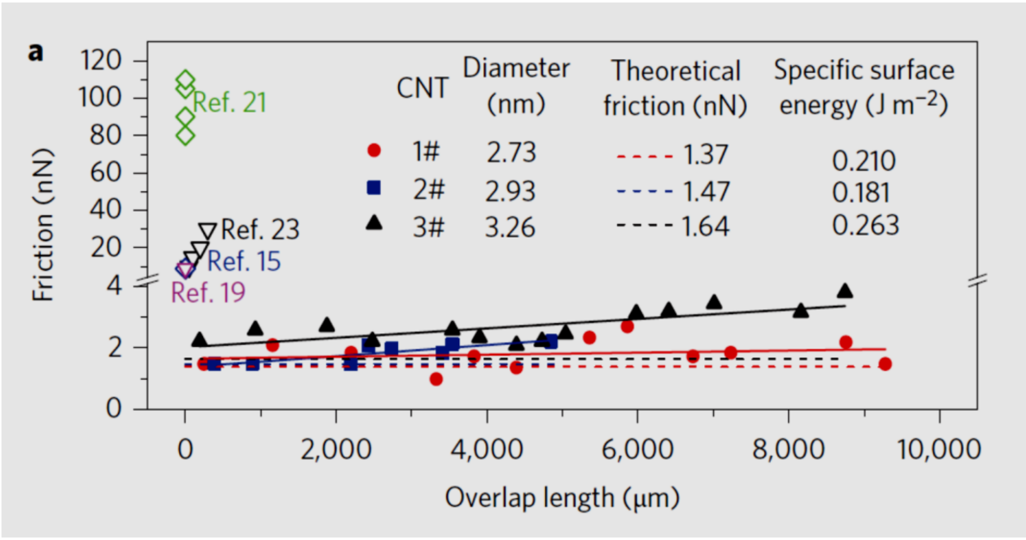




Cumings et al. Science 289, 602 (2000)

➢**Macroscale superlubricity in cm long double walled CNT:**





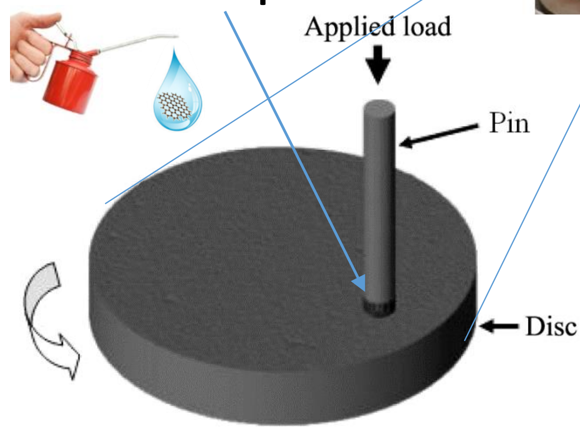
Zhang et al. Nat. Nanotech, 8 (2013)

A new solution: DLC vs Graphene?

Experimental Details:

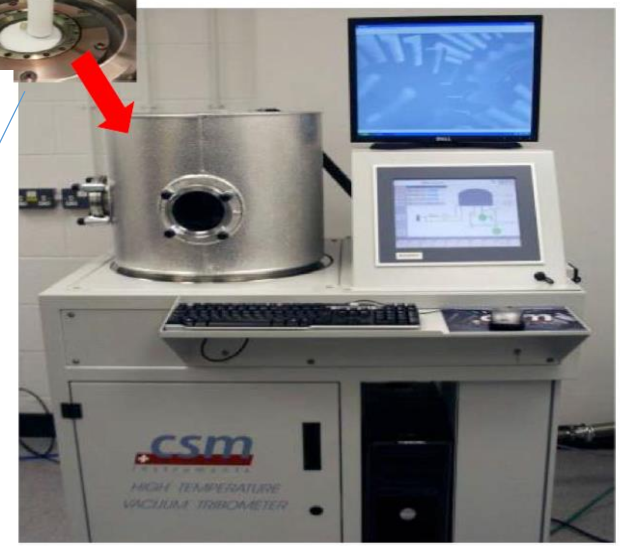
- Graphene on SiO_2 sliding against DLC ball (1µm thick DLC layer on steel ball)
- 0.5 – 3N load variation (Hertz max contact pressure of 0.43 GPa)
- Linear speed of 0.6 - 25 cm/s
- Dry Nitrogen (900 mbar) and ambient environment
  (30% relative humidity)
- Temperature 20-50 ^{o}C

DLC coated pin

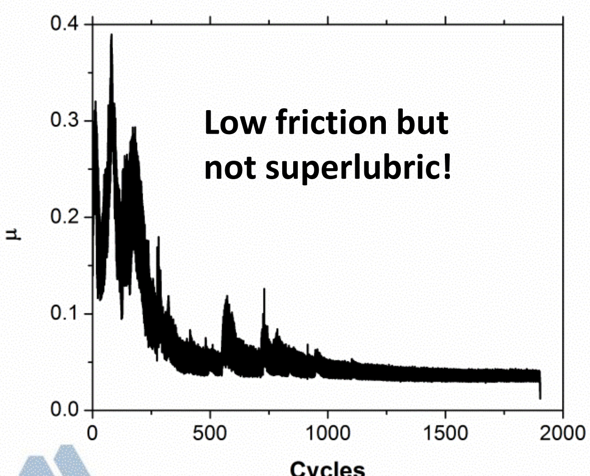


Few layer graphene on SiO_2/Si substrate

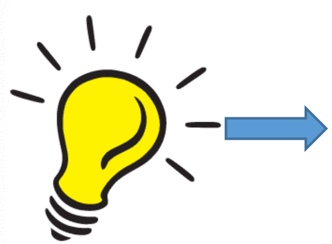
Pin-on-disc high vacuum tribometer



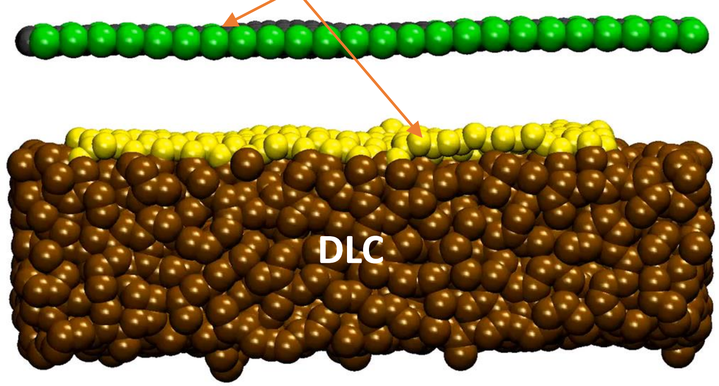
Graphene on SiO_2 against DLC



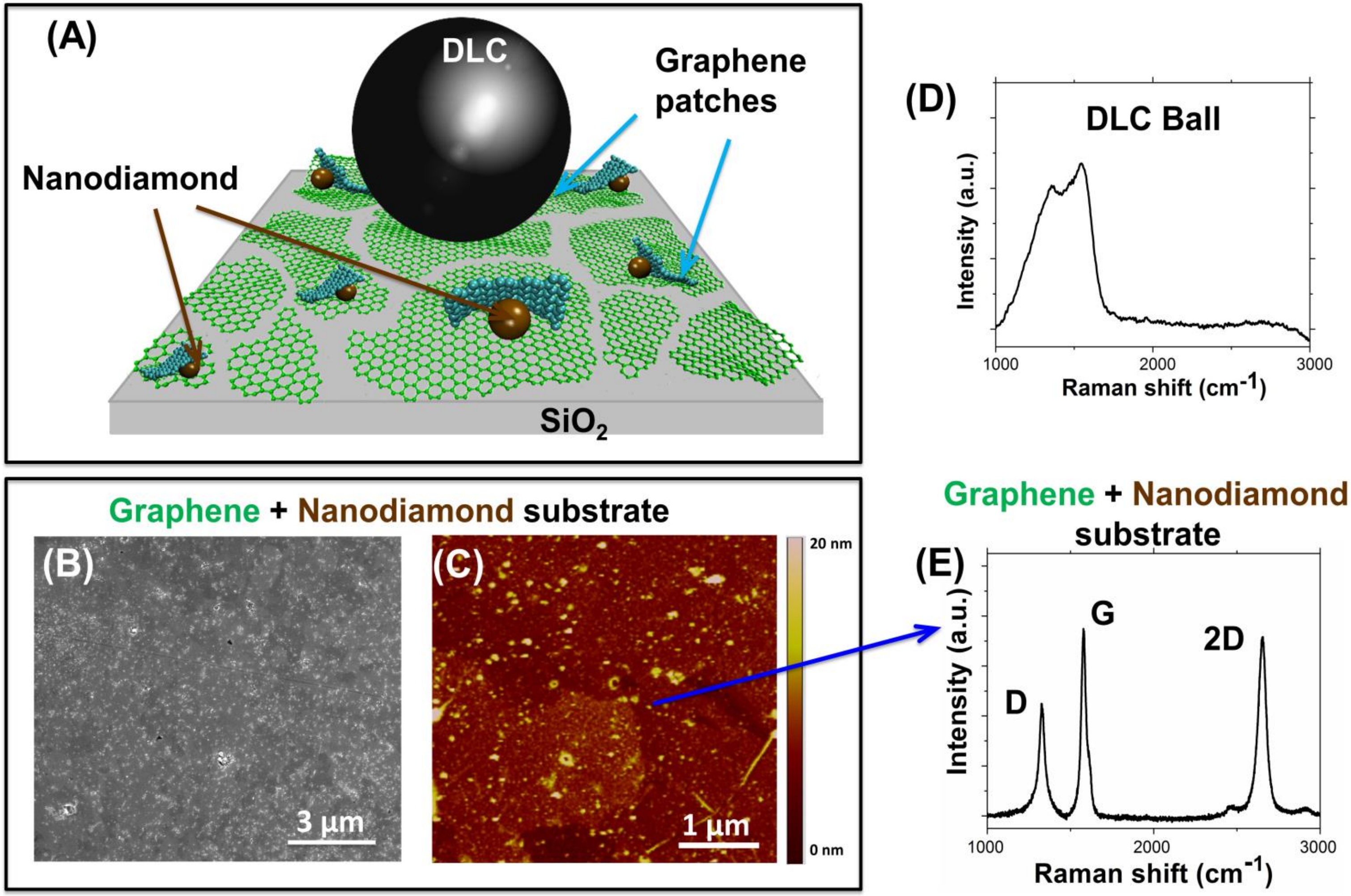
Initial clue!



Graphene



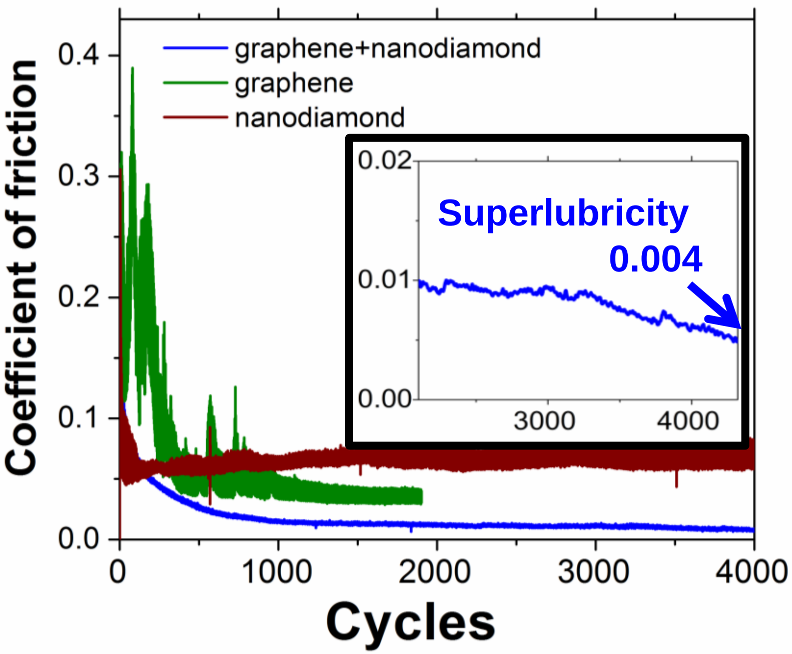
A new solution: DLC vs graphene + nanodiamonds

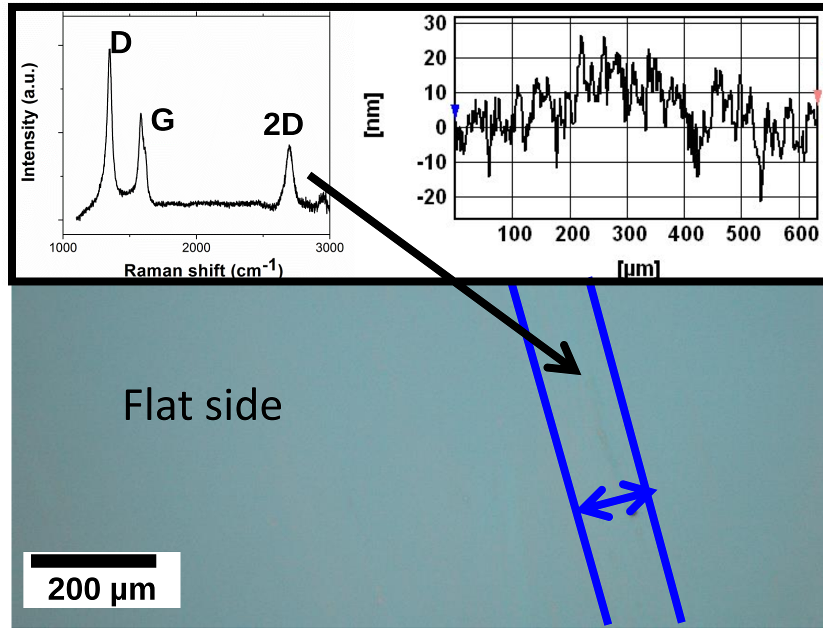


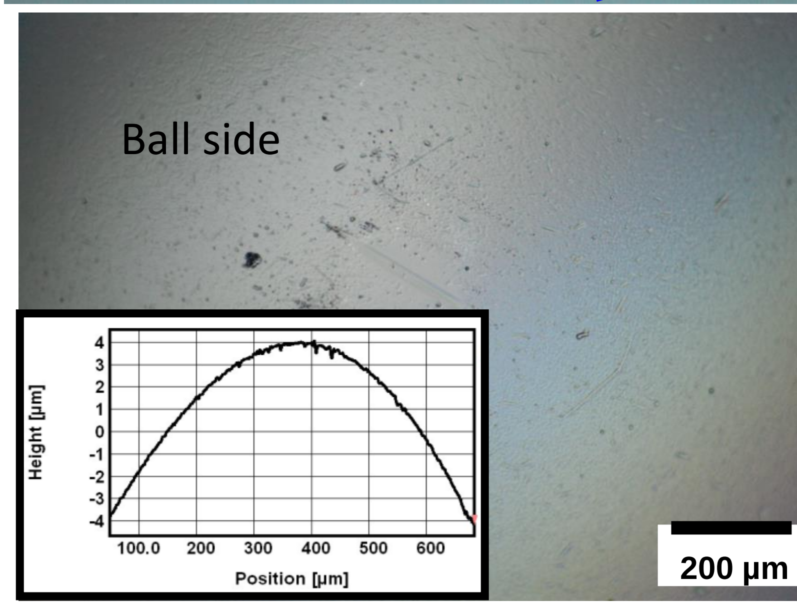
- Graphene deposited on SiO_2 from ethanol solution (1 mg/L) -> 0.5-2 µm flakes with ~75% coverage of the surface.
- Diamond nanoparticles (3-5nm) deposited from DMSO solution -> 10^{11}-10^{13} nanoparticles per cm^2

Superlubricity is achieved in dry N_2 environment

In dry N_2 environment



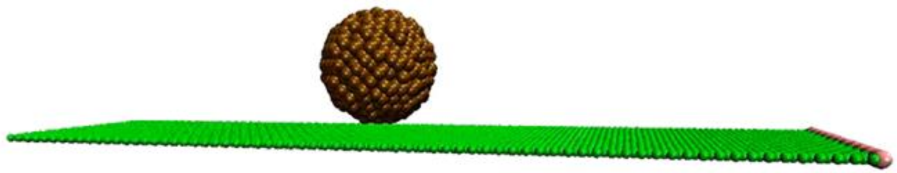




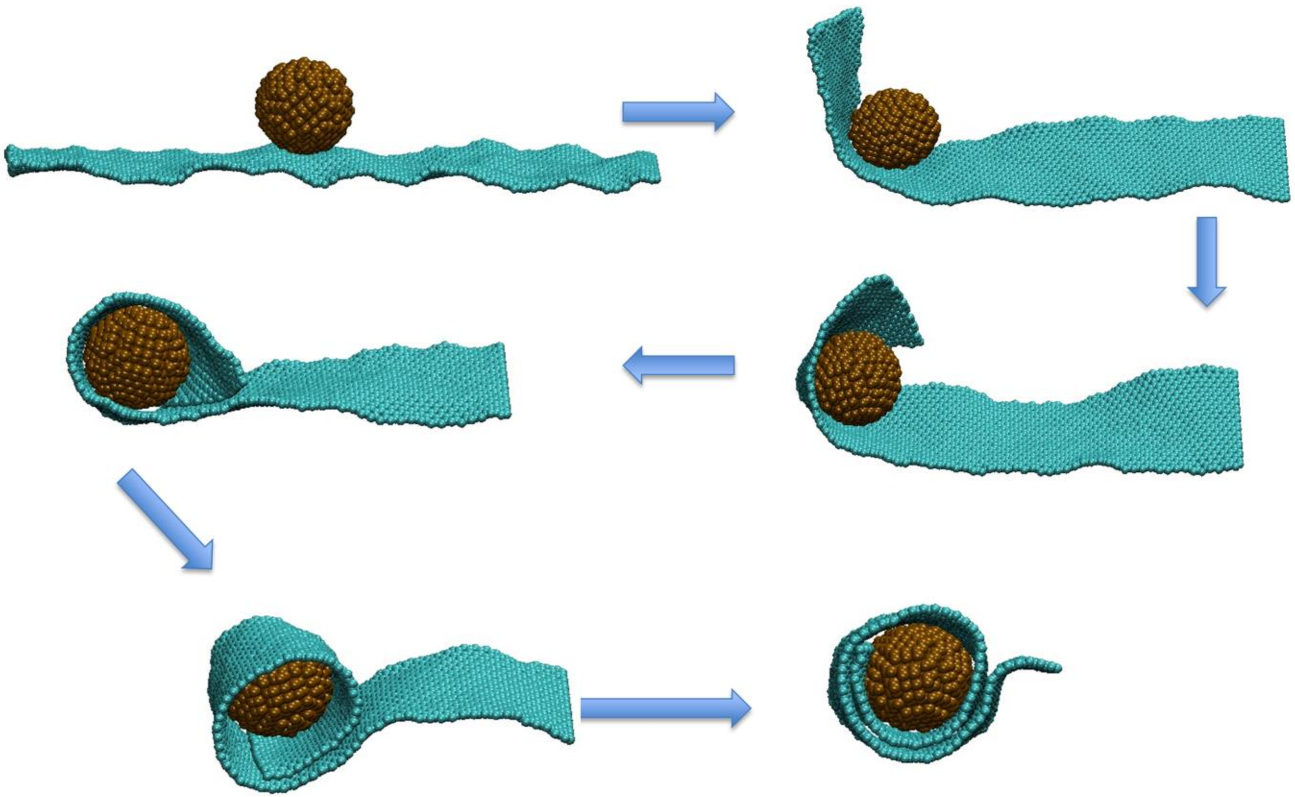
No measurable wear

- **Excellent stability of superlubric state for extended time periods (0.7 km of continuous sliding) in dry N_2 environment**
- **Superlubricity is achieved only with graphene+ nanodiamond combination**
- **No measurable wear on ball and flat surfaces**

The mechanism of graphene nanoscroll formation



The mechanism of graphene nanoscroll formation



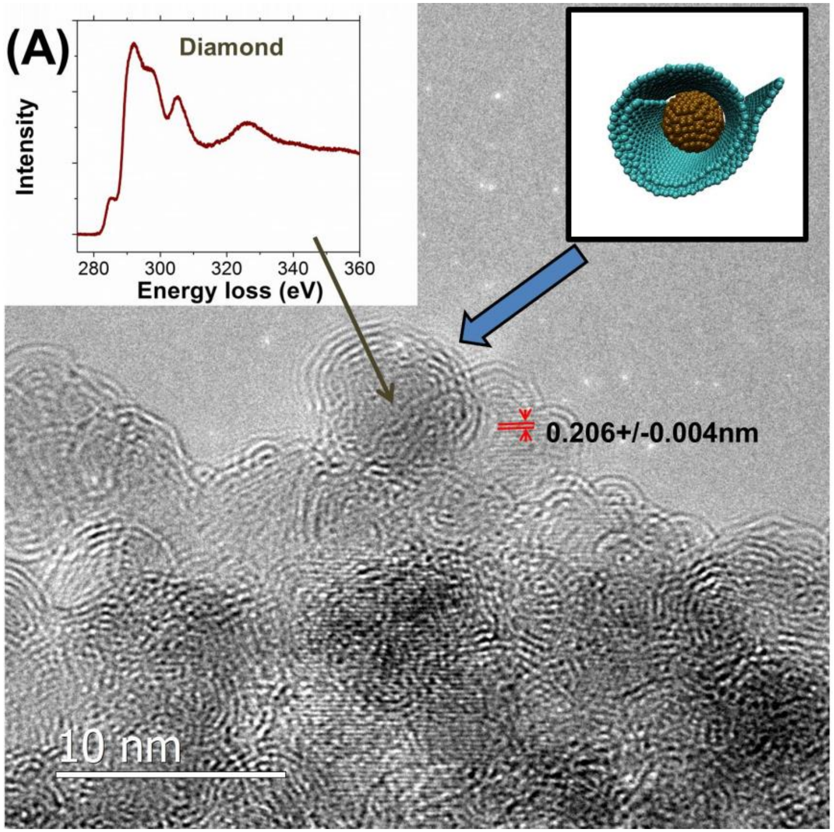
Graphene patch wraps around nanodiamond - > energetically favorable

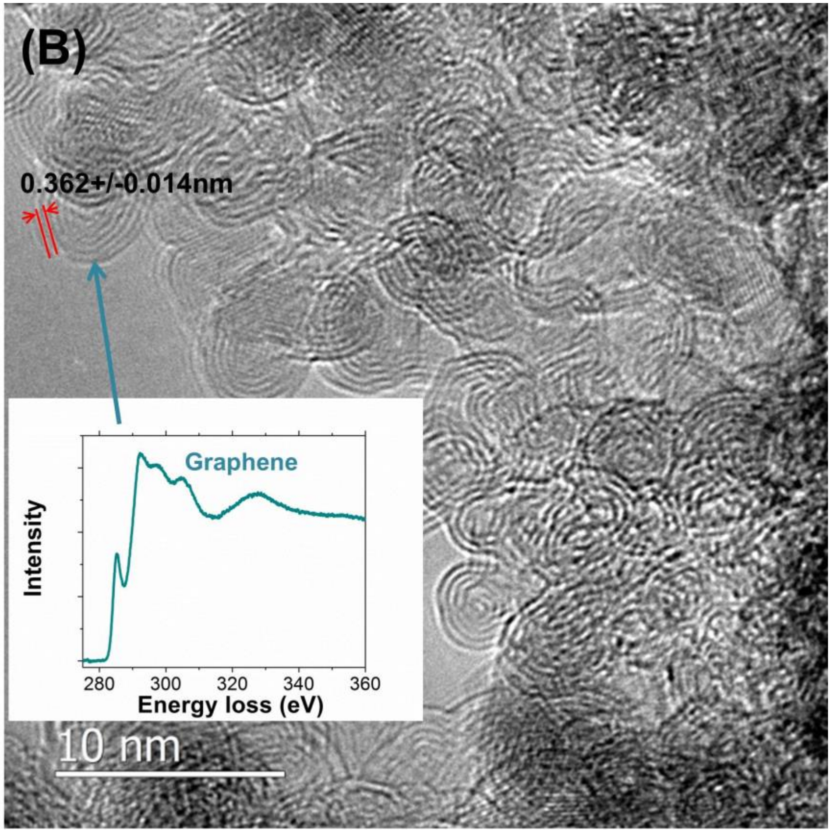
- Graphene patch is highly reactive on the edges and easily attaches to the nanodiamond dangling bonds
- Graphene patch prefers to wrap around nanodiamond 3D structure to promote higher surface contact
- Formation of stable scroll and sliding is determined by following energetics criterion

$$E_{strain} + E_{g\text{-}DLC} < E_{g\text{-}Dia} + E_{kin}$$

- DLC provides an incommensurate contact
- COF depends on contact area between graphene scroll and DLC

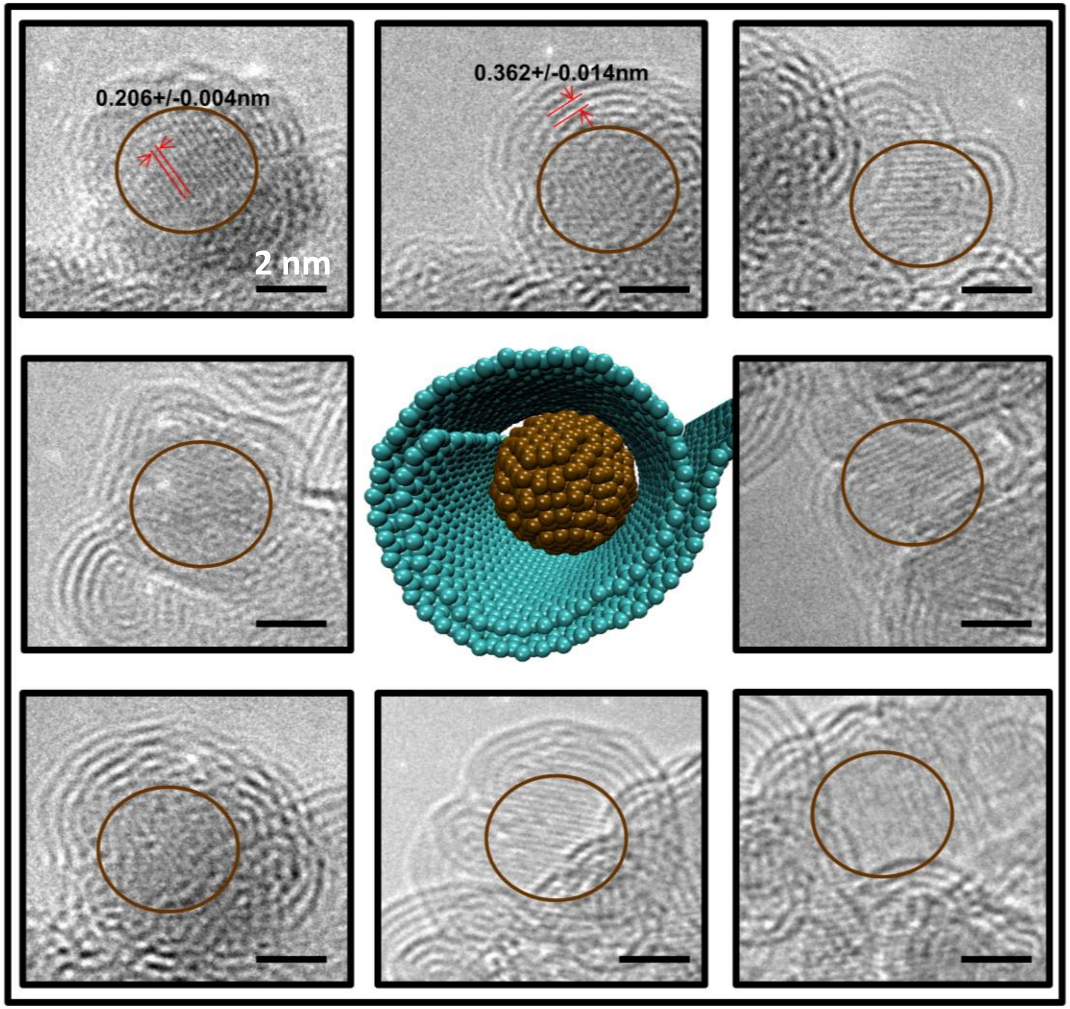
Formation of graphene nanoscrolls in the wear track



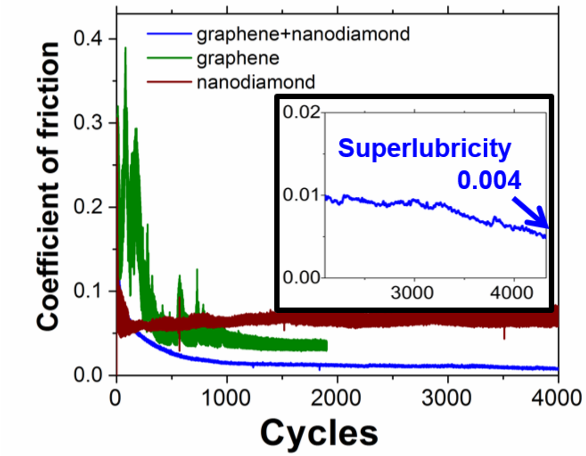


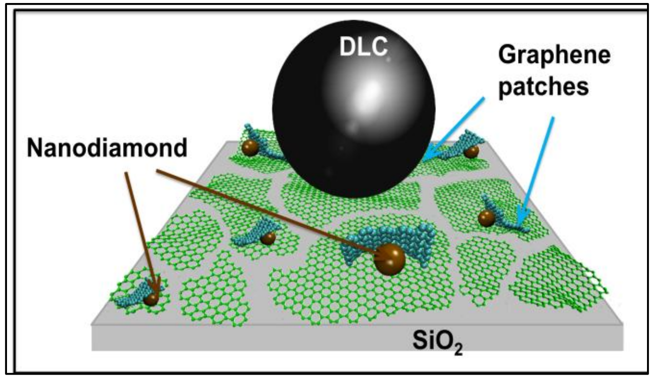
- Wear debris collected from the wear track produced in dry nitrogen environment
- TEM analysis of the wear debris indicates nanoscroll formation: graphene surrounding diamond nanoparticles

Formation of graphene nanoscrolls in the wear track

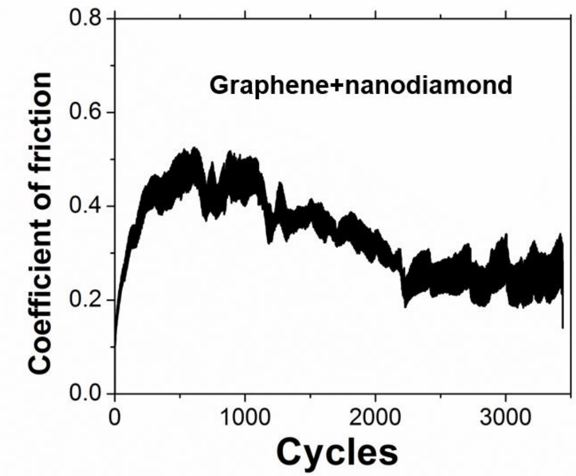


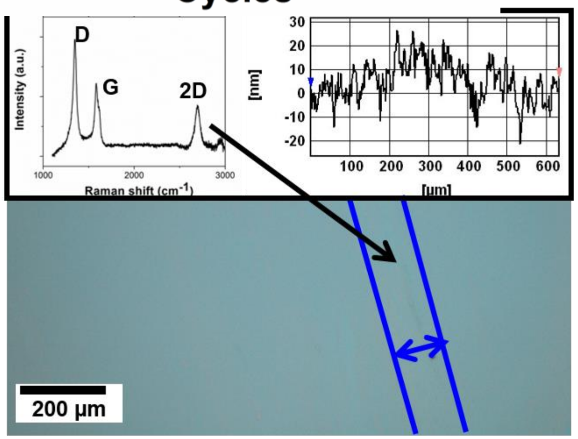
In dry N_2 environment



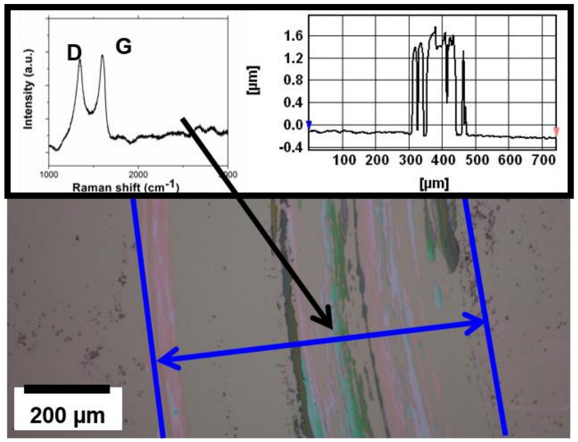


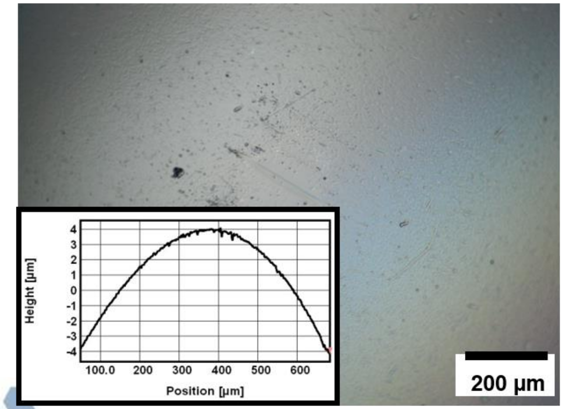
In Humid Air



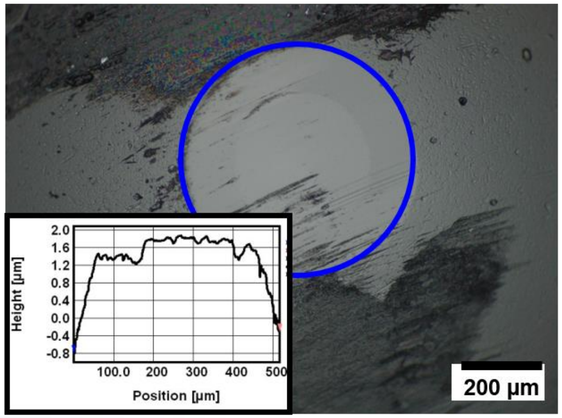


Why?



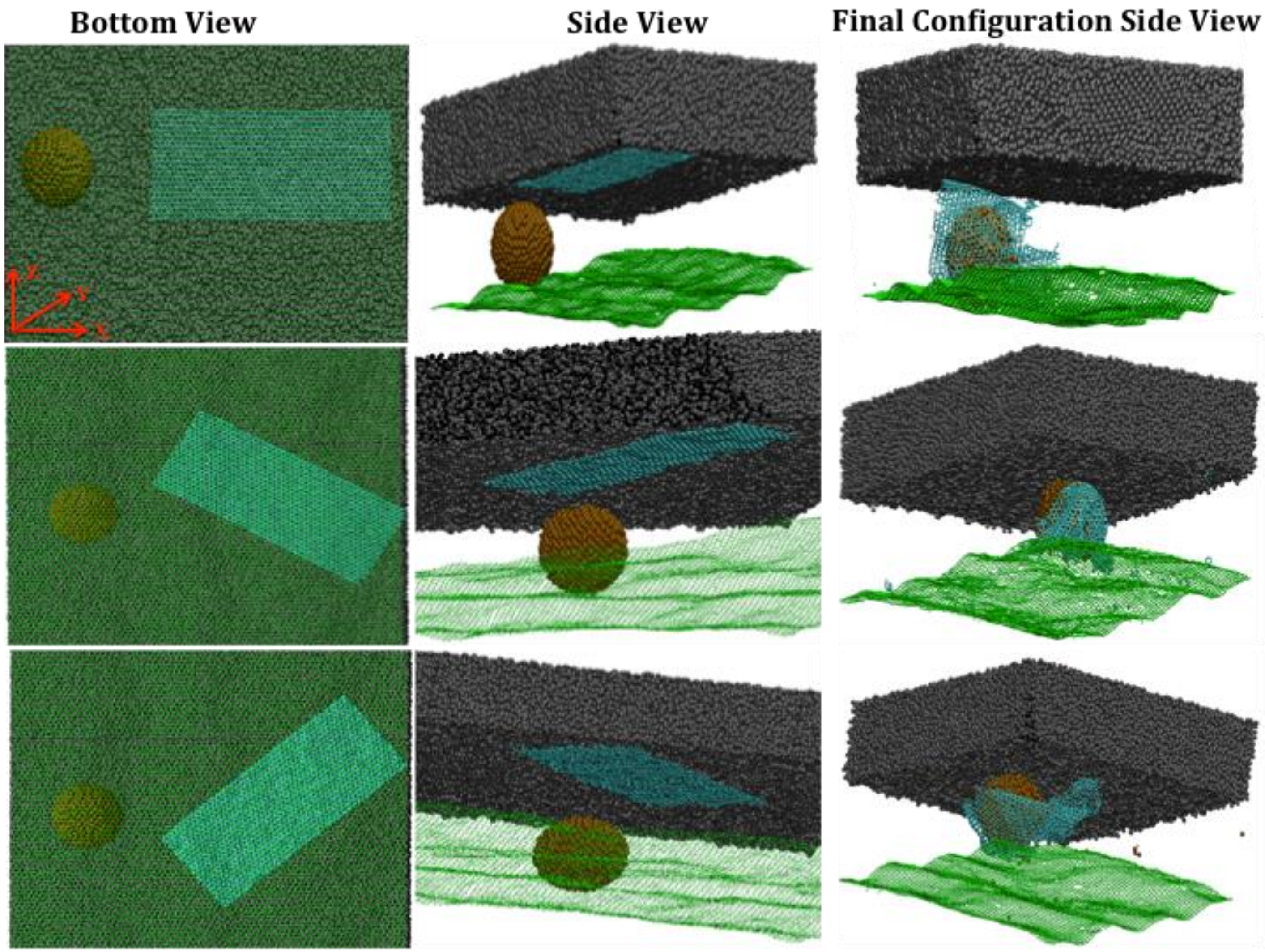


No measurable wear



Wear volume = 6.52 +/- 0.31 x 10^{-4} mm^3

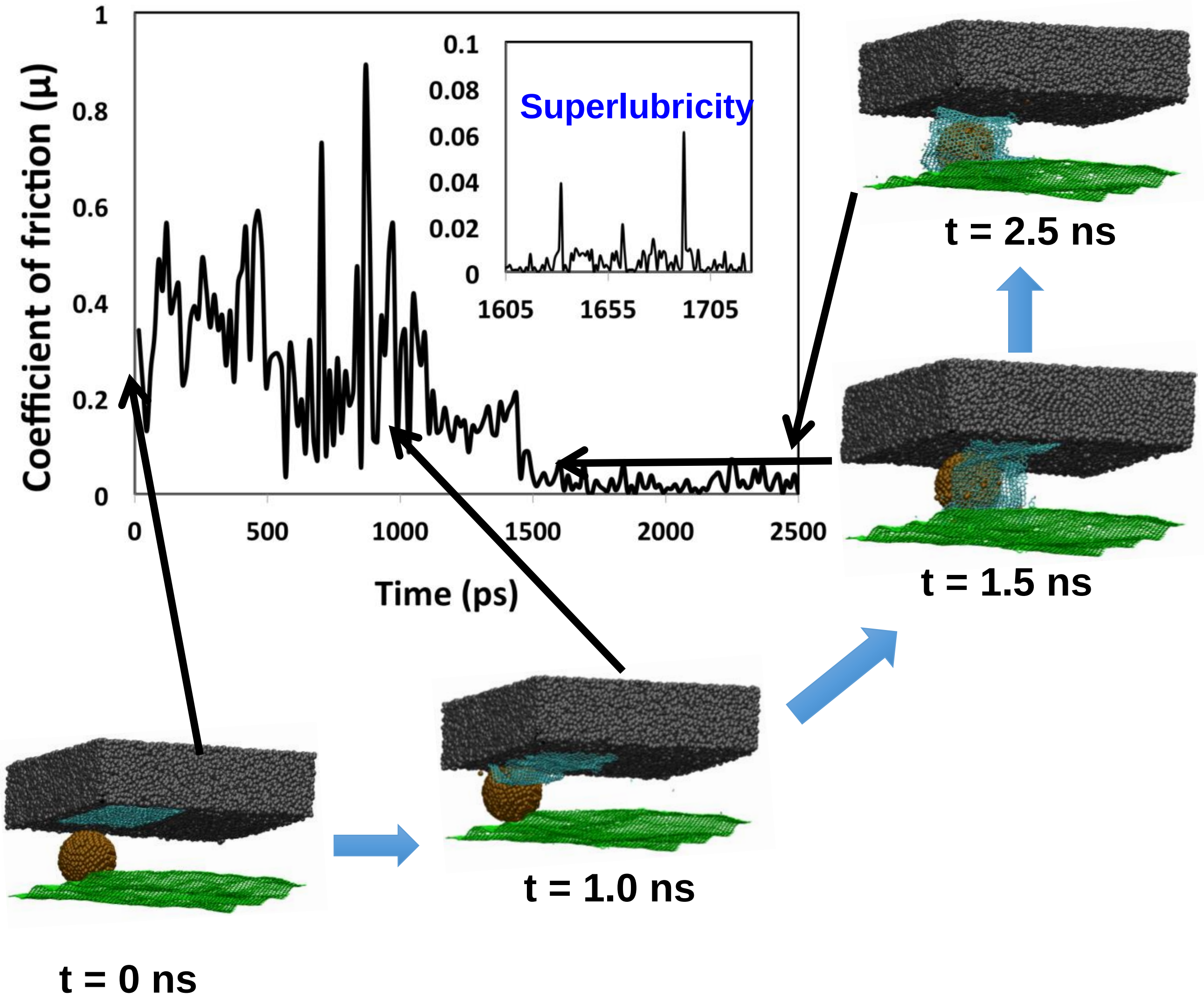
The mechanism of graphene nanoscroll formation



Graphene patch wraps around nanodiamond - > energetically favorable

- DLC 189 Åx130Åx36Å
- single layer graphene patch -> 2024 carbon atoms
- one 3.2 nm in diameter nanodiamond -> 3031 carbon atoms
- Graphene sheet -> 9120 carbon atoms
- AERIBO potential -and LAMMS simulation package
- Sliding of DLC with 40 m/s velocity for 3 ns
- Dry environment – no water molecules present
- Different orientation of graphene patch (-60^o, 0^o, 60^o)

Evolution of friction with scroll formation



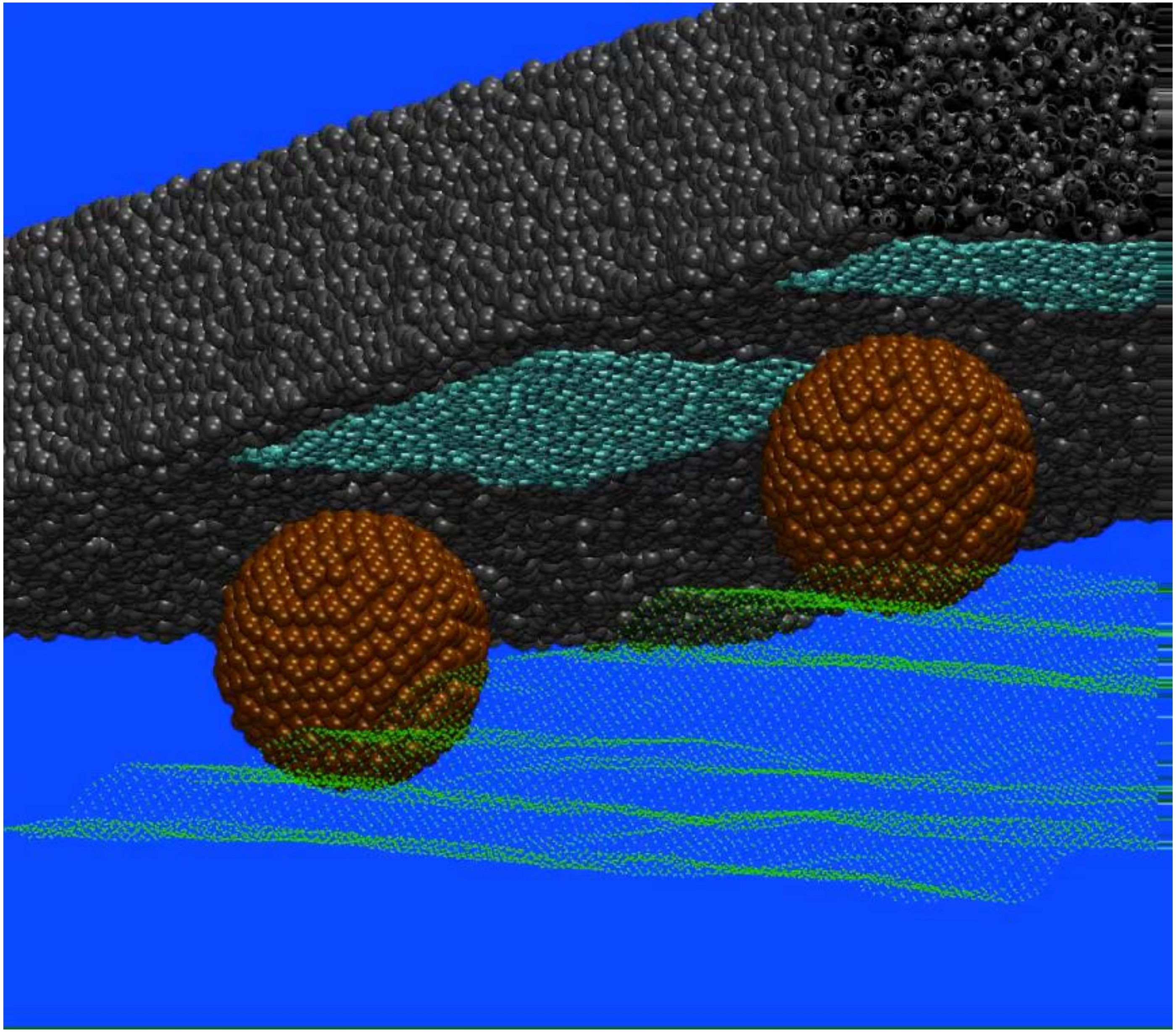
Coefficient of friction: $\mu = \frac{F_x}{F_z}$

- Graphene patch is highly reactive on the edges and easily attaches to the nanodiamond dangling bonds
- Graphene patch prefers to wrap around nanodiamond 3D structure to promote higher surface contact
- Formation of stable scroll and sliding is determined by following energetics criterion

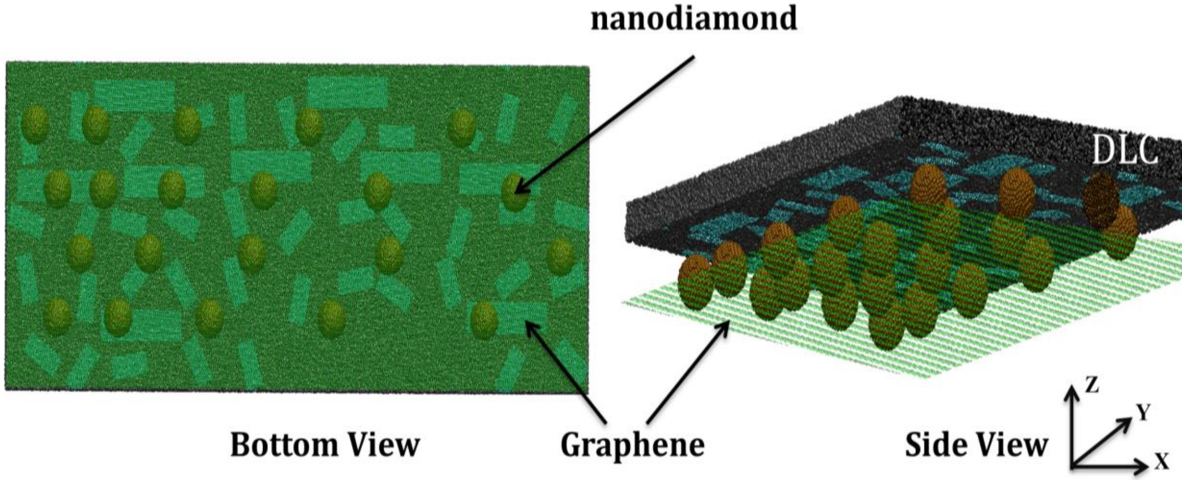
$$E_{strain} + E_{g-DLC} < E_{g-Dia} + E_{kin}$$

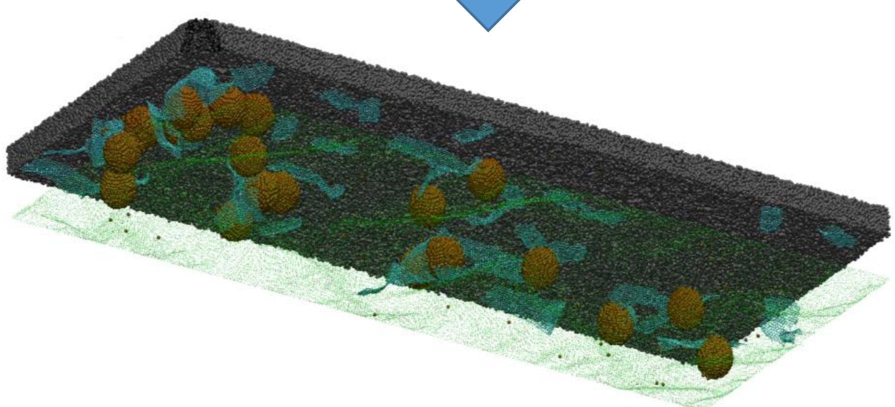
- DLC provides an incommensurate contact
- COF depends on contact area between graphene scroll and DLC

Visualization of scroll formation (simulation)



Link to mesoscale



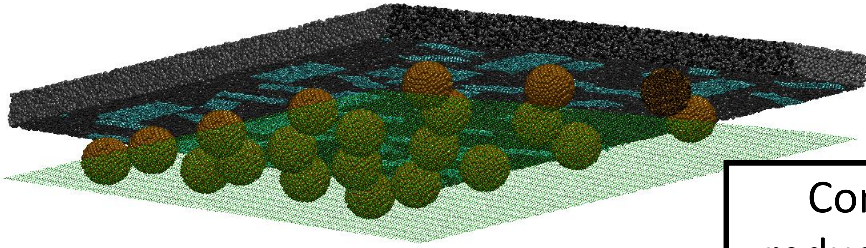


After t = 500 ps

- Large brock of DLC 770Å x 305Å x 22Å
- 55 single layer graphene patch -> random orientation
- 25 nanodiamond (diameter: 32Å) -> randomly placed
- Graphene sheet 770Å x 305Å
- Initial separation between DLC and graphene sheet was 40Å -> ~10 nN load
- Sliding of DLC with 40 m/s velocity for 3 ns
- Dry environment – no water molecules present

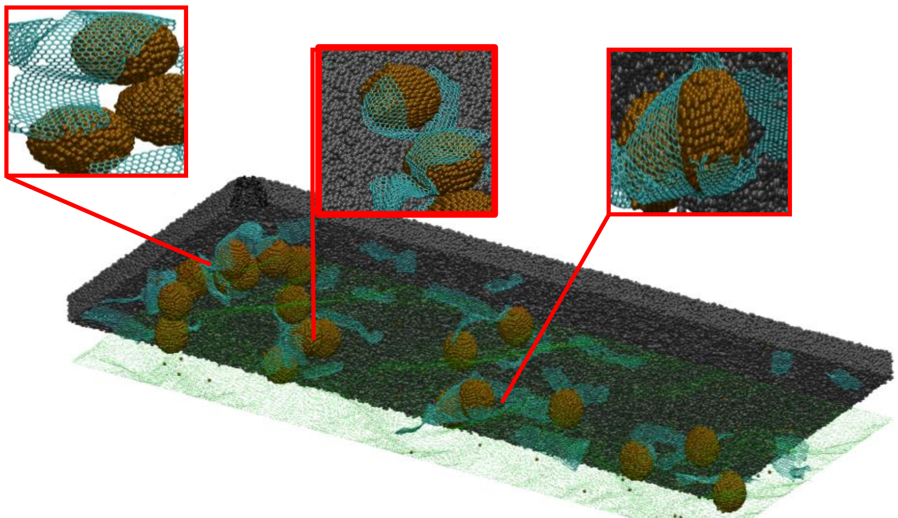
Graphene nanoscrolls formation with an ensemble of graphene patches and nanodiamonds

Link to mesoscale



Initial configuration

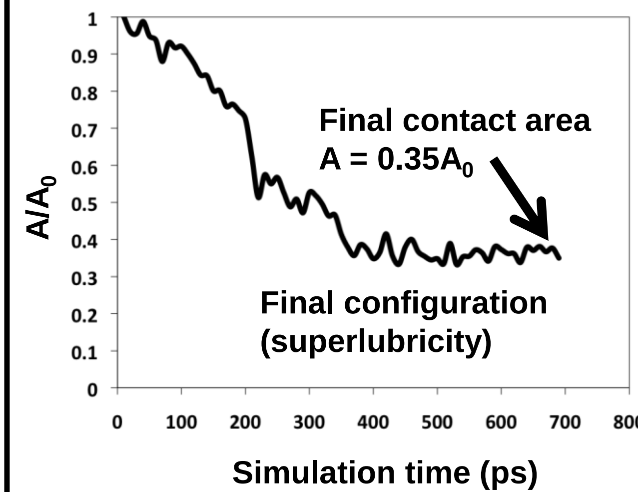
Contact area reduced by ~70% with scroll formation



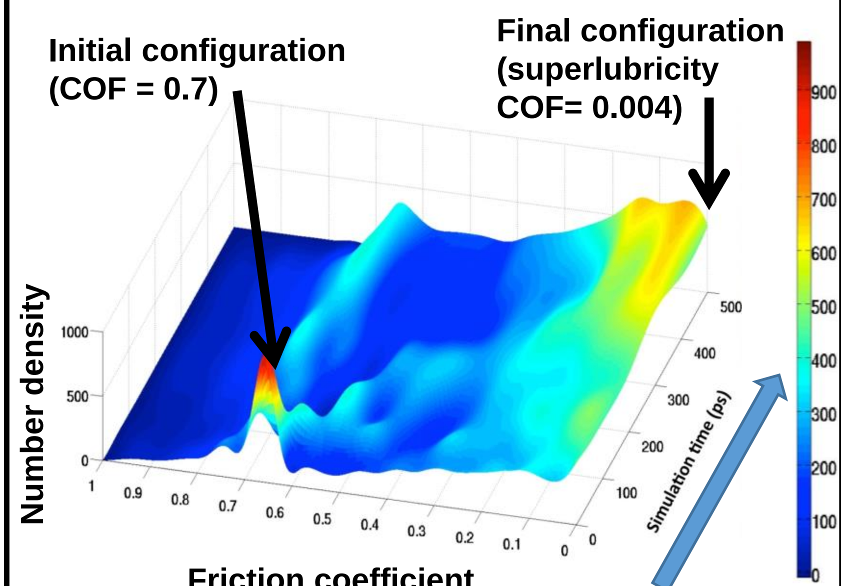
Final configuration
t = 500 ps

Coefficient of friction reduced with scroll formation

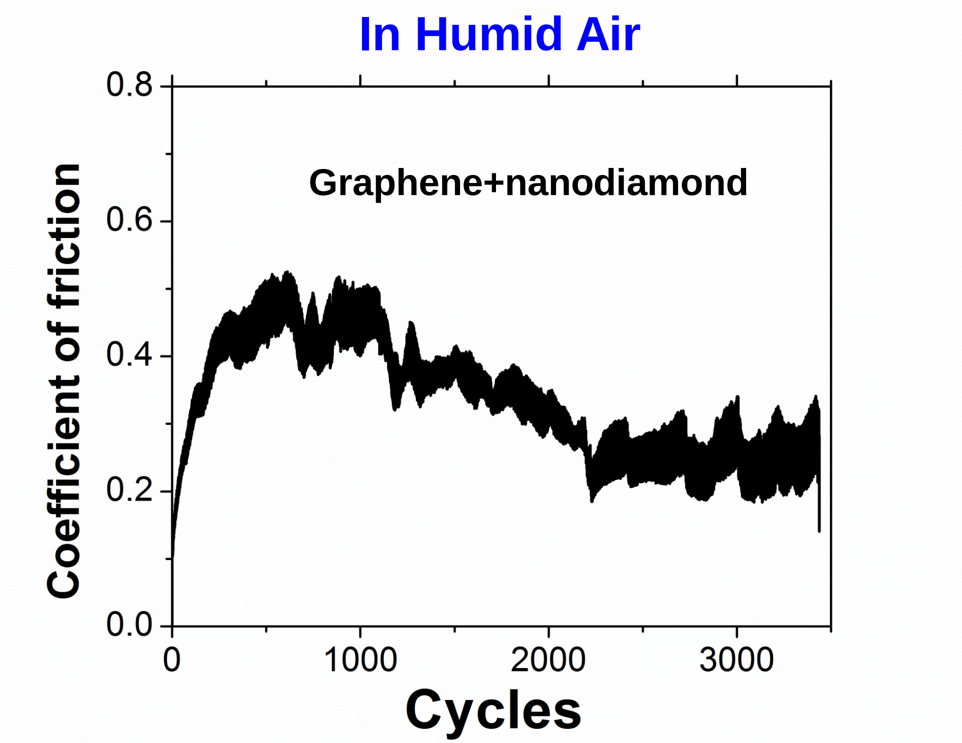
Contact area change

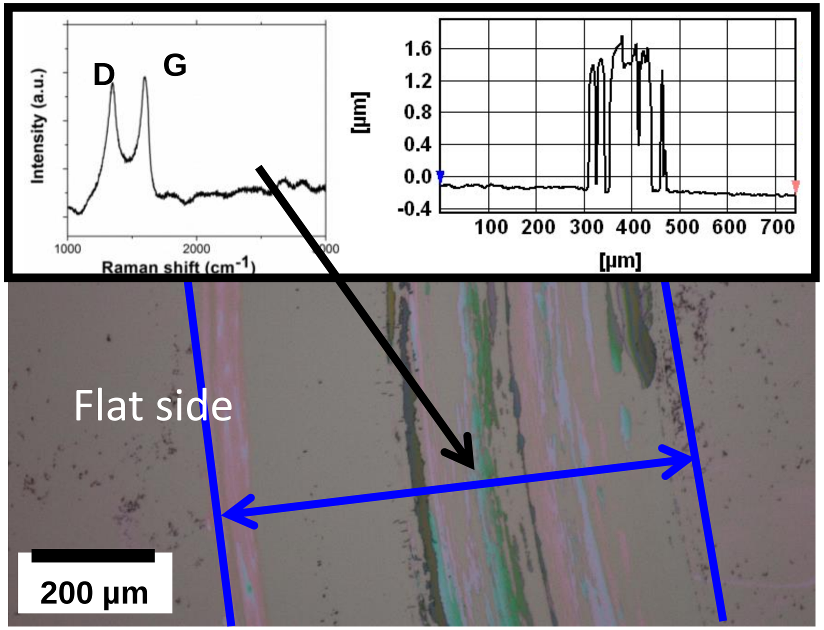


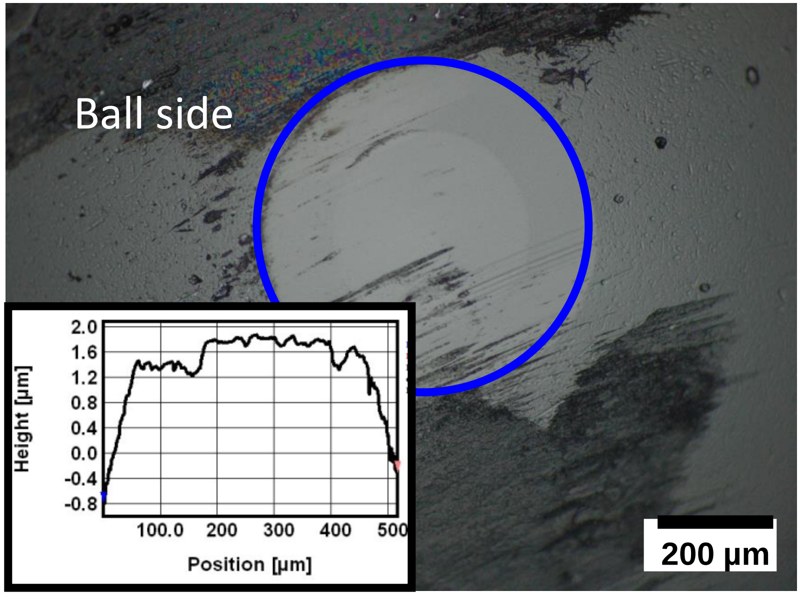
Coefficient of Friction



Superlubricity is lost when tested in humid air



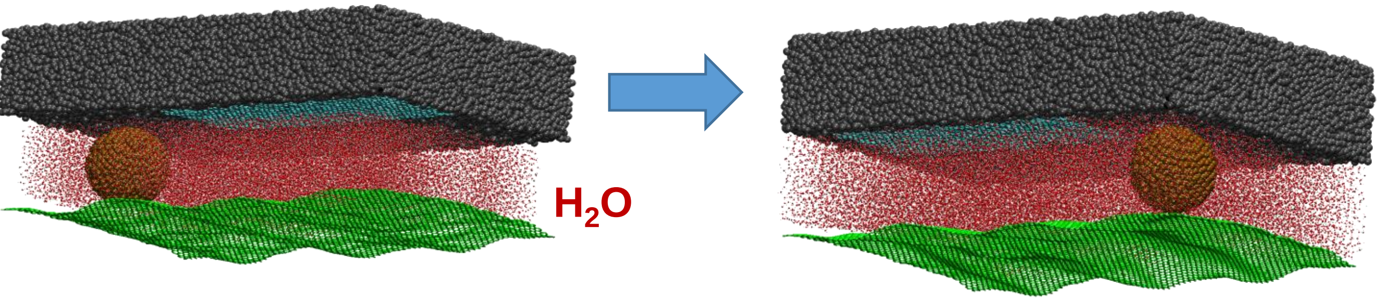




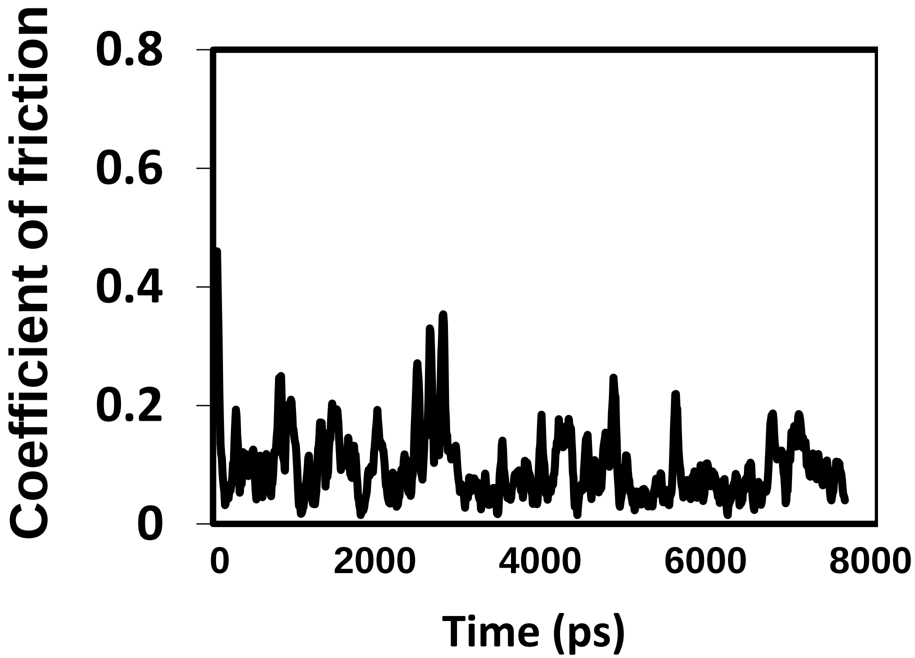
- Superlubricity is lost in ambient air environment
- Both flat and ball side show high wear
- Raman measurements from the wear track indicate highly defective graphene debris

Wear volume = 6.52 +/- 0.31 x 10 $^{-4}$ mm^3

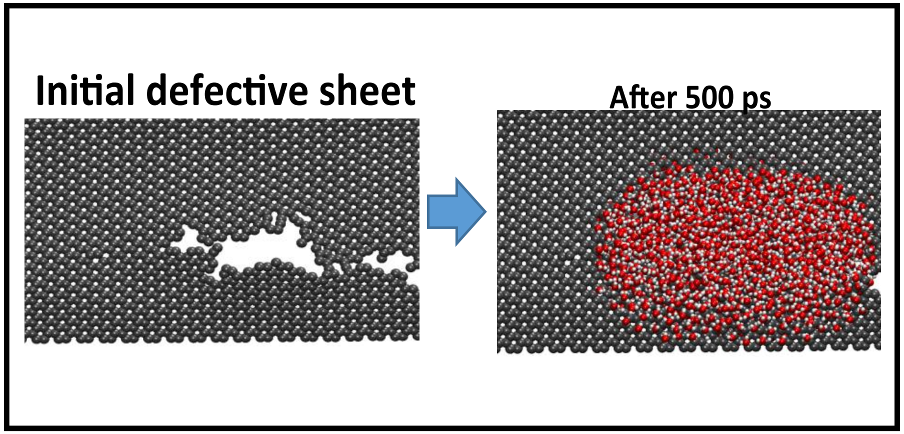
Suppression of scroll formation in presence of water



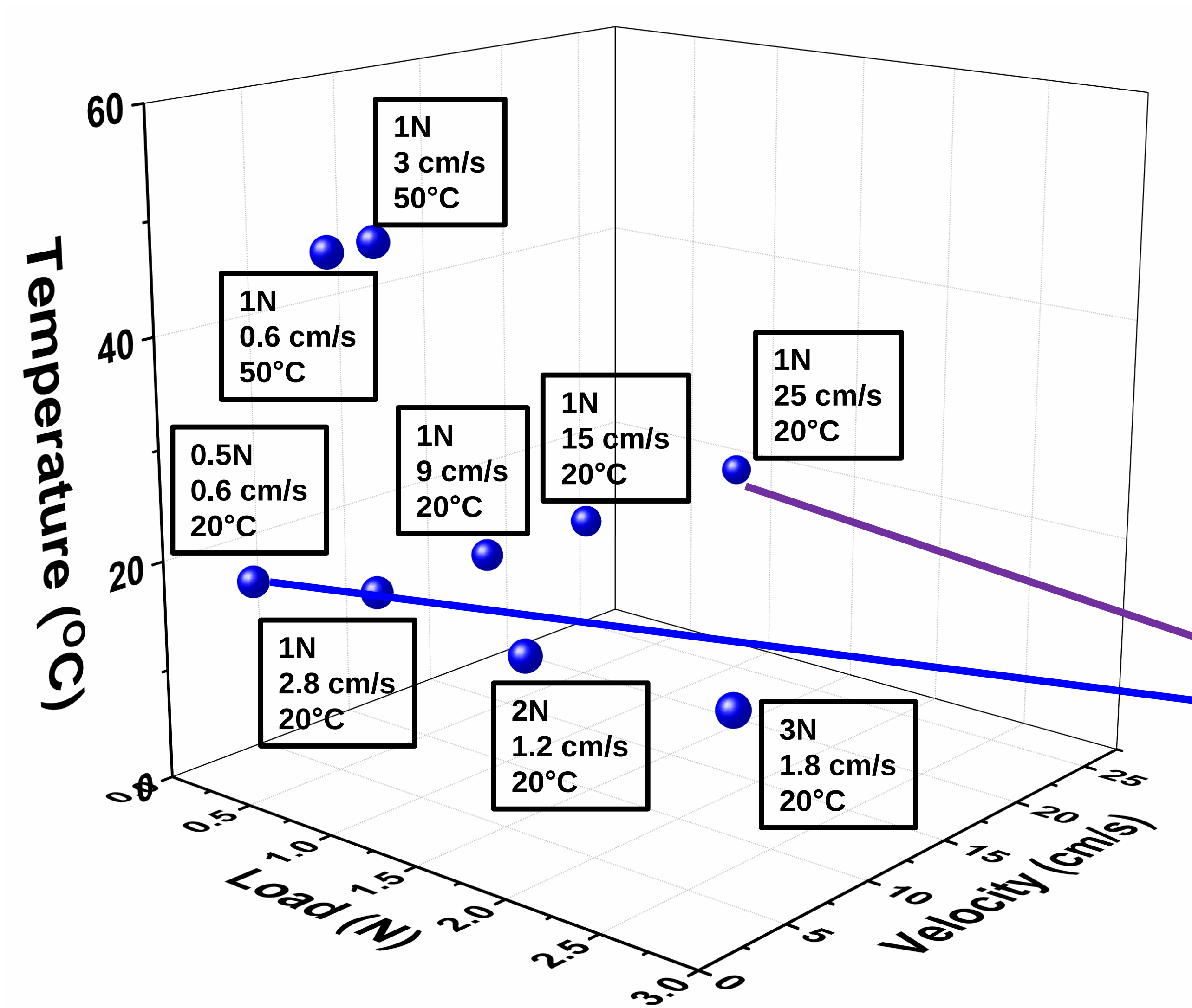
- The same initial DLC-graphene-nanodiamond configuration
- Randomly inserted 30,000 water molecules



- Water layers prevent scroll formation
- Water layers present constant energy barrier for DLC to overcome
- Presence of defects in the system additionally facilitates water adsorption from the ambient atmosphere

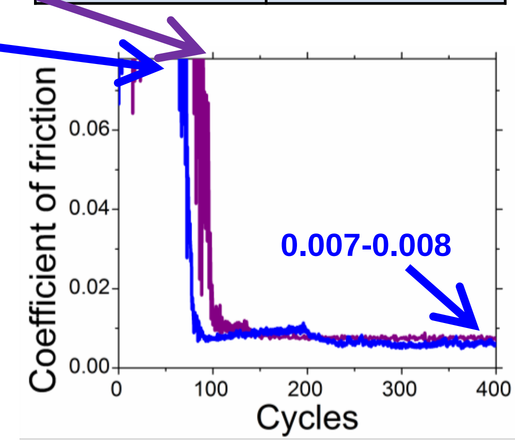


Stability of superlubricity regime



Superlubricity regime is experimentally shown to be stable under a range of loads, velocities, and temperatures.

COF	0.007-0.008 +/- 0.001
Load (N)	0.5 - 3
Velocity (cm/s)	0.6 - 25
Temperature (°C)	20 – 50



Sciencexpress Reports

Macroscale superlubricity enabled by graphene nanoscroll formation

Diana Berman,[1] Sanket A. Deshmukh,[1] Subramanian K. R. S. Sankaranarayanan,[1] Ali Erdemir,[2] Anirudha V. Sumant[1]*

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disulfide (MoS_2) (*15*) has been observed under specific environmental and sliding conditions. However, the exact superlubricity mechanism in above cases is still debatable and is not realized for industrial applications. In recent studies at nano and macroscale, graphene has shown a potential to substantially lower friction (*16–18*) and wear (*19–21*) under specific

Published online May 14, 2015, Science DOI: 10.1126/science.1262024
Published in print June 5, 2015, Science, 348(6239), 1118 (2015)

Press coverage

FRICTION

Macroscale superlubric
graphene nanoscroll fo

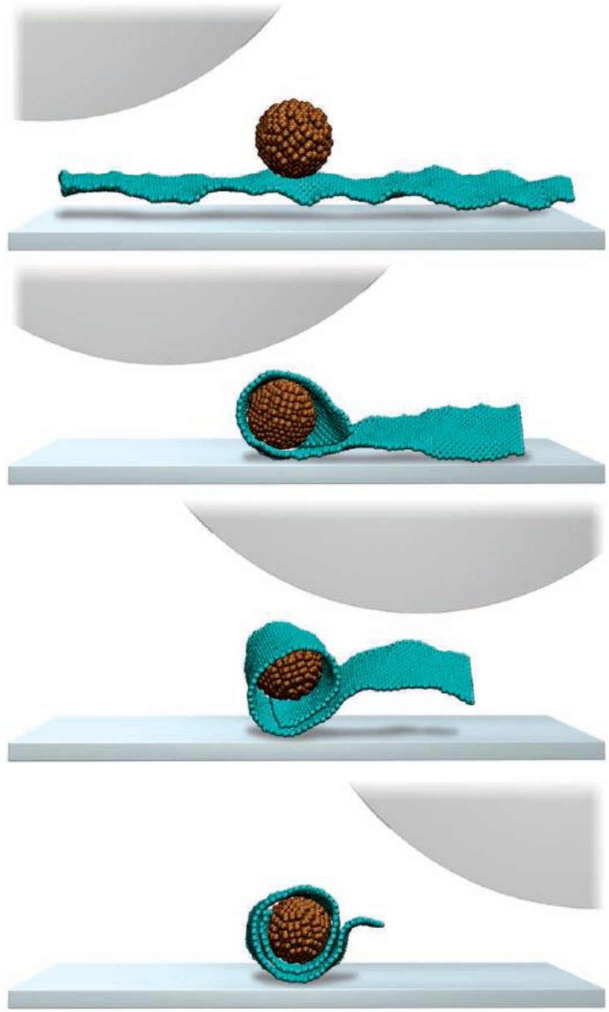
Diana Berman,[1] Sanket A. Deshmukh,[1] Subramanian I
Ali Erdemir,[2] Anirudha V. Sumant[1]*

Friction and wear remain as the primary modes of mec
moving mechanical assemblies; thus, it is desirable to
applications. We demonstrate that superlubricity can be
graphene is used in combination with nanodiamond pa
(DLC). Macroscopic superlubricity originates because g
interface wrap around nanodiamonds to form nanoscro
that slide against the DLC surface, achieving an incomm
reduced coefficient of friction (~0.004). Atomistic sim
mechanism and mesoscopic link bridging the nanoscal
experimental observations.

ROYAL SOCIETY OF CHEMISTRY

Graphene-wrapped diamond ball bearings cut friction to virtually nothing

14 May 2015 Tim Wogan



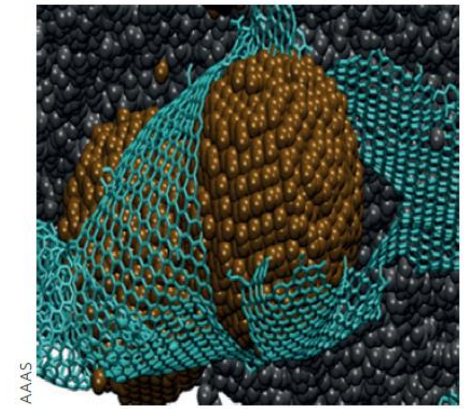
Squeeze wrap. Berman *et al*. found that huge reductions in macroscopic friction ("superlubricity") were achieved where nanodiamonds slid against graphene. The nanodiamonds bonded to graphene nanoplatelets and became wrapped in them, allowing them to slide easily through incommensurate surface effects.

research highlights

FRICTION

Sliding scrolls

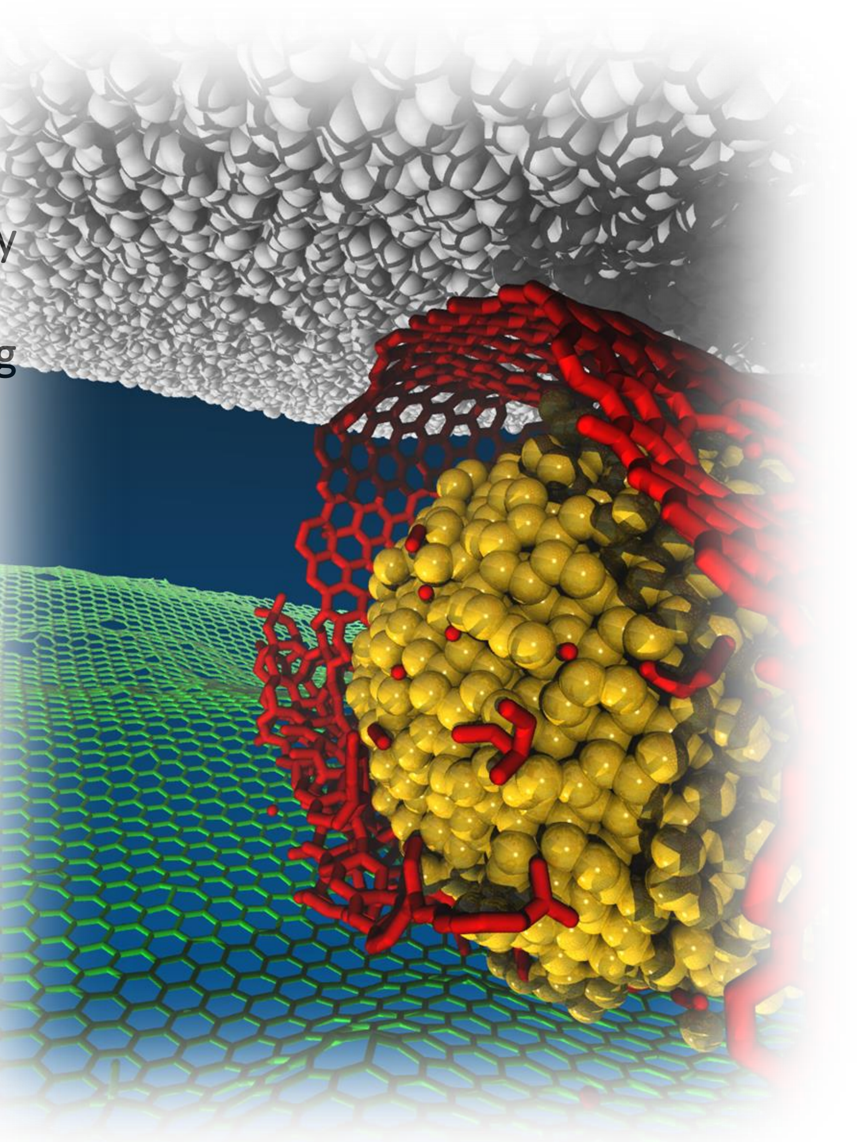
Science **348**, 1118–1122 (2015)



Superlubricity — the condition by which friction between two surfaces essentially tends to zero — has been previously observed for nanoscale sliding structures. Realizing it at the macroscale however is highly desirable for engineering applications, yet problematic due to issues with structural defects. Towards this end, a number of works have proven the beneficial effect that graphene can play in reducing friction. Now, Diana Berman *et al.* have demonstrated that superlubricity can be achieved at the macroscale in a dry environment by the addition of nanodiamonds between graphene flakes on a silicon substrate and a sliding diamond-like carbon interface, reporting a coefficient of friction of approximately 0.004. Analysis of the wear debris reveals that the nanodiamonds become wrapped up in the graphene flakes, forming nanoscrolls. Supporting simulations show that more of the graphene flakes scroll with time, gradually reducing the contact area between the nanoscrolls and the diamond-like carbon contact surface, allowing a superlubric state to be reached. *JP*

Conclusions

- We demonstrate structural superlubricity at true macroscale, with a realistic possibility of scaling-up to the engineering scale.
- We propose a new mechanism of structural lubricity at macroscale facilitated by formation of graphene nanoscroll around nanodiamond sliding against amorphous DLC
- Mesoscopic link to connect nanoscale scroll formation with macroscale experimental observations is presented
- Water presence suppresses scroll formation and results in loss of superlubric behavior under humid environment conditions
- Discovery of macroscale superlubricity offers a direct pathway for designing smart frictionless tribological systems for practical applications of industrial interest.



Acknowledgements

- The use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357
- This research used tribological test facilities of the Energy Systems Division supported by the Vehicle Technologies Program of the Office of Energy Efficiency and Renewable Energy of the U.S. Department of Energy under Contract No. DE-AC02- 06CH11357.
- National Energy Research Scientific Computing Center, supported by the Office of Science of the U.S. Department of Energy under contract No. DE-AC02-05CH11231
- MIRA supercomputer at Argonne under INCITE Program
- Help with TEM by Yuzi Liu (NST) is greatly appreciated
- Tribology group at ES division