Supporting Information

One-pot, in situ synthesis of ZnO-carbon nanotube-epoxy resin hybrid nanocomposites

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Experimental Details

Materials Diethylzinc (1.0 M in hexanes) and acetone (HPLC grade, H_2O max 0.1%) were purchased from Sigma Aldrich. The acetone was dried with molecular sieves before using. The epoxy resin used comprised of a bisphenol-A resin ($M_w < 700$) (ARALDITE LY 556, Vantico) and an aromatic amine hardener (ARALDITE HY 932, Vantico); both components were purchased from commercial suppliers and used as received. All manipulations of diethylzinc solution were carried out using standard Schlenk techniques. After hydrolysis was complete, further steps were carried out in air.

Instrumentation

Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA machine, with heating from 50 to 800°C, in dry air, at a heating rate of 10°C/min. Optical absorption spectra were collected on a Perkin Elmer Lamda 950 spectrophotometer; the sample was mounted on a glass slide. High-resolution Transmission Electron Microscopy (HRTEM) was carried out using a JEOL 2010 microscope at an operating voltage of 200 kV. Thin slices of the nanocomposite samples were prepared using a microtome and mounted on 300-mesh carbon-coated copper grids (Agar Scientific). ^1H and ^{13}C NMR spectra were collected on a Bruker AV-400 machine, using deuterated chloroform as the solvent. UV-vis absorbance spectra were recorded on a Perkin Elmer UV-Visible Lambda 2 spectrophotometer Thermal conductivity analyses were performed using an LFA 447 nanoflash. The apparent viscosity was measured using a Paar Physica MCR Rheometer.

X-ray Diffractometry (XRD) was performed using an X'Pert Pro diffractometer (PANalytical B. V., The Netherlands) and X'Pert Data Collector software, version 2.2b. The instrument was used in the theta/theta reflection mode, fitted with a nickel filter, 0.04 radian Soller slit, 10 mm mask, 1/4 ° fixed divergence slit, and 1/2 ° fixed antiscatter slit. Samples were analysed with a step size of 0.0041778 °, at a scanning speed of 0.027852 $°s^{-1}$. The data was analysed using the X'Pert HighScore software, version 2.2b: the full-width, half-maximum of the peaks of interest were calculated by fitting to a Pseudo-Voigt function and the particle sizes were calculated using the in-built Scherrer calculator, with a shape factor of 0.89 (spheres).

Nanocomposite preparation

1 (5wt% of ZnO): To a solution of Araldite LY556 (5.91 g) in acetone (5 mL), a solution of $ZnEt_2$ (5.00 mL of a 1 M solution in hexane, 5.00 mmol) was added dropwise, under vigorous stirring. The mixture was stirred for 1 hour. Then, a solution of acetone (2 mL) and H_2O (0.18 mL, 10.0 mmol) was added dropwise and the mixture was stirred for 20 h, at room temperature. After this time, the mixture was placed in a sonicator bath for 5 h. The volatile compounds were evaporated *in vacuo*, for 1 h at 50 ^oC. An aromatic amine hardener (HY932, 1.89 g, 100:32 resin:hardener weight percent ratio) was added and the mixture was poured into a mould. The mixture was cured at 120 ^oC for five h. The loading of ZnO in the composite was estimated to be approximately 5 wt% with respect to the precursor compound.

2 (10 wt% of ZnO): The same procedure as for **1** was followed except the quantities used were: Araldite LY566 (5.06 g), acetone (10 mL), $ZnEt_2$ (9.10 mL, 9.10 mmol), acetone (2 mL), water (0.33 mL) and HY932 (1.62 g).

3 (20 wt% of ZnO): The same procedure as for **1** was followed except the quantities used were: Araldite LY566 (2.47 g), acetone (10 mL), $ZnEt_2$ (10 mL, 10 mmol), acetone (2 mL), water (0.36 mL) and HY932 (0.79 g).

4 (30 wt% of ZnO): The same procedure as for **1** was followed except the quantities used were: Araldite LY566 (1.44 g), acetone (10 mL), $ZnEt_2$ (10 mL, 10 mmol), acetone (2 mL), water (0.36 mL) and HY932 (0.46 g).

5 (40 wt% of ZnO): The same procedure as for **1** was followed except the quantities used were: Araldite LY566 (1.85 g), acetone (20 mL), $ZnEt_2$ (20 mL, 20 mmol), acetone (5 mL), water (0.72 mL) and HY932 (0.59 g).

Attempted Synthesis using $ZnCl_2$

A solution of $ZnCl_2$ (0.273 g, 2.0 mmol) in MeOH (20 mL) was added to a mixture of Araldite LY566 (0.974 g) in $CHCl_3$ (20 mL) and NaOH (0.400 g, 10.0 mmol) in MeOH (100 mL) and the resulting suspension stirred for 3 h. The solution was concentrated *in vacuo* and acetone (20 mL) added. The white precipitate was filtered and the volatiles removed from the resulting yellow solution *in vacuo* to yield a yellow powder; ^{1}H NMR ($CDCl_3$): $\delta = 7.11$ (2H, d, $J = 7.0$ Hz, Ar), 6.80 (2H, d, $J = 7.0$ Hz, Ar), 4.13 (1H, q, $J = 4$ Hz, $(ArOCH_2)_2CH$), 3.98 (2H, m, $ArOCH_2$), 3.55 (2H, m, $ArOCH_2CH(OH)R$), 3.39 (3H, s, CH_3O-), 2.85 (1H, COH), 1.61 (3H, s, $(Ar)_2CCH_3$) ppm.). ^{13}C NMR: δ 156.3 (C_6H_4), 143.4 (C_6H_4), 127.7 (C_6H_4), 113.8 (C_6H_4), 77.2 (CH), 73.5 (CH_2), 68.8 (CH), 68.7 (CH_2), 59.2 (CH_3), 41.6 (CH), 30.9 (CH_3). UV-Vis (EtOH): 277, 248 nm. MS-electron ionization (EI) m/e: 404 $[M-284]^+$

Ex situ coating of ZnO onto acid-oxidised carbon nanotubes

Acid-treated CVD-grown multi-walled CNTs were prepared according to Verdejo et al (Chem Comm, 5, 513, 2007). Around 75 mg of CNTs were dispersed in dry acetone (20 ml), 1M $ZnEt_2$ in hexane (0.9 mL, 0.9 mmol) was added dropwise, and the mixture stirred for 1h. 0.5 mL of acetone, containing 32.4 µL of H_2O (1.8 mmol) was added dropwise, and the mixture stirred for another 14 hours at room temperature.The mixture was placed in a bath sonicator for 6 hours. Finally, volatiles were evaporated under vacuum for 14 hours at 60 ^oC, and the resulting solid washed with 15mL of EtOH, sonicated and centrifugated to a black solid. Yield: 91.1 mg, 62 %. Base-washed MWCNT were prepared according to Verdejo et al (Chem Comm, 5, 513, 2007), and coated with ZnO following a similar procedure.

In situ coating of ZnO onto acid-oxidised carbon nanotubes in epoxy

A mixture of Araldite LY566 (3.1 g) and 11 g of acid-treated CNT suspension in acetone (0.37 wt%) was stirred at room temperature for 1 hour. A 1M solution of $ZnEt_2$ in hexane (0.51 mL, 0.51 mmol) was added dropwise with vigorous stirring. After stirring overnight at room temperature, 1 mL of acetone containing 18.4 µL H_2O (1.02 mmol) was added dropwise. The mixture was then stirred for 3 hours and placed in a bath sonicator for 1 hour. Volatiles were evaporated under vacuum for 1 hour at 50^{o}C. An aromatic amine hardener (HY932, 1.89 g, 100:32 resin:hardener weight percent ratio) and the mixture was poured into a mould. The mixture was then cured in an oven at 140 ^oC for four hours. The loading of CNTs and ZnO was estimated to be about 1 wt% in each case.

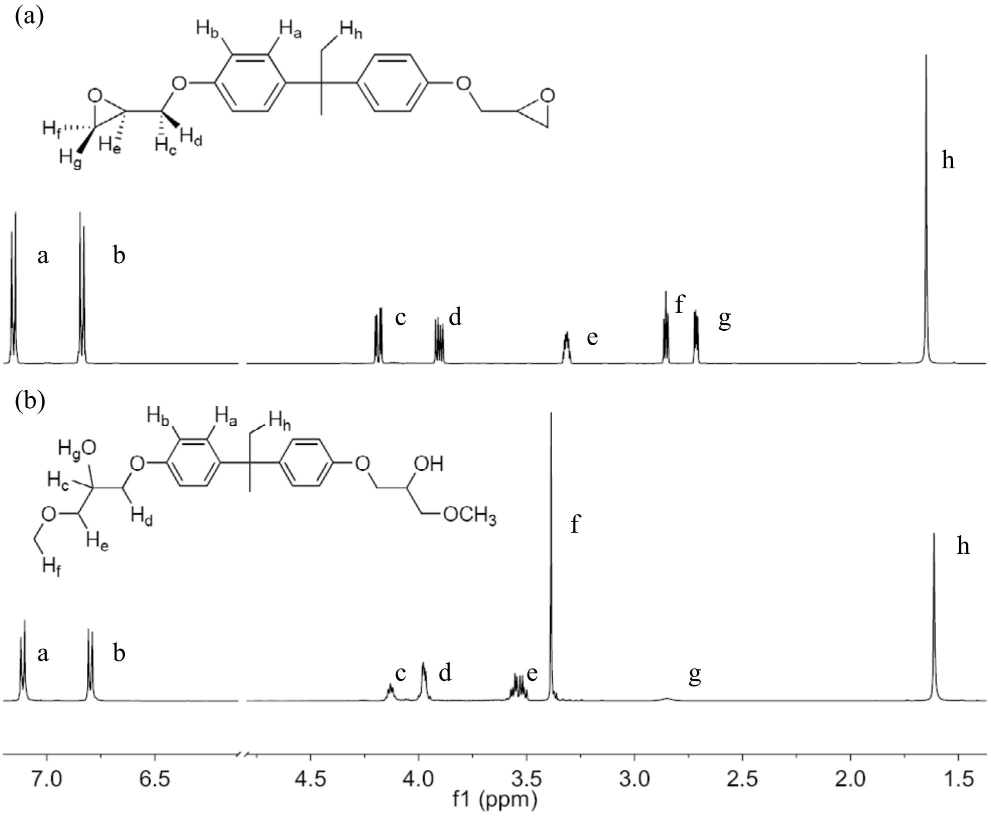

Fig. S1 Comparison of ^{1}H NMR spectra ($CDCl_3$) of (a) Araldite LY566 and (b) product of reaction with ZnCl2, NaOH and MeOH. The change in the chemical shifts of the protons associated with the epoxide functionality, as well as the appearance of the MeO- and –OH resonances ($\delta = 3.39$ and 2.85 ppm respectively), demonstrate the opening of the epoxide rings by methoxide generated *in situ*.

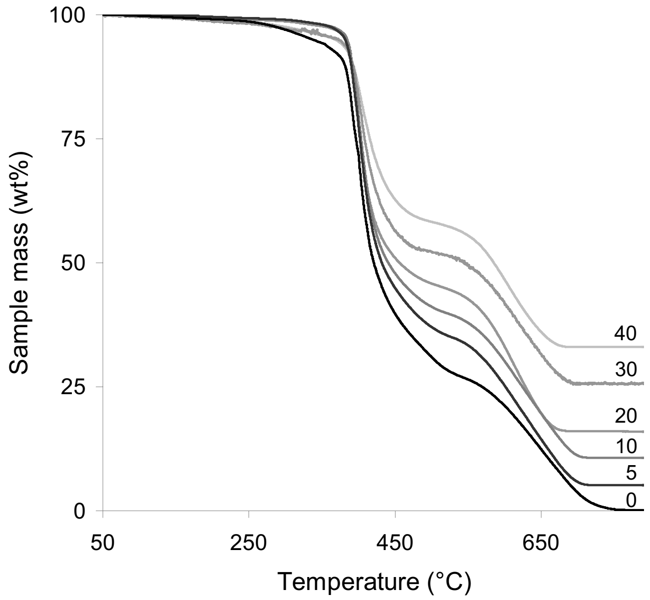

Fig. S2 Thermogravimetric data confirms the intended ZnO content of the nanocomposites, and shows that the thermal degration is unaffected.

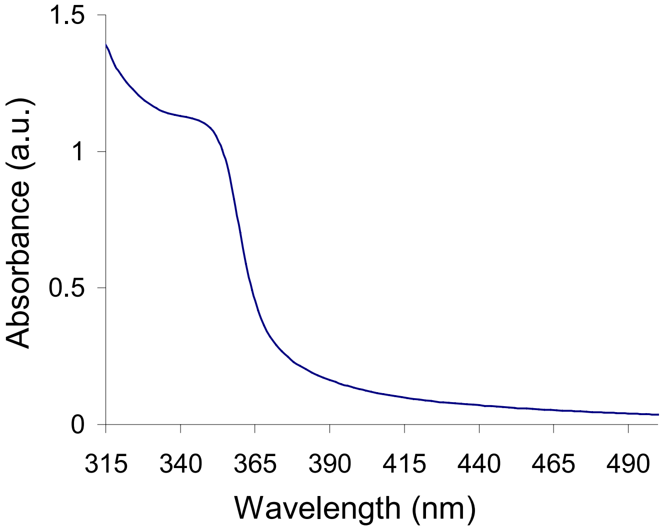

Fig. S3: UV-vis spectrum of ZnO-epoxy nanocomposite: the peak at 350 nm confirms formation of ZnO

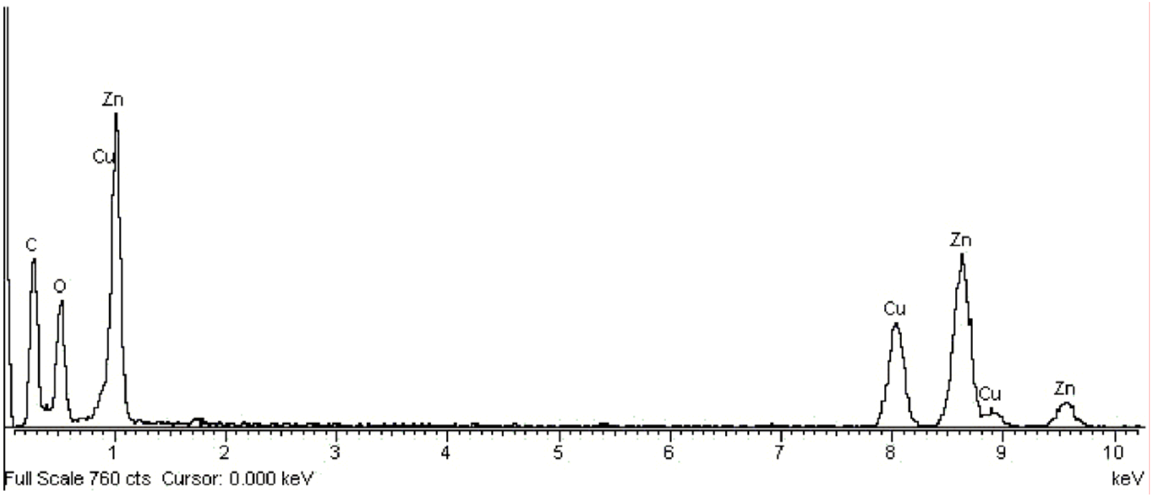

Fig. S4 Representative Electron Dispersive X-ray spectrum for the nanocomposite, showing only Zn, O, and C (Cu results from the TEM grid).