Supporting Information for

Highly Conductive and Stretchable Polymer Composites Based on Graphene/MWCNT Network

Key Laboratory for Ultrafine Materials of Ministry of Education,
School of Materials Science and Engineering,
East China University of Science and Technology,
130 Meilong Road, Shanghai 200237, China.
Fax: +86 21 64250624; Tel: +86 21 64252055;
E-mail: zlingzi@ecust.edu.cn; czli@ecust.edu.cn

Experimental Details

Materials. Pristine MWCNTs synthesized by chemical vapor deposition process (purity was about 95%, average diameter range 10-20 nm, length range 5-20μm) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China. Natural graphite powder (200 mesh) was commercially obtained from Alfa-Aesar. Resorcinol (R, 99%) and formaldehyde solution (F, 36.5% in water) were purchased from Aladdin Chemistry Co., Ltd., Shanghai, China. Poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) prepolymer was prepared by mixing base silicone gel with a curing agent in a 10:1 weight ratio. Sulfuric acid (H_2SO4, 95%), hydrogen peroxide (H_2O_2, 30% in water), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$) and nitric acid (HNO_3, 60%) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China. Dichloromethane (CH_2Cl_2, 98%) was obtained from Shanghai Chemical Reagent CO., Ltd., Shanghai, China. All reactants were analytical purity and used as received. Deionized (DI) water was used throughout the experiments.

Preparation of acid-treated MWCNTs (t-MWCNTs) and graphite oxide (GO). MWCNTs (2g) were placed in a flask and HNO_3 (50 ml)/H_2SO_4 (150 ml) were added slowly to control the generated heat. The mixture was dispersed in an ultrasonic bath for 1 h. Then the reaction flask was immersed in an oil bath equipped with mechanical stirrer and gently heated to 70 °C for 2 h. After cooling to room temperature, the suspension was filtered with a membrane filter, which was then washed to neutral pH and freeze-dried for 24 h to obtain the t-MWCNTs.

Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method. Typically, graphite (2 g)/ $NaNO_3$ (2 g) were added to an ice-cooled solution of H_2SO_4 (96 ml) with vigorously stirring for 15 min. After the graphite was well dispersed, $KMnO_4$ (12 g) was added slowly in the same condition. Then, the reaction mixture was heated to 50 °C and HNO_3 (30 ml) was dropped slowly with mechanical stirring for 2 h. On completion of the reaction, DI (80 ml) was gently added into the mixture, twenty minutes later 10 ml of 30% H_2O_2 was added to the flask under vigorous stirring. After cooling to room temperature, the mixture was centrifuged at low speed for 3 times (5000 rpm, 15 min) and washed with DI for 3 rounds. Finally, the mixture was dialysed for 2 weeks to get GO solutions.

Aerogels and polymer composite films synthesis. The t-MWCNT/graphene-carbon aerogels were prepared using traditional organic sol-gel chemistry method reported elsewhere[1, 2]. Graphenes and t-MWCNTs (the total mass fraction of them was 0.5 wt% in the reaction mixture, the mass ratio of t-MWCNTs to GO was 1:1, 1:2 and 2:1, respectively.) were suspended in DI and dispersed using ultrasonic cell disruptor (model JY96-II, sonic power ~150 W, frequency ~20 kHz, Ningbo Haishu Kesheng Ultrasonic Equipment Co., Ltd., Ningbo, China) for 2 h. When the time was up, Resorcinol (R, 0.247 g, 2.24 mmol), formaldehyde (F, 0.3571 g, 4.41 mmol) and catalyst Na_2CO_3 (C, 1.19 mg, 0.011 mmol) were added to the reaction solution. The starting concentration of resorcinol-formaldehyde (RF) in the mixture was 3.58 wt%, the molar ratio of R:F was 1:2 and R:C was 200:1. Then the mixture solutions were cured in petri dish at 85 °C for 72 h to form organic gels, which were then immersed in water for another 48 h to remove small RF molecules. Freeze-drying was used to dry the t-MWCNT/graphene organic gels, afterwards the dried gels were pyrolyzed at 1000 °C under inert atmosphere and the t-MWCNT/graphene-carbon aerogels were obtained. The t-MWCNT-carbon aerogel (MCA) and graphene-carbon aerogel (GCA) were performed using the same method, the mass fraction of t-MWCNTs or graphene in reaction mixture was also controlled at 0.5 wt%. The PDMS prepolymer was prepared by mixing base silicon gel with curing agent in a weight ratio of 10:1. Then these aerogels were backfilled with PDMS prepolymer using vacuum suction method until no more air escaped and cured at 90 °C for 30 min. These final aerogels/PDMS composites had approximately the same dimensions as the original aerogels.

Graphene/MWCNT/PDMS composite films synthesis. 5g PDMS prepolymer, which was made by mixed base silicone gel with a curing agent in a 10:1 weight ratio, was dissolved in dichloromethane to obtain homogeneous solution. Then 0.0325g graphene and 0.0325g MWCNTs were dispersed in the solution and sonicated for 2h to get stable suspension. The above mixture was dried at room temperature for 12h, and then the resulting compound was moved to vacuum oven at 90 °C for 30 min to obtain the graphene/MWCNT/PDMS composites.

Raman spectra of the MWCNTs and t-MWCNTs were collected on a Lab Ram Infinity Raman spectrometer, using a linearly 514.5nm lasers. The t-MWCNTs, GO, R and F were dispersed in water using a model JY96-II ultrasonic cell disruptor. Then, the organic gels were prepared in an electro-thermostatic water cabinet (model DK-8D, Shanghai Jing Hong Laboratory Instrument Co., Ltd., Shanghai, China) and dried using a freeze-dryer (model FD-1, Shanghai TianFeng Industrial Co., Ltd., Shanghai, China). The morphologies of MCA, GCA and MGCA, the graphitic materials-matrix adhesion of MCA/PDMS, GCA/PDMS and MGCA/PDMS composite films were examined by using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), operating at 5kV. The morphology of MGCA was also characterized by transmission electron microscopy (TEM). Samples were collected on a TEM grid and conducted using a JZM-2100 microscope with an accelerating voltage of 200kV. The electrical conductivity of MGCA/PDMS, MCA/PDMS and GCA/PDMS composite films were measured by four-point probes (model RTS-8, Guangzhou 4Probes Tech Industrial Co., Ltd., Guangzhou, China) contact direct current (dc) conductivity measurement method at room temperature. The tensile tests were performed using a universal testing machine (CMT4204, Sansi Co., Ltd., China).

Supporting Results

Pristine MWCNTs (p-MWCNTs) produced by chemical vapor deposition (CVD) method are agglomerate and have many kinds of impurities, especially the metal catalyst, which will cause negative effect on their performance (electrical and mechanical properties). But suitable acid treatment can increase the solubility and purity of MWCNTs, meanwhile removing amorphous carbons introduced during the CVD process. Therefore, we chose mixed acids of HNO_3 and H_2SO_4 to treat MWCNTs (t-MWCNTs), which was anticipated to improve the hydrophilic of t-MWCNTs for their stable dispersion in aqueous solution. Raman patterns of p-MWCNTs and t-MWCNTs are shown in Fig. 1a, which are used to characterize the damage degree of MWCNTs by acid treatment. The D band at ~1346 cm^{-1} and G band at ~1585 cm^{-1} are corresponding to the amorphous or disorder carbon and crystalline graphitic structures, respectively. Therefore the intensity ratio of D band to G band (I_D/I_G) can indicate the degree of disorder，the smaller I_D/I_G means the better MWCNTs. It is obvious that the D band intensity decreased after acid treatment (I_D/I_G=0.84 and 0.95 for t-MWCNTs and p-MWCNTs, respectively), which implies the oxidation process had little impact on the structures of MWCNTs. That is to say, the acid treatment retained the excellent electrical and mechanical properties of t-MWCNTs and their integrity did not be undermined, meanwhile it improved stable dispersion of the nanotubes in water.

The specific structures of the robust black cylinders of MCA and GCA are shown in field-emission scanning electron micrographs (FE-SEM) images (Fig. S2), which clearly exhibited that the morphology of the aerogels were quite uniform in the large scale. Fig. S2a illustrated that the t-MWCNTs formed the highly porous 3D network structure with pore diameter spread over a few tens to two hundred of nanometers. The randomly oriented t-MWCNTs dispersed very uniformly in the aerogels, which should be attributed to the acid functionalization of MWCNTs and ultrasonic process. The FE-SEM image of graphene carbon aerogel without MWCNTs was shown in Fig. S2b, the graphene sheets overlapped (layer by layer) and aggregated with each other, the pores they formed had heterogeneous pore size distribution, which was spread over dozens to thousands of nanometers. Even more, lots of cracks could be observed in the conductive network, and that would severely impact the mechanical and electrical properties of composite films.

We have prepared three G-MWCNT-CAs with same GO-MWCNT hybrid amount but different initial mass ratios of t-MWCNTs to GO, they were M_1G_2CA ($M_{MWCNTs} : M_{GO} = 1:2$), MGCA ($M_{MWCNTs} : M_{GO} = 1:1$) and M_2G_1CA ($M_{MWCNTs} : M_{GOs} = 2:1$). The porous structures of these resulting graphene-MWCNT hybrid carbon aerogels were exhibited by FE-SEM，as shown in Fig. S3 and Fig. 1B. It is supposed that the structural differences of these three t-MWCNT-graphene carbon aerogels are due to that the GO sheets can adsorb the MWCNTs through the π-stacking interaction[3] and likewise, t-MWCNTs can also prevent the re-stacking of reduced GO sheets[4]. Therefore, the different initial mass ratio of t-MWCNTs to GO would lead to diverse distribution of 2D sheets and 1D nanotubes.

As shown in Fig. S3a and b, when the mass of GO was only half of the mass of t-MWCNTs (M_{MWCNTs}: M_{GO}= 2:1), a large amount of t-MWCNTs were absorbed on the surface of GO sheet by π-stacking interaction and the bushy nanotubes were so dense that they hampered the contacts of GO slices. So the resulting aerogel, M_2G_1CA, showed super macropores and lots of GO sheets were embedded in the networks of MWCNTs.

When the mass of t-MWCNTs and GO was equal (M_{MWCNTs}: M_{GO}= 1:1), as illustrated in Fig. 1B, the newly joined GO sheets induced plentiful contact points that moderate amounts of nanotubes could not only be absorbed on the GO sheets but also connect with each other. Hence, the MGCA had uniformly dispersed t-MWCNT/graphene hybrid and interconnected network in this situation.

Further increased the content of GO till a mass ratio of GO to t-MWCNTs was 2:1 (Fig. S3c and d), this meant large quantities of GOs were added into the structure of uniformly dispersed GO/t-MWCNT hybrid. These new coming GO sheets would adsorb onto the nanotubes and work with the existed GO pieces in the MGCA to co-encase the interconnected t-MWCNTs, the super macropores were also formed in this situation as shown in Fig. S3c and d.

The analysis of structures formed with different mass ratio of GO to MWNCTs might support our assumption mentioned above to a certain extent.

For MWCNT and/or graphene-based elastomers system, few researches have reported composites with electrical conductivities of > 1 S/cm. In general, the higher conductivity (>1 S/cm) demands higher concentration of graphic materials. *Pang et al.* prepared graphene/poly(ethylene) composites with an electrical conductivity of about 0.1 S/cm at 1.3 wt% graphene loading by latex technology[5]. *Li* and *Shimizu* fabricated MWCNTs/poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) composite with an electrical conductivity of about 0.2 S/cm at 5.5 wt% MWCNTs loading by melt blending using a highshear extruder[6]. Seldom articles have focused on composites fabricated from polymer and synergic graphene/carbon nanotubes. Recently, *Hu et al.*[7] have reported a novel approach to fully disperse carbon nanotubes in silicone rubber (Methyl-Vinyl-Silicone, MVQ 110-2) by the addition of graphene, the composites were fabricated through solution blending method. The electrical conductivity of the graphene/MWCNT/MVQ composite was only 1.25×10^{-5} S/cm at 3.5 wt% graphic materials (1 wt% graphene and 2.5 wt% MWCNTs) loading. Here, we also prepared graphene/MWCNT/PDMS composites (see the *Experimental Details*) through solution blending method. The electrical conductivity of this composite could reach 5×10^{-4} S/cm at 1.3 wt% MWCNT/graphene loading. It is noted that the electrical conductivity of our MGCA/PDMS composite film is very high that can reach 2.8 S cm^{-1} when the loading level of MWCNTs plus graphene is only 1.3 wt%, which exhibits an improvement of more than 4 orders of magnitude compared to graphene/MWCNT/PDMS composite prepared through solution blending method. The graphene and MWCNTs in our work formed special-designed 3D network in PDMS matrix, which is responsible for the significantly improved electrical property of the composites.

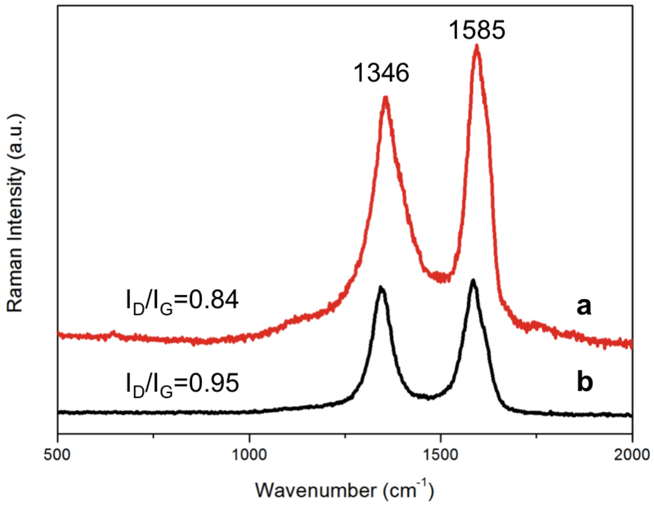

Fig. S1. Raman spectrum of (a) MWCNTs treated with HNO_3/H_2SO_4, (b) p-MWCNTs;

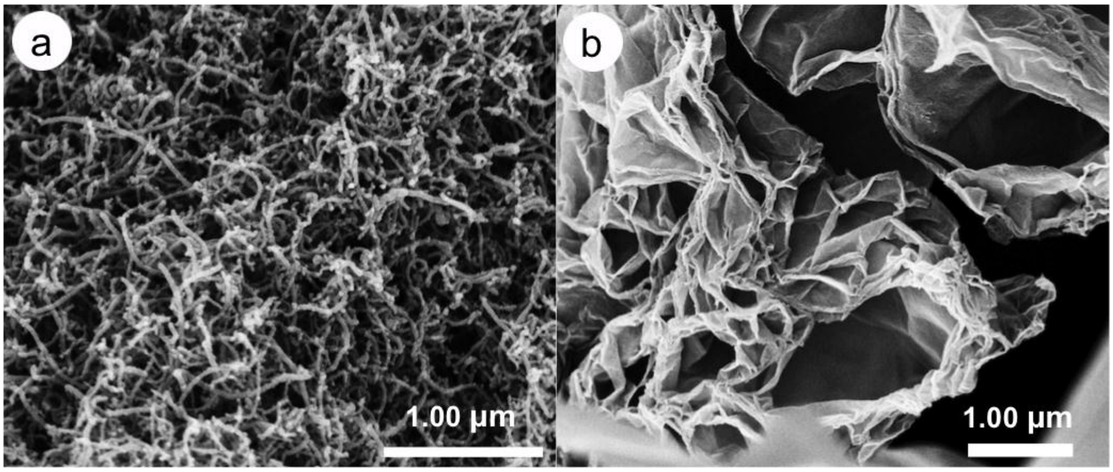

Fig. S2. FE-SEM images for a) MCA and b) GCA.

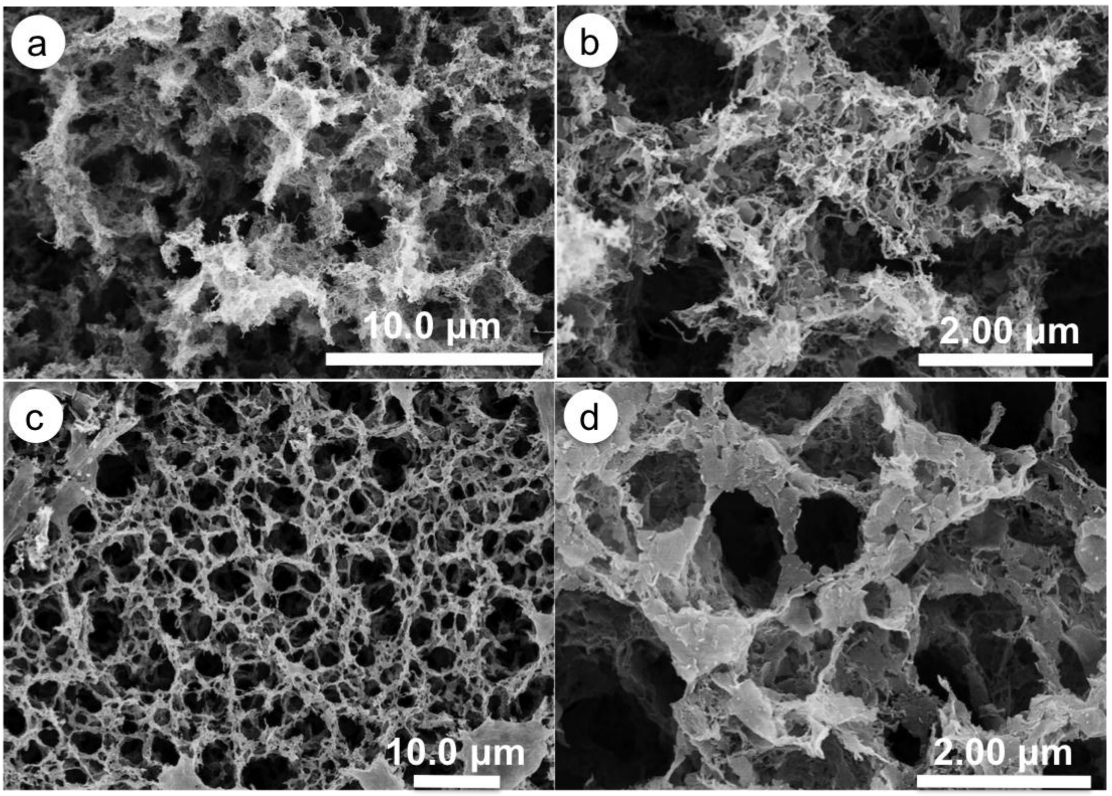

Fig. S3. FE-SEM images of t-MWCNT-graphene carbon aerogels with (a) (b) M_2G_1CA (M_{MWCNTs}: M_{GO}= 1:2) and (c) (d) M_1G_2CA (M_{MWCNTs}: M_{GO}= 2:1) in different amplification factor.

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