

Supporting Information

3D hollow-out TiO₂ nanowire cluster / GOx as ultrasensitive photoelectrochemical glucose biosensor

Wenke Yang,^a Xiaohong Wang,^a Wanjun Hao,^{*a} Qiang Wu,^{*b} Juan Peng,^c

Jinchun Tu,^a and Yang Cao,^{a,d}

^a *State Key Laboratory of Marine Resource Utilization in South China Sea, College of Material Science and Engineering, Hainan University, Haikou 570228, China.*

^b *School of Tropical Medicine and Laboratory Medicine, Key Laboratory of Emergency and Trauma of Ministry of Education, Hainan Medical University, Haikou 571199, China.*

^c *State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China.*

^d *Qiongtai Normal University, Haikou 571127, China.*

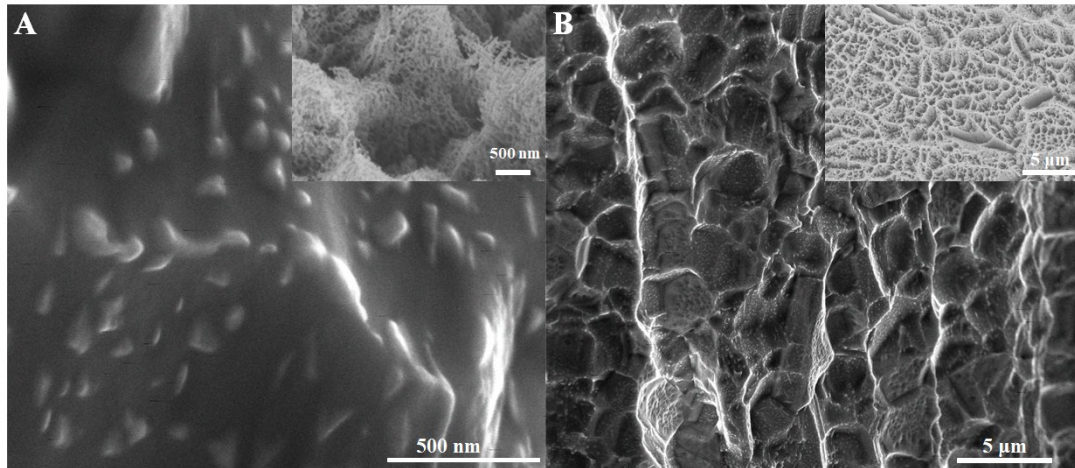


Fig. S1. SEM images (A) and (B) of initial Ti wire mesh at different magnifications. The inset shows the SEM image of the Ti wire mesh after anodization.

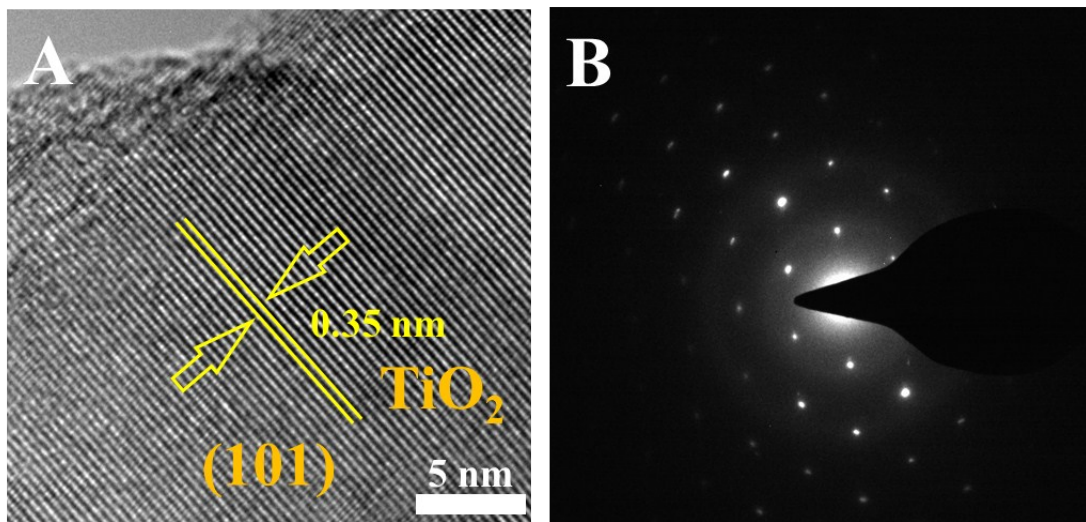


Fig. S2. (A) HR-TEM images of 3D hollow-out TiO₂ NWc of high magnification. (B) SAED pattern of 3D hollow-out TiO₂ NWc.

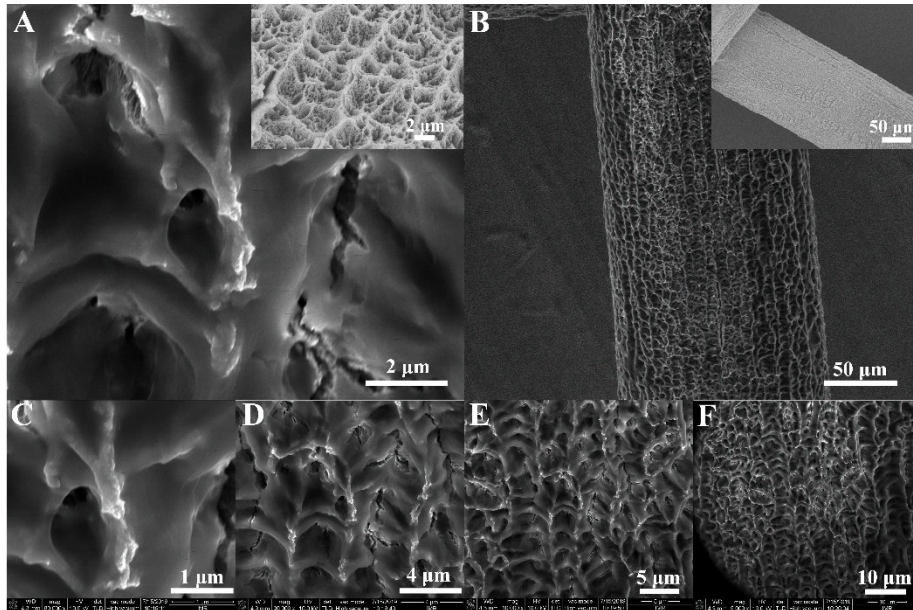


Fig. S3. Partially magnified (A) and complete wire (B) SEM images of 3D hollow-out TiO_2 nanowire cluster loaded with glucose oxidase. SEM images (C, D, E, and F) at different magnifications of 3D hollow-out TiO_2 nanowire cluster after glucose oxidase loading.

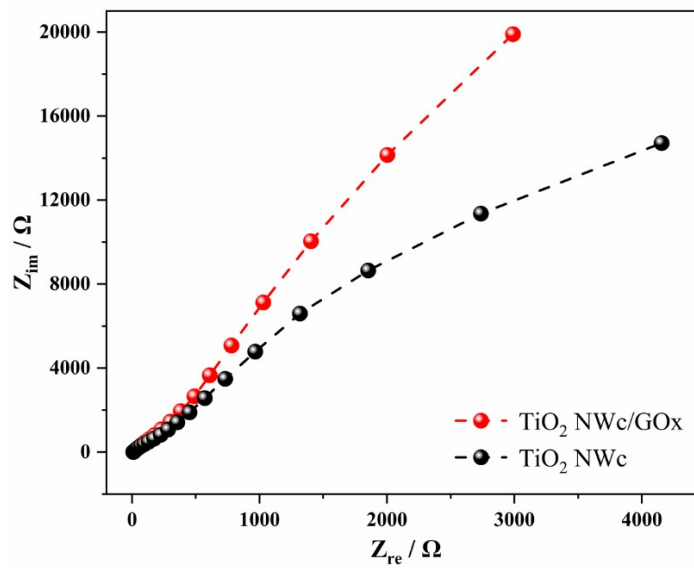


Fig. S4. EIS measurement of TiO_2 NWc before and after GOx loading in 0.1 M PBS (PH=7.4).

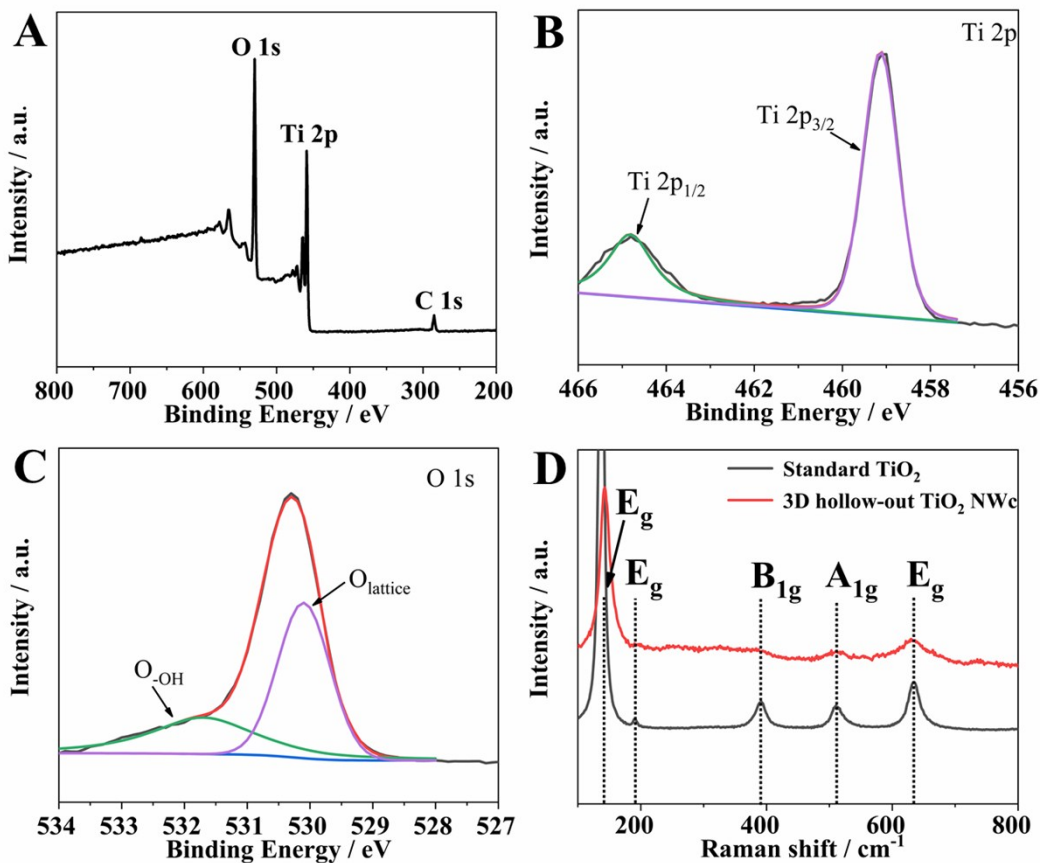


Fig. S5. (A) Wide scan and high-resolution XPS spectra of (B) Ti 2p and (C) O 1s. (D) Raman spectra of 3D hollow-out TiO₂ NWc.

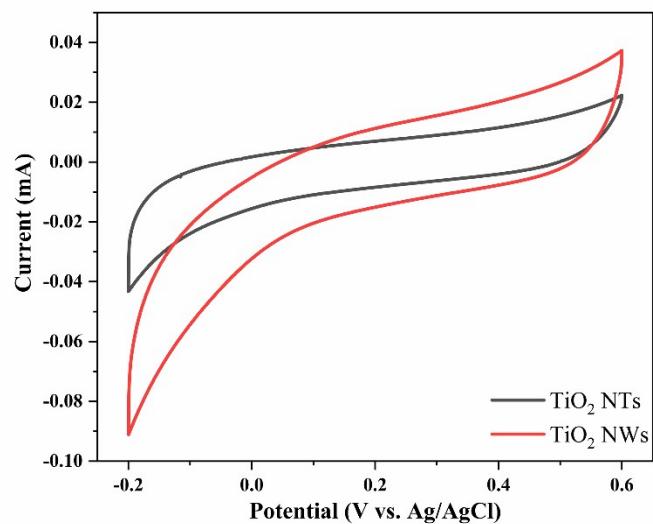


Fig. S6. CV curves for TiO₂ NWc and TiO₂ NTs recorded in 1.0 M PBS (PH=7) at scan rate of 50 mV s⁻¹.

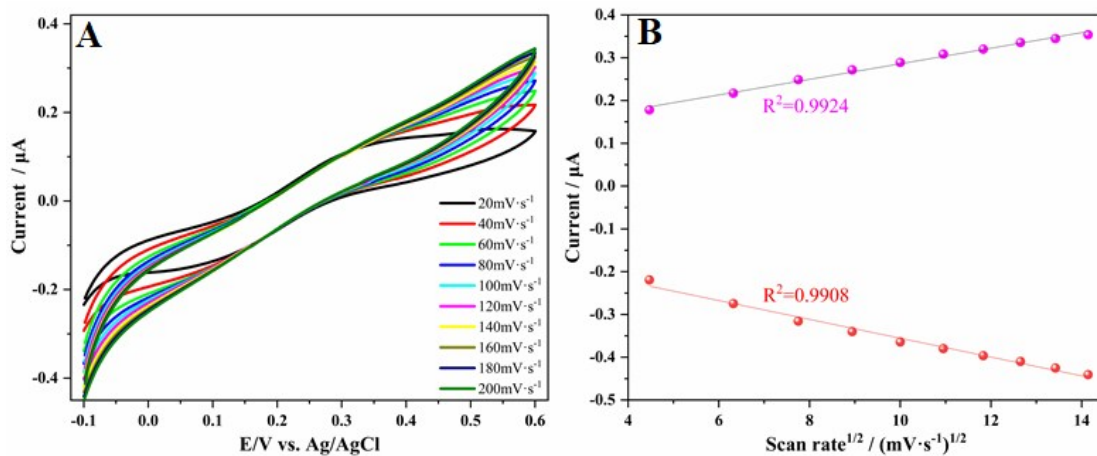


Fig. S7. (A) CV of 3D hollow-out TiO_2 NWc electrode at different scan rates (from $20 \text{ mV}\cdot\text{s}^{-1}$ to $200 \text{ mV}\cdot\text{s}^{-1}$) in a solution containing 10 mM of $\text{Fe}(\text{CN})_6^{3-/4-}$ (0.1 M KCl). (B) Plots of current versus scan rate^{1/2}.

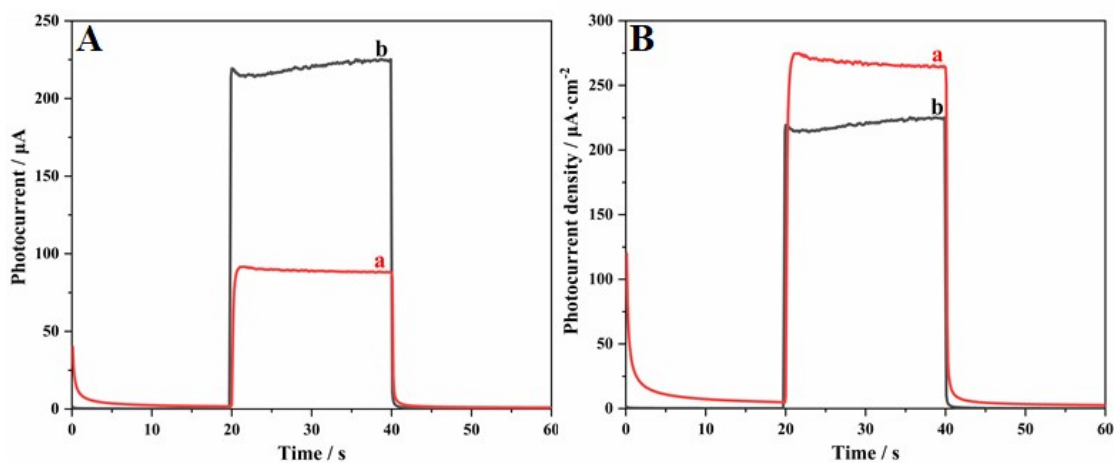


Fig. S8. amperometric *i-t* curve (A) and time–current density curves (B) of 3D hollow-out TiO_2 NWc (curve a) and TiO_2 NTs (curve b).

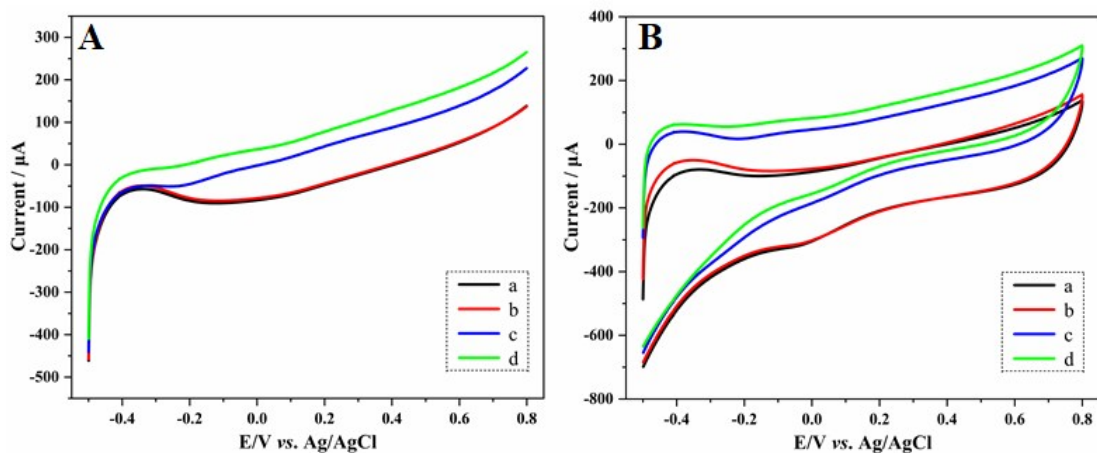


Fig. S9. (A) Linear sweep voltammogram. (B) The CV of the 3D hollow-out TiO_2 NWc

electrode in the (a, c) absence and (b, d) presence of 2 mM glucose under (a, b) lights off and (c, d) on conditions.

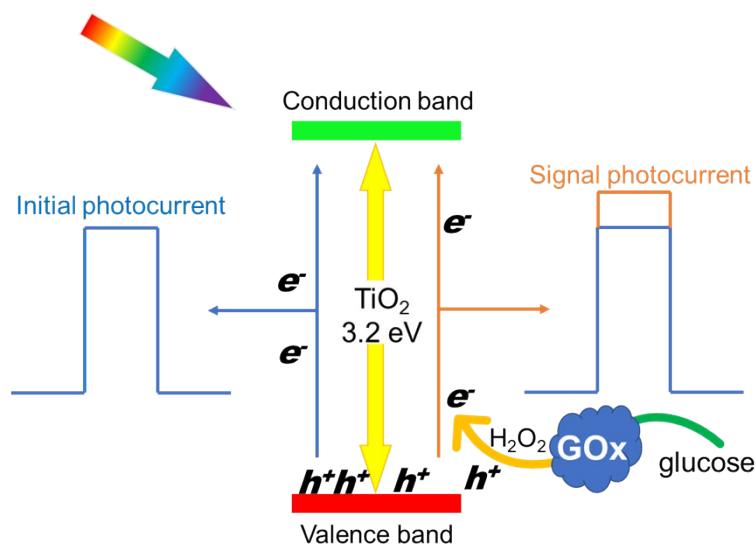


Fig. S10. The mechanism of the photoelectrochemical biosensor.

As shown in Fig. S10, after anatase TiO_2 is irradiated with simulated sunlight, the electrons (e^-) in the valence band absorb the energy of photons and then transition to the conduction band, which forms the initial photocurrent. At the same time, an oxidizing photo-generated hole (h^+) is left in the original position of the electron. In the presence of glucose in the electrolyte, GOx located on the surface of TiO_2 gradually consumes glucose through an enzymatic reaction, thereby generating the active substance H_2O_2 . At this time, the photogenerated holes in TiO_2 will capture the enzymatic products to carry out the redox reaction and generate a signal photocurrent. Different glucose concentrations produce variable electrical signals, which convert biological signals into electrical signals.

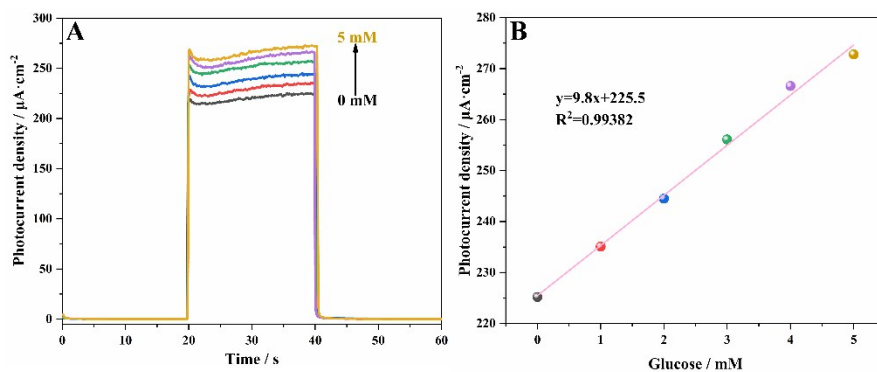


Fig. S11. *i*-*t* responses (A) of TiO₂ NTs/GOx toward Glu at increasing concentrations from 0 mM to 5 mM in electrolyte of 0.1 M PBS (pH 7.4). Linear (B) calibration ([Glu] vs. photocurrent density) curves of TiO₂ NTs/GOx biosensor.