One-Dimensional van der Waals Materials as Efficient Fillers for Composites – Applications in Electromagnetic Shielding

Z. Barani[1], F. Kargar[1], Y. Ghafouri[2], S. Rumyantsev[3], K. Godziszewski[4], G. Cywiński[3], Y. Yashchyshyn[3,4], T.T. Salguero[2] and A.A. Balandin[1]

[1]Department of Electrical and Computer Engineering, University of California, Riverside, California 92521 USA
[2]Department of Chemistry, University of Georgia, Athens, Georgia 30602 USA
[3]CENTERA Laboratories, Institute of High-Pressure Physics, Polish Academy of Sciences, Warsaw 01-142 Poland
[4]Institute of Radioelectronics and Multimedia Technology, Warsaw University of Technology, Warsaw 00-665 Poland
E-mail: balandin@ece.ucr.edu https://balandingroup.ucr.edu

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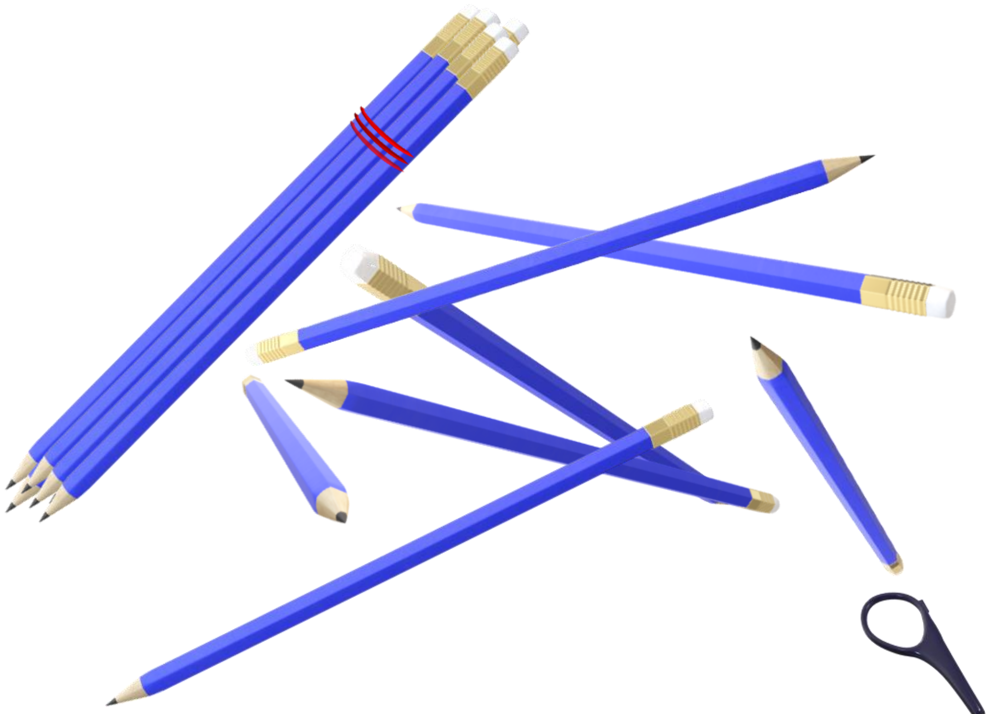
Outline

- **Background and Motivation**
  - Quasi-1D Materials: Structures and Exotic Properties
  - Introduction to EMI Shielding
  - Polymeric Composites with Novel Fillers for EMI Shielding

- **Quasi-1D-Based Composites for EMI Shielding Management**
  - Measurement of EMI Shielding Effectiveness
  - Liquid Phase Exfoliation and Sample Preparation
  - Results and Discussion

- **Summary and Conclusions**

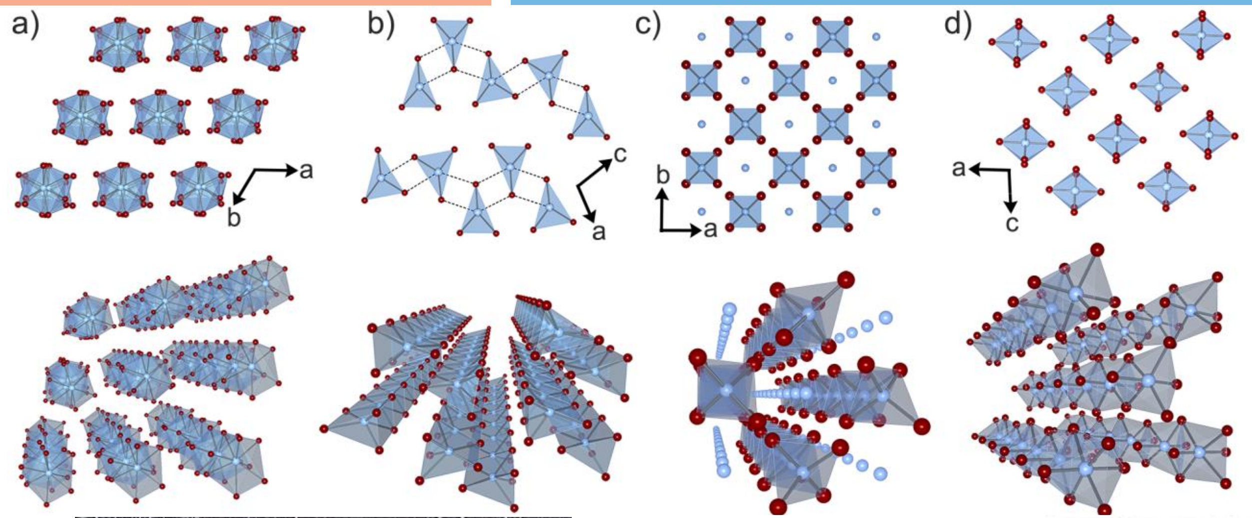
Quasi-1D Materials: "Quasi" and "Quantum" Structures

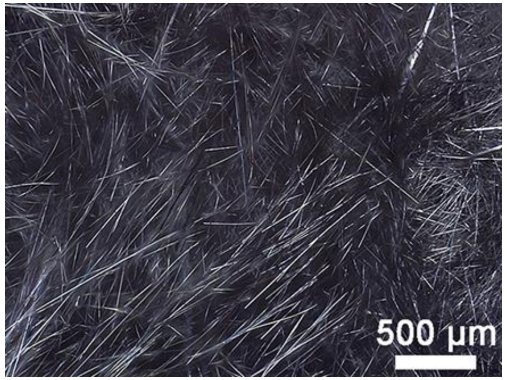


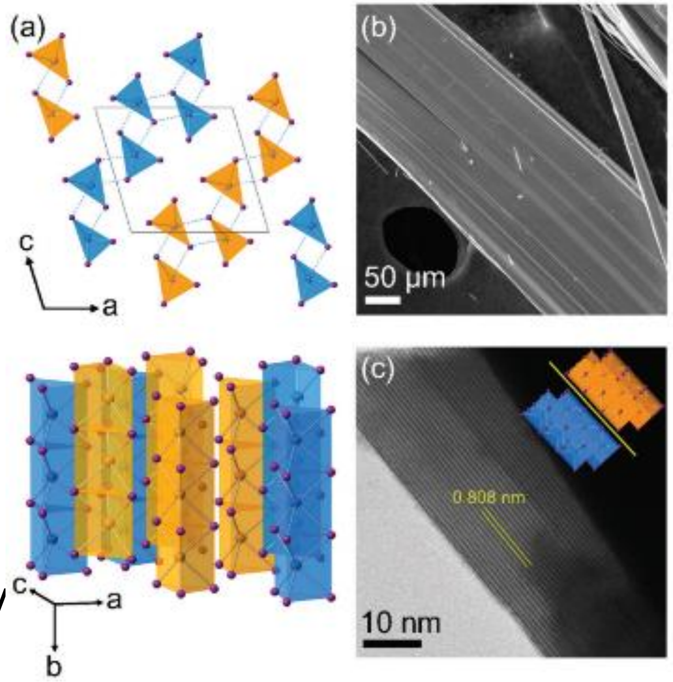
➢ Need a tiny scissor to cut the band

➢ Need a knife to peel

BUT: Need an axe to cut in half





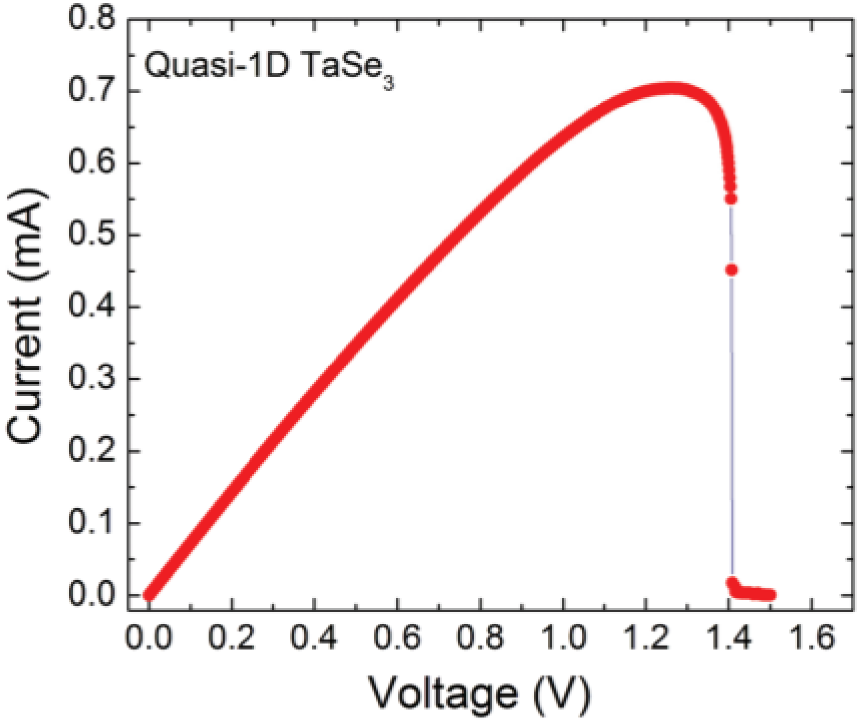


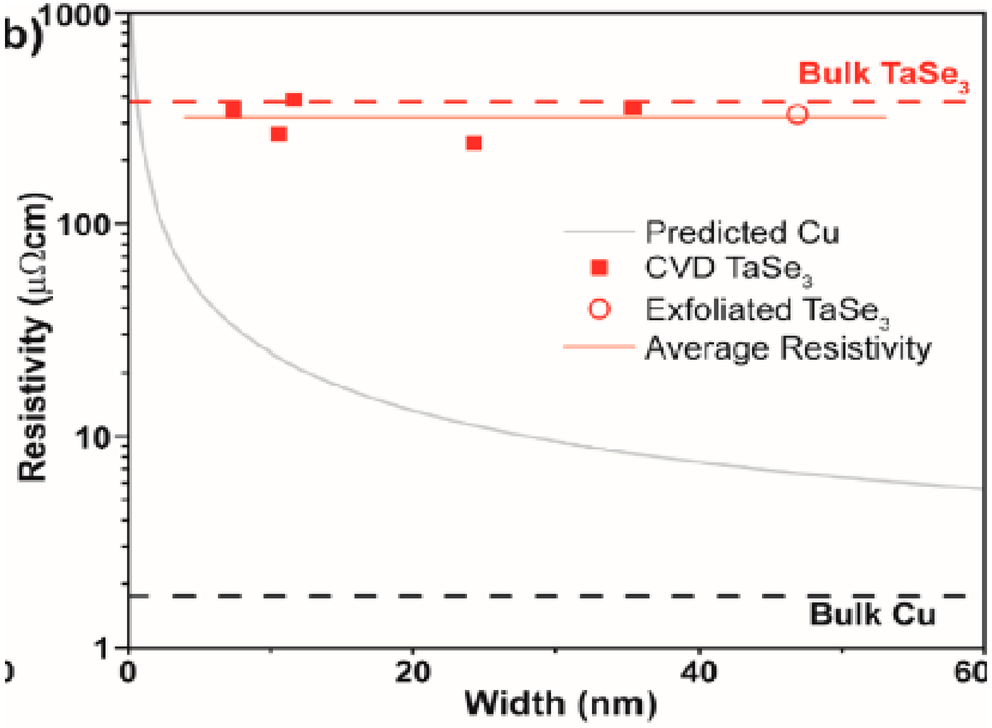
➢ "Quasi" in a sense of a bundle

➢ "Quasi" in a sense that you may have weaker covalent bonds in perpendicular plane

Exotic Properties of MX_3

- MX_3, with M as a transition metal and X as a chalcogen material have special crystal structures causing them to appear as needle-like structures; Rich Material Library





- High-field I–V characteristics showing the breakdown point;
- Extremely high breakdown current density
- $J_{B,TaSe_3} = 32\ \text{MA cm}^{-2}$, $J_{B,ZrTe_3} = 100\ \text{MA cm}^{-2}$ almost 10 and 100 times more than copper;

1. Very high aspect ratio : A strong candidate as filler in EMI shielding composites.
2. Medium-range resistivity of $TaSe_3$.
3. Constant resistivity as Exfoliated: Not like metallic nanowires.
4. Extremely high breakdown current density
5. Anisotropic optical, electrical, thermal, mechanical properties

M.A. Stolyarov… A.A. Balandin, Nanoscale **8**, 15774 (2016).
A. Geremew…A.A. Balandin, IEEE Electron Device Lett. **39**, 735 (2018).
T.A. Empante,…A.A. Balandin, L. Bartels, Nano Lett. 19 (2019) 4355–4361.

Design Requirements for EMI Shielding Applications

Determine the operational frequency → Quantity of shielding required → Material Design → Experimental testing

SE (dB)	Shielding Efficiency (%)
0	0
10	90
20	99
30	99.9
40	99.99
50	99.999
60	99.9999
70	99.99999
80	99.999999

Operational Frequency:

- No composite or material system can shield the whole EM frequency range.
- X-band: 8.2 to 12.4 GHz: Military and most of the communication systems;
- EHF: 30 to 300 GHz, required for the next generation of communication devices.

Shielding Requirements:

- 30 dB shielding would be sufficient in 50% of the industrial cases, and 40 dB would fulfill 95% of their requirements.

30dB = 99.9 % of incident EM wave is blocked.

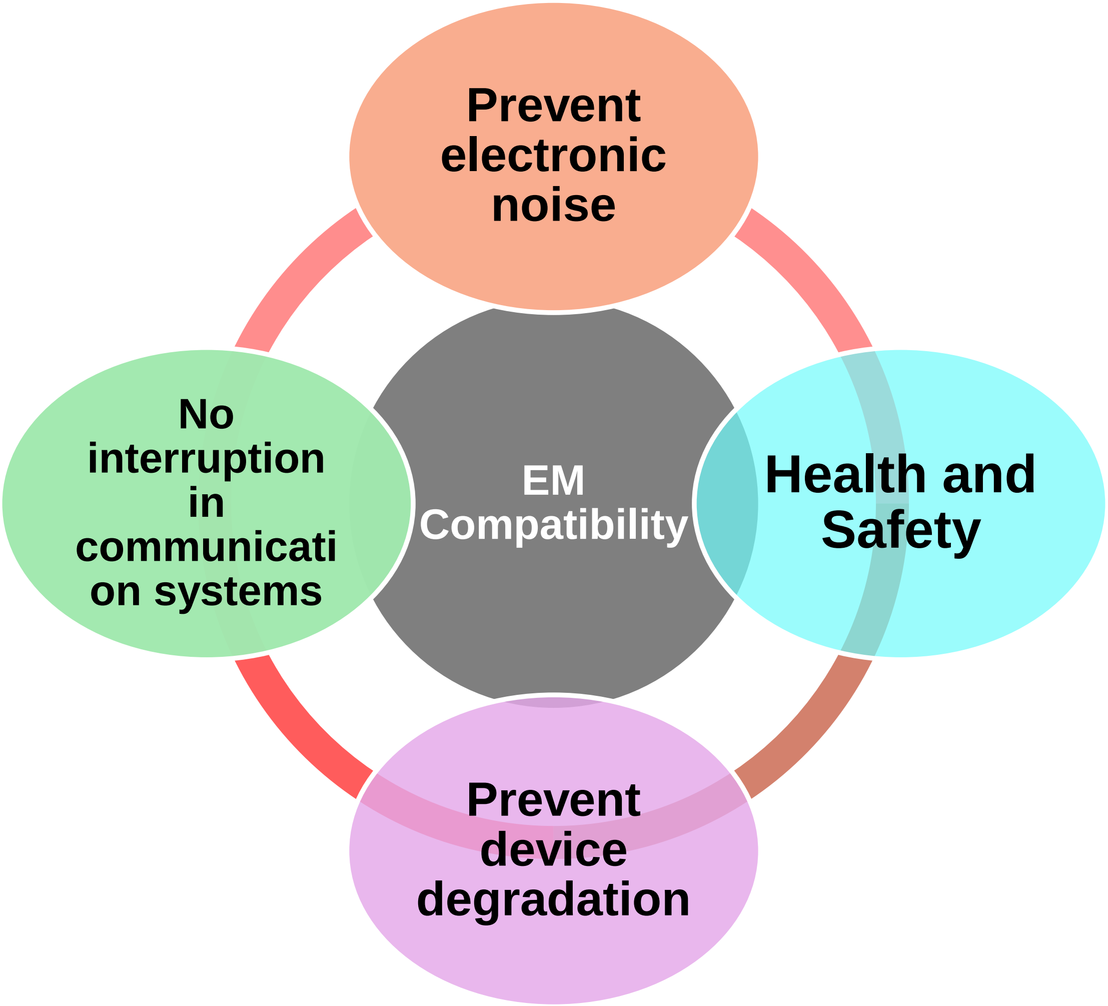
- **Material Design:**

The material system should be light, cost-effective, easy to handle, flexible.

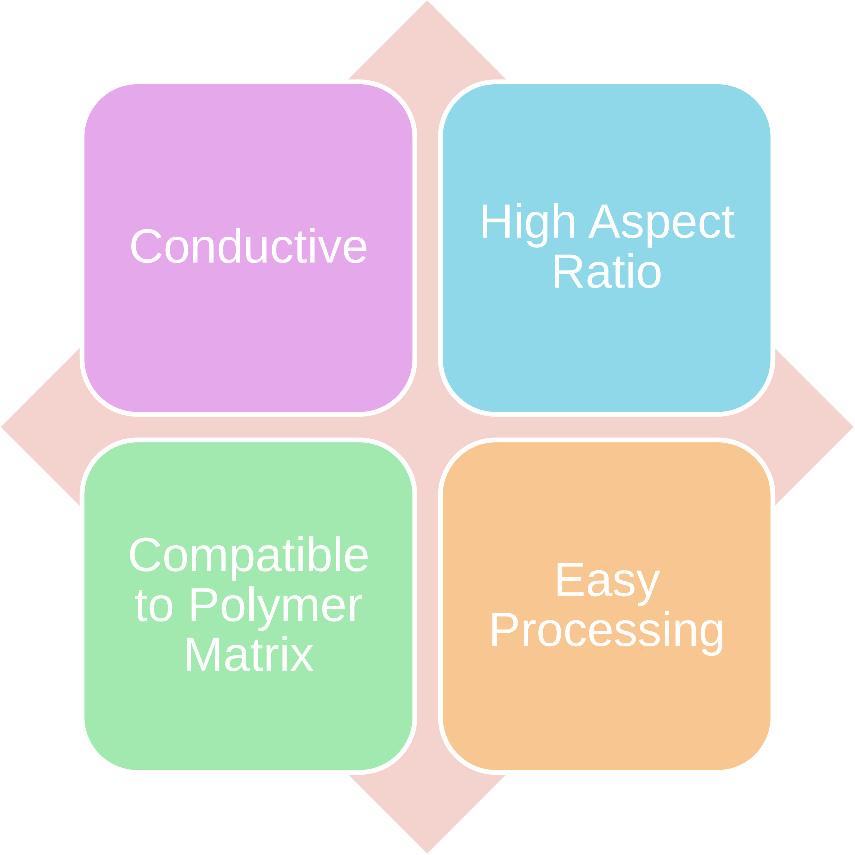
Simon, R. M. EMI Shielding Through Conductive Plastics. *Polym. Plast. Technol. Eng.* **17**, 1–10 (1981).

Composites and EMI Shielding

Electromagnetic Interference: Disturbance generated in a device, or circuit by an external source of EM radiation



- ❑ **Historically Metals**
- ❑ **Polymer/Filler Composites or Films**
  - ➢ Easy manufacturing, flexibility, cheap and stable
  - ➢ Polymers are poor conductors: Need conductive fillers
  - ➢ Classic fillers: Metal fibers, carbon black, graphite



http://www.lessemf.com/plastic.html

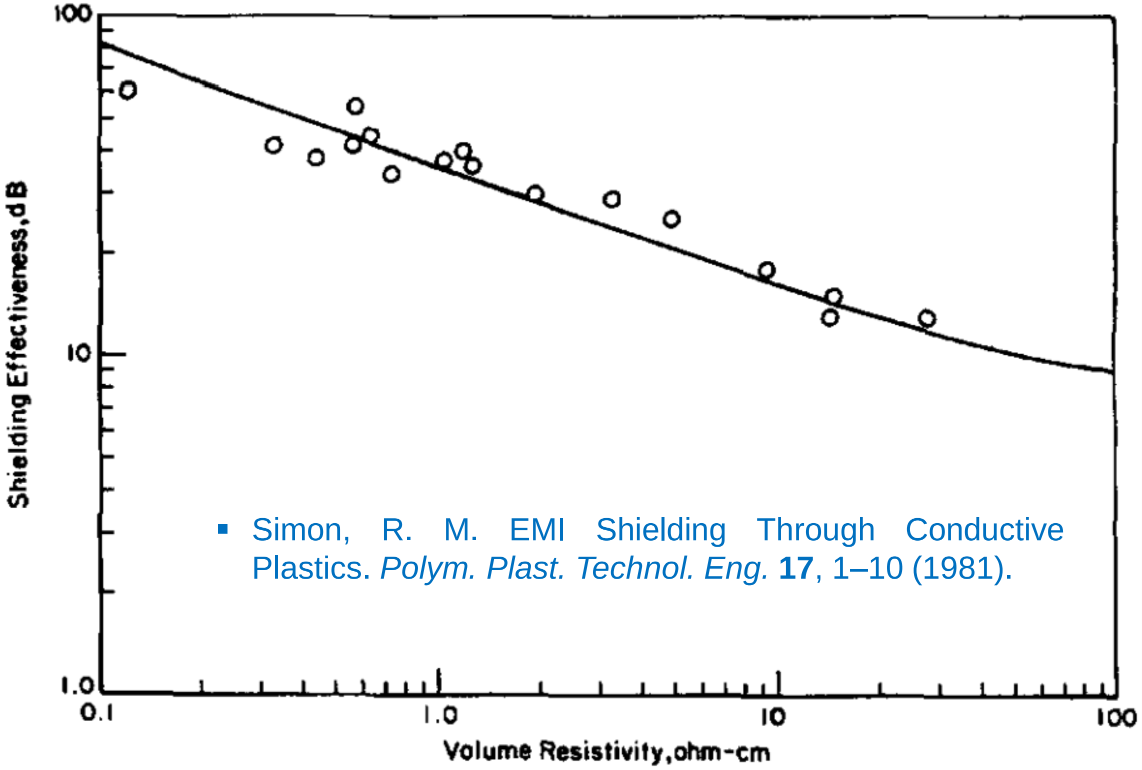
Material Design and Requirements

- EMI shielding is directly related to the bulk resistivity of the composites (Simon's equation):

$$SE_R = 50 + 10\log(\frac{1}{\rho f})$$

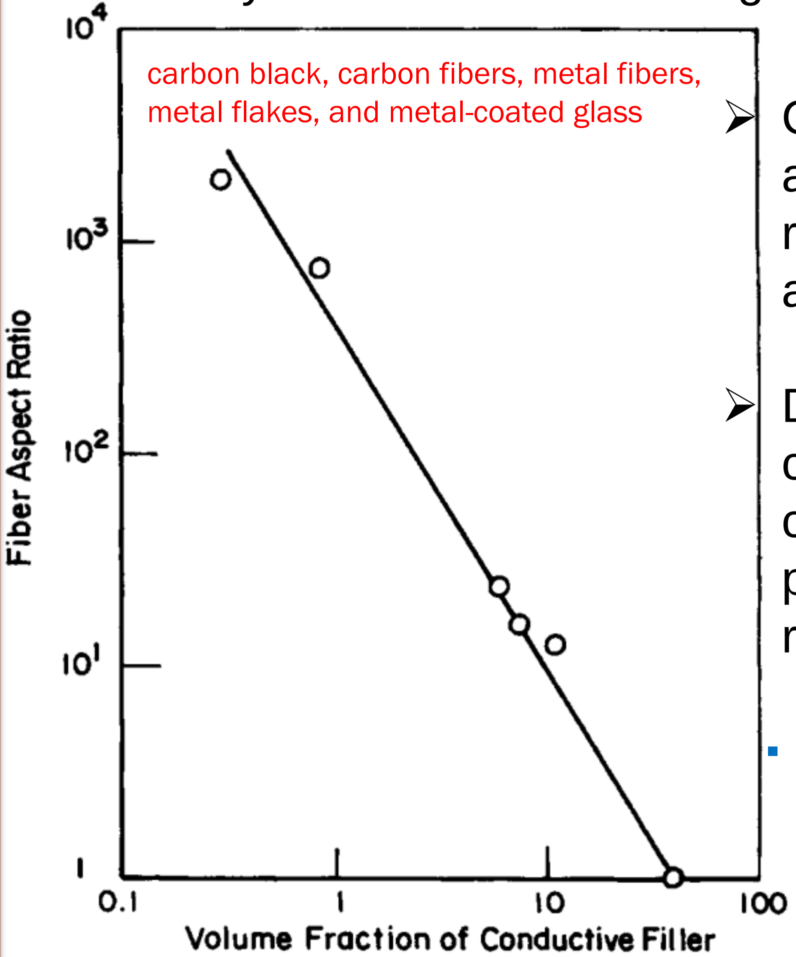
$$SE_A = 1.7t(\frac{f^{0.5}}{\rho})$$

- The lower the resistivity, the higher the EMI shielding;



- Simon, R. M. EMI Shielding Through Conductive Plastics. *Polym. Plast. Technol. Eng.* **17**, 1–10 (1981).

- The resistivity of a composite depends on the filler loading, resistivity of the fillers and their geometry



- Composites with high aspect ratio fillers reach to required electrical resistivity at lower filler loadings.

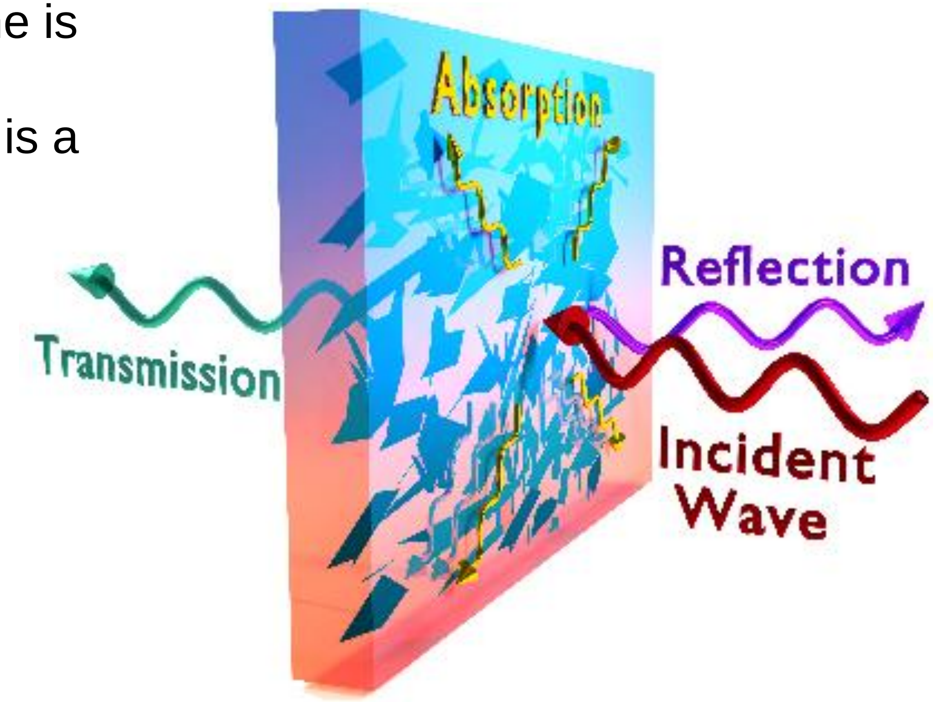
- Dependence of minimum conductive filler concentration required to produce a composite with a resistivity below 100 Ω-cm.

- Bigg, D. M. & Stutz, D. E. Plastic composites for electromagnetic interference shielding applications. *Polym. Compos.* **4**, 40–46 (1983).

Can we envision use of quasi-1D materials for the next generation of EMI shielding composites?

Crucial Parameters in EMI Shielding Performance

- In every material system, part of the incident EM wave is reflected, some is absorbed, and the rest is transmitted: $T + R + A = 1$
- **The electromagnetic interference shielding effectiveness** (EMI SE) is a measure of material's ability to **block** electromagnetic waves.



$$SE_{tot} = 10\log\left(\frac{P_i}{P_t}\right) = SE_R + SE_A, \qquad (dB)$$

$$SE_R = 10\,log\left(\frac{P_i}{P_{i-P_r}}\right) = -10\log(1-R), (dB)$$

$$SE_A = 10\,log[(P_i - P_r)/(P_i - P_r - P_a)] = -10\,log(1 - A_{eff}), (\mathrm{dB})$$

$$A_{eff} = 1 - R - T/1 - R$$

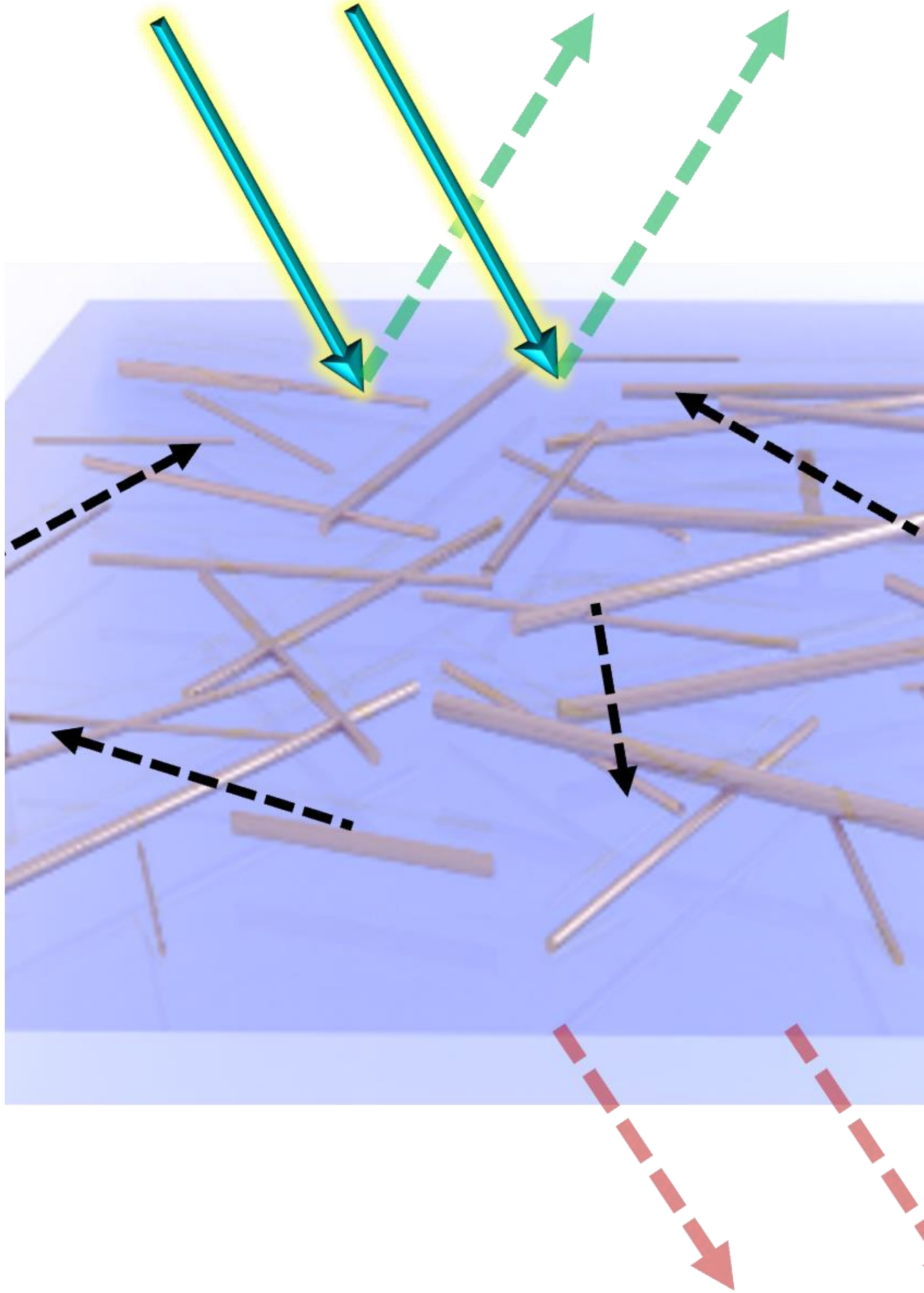
A_{eff}: effective absorption, a true measure for the capability of material to absorb the EM wave after reducing the reflection part.

$P_i, P_r, P_a, and\ P_t$: $incoming, reflected, absorbed, and\ transmitted\ power$

SE_R, SE_A are shielding by reflection and absorption

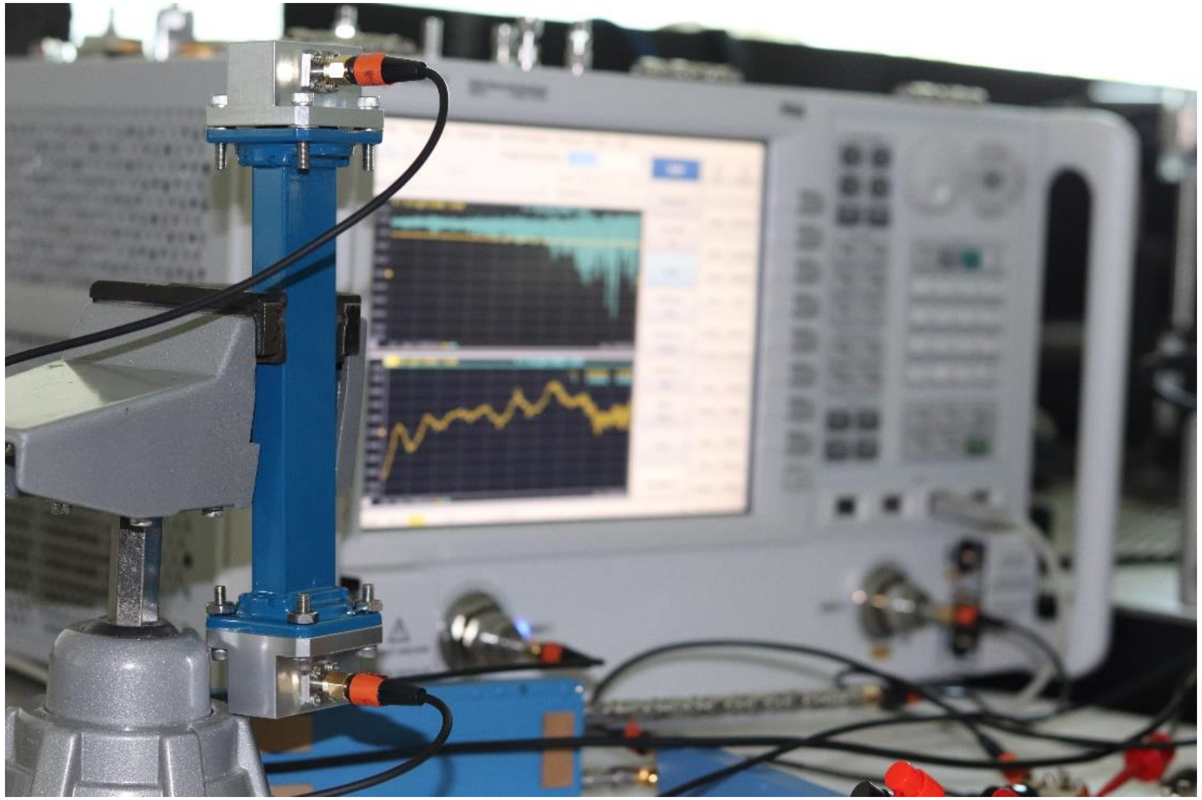
- We need to measure R, T, and A and A_{eff} to calculate the shielding effectiveness parameters;
- The higher the SE, the better the material can shield EM waves.

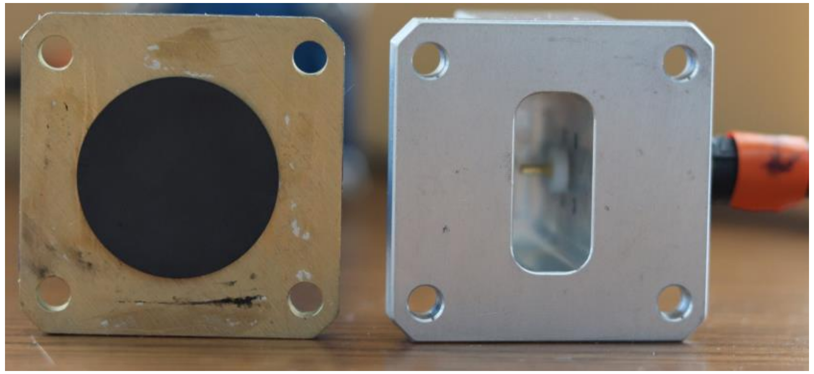
Barani, Z. *et al.* Multifunctional Graphene Composites for Electromagnetic Shielding and Thermal Management at Elevated Temperatures. *Adv. Electron. Mater.* **6**, 2000520 (2020).



EMI Shielding Effectiveness of Composites With Quasi-1D $TaSe_3$ Fillers

Measurement of EMI Shielding





- The reflection (R) and transmission (T) coefficients were obtained from the network analyzer in form of scattering parameters S_{mn}

"m": network analyzer port receiving the EMI radiation

"n" : the port that is transmitting the incident energy

- Vector network analyzer directly gives the output in form of four scattering parameters: S_{11}, S_{12}, S_{21}, and S_{22}

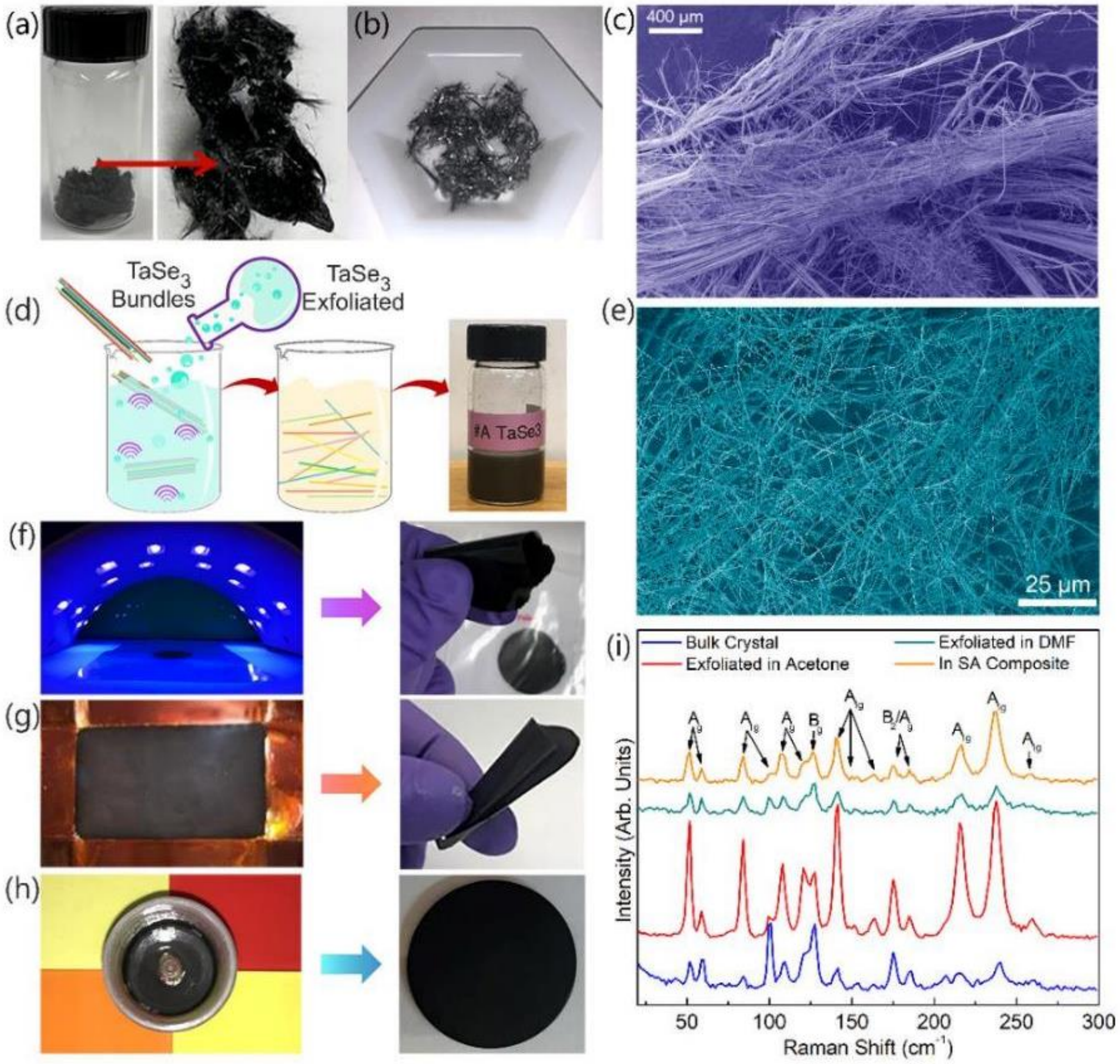
S_{11}: Port 1 sends the EM and measures after reflection from the material ($S_{22} = S_{11}$)

S_{12}: Port 2 sends the EM and port 1 measures the transmitted EM (Transmission coefficient) ($S_{12} = S_{21}$)

- Photo of the actual PNA instrument;

❖ Professor Alexander Khitun kindly made the instrument accessible for all our measurements.

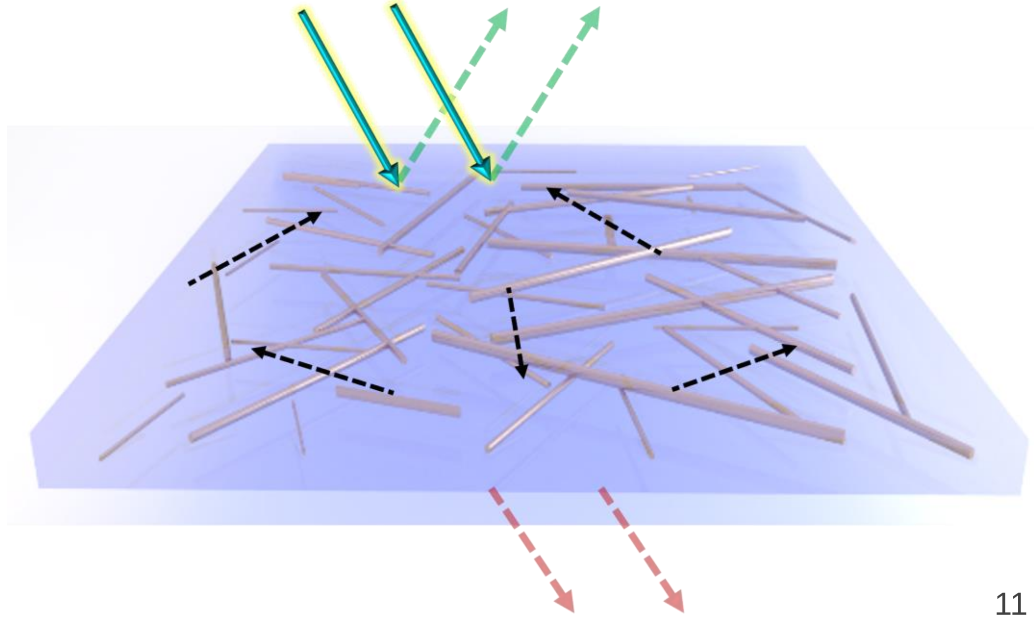
Sample Preparation of Quasi-1D-Based Composites



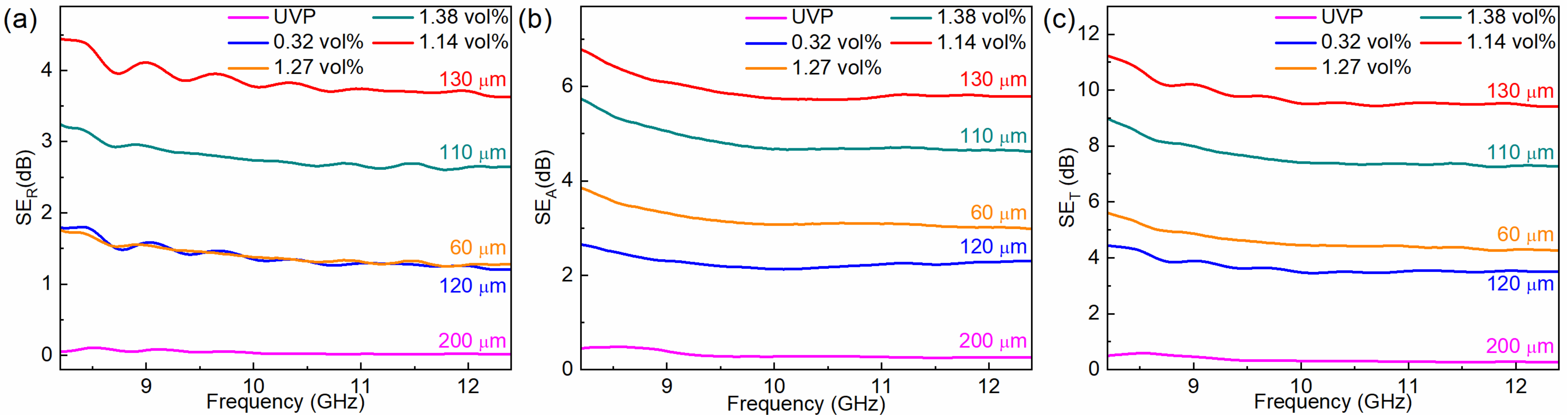
LPE and Compatibility of the filler with the host polymer

- Preparation and characterization of the samples.
- Three different polymers were used.
- Fillers were randomly dispersed into polymers.

Z. Barani, et al. Electrically Insulating Flexible Films with Quasi-1D van der Waals Fillers as Efficient Electromagnetic Shields in the GHz and Sub-THz Frequency Bands, Advanced Materials. 33 (2021) 2007286.



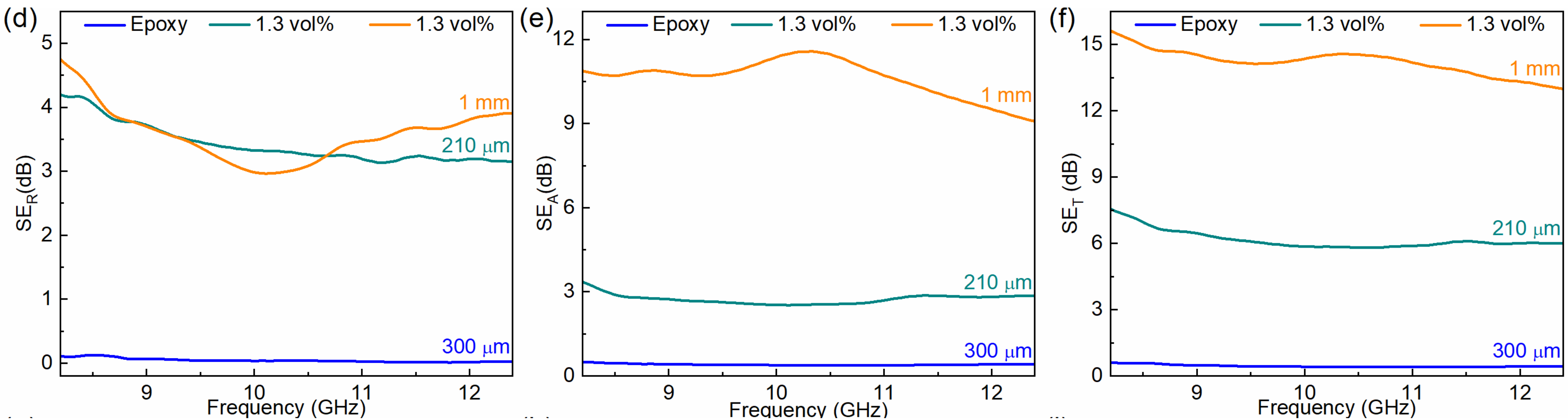
EMI Shielding Effectiveness of UV-Cured Composites



- UVP is a polymer that cures in 2 minutes under UV irradiation. The process prevents agglomeration of the fillers.
- Electromagnetic characteristics of films with low concentration of quasi-1D $TaSe_3$ fillers in X-band frequency range.
- ~11 dB EM shielding with thickness of only 130 µm (1.14 vol%). Samples were Electrically insulator.
- ~65% of the incident wave is reflected at the interface.

Z. Barani, et al. Electrically Insulating Flexible Films with Quasi-1D van der Waals Fillers as Efficient Electromagnetic Shields in the GHz and Sub-THz Frequency Bands, Advanced Materials. 33 (2021) 2007286.

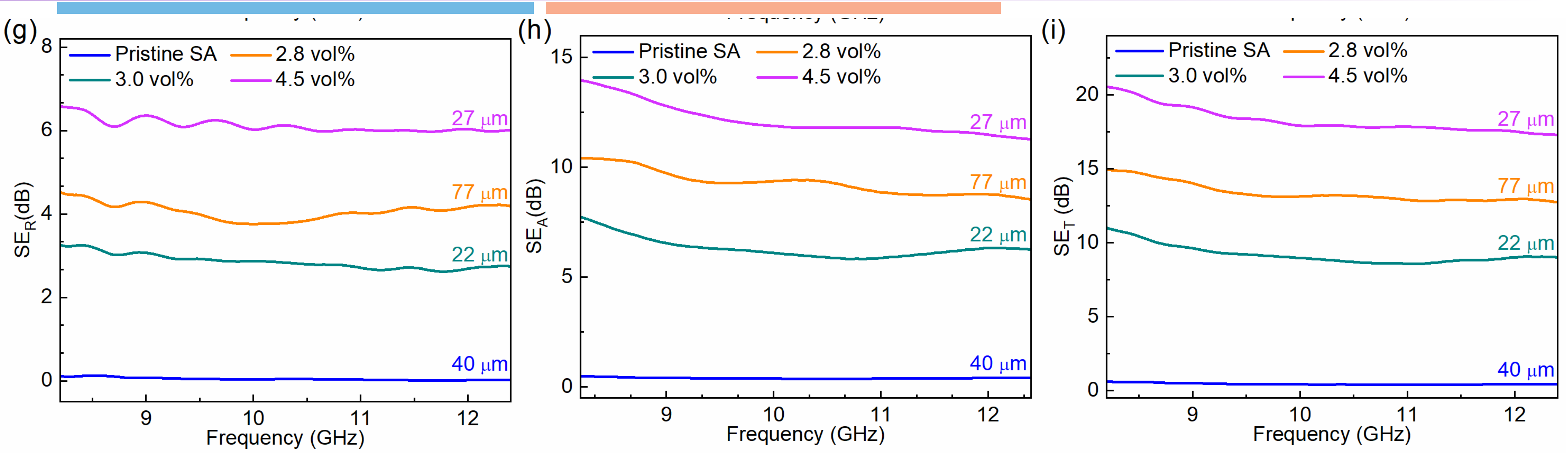
EMI Shielding Effectiveness of Epoxy-Based Composites



- Total shielding of 15 dB at 1.3 vol% of filler is achieved.
- Most of the EM waves are being absorbed.
- Samples were **Electrically insulator** comparing to CNTs with same loading Fraction.

Z. Barani, et al. Electrically Insulating Flexible Films with Quasi-1D van der Waals Fillers as Efficient Electromagnetic Shields in the GHz and Sub-THz Frequency Bands, Advanced Materials. 33 (2021) 2007286.

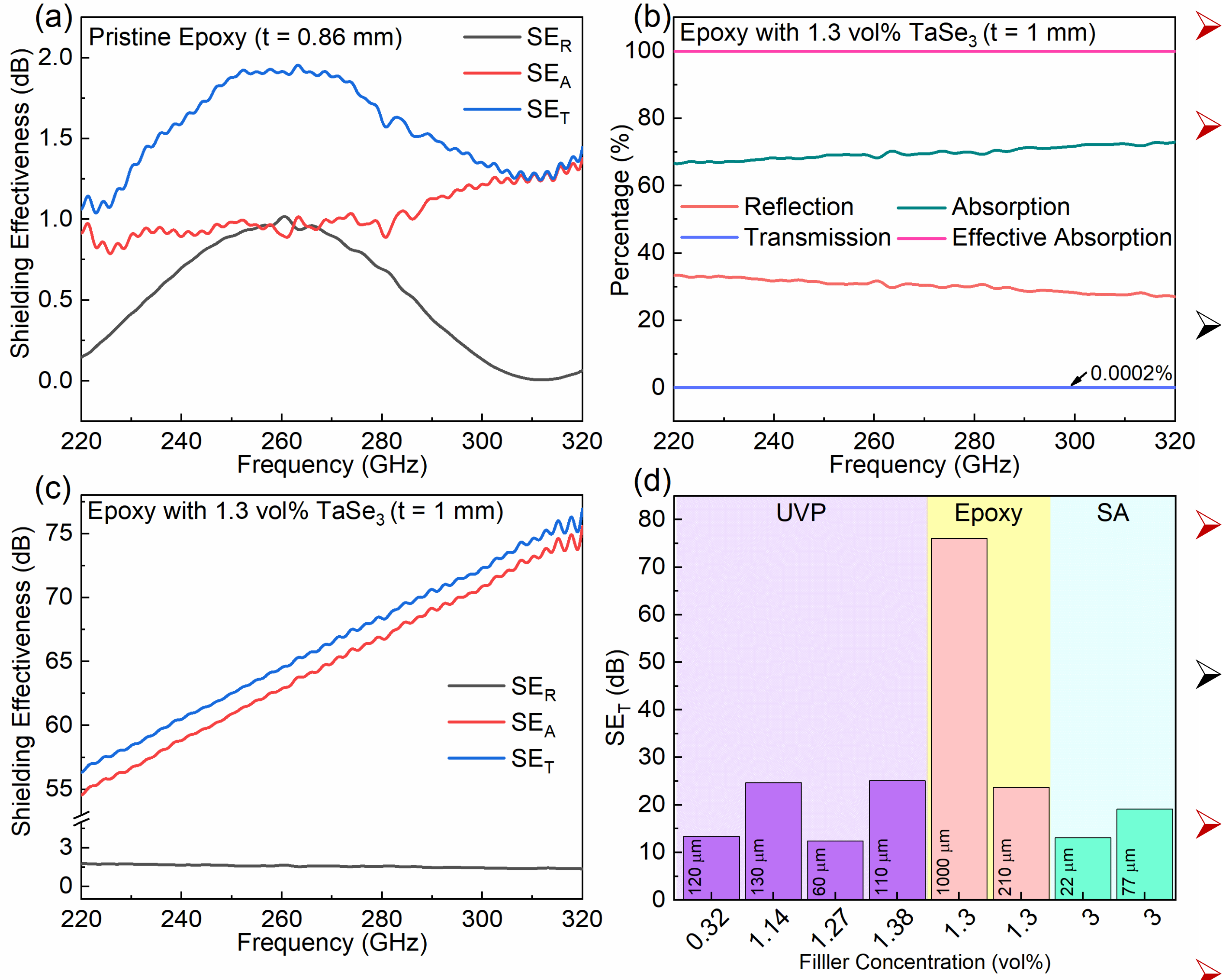
EMI Shielding Effectiveness of SA-Based Composites



- SA-based composites show exceptional EMI shielding properties;
- ~ 20 dB total shielding for samples with thickness of 27 μm and filler loading of 4.5 vol%. (30 dB shielding is sufficient for more than 50% of industrial applications)
- The samples are electrically insulator up to 3 vol% of filler loading.

Z. Barani, et al. Electrically Insulating Flexible Films with Quasi-1D van der Waals Fillers as Efficient Electromagnetic Shields in the GHz and Sub-THz Frequency Bands, Advanced Materials. 33 (2021) 2007286.

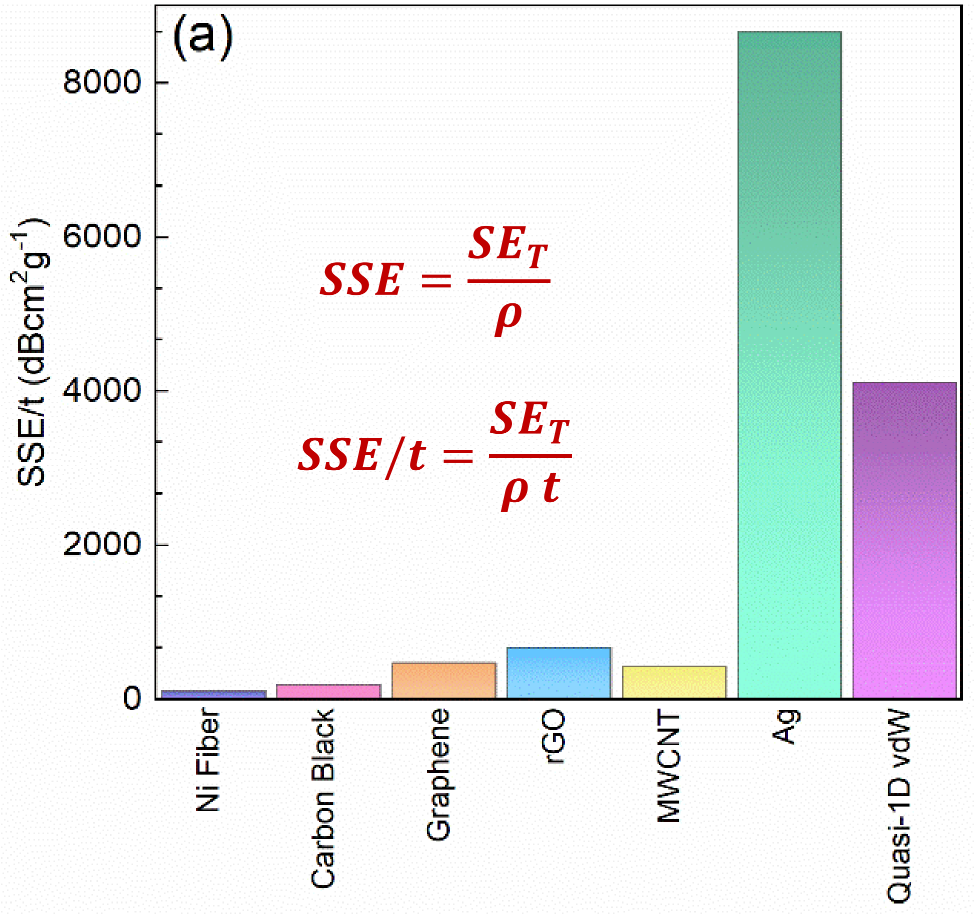
Shielding Performance in EHF Frequency Region

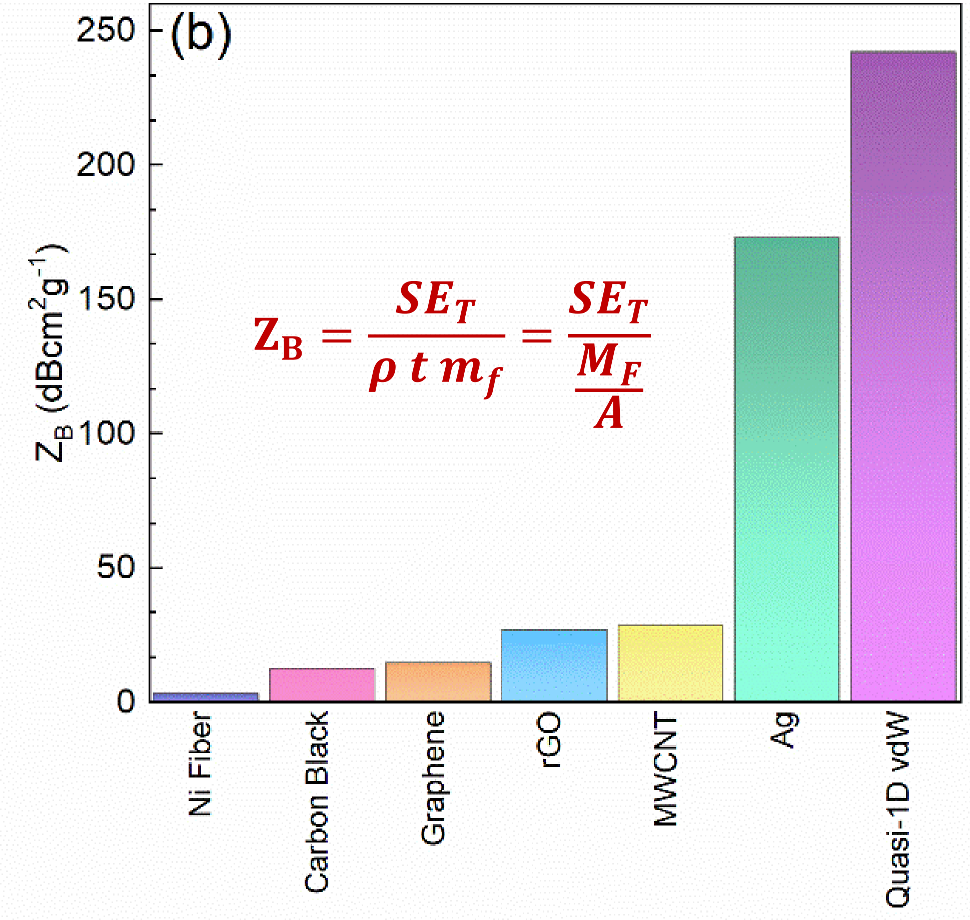


- **(a)** Shielding effectiveness of pristine epoxy;
- **(b)** Reflection, absorption, effective absorption, and transmission **coefficients** of epoxy with only 1.3 vol% loading of the quasi-1D $TaSe_3$ fillers.
- Note that in the EHF range, almost all the incident EM wave energy is blocked and only 0.0002% is transmitted.
- **(c)** Reflection, absorption, and total shielding effectiveness of the same composite.
- Absorption is the dominant mechanism in blocking the EM waves in EHF band.
- **(d)** Total shielding effectiveness of all samples tested at 320 GHz.
- **~75 dB** total shielding at 320 GHz;

Z. Barani, et al. Electrically Insulating Flexible Films with Quasi-1D van der Waals Fillers as Efficient Electromagnetic Shields in the GHz and Sub-THz Frequency Bands, Advanced Materials. 33 (2021) 2007286.

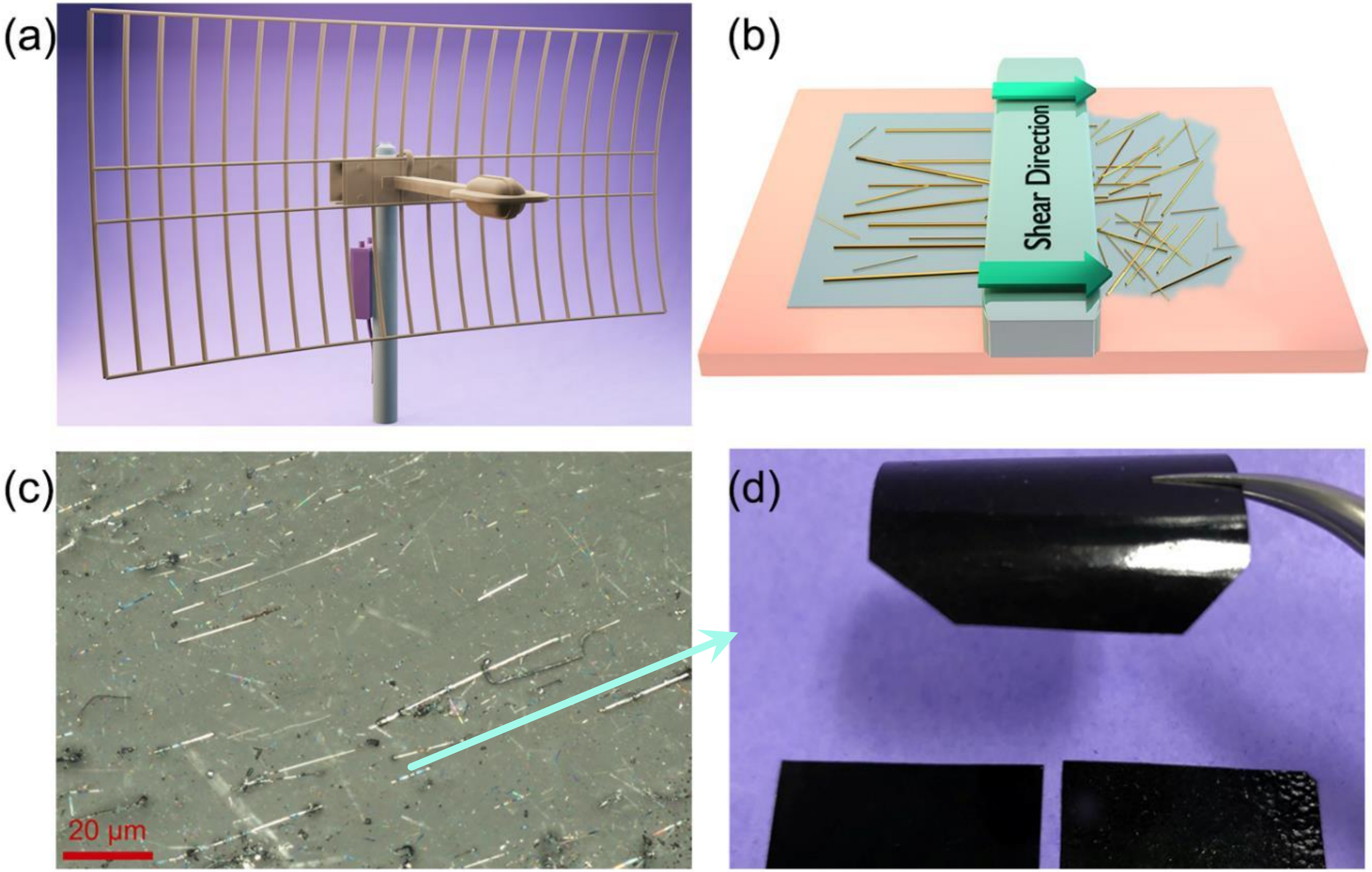
How Does It Compare with Other Material Systems?





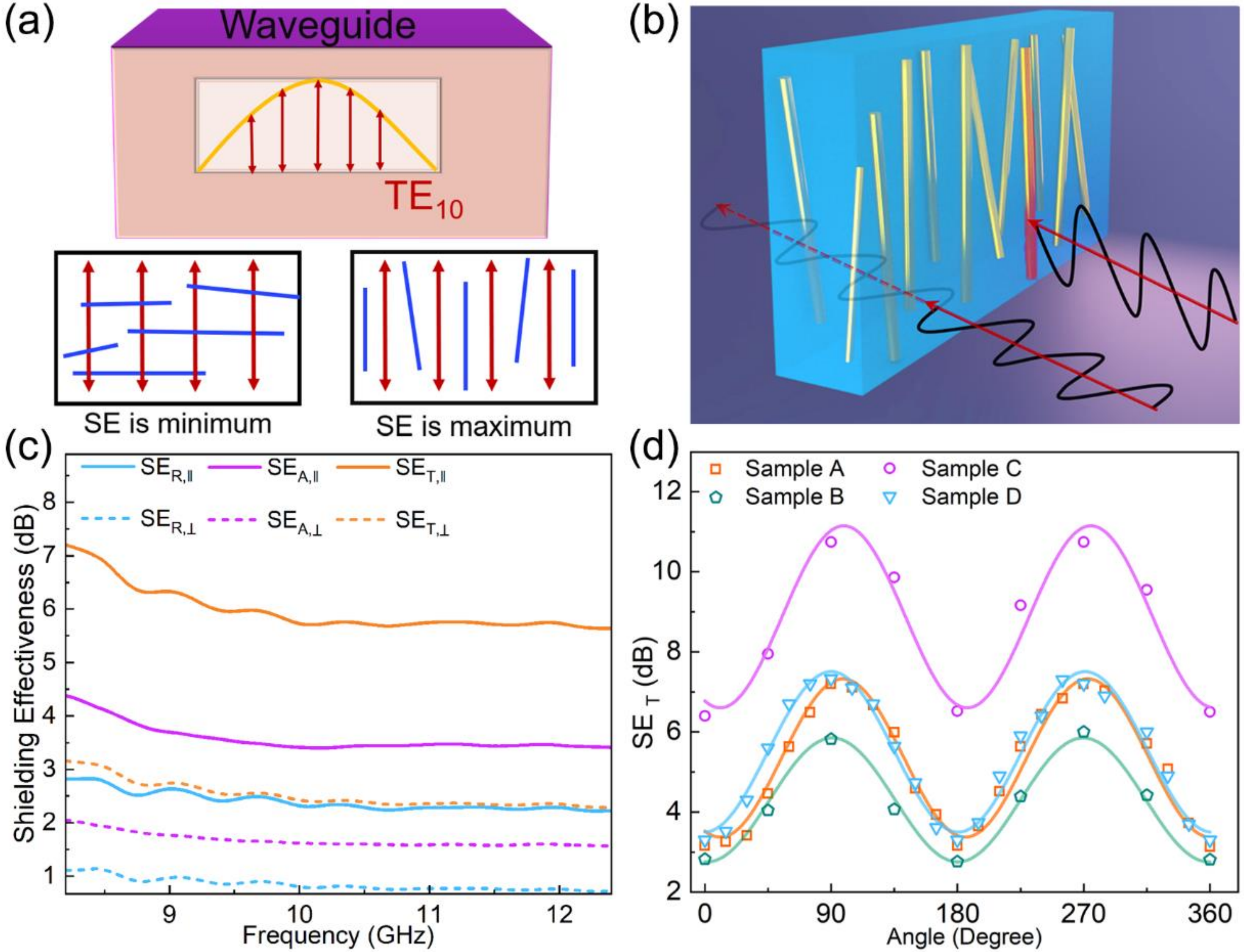
- We introduce a new parameter, Z_B figure-of-merit as follow: $\mathbf{Z_B} = \frac{SE_T}{\rho\, t\, m_f} = \frac{SE_T}{\frac{M_F}{A}}$
- M_F: total weight of filler; m_f: filler mass fraction
- The parameter means the total shielding effectiveness of the films per the areal density of the fillers;

Mechanical Alignment



Z. Barani, et al. Electromagnetic-Polarization-Selective Composites with Quasi-1D Van der Waals Fillers: Nanoscale Material Functionality That Mimics Macroscopic Systems, ACS Appl. Mater. Interfaces. 13 (2021) 21527–21533.

Mechanical Alignment



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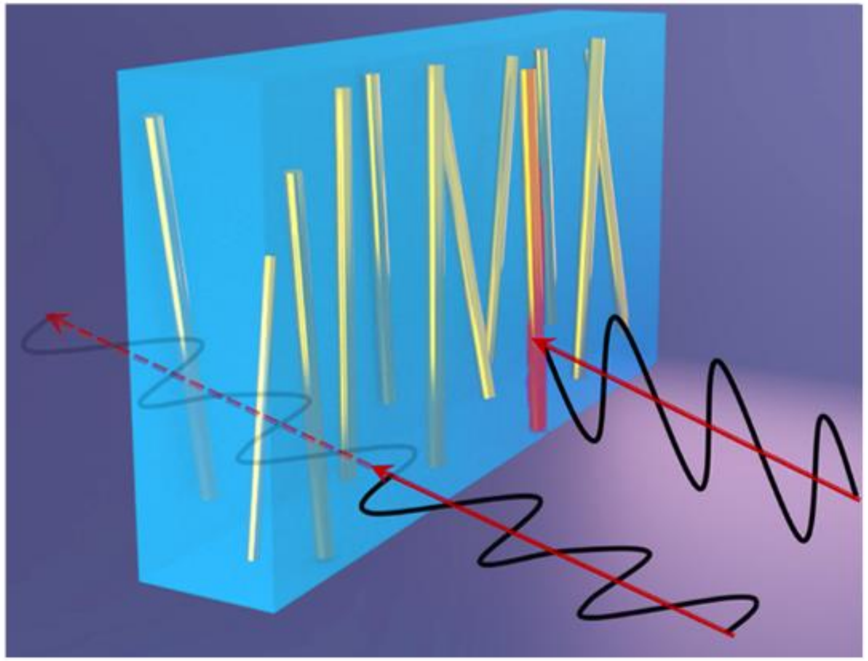
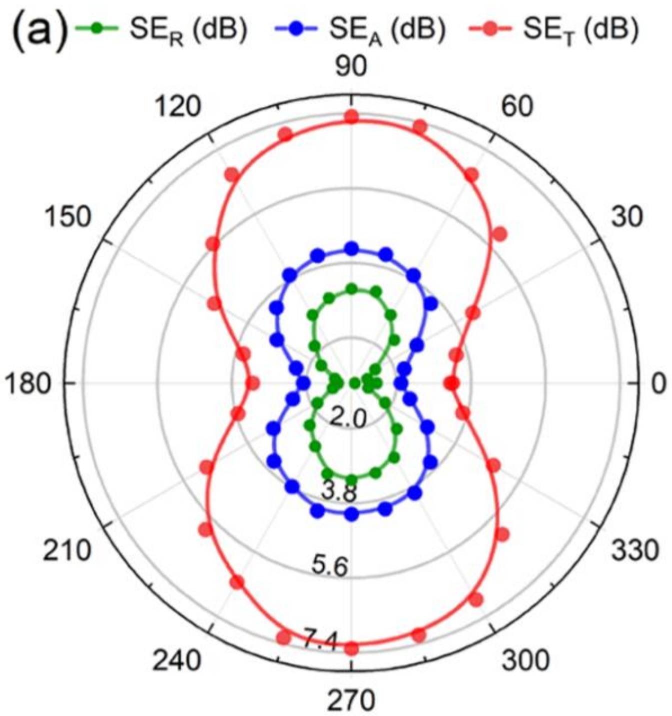
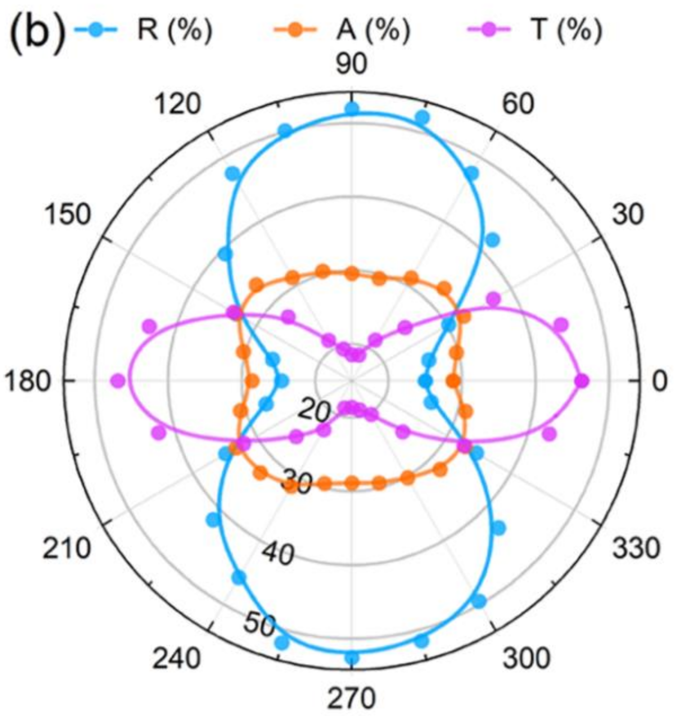
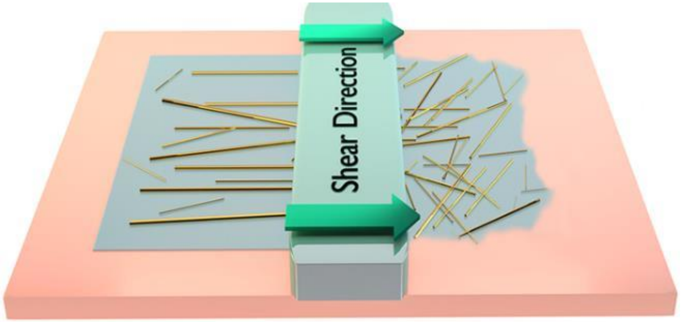
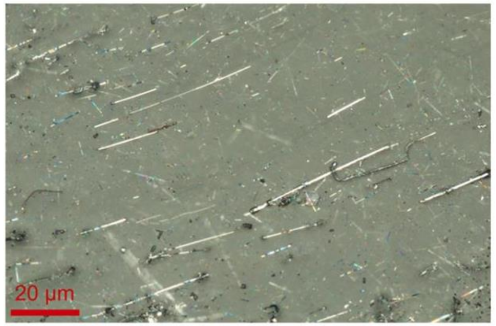
Polarization-Selective Quasi-1D-Based Composites











- Quasi-1D fillers were aligned by mechanical Dr. blade method;
- Composites show anisotropic shielding effectiveness with respect to the polarization of the incident EM wave;

Z. Barani, F. Kargar, Y. Ghafouri, S. Baraghani, S. Sudhindra, A. Mohammadzadeh, T.T. Salguero, and A.A. Balandin, ACS Appl. Mater. Interfaces 13, 21527 (2021).

Summary and Conclusions

- We demonstrated that quasi-1D van der Waals materials can be used as fillers in flexible polymer films providing excellent EMI shielding capability in the X-band and EHF-band.
- Polymer composites films (27 μm thickness) with only 4.5 vol% of quasi-1D $TaSe_3$ fillers delivered **≈ 20 dB** of total EMI shielding in the practically important X-band GHz frequency range.
- The EMI shielding performance of the films with the quasi-1D fillers in the EHF band of sub-THz frequencies was particularly impressive.
- Total shielding effectiveness ~**70 dB** at 320 GHz was achieved with only **1.3 vol%** of filler loading.
- The efficient EMI shielding was achieved with retaining their DC electrically insulating properties at loading less than 3 vol%.

Acknowledgment

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Professor Alexander Balandin, Professor Fariborz Kargar, and Zahra Barani
Department of Electrical and Computer Engineering, University of California, Riverside, California 92521 USA
E-mail: balandin@ece.ucr.edu https://balandingroup.ucr.edu

Professor Tina Salguero and Yasmin Ghafouri
Department of Chemistry, University of Georgia, Athens, Georgia 30602 USA

Dr. Sergey Rumyantsev, K. Godziszewski, G. Cywiński, and Dr. Y. Yashchyshyn
CENTERA Laboratories, Institute of High-Pressure Physics, Polish Academy of Sciences, Warsaw 01-142 Poland
Institute of Radioelectronics and Multimedia Technology, Warsaw University of Technology, Warsaw 00-665 Poland