

## Supporting Information for:

### Thiol-yne click chemistry on carbon nanotubes for mediated bioelectrocatalytic glucose oxidation

Monica Brachi,<sup>a</sup> Fabien Giroud,<sup>a</sup> Serge Cosnier<sup>a,b</sup> and Alan Le Goff<sup>\*a</sup>

<sup>a</sup>Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France

<sup>b</sup>Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Gliwice, Poland.

#### 1. Materials and Methods

##### Chemicals and general procedures.

Multiwalled carbon nanotubes (MWCNT, 10 nm diameter, purity > 99%) were obtained from Sigma-Aldrich and were used as received without any purification. All the reagents were purchased from Sigma-Aldrich and were used without further purification. All solvents were of analytical grade. Ferrocenemethanethiol, 4-ethynylbenzenediazonium tetrafluoroborate<sup>1</sup> and 8-mercapto-N-(1,10-phenanthroline-5-yl) octanamide<sup>2</sup> were prepared as previously described. Distilled water was passed through a Milli-Q water purification system. The electrochemical experiments were carried out in a three-electrode electrochemical cell using a Autolab PGSTAT100 Potentiostat. The MWCNT electrodes were used as working electrodes. Pt wire was used as counter electrode and the reference electrode was based on the Ag/AgNO<sub>3</sub> 10<sup>-2</sup> M reference electrode in MeCN and Saturated Calomel Electrode (SCE) in water. All potentials are given versus Fc/Fc<sup>+</sup> in MeCN and the SCE in water. All current densities are normalized towards the geometrical surface area of the MWCNT/glassy carbon electrode (0.28 cm<sup>2</sup>). Experiments were repeated on at least three electrodes.

XPS analysis was performed using a Thermoelectron ESCALAB 250 device (ICGM, France). The X-ray excitation was provided by a monochromatic Al-K $\alpha$  ( $h\nu=1486.6$  eV) source. The analyzed area was  $\sim 0.15$  mm $^2$ . The background signal was removed using the Shirley $^3$  method. The surface atomic concentrations were determined from photoelectron peak areas using the atomic sensitivity factors reported by Scofield $^4$ . Binding energies (BE) of all core levels were referred to the C=C of C1s carbon at 284.4 eV. Raman spectroscopy was performed on a Witec Alpha 300R (laser He-Ne 633 nm, x50 lens magnification). For measurement purpose, diazonium functionalization of MWCNTs was performed *in situ* using a previously-described chemical diazotisation procedure. $^{5,6}$

*Caution: Perchlorate salts present a potential explosion risk; use with caution!*

### ***Preparation of MWCNT electrode modified with 4-ethynylbenzenediazonium tetrafluoroborate and FAD-GDH***

MWCNT films were prepared by drop coating 20  $\mu$ L of a 5 mg mL $^{-1}$  dispersion of MWCNTs in 1-Methyl-2-pyrrolidinone (NMP) onto the glassy carbon (GC) electrode surface. The deposit was then allowed to dry under vacuum.

Electrografting of 4-ethynylbenzenediazonium tetrafluoroborate on the surface of the MWCNT electrodes was performed by cyclic voltammetry in MeCN with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

For the bioelectrodes preparation, the modified MWCNT GC electrodes were incubated in 20  $\mu$ L of FAD-GDH solution (5 mg mL $^{-1}$ ,  $>900$  U mg $^{-1}$  in 0.1 M phosphate buffer pH 7) for 6 h at 4 $^\circ$ C.

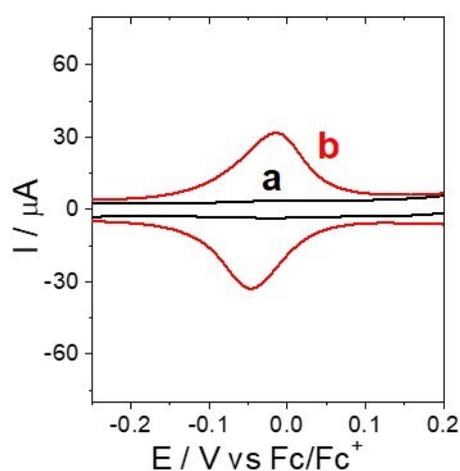


Figure S1. CVs of the pristine MWCNT electrodes functionalized by soaking the electrodes in ferrocenylmethanethiol and 6-ferrocenyl(hexanethiol) (MeCN/0.1 M TBAP, 10 mV s $^{-1}$ ).

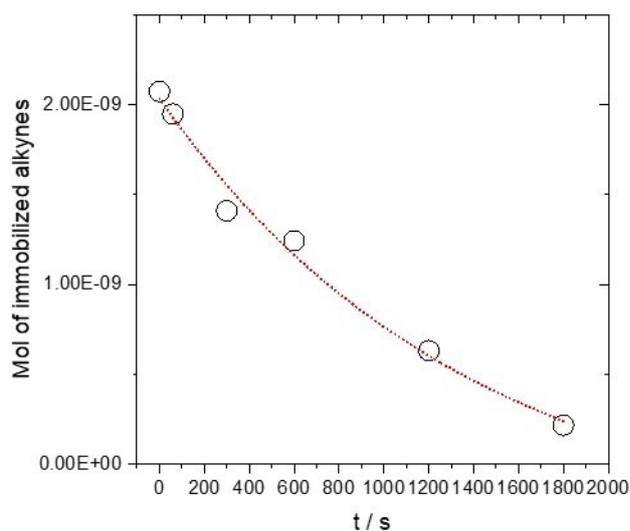


Figure S2. Experimental and fitted curves for the functionalization of alkyne-modified MWCNT electrodes against UV irradiation exposure time.

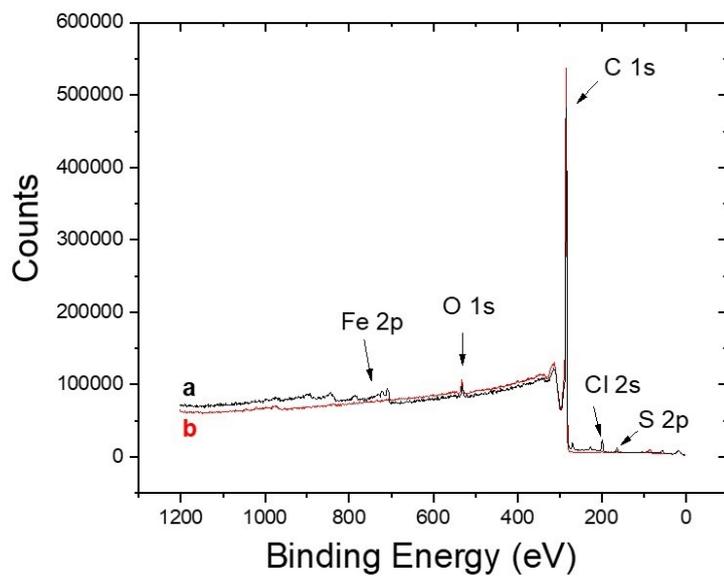


Figure S3. XPS spectra of the alkyne-modified MWCNT electrodes functionalized with ferrocenemethanethiol in the (a) presence and (b) absence of UV irradiation.

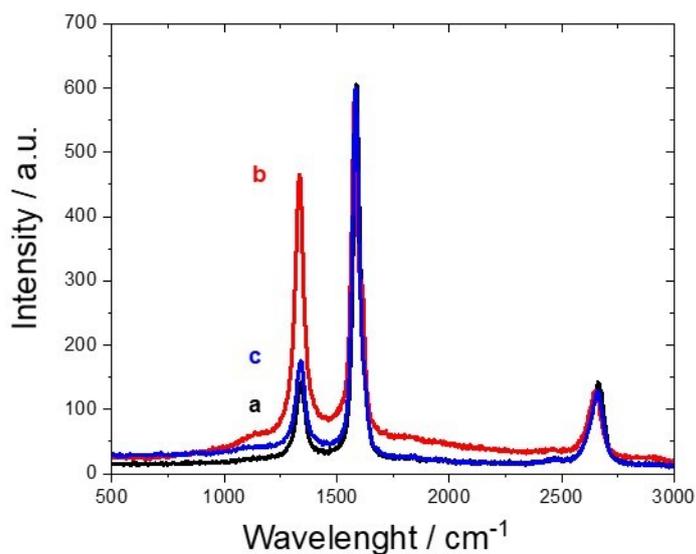


Figure S4. Representative Raman spectrum for (a) pristine MWCNTs, (b) MWCNTs modified by *in situ* 4-ethynylbenzenediazonium functionalization and (c) MWCNTs modified with 1-ethynylpyrene

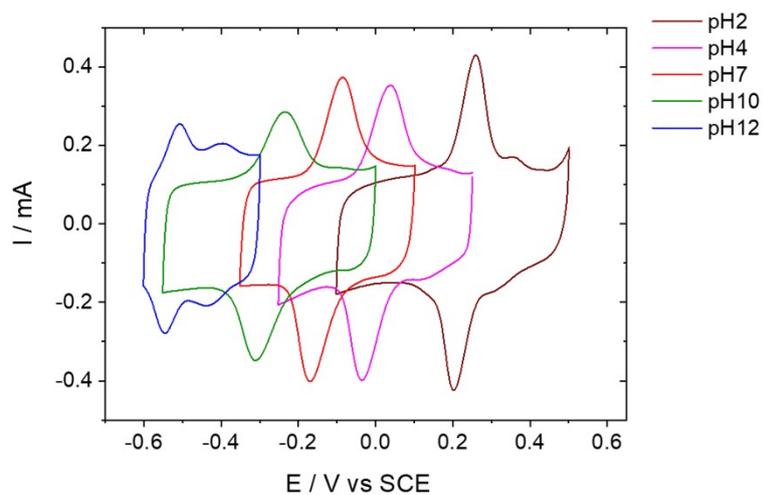


Figure S5. CVs of alkyne-modified MWCNT electrodes functionalized with phenanthrolinequinone by thiol-yne chemistry at different pH (2, 4, 7, 10, 12) (0.1 M phosphate buffer, 10 mV s<sup>-1</sup>).

## References

- (1) Evrard, D.; Lambert, F.; Policar, C.; Balland, V.; Limoges, B. Electrochemical Functionalization of Carbon Surfaces by Aromatic Azide or Alkyne Molecules: A Versatile

- Platform for Click Chemistry. *Chem. Eur. J.* **2008**, *14* (30), 9286–9291. <https://doi.org/10.1002/chem.200801168>.
- (2) Elmes, R. B. P.; Orange, K. N.; Cloonan, S. M.; Williams, D. C.; Gunnlaugsson, T. Luminescent Ruthenium(II) Polypyridyl Functionalized Gold Nanoparticles; Their DNA Binding Abilities and Application As Cellular Imaging Agents. *J. Am. Chem. Soc.* **2011**, *133* (40), 15862–15865. <https://doi.org/10.1021/ja2061159>.
  - (3) Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* **1972**, *5* (12), 4709–4714. <https://doi.org/10.1103/PhysRevB.5.4709>.
  - (4) Scofield, J. H. Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV. *Journal of Electron Spectroscopy and Related Phenomena* **1976**, *8* (2), 129–137. [https://doi.org/10.1016/0368-2048\(76\)80015-1](https://doi.org/10.1016/0368-2048(76)80015-1).
  - (5) Bahr, J. L.; Tour, J. M. Highly Functionalized Carbon Nanotubes Using in Situ Generated Diazonium Compounds. *Chem. Mater.* **2001**, 3823–3824.
  - (6) Lalaoui, N.; Holzinger, M.; Le Goff, A.; Cosnier, S. Diazonium Functionalisation of Carbon Nanotubes for Specific Orientation of Multicopper Oxidases: Controlling Electron Entry Points and Oxygen Diffusion to the Enzyme. *Chem. Eur. J.* **2016**, *22* (30), 10494–10500. <https://doi.org/10.1002/chem.201601377>.