Supplementary Information

PopTube Approach for Ultrafast Carbon Nanotube Growth

Zhen Liu[a], Jialai Wang[b], Vinod Kushvaha[c], Selcuk Poyraz[a], Hareesh Tippur[c], Seongyong Park[d], Moon Kim[d], Yang Liu[a], Johannes Bar[a], Hang Chen[e] and Xinyu Zhang*[a]

[a]Department of Polymer and Fiber Engineering, Auburn University, Auburn, AL 36849, [b]Department of Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL 35487, [c]Department of Mechanical Engineering, Auburn University, Auburn, AL 36849, [d]Department of Materials Engineering, The University of Texas at Dallas, Richardson, TX 75080, [e]Nanotechnology Research Center, Georgia Institute of Technology, Atlanta, GA 30332, USA

1. Synthesis of Conducting Polypyrrole Coated Engineering Materials

   In a typical experiment, 1 g fly ash (glass fiber, glass balloon etc.) was dispersed in 60 mL 1 M aq. HCl under magnetic stirring for 10 min, pyrrole (0.24 M) was then added into the above dispersed fly ash/HCl mixture suspension, stirred for another 10 min, and then 0.03 M ammonium peroxydisulfate (APS) was added into the solution mixture and continued stirring for 4 hrs resulting in PPy coated fly ash in the form of dark precipitates. The resulting black precipitate of PPy coated fly ash was suction filtered, washed with copious amounts of aq. 1 M HCl (3 × 100 mL) and acetone (3 × 100 mL) and finally freeze dried for 12 hrs. The yield of PPy coated fly ash was ~1200 mg.

2. Solid state blending of conductive materials with metallocenes precursors

   In a typical blending process, PPy.Cl or other conductive materials such as ITO, graphite etc. was blended with the same amount of ferrocene (50 mg : 50 mg) in a 10 mL plastic vial and spun in a speed mixer at 3500 rpm for 5 min.

3. Microwave initiated carbon nanotube growth

   In a typical process, 100 mg of conductive materials and metallocene precursors (at 1:1 wt. ratio) were placed in a glass vial and then heated under microwave irradiation for 15 sec.

4. Multiple-step CNT growth

   To promote length increment and higher coverage density of CNT on substrates, one can simply repeat sections 2 and 3 mentioned above. For example, the as-produced CNT coated PPy.Cl can be cooled, washed and dried, and then mixed with additional ferrocene at 1:1 wt. ratio, followed by microwave heating to increase the length and coverage density on the substrates.

5. Hexane assisted CNT growth

   In a typical process, 50 mg of graphite powder and ferrocene mixture (at 1:1 wt. ratio) were placed in a plastic vial and mix with 0.25 mL hexane, and spun in a speed mixer at 3500 rpm for 5 min. Afterwards the mixture of graphite, ferrocene and hexane was placed in a glass vial and then heated in a conventional microwave oven for 30 s.

6. Fracture test sample preparation

Glass microballoons (XLD3000, from 3M Corporation, USA; density 230 kg/m3 and average diameter 30 microns) were used as the filler in epoxy resin to form syntactic foam (SF) [1]. The carbon nanotube grown microballoons were dispersed in a low-viscosity epoxy (Epo-Thin, from Beuhler Inc., USA; Bisphenol-A resin and Amine based hardener; densities 1130 kg/m3 and 961 kg/m3, respectively) to make nanocomposite reinforced syntactic foam (nano-SF). To carry out the comparative static fracture study, SF and nano-SF (containing 15% microballoons by volume, respectively) sheets were cast separately. Cast sheets were machined into test specimens having dimensions of 76.2 mm × 22.0 mm × 8.7 mm. An edge notch with nominal length of 4.4 mm was introduced at mid-span of each specimen using a high-speed diamond impregnated circular saw. The tip of notch was sharpened using a razor blade.

7. Fracture test and results

The three-point bending tests were performed at room temperature using Instron 4465 testing machine, under displacement control mode and a crosshead speed of 0.002 mm/sec. The critical fracture toughness $(KI)_{cr}$ at failure was computed using Eq. 1 [2].

$$K_I^{cr} = \frac{P_{cr} S}{B W^{3/2}} \left[2.9\left(\frac{a}{W}\right)^{1/2} - 4.6\left(\frac{a}{W}\right)^{3/2} + 21.8\left(\frac{a}{W}\right)^{5/2} - 37.6\left(\frac{a}{W}\right)^{7/2} + 38.7\left(\frac{a}{W}\right)^{9/2} \right] \quad (1)$$

where, (KI)cr is critical fracture toughness for mode I fracture, P_{cr} is critical load at failure, a is notch length, B is thickness, S is span and W is width. The $(KI)_{cr}$ values for syntactic and nano syntactic foam are 2.001 0.050 MPa√m (at ultimate cross head displacement of 0.554 0.024 mm) and 2.346 0.064 MPa√m (at ultimate cross head displacement of 0.595 0.030 mm), respectively. The introduction of carbon nanotube grown microballoons enhanced the critical fracture toughness and crosshead displacement at fracture by ~17.0% and ~7.5%, respectively, compared to syntactic foam. To assure the repeatability of experimental results, three specimens of each composite were tested under identical conditions. The results were repeatable within the error range of ~4.0%.

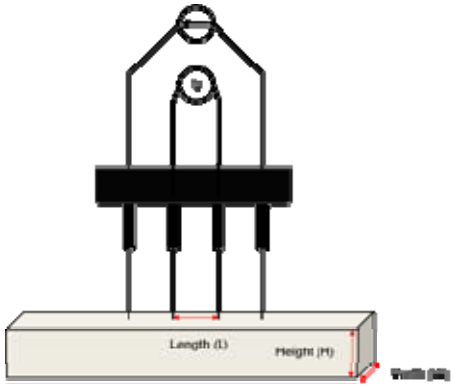
8. Four probe conductivity measurements.

The bulk electrical conductivity of the carbon nanotube coated fly ash was measured by a linear four probe measurement setup described elsewhere.[3] The CNT coated fly ash powder was pressed at 3500 psi in a mode to rectangular thin film, and the four probes were connected to Agilent Technologies 34980A multifunctional switch/measure unit. The conductivity σ (S/cm) is the reciprocal of electrical resistivity and can be expressed as:

$$\sigma = \frac{l}{R \times A}$$

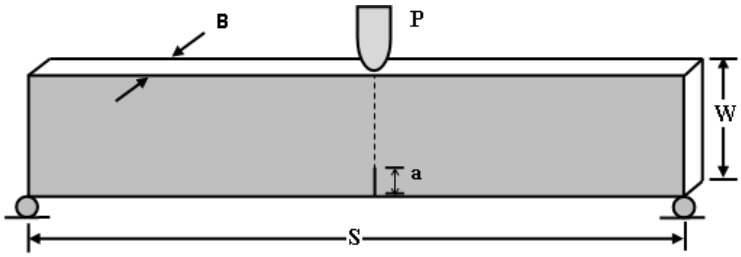
R is the electrical resistance of a uniform specimen of the material (Ω), can be directly read from the Agilent system; *l* is the distance between the inner two probes (cm); A is the cross-sectional area of the specimen (cm^2). In our test, the parameters for the

polypyrrole (PPy) nanoclips sample were: width: 0.2 cm, length: 0.52 cm, thickness: 0.06 cm, resistance from Agilent system: 50.0Ω. The calculated conductivity is 0.87S/cm.



[1]. H. S. Kim and H. H. Oh, J. Appl. Polym. Sci. 2000, 76, 1324.
[2]. D. Broek, in Elementary engineering fracture mechanics, 3rd ed., 1982. Martinus Nijhoff Publishers.
[3]. Haupt, S. G.; Riley, D. R.; Zhao, J.; McDevitt, J. T., 1993 *J. Phys. Chem.* 97, 7796-7799.

Appendix: three-point bending test



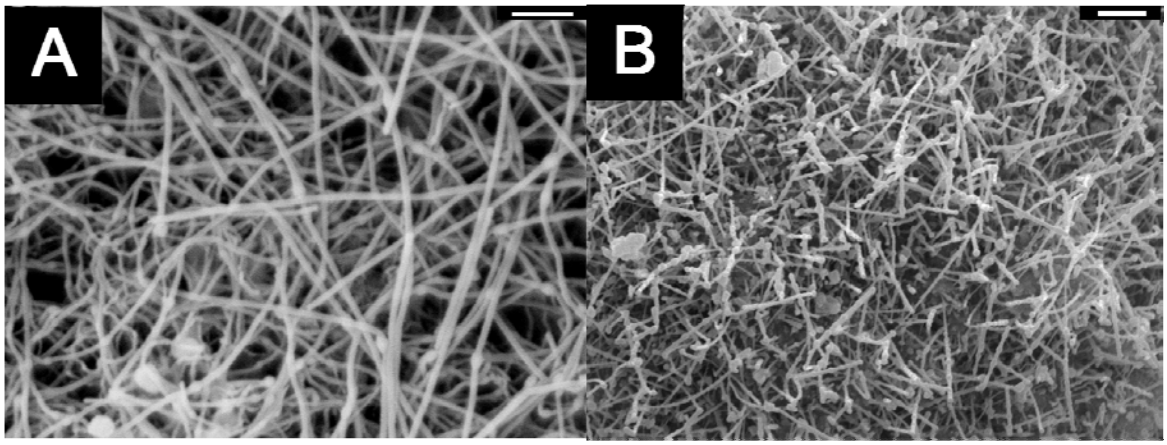


Figure S1. SEM images of CNT deposited on PPy.Cl coated fly ash using (A) bis(cyclopentadienyl)cobalt(II) and (B) 1,1'-Bis(diphenylphosphino) ferrocene as precursors (scale bars: 1μm)

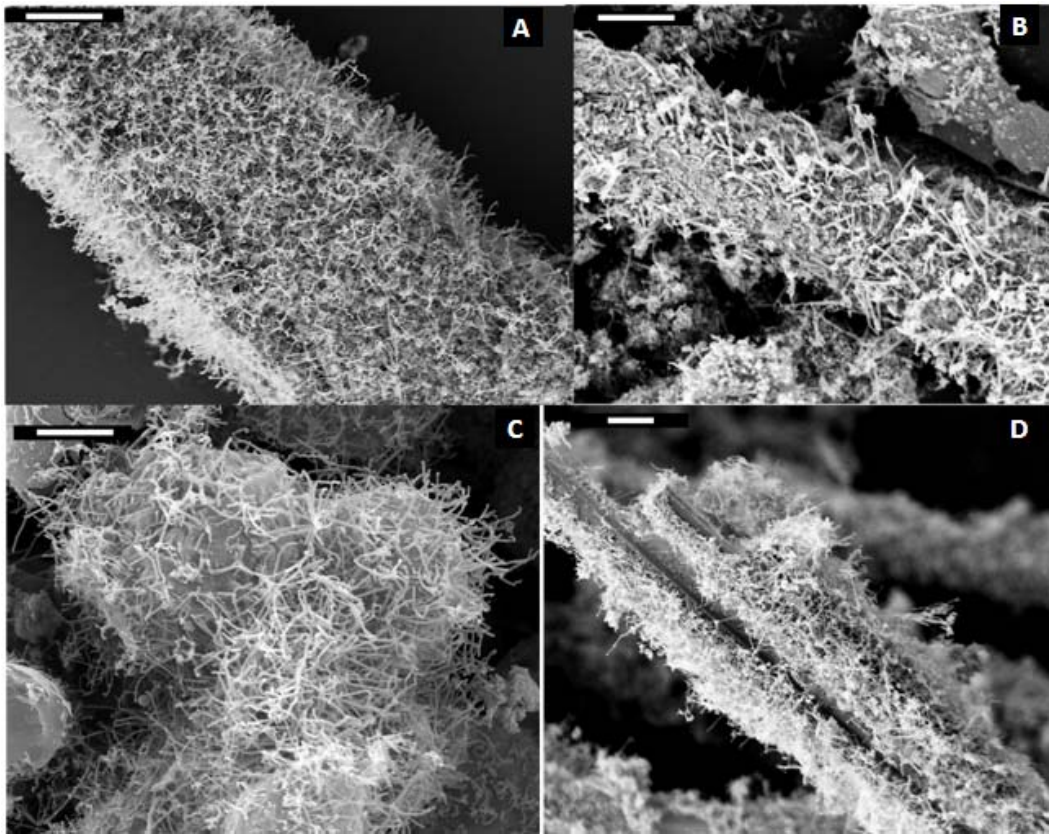


Figure S2. SEM images of CNT coated (A) Kevlar fiber, (B) Basalt fibers, (C) commercial 3M glass microballoons, and (D) carbon fibers (scale bars: 1 μm)

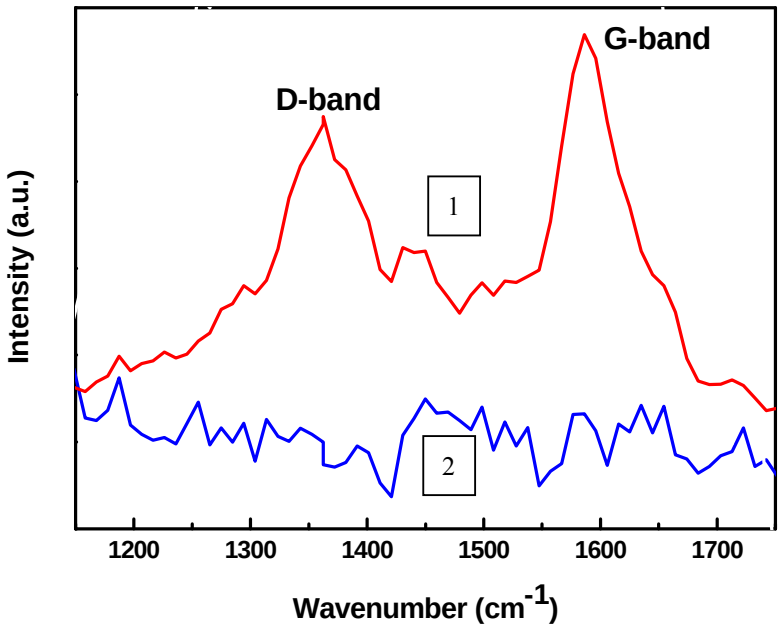


Figure S3. Raman spectra of fly ash with (1) and without (2) CNT coating.

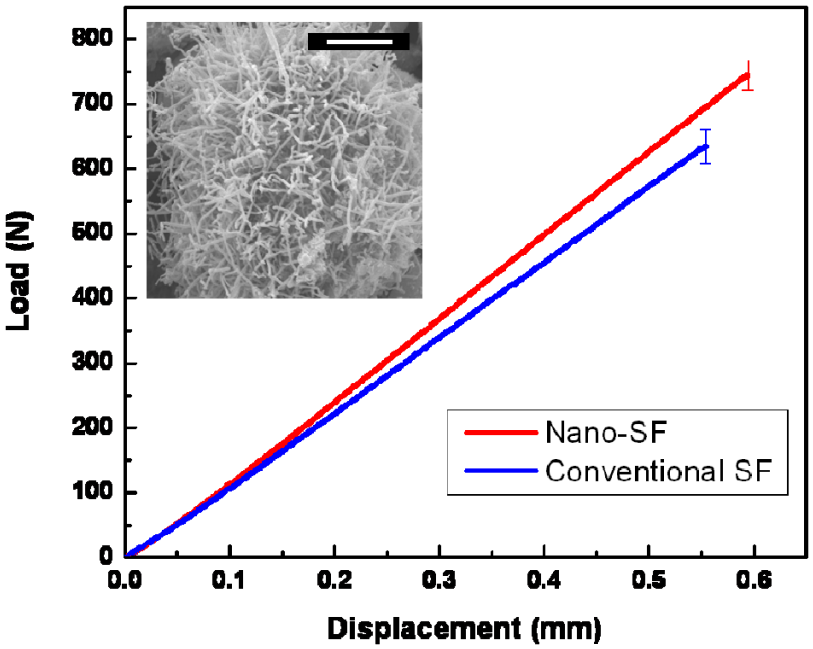


Figure S4. Load-displacement response for conventional SF and nano-SF. Inset: SEM image of the CNT decorated glass microballoon, scale bar: 10 μm)

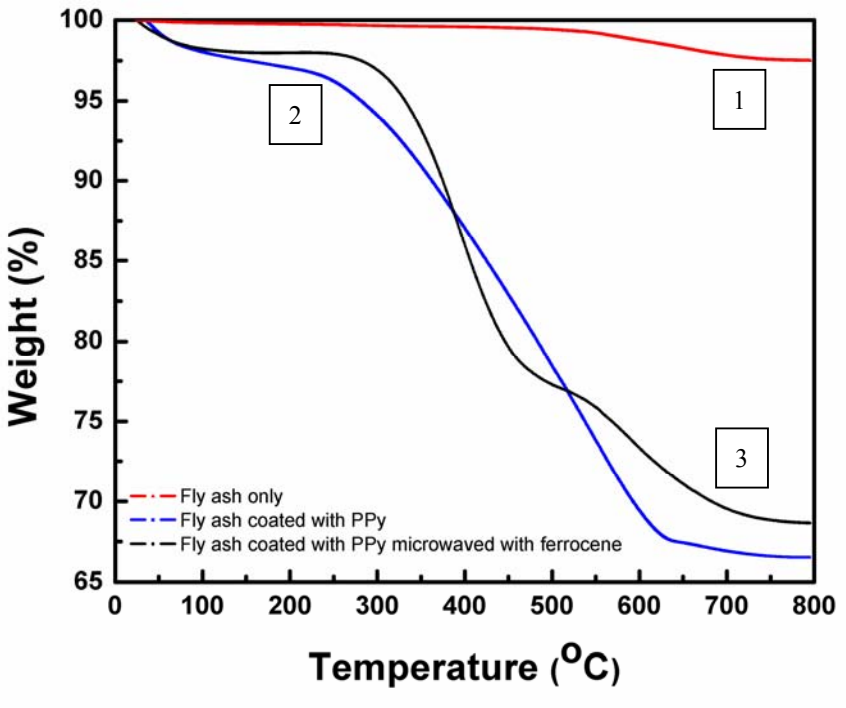


Figure S5. Thermogravimetric Analysis (TGA) of (1) Fly ash; (2) Fly ash coated with PPy and (3) Fly ash coated with PPy microwaved with ferrocene. Heating rate: 10°C/min, under N_2 flow.