

Electronic Supplementary Information

ZnO Nanowire Interfaces for High Strength Multifunctional Composites with Embedded Energy Harvesting

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Characterization Methods of ZnO Nanowires

Scanning electron micrographs of the ZnO nanowire arrays grown on the aramid fibers, the composite cross section, and the fractured surface of the carbon fiber lamina were obtained by a scanning electron microscope (TESCAN VEGA3 LM) at an acceleration voltage of 10 kV. The consistent morphology of silver doped ZnO nanowires (Fig. S1a) and un-doped ZnO nanowires (Fig. S1b) implies that the doping of nanowires does not influence the geometry of the nanowires. Fig. S1c shows a micrograph of surface modified aramid fabrics at low magnification which demonstrates the uniform coverage of the ZnO nanowires over a large area. Furthermore, the growth of the silver doped ZnO nanowires slightly changed the color of the Kevlar fabric. As depicted in Fig. S1d, the difference in color indicates the sections with and without nanowires. The bottom part (darker area) is the section ZnO nanowires coating since it was placed inside the growth solution. Whereas the bright yellow color section is the bare fiber because it was not in the growth solution during the reaction. This results exhibit the scalability of this fabric modification process.

X-ray diffraction (XRD) analysis of the synthesized ZnO nanowires was performed on a PANalytical X'Pert Powder system with a Cu K α irradiation source at a 2 θ range of 10-80°. To further characterize these nanowires, X-ray diffraction (XRD) was performed to examine the crystal structure and verify the existence of Ag ion dopants. The XRD pattern shows the characteristic peaks for hexagonal ZnO, according to JCPDS card no. 36-1451, and demonstrates a lattice spacing shift associated with Ag doping. As seen in Fig. 2c inset, the ZnO [002] peak shifts from a 2 θ of 34.49° to 34.58° when comparing un-doped ZnO to Ag-doped ZnO.¹⁻³ This shift corresponds to a change in lattice constant from 5.197 Å to 5.184 Å, which supports the doping of a smaller Ag ion into the ZnO lattice.¹ The energy-dispersive X-ray spectroscopy (EDS) spectrum of ZnO NWs on aramid fabrics with Ag peaks further supports the evidence of doping (Fig. S2).

XRD Table

	[100] - d(A)/2 θ		[002] - d(A)/2 θ		[101] - d(a)/2 θ	
ZnO	2.8116	31.801	2.5983	34.490	2.4720	36.312
ZnO + Ag	2.8030	31.901	2.5921	34.575	2.4675	36.380

ZnO Ag – d=2.3539, 2T=38.202, Ag Silver-3C

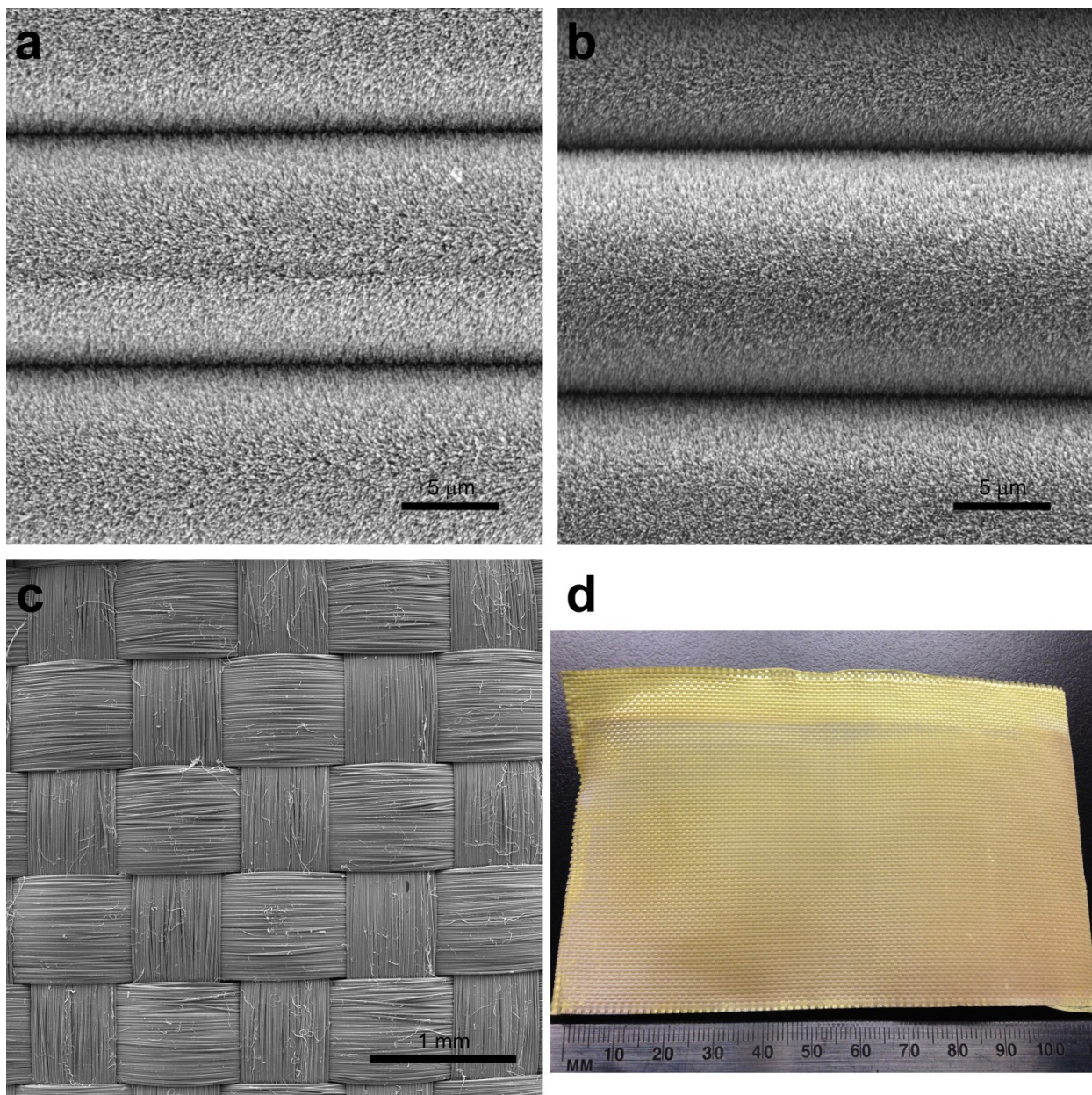


Fig. S1 Scalable synthesis of ZnO nanowire arrays on aramid fabrics. (a) SEM micrograph of Ag-doped ZnO NWs grown on aramid fabric, (b) SEM micrograph of un-doped ZnO NWs grown on aramid fabric showing a very similar morphology as Ag doped ZnO NWs, (c) a low magnified SEM image demonstrating the uniform growth of ZnO nanowires, (d) an optical image of the aramid fabric with Ag doped ZnO nanowires showing a uniform distribution of nanowires on a large area (the bright section does not contain any nanowires since it was kept outside of the solution).

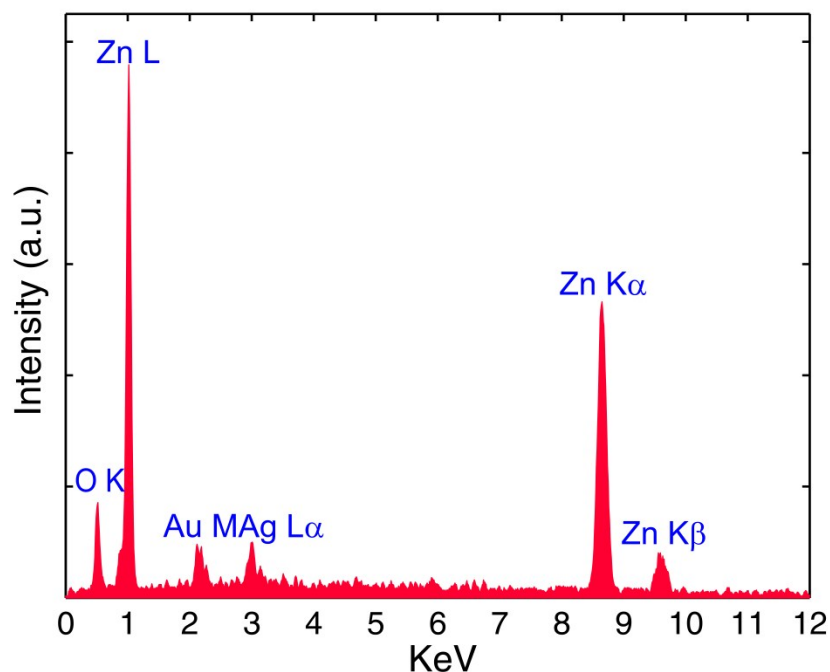


Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) spectrum of Ag-doped ZnO nanowires. The presence of Ag peaks supports the evidence of doping.

Mechanics of Hybrid Composite Energy Harvester

An understanding of the stress distribution across the thickness of an asymmetric cantilever beam is important to explain the piezoelectric energy harvesting function of the fabricated hybrid composites. Assuming that both the fiber and the surrounding matrix phase behave elastically and that the nanowires transfer interfacial shear stress between fiber and matrix during the vibration tests, the complex mechanics of the hybrid composite are simplified. As shown in Figure S3, the neutral axis (NA) of the beam with unsymmetrical layup configuration is placed very close to the lower layer of the ZnO nanowire interface. While the bottom nanowire interface experiences a negligible amount of stress due to their short distance to the neutral axis, the nanowires on the top layer undergo a large stress caused by gradual increase in axial stress from zero at NA to the maximum at the top edge of the composite. Moreover, the difference in elastic modulus of the carbon and aramid plies results in an interlaminar shear stress which further increases the amount of deformation along the length of ZnO nanowires

on the top. Therefore, it can be hypothesized that the large piezoelectric response of ZnO NWs is caused by the highly stressed ZnO nanowires with upward piezoelectric polarization. Since the nanowires with downward polarization on the bottom layer are subjected to a relatively small deformation, the generated charge in the opposite direction of the dominant electron flow can be neglected. However, the mechanics of the hybrid composite energy harvester with woven aramid fabric is very complicated and requires further studies on the polarization of the nanowires. Future studies can be performed by fabrication of unidirectional fiber composites with ZnO nanowire interface.

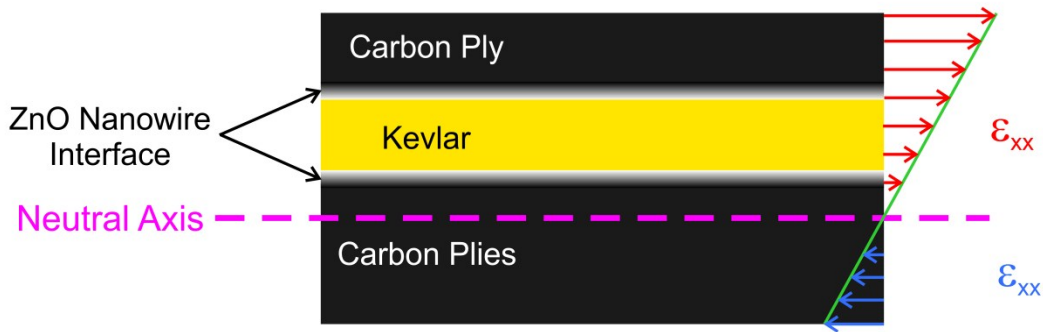


Fig. S3 Schematic of the stressed hybrid composite energy harvester under bending deformation.

Post-Mechanical Testing Characterizations

The nanostructured interfaces created with ZnO NWs in the fiber reinforced composites are very strong and does not damage under dynamic forces. Previously, it was shown that these interfaces in woven carbon fabric composites are stable after performing dynamic mechanical analysis (DMA) test at 100 Hz for two hours.⁴ In order to demonstrate that no failure or debonding occurs after comprehensive vibrational tests, two different cross sectional micrographs from two different samples with doped and un-doped ZnO nanowires have been taken to ensure that the nanostructured interfaces were not damaged during the test. Fig. S4 illustrates the cross section micrographs of these samples.

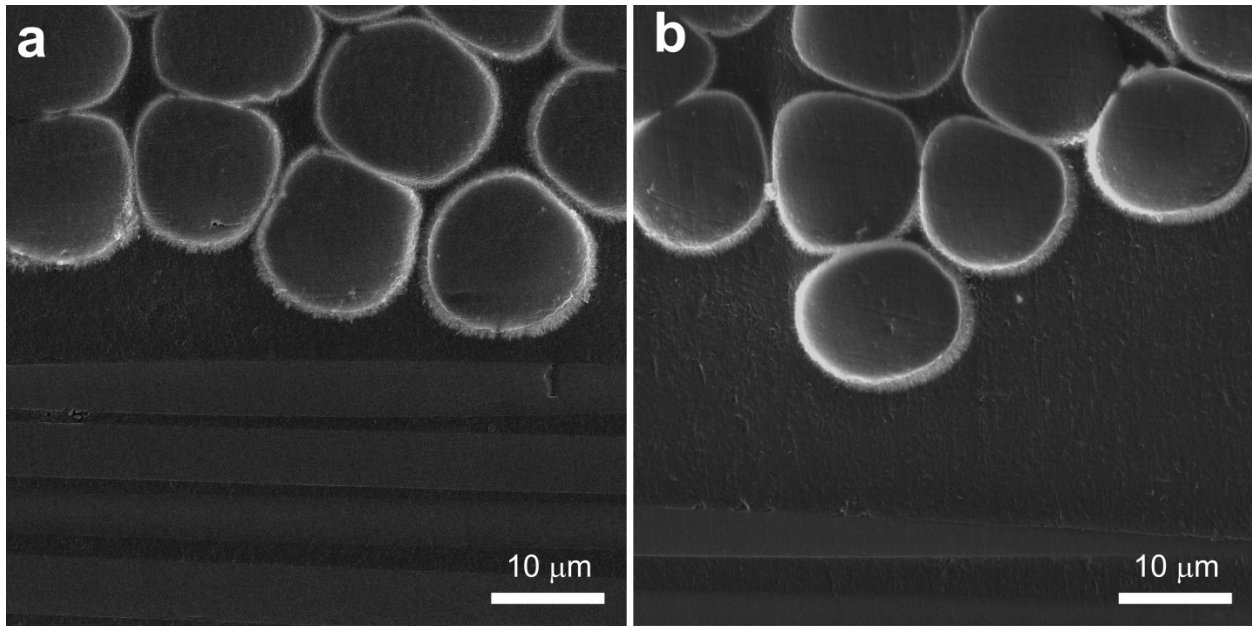


Fig. S4 Post-mechanical testing micrographs of the hybrid composite energy harvesters with different ZnO nanowire interfaces at 5,000 times magnifications: (a) nanostructured interfaces composed of un-doped ZnO nanowires (b) nanostructured interfaces composed of silver doped ZnO nanowires.

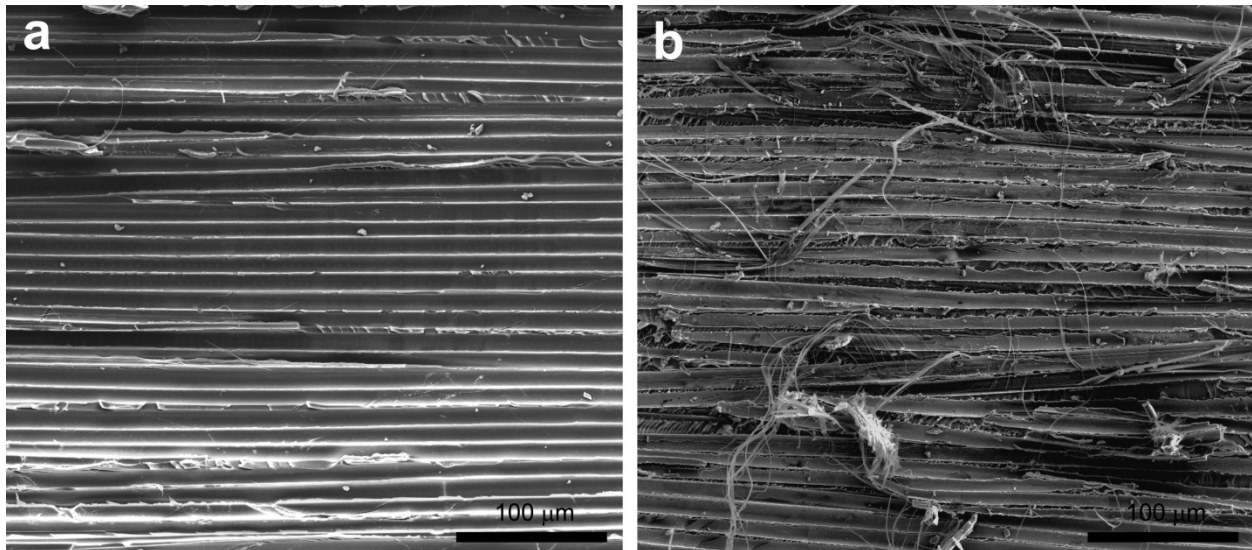


Fig. S5 Fracture surface of the composites after performing tensile test: (a) the SEM image of the neat fracture surface of the base composite (b) the SEM image of the relatively rough fracture surface of the hybrid composites due to the nanostructured interface illustrating fibrillations.

Supplementary References

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