(M_w=[70[000,[Aldrich)[and[poly(styrene[sulfonate)[(PSS,[M_w=[500[000,[Polysciences),[according[to[the[procedure[by[Barker[et[al [20].[T[e[PSS[layer[was[sandwiche[between[two[PAH[layers.[

Tetramethylorthosilicate[(TMOS,[Aldrich)[was[hydrolyzed[under[acidic[onditions[(molar[atio[of[TMOS/HCl/H_2O[was[1:1:55.6)[for[30[min.[T[e[ydrolyzed[solution[was[luted[with[H_2O[n[a[atio[of[1:100.[T[e[luted[solution[was[then[ntrodu[ed[into[a[two-compa[t-[ment[amber[separated[by[the[nanonozzle-array[film.[T[e[eaction[was[arried[out[n[the[presence[of[a[direct-current[electric[field[(80[V[m^{-1}),[with[the[athode[mmersed[n[the[amber[facing[the[sharp[end[and[the[anode[facing[the[large[end.[In[this[arrangement,[the[direction[of[EOF[was[from[the[sharp[end[to[the[large[end.[T[e[e-[action[proceeded[for[15[min,[after[which[the[nanonozzle[array[was[taken[out,[nsed[thoroughly[with[water[and[ed.[

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eryILowIConductivityIThresholdIinI Bulk IsotropicISingle-WalledICarbonI Nanotube–EpoxyIComposites**

By[*MateuszcB.cBryning*,[*MohammadcF.cIslam*,[*JamescM.cKikkawa*, an [*ArjuncG.cYodh**[

Conducting[omposites[are[typically[made[by[embedding[conductive[particles[in[an[otherwise[insulating[matrix.[T[e[e-[sulting[materials[often[exhibit[percolation-like[electrical[on-[uctivity [1][with[a[well-defined[nsulator–conductor[transition[point,[as[a[function[of[filler[oncentration.[Applications[for[these[omposites[include[static-charge[ssipation, [2][adio-fre-[quency[shielding,[and[field-emission[sources.[3,4][Recently,[sin-[gle-walled[carbon[nanotubes[(SWNTs)[have[emerged[as[an[at-[tractive[option[for[onductive[composite[materials.[T[eir[small[size,[large[aspect[ratio,[and[gh[conductivity[make[it[possible[to[eate[onductive[composites[at[very[low[filling[oncentra-[tions[and[with[smaller[inhomogeneities[than[can[be[achieved[with[larger[particles.[Lower[filling[fractions[imply[smaller[per-[turbations[of[bulk[physical[properties,[such[as[strength[and[optical[transparency,[as[well[as[lower[cost.[We[escribe[here[a[simple[procedure[for[making[conductive[SWNT–epoxy[om-[posites[that[esult[n[exceptionally[low[threshold[oncentra-[tions[with[minimal[modification[of[the[epoxy[matrix[material.[

T[us[far,[studies[on[the[onductivity[of[SWNT–polymer[omposites [5–24][ave[eported[low[thresholds[at[volume[frac-[tions[anging[from[7][$\sim 1 \times 10^{-4}$[to[several[percent,[10][n[some[cases[outperforming[current[technologies.[Many[aspects[of[the[problem,[however,[are[poorly[understood[and[optimization[e-[mains[elusive.[The[starting[formulations[of[spersed[SWNTs[frequently[ontain[ense[aggregates[of[nanotubes,[as[well[as[amorphous[arbon[and[metallic[mpurities[that[an[persist[throughout[processing[and[affect[performance.[Stabilizing[the[nanotubes[in[suspension[an[reduce[aggregates,[but[ntroduces[other[problems.[For[example,[ovalent[stabilization[modifies[the[ntrinsic[SWNT[conductivity,[while[steric[stabilization[an[egrade[contacts[between[nanotubes,[and[generally[ntroduces[additional[mpurities[into[the[matrix.[In[addition,[while[well-[spersed[SWNTs[typically[ave[a[gher[length-to-diameter[atio[than[aggregates,[which[s[mportant[for[obtaining[low[thresholds,[25][interactions[between[particles[also[contribute[to[the[formation[of[percolating[networks.[Network[formation[through[particle[aining,[in[particular[[can[be[a[key[factor[n[

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lowering[threshold[concentrations.[In[arbon[black[ompos-[ites,[for[example,[the[threshold[an[be[lowered[by[nducing[particle[aggregation[26][and[through[the[formation[of[diffuse,[or["fluffy"[agglomerates.[27][Long,[flexible[opes[of[aligned[multiwalled[nanotubes[(MWNTs)[ave[also[been[used[to[make[omposites[with[threshold[volume[fractions[as[low[as[$\sim 2 \times 10^{-5}$,[albeit[with[millimeter-scale[inhomogeneities.[28][In[such[cases,[as[n[all[eal[composites,[the[relationship[between[particle[aspect[ratio[and[threshold[concentration[becomes[f-[ficult[to[predict.[In[SWNT[omposites[these[effects[emain[largely[unexplored.[

Here[we[show[how[the[SWNT[length/diameter[aspect[atio[and[the[spontaneous[formation[of[nanotube[networks[affect[the[onductivity[of[bulk[SWNT–epoxy[composites.[We[om-[pare[two[types[of[SWNTs[with[fferent[mean[aspect[ratios,[and[ntroduce[two[nanotube-epoxy[processing[methods[that[nhibit[or[promote[the[formation[of[networks.[We[observe[conductivity[thresholds[at[SWNT[volume[fractions[as[low[as[$5.2[(+1.9/-0.5)[\times[10^{-5}$,[nearly[10[times[lower[than[values[quot-[ed[n[previous[eports[on[SWNT[omposites[n[epoxy[ma-[trices.[5][All[conductivity[thresholds[fall[within[the[semi-dilute[oncentration[egime[of[the[rods,[but[the[effect[of[nanotube[aspect[ratio[on[the[threshold[oncentration[is[only[marginally[explained[by[simple[models[for[od[percolation.[

T[e[key[to[this[work[s[our[starting[formulation,[a[lute[(0.004[wt.-%),[metastable[dispersion[of[pure[SWNTs[n[*N*,*N*-[dimethylformamide[(DMF).[SWNTs[remain[well-dispersed[n[this[suspension[as[solated[SWNTs[and[small[SWNT[bundles[while[under[sonication[(see[F[g.[1g),[but[slowly[eaggregate[when[sonication[s[turned[off.[T[e[absence[of[stabilizing[agents[and[formulation[metastability[permit[networks[to[form[prior[to[curing;[the[low[SWNT[oncentration[reduces[aggre-[gation,[and[so[enables[us[to[benefit[from[the[gh[aspect[atio[of[solated[SWNTs.[T[e[samples[were[processed[under[a[vari-[ety[of[sonication[conditions,[uring[which[time[the[lute[SWNT/DMF[solution[was[slowly[added[to[the[thermoset[epoxy[esin,[and[the[DMF[was[allowed[to[evaporate.[Con-[tinuous[sonication[produced[more[saggregated[composites,[while[stoppage[of[sonication[prior[to[uring[permitted[net-[works[to[form.[Taken[together[[[the[use[of[pristine[SWNTs[and[sonication[allowed[us[to[produce[fairly[omogeneous[ompos-[ites[with[minimal[perturbation[of[the[gh-strength[epoxy.[In-[terestingly,[omposites[n[which[nanotubes[were[allowed[to[reaggregate[exhibited[lower[thresholds,[ompared[to[more[o-[mogenized[ones.[

Laser-oven[(Tubes@Rice)[and[HiPco[(Carbon[Nano-[technologies,[Inc])[SWNTs[were[studied.[T[e[nanotubes[were[purified[to[a[SWNT[ontent[of[>[95[%.[29][Atomic[force[mi-[croscopy[(AFM)[characterization[showed[that[the[laser-oven[(HiPco)[SWNTs[ad[an[average[length,[=[516[±[286[nm[(167[±[90[nm),[and[an[average[ameter,[*de*=[1.35[±[0.15[nm[(1.1[±[0.3[nm).[30][T[ese[mensions[over[the[typical[range[of[SWNT[sizes[available[today.[We[found[that[adding[the[SWNT/DMF[solution[slowly[in[small[discrete[steps[and[allow-[ing[the[DMF[to[evaporate[between[each[step[mproved[the[ef-[fectiveness[of[the[sonication.[Sonication[uring[processing[

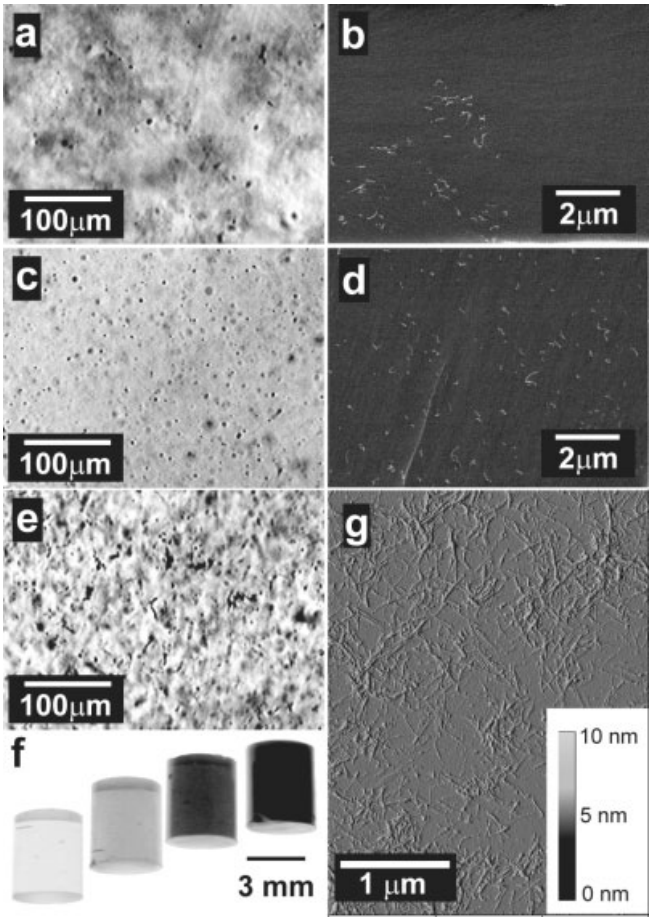

Figure 1. a)–e).8Images8of8composites8(SWNT8volume8fraction82.1×810^{-4}).8 Information8about8SWNT8distribution8in8the8composites8was8obtained8by8 using8transmitted8light8microscopy8of8thin8(~300&μm)8slices8(a,c,e),8and8 from8scanning8electron8microscopy8(SEM)8of8fractured8surfaces8(b,d).8 a) In8a8 *-s onicured* sample,8dark8and8bright8regions8correspond8to8 high8and8low8SWNT8concentrations,8respectively.8b)8In8SEM8images8of8 the8same8non-8onicured8composite,8SWNT8ropes8(white8strips)8appear8in8 ~108μm8clusters8on8the8surface.8Here,8the8ropes8are8present8only8in8the8 lower8left8quadrant8of8the8field8of8view.8c)8The8more8uniform8gray8color8in8 this8*onicured* composite8mplies8a8more8uniform8SWNT8distribution8than8 in8(a).8d)8SEM8image8of8a8sonicured8sample8shows8that8SWNT8ropes8 are8distributed8more8uniformly8across8the8fractured8surface8than8in8(b).8 e)8Dense8aggregates8are8seen8in8a8non-8onicured8composite8made8from8a8 more8concentrated8SWNT/DMF8starting8dispersion8at80.048wt.-%8(see8 text).8f)8Photographs8of8composites.8SWNT8volume8fractions,8from8left8 to8right,8are82.6×810^{-5},85.2×810^{-5},81.0×810^{-4},8and81.5×810^{-4}.8g)8Tapping8 mode8AFM8image8of8laser-oven8SWNTs8adsorbed8for8over8308min8onto8an8 hexamethyldisilazane-treated8silicon8wafer8from8a8well8sonicated,8dilute8 DMF/SWNT suspension.8

tends[to[break[up[transient[SWNT[networks[and[nhibit[the[formation[of[new[ones.[Once[the[esired[SWNT[oncentra-[tion[was[eached[n[the[sonicating[esin[as[escribed[above,[an[aliphatic[amine[osslinker[was[stirred[into[the[solution.[At[this[stage,[the[samples[were[vided[into[two[categories.[In[the[first[set,[samples[were[placed[into[a[hot[water[bath[to[cure[at[90[°C[for[30[min;[curing[proceeded[without[sonication.[Here-[after,[we[efer[to[these[samples[as["non-sonicured".[In[the[second[set,[samples[were[placed[in[the[sonicator[bath[at[80[°C,[

and[were[ured[under[sonication[for[30[min.[We[efer[to[these[samples[as["sonicured".[We[found[that["sonicured"[samples[were[more[omogeneous[than["non-sonicured"[ones,[mply-[ing[that[SWNT[networks[that[formed[during[sample[process-[ing[were[successfully[spersed.[

A[series[of[composite[samples[with[increasing[SWNT[on-[entration[is[shown[in[F[gure[1f.[Our[SWNT–epoxy[ompos-[tes[exhibited[a[ange[of[microscopic[morphologies[evident[from[optical[microscopy[of[thin[sections[and[SEM[of[frac-[tured[surfaces[(see[F[g.[1).[An[example[of[a["non-sonicured"[sample[s[shown[n[F[gures[1a,b.[Reaggregation[of[SWNTs[was[clearly[evident[as[bright[and[ark[regions[on[the[optical[images.[T[ese[diffuse[aggregates[were[roughly[10[μm[n[am-[eter.[SEM[maging[onfirmed[that[nanotube[density[varied[on[a[similar[length[scale.[Ropes[of[SWNTs[were[stributed[n[lusters[on[the[fractured[surfaces.[T[ese[lusters[were[easily[spersed[by[ontinued[sonication[just[prior[to[uring.[An[example[of[a[saggregated["sonicured"[sample[s[shown[n[F[gures[1c,[.[T[e[optical[and[SEM[mages[show[that[the[SWNT[distribution[was[quite[omogeneous[down[to[a[few[mi-[crometers,[and[although[some[aggregates[were[present,[their[ensity[was[elatively[low.[We[suspect[the[epoxy[esin[tself[partially[stabilizes[the[suspension[31][once[the[DMF[evapo-[rates,[facilitating[this[dispersion.[It[s[important[to[stinguish[the[ffuse[features[n[our["non-sonicured"[samples[from[dense[aggregates,[which[result[from[a[poor[nitial[spersion.[Fo[example,[a[sample[made[from[a[0.04[wt.-%[SWNT/DMF[suspension,[shown[n[F[gure[1e,[ad[a[substantially[larger[number[of[dense[aggregates,[which[presumably[existed[in[the[more[oncentrated[starting[suspensions[and[persisted[throughout[processing.[

T[e[electrical[conductivity[of[the[SWNT–epoxy[omposites[was[etermined[by[two-[and[four[point[ontact[ect-current[(dc)[onductivity[measurements.[Most[of[the[measurements[were[obtained[by[the[four[point[method,[in[order[to[eliminate[contact-resistance[effects.[Samples[were[prepared[for[the[mea-[surements[as[shown[n[the[nset[n[F[gure[2.[T[e[four[point[current–voltage[(*I–V)c*urves[were[linear[in[the[range[studied,[as[shown[in[the[same[figure.[In[F[gure[3,[we[show[the[onduc-[

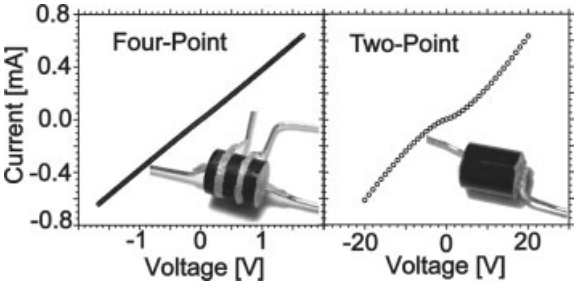

Figure Two-point&nd&four-point&*I–V* curves&for&a&non-sonicured&iPco&SWNT&composite&at&1.6&x&10^{-48}SWNT&volume&fraction&show&the&ypical&re-&sponse&of&our&samples.&The&insets&show&composite&samples&mounted&for&two-&and&four-point&conductivity&measurements.&At&a&given&current,&the&measured&oltage&n&the&two-point&measurement&s&significantly&high-&er&than&in&that&in&the&four-point,&due&to&both&contact&resistance&and&a&larger&separation&between&the&electrodes.&

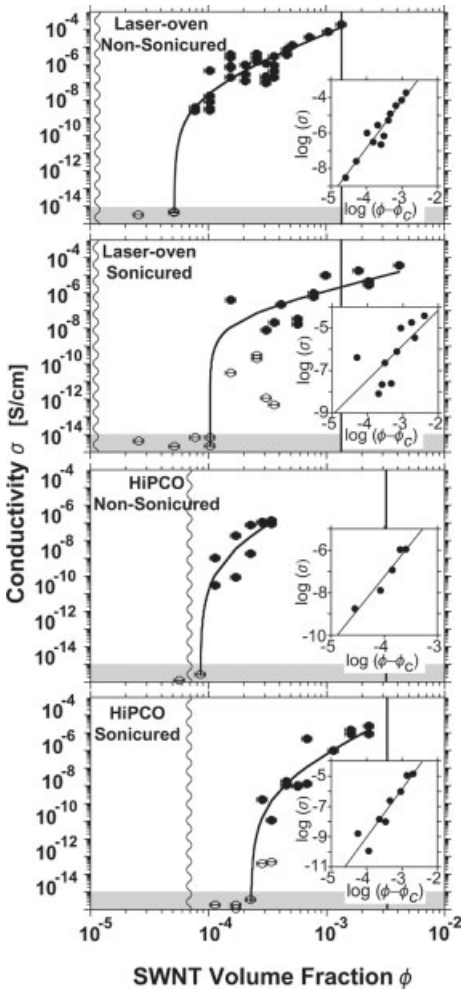

Figure 3. onductivity,&σ,&as&a&function&of&SWNT&volume&fraction,&φ,&for&non-sonicured&and&sonicured&laser-oven&and&HiPco&samples.&The&vertical&lines&on&the&charts&ndicate&approximate&transitions&from&dilute&to&semi-&dilute&regimes&(wavy),&and&semi-dilute&to&concentrated&regimes&(solid).&Each&point&on&the&plot&represents&a&separately&made&composite.&The&ob-&served&scatter&n&conductivity&s&likely&caused&by&small&variations&n&pro-&cessing&conditions&between&samples.&In&contrast,&the&conductivities&of&different&sections&of&the&same&sample&were&never&more&than&50%&of&each&other.&Filled&circles&represent&four-point&measurements.&Open&cir-&cles&depict&two-point&alternating&bias&measurements.&Points&in&shaded&areas&are&below&the&baseline&of&our&equipment.& onnecting&curves&reflect&the&predicted&behavior&according&to&the&best&fits&for&the&observed&thresh-&old,&ϕ_c,&and&the&exponent,&*s*.&Insets&show&plots&of&log(σ)&as&function&of&log($\phi - \phi_c$)&for&the&same&data&sets,&where&multiple&points&at&the&same&concentration&have&been&binned&prior&to&fitting.&Best-fit&lines&determining&ϕ_c&and&& are&shown.&

tivity,[σ,[of[the[non-sonicured[and[sonicured[laser[oven[and[HiPco[composites[as[a[function[of[SWNT[volume[fraction,[φ.[All[four[sets[of[composites[exhibited[a[jump[in[the[value[of[σ of[2[to[6[orders[of[magnitude[over[a[small[ange[n[φ,[i.e.,[a[percolation-like[behavior.[Near[this[threshold,[we[found[$\sigma \propto (\phi - \phi)^s$;[ereafter[we[efer[to[φ as[the[threshold[volume[fraction.[To[etermine[φ and[*s*,[logarithms[of[the[measured[conductivity[and[volume[fraction[were[ompared[to[the[equa-[tion[log[(σ)[=[log[(C_0[+ A($\phi - \phi$)$^{sc}\Theta$ ($\phi - \phi$)),[where[C_0[s[the[

constant[background[onductivity[of[the[points[below[the[threshold,[A is[a[constant[that[depends[on[nanotube[onduc-[tivity[and[network[morphology,[and[$\Theta(\phi-\phi_c)$[s[the[Heaviside[step[function,[such[that[$\Theta(x)$[=[0[when[$x<0$[and[$\Theta(x)$[=[1[when[$x>0$.[Two-point[measurements[above[the[threshold[were[ex-[luded[from[the[fits[to[avoid[systematic[errors[due[to[ontact[resistance.[

A[least-squares[analysis[of[the[fits[showed[that[ϕ_c for[each[set[of[ompos]ites[was]strongly[bounded[by[the[regions[between[the[gh[est[insulating[and[lowest[ondu]cting[points.[T[e[expo-[nent[s,[however[[was[not[well[bounded.[T[e[fit[results[for[ϕ_c and[s are]summari]ed[in[Table[1.[Plots[of[$\log(\sigma)$[versus[$\log(\phi-\phi_c)$[n[the[nsets[of[F]gure[3[show[the[onduct[ng[ompos[te[samples[with[best-f]t[lines[whose[slopes[provide[the[best-fit[exponent,[s.[T[e[lowest[measu[ed[threshold[volume[fraction[was[obtaine[for[the[non-son[ured[laser]oven[SWNTs;]its]val-[ue[of[5.2][(+1.9/–0.5)][×][10^{-5}[s[approx]mately[10[times[smaller[than[the[lowest[threshol[oncent[ation[eported[to[ate[for[SWNTs[in[epoxy.[5][Electrostatic[dissi]ation[applications[typi-[ally[equi[e[a[ondu[tivity[of[about[10^{-5}[Sc[m^{-1},[which[was[eache[when[$\phi \approx 5\times10^{-4}$[($\sigma \approx 10^{-4}$[Sc[$m^{-1}$[at[$\phi = 10^{-3}$).[T[e[magnitude[of[the[ondu[tivity[s[comparable[to[some[esults[obtained[for[MWNTs[in[epoxy[ompos]ites;[note,[owever[that[the[length[scale[for[inhomogeneity[s[~ 10[μm[o[less[for[son-[ured[and[non-son[ured[samples[(F]g.[1),[ompare[with[~ 1[mm[n[MWNT–epoxy[samples.[28][Two[other[facts[are[learly[evealed[in[the[data.[F]rst,[the[threshol]s[observed[n[the[sonicu[ed[samples[were[gher[(i.e.,[by[~2×)[than[the[non-[sonicu[ed[samples.[Evidently,[sonicati]n[disaggr]gated[and[omogen[zed[SWNTs[better[just[prior[to[curing,[but[the[more[reaggr]gated[ompos]ites[percolated[more[readily.[Second,[the[laser]oven[SWNT[ompos[tes[ad[approx]mately[twofold[low-[er[thresh]lds[than[corresponding[HiPco[SWNT[composi]es.[This[trend[is[qualitatively[consistent[with[the[expectations[of[simple[models[for[percolation[n[andom[od[netwo]ks[s-[ussed[below,]which[scale[with[od[length[and[amete[.[

Since[individual[SWNTs[behave[somewhat[like[gid[ods[n[solution,[32][t[is[useful[to[onsider[our[observations[in[light[of[the[predictions[made[by[simple[percolation[models[for[sotro-[pic[spersions[of[od-like[particles.[Such[spersions[an[be[lassified[by[Doi–Edwards[theory[nto[dilute,[semi-dilute,[and[oncentrated[regimes.[33][Fo[non-interacting[rods,[the[percola-[tion[threshold[occurs[near[the[transition[between[the[semi-di-[lute[and[oncentrated[regimes,[where[the[od[number[ensity[s[oughly[the[eciprocal[of[the[excluded[volume[of[the[od,[ν_{excl},[25,34,35][which[ere[can]be[approximated[by[$\nu_{excl}[\approx \pi$ $^{2}[d/2$,[where[d and[are[as[efined[earlier][T[e[threshold[s[thus[predicted[to[be[at[a[volume[fraction[$\phi_1[\approx d/2$[.[While[valid[for[systems[of[non-interacting[rods,[this[model[as[ad[limited[success]predicting[the[percolation-like[behavior[of[strongly[n-[teracting[nanotube[systems.[Attractive[nteractions[can[lower[threshold[concentrations[when[the[particles[assemble[to[form[long[chains.[T[e[simplest[model[for[these[attractive[systems[assumes[that[the[limiting[oncentration[at[which[ontinuous[ains[can[form[occurs[near[the[transition[between[dilute[and[semi-dilute[regimes,[where[the[rotational[motion[of[each[od[s[obstructed[by[the[presence[of[other[rods.[36–38][Here,[the volume[occupied[by[each[od[s[a[sphere[of[ameter[, o [$\nu_0[\approx \pi$ $^{3}/6$,[and[the[critical[volume[fraction[s[$\phi_0[\approx 3d^2/2$[^{2}. T[s[model[predicts[a[significantly[lower[threshold[than[the[ex-[cluded-volume[picture[escribed[above,[and[provides[a[lower-[bound[for[the[position[of[the[threshold[when[the[rods[are[s-[tributed[randomly.[It[s[thus[easonable[that[the[threshold[should]be[observed[in[the[semi-dilute[regime[between[the[two[limiting[ases[escribed[above.[

While[these[models[oversimplify[the[situation[in[our[om-[posites,[they[o[give[a[ange[of[oncentrations[where[the[threshold[can]be[expected.[If[we[approximate[our[laser-oven[(HiPco)[samples[as[omogeneous[od[stributions[with[length[516[nm[(167[nm)[and[ameter[1.35[nm[(1.1[nm),[then[we[an[define[limiting[theoretical[percolation[thresholds[using[the[simple[models[outlined[above.[The[wavy[and[solid[lines[n[F]gure[3[orrespond[to[dilute/semi-dilute[and[semi-dilute/con-[entrated[transition[points,[respectively.[T[esholds[for[all[four[sets[of[omposites[were[observed[n[the[semi-dilute[e-[gime,[as[expected[in[a[system[of[attractive[rods.[T[s[esult[s[also[consistent[with[rheological[studies[of[surfactant-stabilized[SWNTs[n[solution,[where[gidity[percolation[was[observed[in[the[semi-dilute[regime.[39][T[e[models[also[make[quantita-[tive[predictions[about[the[atio[of[the[HiPco[threshold[to[the[laser-oven[threshold.[T[e[observed[threshold[ratio[for[our[composites[was[1.7[for[non-sonicured[samples[and[2.2[for[so-[nicured[samples.[If[the[samples[are[overlap-volume[limited[(i.e.,[v_0[limited),[then[the[predicted[atio[is[6.5.[If[the[samples[are[excluded-volume[limited[(i.e.,[$1/\nu_{excl}$[limited),[then[the[ob-[served[atios[are[predicted[to[be[2.5.[Although[loser[to[the[

Table 1. Observed thresholds, exponents, and predicted thresholds for the four data sets. All numbers are given in terms of SWNT volume fraction.

	Laser-oven		iPco	
	Non-sonicured	Sonicured	Non-sonicured	Sonicured
Threshold volume fraction ($\phi_c \times 10^{-5}$)	5.2 (+1.9/-0.5)	10 (+2/-1)	8.5 (+1.0/-0.9)	23 (+2/-2)
Best-fit exponent (s)	2.7 (+0.4/-0.8)	1.6 (+0.5/-0.6)	3.1 (+1.2/-1.7)	3.2 (+0.5/-0.6)
Dilute/semi-dilute transition (ϕ_0)	$\times 10^{-5}$	$\times 10^{-5}$	6.5×10^{-5}	6.5×10^{-5}
Semi-dilute/concentrated transition (ϕ_1)	1.3×10^{-3}	1.3×10^{-3}	3.3×10^{-3}	3.3×10^{-3}

latter ratio, our observations do not agree with either model. Another potentially testable prediction is the percolation exponent, *s*. The confidence intervals for our exponents were large and their best fits ranged from 1.6 (+0.5/–0.6) to 3.2 (+0.5/–0.6). Computer models of conductivity percolation predict a critical exponent value [40] of 2. Other experimental studies of carbon nanotube composites have frequently cited values [5,9,13,28] between 1.3 and 2, while exponents of 3.1 were observed in disordered, short-carbon-fiber composites. [41]

In summary, we have developed a methodology to disperse purified SWNTs into epoxy and we have investigated the electrical conductivity in these composites as a function of SWNT length, type, and dispersion homogeneity. All four varieties of our composites exhibited percolation-like thresholds in the semi-dilute concentration regime. The lowest thresholds were observed when the SWNTs were allowed to reaggregate, and these were significantly lower than ever been previously reported for SWNTs in epoxy.

Experimental

Nanotubes were obtained in raw form and purified according to procedures largely described in previous publications [42] and [43]. The suspensions were magnetically fractionated, reducing the magnetic-catalyst fraction to ≤ 0.7 wt.-%, and then the nanotubes were annealed at 1150 °C. A combination of X-ray and thermogravimetric analysis (TGA) measurements suggested that the resultant purified nanotubes contained > 95 wt.-% SWNTs and < 5 wt.-% carbon-derivative (amorphous carbon, graphite) impurities, in addition to the above-mentioned small quantities of catalyst particles. Details of the TGA and X-ray analyses are given in previous publications ([29] and [44], respectively). The purified nanotubes were dispersed using a low-power high-frequency sonicator (Cole-Parmer model 08849-00, 1 pint, 17 W) at concentrations of 0.004 wt.-% and 0.04 wt.-% in *N*,*N*-methylformamide (DMF). To characterize the dispersion, we deposited SWNTs onto a hexamethyldisilazane (HMDS)-treated silicon wafer by dipping the wafer into the SWNT suspensions and then measured the eight of the deposited nanotubes using atomic force microscopy. Figure 1g shows an AFM image of a wafer that was left in solution for 30 min; our quantitative dispersion data, however, were derived from similar images of wafers that were only briefly dipped into the solution, and therefore contained a much lower density of adsorbed SWNTs. The 0.004 wt.-% SWNT/DMF dispersion contained a mixture of isolated nanotubes (< 10 %) and small bundles (> 90 %, mean height < 6 nm), whereas the 0.04 wt.-% SWNT-DMF dispersion contained many significantly larger bundles.

Our thermoset epoxy was Shell Epon 828 (Bisphenol-A, Miller Stephenson, density: 1.16 g m^{-3}) epoxy resin with EpiKure 3234 cross-linker (Triethylenetetramine, Miller Stephenson, density: 0.98 g m^{-3}). The density of cured epoxy was found to be 1.2 ± 0.02 g m^{-3}. We used the cured epoxy density along with the calculated value of 1.4 g m^{-3} for nanotube density [9] to convert from units of weight percent to volume fraction. For each SWNT-composite sample, 0.5 g of epoxy resin was placed in a low-power high-frequency bath sonicator. The sonicator temperature was maintained at 80 °C. SWNT/DMF suspension was added to the heated and sonicating epoxy resin with a glass syringe in 1 mL increments every 30 min, until the desired nanotube concentration was reached. The elevated sonication temperature reduced the viscosity of the epoxy resin; this step was necessary for effective sonication and fast DMF evaporation. The resultant sample was left in the sonicator for an additional 2–3 h to ensure complete evaporation of DMF. We then added 65 μL of cross-linker to the sonicating SWNT/epoxy resin mixture. We stirred the mixture mechanically for two minutes, and then loaded it into a thin-walled cylindrical Teflon mold. Curing proceeded either under continued sonication or without, as described above. All samples were subsequently annealed in an oven at 120 °C for two hours. Thus prepared, the samples were cut with a diamond saw into 5.4 mm, 2.5 mm, and 300 μm thick pieces, and the flat ends were polished on 5 μm grain polishing paper.

For two-point measurements, the flat surfaces of the cylindrical composite samples were painted with conductive paint (product number 4929N, DuPont). For four-point measurements, the samples were further prepared by roughening the curved surface of the cylindrical samples and painting conductive rings around their circumference with a spacing of approximately 1 mm. Copper leads were attached to these electrodes with the same conductive paint. (See insets in Fig. 2.) Samples with conductivities of less than 1×10^{-10} S m^{-1} were measured by an alternating-bias two-point method that utilized capacitive decay curves to extract conductivity [45]. The measurement error for the conductivity was ≤ 1 %, and the nanotube volume fraction was known to within 10 %. The sensitivity limit of our apparatus was approximately 1×10^{-14} S m^{-1}, as indicated by the shaded gray areas in Figure 3. We confirmed the conductivity was isotropic; conductivities measured along three perpendicular axes were within 25 % of one another. Weak aging effects were observed in our composites. After a period of two months, the conductivities of all samples were observed to decrease by approximately 50 %. The conductivity recovered to 75 %–100 % of its original value after heating at 110 °C for 1 h. To account the possibility of conduction through any remaining solvent, control samples were prepared that underwent the same processing with pure DMF in place of the SWNT/DMF dispersion. All of these control samples were insulating below the noise floor of the measurement.

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Phthalocyanine Composites as High-Mobility Semiconductors for Organic Thin-Film Transistors**

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T[ere[is[a[growing[esearch[effort[in[organic[thin-film[tran-[sistors[(OTFTs)[because[organic[semiconductors[possess[numerous[advantages,[ncluding[large-area[coverage,[easy[processing,[good[compatibility[with[a[variety[of[substrates[n-[cluding[flexible[plastics,[and[great[opportunities[for[structural[modification.[1–4][A[lot[of[esearch[as[been[arried[out[by[emists[to[synthesize[new[materials[with[promising[proper-[ties,[such[as[gh[mobilities[and[gh[on/off[ratios.[5–7][Semi-[onducting[materials[with[gh[performance[an[also[be[formed[by[the[incorporation[of[two[different[organic[materi-[als.[8][However,[omposites[of[organic[semiconductors[ave[scarcely[been[nvestigated[in[OTFTs.[9,10][Also,[the[mobility[of[the[composites[are[relatively[low.[

Phthalocyanines[(Pcs)[are[a[large[family[of[onjugated[mol-[ecules[with[gh[chemical[and[thermal[stabilities.[11][T[e[out-[standing[optical[and[electrical[properties[of[these[materials[open[up[a[wide[range[of[applications,[including[electrochemi-[al[devices,[optical[switches,[data-storage[media,[gas[sensors,[solar[cells,[and[OTFTs.[12–17] Our[esults[on[OTFTs[aving[source[and[ain[electrodes[sandwiched[between[opper[phthalocyanine[(CuPc)[and[obalt[phthalocyanine[(CoPc)[layers[eveal[that[omposites[of[the[two[Pcs[ave[fferent[aracteristics[than[the[pure[materials.[18][A[omposite[of[CuPc[and[nickel[phthalocyanine[(NiPc),[CuPc–NiPc,[s[nves-[tigated[as[the[active[layer[n[an[OTFT[n[this[article.[An[OTFT[n[top-contact[onfiguration[s[schematically[epicted[in[Figure[1.[CuPc[and[NiPc[films[have[been[eposited[to[om-[pare[the[structures[of[the[materials.[

Representative[transfer[aracteristics[are[shown[n[F[g-[ure[1[for[OTFTs[based[on[CuPc–NiPc[(9:1[w/w)[films.[F[om[the[square[oot[of[the[ain[urrent[($I_D^{1/2}$)[vs.[gate[voltage[(V_G)[curve[at[a[fixed[drain–source[voltage[(V_D)[of[–40[V,[the[field-effect[mobility[(μ)[n[the[saturation[egime[for[the[CuPc–NiPc[(9:1)[evice[s[estimated[to[be[0.050[$m^2V^{-1}s^{-1}$. T[e[corresponding[linear-regime[mobility[is[0.025[$m^2V^{-1}s^{-1}$. T[s[reduction[of[linear-regime[mobility[relative[to[the[satura-[tion-regime[value[may[be[attributed[to[traps[n[the[organic[

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