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Center for Advanced Construction Materials

Multiscale Characterization and Modeling of Electron Kinetics in Concrete Engineered with Carbon-Based Nanomaterial Networks

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ACI Fall Convention 2023
Measuring, Monitoring and Modeling Concrete's Electrical and Thermal Properties
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Boston, MA

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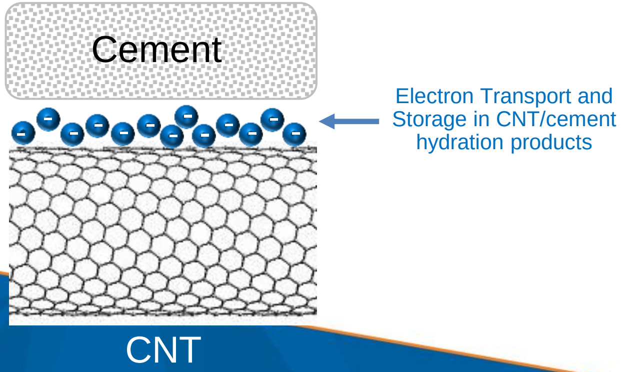
Modification of Electron Kinetics in Nanoengineered Concrete Using Highly Conducting Carbon-based Nanomaterials

Nano-scale

Formation of conducting network of continuously interconnected carbon-based nanomaterials, i.e., carbon nanotubes (CNTs)

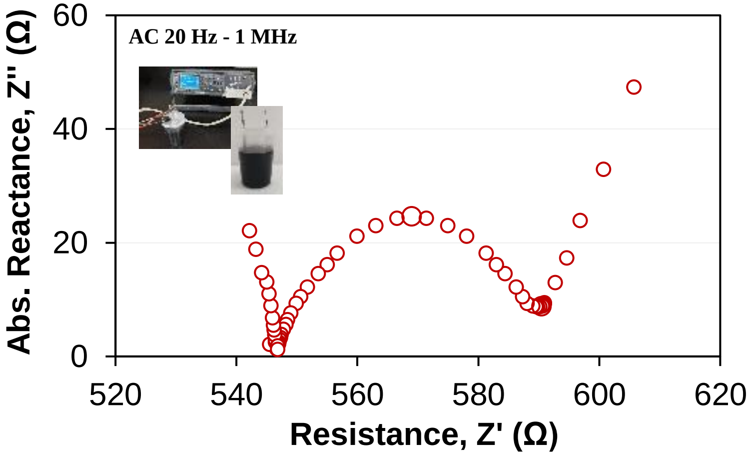
- ✓ Increased electron tunneling by minimizing the CNT-CNT distance, a.k.a. tunneling distance, d_t
- ✓ Controlled concentration of electrons available for electrical conduction, i.e., energy density, *dI/dV*



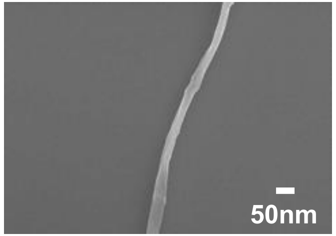
Macro-scale

E-Conducting Concrete with unique electrical properties

- ✓ High electrical conductivity
- ✓ Controlled dielectric permittivity



Materials and Experimental Program



SEM image of monodispersed CNT

Type	Diameter, R nm	Length, l µm	Waviness, *u*	Electrical conductivity, σ_i (S/m)
CNTs	20 - 45	10	0.95	10^6

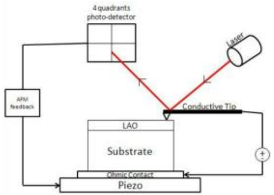
28-day Cement Mortar
w/c/s: 0.485/1.0/2.75
CNTs: 0.05 - 0.3 wt%

Specimens
Diameter: 1.2" (30 mm)
Height: 0.6" (14mm)

Tunneling AFM (TUNA AFM)

Electrical Property Mapping at the nanoscale

- ✓ Tunneling distance, d_t
- ✓ Electron Density, dI/dV



Tunneling AFM Block diagram

Parameters	Input values
Peak force	10nN
Scan rate	0.3Hz
Voltage	2V
Resolution	64x64

Electrical Conductivity, σ

True material property that indicates the material's ability to conduct an electric current

$$\sigma = \sigma_m \exp\left(-\frac{\sigma_i}{\boldsymbol{d_t}}\frac{2.4uR^2}{l\left(V_{eff}\right)^{2/3}}\right)$$

σ_m, electrical conductivity of the matrix (S/m)
V_{eff}, effective volume of nanofiber in the matrix

Dielectric Permittivity, ε

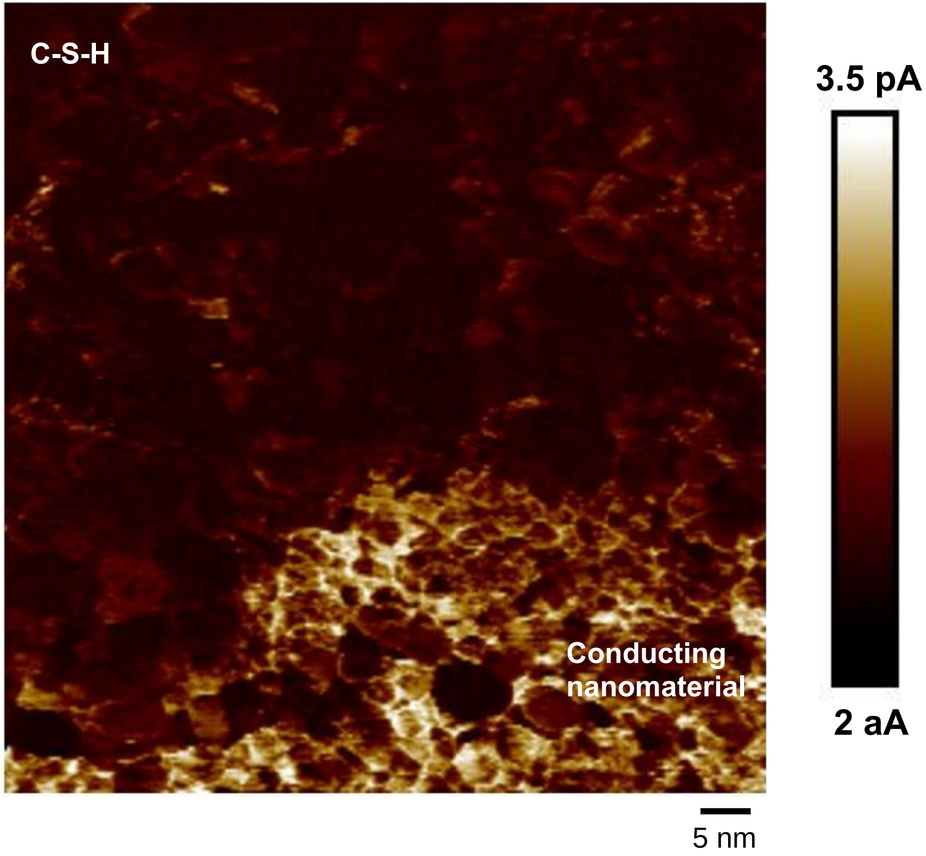
True material property that represents the material's capacity to store electrical energy

$$\varepsilon = \frac{1}{\frac{\boldsymbol{dI}}{\boldsymbol{dV}}}\varepsilon_0 A$$

ε_0, Dielectric permittivity of vacuum
A, Area of in-plane current path

1) Shah, S.P., Konsta-Gdoutos, M.S., Metaxa, Z.S.. United States Patent US9,365,456 (B2) — 2016-06-14
2) Hersam, M.C., Seo, J-W.T. , Shah, S.P., Konsta-Gdoutos, M.S., Metaxa, Z.S.. United States Patent, US8,865,107(B2)- 2014-10-14
3) Shah, S.P., Konsta-Gdoutos, M.S., Metaxa, Z.S.. United States Patent No. 9,499,439 (B2) — 2016-11-22

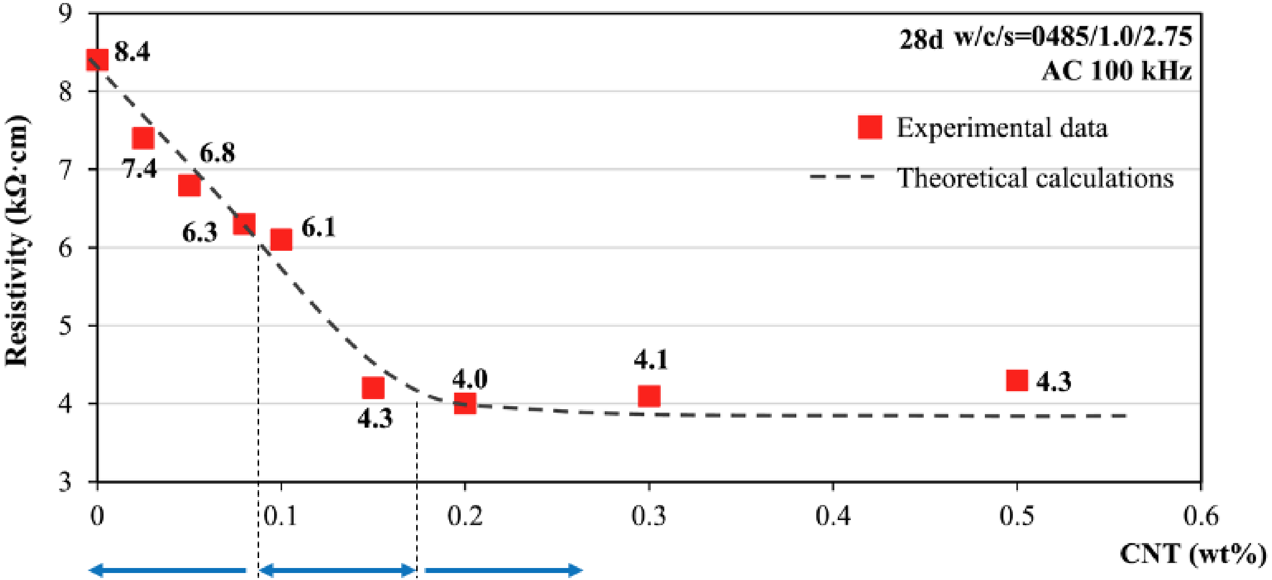
Topographical Imaging and Property Mapping in Nanomodified Cementitious System



- ➢ 5 nm Topographical Imaging of 28-day CNT reinforced mortar
- ➢ Ultra-low Current Mapping
  - *Pikoampere (pA): 10^{-15} A*
  - *Attoampere (aA): 10^{-18} A*

Electrical Resistivity of CNT Reinforced Mortars

Electrochemical Impedance Spectroscopy Measurements

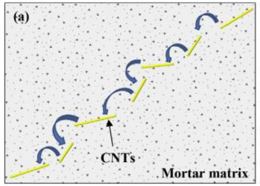


Non continuous CNT network

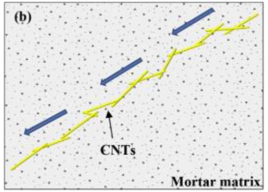
Percolation Threshold

Continuous CNT network

Electron Hopping



Electron Tunneling



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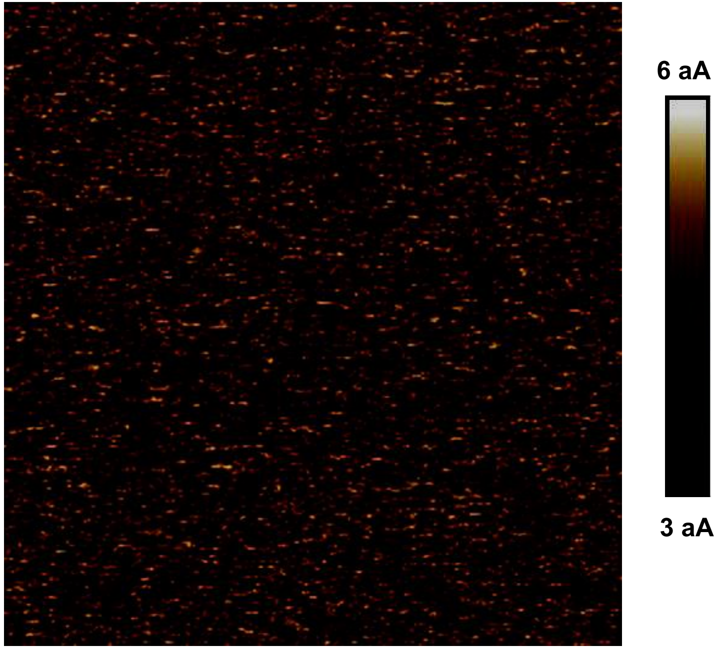
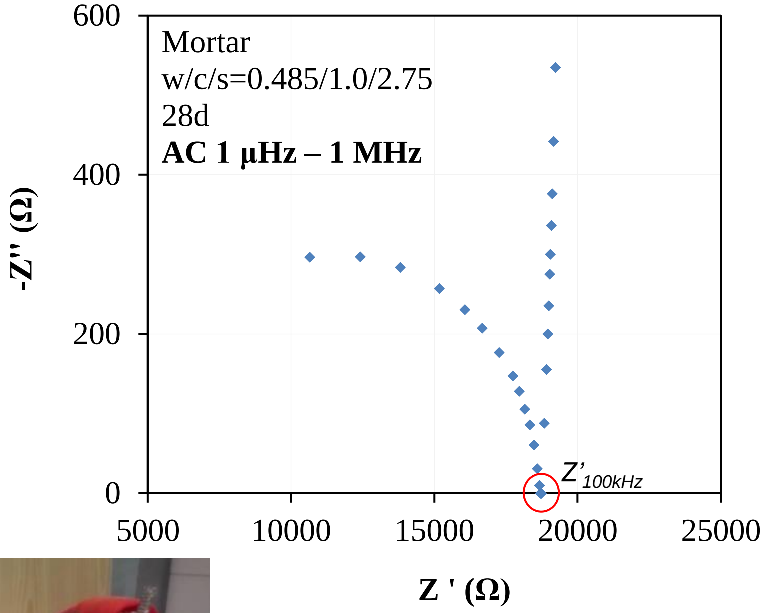
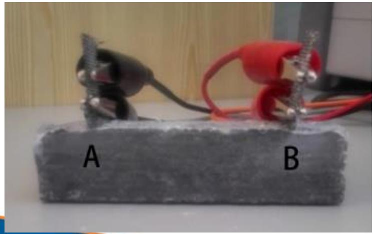
Electron Mobility is not Detected Within the Insulating Cementitious Matrix



Tunneling distance, d_t : N/A

Electrical Conductivity, σ_m, of 28-day mortar, σ_m, was calculated through Electrochemical Impedance Spectroscopy measurements





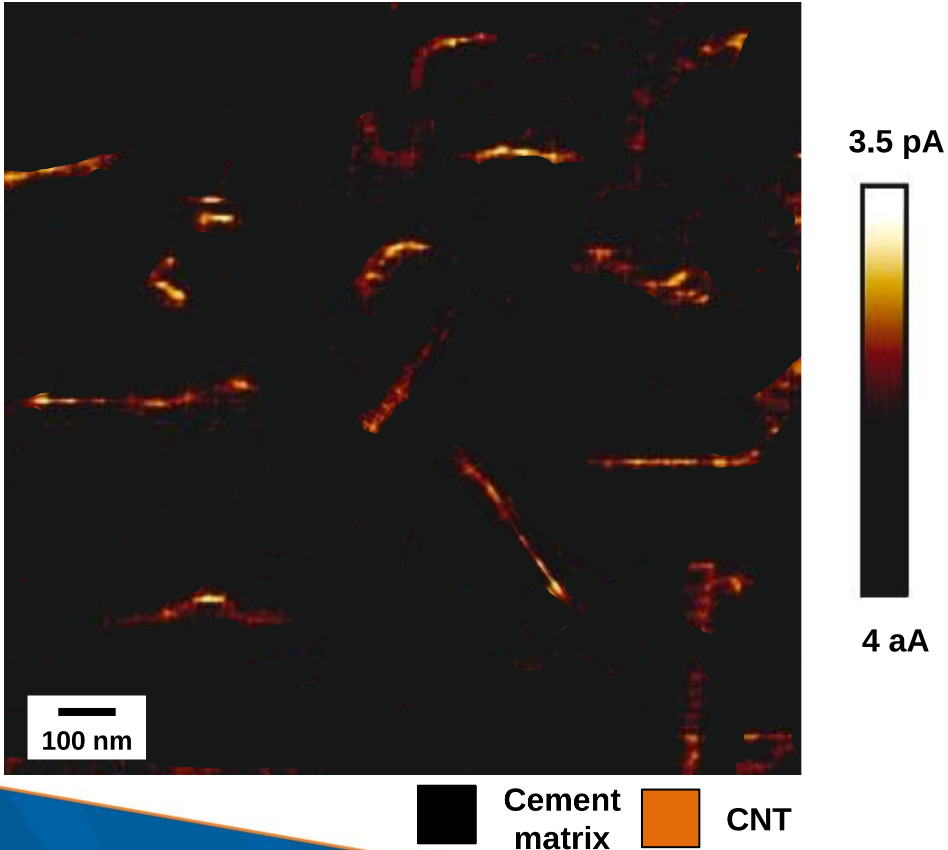
$$\sigma_m = \frac{L}{Z'_{100kHz} S}$$

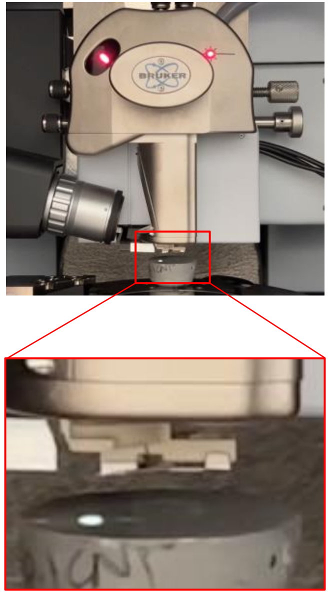
$$\sigma_m = 1.1\ S/m$$

S: Cross section of the specimen
L: the distance between electrodes

Electron Mobility Mechanism of CNT Networks Within Cementitious Matrix

Current Mapping in 0.05 wt% CNT Mortars



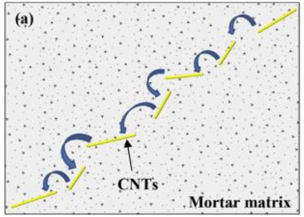


Electron Mobility Mechanism of CNT Networks Within Cementitious Matrix

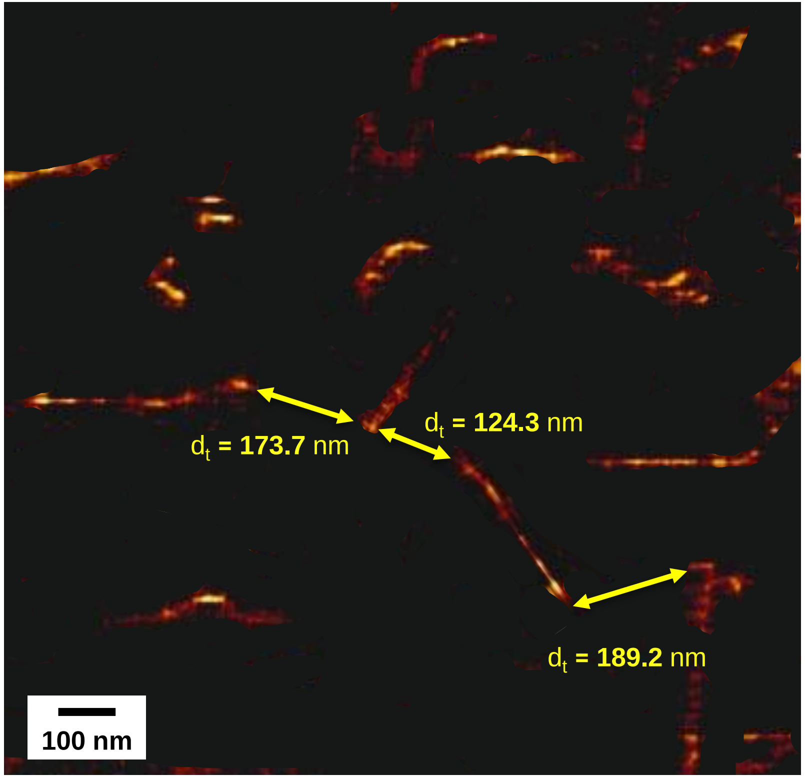
Tunneling Distance in 0.05 wt% CNT Mortars

High Tunneling Distance d_t

Electron Hopping



Low electron mobility

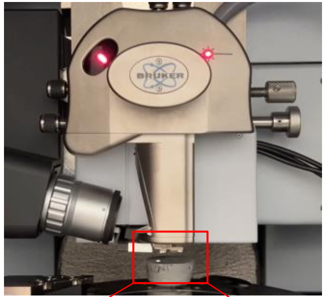


3.5 pA

4 aA

Cement matrix

CNT



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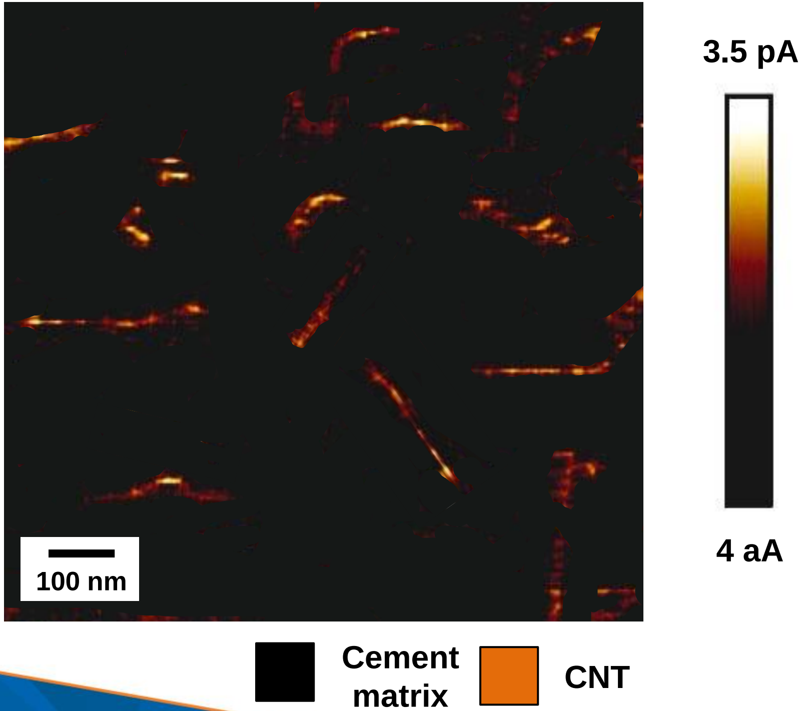
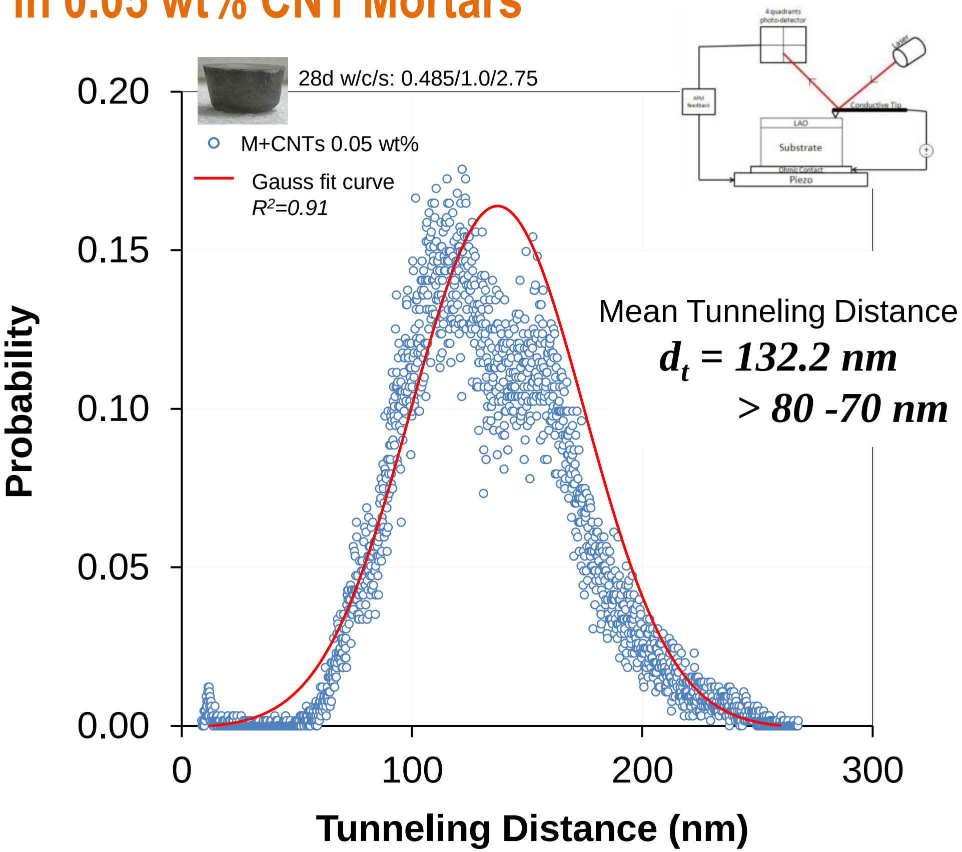
Electron Mobility Mechanism of CNT Networks Within Cementitious Matrix

Tunneling Distance in 0.05 wt% CNT Mortars



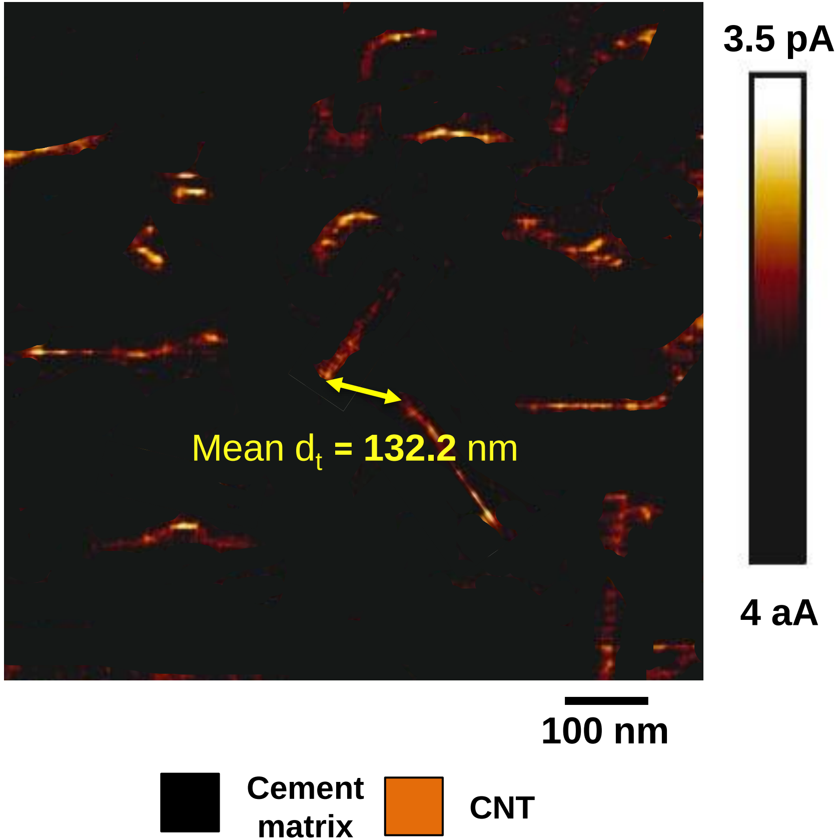


Danoglidis, P.A., Konsta-Gdoutos, M.S. and Shah, S.P., 2019. Carbon, 145, pp.218-228.

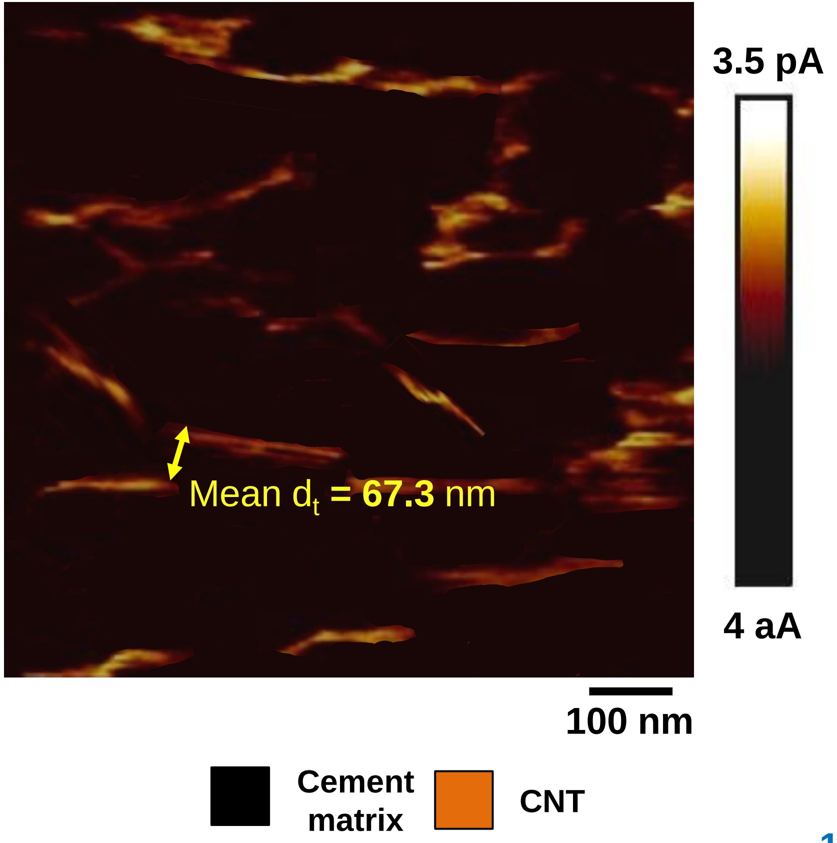
Zare, Y. and Rhee, K.Y., 2020. Polymers, 12(1), p.114.

Current Mapping of CNT Mortars

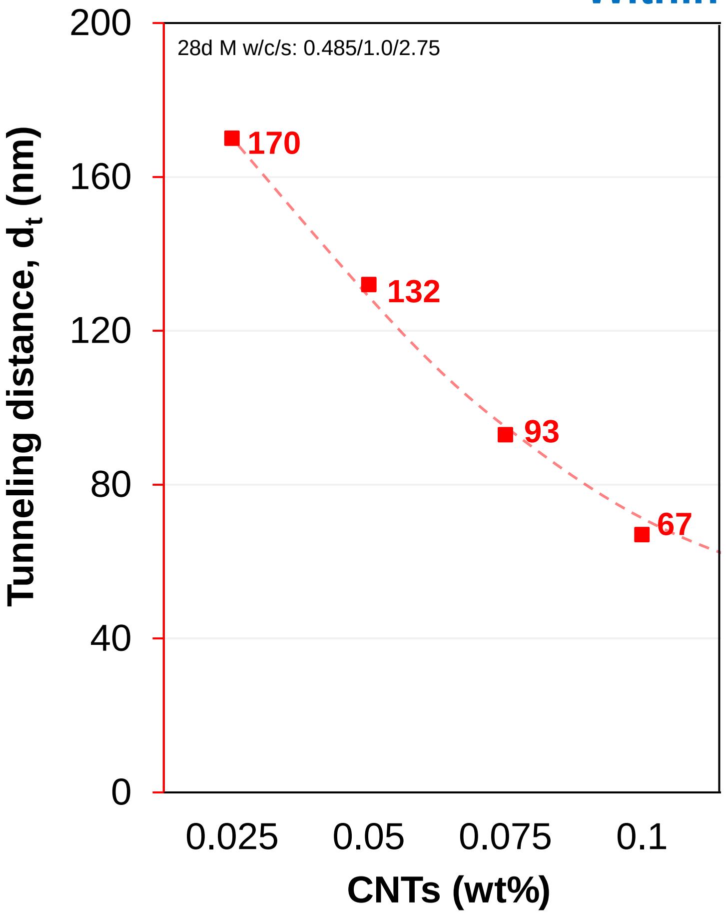
M + CNTs 0.05 wt%



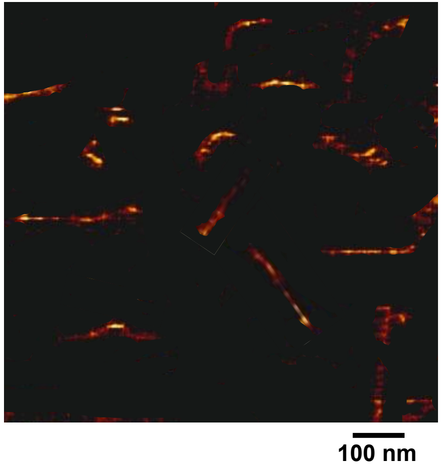
M + CNTs 0.1 wt%



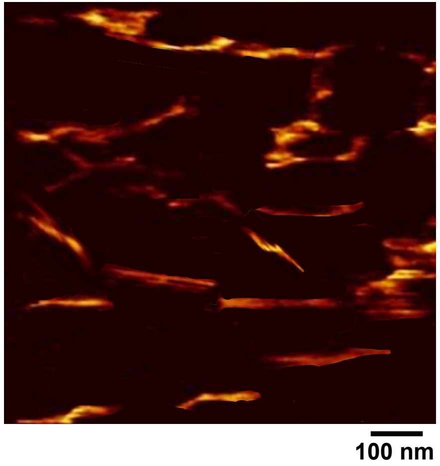
Gradual Formation of Continuous CNT Networks Within Cementitious Matrix



M + CNTs 0.05 wt%



M + CNTs 0.1 wt%



0.1 wt% CNT mortars
d_t = 67 nm < 80 -70 nm

0.1 wt% is the critical amount of CNTs that denotes the formation of a continuous electrically conductive network, i.e., percolation threshold

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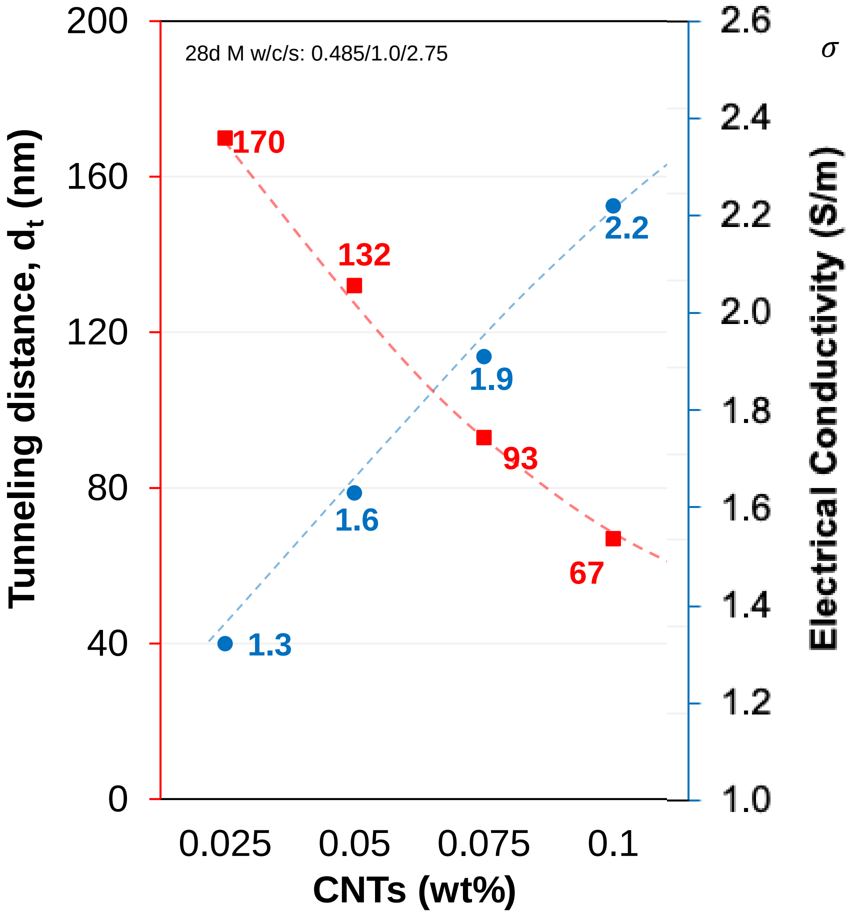
Electrical Conductivity of CNT Reinforced Mortars



$$\sigma = \sigma_m \exp\left(-\frac{\sigma_i}{\boldsymbol{d_t}}\frac{2.4uR^2}{l(V_{eff})^{2/3}}\right)$$

- ✓ Decrease of d_t in CNT networks

⇩

- ✓ **+70%** Higher electrical conductivity using 0.1 wt% CNTs

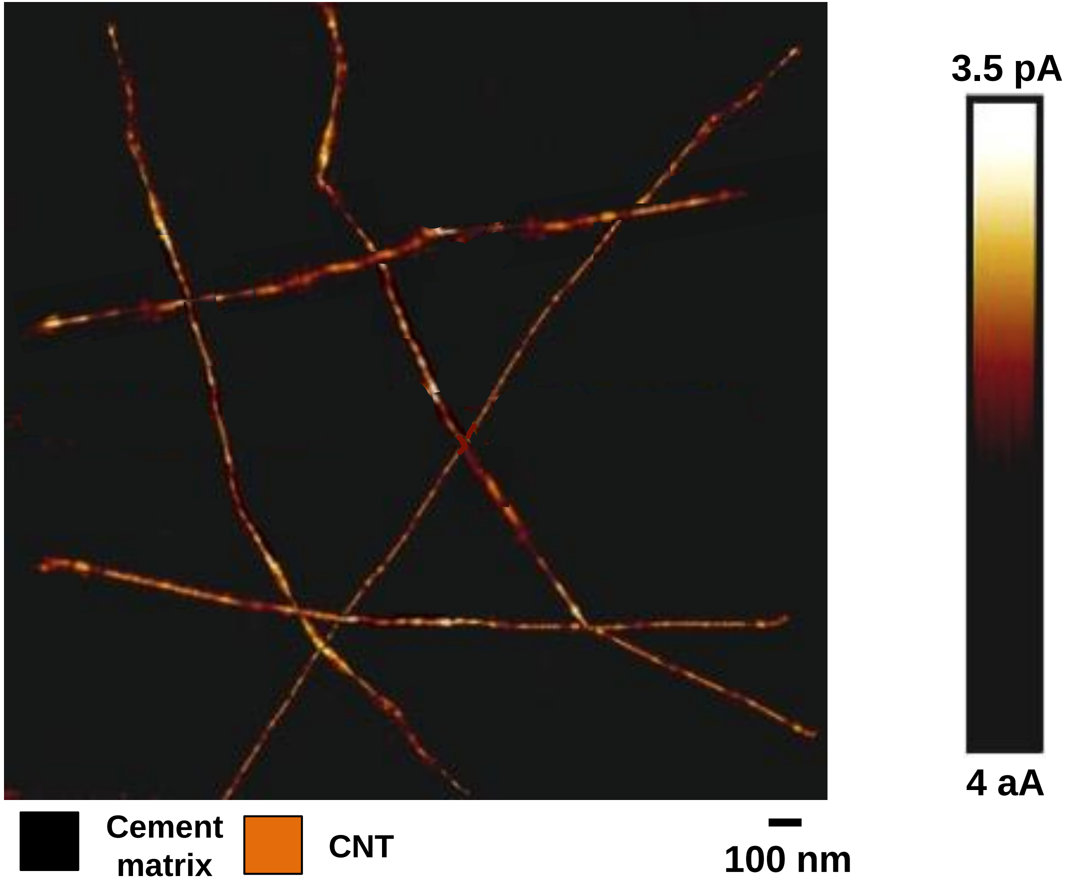
*Electrical conductivity values obtained from Electrochemical Impedance Spectroscopy Measurements**

	Electrical conductivity (S/m)
Mortar (M)	1.1 ± 0.2
M + CNTs 0.025 wt%	1.3 ± 0.2
M + CNTs 0.05 wt%	1.6 ± 0.2
M + CNTs 0.08 wt%	1.9 ± 0.1
M + CNTs 0.1 wt%	2.2 ± 0.1

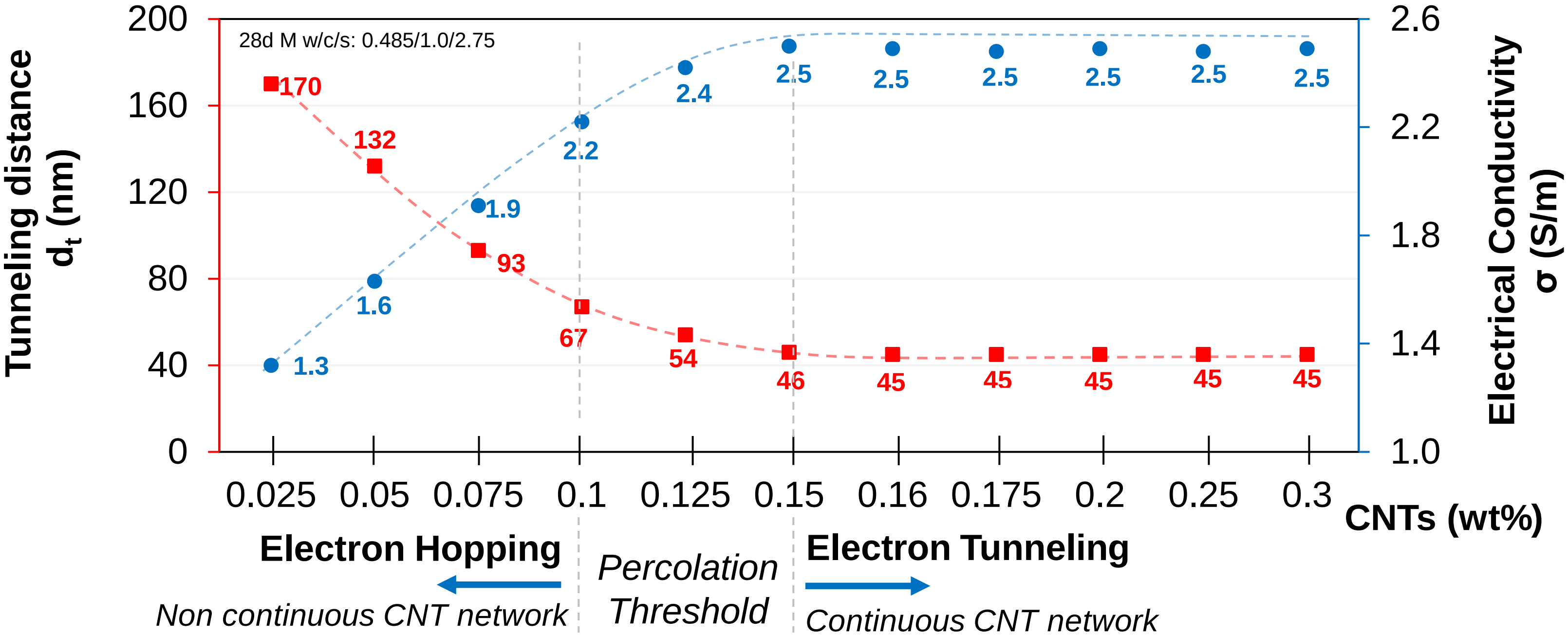
Danoglidis, P.A., Konsta-Gdoutos, M.S. and Shah, S.P., 2019. Carbon, 145, pp.218-228.

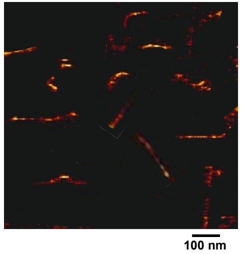
Uninterrupted Electron Mobility Through Percolative CNT Networks

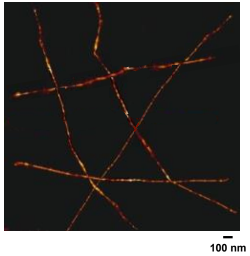
CNTs 0.15 wt%



Electron Mobility Mechanism in non-percolative and percolative CNT networks within cementitious matrix



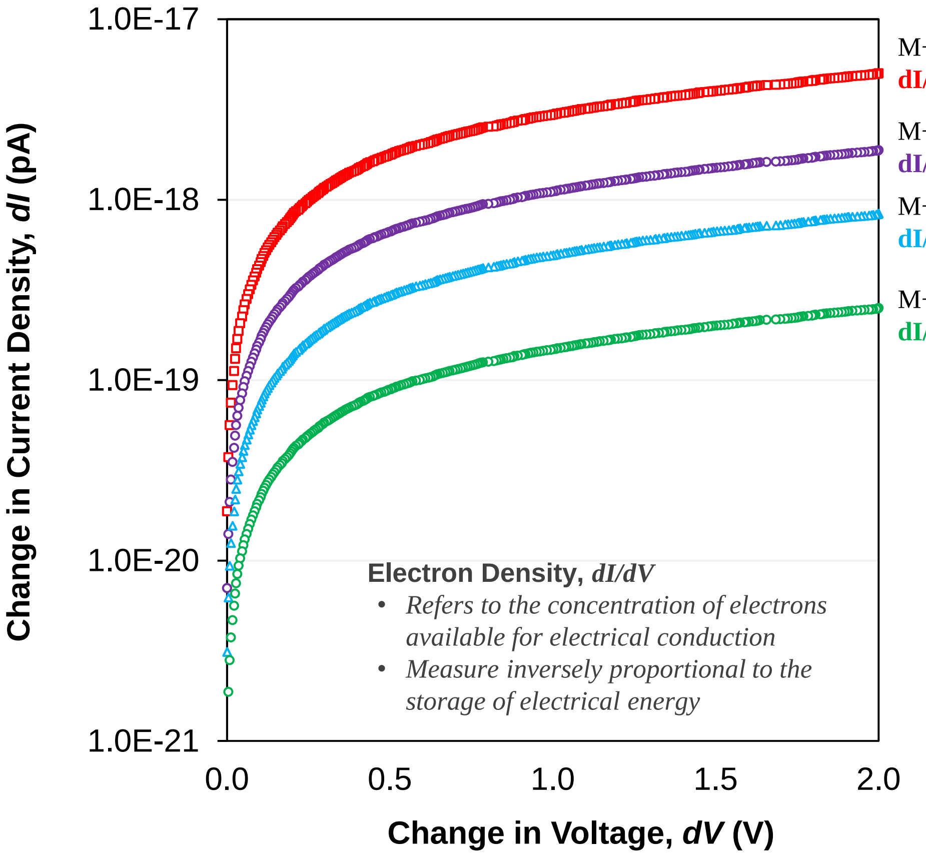




$$\sigma = \sigma_m \exp\left(-\frac{\sigma_i}{\boldsymbol{d_t}} \frac{2.4uR^2}{l\left(V_{eff}\right)^{2/3}}\right)$$

Electron Density in CNT Reinforced Mortars

CNT amounts up to 0.1 wt% (percolation threshold)



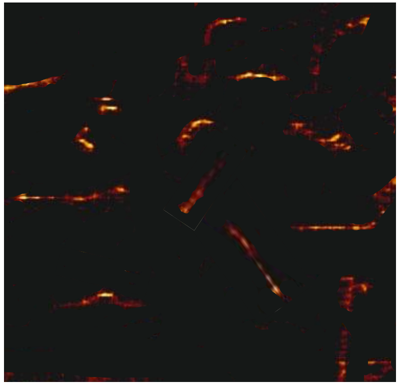
M+CNTs **0.1** wt%
dI/dV = 25 · 10^{-19}

M+CNTs **0.08** wt%
dI/dV = 9.4 · 10^{-19}

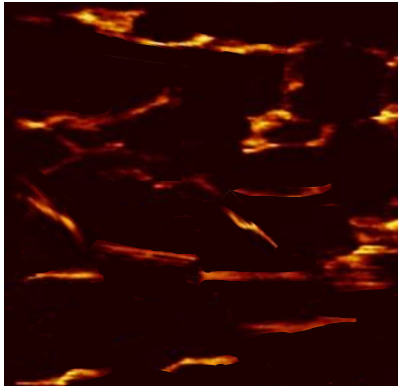
M+CNTs **0.05** wt%
dI/dV = 4.1 · 10^{-19}

M+CNTs **0.025** wt%
dI/dV = 1.3 · 10^{-19}

500%
higher current density



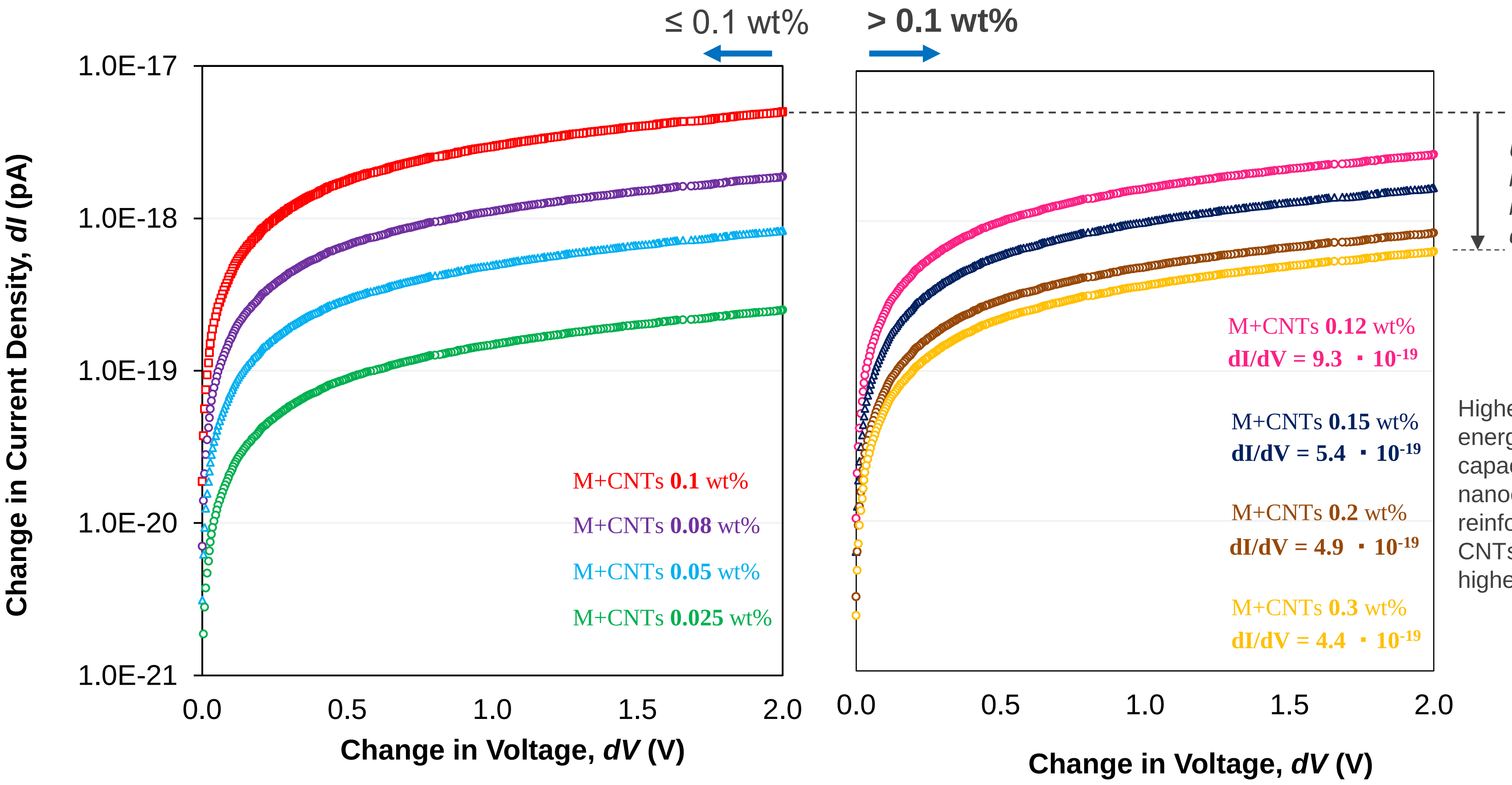
M+CNTs **0.05** wt%



M+CNTs **0.1** wt%

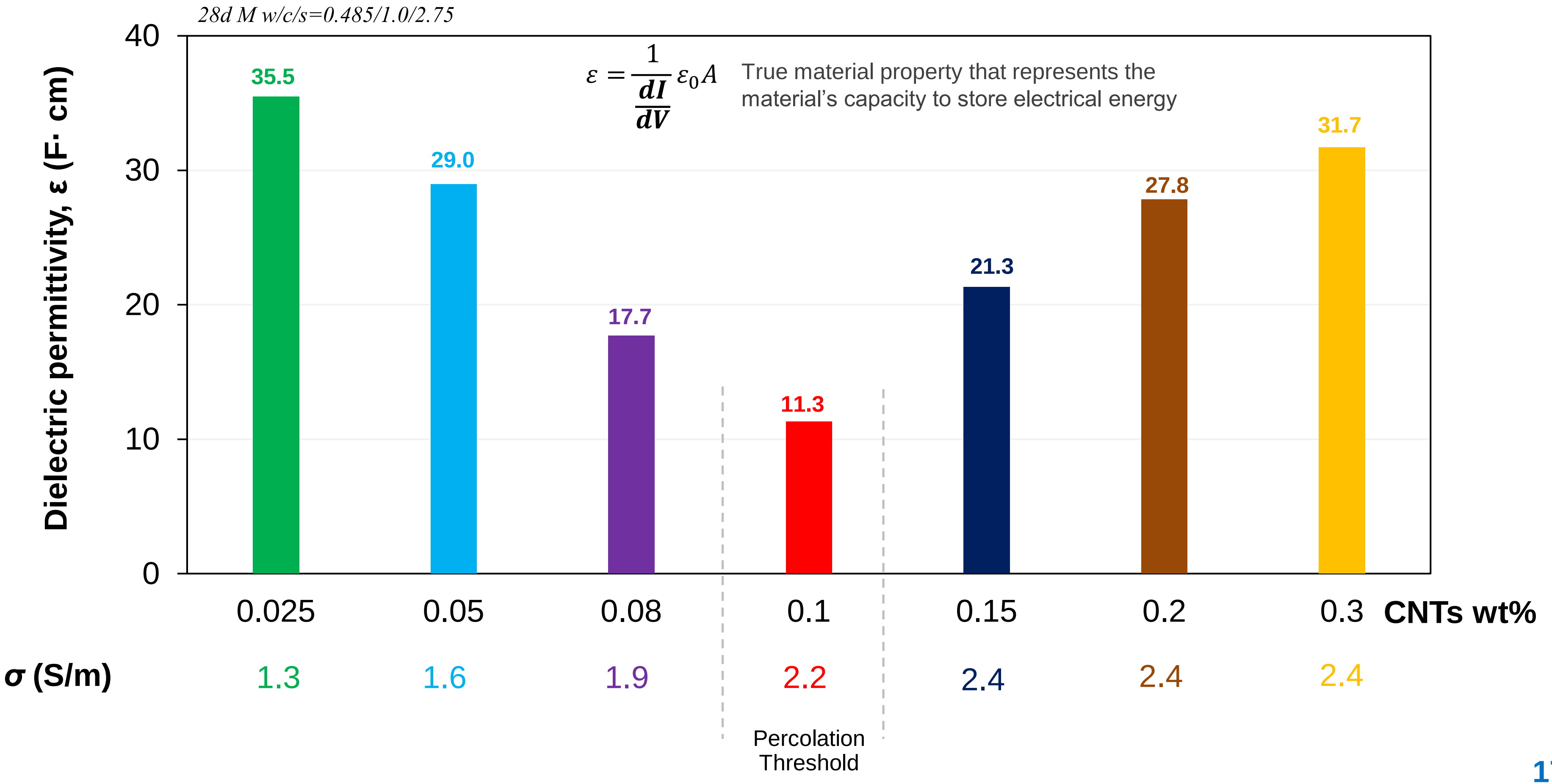
Electron Density in CNT Reinforced Mortars

CNT amounts higher than 0.1 wt%

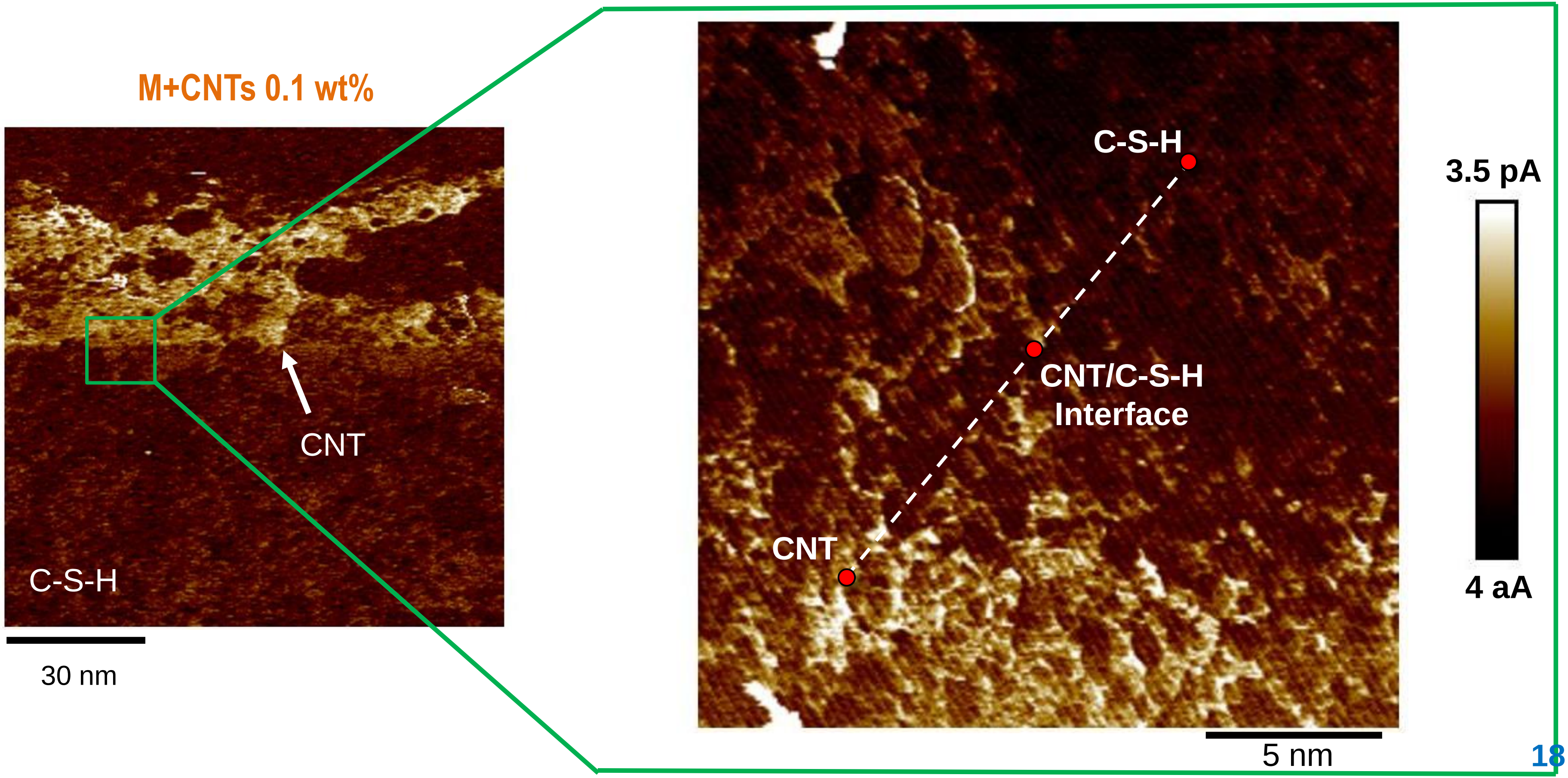


Higher electrical energy absorption capacity of nanocomposites reinforced with CNTs at amounts higher than 0.1 wt%

Dielectric Permittivity of CNT Reinforced Mortars

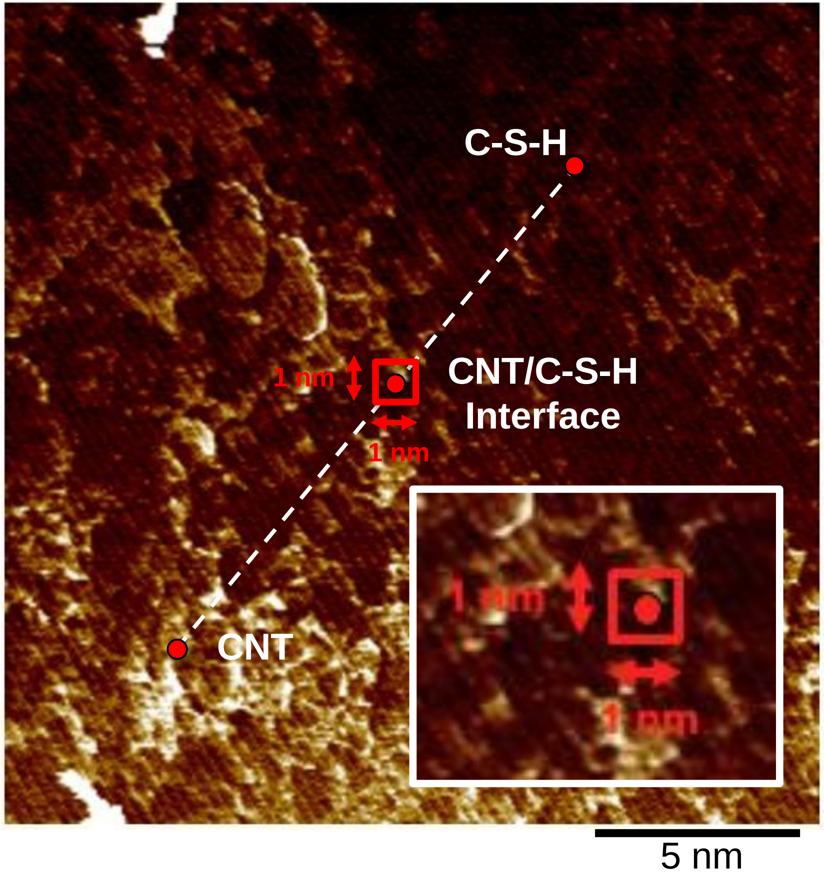


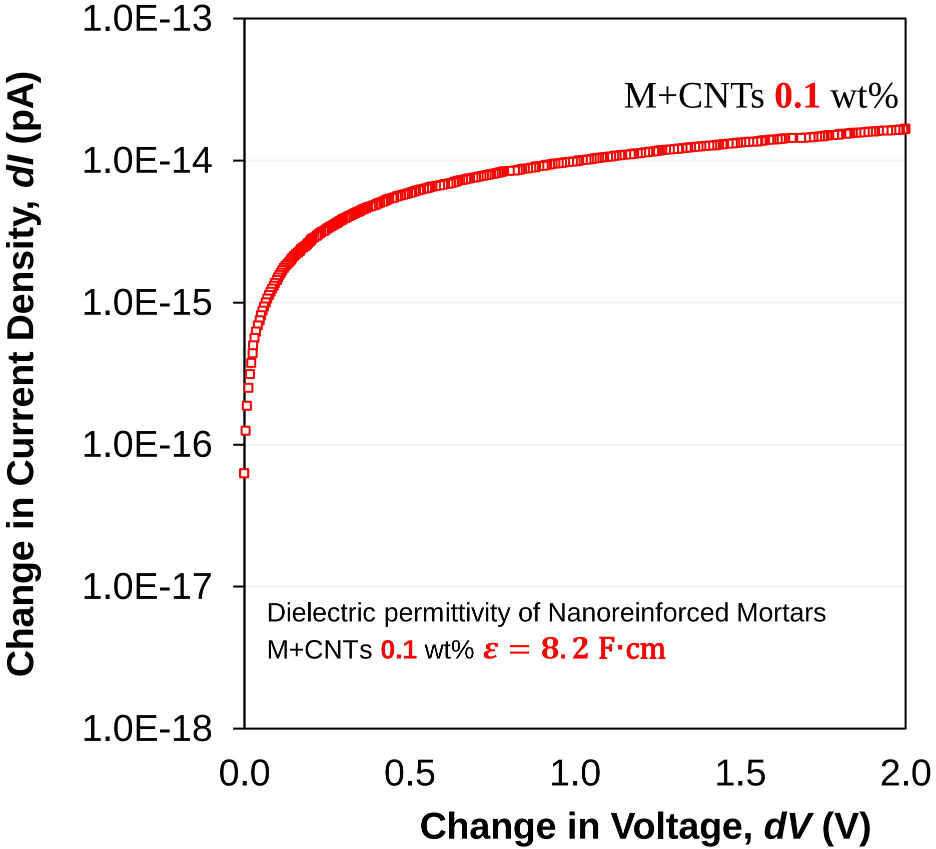
Nanoscale interfaces Play a Key Role on the Bulk Electrical Properties of Nanoengineered Concrete



Electron Density of the CNT/C-S-H Interface

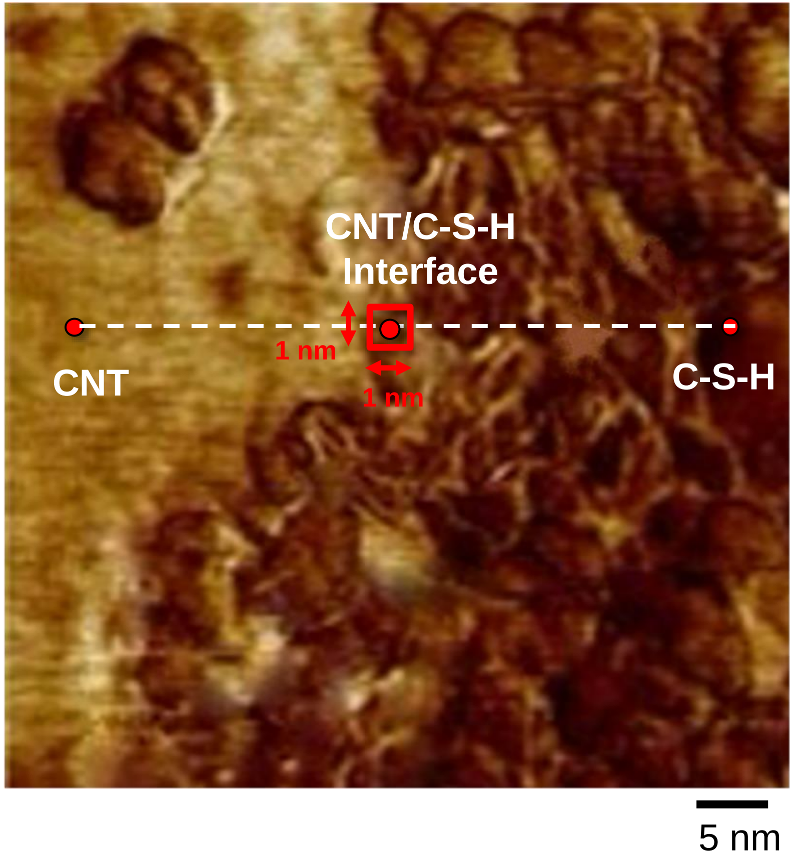
M+CNTs 0.1 wt%

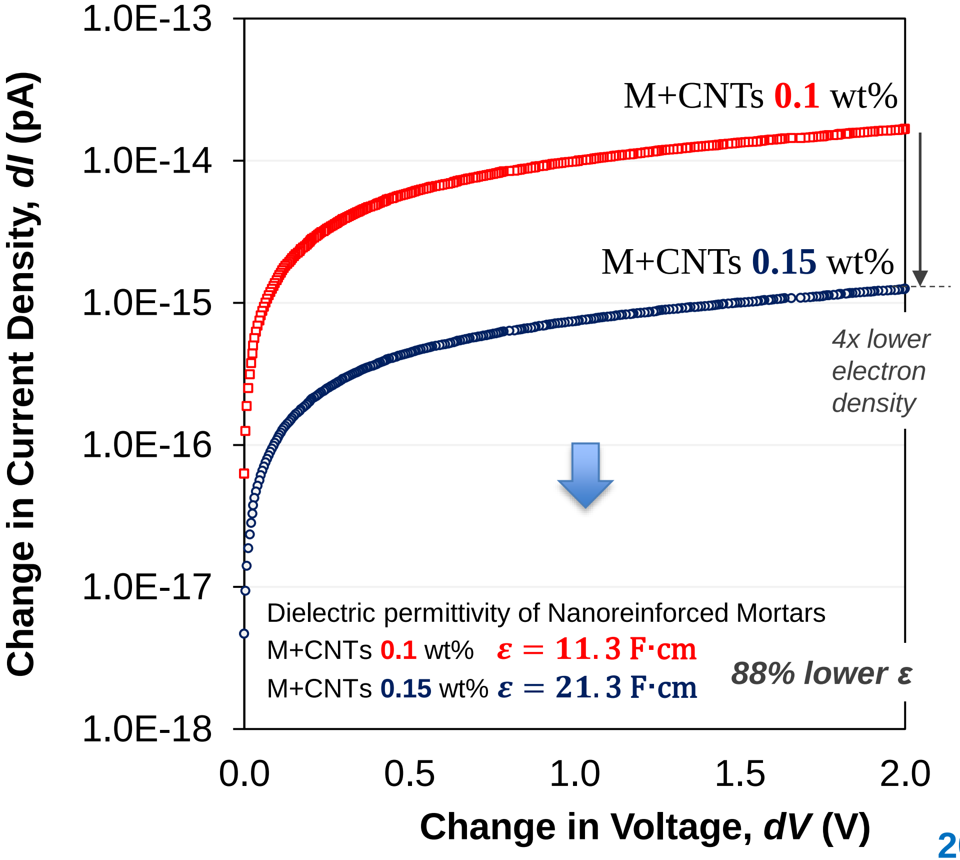




Dielectric Permittivity of the CNT/C-S-H Interface

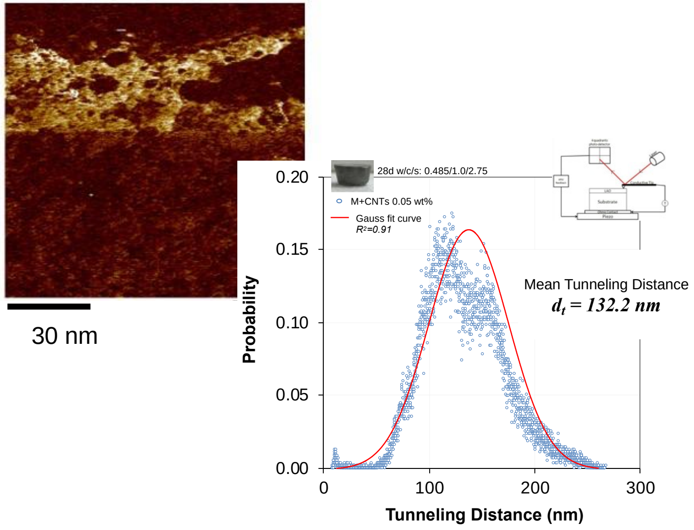
M+CNTs 0.15 wt%



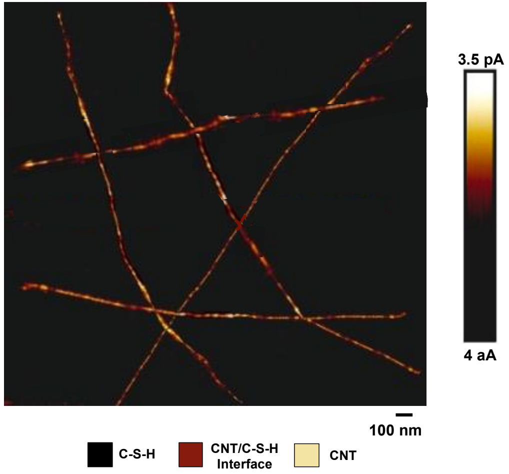


Conclusions

- ➢ Tunneling AFM is a useful tool for identifying the tunneling distance and electron density related to the electron mobility in nanostructured systems
- ➢ Tunneling distance and electron density are essential for the evaluation of the bulk electrical conductivity and dielectric permittivity of nanocomposites



- ➢ Use of CNTs at amounts
  - Up to 0.1 wt% (percolation threshold) ➡ Gradual formation of continuous CNT networks
    - ✓ *Reduced tunneling distance → Higher Electrical Conductivity*
    - ✓ *Increased electron density → Lower Dielectric Permittivity*
  - > 0.1 wt% ➡ Continuous CNT network is established
    - ✓ *Negligible tunneling distance → High Electrical Conductivity of 2.5 S/m*
    - ✓ *Decreased electron density → Higher Dielectric Permittivity*



Current mapping of Percolative CNT networks

Acknowledgements

The authors would like to acknowledge the financial support of the National Science Foundation – Partnerships for International Research and Education (PIRE) Research Funding Program "Advancing International Partnerships in Research for Decoupling Concrete Manufacturing and Global Greenhouse Gas Emissions" (NSF – PIRE – 2230747).

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Advancing International Partnerships in Research for Decoupling Concrete Manufacturing and Global Greenhouse Gas Emissions

National Science Foundation

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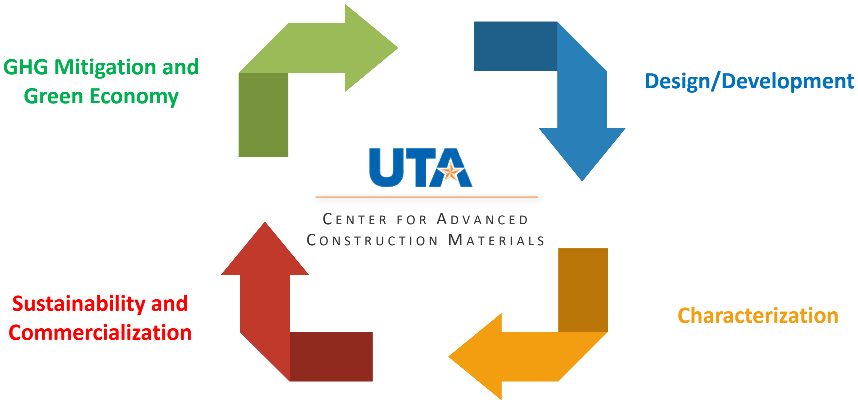
Thank you!



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