

SUPPORTING INFORMATION FOR

Fast Mechanochemical Synthesis of Carbon Nanotube-Polyaniline

Hybrid Materials

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S.I. Screening Experiments

We tested whether sonication previous to ball milling would contribute to the dispersion of the nanotubes in the final hybrid material. Since nitrogen-doped multi-walled carbon nanotubes (CN_x-MWCNT) are more dispersible than undoped MWCNT in polar solvents we only did these tests with CN_x.

We sonicated 40.4 mg CN_x in 7 mL water for 60, 30 or 0 min, followed by milling for 20 min, with 8.34 g FeCl₃ and 2.02 g aniline (molar ratio 2:1 FeCl₃:Ani·HCl).

The polymerization yields (**Y**) in these experiments were, as expected, independent of the sonication times (for t_s=0 min, **Y**=1.86 % ±0.19; for t_s=30, **Y**=1.75 % ±0.25; and for t_s=60, **Y**=1.63 % ±0.05). We also should note that after sonication for 30 and even 60 min in deionized water, the CN_x still flocculated, even though they are much more dispersible in polar solvents than the undoped nanotubes. We found that prior sonication of CNT did not affect the final dispersion in the composite, indicating that the vigorous and energetic mixing that occurs during ball milling is enough to disperse the nanotubes in the polymer. Thus, we omitted prior sonication in later experiments.

We observed that yields were significantly lower ($Y=0.3\%$) when water was not added. Therefore we made an initial experimental design to study the effect of water volume (V_w), together with the molar ratio of oxidant to aniline (Ox) and the milling time (t_m). We used a $\frac{1}{2}2^k$ factorial design to halve the number of screening experiments. The levels of each variable and the polymer yields of each run are shown in table S.I, which shows that V_w actually had a clear effect in increasing the yield.

Table S.I. Levels used for the variables studied and conversion rates of aniline in the $\frac{1}{2}2^k$ experimental design

Run	t_m (milling time, min)	V_w H ₂ O volume (mL)	Ox (molar ratio Oxidant* to Aniline)	Y PAni yield (%)
1	20	2	2:1	1.70
2	60	2	1:1	1.54
3	20	12	1:1	2.72
4	60	12	2:1	2.87
*FeCl ₃ ·6H ₂ O, 4.17 or 8.34 g to 2.02 g Ani·HCl				

The effect of the other variables is not as evident from table S.I but by statistical analysis of the results we obtained a regression model (equation S.1) for the principal factorial effects.

$$Y = 2.21 - 0.0025(t_m) + 0.585(V_w) + 0.0775(Ox) \quad (eq. S.1)$$

The results in table S.I show that there is no advantage to using milling times longer than 20 min. The regression model reflects this with a very small coefficient for this variable, which we consider to actually be close to zero within experimental error. The negative sign for the milling time in the regression model may be due to ball milling induced polymer bond breaking, as discussed in the main paper. The regression model shows a small coefficient for the oxidant to aniline ratio, thus, to ensure that there was a stoichiometric excess of FeCl₃, we decided to keep the larger molar ratio of 2:1 in other experiments.

S.II Optimization Experiments

The design of experiments and the chosen variables are explained in the main paper (see Table I, and section III.B). The table, as arranged by ascending water volumes makes evident that V_w is a critical variable for PANi yield (Y), which varied from 1.45 to 3.15% (average 2.05 ± 0.48 %). The best regression model for yield, by analysis of variance (ANOVA) is shown in equation S.2, and it has a coefficient of determination $R^2=0.776$. This model captures adequately the main features of this process including only the main factors and ignoring interactions between variables and quadratic terms of factors, which are not significant. The largest coefficient is that for V_w , again. The amounts or type of nanotube would not be expected to interfere in the polymer yield, as they would not participate in the aniline oxidation reaction, and accordingly the regression model shows similarly small coefficients for those variables.

$$Y = 2.05 + 0.064(MWCNT) + 0.065(CN_x) + 0.59(V_w) \quad (eq. S.2)$$

Electrical conductivity (σ) varied from $\sim 10^{-4}$ (pure PANi) to $4.51 \text{ S} \cdot \text{cm}^{-1}$, with a mean value of $2.76 \pm 1.25\% \text{ S} \cdot \text{cm}^{-1}$.

Both types of CNT increase the conductivity significantly and to similar orders of magnitude. CNT contents above 25% increase conductivity only slightly further indicating that the CNT concentrations are well above the percolation threshold.

It is clear that nanotubes of either type increased conductivity significantly, to values four orders of magnitude higher than those of PANi synthesized under the same ball milling conditions. The data model for σ (equation S.3) shows that ($MWCNT$) was a more significant factor to increase conductivity than (CN_x). The negative coefficient for V_w is consistent with its large effect on the yield: more polymer is produced with larger water volumes and a smaller %CNT means a slightly lower conductivity for the

composite. The $R^2 = 0.748$ for the model, indicates that it is a fair representation of the factorial variability of electrical conductivity in these composites.

$$\sigma = 2.72 + 0.88(MWCNT) - 0.20(CN_x) - 0.38(V_w) + 0.92(MWCNT)(CN_x) - 0.60(MWCNT)(V_w) - 0.84(MWCNT)^2 + 0.92(V_w)^2 \quad (eq. S.3)$$

A visual representation of both regression models as response surfaces is shown in the main paper (figure 1), and discussed in more detail there. The relation between conductivity and nanotube concentration is represented in figure S.1 below. A greater percentage of nanotubes generally increases conductivity, but other variables are also playing a role here, and the data points are too scattered to provide a simple direct relationship. They also show slight increases in σ with increasing amounts of CN_x from a lowest point of 1.6 to 2.9 $S \cdot cm^{-1}$, which is likely due to the quadratic factor $(MWCNT)(CN_x)$; if we have a low level of $(MWCNT)$, this quadratic factor results in positive contributions to σ with high levels of CN_x , as seen in figure 1(B). The effect of water lowering the conductivity is more easily seen in the extreme of highest MWCNT level in figure 1(C).

