Supplementary Information

New design of organic radical batteries (ORBs):
Carbon nanotubes buckypaper electrode functionalized by electrografting

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Contents
S1 Materials and techniques
S2 Monomer synthesis
S3 Electrografting of the monomer
S4 Polymer oxidation
S5 Bucky paper preparation
S6 TGA analysis
S7 Electrochemical measurements
S8 BP functionalized by chemical crosslinking

S1 - Materials and techniques

Materials: The multiwalled carbon nanotubes were purchased from Nanocyl and used without any further purification. All other reagents, including 4-Hydroxy-TEMPO, (1-bromoethyl) benzene, Cu₀ powder (75 μm), CuBr, CuBr₂, N,N,N’,N’’,N’’’-pentamethyldiethylenetriamine (PMDETA), anisole, triethylamine and acryloyl chloride were purchased from Aldrich. All solvents were purchased from Aldrich with the highest purity available and dried before use. Electrolyte LP-71 (1 M LiPF₆ in EthyleneCarbonate:Diethylcarbonate:Dimethylcarbonate 1:1:1, EC:DEC:DMC) was supplied by Merck.

Techniques:

NMR spectra were recorded on a Bruker instrument operating at 250 MHz. The TGA measurement was carried out under a stream of O₂ at a heating rate of 10°C/min using a TG/DTA6300 instrument. The microscopic features of the products were characterized by scanning electron microscopy (SEM, JEOL–6701F) and transmission electron microscopy (TEM, JEM-2100). For TEM analysis, the modified buckypaper was dispersed by sonication in acetonitrile and drop cast on a carbon-film-coated copper grid.

S2 - Monomer synthesis
Synthesis of the 1-Phenylethylhydroxy-TEMPO Alkoxyamine (1-(1-Phenylethoxy)-2,2,6,6-tetramethylpiperidin-4-ol), 1.:  
A Schlenk flask was charged with hydroxy-TEMPO (7.89 g, 45.8 mmol), copper powder (11.6 g, 183 mmol), copper bromide (52.5 mg, 0.366 mmol), and 50 mL of anisole. The solution was degassed by bubbling with nitrogen for 30 min, and then PMDETA (76.6 µL, 0.366 mmol) was added. After 5 min, (1-bromoethyl)benzene (5 mL, 36.6 mmol) was added, and the solution was then heated to 40°C for 18 h. The solution was filtered and concentrated under vacuum. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (95/5 gradually increasing to 5/5) to afford 8.15 g (yield=80.2%) of a white solid. 1H NMR (CDCl3) δ: δ = 7.34-7.18 (m, 5H, Ar-H); 4.77 (q, J = 6.7 Hz, 1H, CHON); 3.75-4.08 (m, 1H, CHOC(O)); 1.88-1.50 (m, 4H, 2×CH2); 1.48 (d, J = 6.7 Hz, 3H, CH3CHON); 1.33 (s, 3H, CH3); 1.27 (s, 3H, CH3); 1.13 (s, 3H, CH3); 0.66 (s, 3H, CH3) ppm.

Synthesis of the (4-acryloyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (APEOT), 2.:  
4. 1-Phenylethylhydroxy-TEMPO alkoxyamine (1) (3 g, 10.9 mmol) The reaction mixture was cooled to 0°C and triethylamine (1.8 mL, 13.08 mol) was added. Acryloyl chloride (1.08 mL, 0.013 mol) was added drop-wise via an addition funnel. The reaction was allowed to proceed for 6 h. The product mixture was washed with basic water (pH = 9), filtered and concentrated under vacuum. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (95/5 gradually increasing to 5/5) to afford 2.69 g (yield~75%) of a white solid. 1H-NMR (300 MHz, CDCl3): δ = 7.34-7.18 (m, 5H, Ar-H); 6.35 (d, 1H, =CH); 6.04 (d, 1H, HHC=C); 5.53 (d, 1H, HHC=C); 5.11-4.98 (m, 1H, CHOC(O)); 4.77 (q, J = 6.7 Hz, 1H, CHON); 1.88-1.50 (m, 4H, 2×CH2); 1.48 (d, J = 6.7 Hz, 3H, CH3CHON); 1.33 (s, 3H, CH3); 1.27 (s, 3H, CH3); 1.13 (s, 3H, CH3); 0.66 (s, 3H, CH3) ppm.
S3 - Electrografting of the monomer

**Methods:** All the electrografting experiments were carried out under dry nitrogen. Dimethylformamide (DMF, Aldrich) was dried over P₂O₅ and distilled under reduced pressure. Tetraethylammonium perchlorate (TEAP, Fluka) was heated in vacuum at 80°C for 12 h prior to use. The BP electrodes were previously dried overnight at 150°C under vacuum, just before use. Electrografting experiments were carried out in a three-compartment cell equipped with a Pt pseudo-reference electrode, a Pt counter-electrode, and a working electrode (stainless steel or BP) with a PAR EG&G potentiostat (Model 273A). All electrochemical experiments were carried out in a glove box under a dry and inert atmosphere (N₂). All the electrografted films of APEOT were prepared by, respectively, two or three scans of the potential between the initial potential of the open circuit and the potential at the top of the first peak, where it is kept for 5 s. APEOT was dissolved in dry dimethylformamide (0.5-1.5 M) containing tetraethylammonium perchlorate (TEAP) (0.05 M) as a conducting salt. The water content of this solution was measured by the Karl Fischer method (Tacussel aqua-processor) and ascertained to be lower than 10 ppm.
**S4 Polymer oxidation**

Electron spin resonance (ESR) spectroscopy is used to follow the formation of the nitroxide by heating APEOT in DMF at 120°C in the ESR cavity. ESR studies were carried out with a Miniscope MS400 (Magnettech, Berlin, Germany) benchtop spectrometer working at X-band with a modulation amplitude of 2G, a sweep width of 68G, a sweep time of 30 s, and a microwave power of 10mW. The temperature was adjusted with the temperature controlled unit TC H03 (Magnettech), providing an electronic adjustment in steps of 0.1°C in the range of -170°C to 250°C. The solutions were ramp heated to 120°C for the ESR measurements.
The deprotection of PTMPM was quantified using UV-Vis spectroscopy by taking advantage of the color change that occurred after oxidation. First the molar absorptivity of the repeat radical unit was determined by analyzing TEMPO-OH at varying concentrations. This was achieved utilizing Beer’s Law to relate the absorbance to molar absorptivity. To determine the conversion of radical sites, alkoxyamine-based polymer was dissolved in tert-butylbenzene (c = 0.01 g/mL), and the mixture was heated to 120°C for 5 h with a reflux condenser. During the reaction air was bubbled through the solution. The solvent was evaporated, and the crude mixture was dissolved in a small amount of CH2Cl2. A mixture of pentane/Et2O (1:1 v/v, ca. 25 mL) was added slowly, and the precipitate was collected. This procedure was repeated, and the nitroxide-based polymer was isolated as a red solid after drying in vacuo. The samples were filtered and characterized by UV-Vis and the absorbance was related through Beer’s Law to obtain the concentration of radical sites. It is important to note that PTMPM is a white powder and colorless in the solution. As such, there is no absorbance in the UV-Vis spectra of the PTMPM precursor polymers.
Figure S4b: (A) calibration curve of molar absorptivity of the radical unit determined by
UV–vis (wavelength: 461 nm) of TEMPO-OH at varying concentrations. (B) Evolution of
oxidation yield during the time estimated by UV–vis spectroscopy.

The preparation of the polymer brush bearing the redox-active TEMPO on modified
electrodes (flat stainless steel substrate or BP) was achieved by heating the electrode in DMF
at 120°C under air during 24h.

S5 - Buckypaper (BP) preparation

CNTs were dispersed in n-butanol with the aid of sonications. Typically, 200 mg of CNTs
were added to 1 liter of solvent and the dispersion sonicated for more than 12 h using typical
bath sonicator (power = 100w, frequency = 42kHz). The suspension presented no large
agglomerate and was found to be stable for a duration of 1 to 2 h. For the preparation of the
buckypaper electrodes, the freshly prepared CNT dispersion was vacuum filtered (Millipore
system) using a Nylon filter (pore size = 0.45µm). The amount of the filtered suspension
defines the mass and areal loading of the BP, with typical loadings of 2 mg/cm².

Figure S5: Morphology of the pristine buckypaper.

S6 - TGA analysis of modified buckypaper
S7 - Electrochemical measurements

Cyclic voltammogram (CV) of PTMA brush-stainless steel electrode: In the electrochemical cell, a PTMA brush-modified stainless steel electrode and platinum plate were used as working and counter electrodes, respectively. The distance between the working and the counter electrode was fixed at 2 cm. For the cyclic voltammogram (CV), cells were observed between 0.0 and 0.9 V at a scan rate of 5.0 mV/s, in acetonitrile using Ag/AgNO$_3$ as reference and 0.1 M of TEAP as an electrolyte.

Battery tests of PTMA brush-modified buckypaper: Coin cells (CR2032) were used and assembled in an Ar-filled glove box (MBraun). Measurements were carried out on the modified surface after generation of radical species by thermal treatment in DMF at 120°C overnight. After rinsing with DMF to remove the non-grafted polymer, and in acetonitrile, the BP electrodes were dried overnight at 100°C under vacuum, just before use. PTMA brush-modified buckypaper and lithium metal foil were used as the cathode and anode, respectively. A Celgard separator soaked with 100 µl of LP71 (1 M LiPF$_6$ in EC:DEC:DMC 1:1:1) electrolyte was placed in-between. CV was carried out at a scan rate of 0.5 mV/s over the potential window of 2.7 - 3.9 V(vs. Li/Li$^+$). Charge–discharge curves were recorded at C/10 between 2.7 and 3.9 V (vs. Li/Li$^+$) with a Biologic VMP3 multichannel potentiostat. For the calculation of the energy density of polymer brushes, the mass of polymer brushes on the BP electrode was determined by TGA analysis.
S8- BP functionalized by chemical crosslinking

Cross-linked PTMA: Functionalized buckypaper prepared by chemical crosslinking of APEOT (1 M) was performed in DMF using EGDA (0.1 M) as crosslinking agent and V70 (0.02 M) as an initiator. The mixture was filtered first through the buckypaper filter, then the electrode was heated under inert atmosphere. To enhance the weight fraction of PAPEOT, the cycle filtration/thermal treatment was repeated three times. Electrochemical measurements were carried out on the cross linked surface after generation of radical species by thermal treatment in DMF at 120°C overnight using the same protocol reported above.

Figure S8a: Typical CV for coin-cells with crosslinked PTMA-modified buckypaper and lithium metal foil used as the cathode and anode, respectively, at a scan rate of 0.5 mV/s.
Figure S8b: SEM analysis of the PTMA-g-CNT materials obtained by chemical crosslinking using filtration

**Note:** The formula weight-based theoretical capacity (in mAh g\(^{-1}\)) was calculated according to 1000 nFM\(^{-1}\) (3600)\(^{-1}\), where n, F and M are the stoichiometric number of electrons, the Faraday constant and the molar mass of the pendant-TEMPO unit, respectively. The redox capacity (in mAh g\(^{-1}\)) was obtained by employing 1000 Qm\(^{-1}\) (3600)\(^{-1}\), where Q and m are the charge passed in electrolysis and the loading weight of the polymer, respectively. The 1 C rate is defined as the current density at which the charging or discharging of the cell takes 1 h.