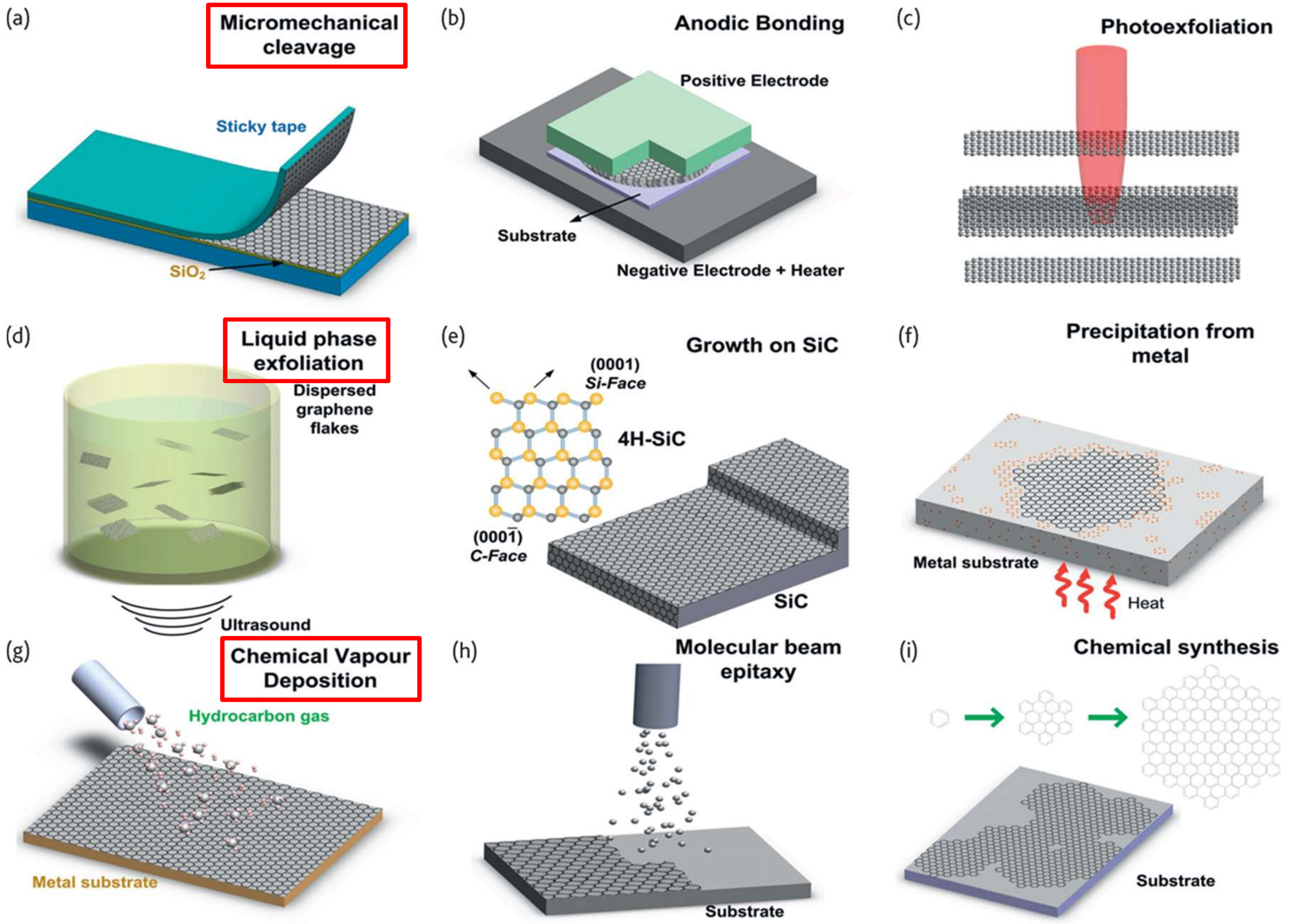
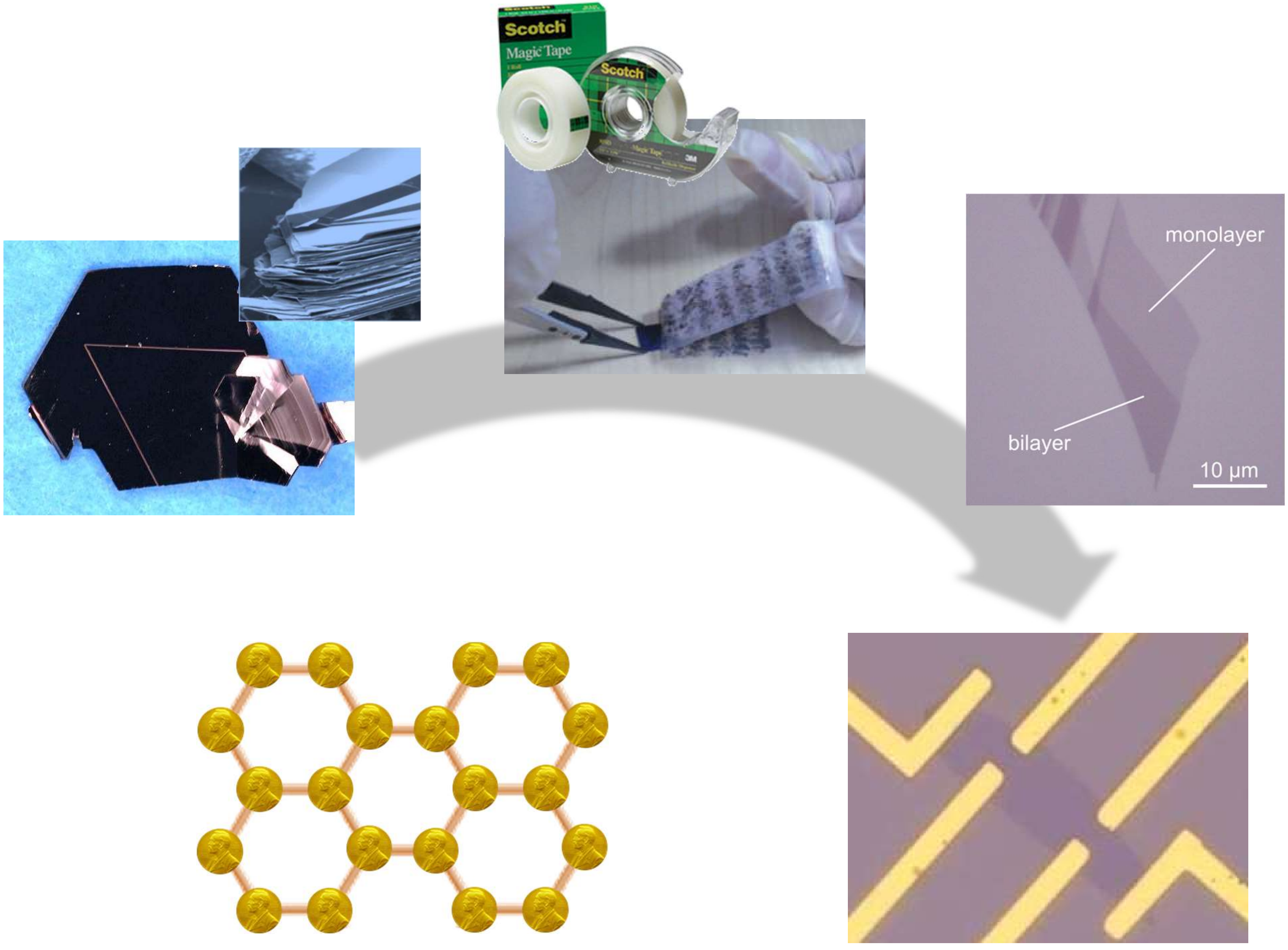
5. Production of 2D Materials
Part 1

How to Make 2D Materials



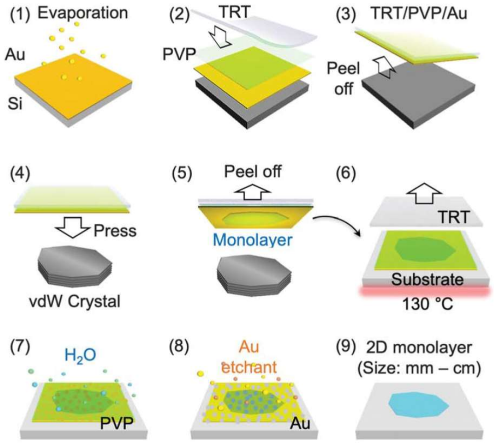
F. Bonaccorso et al. Materials Today (2012)

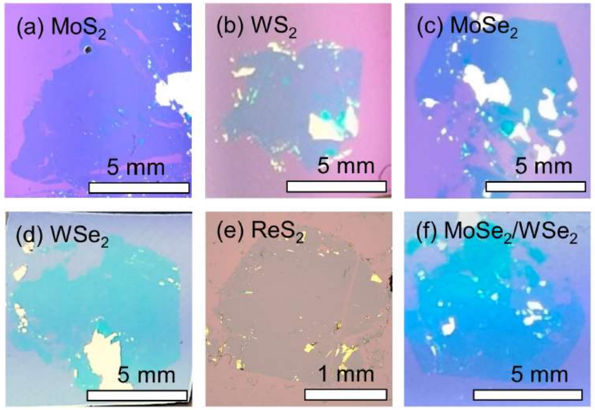
Mechanical Exfoliation (Scotch Tape Method)

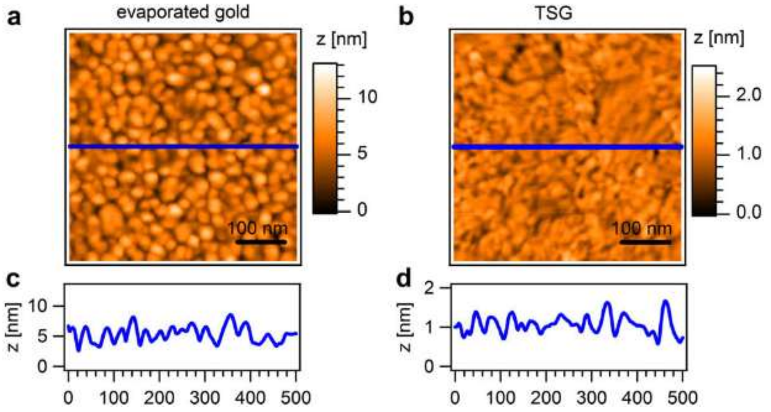


Advanced Mechanical Exfoliation

Mechanical exfoliation by using flat Au film

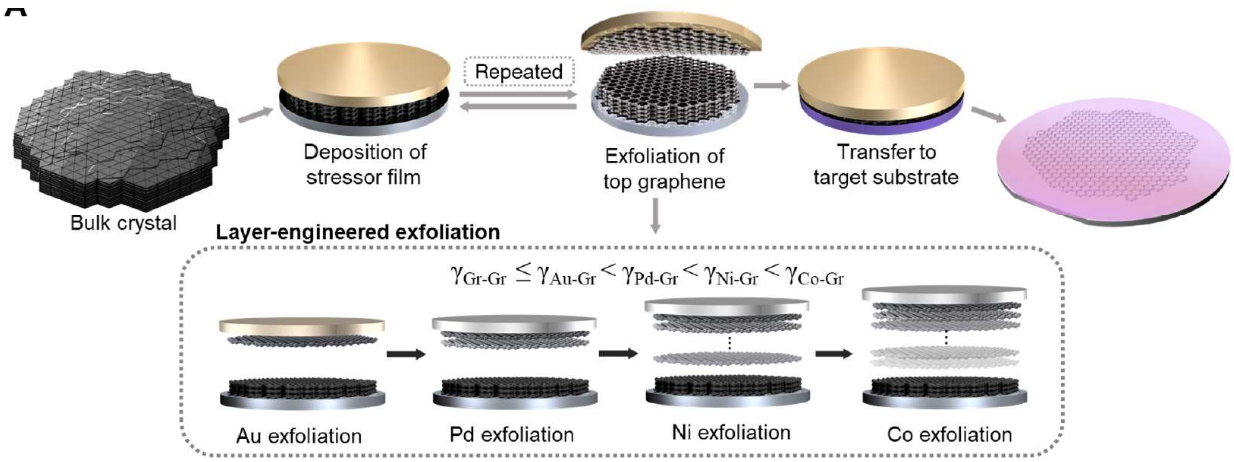


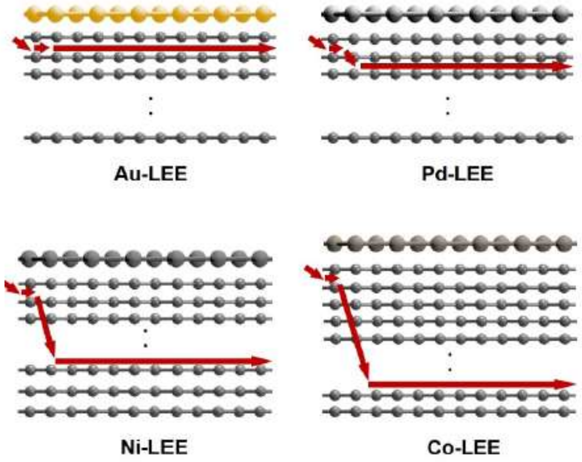




A. Rueda et al. Surface Science (2009)

Layer-engineered exfoliation by using deposited metal films

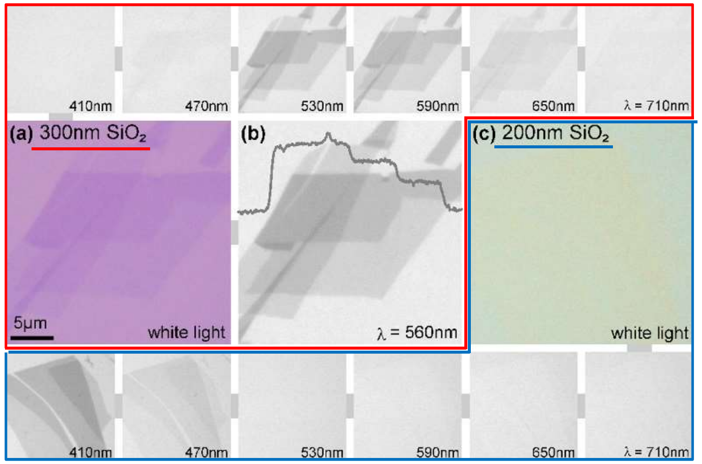


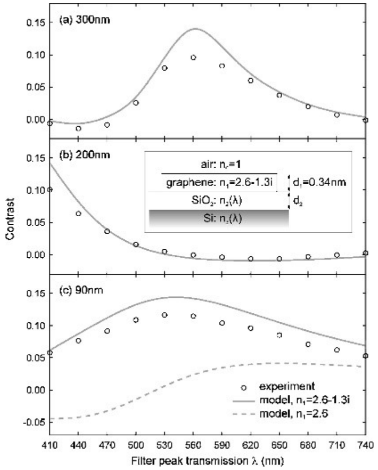


Moon et al., Sci. Adv. (2020)

Optical Contrast of Graphene

Graphene's visibility depending on substrate and light wavelength



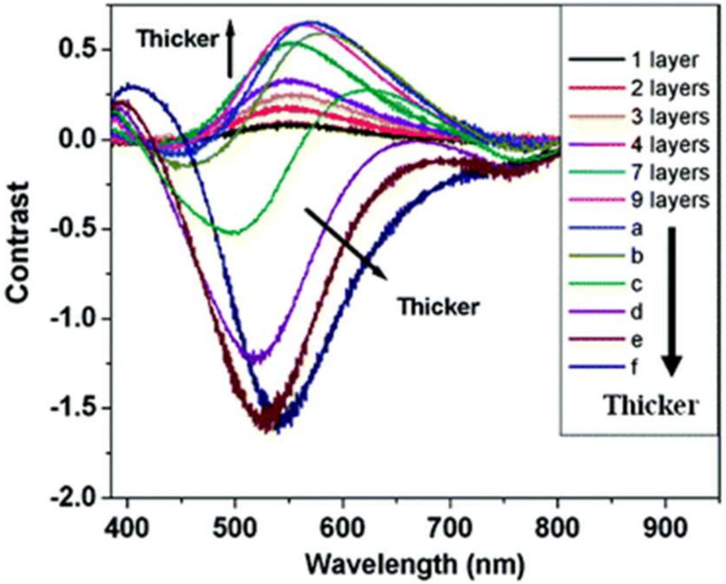


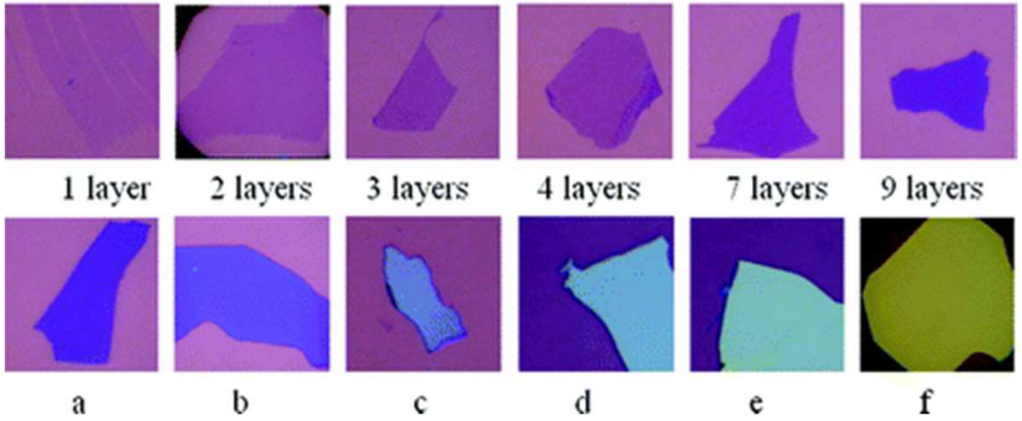
$$Contrast\ (\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}$$

where, $R_0(\lambda)$ is the reflection spectrum from the SiO_2/Si substrate and $R(\lambda)$ is the reflection spectrum from graphene sheet.

P. Blake et al. Applied Physics Letters (2007)

Optical contrast depending on number of layers





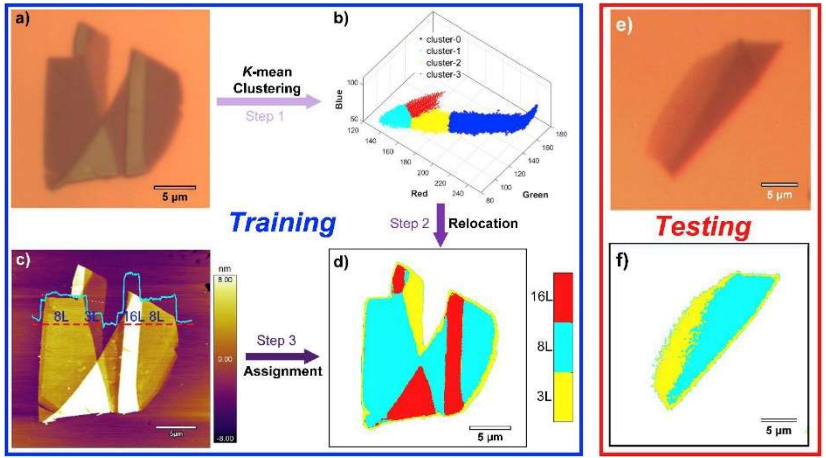
Sample a, b, c, d, e, f > 10 layers

I. Jung et al. Nano Letters (2007)

Z. H. Ni et al. Nano letters (2007)

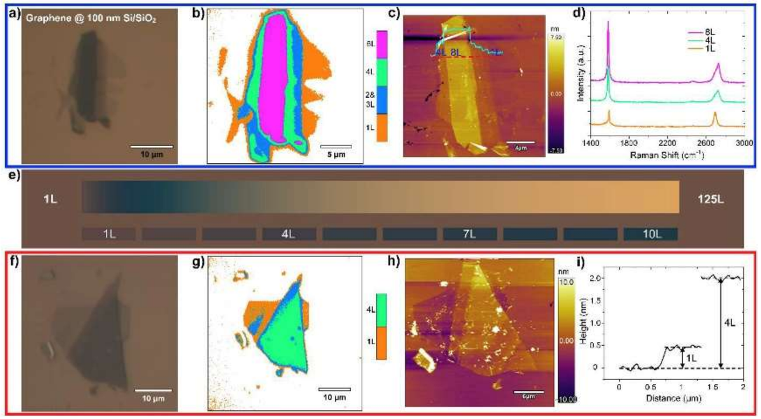
Identification of Number of Layer Number

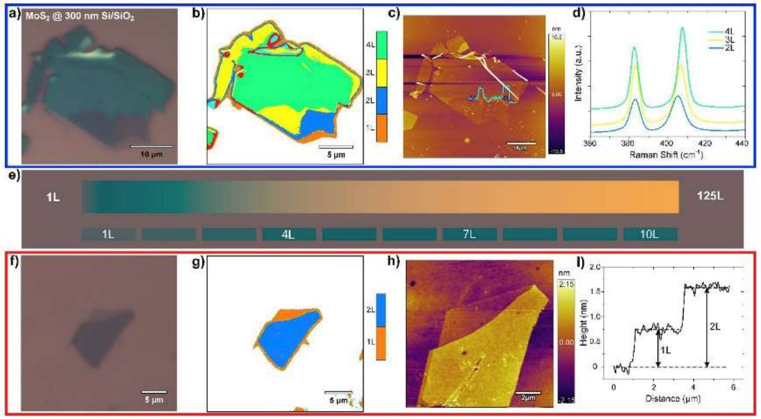
machine learning



graphene

MoS$_2$





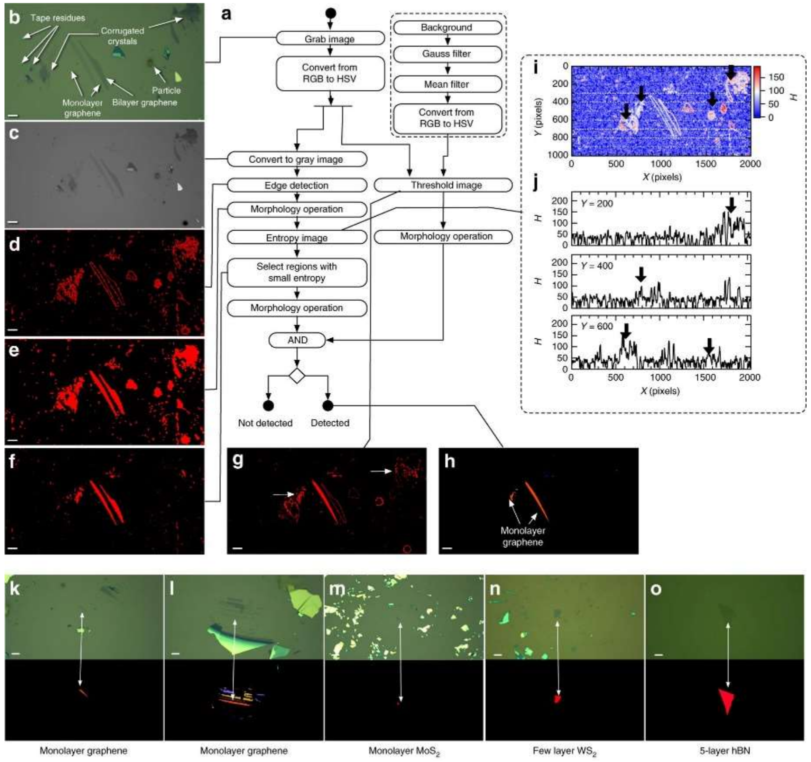
Three effective indexes

- optical contrast
- total color difference
- red-green-blue

Y. Li et al. Journal of Materiomics (2019)

Auto-finding Flakes of 2D Materials

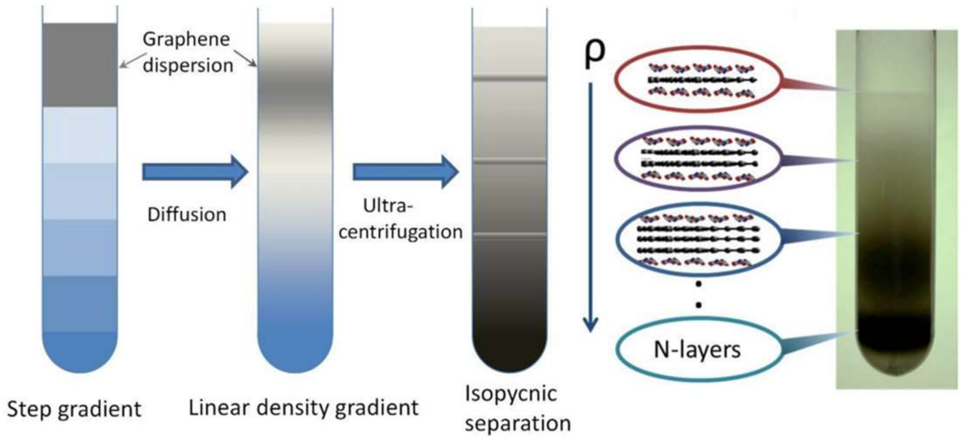
Auto-finding flakes of 2D materials

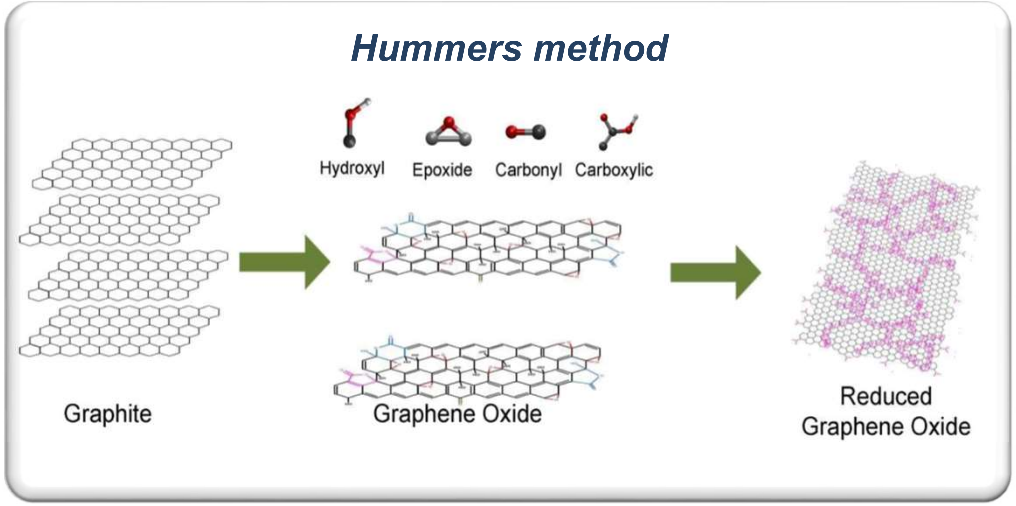


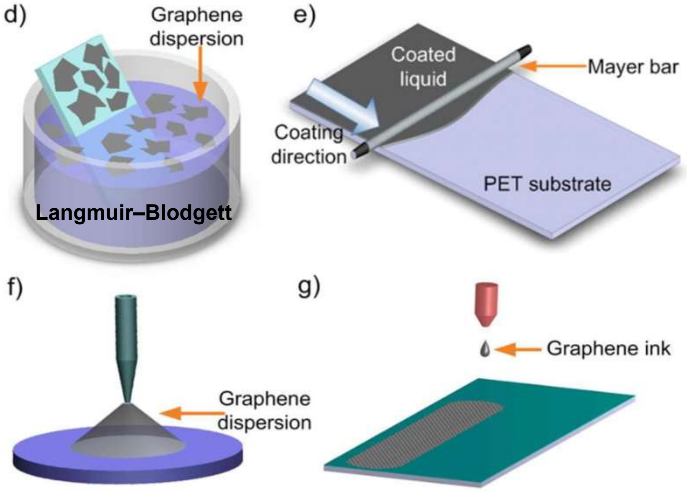
Scan for 2D crystals

S. Masubuchi et al. Nature Commun. (2018)

Liquid Exfoliation



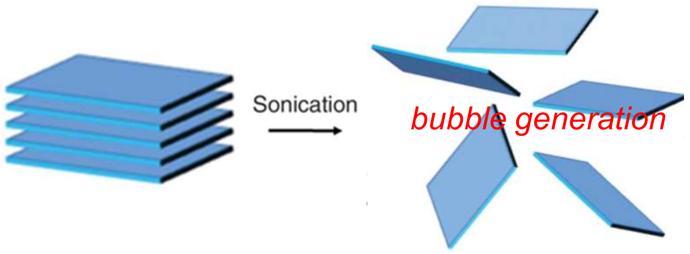

Hummers method



F. Bonaccorso et al. Materials Today (2012)
K. R. Paton et al. Nature Materials (2014)
A. C. Ferrari et al. Nanoscale (2014)

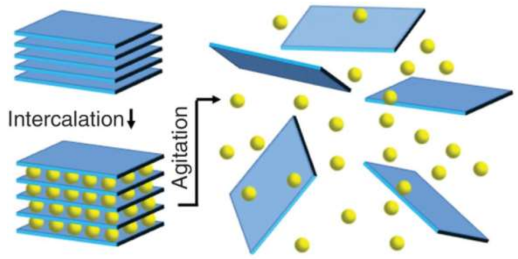
Liquid Exfoliation

Ultrasonication method



V. Nicolosi et al. Science (2013)

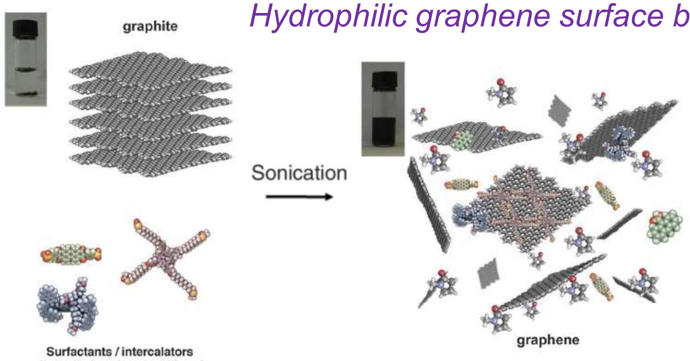
Hummers method



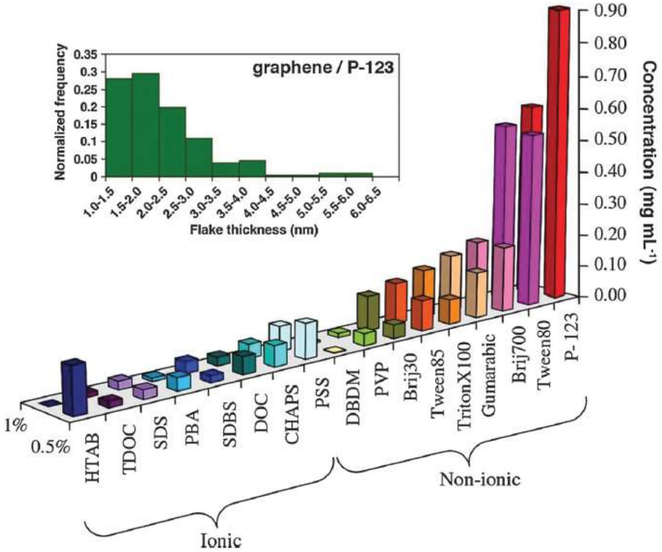
Graphene oxidation (H_2SO_4 or $KMnO_4$) → Formation of hydroxyl or epoxide groups → Water Intercalation by hydrophilicity → Ultrasonication → Reduction

Intercalation method

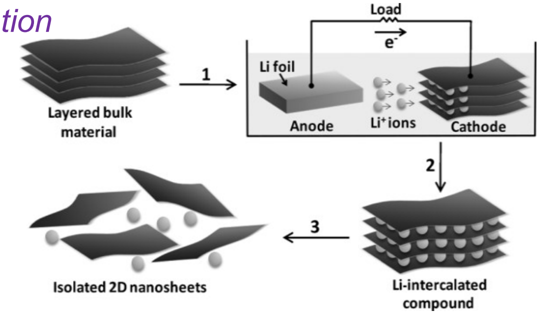
Hydrophilic graphene surface by surfactant



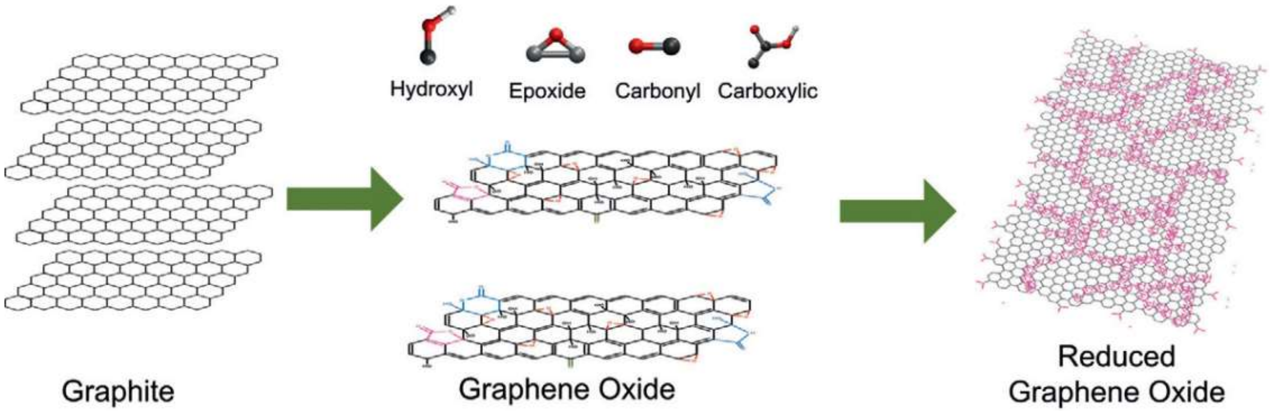
A. Ciesielski et al. Chem. Soc. Rev. (2014)

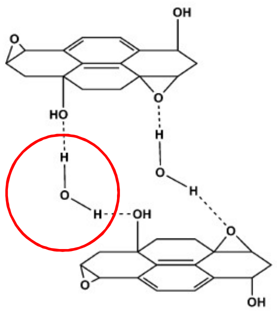


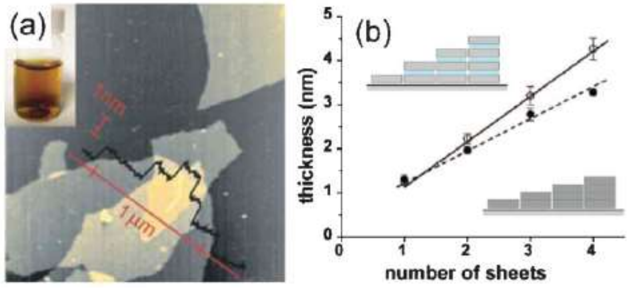
Li intercalation



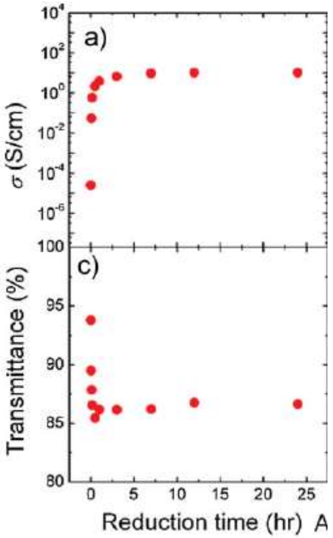
Oxidation/Reduction for rGO

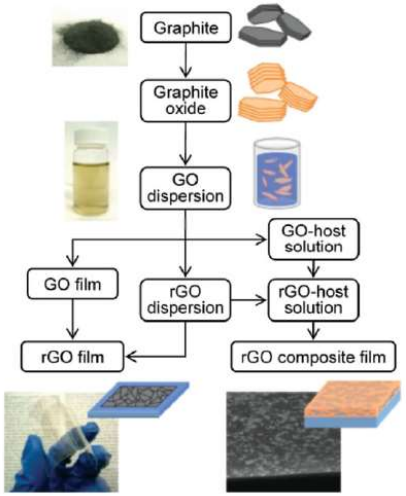






	Oxidation / Reduction
Mechanism	Attachment/detachment of functional groups including oxygen
Properties	Control of property by varying types/amounts of oxide Scattering of electrons due to chemical groups/defects

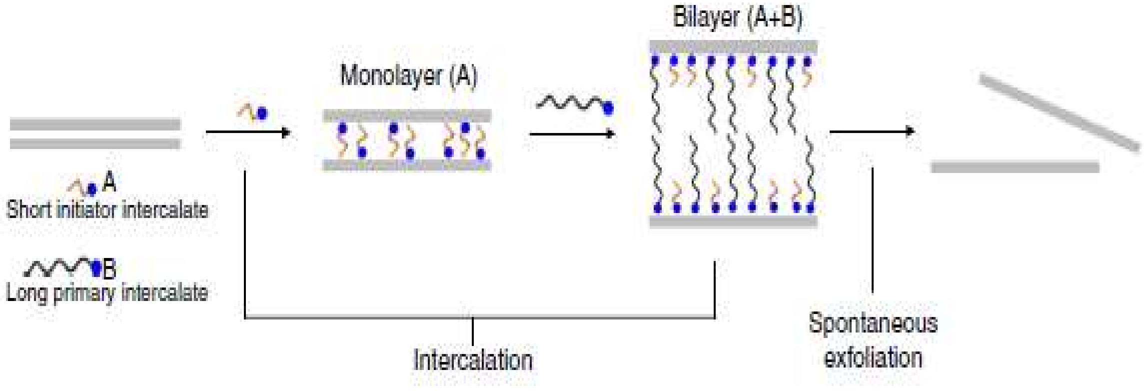


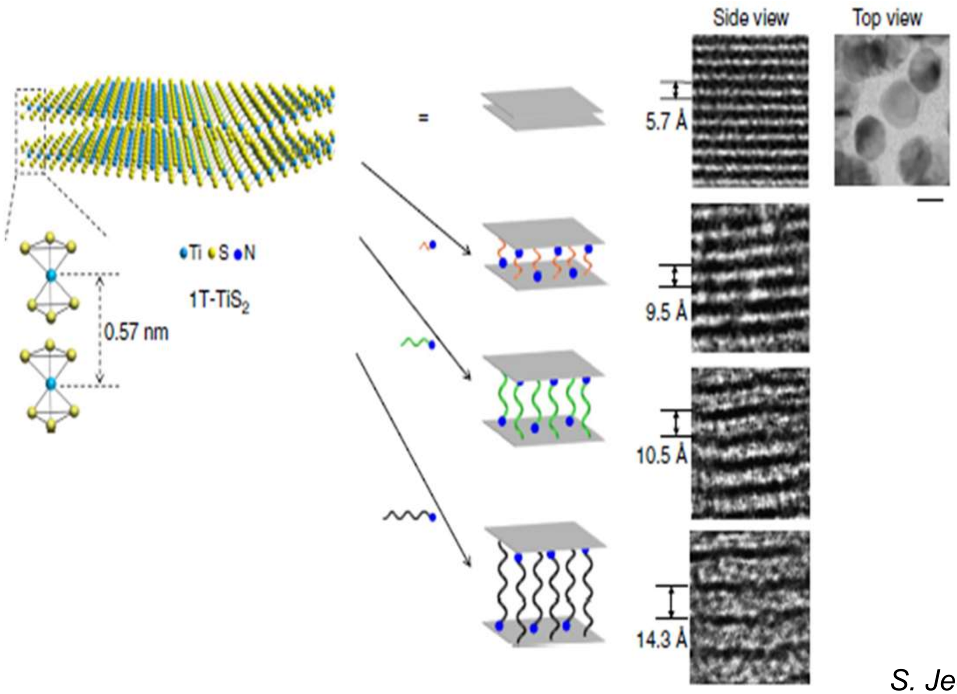


F. Bonaccorso et al. Materials Today (2012)

Advanced Liquid Exfoliation

Tandem molecular intercalation

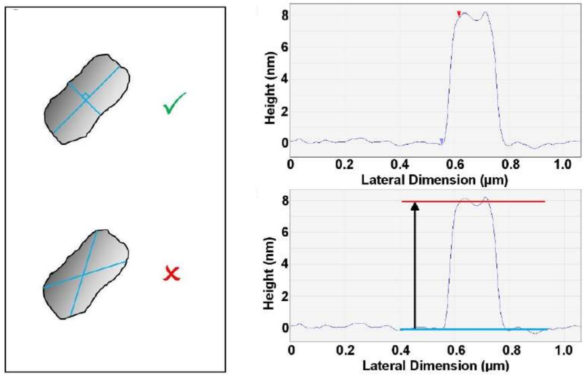




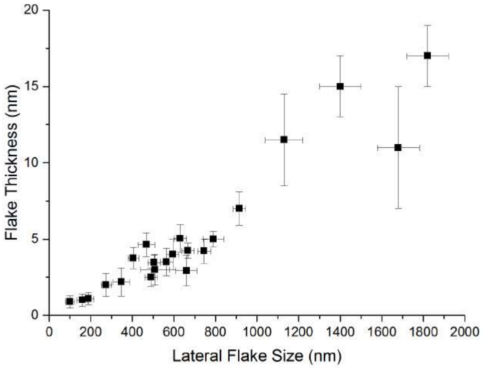
S. Jeong et al. Nature Commun. (2015)

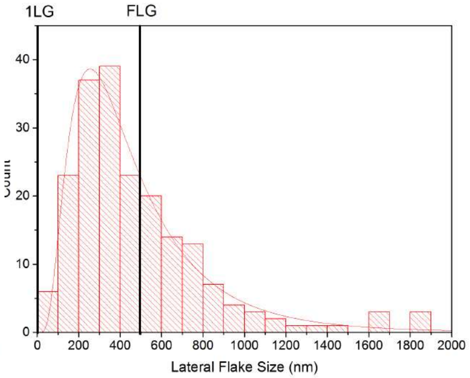
Standard Category of Graphene

Determination of thickness and size of graphene flakes



Distribution of graphene flakes





Graphene; graphene layer; single layer graphene; monolayer graphene
Single layer of carbon atoms with each atom bound to three neighbors in a honeycomb structure

Bilayer graphene (2LG)
Two-dimensional material consisting of two well-defined stacked graphene layers

Few-layer graphene (FLG)
Two-dimensional material consisting of three to ten well-defined stacked graphene layers

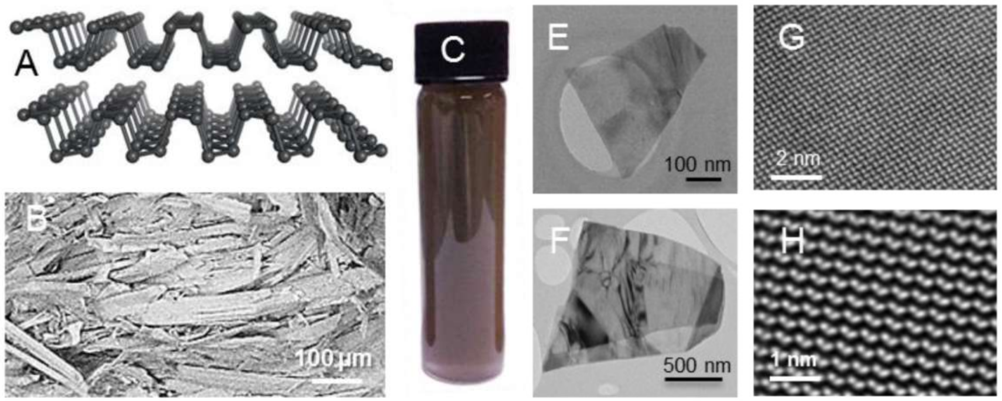
Graphene nanoplatelet (GNP)
Thickness between 1 and 3 nm and lateral dimensions ranging from ≈100 nm to 100 μm.

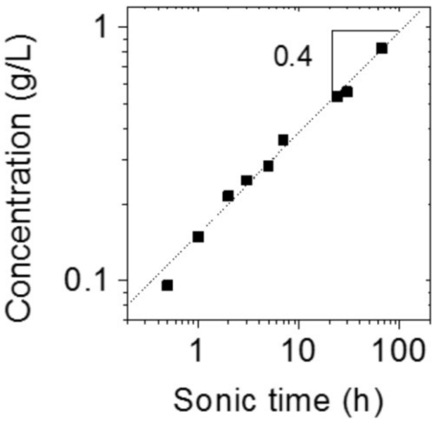
Thickness of graphene monolayer is 0.34 nm. But, it is not correspond to single layer graphene on substrate because interaction between substrate and graphene is different from that between graphene layers. So, we have to confirm the number of layers of graphene on substrate using Raman spectroscopy and AFM. For example, even though the thickness of a graphene flake is measured as 1.0 nm with AFM, it might be a single layer graphene as confirmed by Raman spectroscopy. Nevertheless, subsequent layers have a corresponding 0.34 nm step height (*i.e.* 2LG is ~1.34 nm and 3LG is ~1.68 nm-thick).

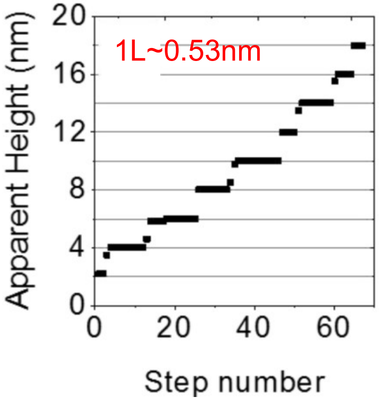
A. P. Kauling et al. Adv. Mater. (2018)
A. J. Pollard et al. “Characterisation of the structure of graphene”, NPL, (2017)

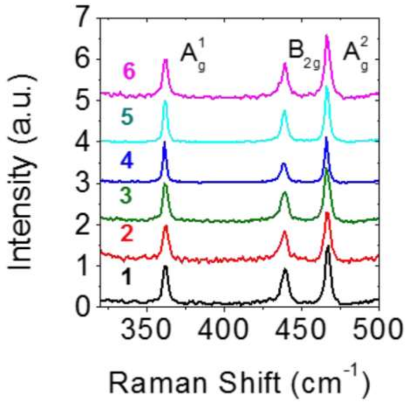
Liquid Exfoliation of Black Phosphorous

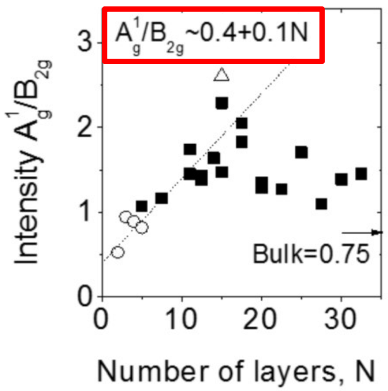
Sonication in N-cyclohexyl-2-pyrrolidone (CHP)







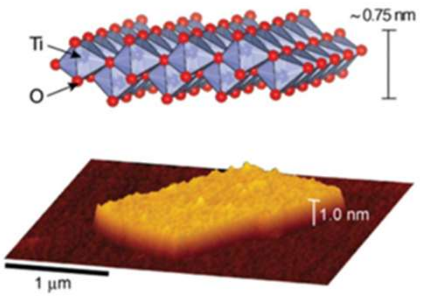


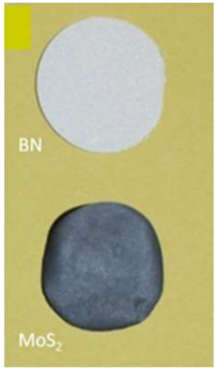


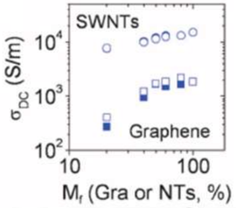
D. Hanlon et al. Nature Commun (2015)

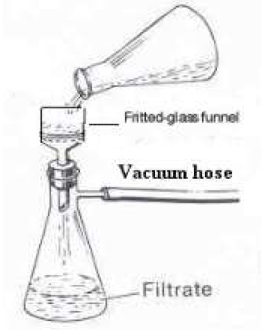
Applications of Liquid-Exfoliated 2D sheets

Formation of thin or free-standing films

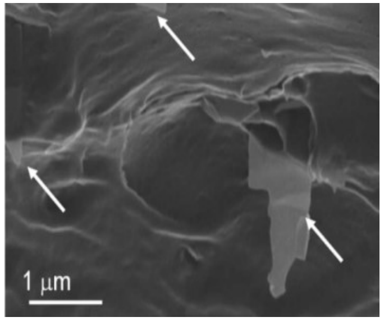


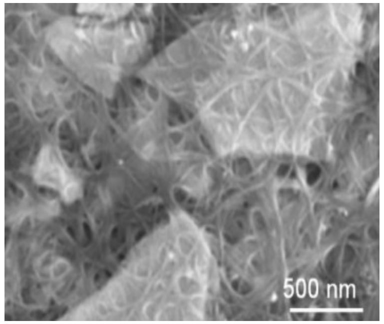




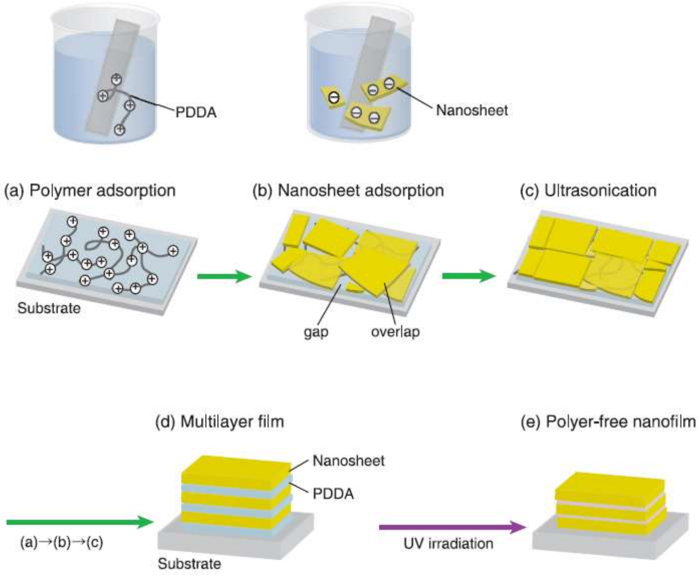


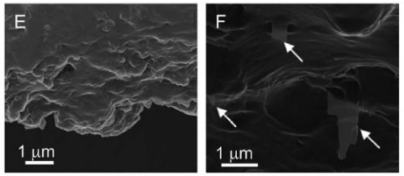
Mixing with other materials (polymer composites)

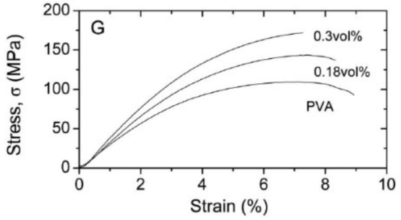




Formation of 2D oxide films

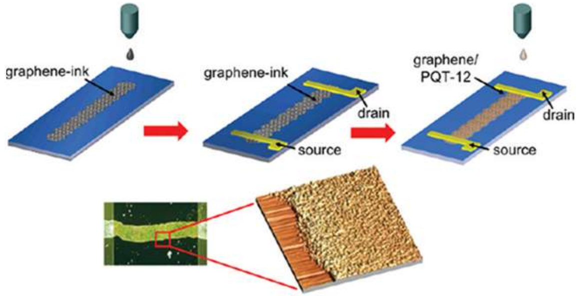


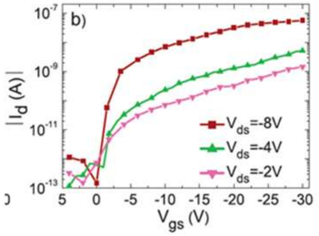




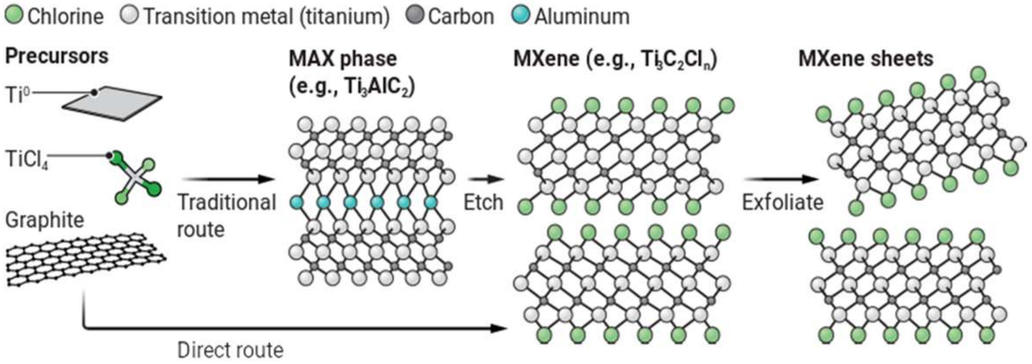
	Ti$_{0.87}$O$_2$ nanosheet	TiO$_2$ (rutile)	TiO$_2$ (anatase)
Dielectric constant (exp.)	125	80–100	30–40
Electronic permittivity (calc.)	9.81	8.22	6.05

Printing of 2D materials





Direct route to synthesize Mxene

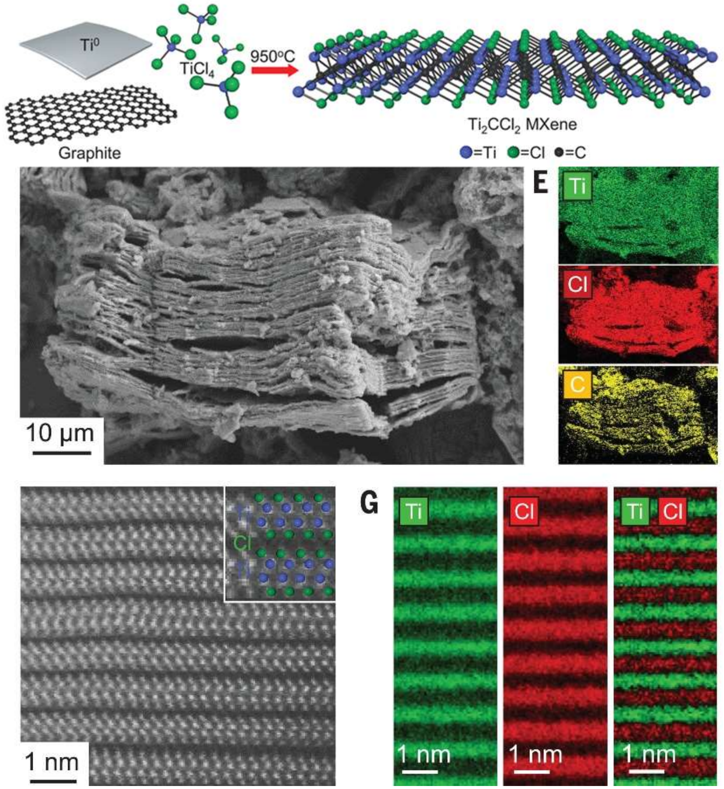


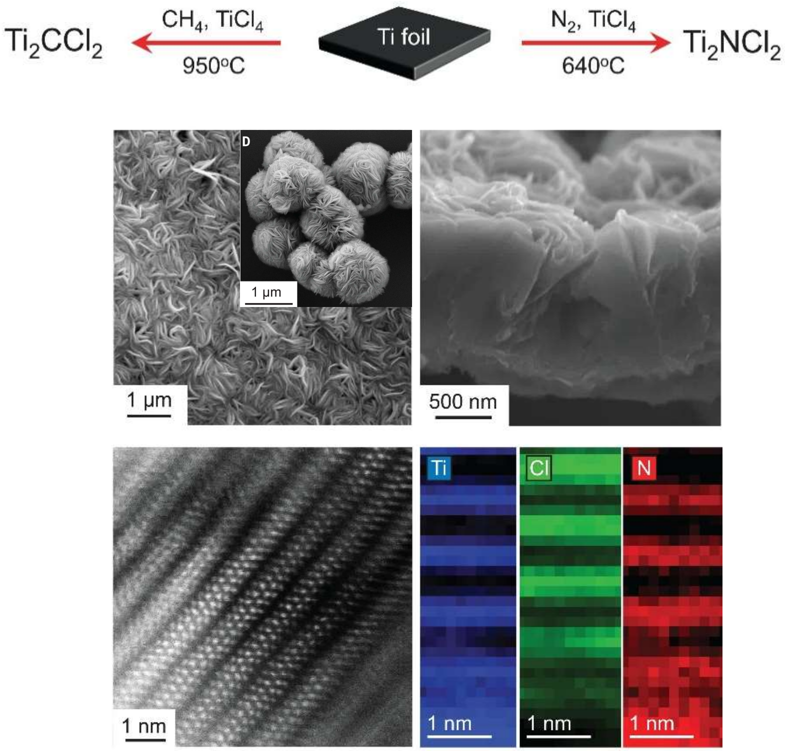
Precursors of the desired elements are heated together to produce a MAX phase.

Once synthesized, the MAX phase is treated with hydrofluoric acid or another etchant to remove A atoms and produce a layered MXene phase.

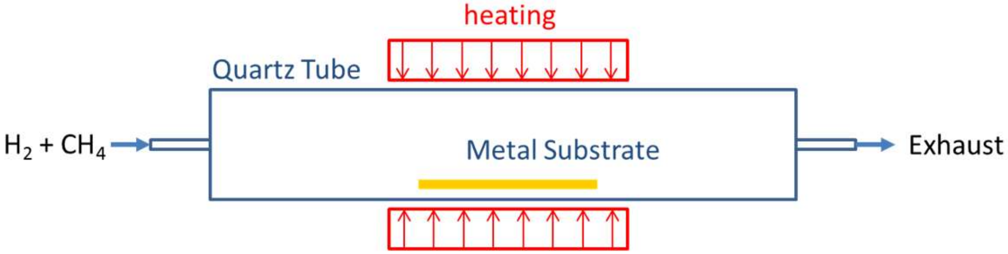
The bulk MXene material can then be exfoliated into individual sheets for applications.

Science 379, 1189-1190 (2023)





Chemical Vapor Deposition (CVD)

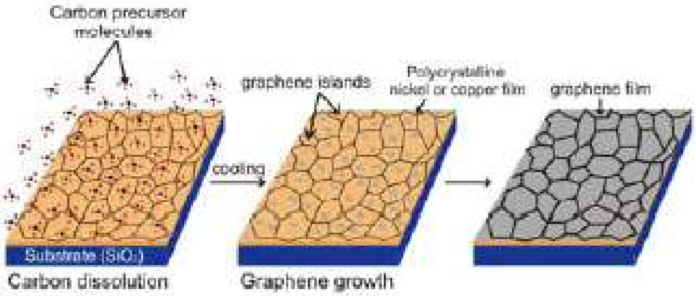

heating

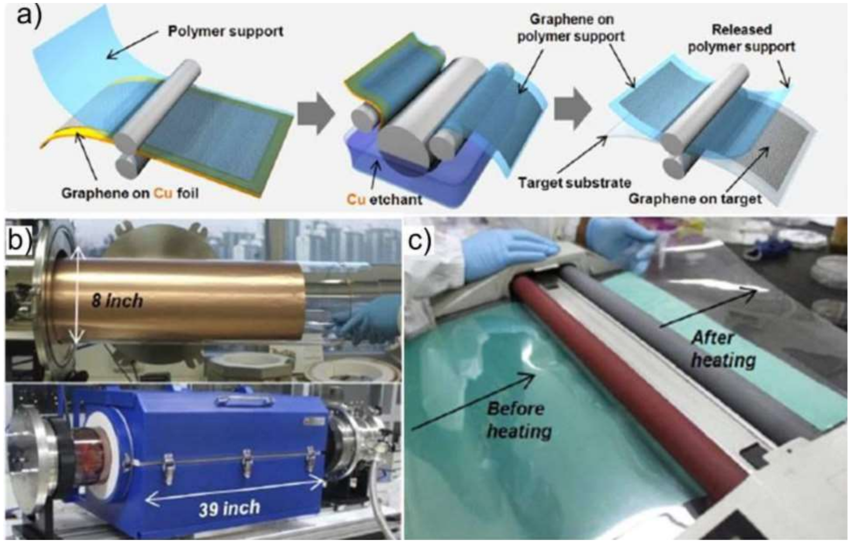
Quartz Tube

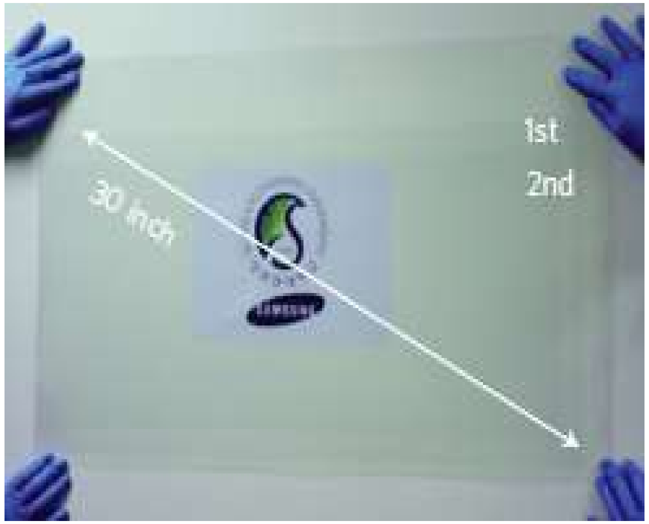
$H_2 + CH_4$

Metal Substrate

Exhaust







X. Li et al. Science (2009)
S. Bae et al. Nature Nanotech. (2010)
D. Jariwala et J Nanosci Nanotechnol.. (2011)

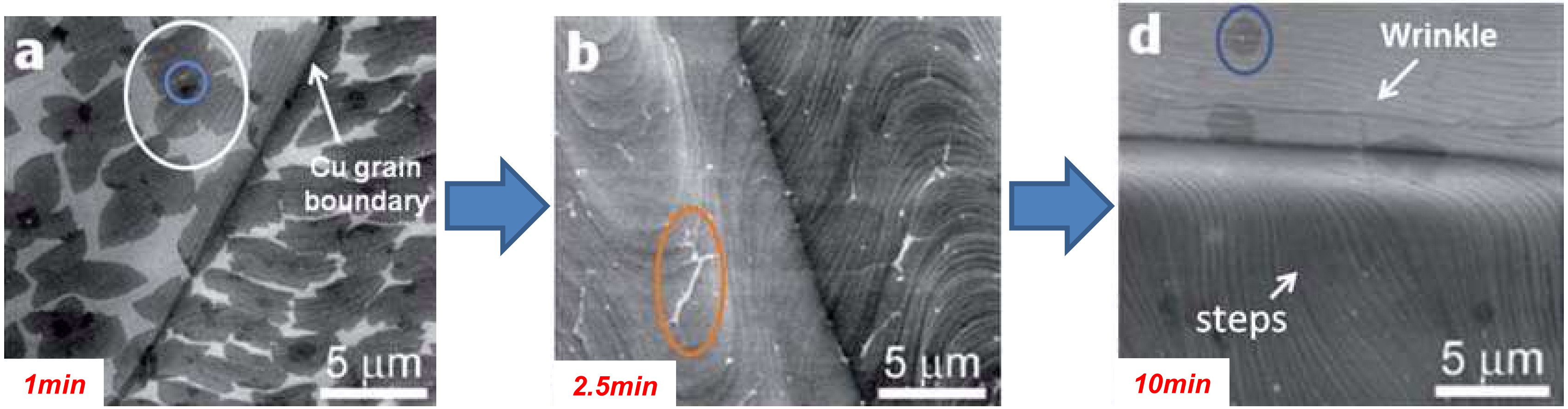
Chemical Vapor Deposition (CVD)

Factors to Influence Characteristics of Graphene

- *Nucleation : density of grains, homogeneity*
  - *Pre-treatment condition*
  - *Partial pressure of methane and total growth pressure*
  - *Nucleation sites – atomically thin terraces, defects, protrusions, evaporated copper during process*

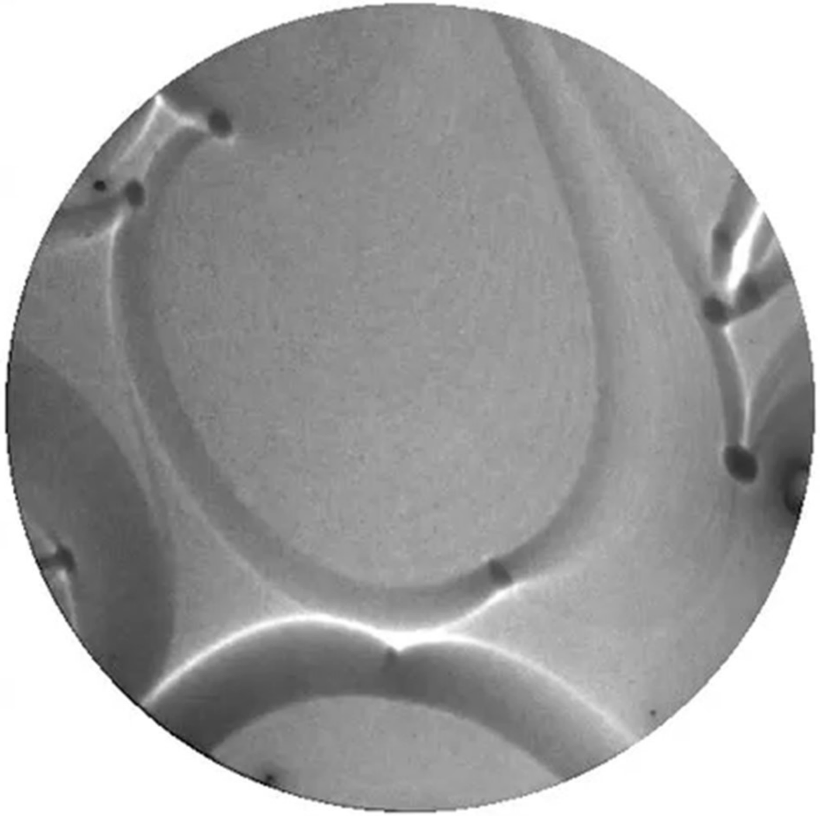
- *Growth : grain size, shape*
  - *Partial pressure of hydrogen and methane and total pressure*
  - *Growth time*

- *Metal substrate : Cu, Ni, Au, Pt, Fe …*
  - *Catalytic effect (e.g. Cu)*
  - *Precipitation and surface segregation (e.g. Ni)*
  - *Roughness, crystal orientation*



X. Li et al., Science (2009)

Chemical Vapor Deposition (CVD)



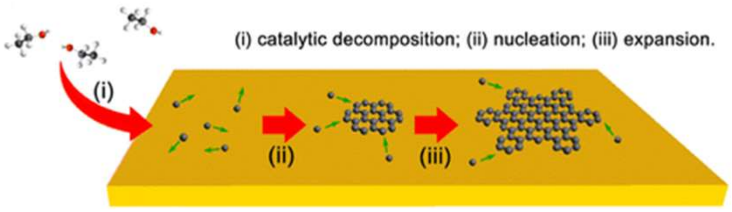
S2.mov

S3.mov

J. M. Wofford et al. Nano Lett (2010)

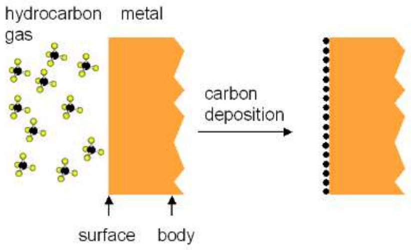
Effect of Growth Templates in CVD

Growth of graphene on Cu



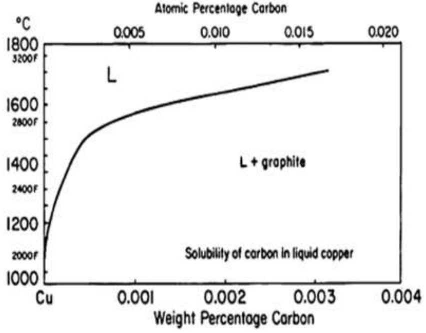
J. Phys. Chem. (2013)

Self –limiting process



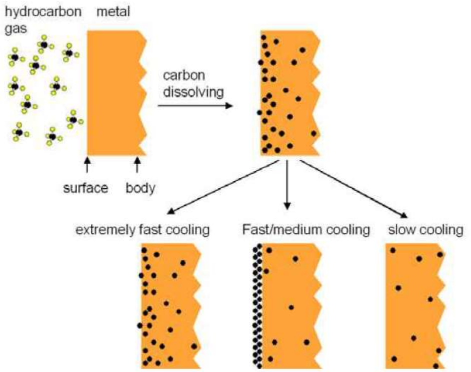
Appl. Phys. Lett (2008)

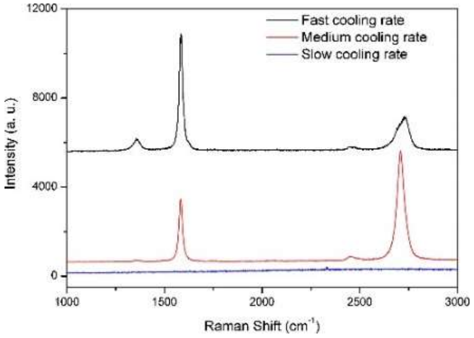
Low carbon dissolvability



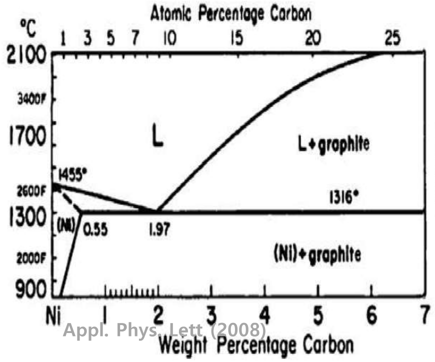
- Cu is a efficient catalyst for decomposing of hydrocarbon gas.
- Extremely low carbon dissolvability
- No formation of copper carbides.

Growth of graphene on Ni





High carbon dissolvability

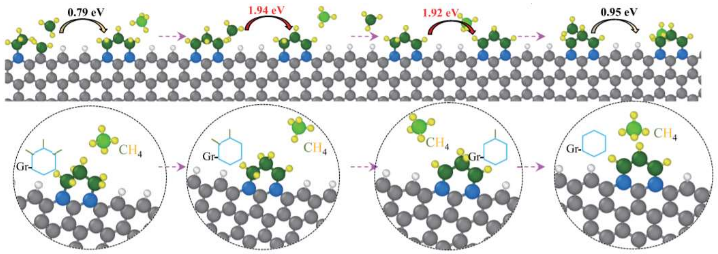


Appl. Phys. Lett (2008)

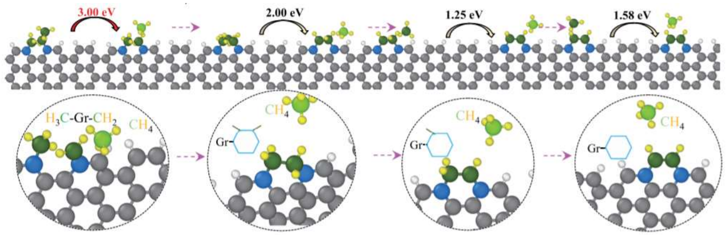
- Cooling rate determines the thickness of graphene.
- Growth of graphene through dissolution and precipitation process of carbon atoms.

Growth of graphene on insulator

Zigzag edge (ZZ)



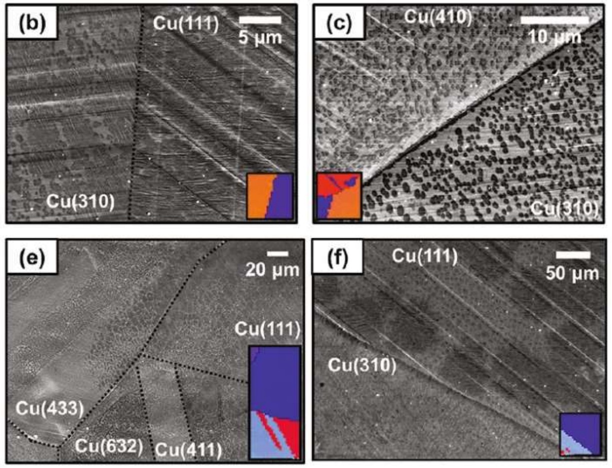
Armchair edge (AC)



- Growth rate of graphene on an insulator is very slow because of high threshold reaction barrier.

Effect of Substrate in CVD

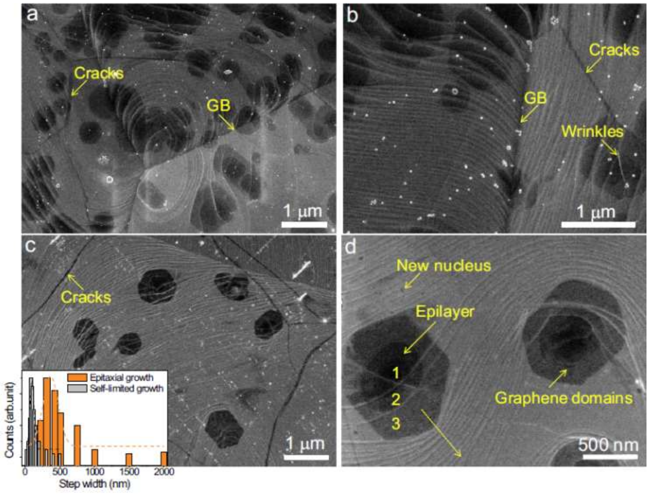
Effect of Copper Surface

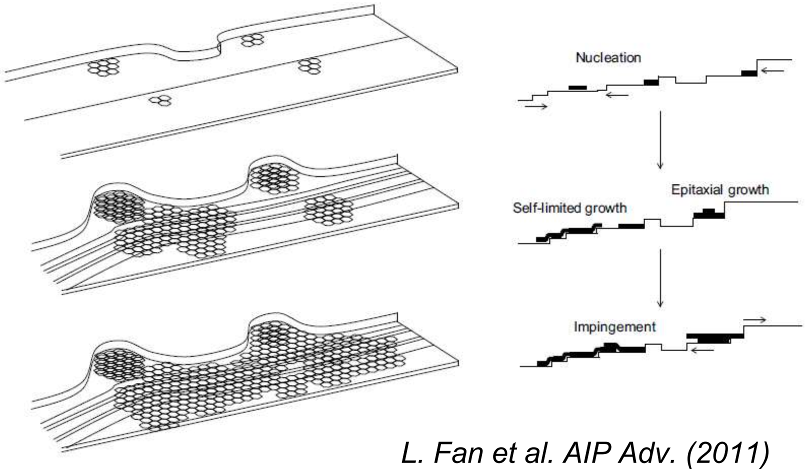


J. Wood et al. Nano Lett (2011)

Low-index Cu facets
More monolayer graphene and fewer defects due to high diffusion and improved adsorption of carbon-containing species on Cu(111)

High-index Cu facets
Compact graphene islands due to lowered diffusion, nucleation, and pinning at rough surface sites

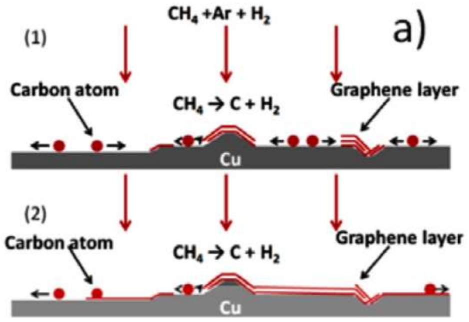


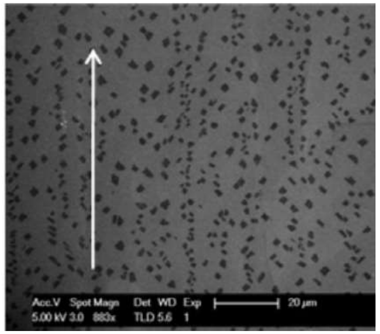


L. Fan et al. AIP Adv. (2011)

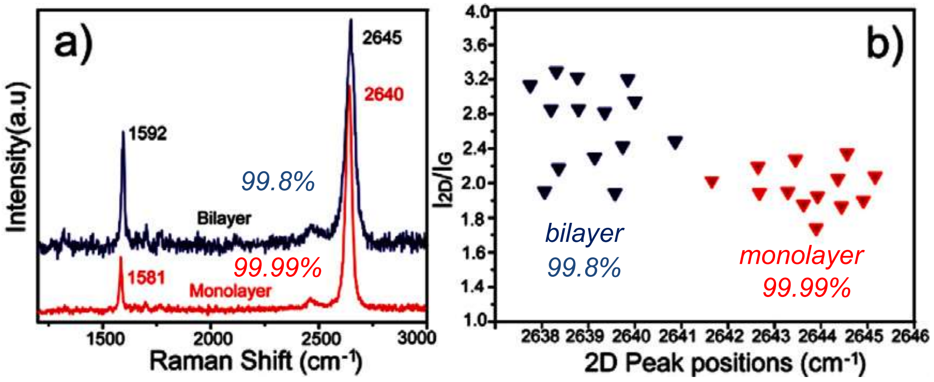
Effect of Substrate in CVD

Formation of bilayer patch





Effect of copper purity

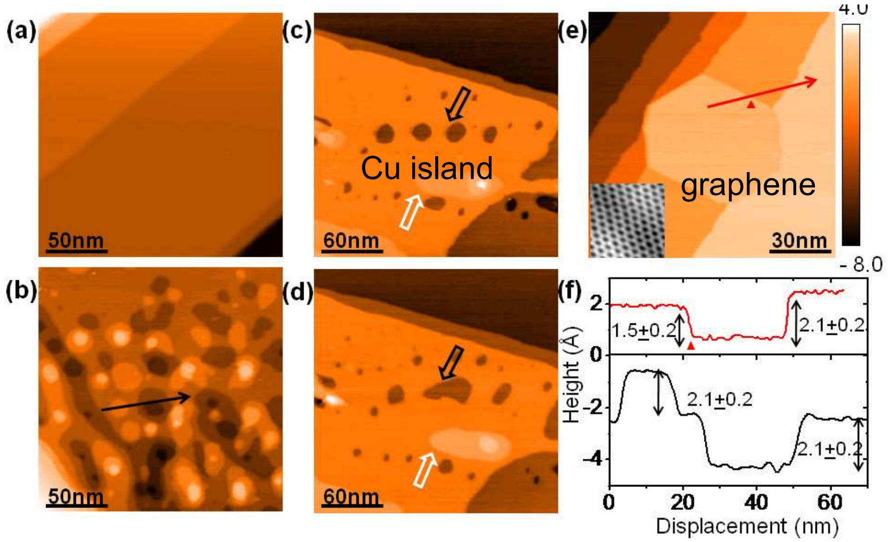


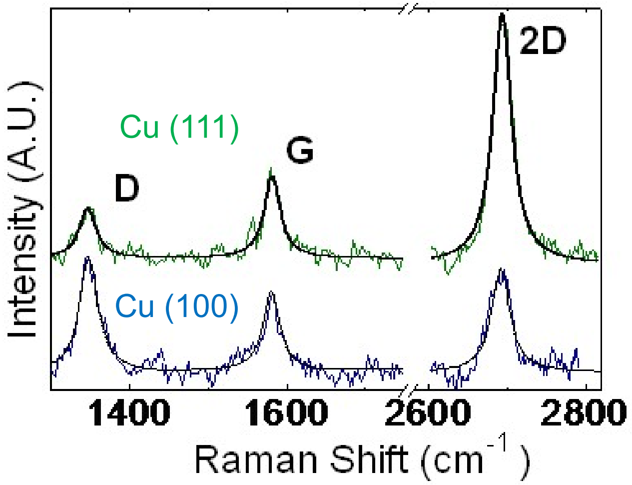
Nucleation of graphene nuclii at steps and grain boundaries.

Diffused impurity atoms onto surface result in growth of bilayer.

W. Liu et al, Carbon (2011)

Growth of graphene on Cu single crystal

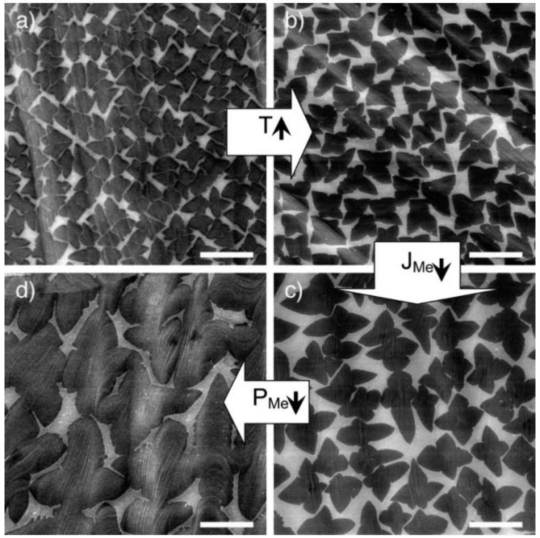




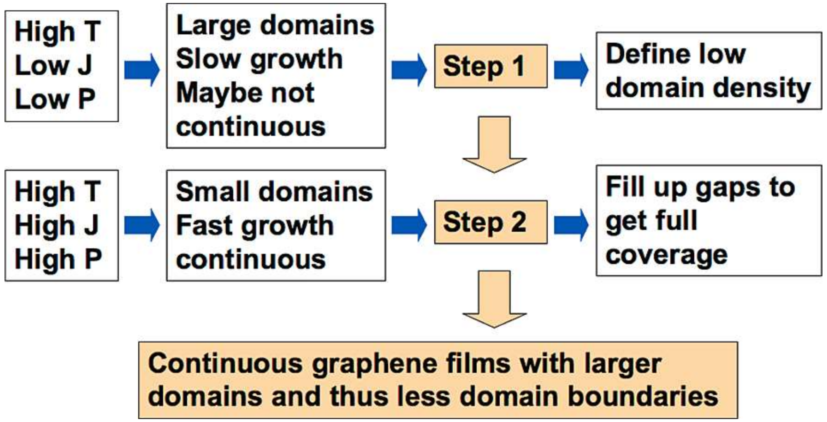
L. Zhao et al. Solid State Communications (2011)

Effect of Growth Conditions in CVD

Effect of Growth Conditions



Two-step process for large grain size



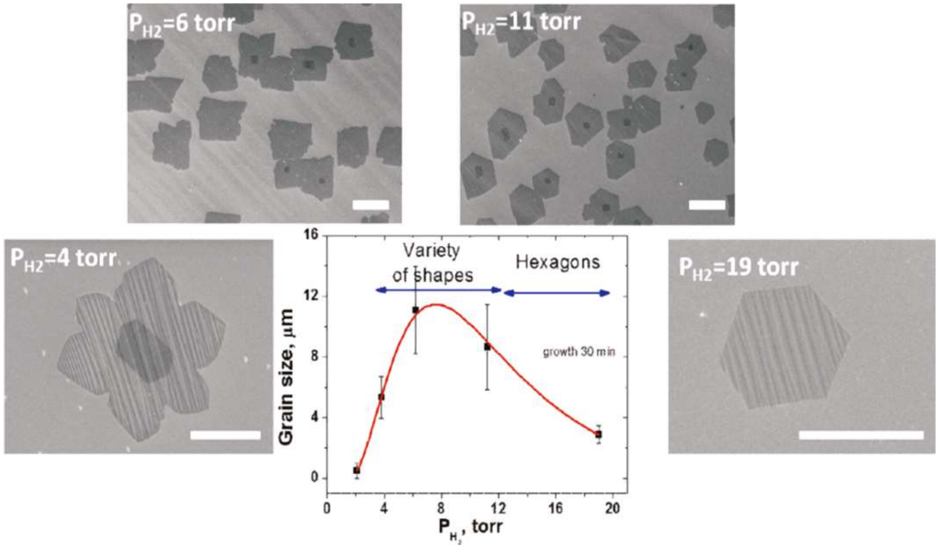
High T
Low J
Low P
→
Large domains
Slow growth
Maybe not continuous
→ **Step 1** → **Define low domain density**

High T
High J
High P
→
Small domains
Fast growth
continuous
→ **Step 2** → **Fill up gaps to get full coverage**

Continuous graphene films with larger domains and thus less domain boundaries

X. Li et al. Nano Letter (2010)

Role of Hydrogen in Chemical Vapor Deposition

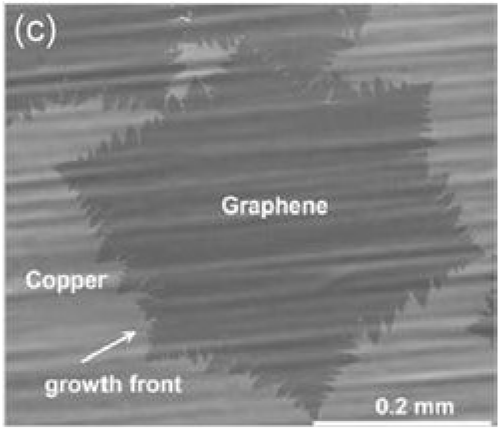


I. Vlassioul et al. ACS Nano (2011)

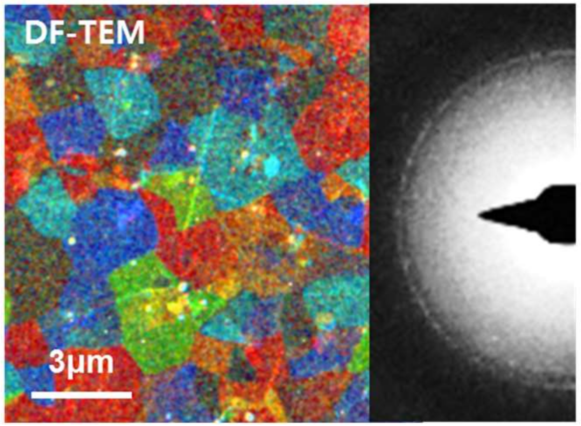
Effect of Growth Conditions in CVD

Pita pocket growth

X. Li et al. J. Am. Chem. Soc. (2011)

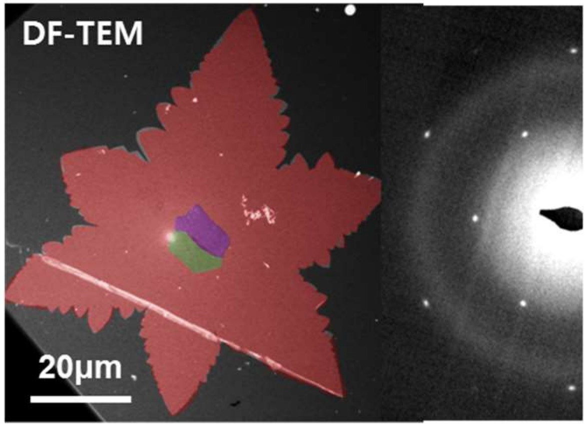


Small Grain Graphene



- Pressure: 300 mTorr
- Flow rate: 35 sccm methane
- Directly exposed on copper foil
→ multi-grain graphene with 1-5μm size

Large Grain Graphene

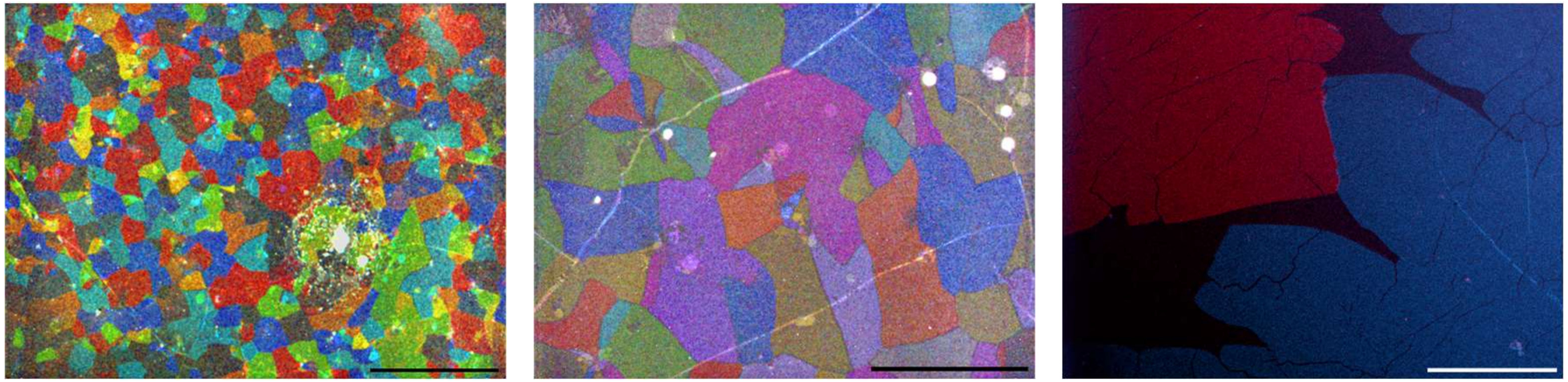


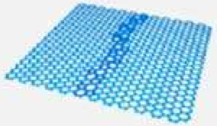
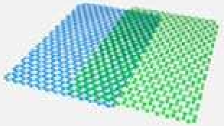
- Pressure: <50 mTorr
- Flow rate: 1 sccm Methane
- Enclosed copper foil (by Ruoff group)
→ single-grain graphene with 100-150μm

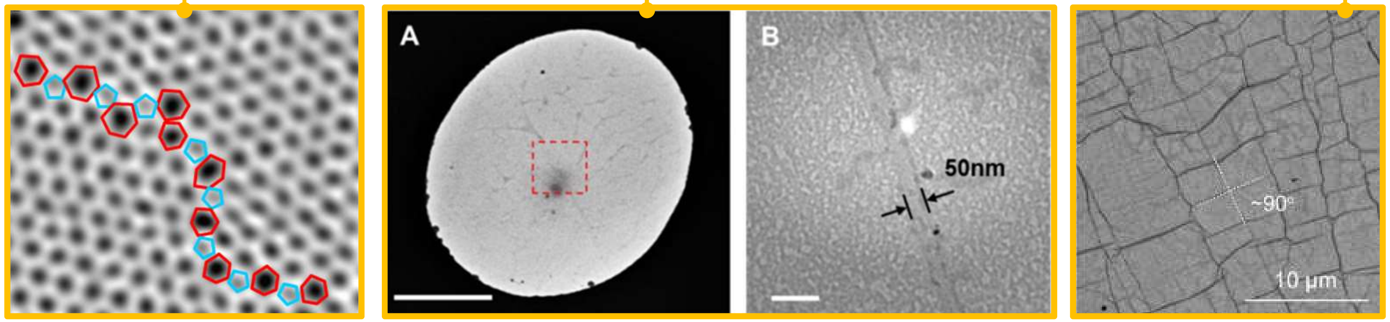
G. H. Lee et al. Science (2013)

Types of Grain Boundaries in CVD-grown Graphene

Larger grain size (lower flow of CH_4)

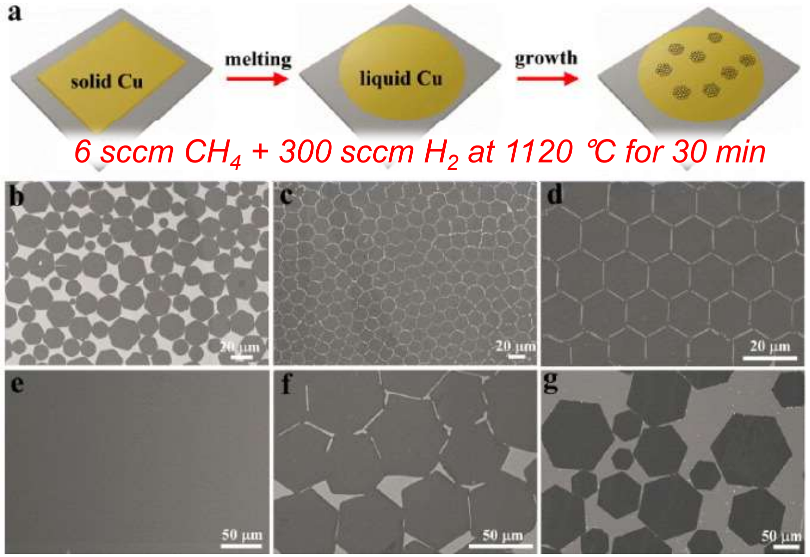


	Stitched GB	Overlapped GB	Standing Collapsed Wrinkle	Folded Wrinkle
Shape				
Width	3 ~ 4 Å	10 ~ 50 nm	~ 2 nm (first observed)	~ 100 nm
Height			2 ~ 6 nm	~1 nm

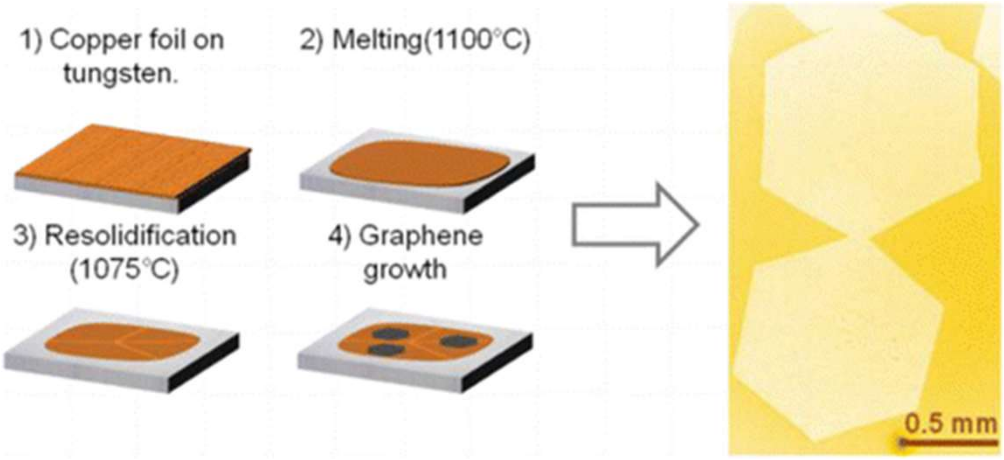


Effect of Growth Conditions in CVD

Graphene growth on melting copper

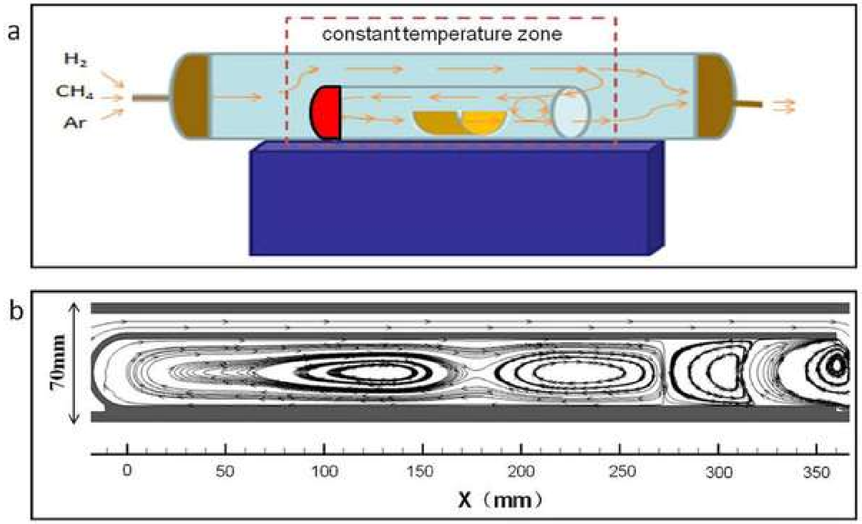


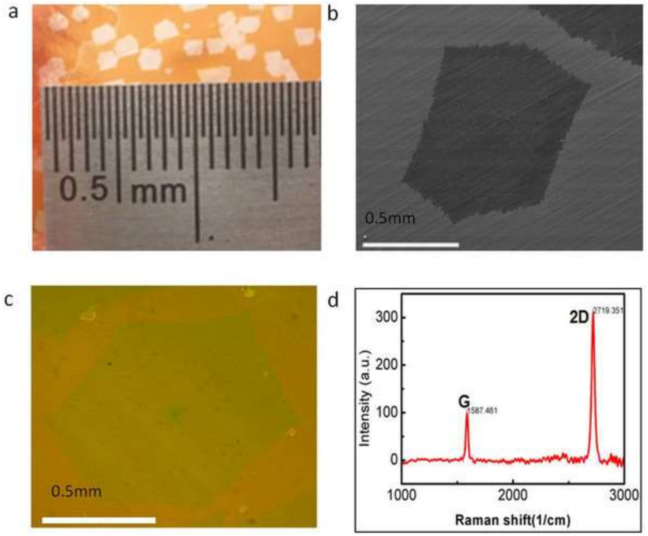
6 sccm CH_4 + 300 sccm H_2 at 1120 ℃ for 30 min



D. Genget al. PNAS (2012) & A. Mohsin et al. ACS Nano (2013)

Circumfluence CVD

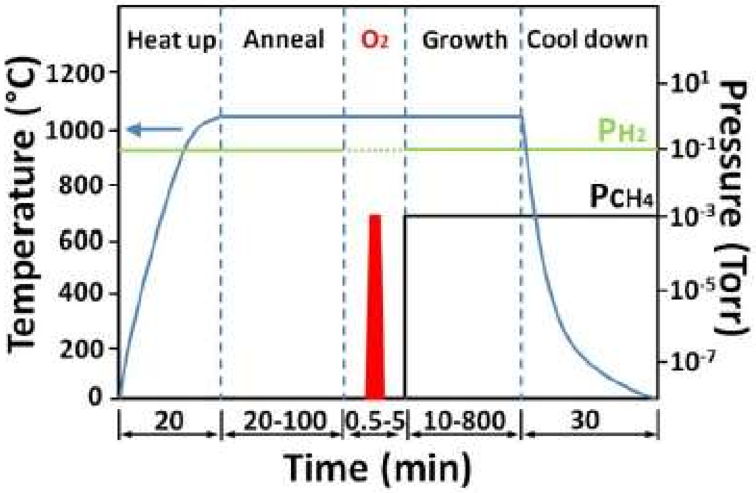




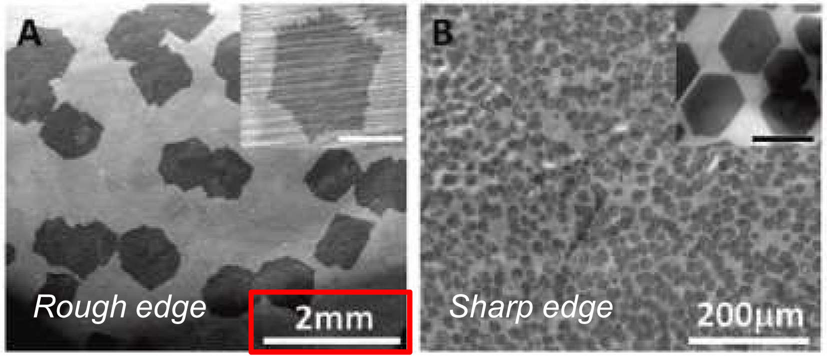
C. Wang et al. Sci. Rep. (2014)

Effect of Growth Conditions in CVD

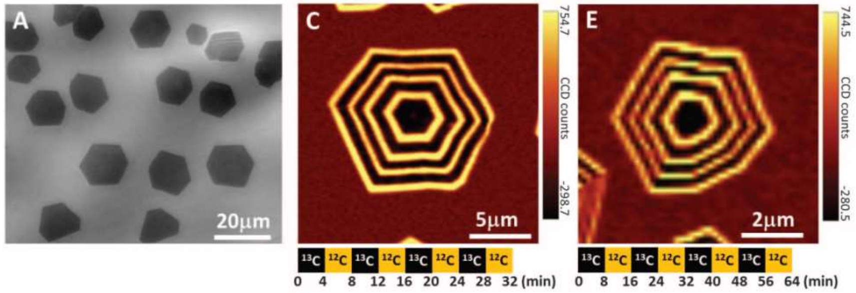
Suppression of graphene nucleation by oxygen on the copper surface



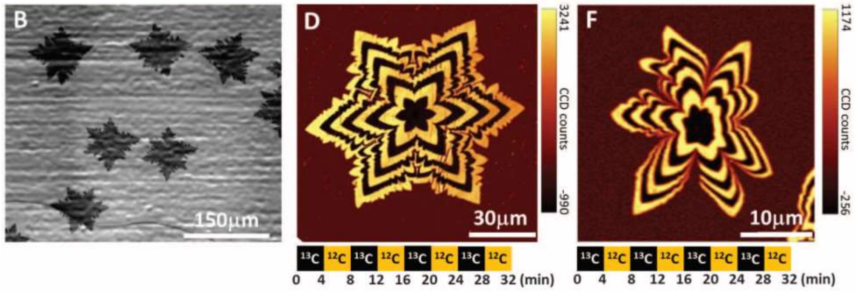
Oxygen-rich Cu *Oxygen-free Cu*



Oxygen-rich Cu



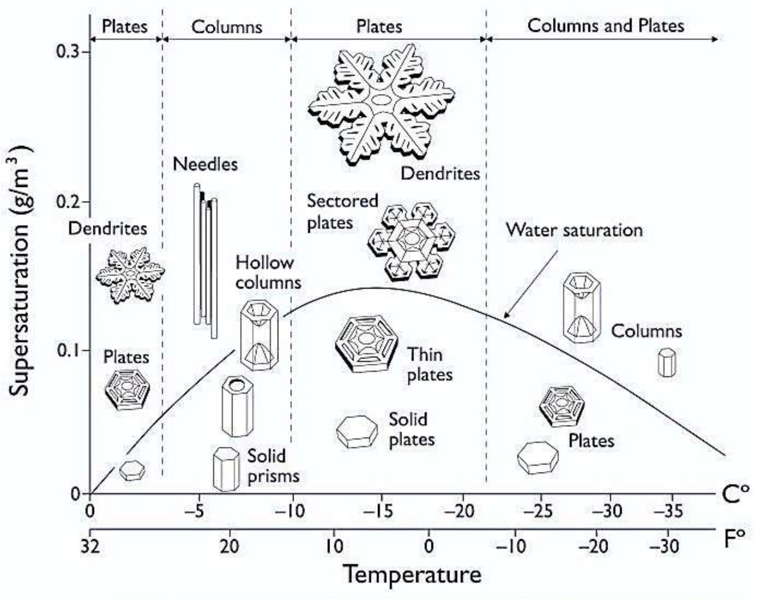
Oxygen-free Cu



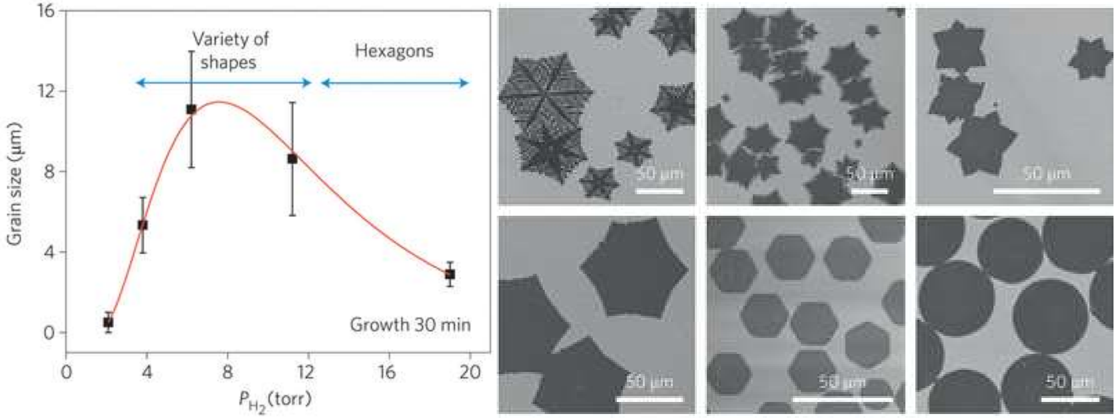
Y. Hao et al. Science (2013)

Shape Control of CVD-Grown Graphene

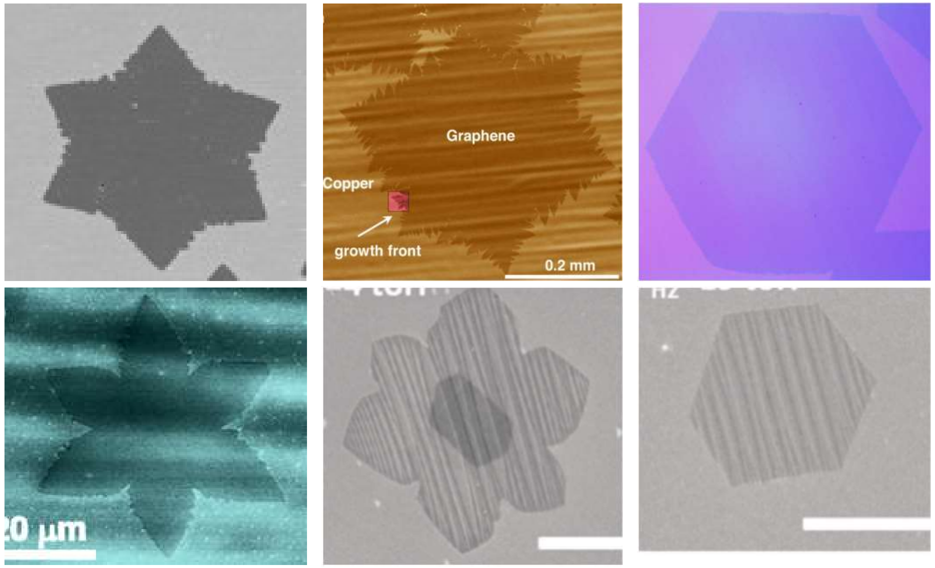
Map of ice formation



CH_4 / H_2 ratio

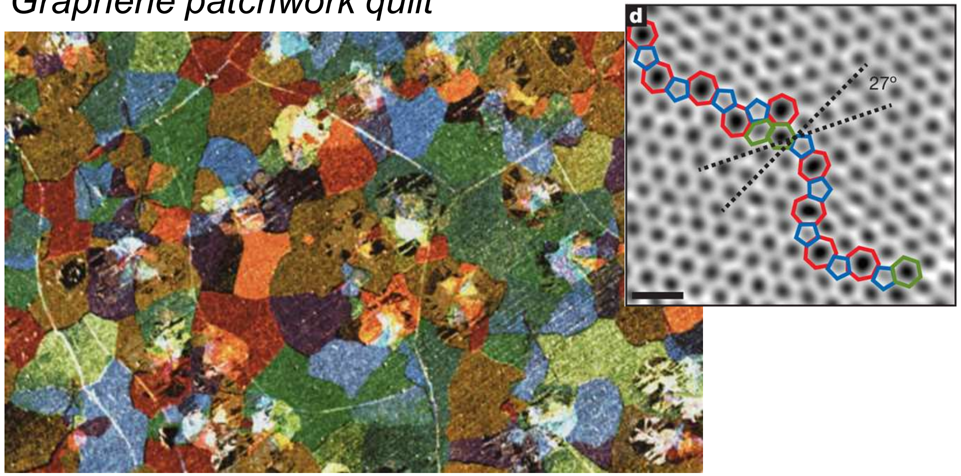


O. V. Yazyev et al. Nature Nanotechnol. (2014)



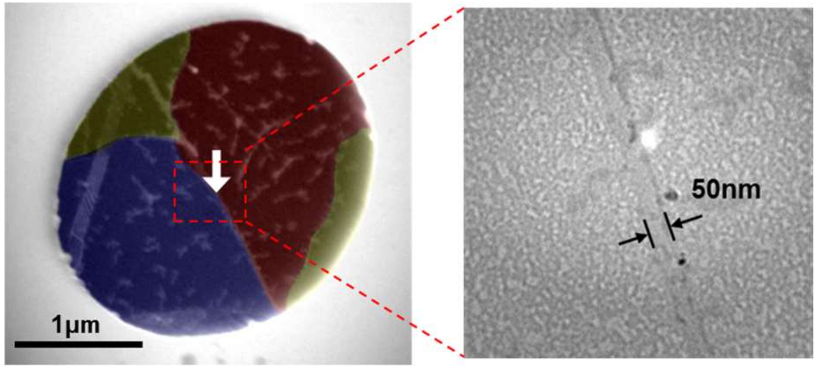
Grain Boundaries of CVD-Grown Graphene

Graphene patchwork quilt



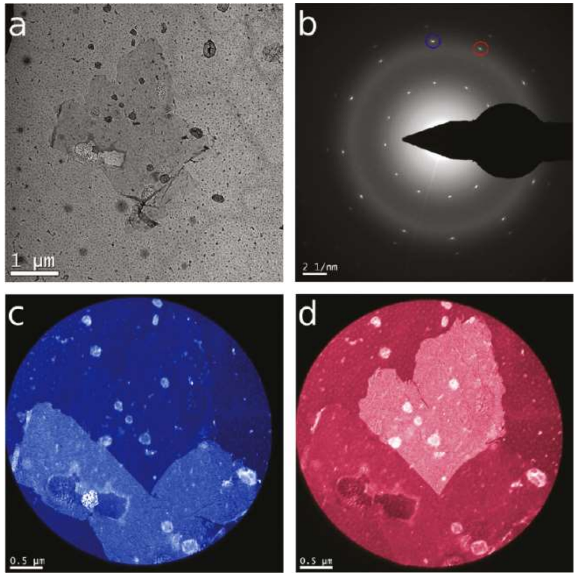
P. Huang et al. Nature (2011)

Overlapped Grain Boundaries (Un-stitched)

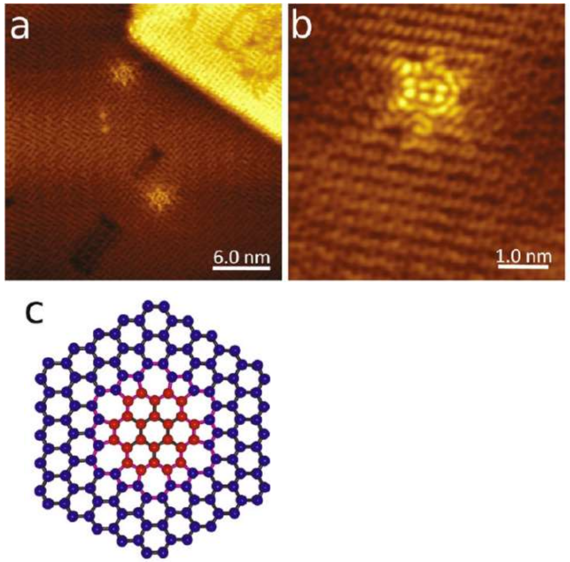


G. H. Lee et al. Science (2013)

Graphene grown Cu (100) single crystal

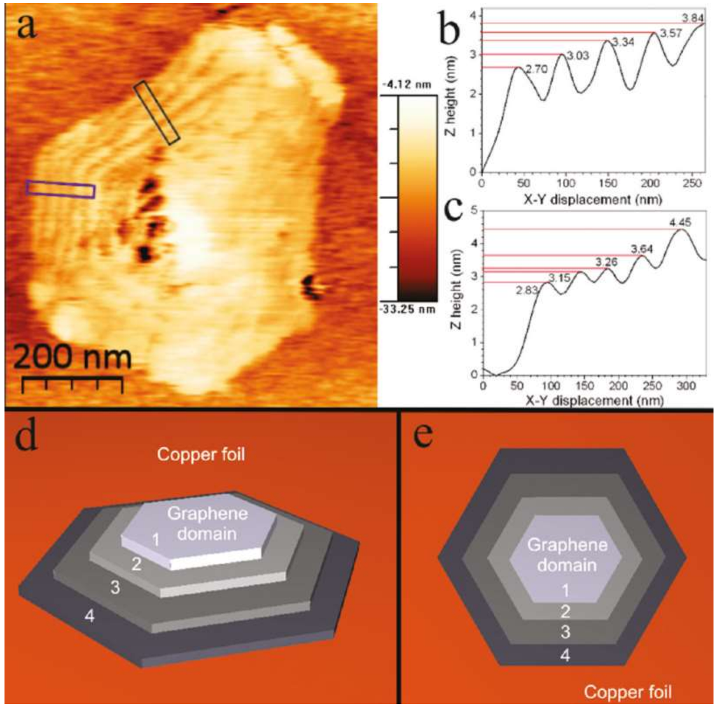


H. Rasool et al. JACS (2011)



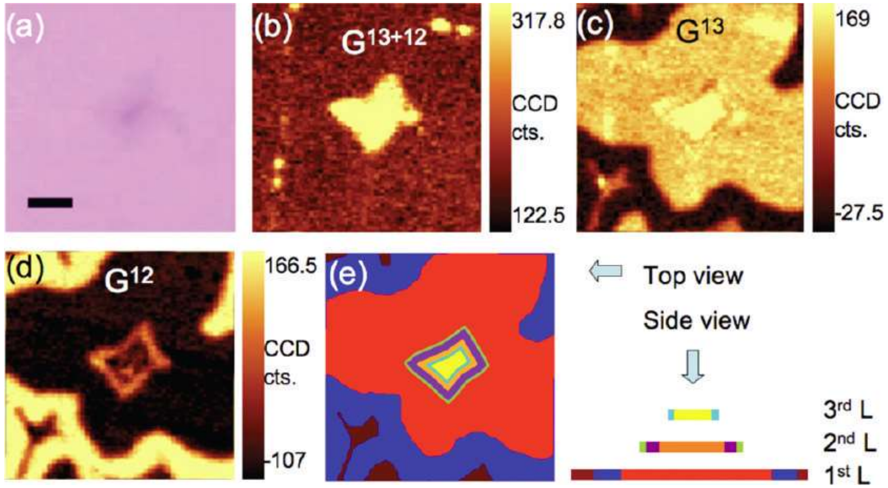
“flower” structures at small protrusions

Growth of Multilayer Graphene Islands



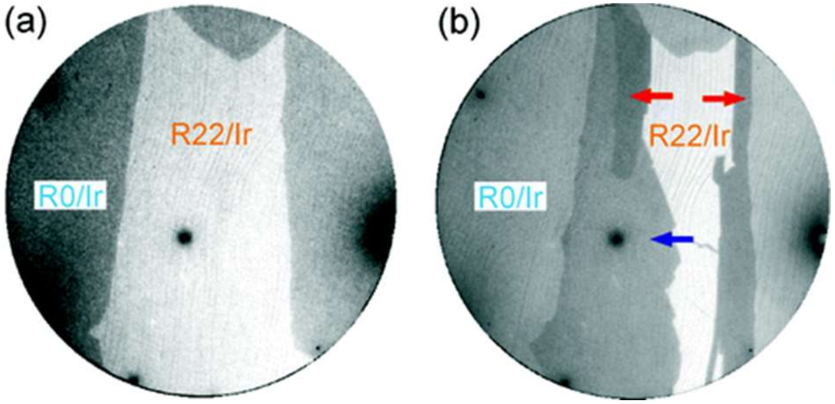
A. W. Robertson et al. Nano Lett. (2011)

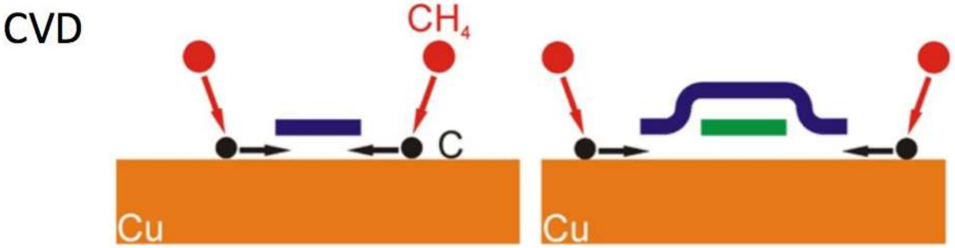
Raman mapping using carbon isotopes



X. Li et al. Nano Lett. (2009)

Growth from below: graphene bilayers

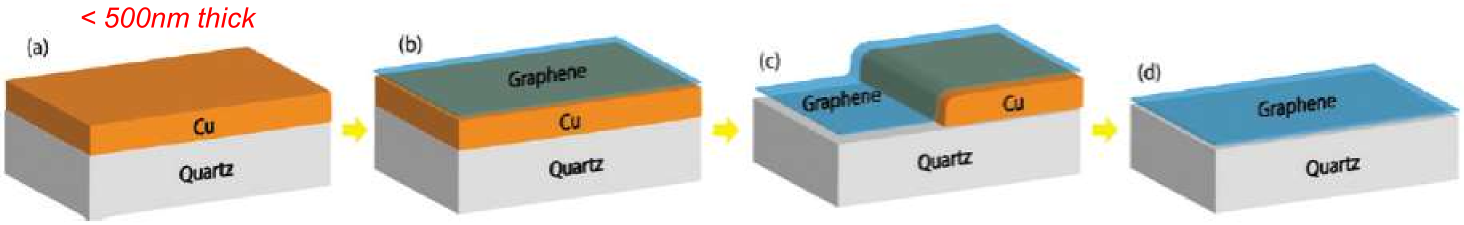




S. Nie et al. ACS Nano (2011)

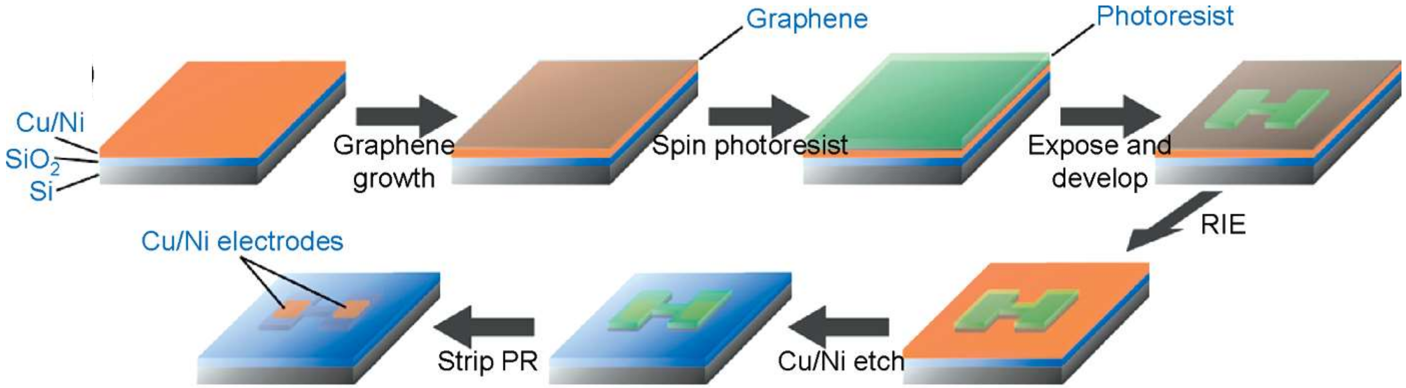
Advances in CVD Process for Graphene

Direct transfer of CVD-grown graphene onto SiO_2 substrate



A. Ismach et al. Nano Lett. (2010)

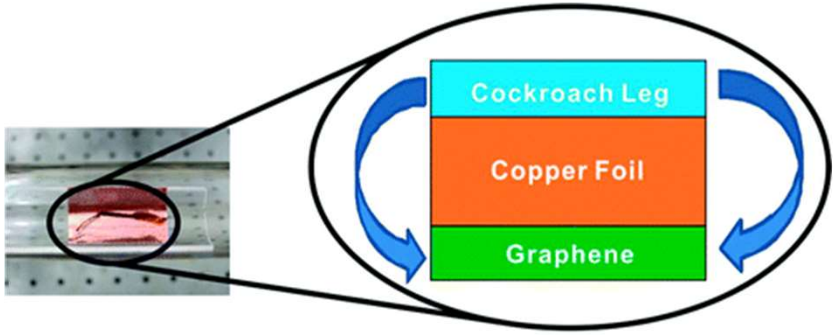
Direct fabrication of electrode in CVD-grown graphene devices



M. P. Levendorf et al. Nano Lett. (2009)

Advances in CVD Process for Graphene

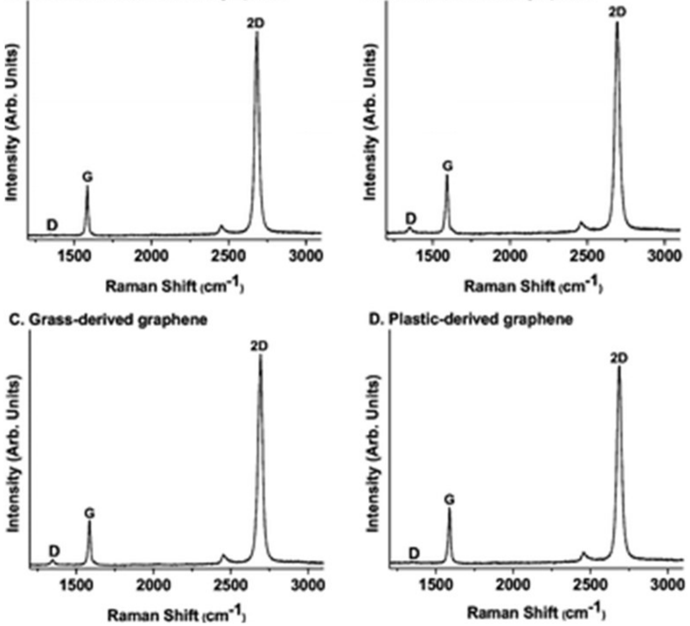
Growth of Graphene from Food, Insects, and Waste



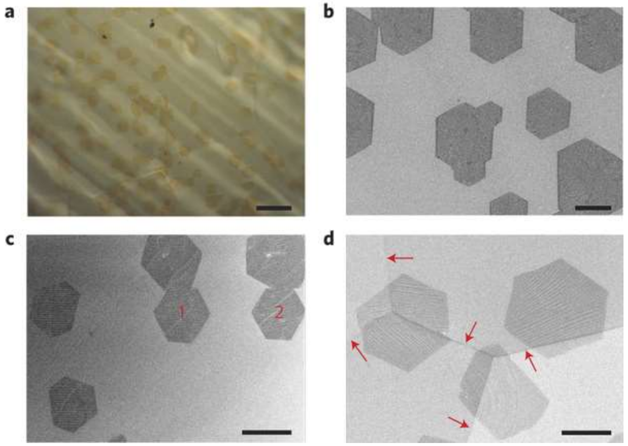
Cockroach leg before conversion to graphene

Cross view of the growth of graphene on the backside of the Cu foil

G. Ruan et al. ACS Nano (2011)

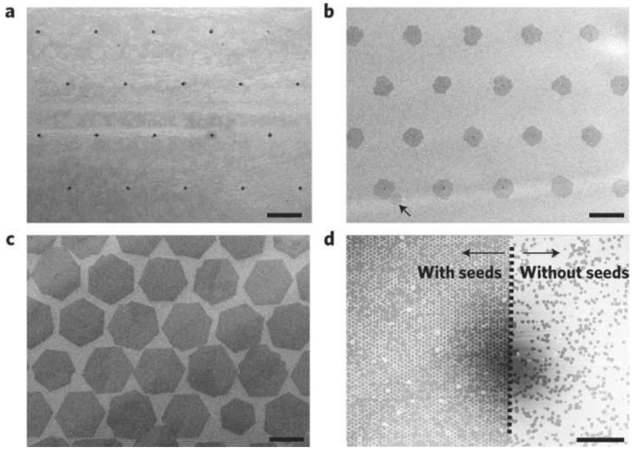


Aligned growth of large-size graphene grains



Growth at 1050 °C for ~10 min under 300 sccm diluted CH_4 (8 ppm in Ar) and 10 sccm of H_2

Seeded growth of graphene

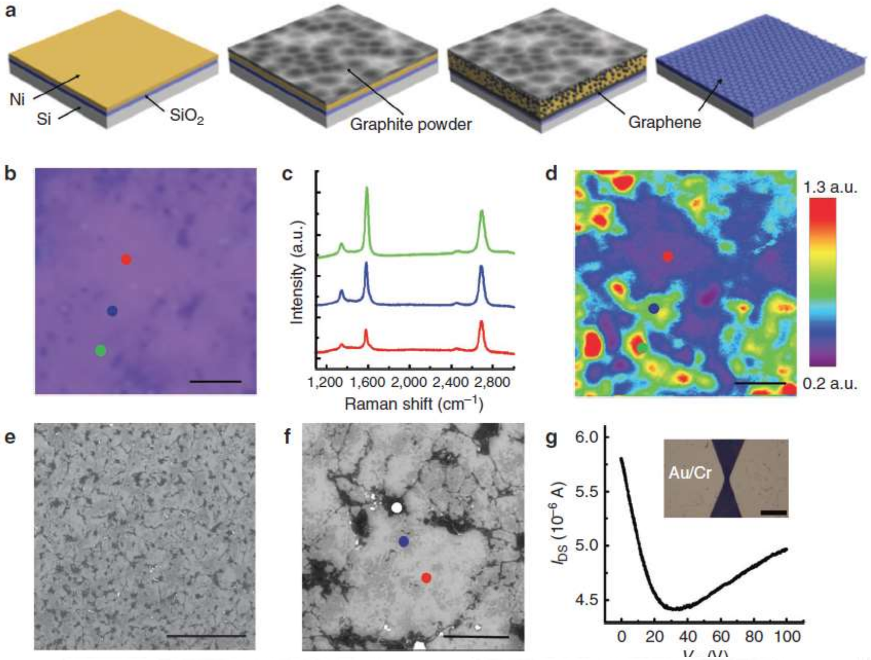


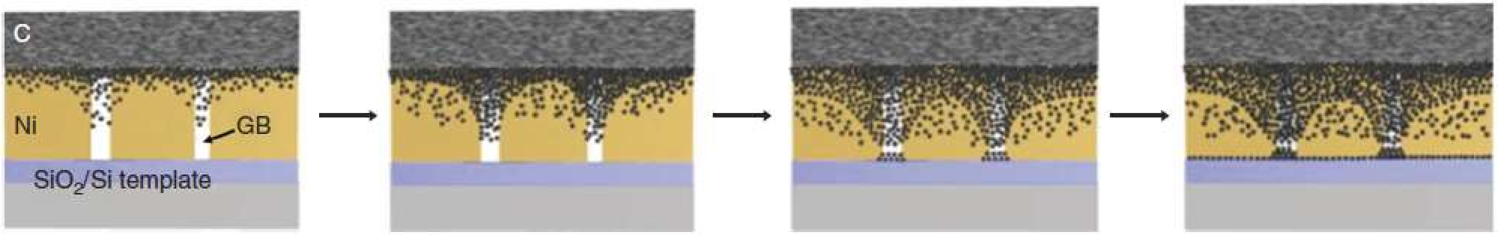
Seeds of patterned graphene for control of nucleation sites

Q. Yu et al., Nature Materials (2011)

Advances in CVD Process for Graphene

Near room-temperature synthesis of transfer-free graphene films

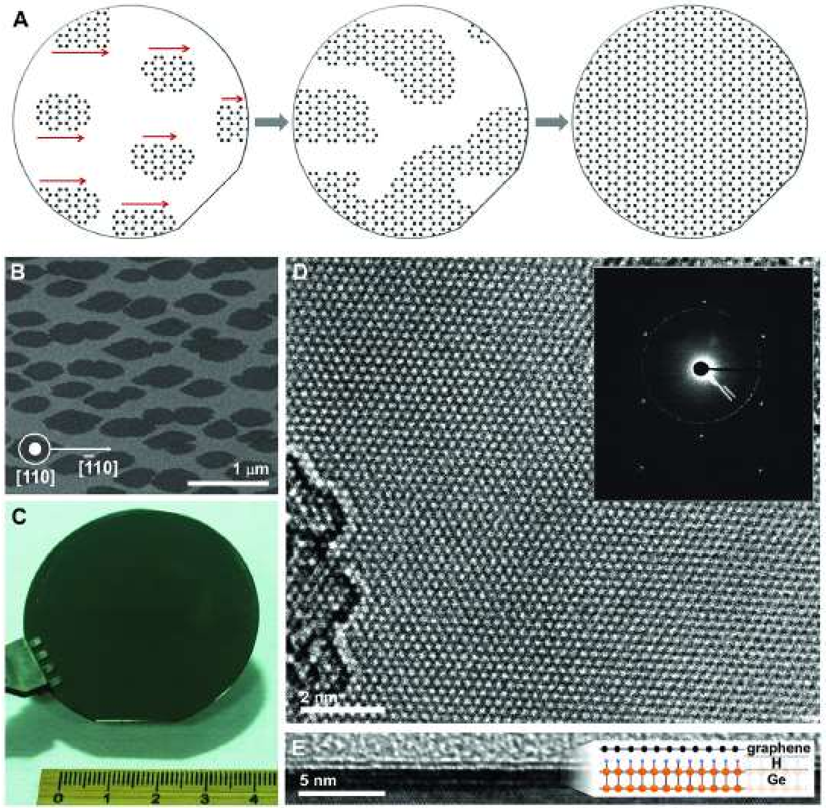




J. Kwak et al. Nature Commun. (2012)

Advances in CVD Process for Graphene

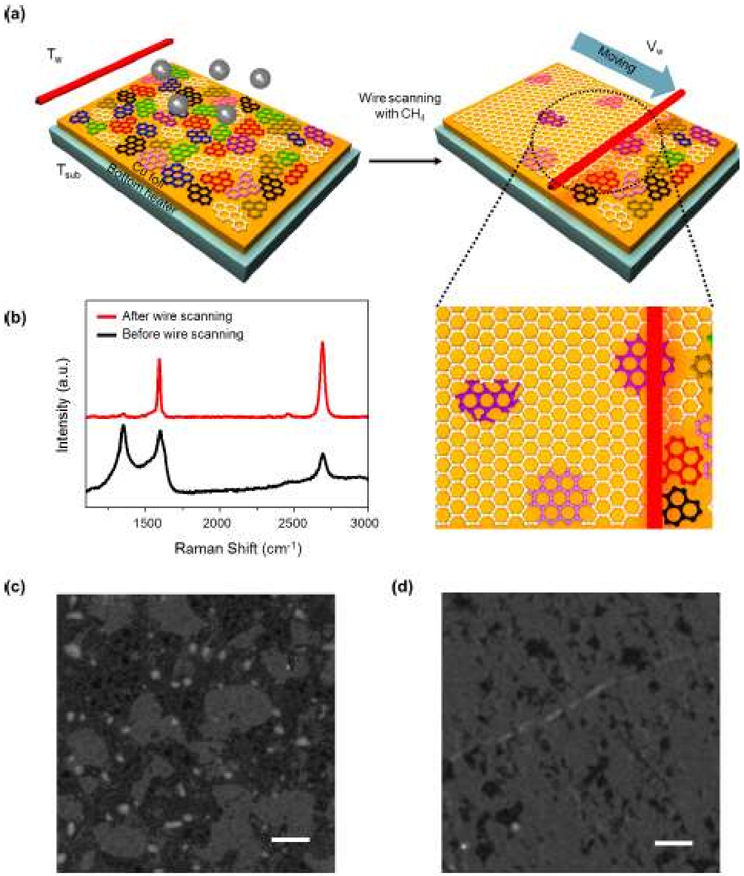
Large-Single-Crystal Graphene



Growth of graphene on H_2 terminated Ge surface

J. H. Lee et al. Science (2014)

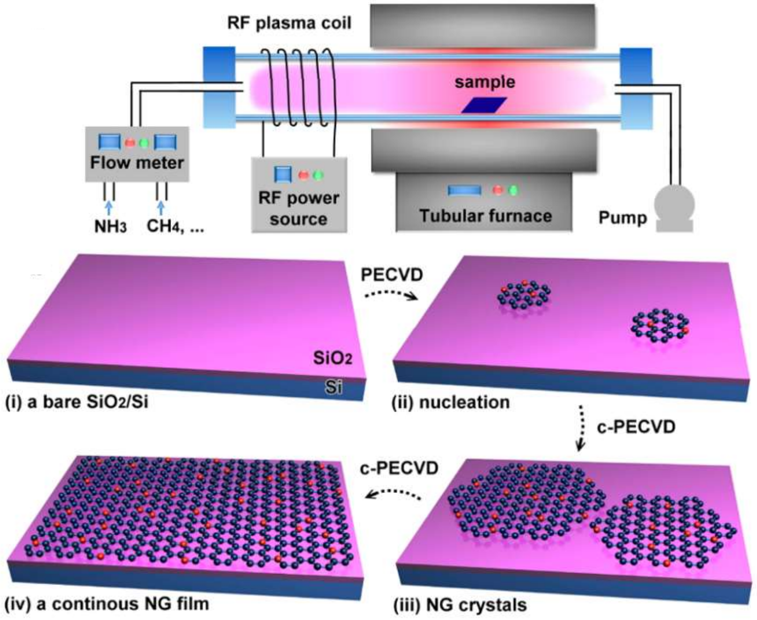
Removal of Grain Boundaries



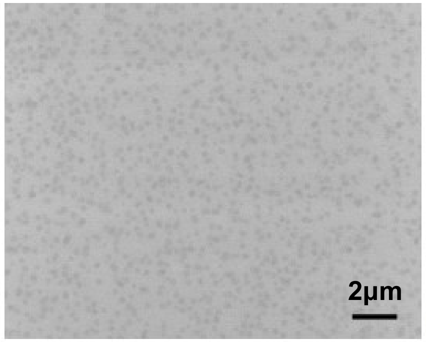
J. Lee et al. Nano Lett. (2014)

Advances in CVD Process for Graphene

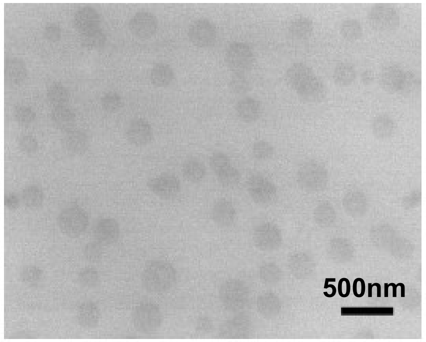
N-doped graphene growth on SiO_2 using PECVD under 700 ℃



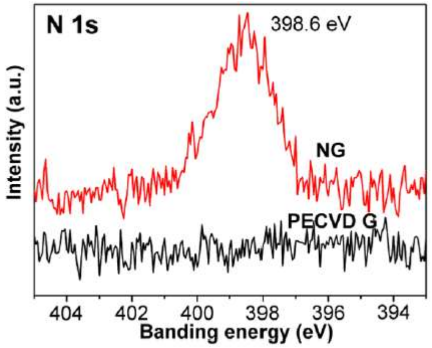
Seed nucleation at 700℃



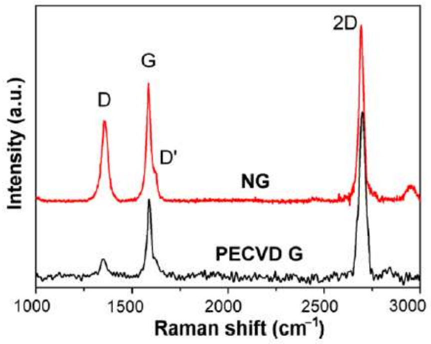
Growth at 650℃



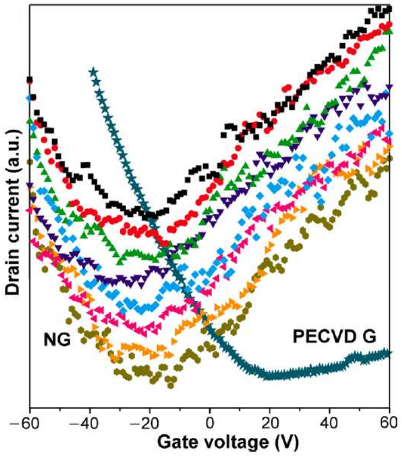
XPS of NG and PECVD G



Raman spectrum of NG and PECVD G



Transfer curve of NG and PECVD G



NG – nitrogen doped graphene made by CH_4 + NH_3 in PECVD

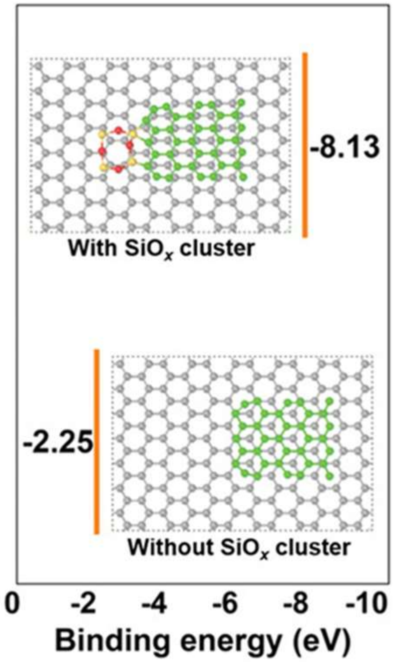
PECVD G – pristine graphene made by CH_4 + H_2 in PECVD

D. Wei et al. ACS Nano (2015)

Advances in CVD Process for Graphene

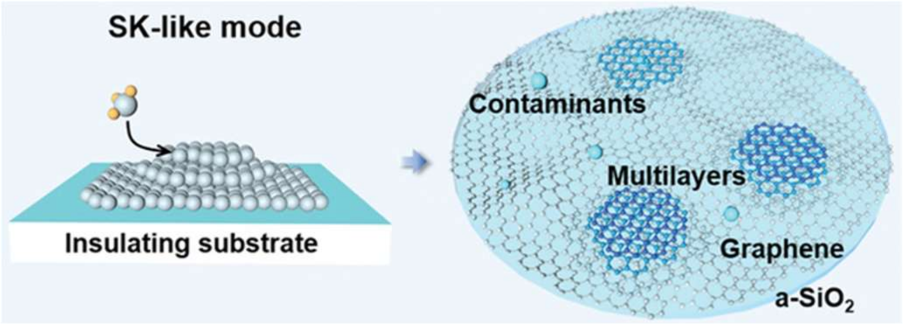
Graphene nucleation and growth behaviors over amorphous SiO_2 substrate

Binding energy of graphene

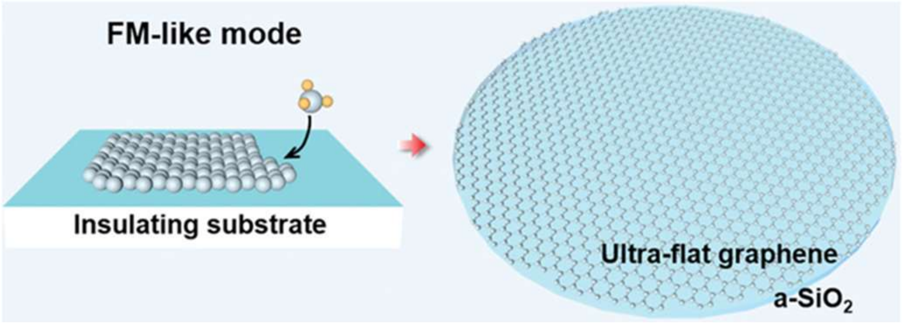


Binding energy of underlayer and overlayer with the presence of Si_4O_4 cluster is −8.13 eV, much higher than that of bare graphene (−2.25 eV), indicating that unsaturated carbon atoms of nanofragments are prone to deposit on the surface of graphene aided by Si_4O_4 cluster.

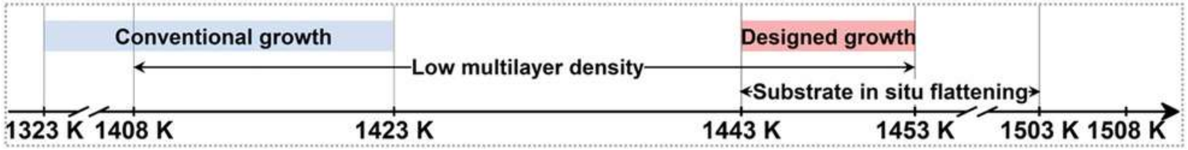
Conventional CVD



Designed CVD

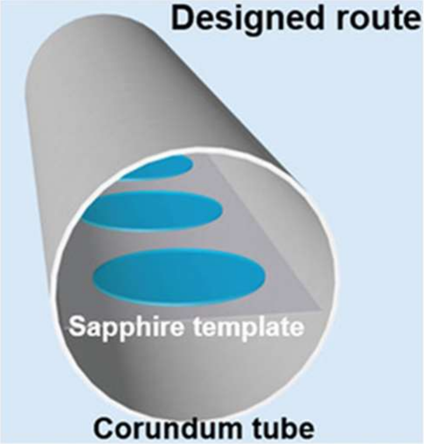


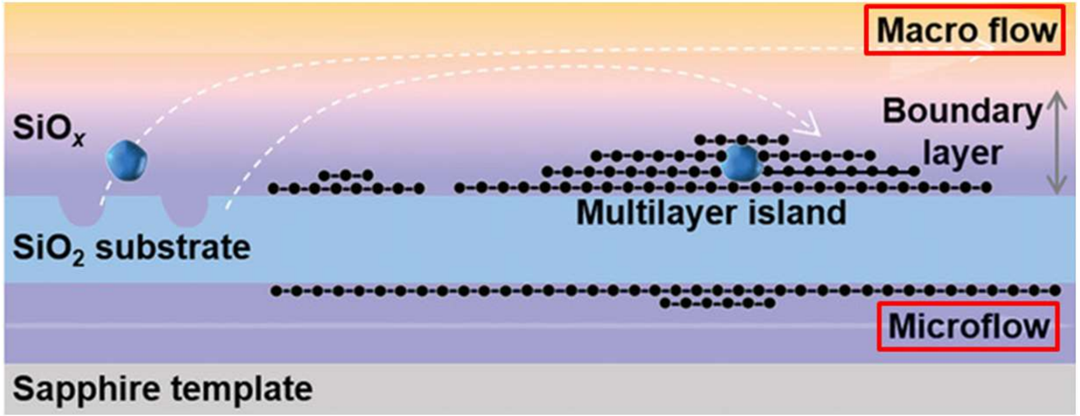
Temperature ranges for designed and conventional CVD

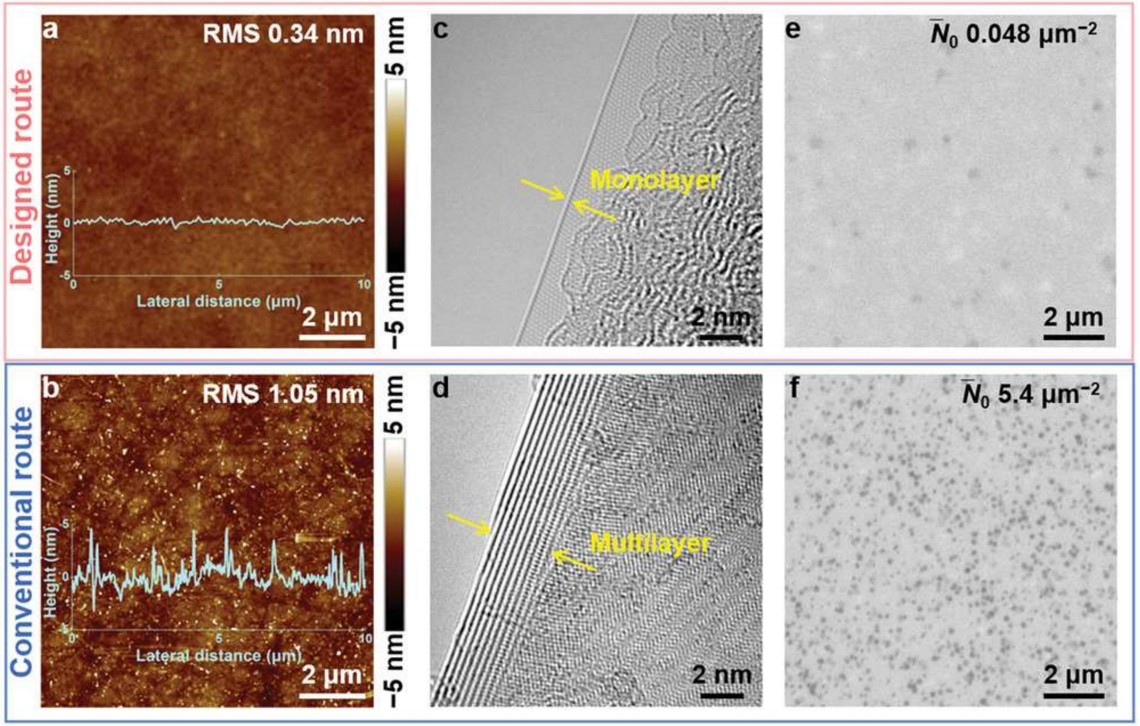


B. Jiang et al. Adv. Funct. Mater. (2022)

Advances in CVD Process for Graphene



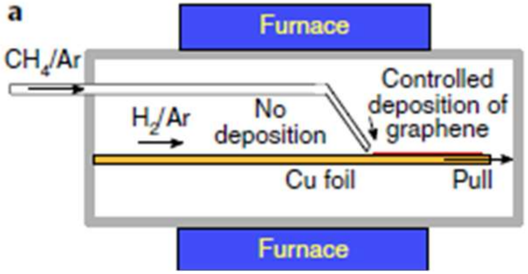


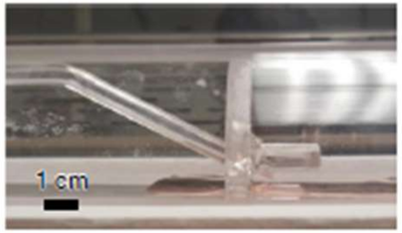


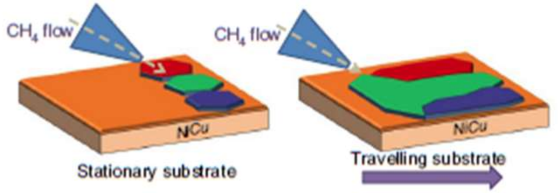
B. Jiang et al. Adv. Funct. Mater. (2022)

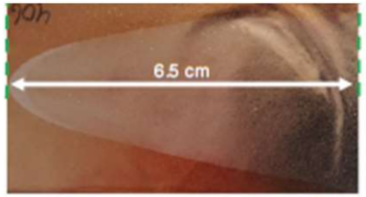
Advances in CVD Process for Graphene

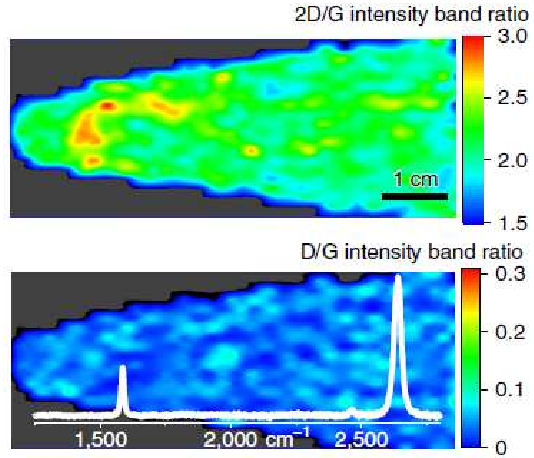
Advancing Local Control CVD (ALC CVD)







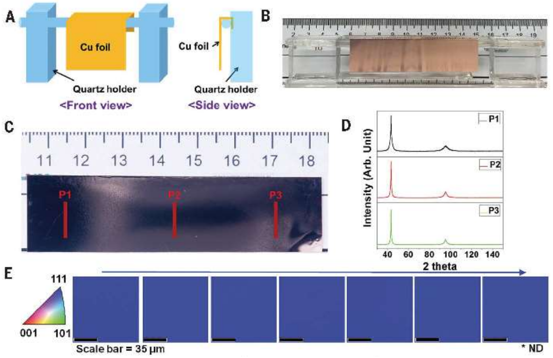


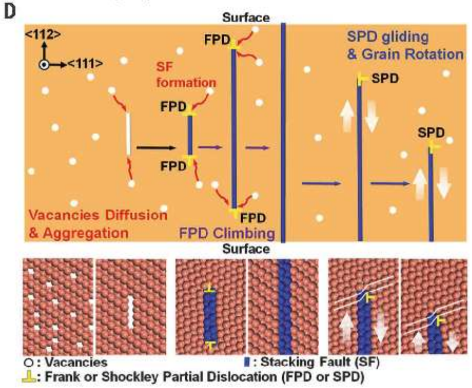


I. Vlassiouk et al. Nature Materials (2018)

Growth of graphene on Cu (111) single crystal

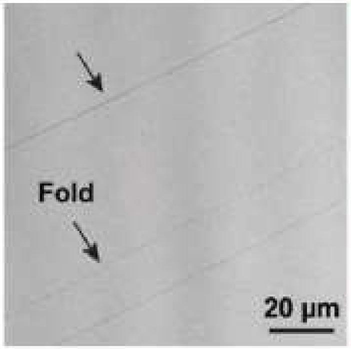
Contact free annealing (CFA) of Cu



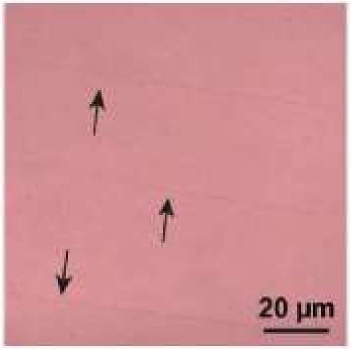


S. Jung et al. Science (2019)

SEM image of graphene on a Cu (111) foil



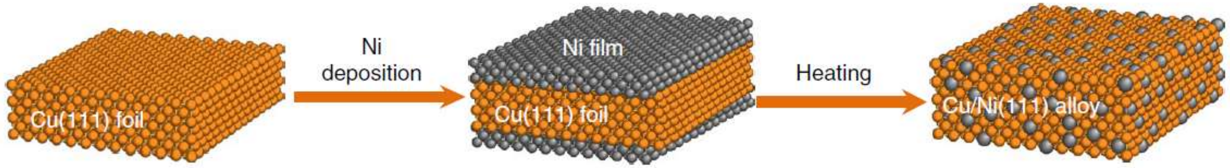
OM image of and graphene transfer to a 300 nm SiO_2/Si

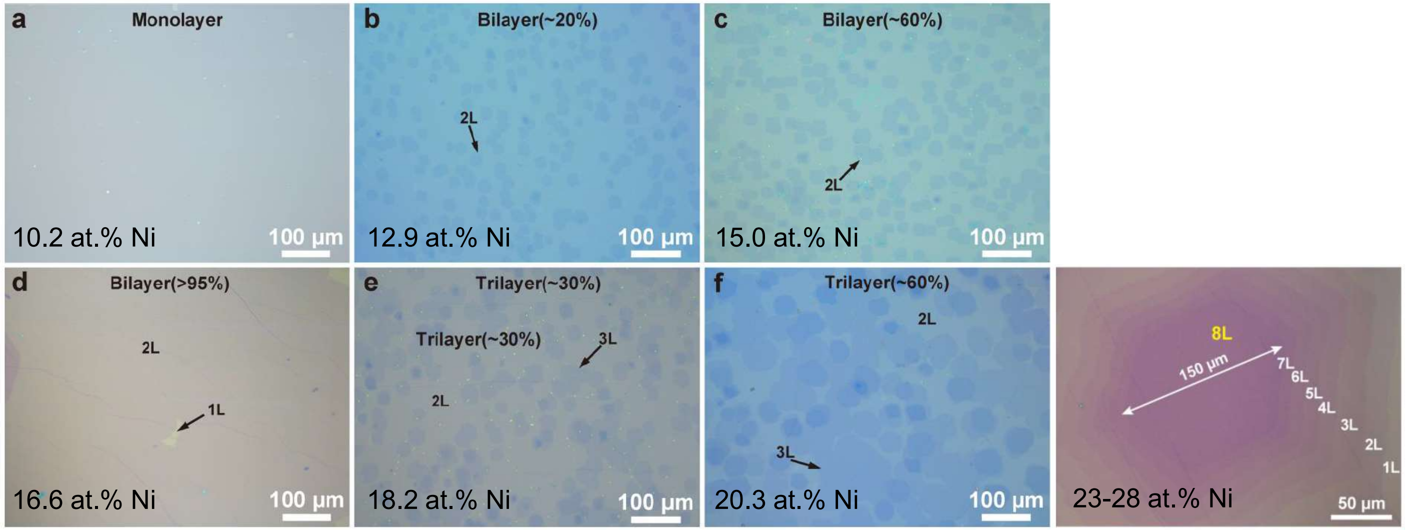


D. Luo et al. Adv. Mater. (2019)

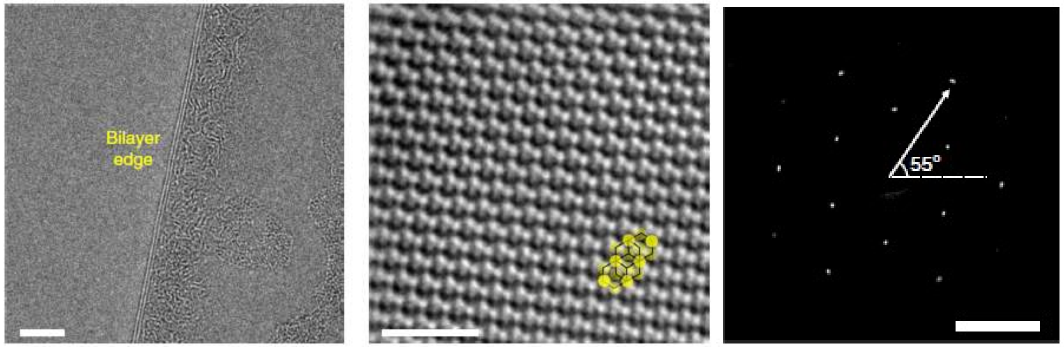
Advances in CVD Process for Graphene

Layer control of graphene using Cu/Ni(111) alloy



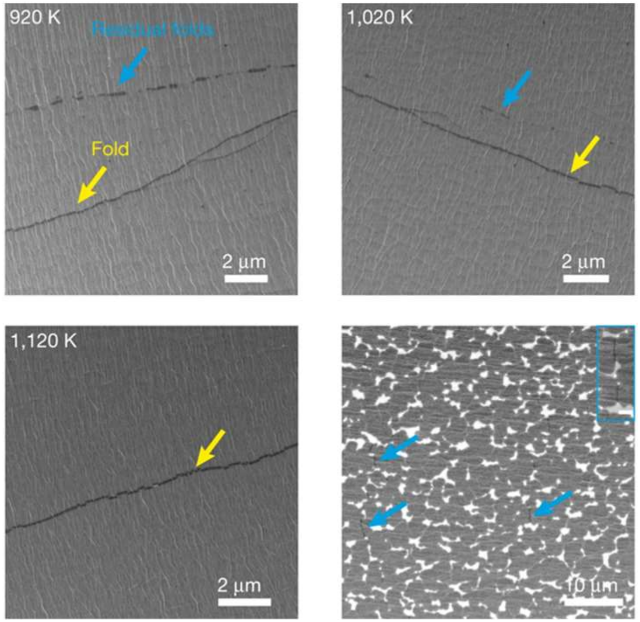


AB stacked bilayer graphene

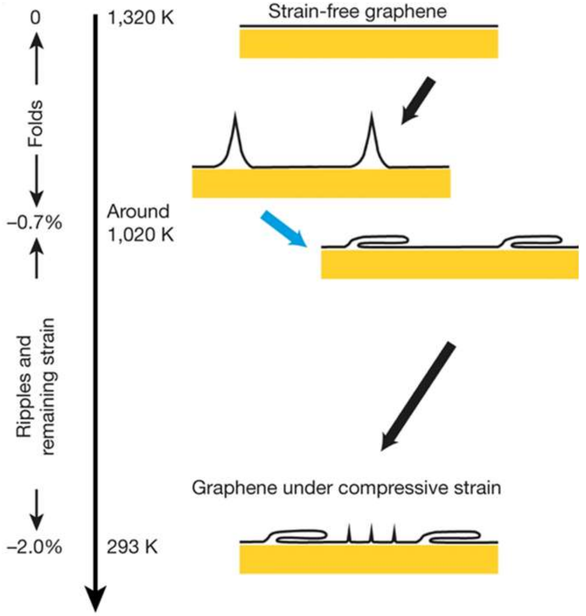


M. Huang et al. Nature Nanotech (2020)

Advances in CVD Process for Graphene

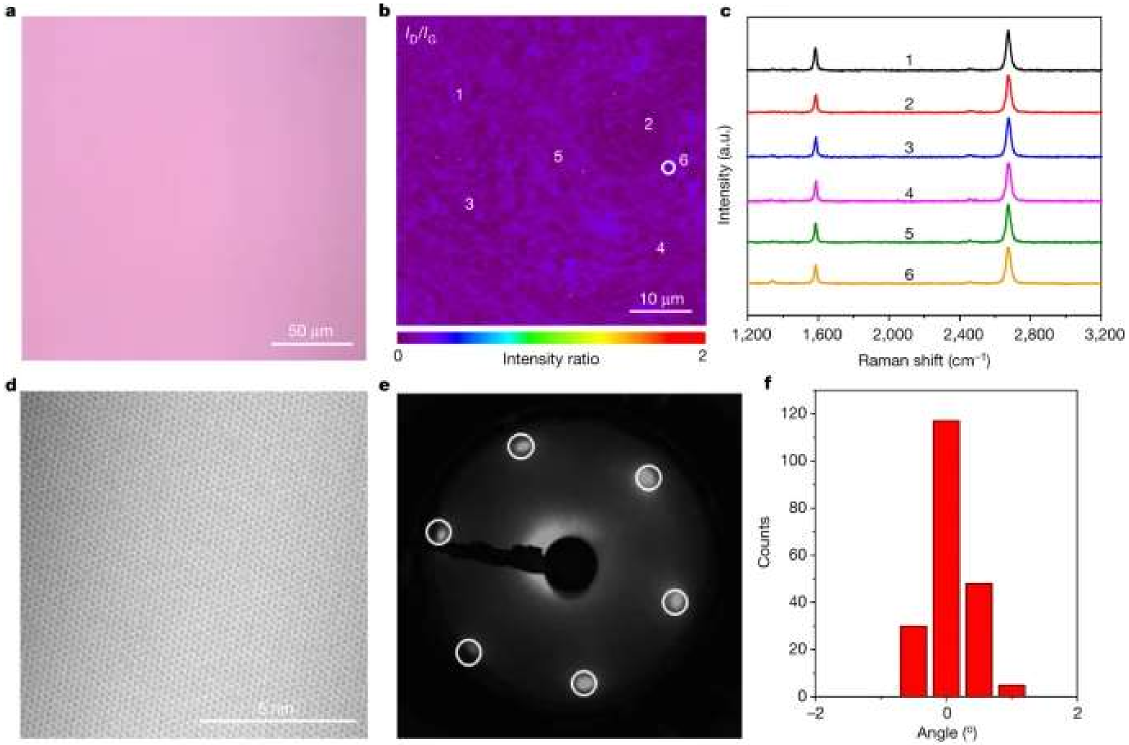


Cycling experiment: Growth at 1320K, then cooling to different temperatures (920K, 1,020K, 1120K) and stabilizing for 10 min, followed by regrowth at 1,320 K for 30 min



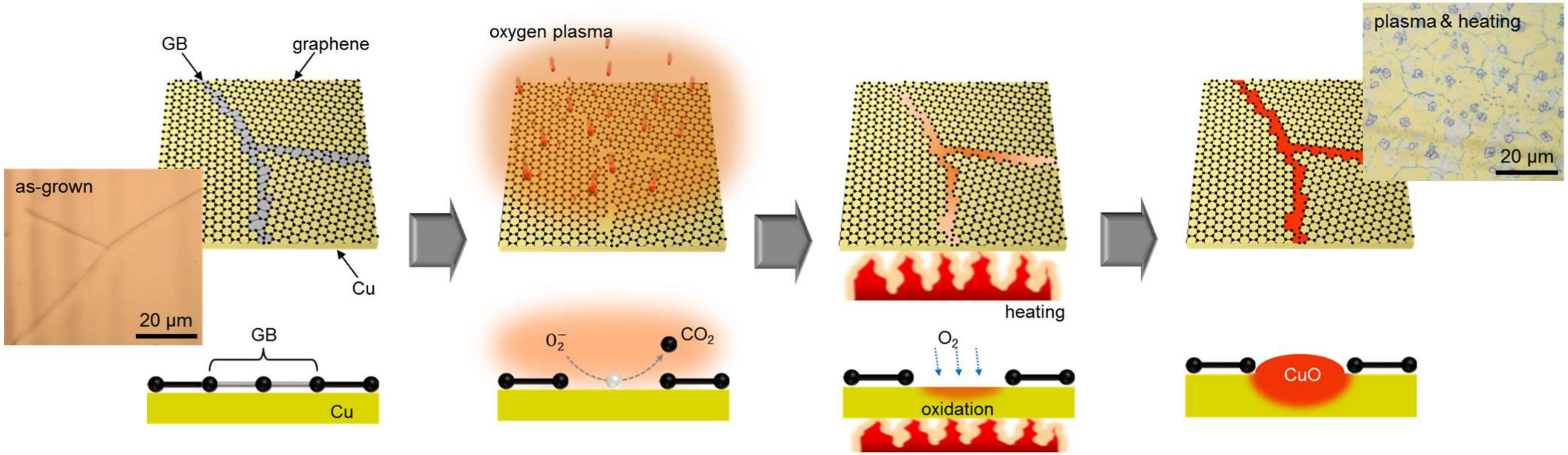
Single-crystal, large-area, fold-free monolayer graphene

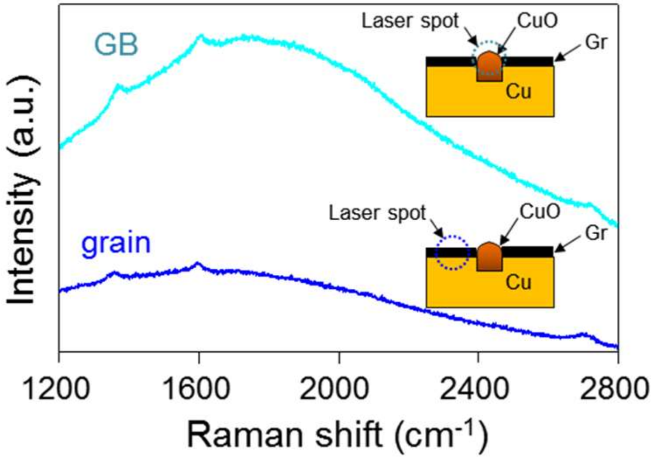
: Critical temperature for the formation of folds is 1030K on Cu–Ni(111) alloy foil with ethylene (carbon precursor)

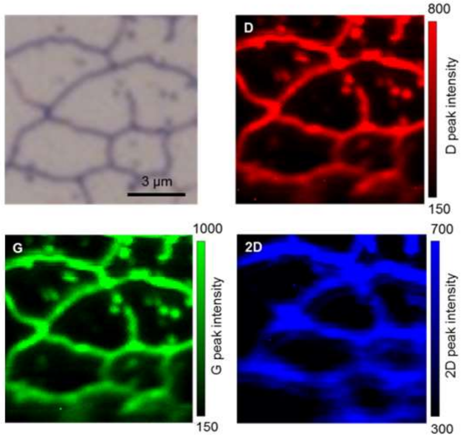


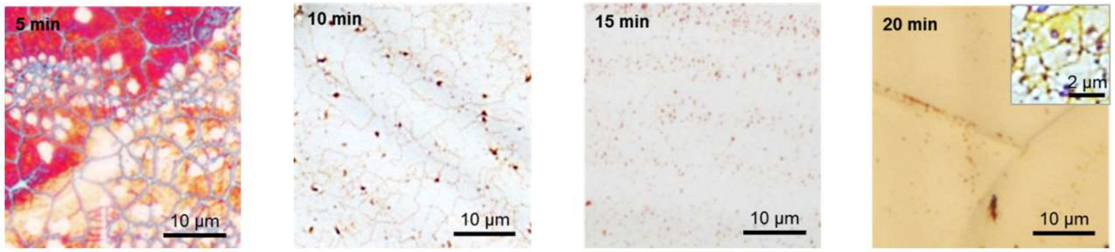
Nature 596, 519–524 (2021)

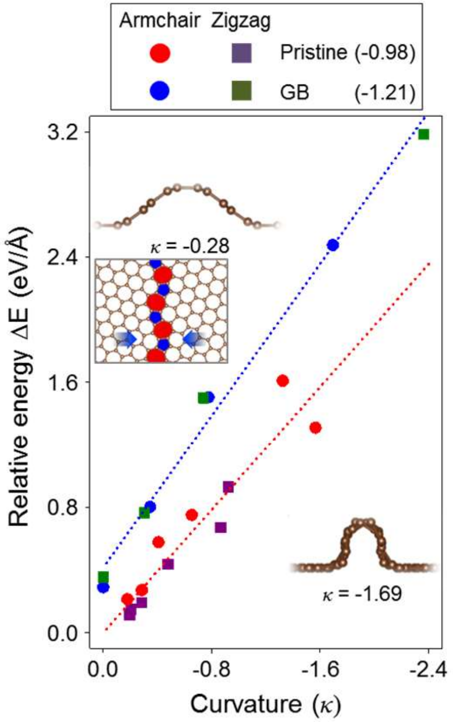
Observation of Grain Boundaries in Graphene











J.Y. Lee, G.H. Lee ***Carbon*** *(2017)*