Visualizing 2D Sheets by Fluorescence Quenching Microscopy: An Update

FORMEN

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 6th Go to GO Symposium

 December 28, 2021

Co-presenters





Seeing two-dimensional materials



Science 2004

Seeing two-dimensional materials

Techniques	Mechanism	Relative speed	Requirement on substrate	Solution observation	Other requirement
Optical Microscopy	Interference	Fast	Dielectrics coated Si	No	Optimized dielectric thickness and wavelength
	Ellipsometry	Fast	Dielectrics coated Si	No	
AFM	Force between sample and tip	Low (scanning)	Smooth surface (e.g., Si, mica, quartz)	No	Vibration isolation
STM	Electron tunneling	Low (scanning)	Conductive, atomically smooth	No	Vacuum
SEM	Secondary and scattered electrons	Medium (scanning)	Conductive	No	Vacuum
TEM	Absorbed electrons	Slow	Transparent to electron	No	Vacuum
Raman	Inelastic photon scattering	Fast	Low fluorescence, effective heat dissipation	No	Laser



SEM and AFM are the main workhorse techniques

Mater. Today, 2010, 13, 28-38

Fluorescence quenching microscopy (FQM)





Kim, J. et al., JACS, 2010

Mechanism

Swathi, R. S., and Sebastian, K. L., *J. Chem. Phys.* **2009**, 086101

Long range resonance energy transfer from a dye molecule to graphene has (distance)⁻⁴ dependence

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We estimate that quenching would be observable up to a distance of about 300 Å, which is much longer than for any other surface, suggesting interesting possibilities for having a ruler for measuring distances at the nanoscale.

Quenching distance: Observable up to 30 nm



Turro, N. J., *et al., Principles of molecular photochemistry : An introduction*

(Forster resonance energy transfer)

FRET



Ground State

High contrast and layer resolution of FQM images



High contrast and layer resolution comparable to AFM and SEM

Fluorescence quenching microscope (FQM)



The new carbon age Nanotubes and Graphene a transparent future ahead



Apply (or pre-apply) a layer of fluorescent sensitizer, above or below the graphene layer \rightarrow Observe under a common fluorescent microscope

Works well for graphene family and TMDCs on arbitrary substrates and even in solution



Small, 2013, 9, 3253-3258

Materials Matter, **2015**, 10, 64-66

smal

Weakly quenching sheets: Clay and metal oxides

Silicate

Titania

 $Na_{0.75} \ ^{inter.} [Mg_{2.25}Li_{0.25}]^{oct.} <\!Si_4\!\!>^{tetr.} \!O_{10}F_2$



O Si Li[⁺],Na⁺ Li, Al, Mg ● ● ● ●

Electrostatic bonding

Ti_{0.87}O₂^{0.56-}



Clay nanosheets

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- Great cation exchange capacity
- High surface reactivity and adsorption

Metal oxide nanosheets

- High-κ ferroelectricity
- Superconductivity
- Great photocatalytic properties





Prof. Josef Breu





Prof. Takayoshi Sasaki

Visualizing transparent 2D sheets by FQM



Visualizing transparent 2D sheets by FQM



Exploring different strongly quenching substrates

a Dye-polymer layer
 Weakly quenching sheet –
 Strongly quenching substrate –





• When deposited on a strongly quenching substrate, these dielectric sheets can act as a separator to reduce the degree of fluorescence quenching by the substrate, thus appearing as bright sheets in a dark background

High contrast and layer resolution of FQM images



Substrate: Si

 FQM can image these sheets with high contrast and layer resolution comparable to AFM and SEM

Visualizing 2D heterojunctions by FQM



 FQM can resolve stacking sequence in vertical heterojunctions made of different 2D materials

Summary: FQM imaging of strong quencher (SQ) and weak quencher (WQ)



SQ material on WQ substrate (e.g., graphene on glass): sample looks dark

WQ material on SQ substrate (e.g., clay on graphene/metal/ITO/doped Si): sample looks bright

Recommendation: ITO substrates



 ITO is found to have intermediate quenching capability, making it a suitable type of FQM substrate for seeing a broad range of 2D materials
 Small Methods 2020, 4, 2000036

Acknowledgements





Group: https://www.jxhuang-lab.com/

Collaborators: Dr. Matthias Daab Dr. Hitomi Yano Prof. Josef Breu Prof. Takayoshi Sasaki Prof. SonBinh T. Nguyen



