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Edge-to-edge Interaction between Carbon Nanotube-Pyrene Complexes and Electrodes for Biosensing and Electrocatalytic Applications

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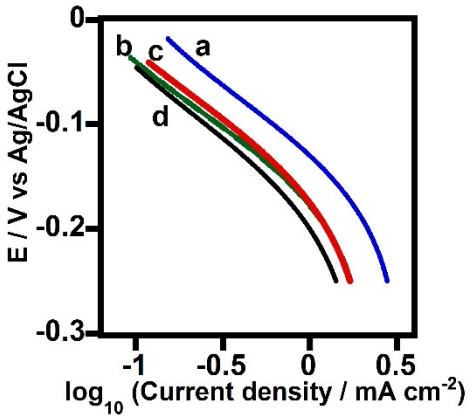

Figure S1. Tafel plots for peroxide reduction by MWNT/Py-Mb films on **a**. EP, **b.** BP, **c.** GC, and **d.** Au electrodes for the catalytic voltammograms shown in Figure 2.

Experimental

Chemicals and materials

Disk electrodes made of purely EP or purely BP (Momentive Performance Materials Ltd.), and non-graphitic Au and GC electrodes (CH Instruments) were used in this study (geometric area of each electrode was 0.2 cm^2). MWNT (outer diameter 10–15 nm, inner diameter 2–6 nm, length 0.1–10 μm), equine heart myoglobin (Mb, ≥ 90%, SDS-PAGE), dimethyl formamide (DMF), 1-pyrenebutyric acid (Py), t-Butyl hydroperoxide (t-BuOOH), 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride, and N-hydroxysuccinimide were purchased from Sigma (Milwaukee, USA). All other chemicals were analytical grade.

Preparation of protein films on various electrodes modified with MWNT/Py units.

The procedure to covalently attach myoglobin to MWNT/Py-modified electrodes to obtain MWNT/Py-Mb films was similar to that described in our prior reports.[1,2] Briefly, 15 μL of 1 mg mL^{-1} MWNT in DMF were dry coated on electrodes and π-π stacked with Py (10 mM in DMF) molecules. The Mb surface lysine residues (PDB: 2FRF) were covalently attached to the –COOH groups of the MWNT/Py surface of various electrodes by amine-carboxylic acid coupling chemistry (denoted as electrode/MWNT/Py-Mb, where electrode = EP, BP, GC, or Au). The electrochemical and electrocatalytic peroxide reduction properties of immobilized Mb on the designed electrode materials were investigated by cyclic voltammetry and rotating disk voltammetry (RDV) methods, respectively.

Instrumentation

Electrochemical measurements were performed using a CH instrument (Model: CHI 6017E, Texas, USA). RDV was performed to study the catalytic reduction rate of t-BuOOH at a rotation rate of 1000 rpm (EcoChemie Autolab rotator supplied with a motor controller, Metrohm Inc.). A three-electrode electrochemical cell equipped with an Ag/AgCl reference

(3 M KCl), a Pt-wire counter electrode, and MWNT/Py-Mb films on the various working electrodes were used. Fluorescence emission spectra of Py solutions were obtained using a Varian Cary eclipse fluorescence spectrophotometer. The excitation and emission slit widths were set at 5 nm. The excitation wavelength was set at 284 nm and emission was monitored at 377 nm. The X-ray photoelectron spectroscopy (XPS) analyses were performed using the Mg anode of a PHI 300 W twin anode X-ray source and the PHI double-pass cylindrical mirror analyzer as the detector with a pass energy of 100 eV. The instrument was equipped with a surface analysis system with a base pressure of 2 x 10^{-10} Torr. General survey scans were carried out for the EP/MWNT/Py-Mb and BP/MWNT/Py-Mb electrodes to qualitatively assess how the edge and basal plane effects on MWNT/Py modification and influence the surface density of immobilized Mb molecules.

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1 C. Walgama and S. Krishnan, *J. Electrochem. Soc.,* 2014, **161**, H47.

2 S. Krishnan and F. A. Armstrong, *Chem. Sci.,* 2012, **3**, 1015.