Supplementary Information

Coaxial cable-like polyaniline@titania nanofibers: facile synthesis and low power electrorheological fluid application

Jianbo Yin*, Xiang Xia, Liqin Xiang and Xiaopeng Zhao*

Smart Materials Laboratory, Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710129, P. R. China. E-mail: jbyin@nwpu.edu.cn , xpzhao@nwpu.edu.cn; Fax: +86-29-88491000; Tel: +86-29-88431662

Experimental

Materials

Aniline monomer, ammonium per-sulfate (APS), citric acid, and ethanol were pursed from Sinopharm Chemical Reagent Co. Ltd. of China and titanium tetrabutyl titanate (TBT) was pursed from Kermel Chemical Reagent Co. Ltd. of China. All the reagents were of analytical grade purity and other reagents used as received except for aniline monomer being distilled before using.

Synthesis of conducting PANI nanofibers

5.7 g of aniline and 4.0 g of citric acid were mixed in 300 mL of distilled water to form mixture solution with a middle acidity (pH=4.0). Then, an aqueous solution of APS (13.6 g of APS in 150 mL of distilled water) was rapidly added into the above mixture solution with vigorous stirring. After 30 s, the stirring was stopped and the

resulting solution was left standing for 24 h at 4 ^{o}C in refrigerator. After that, a dark green PANI nanofiber suspension with high-suspended stability was formed. PANI nanofiber suspension was filtered, washed with distilled water and ethanol to remove residual, and then obtained PANI nanofibers were further dispersed in 200 mL of water-free ethanol by ultrasonic.

Synthesis of PANI@titania nanofibers

40 mL of the above PANI nanofiber/ethanol suspension was diluted by 50 mL of ethanol. Then 1.0 mL of water was added into the diluted PANI nanofiber/ethanol suspension and the mixture was stirred for 30 min at 25 ^{o}C followed by the addition of 3 mL of tetrabutyl titanate. After being stirred for 2 h at 25 ^{o}C, the mixture were filtered, washed with ethanol three times, and then dried at 100 ^{o}C to obtain PANI@titania coaxial nanofibers.

PANI@titania nanofibers with various sheath thickness could be prepared simply by adjusting the amount (0.5 mL, 1.5 mL or 2.0 mL) of water in the reaction. Fig. S2 shows SEM images of PANI@titania nanofibers with various sheath thickness. It can be found that the sheath thickness increases with the amount of water.

Characterization

The morphology was characterized by the scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, FEI Tecnai F30 G^2). The structure was determined by the powder x-ray diffraction pattern (XRD, Philips X'Pert Pro) using Cu K_α radiation. The chemical groups were determined by the Fourier transform infrared spectra (FT-IR, JASCO FT/IR-470 Plus). The thermal

property of PANI@titania nanofibers was determined by the thermogravimetric analyzer (TGA, Universal V3.8B TA instrument) in air with a heating rate of 10 ^{o}C min^{-1} in the temperature range of 20 - 600 ^{o}C.

Preparation of ER suspensions

The PANI@titania coaxial nanofibers were further dried at 150 ^{o}C until their conductivity no longer depended on the drying time. ER suspensions were prepared by dispersing the dried PANI@titania nanofibers in silicone oil (Dielectric constant of 2.7~2.9, viscosity of 50 mPa·s, density of 0.96 g/cm^3 at 25 ^{o}C) with a mechanical stirring and ultrasonic. The volume fraction of nanofibers in suspensions was defined by the ratio of nanofiber volume to total suspension volume. The density of nanofibers was measured by a pycnometer filled with silicone oil (density of 0.96 g/cm^3 at 25 ^{o}C). To decrease the effect of porosity on density, the pycnometer was placed in an ultrasonic cleaning bath and connected to a vacuum pump. After sonication under reduced pressure for 10 min, the density was measured.

Electrorheological measurements

The ER properties of PANI@titania nanofibers suspensions were measured by a stress-controlled electrorheometer (Thermal-Haake RS600) with a plate-plate system (PP ER35, the gap between plates was 1.0 mm.), WYZ-010 dc high-voltage generator (0-10 kV, 0-2 mA), oil bath system (-25-125 ^{o}C, Phoenix), and PC computer. Under electrical fields, the yield stress and dynamic viscoelastic properties were used to characterize ER effect of suspensions. The yield stress obtained by the controlled shear stress mode. In the dynamic experiment, the stress amplitude sweep test of

modulus as a function of stress at a constant frequency (0.5Hz) was initially attempted to find a linear viscoelastic region, and then the dynamic viscoelastic properties were measured as a function of frequency at the stress in the linear regions. The same stress was chosen for all PANI@titania nanofiber suspensions in order to make a comparable investigation. To ensure data consistency, all the measurements were repeated three times. The current through ER suspensions were recorded by an ampere meter connected with electrorheometer.

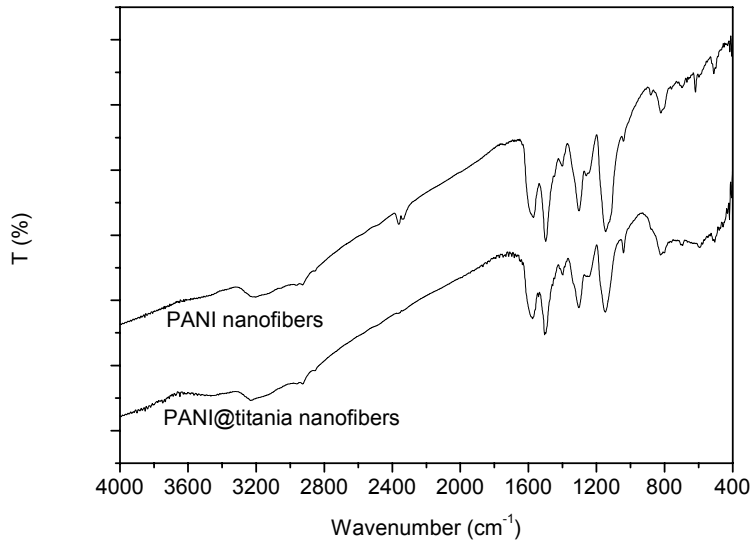

Fig. S1 FT-IR spectra of as-made PANI nanofibers and resulted PANI@titania nanofibers

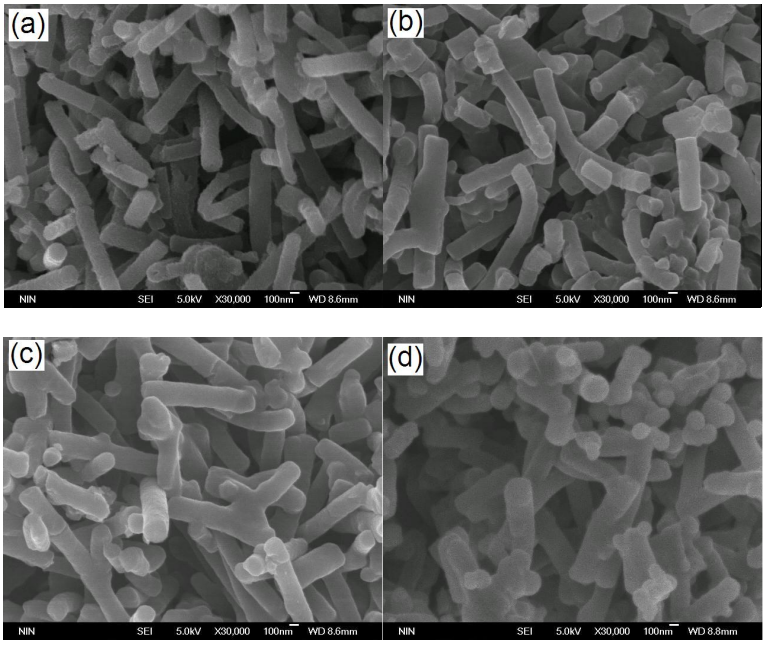

Fig. S2 SEM images of PANI@titania nanofibers with different sheath thickness synthesized by varying the amount of water: (a) 0.5 mL, (b)1.0 mL, (c) 1.5 mL, and (d) 2.0 mL.

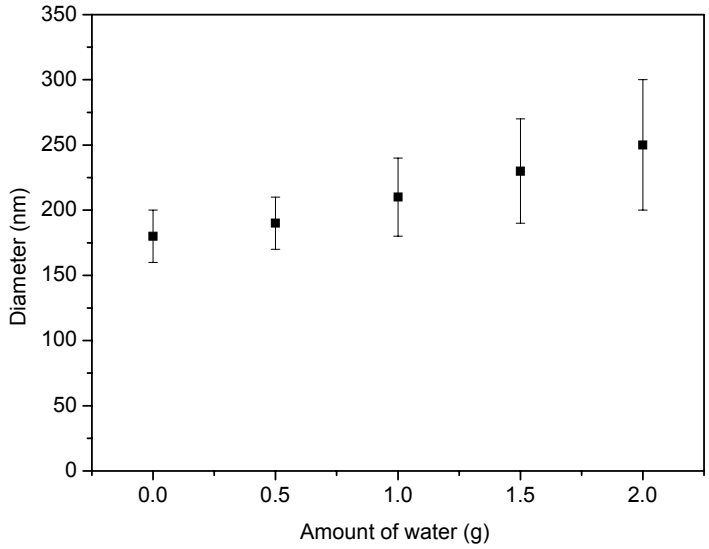

Fig. S3 Diameter change of PANI@titania nanofibers with the amount of water.

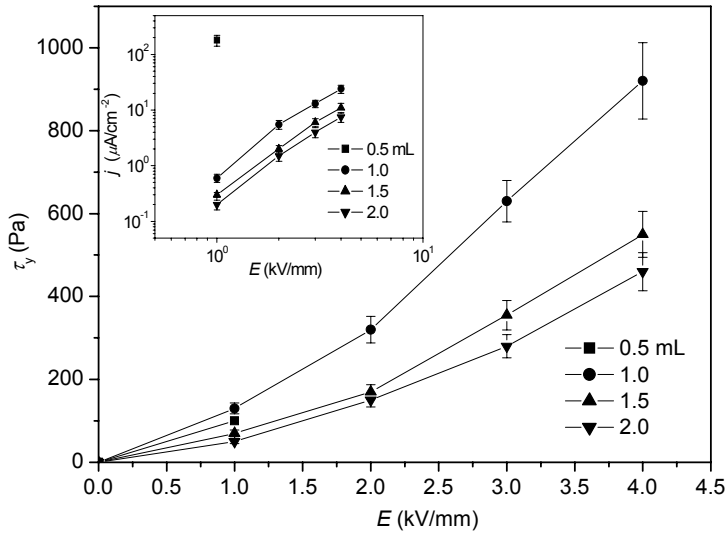

Fig. S4 Yield stress and current density (inset) as a function of electric field strengths for the suspensions of PANI@titania nanofibers synthesized with different amount of water (T=23 ^{o}C, 10 vol%).