
Carbon nanotube-functionalized silicon surfaces with efficient redox communication

Fanny Hauquier[a], Giorgia Pastorin[b], Philippe Hapiot[a], Maurizio Prato*[c], Alberto Bianco*[b] and Bruno Fabre*[a]

[a] *Matière Condensée et Systèmes Electroactifs MaCSE, Sciences Chimiques de Rennes, UMR 6226 CNRS, Campus de Beaulieu, Université de Rennes 1, 35042 Rennes Cedex, France*

[b] *Institut de Biologie Moléculaire et Cellulaire, UPR 9021 CNRS, Immunologie et Chimie Thérapeutiques, 67084 Strasbourg, France*

[c] *Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy*

General. All reagents and solvents were obtained from commercial suppliers and used without further purification. The reactions were monitored by thin-layer chromatography (TLC) on silica gel (F_{254} Merck) and the products were visualised on aqueous potassium permanganate or ninhydrine spray followed by heating. Infrared spectra (FT-IR) were measured on a Perkin Elmer Spectrum One ATR-FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker DPX 300 spectrometer. Peak values were given as ppm (δ) and referenced to the solvent. Chromatographic purifications were done with silica gel Merck (Kiesegel 60, 40-60 μm, 230-400 mesh ASTM) using standard column. Organic phases were dried with sodium sulphate. Multi-walled carbon nanotubes (MWNT) were purchased from Nanostructured & Amorphous Materials Inc. (Huston, TX). MWNT used in this study were 94% pure, stock #: 1240XH. Transmission electron microscopy (TEM) analyses were performed on a TEM Hitachi 600 HS.

Synthesis of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH_2

A solution of chlorotriphenylmethane (Trt-Cl) (3.76 g, 13.5 mmol) in DCM (50 ml) was added dropwise to a solution of 2,2'-(ethylene-dioxy)bis(ethylamine) (20 g, 135 mmol) in DCM (100 ml). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue dissolved in DCM (50 ml), washed with water (3×40 ml), dried (Na_2SO_4) and evaporated. The unreacted diamine was removed by flash chromatography using DCM/MeOH 7:2 as eluant. Yield: 3.95 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.14 (m, 15 H), 3.63-3.46 (m, 8H), 2.80 (m, 2 H), 2.34 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.93, 128.55, 127.65, 126.12, 72.68, 71.09, 70.08, 69.90, 50.01, 42.90, 41.34.

Synthesis of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH-CH_2-COOBzl

To a solution of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH_2 (3.95 g, 10 mmol) in DCM (50 ml), cooled at 0 °C, a solution of benzylbromoacetate (0.8 g, 3.4 mmol) in DCM (15 ml) was added dropwise over a period of 1.5 hours. The reaction mixture was allowed to reach the room temperature and was stirred overnight. The solvent was removed under reduced pressure. The final product was purified by flash chromatography using DCM/MeOH 9.5:0.5 as eluant. Yield: 1.6 g (89%). FT-IR: 3331, 1741, 1632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.18 (m, 20H), 5.16 (s, 2H), 3.63-3.52 (m, 8H), 3.44 (s, 2H), 2.78 (m, 2H), 2.37 (m, 2H), 2.09 (m 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.98, 145.95, 135.51, 128.51, 128.39, 128.39, 128.16, 127.60, 126,04, 71.07, 70.54, 70.46, 70.08, 69.88, 66.24, 50.74, 48.57, 42.88.

Synthesis of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH-CH_2-COOH

To a solution of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH-CH_2-COOBzl (1.6 g, 3.0 mmol) in MeOH (40 ml) were added 160 mg (10%)of Pd/C. A stream of H_2 was subsequently applied and the reaction mixture was stirred for 5 hours at room temperature. The solution was filtered through a celite pad and the solvent was evaporated under reduced pressure. The product was recrystallized from MeOH/cold diethyl ether. Yield: 0.9 g (70%). FT-IR: 3394, 1638, 1558 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.13 (m, 15H), 3.72-3.47 (m, 12H), 3.13 (m, 2H), 2.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.24, 145.93, 128.59, 127.76, 126.23, 71.15, 70.63, 70.12, 69.79, 66.33, 46.73, 42.97.

Preparation of functionalized MWNT (1)

CNT (80 mg) and paraformaldehyde (3 × 160 mg every 24 hours) were suspended in 100 ml of DMF. 270 mg of Trt-NH-$(CH_2CH_2O)_2$-CH_2CH_2-NH-CH_2-COOH were added and the reaction was heated at 125 °C for 72 hours. The heating was stopped. Unreacted CNT remained completely insoluble in DMF and were separated from the soluble functionalized tubes by centrifugation. The solvent was evaporated and the brown residue was dissolved in DCM, washed once with water and dried over Na_2SO_4. The solvent was evaporated and the product was reprecipitated several times from DCM/diethyl ether. Functionalised MWNT were characterized by TEM (Figure S1).

Cleavage of the Trt protecting group

A solution of HCl 4 M in dioxane was added to functionalized MWNT (5 mg) and the mixture was stirred for 3 hours at room temperature. The solvent was removed under reduced pressure and the product was reprecipitated several times from MeOH/diethyl ether. Ammonium-functionalized MWNT **1** were again characterized by TEM. Quantitative Kaiser test afforded a loading of 0.50 mmol/g of free NH_2.

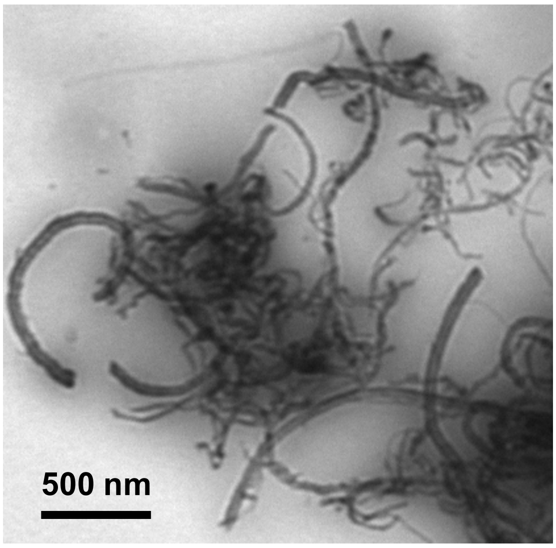

Figure S1. TEM image of functionalized MWNT.

Covalent attachment of 1 on Si(111)

A single side polished silicon(111) shard (1.5 x 1.5 cm^2, 1-5 Ω cm, *p*-type, boron doped, thickness = 525 ± 25 µm, Siltronix) was sonicated for 10 min successively in acetone (min. 99.8%, Carlo Erba), methanol (min. 99.9%, Carlo Erba) and ultra-pure 18.2 MΩ cm water. It was then cleaned in 3:1 v/v concentrated 96% H_2SO_4/30% H_2O_2 (VLSI semiconductor grade, Riedel-de-Haën) at 100°C for 30 min, followed by copious rinsing with ultra-pure water.

***Caution**: The concentrated H_2SO_4:H_2O_2 (aq) piranha solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully.*

The surface was etched with ppb grade 40% aqueous argon-deaerated NH_4F (VLSI semiconductor grade, Riedel-de-Haën) for 15 min to obtain atomically flat Si(111)-H.[1] It was then dipped in argon-deaerated ultrapure water for several seconds, dried under an argon stream and transferred immediately into a Pyrex Schlenk tube containing ca. 10 mL of deoxygenated undecylenic acid (99%, Acros) which had been previously passed through a neutral, activated alumina column. The solution was thoroughly purged with argon for 30 min, the Schlenk tube was sealed with paraffin film (Parafilm M), and the solution was irradiated for 3.5 hr in a Rayonet photochemical reactor (300 nm).[2] The undecanoic acid-modified Si(111) surface was rinsed copiously with tetrahydrofuran (HPLC grade, SDS), hot acetic acid (glacial ACS, Acros)[2a] and methylene chloride (anhydrous analytical grade, SDS), and dried under an argon stream.

It has been demonstrated that this direct hydrosilylation route does not lead to appreciable reaction between the carboxyl groups and the surface provided that short UV irradiation times are used (typically, less than 4 h).[3] Then, the terminal COOH groups were activated with *N*-hydroxysuccinimide (NHS) by immersing the modified silicon surface for 3 hr in a freshly prepared mixture of a deaerated solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (Acros, 98+%) at 0.2 M in dimethylformamide (DMF, anhydrous, SDS) (5 mL) and a deaerated solution of NHS (Acros, 98+%) at 0.1 M in DMF (5 mL).[2b,4,5] The mixture was gently purged by bubbling with argon. The surface was then rinsed with DMF and used immediately for the coupling reaction with **1**.

The covalent attachment of MWNTs on Si(111) was performed at rt by immersing overnight the NHS-activated silicon surface in a DMF solution (1 mL) containing ca. 1 mg mL^{-1} of **1** previously neutralized with diisopropylethylamine (10 μL, 99.5+%, Acros). The MWNT-modified surface was rinsed with DMF, ethanol (puriss, Riedel-de-Haën) and methylene chloride, and dried under an argon stream.

SECM measurements

Scanning electrochemical microscopy experiments were carried out with a homemade SECM based on technical description previously published in the literature.[6] The microelectrode tip was moved by a horizontal translation stage (speed 2 μm/s) driven by an electrical micro step motor piloted by a computer. The micro step motors driven by a Pico SPM II (Molecular Imaging) classically used in AFM or STM experiments. The electrode potential tip was controlled using a PAR potentiostat/galvanostat model M273 (EG&G) that also measures and digitalizes the current. The potential applied to the tip electrode was chosen as to be at the level of the diffusion plateau of the mediator. The approach curve showing feedback was then recorded and the coordinate of substrate/solution interface ($d = 0$) was determined from the shape change of the tip current that occurred when the tip just touched the substrate surface. The procedure was checked by considering similar approach in conditions of insulating substrate.[6] Diffusion coefficients, D, of the mediators were measured in DMF + 0.1 mol L^{-1} NBu_4ClO_4 by cyclic voltammetry on a millimetric electrode. Values of 8.2×10^{-6} cm^2 s^{-1} and 7.6×10^{-6} cm^2 s^{-1} were determined for the ferrocene/ferrocenium and azobenzene/azobenzene$^{\bullet -}$ couples respectively.

The ultramicroelectrodes (UME) used for these SECM experiments were prepared in the laboratory following general published procedure.[6] Disk-shaped UME of 10 μm radius was made by sealing platinum wires (GoodFellow) in a soft glass tube that was subsequently ground at one end. The glass edge was conically shaped with an outer diameter of approximately 100 μm ($5 < RG < 10$). Prior to use, the UME was polished using diamond pastes with decreasing grain sizes. Electrode diameter was measured by studying the steady-steady current of the ferrocene oxidation with a defined concentration of mediator. A homemade electrochemical cell was used for SECM experiments similar to the one previously described for electrochemical AFM experiments.[7] The reference electrode was a quasi-reference electrode, made with an Ag wire covered with $AgNO_3$. Its potential was checked versus the ferrocene/ferrocenium couple. A 0.5 mm-diameter platinum wire was used as the auxiliary electrode.

Fitting of the SECM approach curves

The apparent charge-transfer rate constant k_{app} obtained at the modified Si(111) surfaces was measured using the formalism previously introduced by Mirkin and Bard.[6,8]

When the interfacial electron transfer at the substrate/solution is the rate-determining step, the normalized current I_T in the SECM approach curves can be described by the following set of equations:

$$I_T = I_S^k \left(1 - \frac{I_T^{ins}}{I_T^c} \right) + I_T^{ins} \tag{1}$$

where I_T^c is the normalized tip current associated to the tip current for the diffusion-controlled regeneration

$$I_T^c = 0.68 + \frac{0.78377}{L} + 0.3315 \; e^{\left(-1.0672/L\right)} \tag{2}$$

I_S^k is the normalized tip current for the kinetically controlled electron transfer at the substrate interface. I_S^k depends on a single adimensional parameter $\kappa = k_{app}a/D$ where a is the electrode tip radius and D is the diffusion coefficient of the mediator. For $L < 2$ and $0.01 < \kappa < 1000$, I_S^k can be approximated by the following equation:

$$I_S^k = \frac{0.78377}{L(1+1/\Lambda)} + \left[\frac{0.68 + 0.3315 \; e^{\left(-1.0672/L\right)}}{1 + F(L,\Lambda)} \right] \tag{3}$$

$$\text{with } F(L,\Lambda) = \frac{(11 + 7.3\Lambda)}{\Lambda(110 - 40L)} \text{ and } \Lambda = \kappa L$$

I_T^{ins} is the normalized tip current corresponding to a totally insulating surface:

$$I_T^{ins} = \left(0.15 + \frac{1.5358}{L} + 0.58 e^{\left(-1.14/L\right)} + 0.0908 e^{\left(L - 6.3/1.017L\right)} \right)^{-1} \tag{4}$$

It depends only on the adimensional distance *L*. The approach curve at an insulating surface can be used for a precise determination of the distance origin if the electrode radius has been measured beforehand.

The experimental approach curves obtained at different modified *p*-type Si(111) surfaces are shown in Figures S2 and S3 using ferrocene and azobenzene as redox mediators respectively. These were fitted with the theoretical curves to extract the apparent charge-transfer rate constant k_{app}. The anodic oxidation of ferrocene and the cathodic reduction of azobenzene were performed at a Pt UME tip. The k_{app} values are gathered in Table S1.

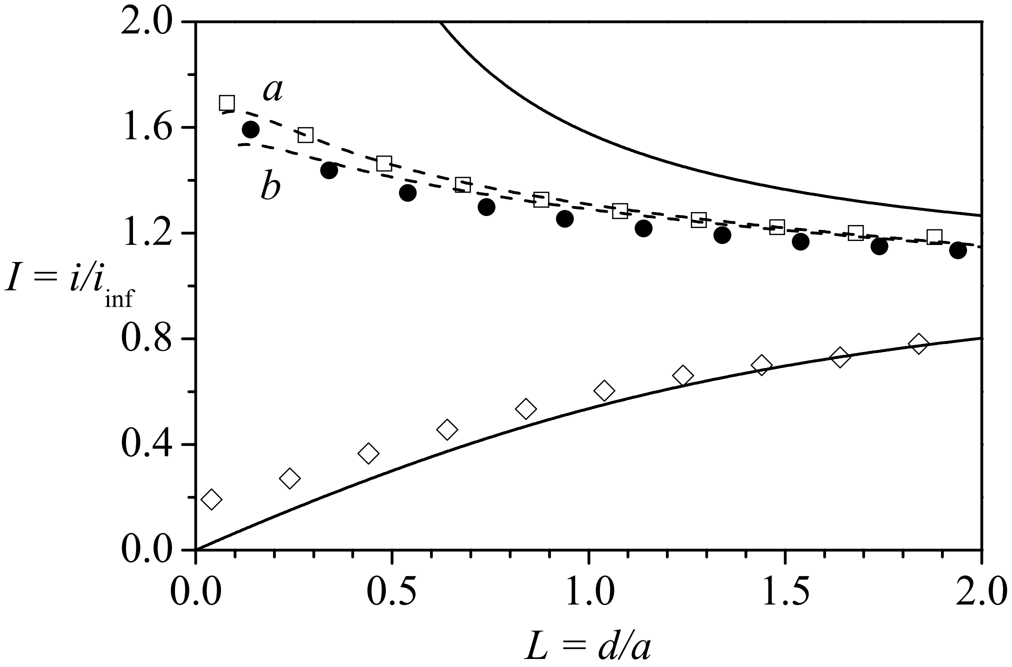

Figure S2. SECM approach curves with L ranging from 0 to 2 obtained at the (□) MWNT-, (◇) undecanoic acid monolayer-modified and (●) hydrogen-terminated Si(111) surfaces in DMF + 0.1 M Bu_4NClO_4 containing 10^{-2} M ferrocene. The bottom and top solid lines are theoretical SECM curves for totally insulating and conducting substrates respectively. The dashed lines correspond to a finite charge transfer kinetic with (a) $k_{app} = 1.5 \times 10^{-2}$ cm s^{-1} and (b) $k_{app} = 1.3 \times 10^{-2}$ cm s^{-1}. The UME tip was a 10 μm-radius platinum disk.

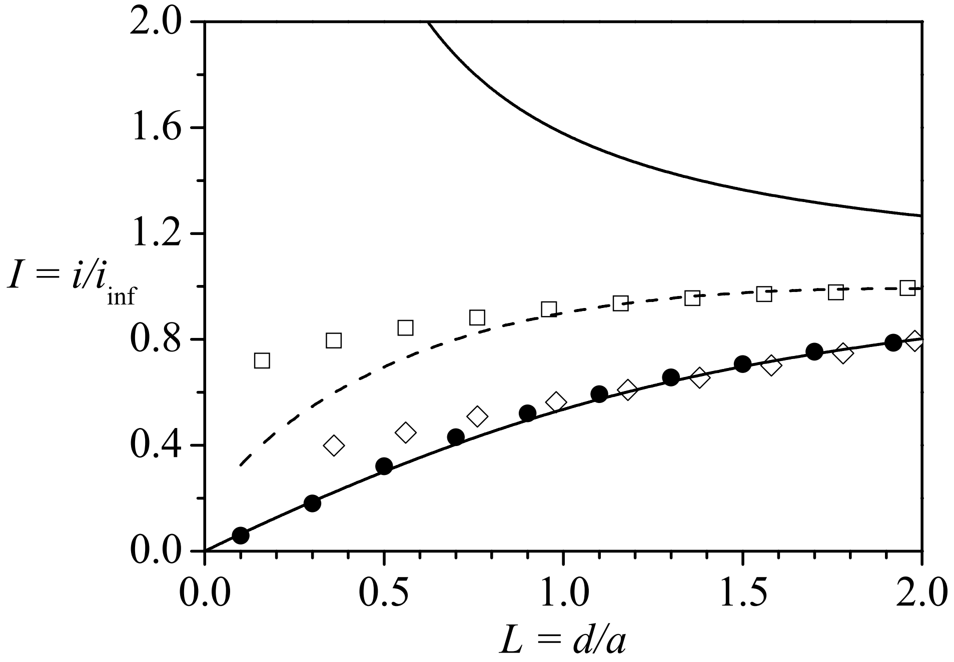

Figure S3. SECM approach curves with *L* ranging from 0 to 2 obtained at the (□) MWNT-, (◇) undecanoic acid monolayer-modified and (●) hydrogen-terminated Si(111) surfaces in DMF + 0.1 M Bu_4NClO_4 containing 10 mM azobenzene. The bottom and top solid lines are theoretical SECM curves for totally insulating and conducting substrates respectively. The dashed line corresponds to a finite charge transfer kinetic with $k_{app} = 1.7 \times 10^{-3}$ cm s^{-1}. The UME tip was a 10 μm-radius platinum disk.

Table S1. Apparent charge-transfer rate constants k_{app} determined from the fitting of SECM data on different modified *p*-type Si(111) surfaces. Electrolyte: DMF + 0.1 M Bu_4NClO_4 containing 10 mM ferrocene or azobenzene. $a = 10\ \mu m$.

Surface	k_{app} / cm s^{-1}	
	Ferrocene ($E^{\circ\prime}$ = 0.45 V vs SCE)	Azobenzene ($E^{\circ\prime}$ = -1.3 V vs SCE)
Undecanoic acid-modified Si(111)	8×10^{-5}	_[a]
MWNT-modified Si(111)	1.5×10^{-2}	1.7×10^{-3}
Hydrogen-terminated Si(111)	1.3×10^{-2}	_[a]

[a] Too low to measure under these experimental conditions.

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