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Supporting Information

Transparent Carbon Nanotube Network for Efficient Electrochemiluminescence Devices

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Supplementary Informations

SWCNT electrode synthesis.

SWCNT-SALT PREPARATION[1] requires the preparation of a naphthalene salt in THF upon intercalation with metallic potassium. Naphthalene shows high reduction potential to reduce SWCNTs.
After two hours under reflux the solution becomes dark-green as expected for the successful reduction reaction. Once naphthalene salt is obtained, nanotubes can be added stoichiometrically. CNTs undergo reduction by naphthalene radical anions resulting in a polyelectrolyte salt of nanotubes.
50 *mg* of single-walled carbon nanotubes were chosen to prepare the corresponding nanotube salt.

$$Naphthalene + K \xrightarrow{THF} [\![Naphth^{-}K^{+}]\!]\,(THF)_x$$

$$[Naphth^{-}K^{+}]\,(THF)_x + CNTs \rightarrow [K^{+}CNTs^{-}](THF)_X + Naphthalene$$

The solution was filtered in a polyvinylidene difluoride membrane (PVDF) of 0.45 μm in pore size and the remaining powder was rinsed with distilled THF until filtration remains colorless. The product obtained is the SWCNT-salt. The obtained material contains one positive charge per potassium atom, hence one negative charge per 10 carbon atoms in the case of KC_{10} stoichiometry.
Stirring SWCNT-salt overnight in dry DMSO results in a homogeneous SWCNT-solution after centrifugation (2500 g, 1 hour) to remove insoluble material. The relation used was 2 mg of SWCNT-salt per mL of DMSO.

SWCNT Films
Dilutions were prepared in clean and dry DMSO. Whatman Anodisc Filter Membranes (0.02 μm pore size; diameter=47 *mm*) from Fisher Scientific were used to prepare SWCNT films.
During re-oxidation (neutralization) step, films were placed hermetically in a sealed box and transferred outside glovebox under a control flow of dry air per 2h at least.

Transfer to Polystyrene (PS)
The dissolution of the alumina membrane results in films made exclusively of SWCNTs. A bath of sodium hydroxide (1.5 *M*) was used to dissolve the alumina; it takes 8-9 minutes to get dissolved. Exceeding 12 minutes SWCNT films could be damaged. The bath was neutralized by rinsing with deionized water until pH~7. After that, **PS** foil was placed at the bottom and SWCNT films were deposited on it by removal of the bath. They were dried in the oven overnight at 40-50 *°C*.

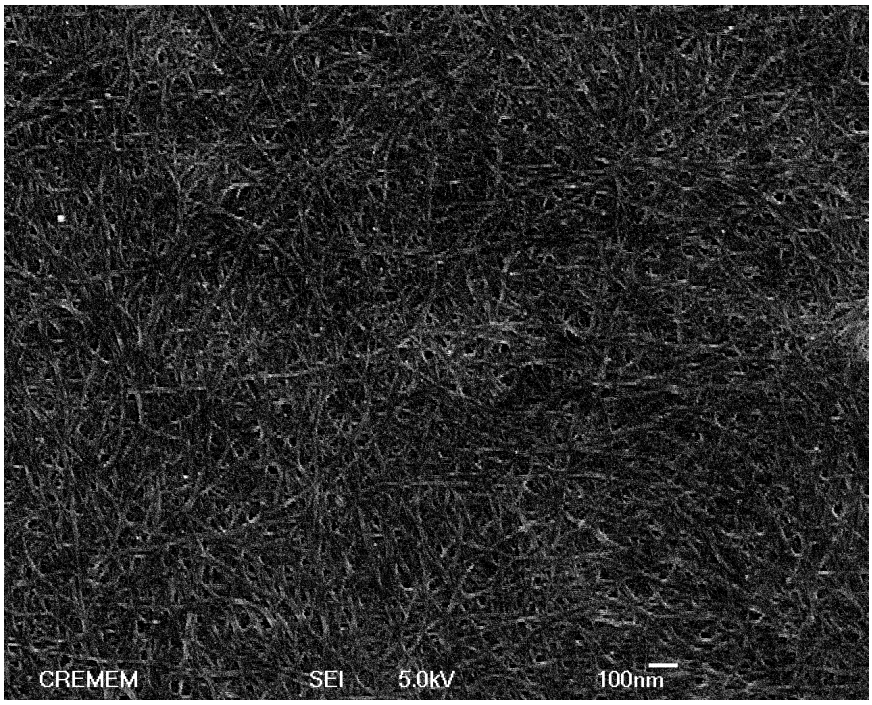

Figure S1. SEM of the CNT-based electrode. No traces of catalyst residues or aggregates are visible. SWCNT film surface appears to be clean and homogeneous.

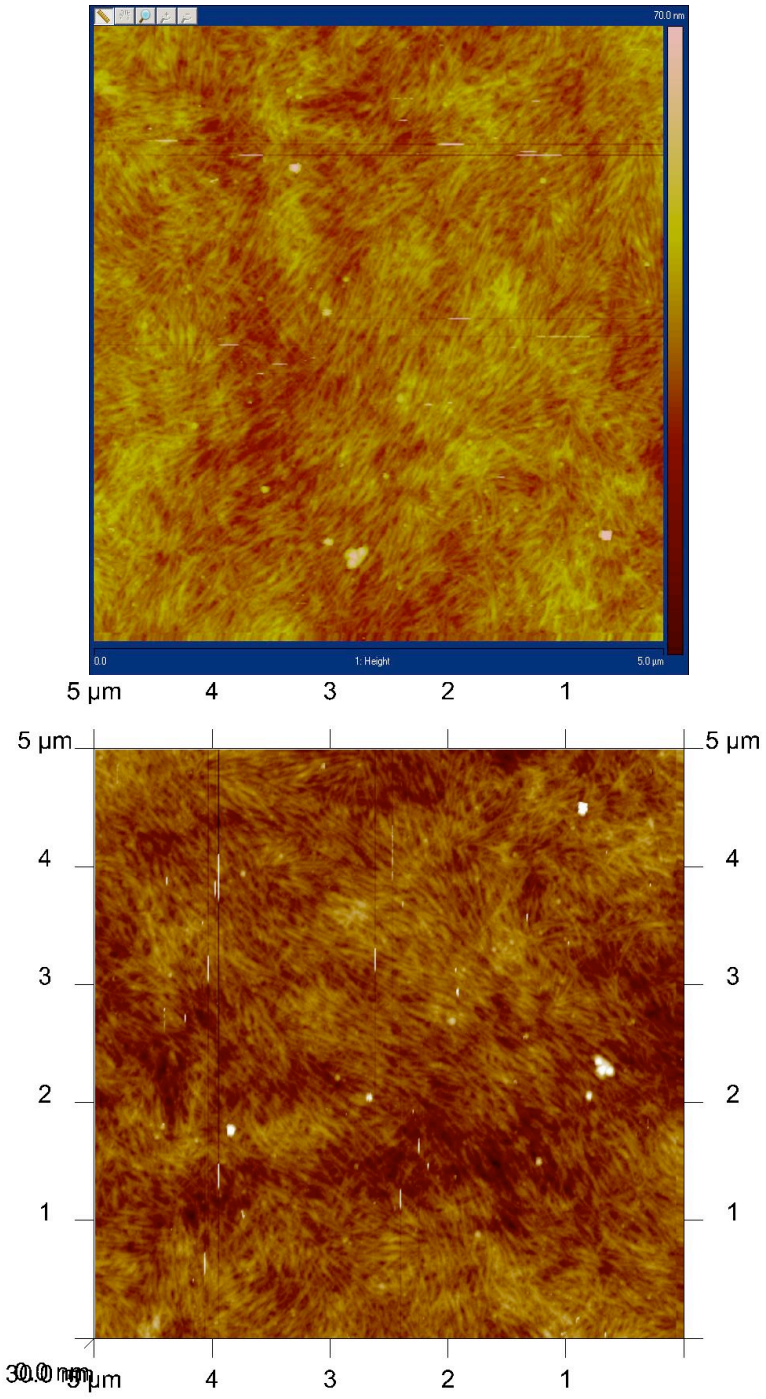

Figure S2. AFM image of the CNT based electrode. It can be described like a nest of nanotubes where deeper (darker) zones could be formed during dissolution of the alumina membrane where tubes are partially lost.

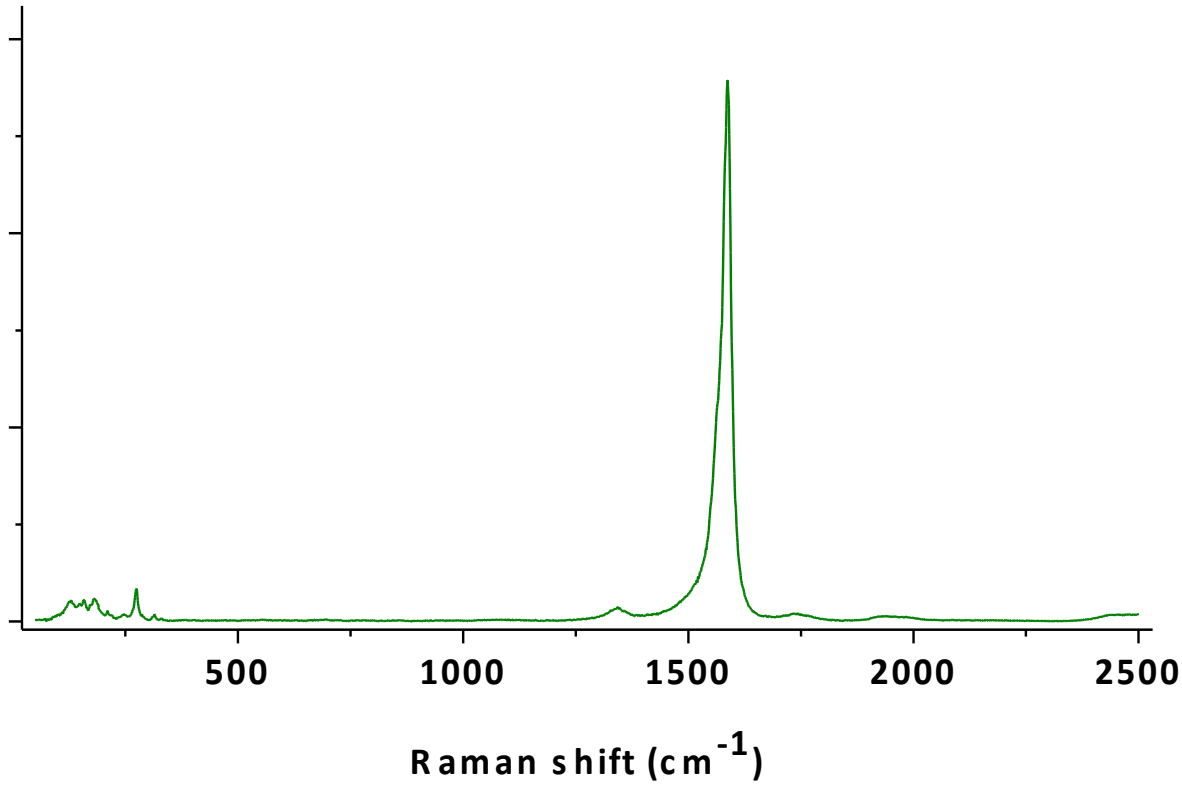

Figure S3. RAMAN of the CNT-based electrode shows characteristic radial breathing modes of nanotubes (RBMs) at the lowest raman shifts (~150-350 cm^{-1}). At higher wavenumber (~1600 cm^{-1}) the intensity of this band, called G-band, informs about the degree of sp^2 hybridation in the system; below in wavenumber (~1300cm^{-1}), appears the D-band. This D-band indicates the degree of disorder/defects in the system or carbons that present a sp^3 hybridation. The CNT-based electrode here presented appears to be a system where the majority of carbons present a sp^2 hybridation resulting in an intense band at ~1600 cm^{-1}.

Kinetic behaviour at the CNT electrode.

We used electrochemical impedance spectroscopy (EIS) in order to estimate the k_{her} and the capacitance of the double layer C_{dl} of the new electrode. The experiments were carried out at 1 V vs Ag/AgCl 3M and thus at a potential higher then the TPrA/TPrA $^{+}$ standard potential with various TPrA concentration. The R_{CT} and C_{dl} values were obtained through the fitting of EIS with the classical Randles circuit (at each concentration) and the parameter are reported in Table S1. The increase of the electroactive surface area was evaluated by the comparison between the capacitance of the double layer for the two materials.

Table 1

	CNT based electrode			*ITO*		
TPrA concentration	*R (Ω)*	*C_{dl}(μF)*	*R_{CT}(Ω)*	*R (Ω)*	*C_{dl}(μF)*	*R_{CT}(Ω)*
$Fe[(CN)_6]^{4-}/Fe[(CN)_6]^{3-}$(1:1)[a]	230	116	-	437	34	-
No[b]	194	400	-	-	-	-
1mM[b]	197	300	3400	1430	17	$11x10^6$
10mM[b]	190	400	1400	1420	17	$5x10^6$
50mM[b]	192	400	50	1500	17	-
100mM[b]	180	350	36	1500	17	$1.5x10^6$
180mM	171	350	21	1400	17	$0.7x10^6$

The R_{CT} is described by the following equation:[2]

$$R_{ct} = \frac{RT}{nFi_0}$$

where

$$i_0 = FAk^0C$$

Plotting therefore the reciprocal of R_{CT} as function of the TPrA concentration we evaluated the kinetic constant for the heterogeneous oxidation (see figure S4). The two electrode materials, CNT and ITO, were compared in the same experimental condition, i.e. normalizing for the electroactive surface area.

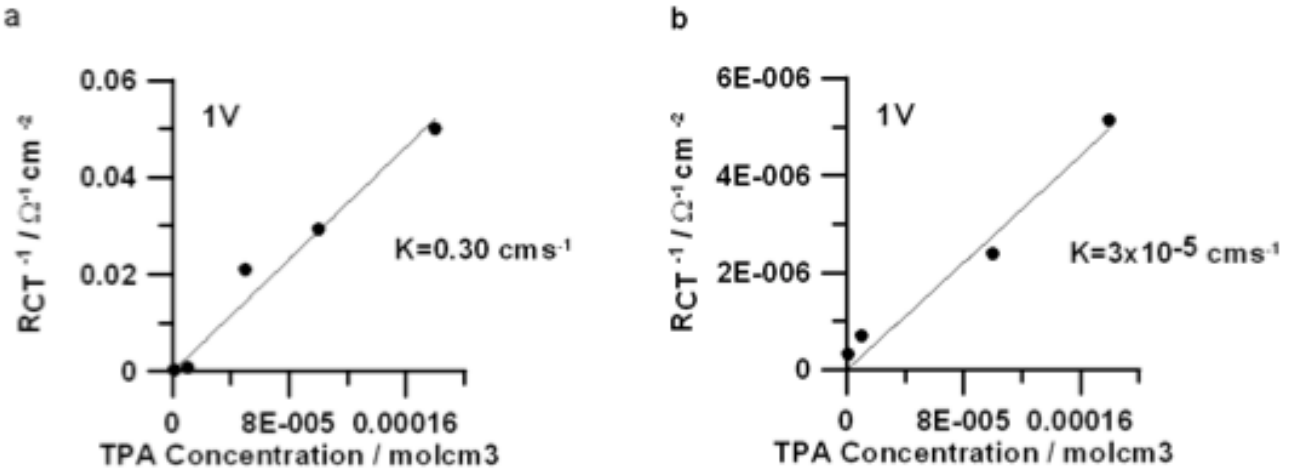

Figure S4. R_{CT}^{-1} as a function of the TPrA concentration for (a) CNT based electrode and (b) ITO.

In this case the concentration of TPrA is crucial parameter for the accurate k_{her} determination and at the experimental pH carried on the deprotonated TPrA concentration is governed by the pka, and thus we modified the equation used for the fitting as follows:

$$\frac{1}{R_{CT}} = \frac{k^{\circ}F^2}{RT}\frac{K_a}{[H^+]}[TPA]$$

Where F is the faraday constant (96500 C mol^{-1}), R the gas constant (8.31 J K^{-1} mol^{-1}), T the temperature (298 K), ka the dissociation constant for TPrA and [H+] is the proton concentration (pH 6.8).

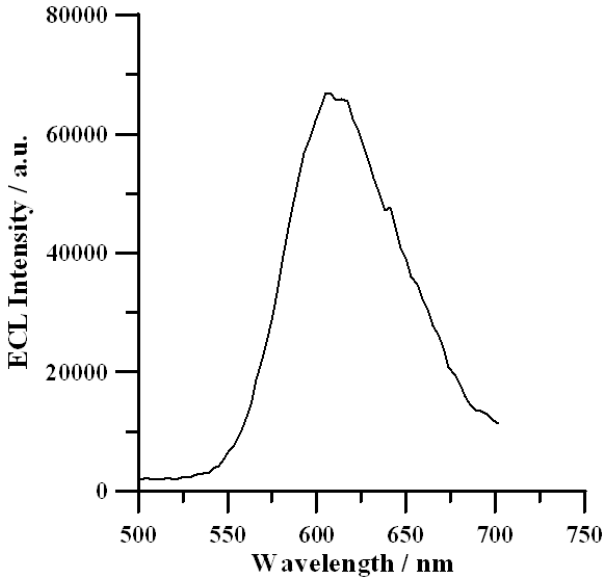

Figure S5. ECL Spectrum for CNT electrode acquired at 1.2V with a solution of 10 mM $Ru(bpy)_3^{2+}$, 80mM TPrA in phosphate buffer 0.1M. The ECL maximum at 610 nm characteristic of the $Ru(bpy)_3^{2+}$* excite state. [3]

Reference

[1] Penicaud, A.; Poulin, P.; Derre´, A.; Anglaret, E.; Petit, P. *J. Am. Chem. Soc.* **2005**, *127*, 8.

[2] Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley: New York, **2001**.

[3] M. Montalti, A. Credi, L. Prodi, T. Gandolfi, *Handbook of Photochemistry, 3rd ed.,* Taylor & Francis: Boca Raton, FL, **2006**.