

Electronic Supplementary Information for

Enhanced Enzymatic Reaction Using a Triphase System Based on Superhydrophobic Mesoporous Nanowire Arrays

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Materials and methods

Growth of mesoporous ZnO nanowire (NW) arrays. A fluorine-doped tin oxide (FTO) coated glass substrate was firstly sonicated consecutively in ethanol, acetone and deionized water for 15 min, respectively. The cleaned FTO-substrates were loaded into a reactor containing an aqueous solution of zinc nitrate (0.03 M), hexamethylenetetramine (0.03 M), tetrabutylammonium fluoride (0.015 M). The reactor was then heated to 80 °C and maintained at this temperature from 15 min to 6 h. After being annealed at 400 °C for one-hour, mesoporous ZnO NW arrays were obtained. ZnO NWs with different lengths can be obtained by using different growth time.

Triphase enzymatic system with a gas-solid-liquid joint interface. Nanostructured H₂O₂ electrocatalysts sensitized ZnO NWs were obtained by dropping an aliquot of H₂PtCl₆ solution onto the surface of NW arrays, and subsequent calcining at 350 °C for 30 min. The Pt-decorated ZnO NWs was then immersed in a cyclohexane solution of PFOS for 1 hour. Thus-prepared superhydrophobic ZnO NW arrays were then treated by low power oxygen plasma for a short time (1-2s) to make (only) the top surface of NWs hydrophilic, then 12 μL of a mixed solution of glucose oxidase (GOx, EC 1.1.3.4, 126,000 U/g) (20 mg/mL in DI-water), nafion (1 wt% in DI-water) and DI-water volume ratio of 25:1:24 was drop cast onto the top of NWs with a size of 0.25 cm² and allowed to dry naturally.

Characterization. The scanning electron microscope (SEM) images were obtained by using a field emission scanning electron microscope (FE-SEM, HITACHI-SU8010, Japan), coupled with an energy dispersive X-ray (EDX). X-ray diffraction (XRD) analysis was performed using an X-ray powder diffractometer (X'Pert Pro MPD, Holland Panalytical). The transmission electron microscopy (TEM) images were recorded with a Tecnai F20 (FEI, Hillsboro, OR, USA) microscope at an accelerating voltage of 200 kV.

Electrochemical experiments. In electrochemical experiments, the as-prepared triphase reaction system was placed vertically into the electrolyte solution with the GOx/nafion covered area submerged and a portion of the superhydrophobic region kept above the solution level. All of the electrochemical measurements were performed with a CHI 660E electrochemical workstation (CHI Instruments Inc., Austin, USA). The working electrode, Ag/AgCl reference electrode and Pt wire counter electrode were inserted in a cell containing 10 mL solution (0.2 M phosphate buffer solution, PBS, pH 7.2). A stirring rate of 400 rpm was employed during measurements. In the case of nitrogen atmosphere, the gas environment was purged with nitrogen to the bioassay interface. Linear sweep voltammetry experiments were performed at the sweep speed of 50 mV/s, allowing a constant background current to be obtained, and adding the desired concentration of glucose. The current difference was recorded and used to plot the current-concentration curves.

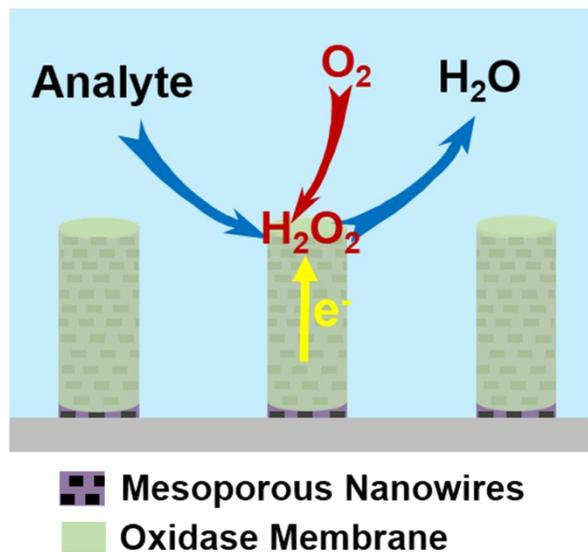


Fig. S1 Schematic illustration of conventional solid-liquid diphasic enzyme electrode system. The availability of oxygen at the reaction interface depends upon its mass transfer through the liquid phase. The low solubility and slow mass transport rate of oxygen in aqueous solutions suppress the oxidase kinetics, and thus the amount of H_2O_2 production, and consequently the performance of the bio-electronic device.

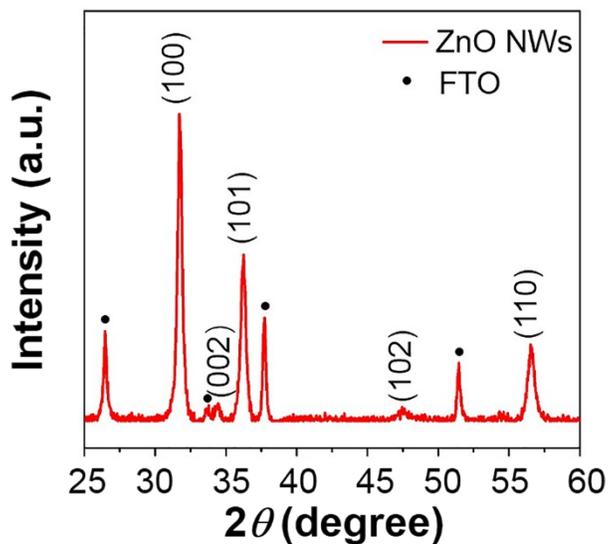


Fig. S2 XRD pattern of the as-prepared mesoporous ZnO nanowire arrays.

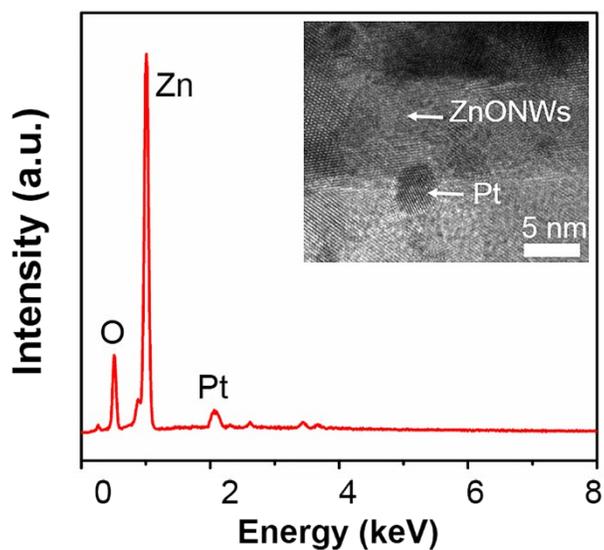


Fig. S3 Energy Dispersive X-ray (EDX) spectra for ZnO nanowires modified with electrocatalyst Pt. Inset: High-resolution transmission electron microscopy (HR-TEM) image of Pt on the nanowire.

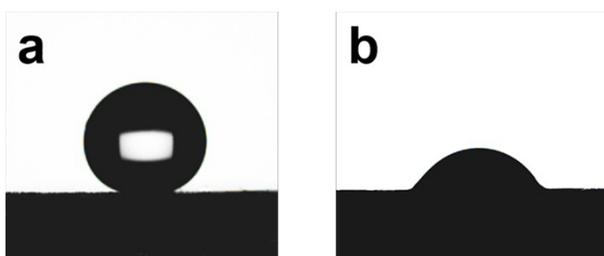


Fig. S4 (a) A spherical water droplet placed on the ZnO NWs after PFOS treating. The water contact angle (CA) is measured to be $151 \pm 2^\circ$. (b) A water droplet placed on the top of GOx immobilized NWs. The surface became hydrophilic with a water CA of $57 \pm 2^\circ$.

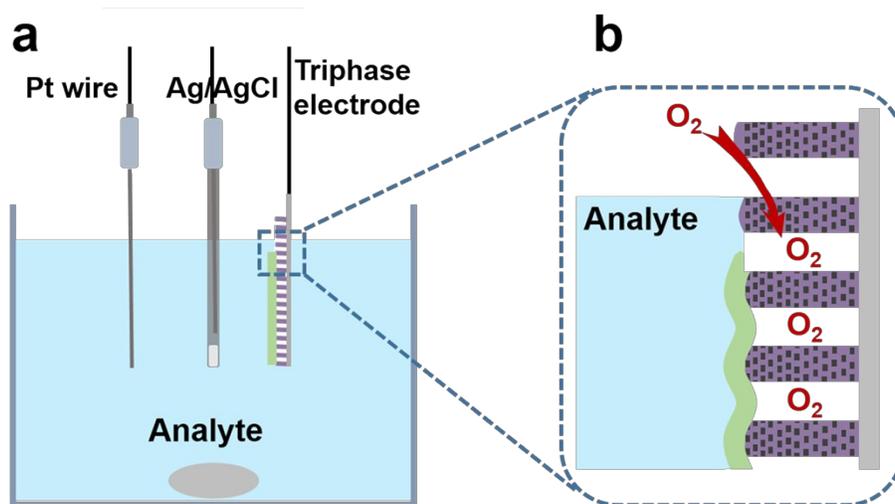


Fig. S5 Schematic representation of the experimental setup based upon the triphase enzyme electrode.

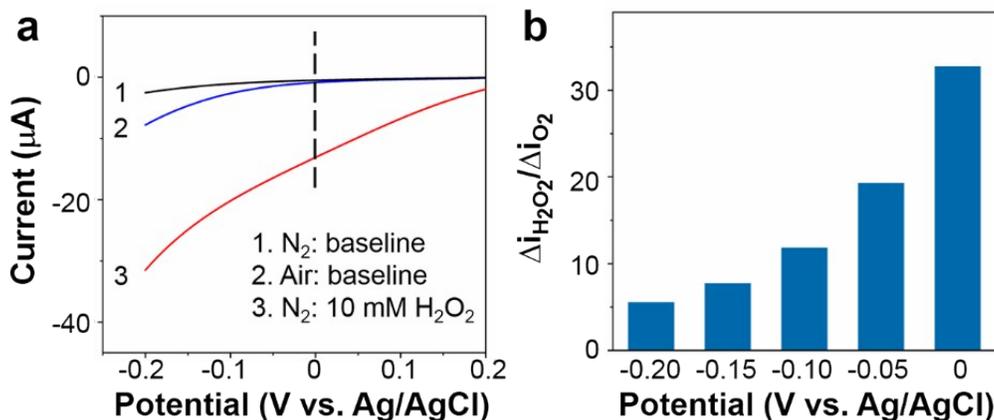


Fig. S6 Influence of oxygen reduction on H_2O_2 detection. (a) LSVs of electrode under different conditions. (b) Relative current response ($\Delta i_{\text{H}_2\text{O}_2} / \Delta i_{\text{O}_2}$) for electrode at different potentials. $i_{\text{H}_2\text{O}_2}$ (black line) and i_{O_2} (blue line) are the current response inside solutions in the absence and presence of air, respectively; $i_{\text{H}_2\text{O}_2}$ (red line) is the current response measured in 10 mM H_2O_2 solution in the absence of oxygen. $\Delta i_{\text{H}_2\text{O}_2} = i_{\text{H}_2\text{O}_2} - i_{\text{H}_2\text{O}_2 - \text{N}_2}$, $\Delta i_{\text{O}_2} = i_{\text{O}_2} - i_{\text{O}_2 - \text{N}_2}$. Cathodic detection was used to monitor the oxidase catalytic kinetics as it can naturally avoid interferences from easily oxidizable species in biological solutions. To minimize current response from oxygen a potential of 0 V was used, the potential that provides the lowest oxygen reduction background current and the highest relative current response ($\Delta i_{\text{H}_2\text{O}_2} / \Delta i_{\text{O}_2}$).

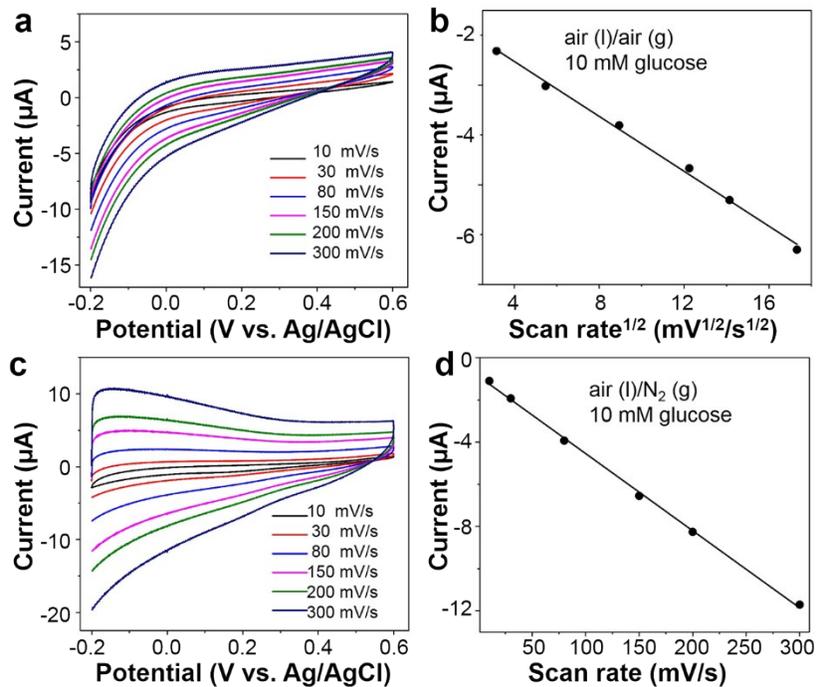


Fig. S7 Cyclic voltammograms of triphase electrode under air atmosphere (a) and nitrogen atmosphere (c) at different scan rates in 0.20 M PBS (pH 7.2) containing 10 mM glucose. (b) The dependence of the cathodic current of glucose (10 mM) on scan rate $v^{1/2}$ using triphase electrode under air atmosphere at 0 V (vs. Ag/AgCl). (d) Plot of current vs. scan rate v under nitrogen atmosphere at 0 V (vs. Ag/AgCl).

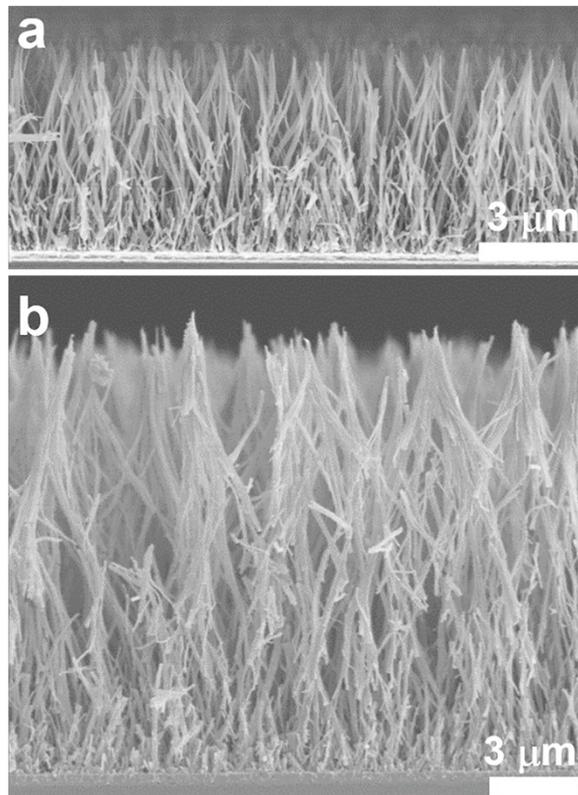


Fig. S8 (a) and (b) are side-views of the ZnO NWs with a length of about 6 μm and 15 μm , respectively.

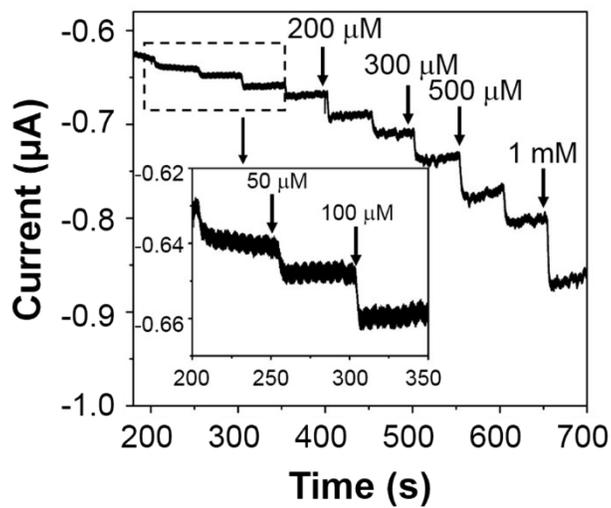


Fig. S9 Amperometric response of triphase electrode after successive addition of glucose. Working potential: 0 V (vs. Ag/AgCl), supporting electrolyte: 0.2 M PBS (pH 7.2).