Supplementary Information for "Ionic liquid–carbon nanotube composites as scaffolds in the determination of tetrachlorobenzene: electrochemical impedance technique"

Experimental Section

Chemical Reagents. 1,2,4,5-tetrachlorobenzene (TeCB) was purchased from 125 Market ST. New Haven, CT 06513, USA. N-ethylbimethylpropylammonium bis(trifluoro- methylsolfonyl)imid ($[N_{2113}][NTf_2]$) was supplied by Merck KGaA (Darmstadt, Germany). Multi-walled carbon nanotubes (MWCNT) used in the experiments was "bamboo-like" MWCNT manufactured by NanoLab (Brighton, MA) with 30±10 nm in diameter and 5 - 20 nm in length (purity > 95%). Other reagents and solvents were commercially available from Sinopharm Chemical Reagent Co., Ltd (China) with analytical grade and used as received without further purification. All experiments were carried out at temperature of 23±3°C.

Apparatus. Electrochemical experiments were all performed with screen printed carbon electrode (SPCE) (ref. 110, DropSens, Edificio Severo Ochoa, Spain). The electrochemical cell consists of a three-electrode arrangement with a carbon (4 mm diameter) serving as the working electrode, with a carbon used as the counter electrode. A silver pseudoreference electrode completed the circuit. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a CHI660D potentiostat (Shanghai, China). Prior to the experiments, the ionic liquid was purged under vacuum (Edwards high-vacuum pump, model ES 50) for at least 24 hrs to remove impurities (trace of atmospheric oxygen or moisture). The impedance spectra were recorded within a frequency range of 1 Hz-100 kHz. The amplitude is 5 mV. The scan rate is 100 mV s^{-1}.

The morphology of ionic liquid-carbon nanotubes on electrode surface was verified by field-emission scanning electronic microscope (FESEM, Quanta 200 FEG, FEI Company, USA). X-ray photoelectron spectroscopy (XPS) was carried out by electron spectroscopy for chemical analysis 2000. Fourier transform infrared (FT-IR) spectrum was recorded on a Nexus-870 spectrophotometer. The Raman spectrum was recorded with a Jobin Yvon LABRAMHR spectrometer with argon ion laser beam focusing on the sample surface at room temperature.

MWCNTs Purification. The pristine MWCNT were heated in an oven at 360 °C for more than 4 h to remove the probable amorphous carbons, graphitic nanoparticles and catalyst impurities, then cooled at room temperature and used for acid treatment. The process of MWCNT acidulation were: 50 mg MWCNT were dispersed in 150 mL concentrated nitric acid (63 wt%) and refluxed in oil bath at 100 °C for 8 h. Thereafter, the MWCNT suspension was filtered (0.1 μm nitrocellulose membranes, Advantec MFS, Inc.) and washed with double deionized water and ethanol until neutral pH was reached, and then dried at 80 °C in vacuum.

Preparation of ionic liquid-carbon nanotube composite electrode. The MWCNT suspension was prepared by dispersing 1 mg acidulated MWCNT in 15 mL ethanol with the assist of ultrasonic agitation. Composite material comprising viscous ionic liquid with embedded MWCNT was prepared by mixing acidulated MWCNT with ionic liquid at different loadings (volume, 10, 20, 40, 60, 80%). The ethanol solvent was evaporated off by placing the electrode under vacuum. The working electrode of disposable SPCE was coated by casting several microliters of the prepared ionic liquid-carbon nanotube composite. Due to the viscosity of ionic liquid and binding of carbon nanotube, the composite material could be held on the working area of SPCE. The pristine MWCNT without acid treatment modified SPCE was similarly fabricated as a comparison.

Procedures. Standard stock solutions of TeCB (25 mg L^{-1}) and other interfence test samples (20 mg L^{-1}) were prepared in methanol. All solutions were stored in the dark at 4 ^{o}C. Working solutions were prepared by dilution of standard stock solutions with distilled water. A typical experiment involves a two-step procedure: an accumulation at open-circuit followed by a cyclic voltammetry and electrochemical impedance spectroscopydetection. The modified electrode was immersed for a given period of time in the accumulation cell containing the TeCB solution at a selected concentration. Preconcentration was achieved at open circuit and under constant stirring. The electrode was then removed from the solution, copiously rinsed with water, and transferred into the voltammetric cell containing 50 mL of the electrolyte solution (5 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl). Repetitive preconcentration-measurement-regeneration cycles were performed to characterize the reproducibility of the electrode performance by transferring the electrode after determination to ethanol saturated solution of sodium acetate and then scanning in the same potential window achieved regeneration.

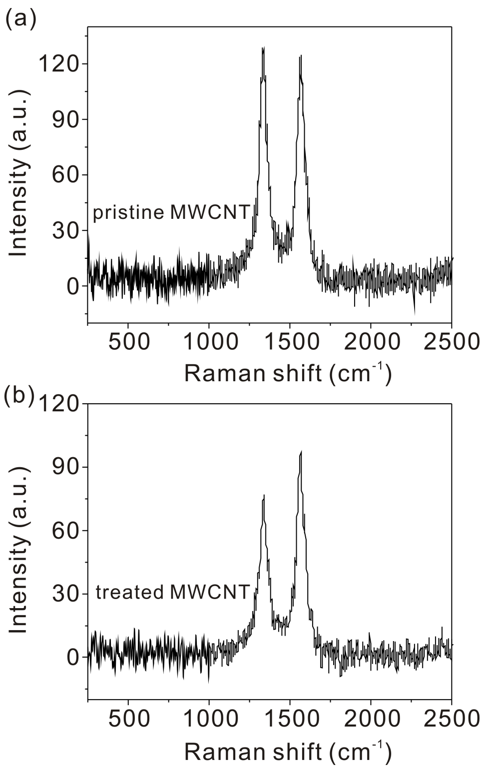

Fig. S1 Raman spectra of MWCNT (a) before and (b) after treatment.

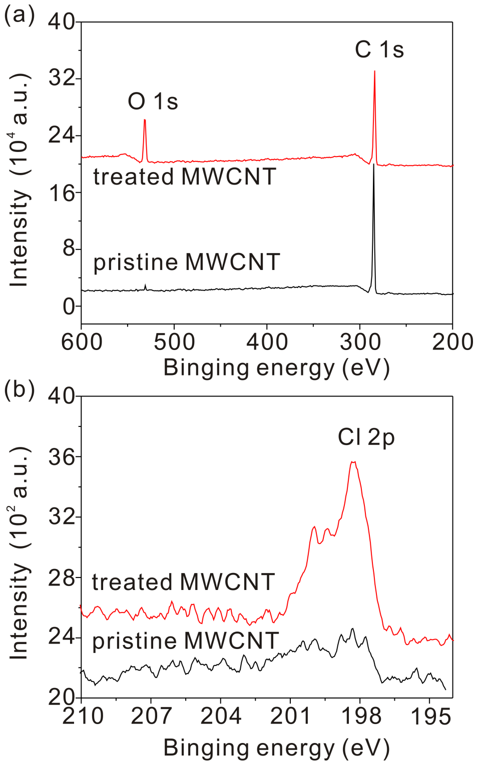

Fig. S2 (a) XPS wide scan of the pristine and treated MWCNT after adsorption of 2 μM TeCB. (b) High-resolution Cl 2p spectrum the two MWCNT samples after adsorption of 2 μM TeCB.

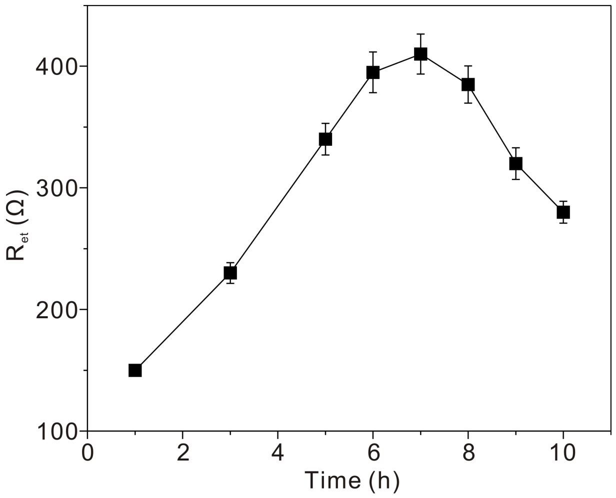

Fig. S3 The effect of preconcentration time of TeCB on the electrochemical impedance response, Data were collected from Nyquist diagrams of experiments. Each point is expressed as mean ± standard deviation (n = 3).