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## Supplemental Information

# WO<sub>3</sub> Nanoparticles Decorated Core Shell TiC/C Nanofiber Arrays for Highly Sensitive Non-Enzyme Photoelectrochemical Biosensing

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### †Electronic Supplementary Information (ESI)†

#### Experimental

##### Preparation of core shell TiC/C nanofibers on Ti substrate

The pristine Ti foils (99.6% purchased from Aldrich) were cut to dimensions of 10 x 10 x 1 mm<sup>3</sup>, polished by SiC paper, and ultrasonically cleaned in acetone, ethanol, and distilled water sequentially. The Ti foils were implanted with Al for 15 min at a pulsed high voltage of -20 kV using a plasma immersion ion implanter (PIII) equipped with a cathodic arc metal ion source at City University of Hong Kong. The thermochemical reaction between the pristine Al ion-implanted Ti foil and acetone vapor is conducted in a horizontal tube furnace. The Al ion-implanted Ti foils were put on a ceramic substrate in the center of an alumina tube. The reactor was purged with argon (Ar) several times to remove residual oxygen and/or moisture before heating to 800 °C. Acetone was introduced into the chamber with Ar as the carrier gas. After 2 h, the sample was cooled to room temperature under flowing Ar to produce the TiC/C core-shell NF arrays on Ti.

##### Synthesis of WO<sub>3</sub> nanoparticles modified TiC/C nanofiber electrode

The WO<sub>3</sub> NPs decorated TiC/C NF arrays were synthesized by thermal evaporation of WO<sub>3</sub> precursors (99.6% purchased from Aldrich) under 10 sccm H<sub>2</sub> flow at 800°C for 2 h. The WO<sub>3</sub> powders were loaded on a ceramic boat in a quartz tube 1 cm in diameter and then inserted into the center of a horizontal tube furnace. The Ti foil with TiC/C NFs was ultrasonically cleaned

in acetone and distilled water sequentially, dried in nitrogen, and faced down to the WO<sub>3</sub> powders with 2 mm distance. The system was heated to the desired temperature for 2 h at a low pressure of 4 torr under 10 sccm H<sub>2</sub> flow. Afterwards, the reactor was cooled to room temperature under evacuation.

##### Materials characterization

The samples were characterized by glancing angle X-ray diffraction at 1° incidence (GAXRD, Philips X' Pert Pro). In addition, contact angle measurements, field-emission scanning electron microscopy (FE-SEM, JSM-820), transmission electron microscopy (TEM, Philips CM20), and high-resolution TEM (HR-TEM, JEM-2010F) were performed to determine the various surface properties and morphology. Micro-Raman spectra were acquired using the 514.5 nm argon laser (HR LabRam).

##### Electrochemical and photoelectrochemical performance of the WO<sub>3</sub>@TiC/C electrode

The electrochemical experiments were conducted on a Zahner Zennium electrochemical workstation using the conventional three-electrode technique. The potential was referenced to a saturated Hg/Hg<sub>2</sub>Cl<sub>2</sub> and the counter electrode was a platinum sheet and the pristine TiC/C or WO<sub>3</sub>@TiC/C NFs being the working electrode. The electrode sealed with a size of 0.5 cm<sup>2</sup> was put in the front of a PEC cell with 15 ml electrolyte. The electrochemical impedance measurement was carried out in a 0.1 M phosphate buffer solution (PBS pH = 7.4) containing 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) as a redox probe by applying an amplitude of 5 mV.

The PEC characteristics of the bare TiC/C and WO<sub>3</sub>@TiC/C electrode were evaluated by linear sweep voltammetry at a scanning rate of 10 mV/s in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution under monochromatic irradiation (400 nm) and photointensity of 5 mW/cm<sup>2</sup>.

### Photoelectrochemical and electrochemical biosensing

The PEC and EC biosensing properties were assessed by determining the amperometric response of the bare TiC/C and WO<sub>3</sub>@TiC/C electrodes in the presence and absence of target compounds in 0.1 M PBS (15 ml). The exposed area on the working electrode was 0.5 cm<sup>2</sup>. A platinum foil and saturated Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode served as the counter electrode and reference electrode, respectively. Monochromatic light (400 nm) with power of 5 mW/cm<sup>2</sup> and 50 mW/cm<sup>2</sup> respectively impacted the electrode and the current was monitored on the Zahner Zennium electrochemical workstation. When the electrolyte was changed, the electrode just was rinsed by ethanol and DI water several times.

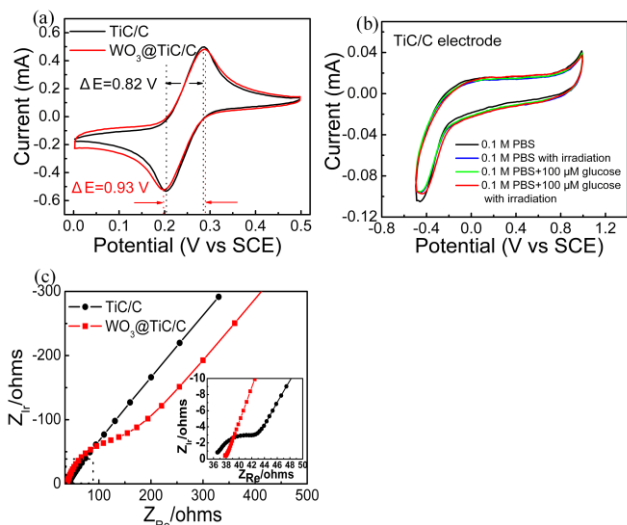


Fig.S1 (a) CV profiles of the bare TiC/C and WO<sub>3</sub>@TiC/C electrodes at a scanning rate of 100 mV/s in a 0.1 M PBS containing 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) as the redox probe. (b) CV profiles of bare TiC/C at a scanning rate of 100 mV/s in 0.1 M PBS with or without additional 100 μM glucose and irradiation. (c) Nyquist plots for bare TiC/C and WO<sub>3</sub>@TiC/C electrodes by applying amplitude of 5 mV under open circuit potential conditions in a frequency range between 10<sup>5</sup> and 0.01 Hz. A 0.1 M PBS containing 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) mixture solution serves as the redox probe.

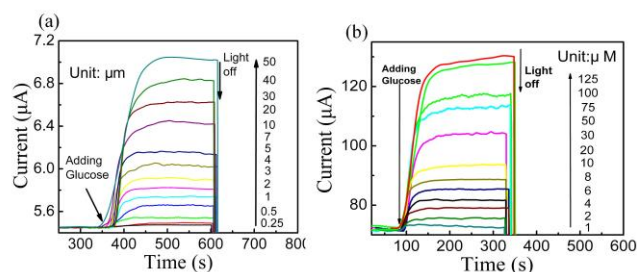


Fig. S2 (a) Transient photocurrent response for different concentrations of glucose (0.25 - 50 μM) under illumination at applied potential of +0.6V in 0.1 M PBS (5mW/cm<sup>2</sup>); (b) Transient photocurrent response for different concentrations of glucose (1 - 125 μM) under high power illumination (50mW/cm<sup>2</sup>) at applied potential of +0.6V in 0.1 M PBS;

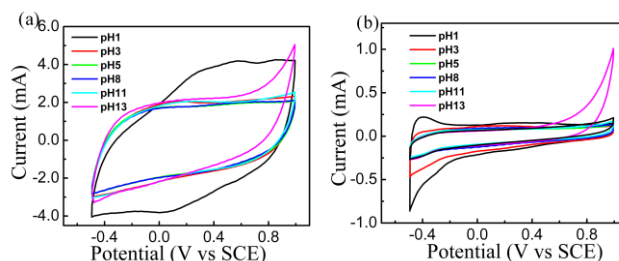


Fig. S3 The CV profiles of the pristine TiC/C (a) and WO<sub>3</sub>@TiC/C (b) electrode in 0.5 M Na<sub>2</sub>SO<sub>4</sub> with different pH value. (adjust by 1M HCl and 1M NaOH)

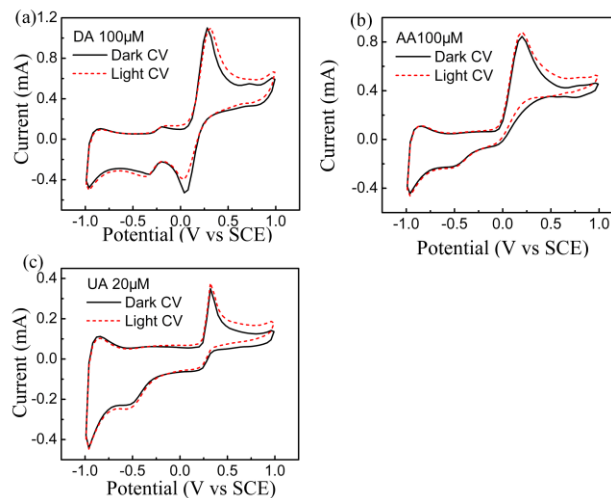


Fig. S4. CV profiles of WO<sub>3</sub>@TiC/C electrode at a scanning rate of 100 mV/s in 0.1 M PBS containing different interferent with or without irradiation. (a) 100 μM dopamine, (b) 100 μM ascorbic acid and (c) 20 μM uric acid.