

Dual synergistic effect of a carbon/metal hybrid network on mechanical and electromagnetic interference shielding performance in self-assembly enhanced epoxy curing network

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1. Electromagnetic Interference (EMI) Shielding Measurements

The physical parameters for evaluating the EMI performance can be calculated based on the scattering parameters (S_{11} and S_{21}). The relevant formulas are shown as follows:

$$R = |S_{11}|^2$$

$$T = |S_{21}|^2$$

$$A + R + T = 1$$

$$SE_{\text{Total}} = -10 \log T$$

$$SER = -10 \log (1 - R)$$

$$SEA = SE_{\text{Total}} - SER$$

where A , R and T are the absorption, reflection and transmission coefficients, respectively. SE_{Total} , SE_{R} , and SE_{A} are the total, reflective, and absorptive EMI shielding effectiveness, respectively.

2. Figures and Tables

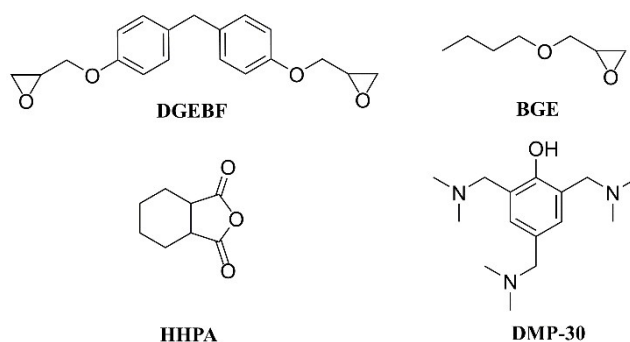


Figure S1. Chemical structures of the epoxy curing system used in this study.

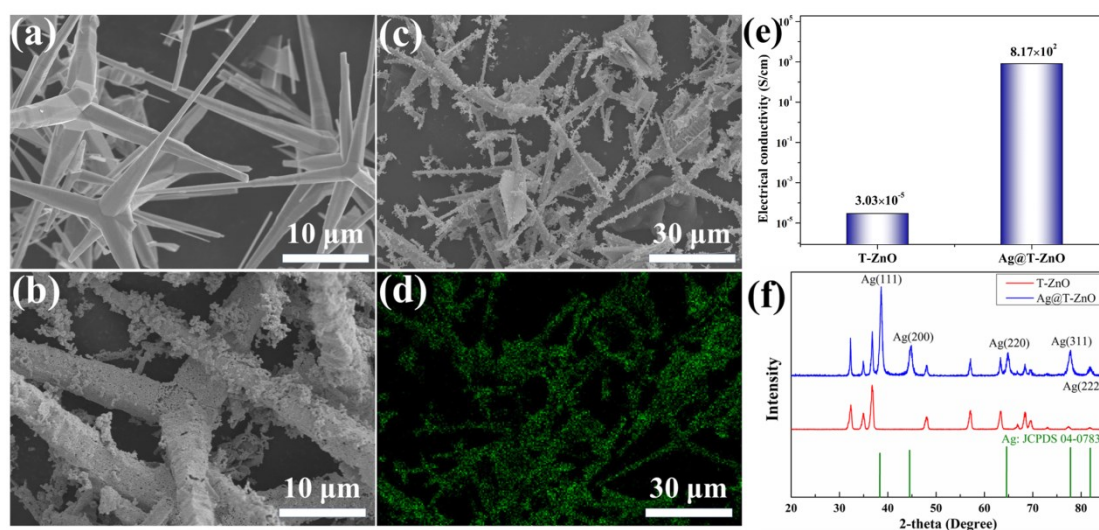


Figure S2. Characterization of Ag@T-ZnO conductive fillers: SEM morphology of (a) T-ZnO whiskers; (b-c) Ag@T-ZnO fillers; (d) SEM elemental mapping of the Ag@T-ZnO fillers shown in (c); (e) electrical conductivity of T-ZnO whiskers and Ag@T-ZnO fillers; (f) XRD patterns of T-ZnO whiskers and Ag@T-ZnO fillers.

In **Figure S2**, Ag@T-ZnO fillers can be observed a compact Ag layer on the surface of T-ZnO whiskers (**Figure S2(b)** and **(c)**) compared with pristine T-ZnO whiskers shown in **Figure S2(a)**. Besides, in **Figure S2(d)**, the elemental mapping result of Ag@T-ZnO fillers corresponding to **Figure S2(c)** can further prove the existence of the Ag layer on the T-ZnO whiskers. The above result is consistent with the ultrahigh electrical conductivity of Ag@T-ZnO fillers (81700 S/m) shown in **Figure S2(e)**. Moreover, the diffraction peaks at 38° , 44° , 64° , and 77° in the XRD patterns of the Ag@T-ZnO fillers are attributed to the (111), (200), (220), and (311) faces of the face-centered cubic structure of Ag.^{1, 2} In conclusion, all the result of SEM morphology, electrical conductivity, and XRD patterns can prove that Ag has successfully deposited on the surface of T-ZnO whiskers. Besides, it is expected that conductive network structure can be easily formed due to the unique 3D four-needed structure of Ag@T-ZnO fillers.

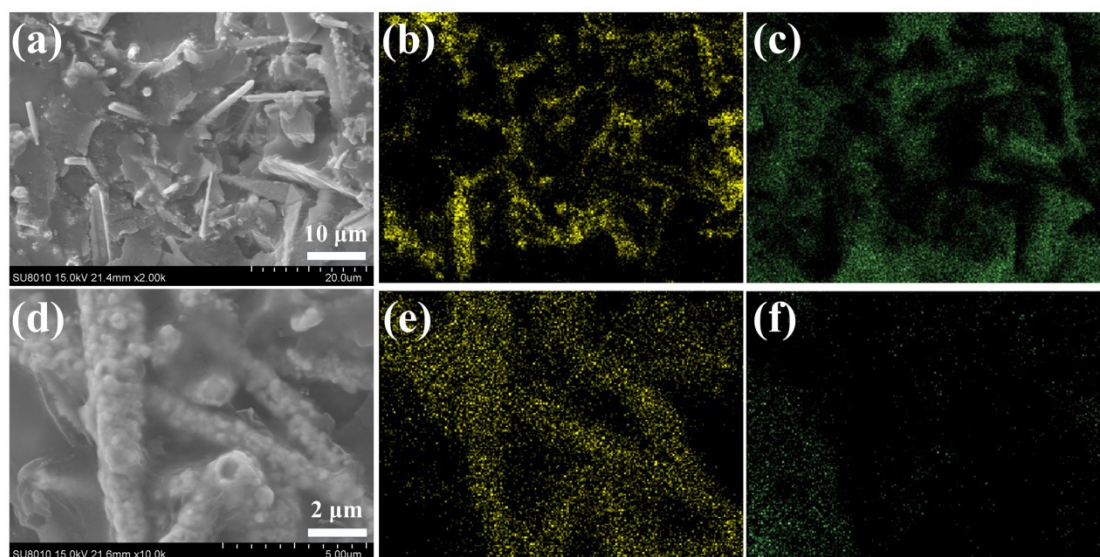


Figure S3. SEM images of (a)(d) T:M=9:1 system; (b) Ag EDS of (a); (c) C EDS of (a); (e) Ag EDS of (d); (f) C EDS of (d)

As shown in **Figure S3**, it can be observed that the electrical conductive network of the hybrid fillers in the T:M=9:1 system is mainly formed by the Ag@T-ZnO

fillers. However, MWCNTs is hard to be recognized because of two reasons. On the one hand, both the EP matrix and MWCNTs contain C element. On the other hand, the content of MWCNTs (2 wt%) is much lower than that of EP in the composites. Therefore, the above two facts are the reasons that we further carried out the SEM analysis of the preformed deposited conductive network structure (without EP matrix) formed by hybrid MWCNTs and Ag@T-ZnO particles (mass ratio of Ag@T-ZnO and MWCNTs is 9:1) shown in **Figure 3** of the manuscript and **Figure S4**, so that the influence of EP matrix on observing the morphologies of MWCNTs can be eliminated and the interfacial interfaces of Ag@T-ZnO and MWCNTs can be further clarified.

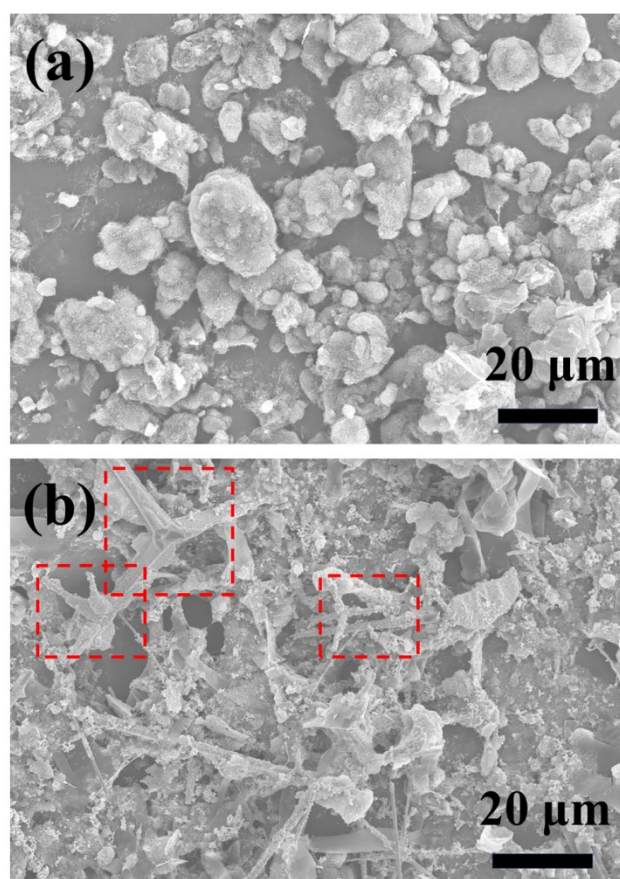


Figure S4. SEM morphologies of (a) neat MWCNTs particles and (b) preformed deposited conductive network structure of Ag@T-ZnO and MWCNTs hybrid fillers (mass ratio of Ag@T-ZnO and MWCNTs is 9:1)

Table S1 The electrical conductivity of the T:M=m:n system tested from different surfaces of the sample

System	T:M=0:1	T:M=7:3	T:M=8:2	T:M=9:1	T:M=12:	T:M=10:
	0				1	0
Top surface (S/cm)	0.35×10^{-5}	0.88×10^{-6}	0.63×10^{-6}	0.32×10^{-6}	0.24×10^{-6}	0.19×10^{-6}
Bottom surface (S/cm)	0.31	12.50	46.25	354.80	365.75	287.46

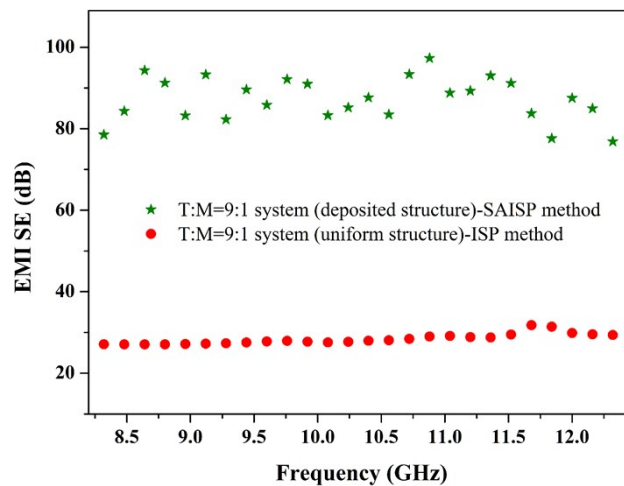


Figure S5 Comparison of the EMI SE curves of the T:M=9:1 systems prepared by SAISP method (deposited structure) and ISP method (uniform structure) in X band.

The EMI shielding performance of the Ag@T-ZnO/MWCNTs/EP sample prepared by SAISP method (deposited structure, T:M=9:1 system in the manuscript) and traditional in-situ polymerization (ISP) method (uniform structure) was compared. In **Figure S5**, it can be observed that the average EMI SE value of the T:M=9:1 system with uniform structure (prepared by ISP method) is only 28.2 dB, which is much lower than that of the T:M=9:1 system with deposited structure (prepared by SAISP method). The above data can not only prove that the EMI shielding performance of the composites with deposited conductive network is higher than that with uniform conductive network structure, but also further prove that the dense

deposited conductive network structure formed by the SAISP method is one of the reason that the ternary Ag@T-ZnO/MWCNTs/EP composites can possess ultrahigh EMI shielding performance.

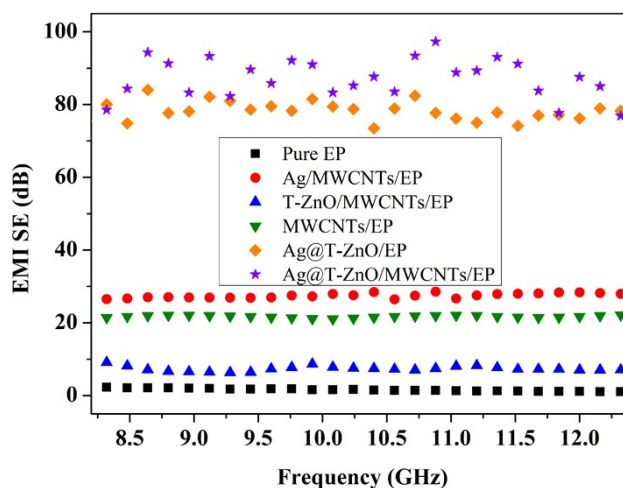


Figure S6 EMI SE curves of different epoxy composites with 20 wt% filler content (all the mass ratio of Ag:MWCNTs, T-ZnO:MWCNTs, and Ag@T-ZnO:MWCNTs in the ternary composites is 9:1)

In order to further clarify the contribution of each ingredient for the EMI shielding performance of the ternary Ag@T-ZnO/MWCNTs/EP composites. The EMI SE value of pure EP, Ag/MWCNTs/EP, T-ZnO/MWCNTs/EP, MWCNTs/EP, Ag@T-ZnO/EP, and Ag@T-ZnO/MWCNTs/EP systems were compared. Due to the fact that T:M=9:1 system possesses the highest EMI SE in all the T:M=m:n systems (total filler loading is 20 wt%) and T:M=10:0 as well as T:M=0:10 system is actually pure Ag@T-ZnO and pure MWCNTs systems, we prepared ternary Ag/MWCNTs/EP and T-ZnO/MWCNTs/EP composites in which the total filler loading is 20 wt% and the mass ratio of Ag:MWCNTs as well as T-ZnO:MWCNTs is 9:1 by SAISP method. Besides, pure EP system was also prepared. The EMI SE curves of pure EP, Ag/MWCNTs/EP, T-ZnO/MWCNTs/EP, MWCNTs/EP, Ag@T-ZnO/EP, and

Ag@T-ZnO/MWCNTs/EP systems were shown in **Figure S6**, respectively. It should be noted that the MWCNTs/EP, Ag@T-ZnO/EP, and Ag@T-ZnO/MWCNTs/EP system is actually T:M=0:10, T:M=10:0, and T:M=9:1 system in the main manuscript, respectively. Pure EP system can only exhibit an average EMI SE value of 2 dB due to the insulating epoxy curing network. Besides, the average EMI SE value of the T-ZnO/MWCNTs/EP system is still lower than 10 dB due to the high loading of T-ZnO, which is a type of low dielectric materials. To our surprise, the average EMI SE value of the Ag/MWCNTs/EP system can only reach 27.4 dB, which is only slightly higher than that of the MWCNTs/EP system (21.6 dB) but far lower than that of Ag@T-ZnO/EP system (78.2 dB) and Ag@T-ZnO/MWCNTs/EP system (88.1 dB) considering the fact that the electrical conductivity of Ag (1174 S/cm) is higher than that of Ag@T-ZnO (817 S/cm) and MWCNTs (0.68 S/cm) used in this study.

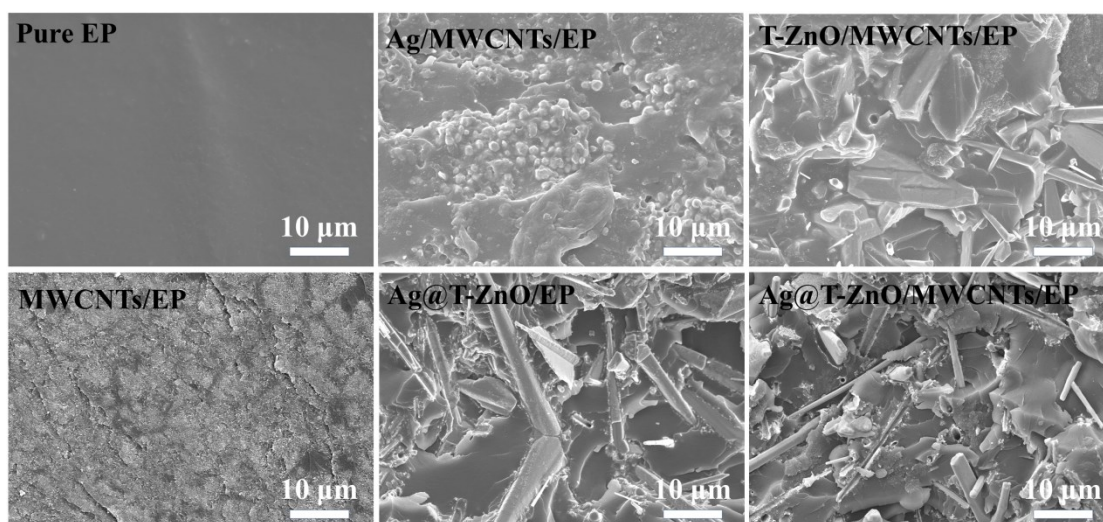


Figure S7 SEM morphologies of different epoxy composites with 20 wt% filler content (all the mass ratio of Ag:MWCNTs, T-ZnO:MWCNTs, and Ag@T-ZnO:MWCNTs in the ternary composites is 9:1)

In order to clarify the above facts determined by **Figure S6**, SEM morphologies of the above 6 systems were shown in **Figure S7**. It can be observed dense conductive

pathways in the MWCNTs/EP system. On the contrary, though the electrical conductivity of Ag is much higher than that of MWCNTs, the spherical Ag particles (with an average diameter of 1.5 μm) are hard to form dense electrical conductive network even the filler loading of Ag is 18 wt% (the other 2 wt% is MWCNTs), which may be the reason that the EMI SE of the Ag/MWCNTs/EP system is only slightly higher than that of the MWCNTs/EP system. Besides, due to the superior tetrapod spatial structures of T-ZnO, either the T-ZnO or Ag@T-ZnO fillers are easier to connect with each in the final composites, demonstrating dense conductive network structure and excellent EMI SE in the Ag@T-ZnO/EP and Ag@T-ZnO/MWCNTs/EP systems.

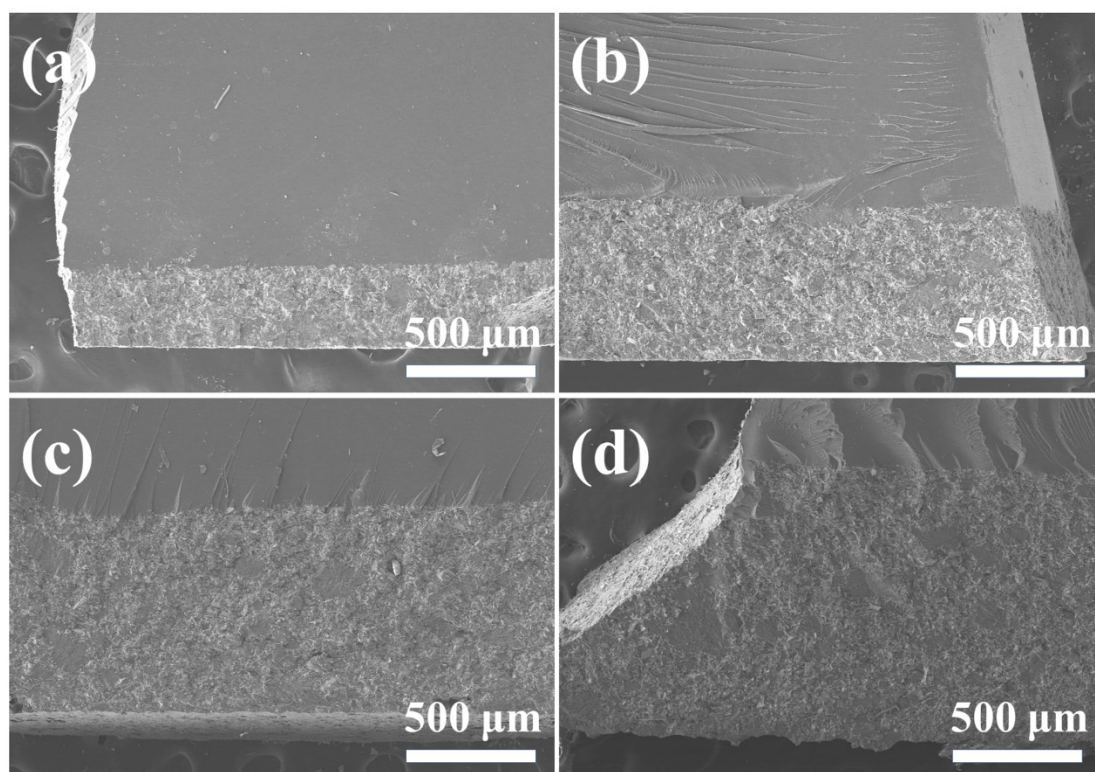


Figure S8. SEM images of the EP_{BD-X} systems: (a) EP_{BD-5} sample; (b) EP_{BD-10} sample; (c) EP_{BD-15} sample; (d) EP_{BD-20} sample.

In **Figure S8**, it is obvious that the thickness of the conductive layer (formed by

the Ag@T-ZnO and MWCNTs hybrid fillers) can be increased with the increasing content of the hybrid fillers. The thickness of the EP_{BD-5}, EP_{BD-10}, EP_{BD-15}, and EP_{BD-20} systems is 0.35, 0.63, 0.80, and 1.06 mm, respectively.

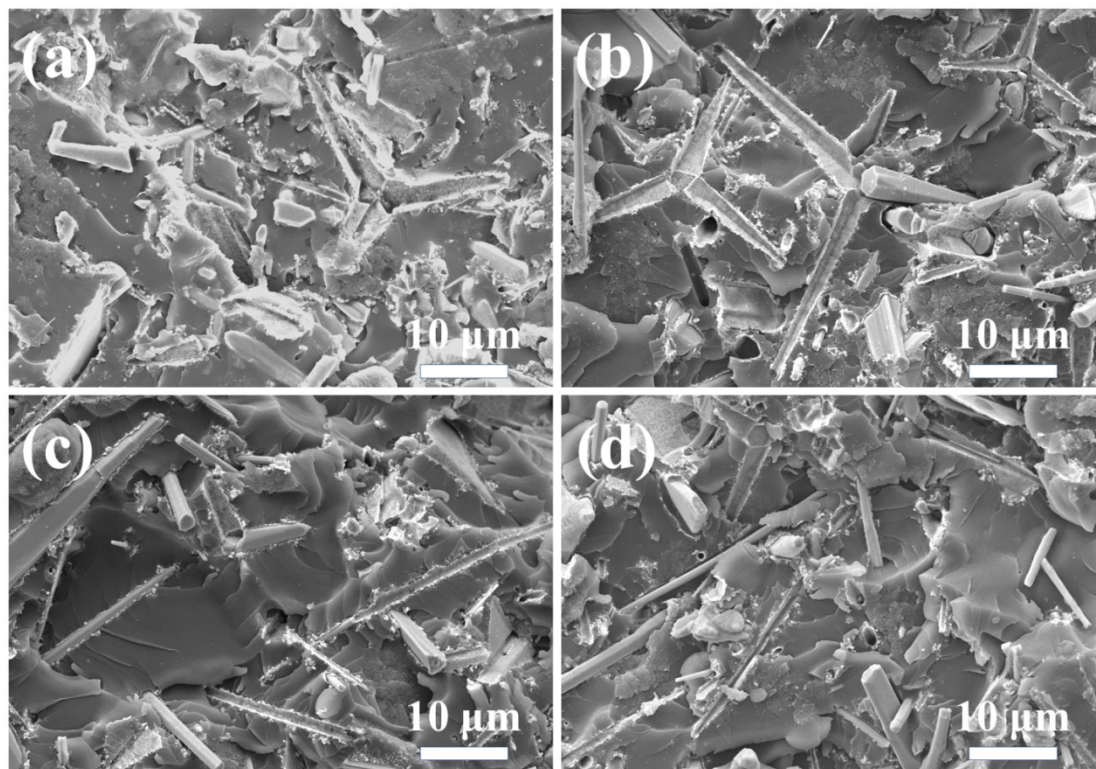


Figure S9. SEM morphologies on the bottom layer of the fractured interface (broken in liquid nitrogen) of the EP_{BD-X} systems: (a) EP_{BD-5} sample; (b) EP_{BD-10} sample; (c) EP_{BD-15} sample; (d) EP_{BD-20} sample.

References

1. T. Lee, S. Lee and Y. G. Jeong, *ACS Appl. Mater. Interfaces*, 2016, **8**, 13123-13132.
2. S. Lin, C. M. Ma, S. Hsiao, Y. Wang, C. Yang, W. Liao, S. Li, J. Wang, T. Cheng and C. Lin, *Appl. Surf. Sci.*, 2016, **385**, 436-444.

