

## Electronic Supplementary Information

### Electrochemical activation of polymer chains mediated with radical transfer reactions

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#### Experimental methods

**Materials.** 4-bromobenzenediazonium tetrafluoroborate ( $\text{BrPhN}_2^+\text{BF}_4^-$ , 96%) and tetraethylammonium hexafluorophosphate ( $\text{Et}_4\text{NPF}_6$ , 98%) were purchased from Alfa Aesar and used as received. Polyethylene glycol (PEG, molecular weight: 2000 Da) was purchased from Fluka and used as received. Polyvinyl butyral (PVB) was received from Chang Chun Group, Taiwan (Product code: PVB B18FS). Polybenzoxazine PBz) was prepared in our laboratory (Li *et al.*, *Adv. Mater. Interfaces* **2015**, *2*, 1500065). The number-averaged molecular weight and polydispersity of the utilized PBz are about 6,800 Da and 6.2, respectively. Carbon nanotubes (CNT, 97%) were received from the Carbon Nanotube Co. (Incheon, Korea). The used CNTs have an average diameter of about 20 nm and a length in 10-100  $\mu\text{m}$ . Laboratory made reduced graphene oxide (rGO, *Chem. Mater.* **2014**, *26*, 2983-2990) was from Professor W. S. Hung (National Taiwan University of Science and Technology, Taiwan).

**Measurements.** Raman spectra were recorded with a Renishaw InVia Raman spectrometer using He-Ne laser of 632.8 nm as the incident radiation. High-resolution transmission electron microscopy (HRTEM) was conducted with a JEOL JEM-2010 HRTEM. X-ray photoelectron spectroscopy (XPS) measurements were recorded with an XPS instrument from Thermo VG-Scientific Co. (Model: Sigma Probe) using a  $\text{Mg-K}\alpha$  line as the radiation source. TGA measurements were carried out with a Thermal Analysis (TA) TGA Q-500 instrument under a nitrogen atmosphere. The heating rate is  $10\text{ }^\circ\text{C min}^{-1}$  and the nitrogen gas flow rate is  $100\text{ mL min}^{-1}$ . Differential scanning calorimetric (DSC) thermograms were recorded with a TA DSC Q-100 instrument under a nitrogen flow at  $50\text{ mL min}^{-1}$  and a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Atomic force microscopy (AFM) images were recorded with a Nano Scope IIIa instrument from the Digital Instruments (Germany). The measurements were carried out in tapping mode at a scan rate of 0.5 Hz with a  $125\text{ }\mu\text{m}$  noncontact silicon cantilever (model NCH-50). The rGO samples dispersed in methanol ( $0.1\text{ mg mL}^{-1}$ ) were applied to freshly cleaved mica surfaces by spin coating. A potentiostat/galvanostat instrument from Metrohm (Autolab PGSTAT204) was employed for electrochemical reactions.

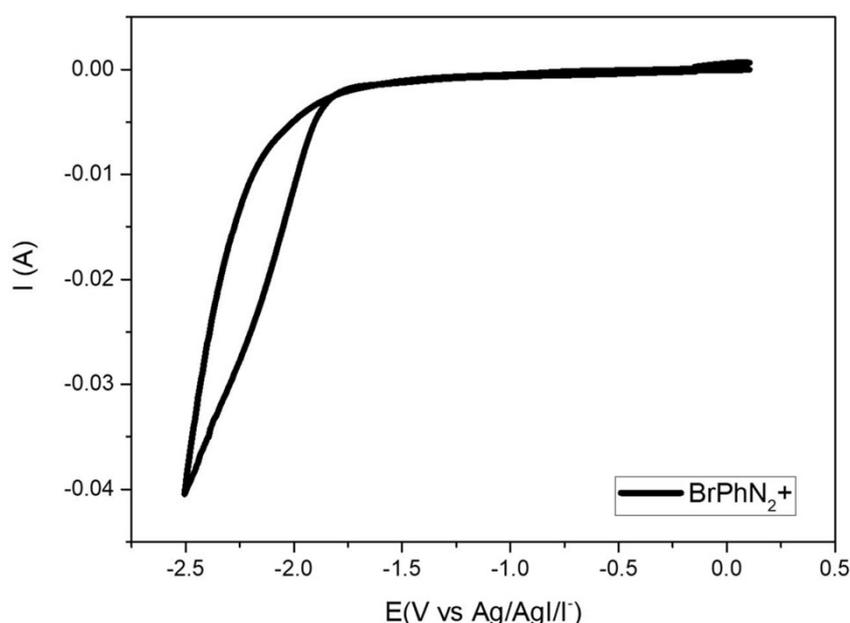
**Cyclic voltammetry (CV) analysis.** CV tests on  $\text{BrPhN}_2^+$  have been carried out (Figure S1) according to the reported method (Wang *et al.*, *Macromolecules* **2017**, *50*, 7872–7879). A general five-necked electrochemical reaction cell equipped with Pt disk working electrode (WE), Pt wire counter electrode (CE) and  $\text{Ag|AgCl|0.1 M } n\text{-Bu}_4\text{NI}$  in *N,N*-dimethylformamide (DMF) reference electrode (RE). The solution of  $\text{Et}_4\text{NPF}_6$  in DMSO (0.1 M) was employed as the electrolyte and reaction medium.  $\text{BrPhN}_2^+\text{BF}_4^-$  was dissolved in the electrolyte with a concentration of 7 mM. The RE was calibrated against the saturated calomel electrode (SCE) scale by measuring potential difference ( $\Delta E$ ) between a SCE at scan rate ( $v$ ) of  $100\text{ mV s}^{-1}$ .

**Electrochemical reaction between  $\text{BrPhN}_2^+$  and CNT.** A five-neck electrochemical reaction cell equipped with the above-mentioned electrodes was employed. After charging  $\text{Et}_4\text{NPF}_6$  (0.220 g, 0.8 mmol) and

$\text{BrPhN}_2^+\text{BF}_4^-$  (0.016 g, 0.06 mmol) into the cell, a CNT (0.03 g) dispersion in DMF (10 mL) was added. The solution of  $\text{Et}_4\text{NPF}_6$  in DMSO (0.01M) was employed as the electrolyte and reaction medium.  $\text{BrPhN}_2^+\text{BF}_4^-$  (0.018 g) and CNT (0.05 g) were charged into a 25 mL electrolyte. The reaction was carried out at a fixed applied potential of -2.3 V vs. SCE, which is equal to the cathodic peak potential for  $\text{BrPhN}_2^+\text{BF}_4^-$ . The reaction was carried out at room temperature for 3 h under nitrogen with suitable potential being applied. The CNTs were precipitated from methanol, collected with filtration, and dried under vacuum at room temperature. The obtained product is bromophenyl-functionalized CNT (BrPh-CNT).

**Electrochemical activation of polymer chains for preparation of polymer-CNT nanohybrids.** Similar to the method for preparation of BrPh-CNT, PBz (0.01 g) was added to the reaction cell. The collected CNT is PBz-functionalized CNT (PBz-CNT). A polymer/CNT weight ratio of 1/3 is applied to provide enough polymers chains chemically adding to CNTs. The other two samples (PEG-CNT and PVB-CNT) were obtained with the same manner. Preparations of each polymer-CNT nanohybrid samples have been repeated for 3 times. The results support to good reproducibility of the synthesis approaches.

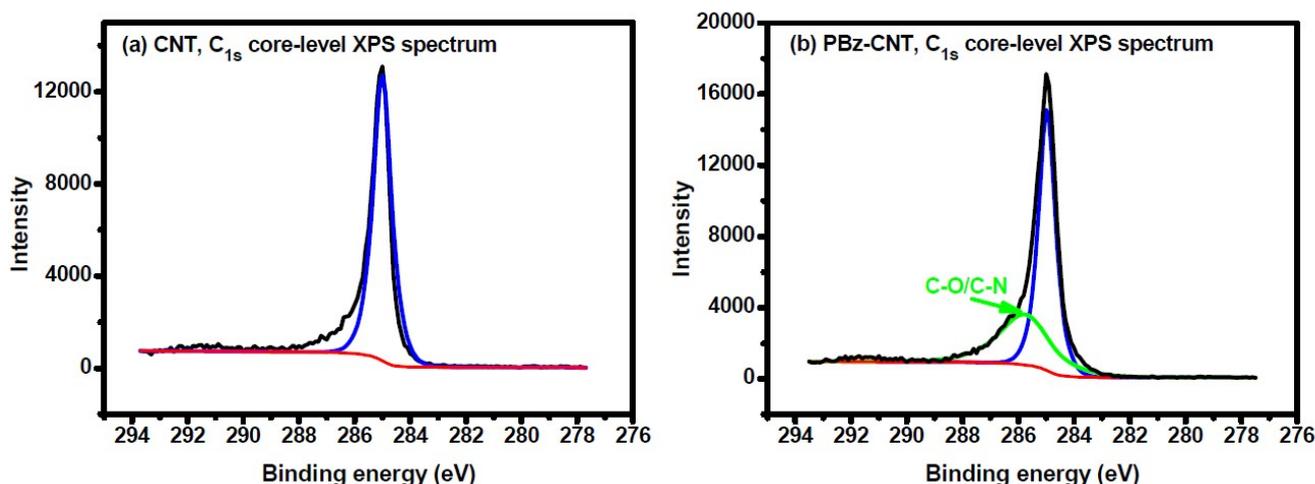
**Electrochemical activation of polymer chains for preparation of PBz-rGO nanohybrids.** Similar to the method for preparation of PBz-CNT, rGO was employed to replace CNT. The obtained sample is PBz-functionalized rGO (PBz-rGO). Preparation of PBz-rGO nanohybrid sample has been repeated for 3 times. The results support to good reproducibility of the synthesis approaches.



**Figure S1.** Cyclic voltammety curve recorded on a  $\text{BrPhN}_2^+\text{BF}_4^-$  solution in the employed electrolyte (7 mM). WE: Pt disk; CE: Pt wire; RE: Ag|AgCl|0.1 M  $n\text{-Bu}_4\text{NI}$  in DMF; electrolyte:  $\text{Et}_4\text{NPF}_6$  in DMSO (0.1 M).

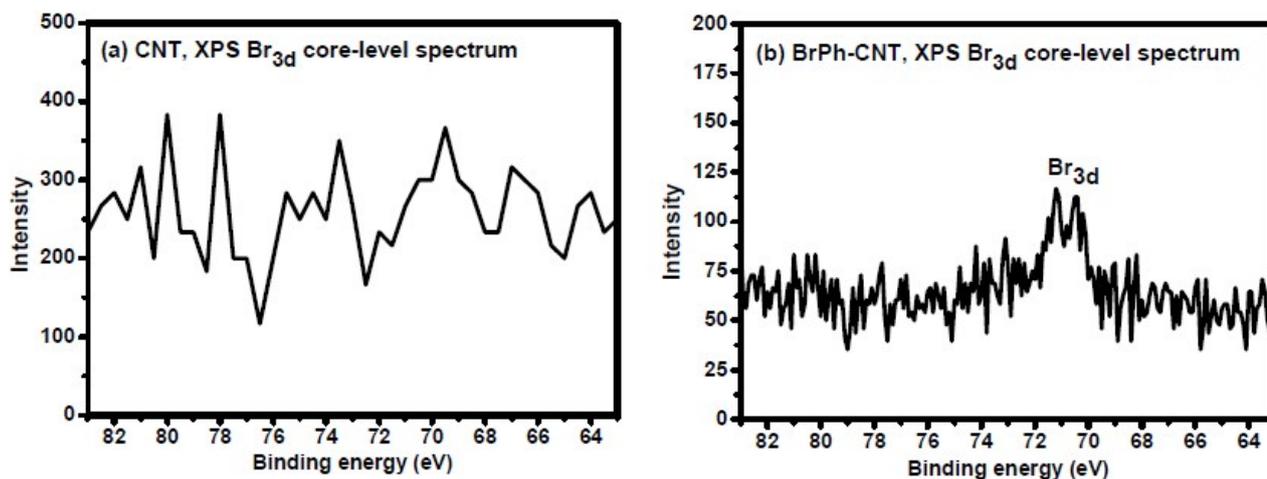
## Supporting figures and discussion mentioned in the main text

For **PBz-CNT hybrid**, the presence of PBz chains is also supported with the changes in the  $C_{1s}$  core-level XPS spectra (**Figure S2**). In addition to the peak at 285.0 eV observed with the neat CNT sample, PBz-CNT demonstrates another peak at about 286.0 eV corresponding to C-O and C-N groups, which are associated to the chemical structure of PBz.

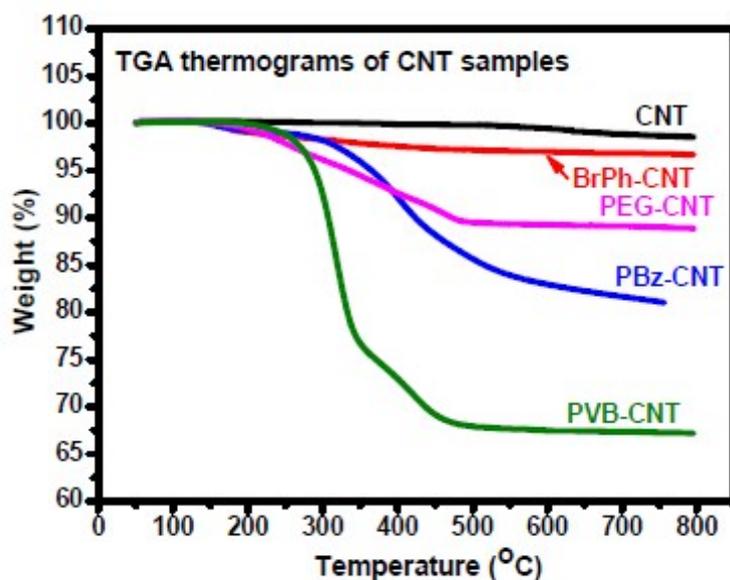


**Figure S2.**  $C_{1s}$  core-level XPS spectrum of (a) CNT and (b) PBz-CNT. The appearance of the C-O/C-N signal in the spectrum of PBz-CNT supporting to the radical addition reaction of PBz chains toward CNTs.

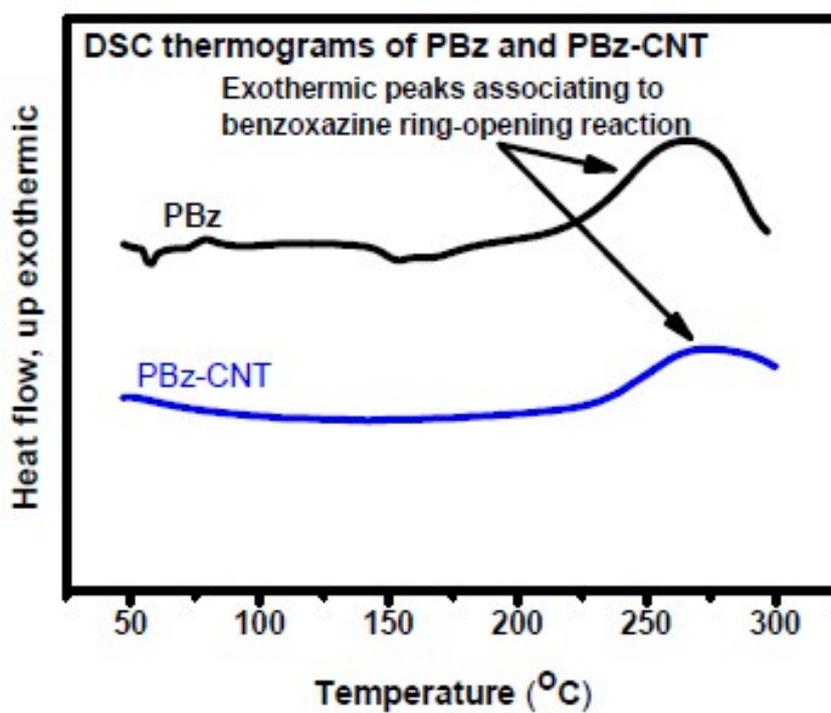
The **BrPh-CNT sample**, which was collected from the polymer-free reaction system, shows a  $Br_{3d}$  signal at about 70 eV (**Figure S3**), indicating that BrPh-CNT possesses bromide atoms due to occurrence of the radical addition reaction of bromophenyl radicals to CNTs.



**Figure S3.**  $Br_{3d}$  core-level XPS spectrum of (a) CNT and (b) BrPh-CNT. The appearance of the Br signal in the spectrum of BrPh-CNT, supporting the radical addition reaction of bromophenyl radicals toward CNTs.

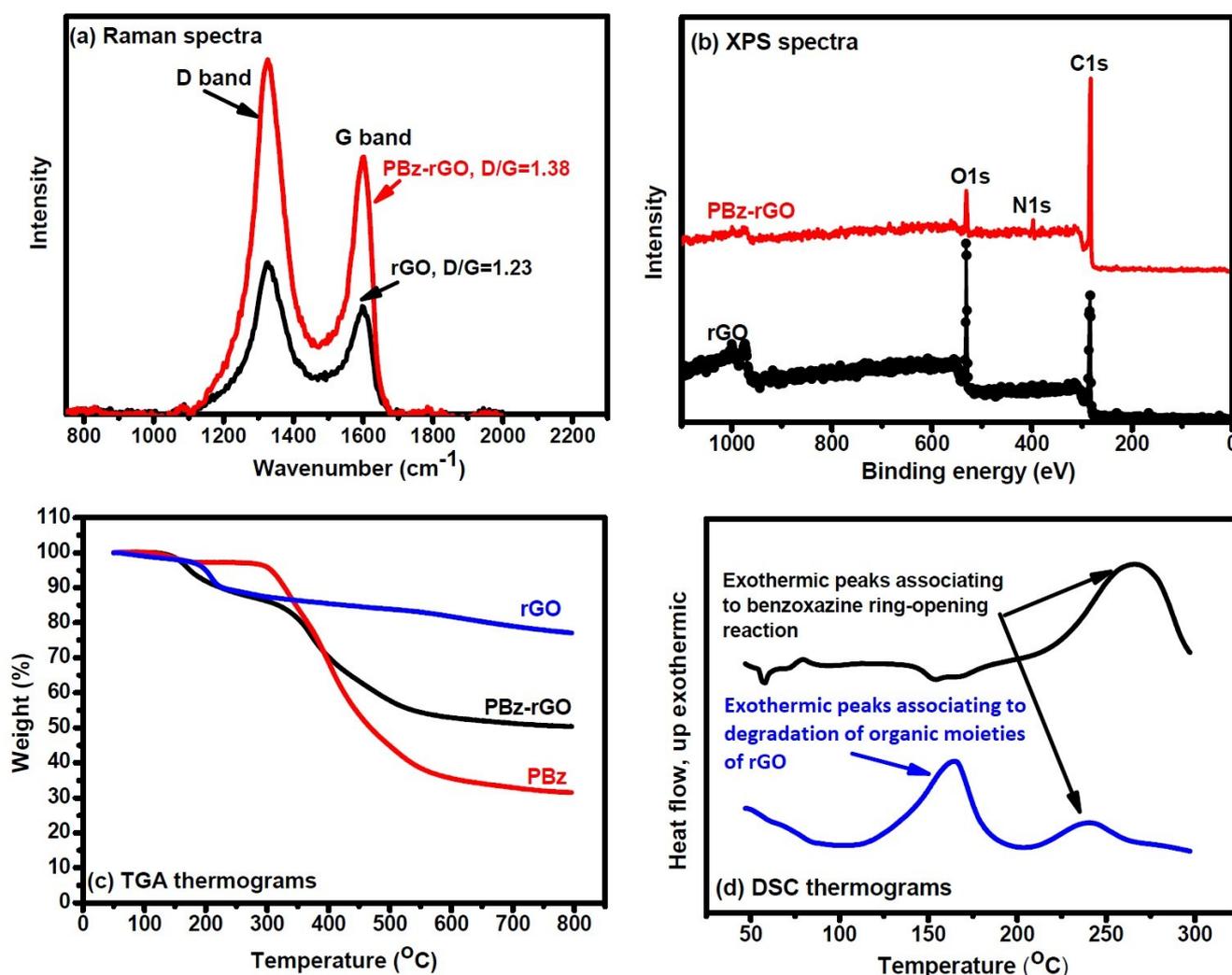


**Figure S4.** TGA thermograms of the neat CNT and the prepared polymer-functionalized CNT nanohybrids.



**Figure S5.** DSC thermograms of the neat CNT and PBz-CNT nanohybrid. The exothermic peaks are associated to the thermally-induced ring-opening reaction of benzoxazine groups of PBz chains.

**Characterization of PBz-rGO.** rGO shows D band and G band peaks with a D/G ratio of 1.23 in Raman analysis. As PBz-rGO also exhibit similar D-band and G-band peaks at similar Raman shifts with a D/G ratio of 1.38, the increase in the D/G ratio supports to the chemical reaction between activated PBz chains and rGO at the  $sp^2$ -hybrid carbon groups of rGO. The N signal appearing in the wide-scanning XPS spectrum of PBz-rGO indicates the presence of benzoxazine groups in the sample. Based on the high C/O ratio of PBz chains ( $C/O = 10.3$ ), PBz-rGO shows a relatively high C/O ratio (7.8) compared to rGO (2.8). The spectral analysis result is coincident to the experimental work of incorporation of PBz chains to the rGO surfaces. In TGA measurement, PBz-rGO shows a two-stage weight loss. The first stage weight loss occurring at about 200 °C corresponds to the rGO fraction and the second stage at about 400 °C is attributed to the degradation of PBz chains. Based on the char yields of the samples in TGA measurements, the PBz weight fraction of PBz-rGO is about 43 wt%. Like PBz-CNT, PBz-rGO still exhibits an exothermic peak in DSC measurement associating to the ring-opening reaction of benzoxazine groups. The results support the successful incorporation of PBz chains to rGO and PBz-rGO still possesses benzoxazine ring groups. An additional exothermic peak appearing at relatively low temperature has been assigned to the degradation of organic moieties of rGO.



**Figure S6.** Spectral characterization and thermal analysis on rGO and PBz-rGO. (a) Raman analysis, (b) XPS analysis, (c) TGA measurements, and (d) DSC measurements.