Supporting Information

TiO_2 nanoparticles-induced nanowires formation facilitates extracellular electron transfer

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Construction and operation of the bioelectrochemical system. A reactor with a liquid volume of 6 ml was constructed, in which the ITO electrode or nanoparticles-coated ITO electrode was used as working electrode, an saturated calomel electrode (SCE) as the reference electrode, and the Ti wire as the counter electrode. Log-phase cells [cell density reached A_{600} of ca. 0.2; 5% (v/v) inocula] were inoculated into the chamber, which contained the freshwater medium supplemented with 16 mM acetate as the electron donor. All potentials were determined relative to the SCE, and the potential of SCE with respect to standard hydrogen electrode is +0.2415 V.

Measurement of electrical conductivity. The electrical conductivity of ITO and NPs-coated ITO was measured at 25 °C by four-probe method using a FT-330 resistance meter (Ningbo Argal instrument Co., Ltd, China). For each electrode, 3 replicates were prepared, and the conductivity was measured at various positions of the pellets by the four probe to collect at least 50 data, and the average value was given in Table S1.

Calculation of electrochemically active surface area (EASA). In order to determine the EASA, cyclic voltammetry (CV) was conducted after immersing the electrodes in deaerated solutions containing 0.1 M $K_4Fe(CN)_6$ and 0.1 M KNO_3. CV tests were carried out at different scan rates in a range of 5 to 100 mV/s and over a potential range of -0.4 to 0.8 V (vs SCE). The CVs obtained using different electrodes were shown in Figure S3. The Randles-Sevcik plots were derived from the anodic peak currents, and the slopes of the Randles-Sevcik plots were then used to determine the EASA of the electrodes (Table S1).

RT-qPCR. Total RNA was extracted from electrode-grown cells when the current generation reached a peak plateau by using TRIzol (Invitrogen), and treated with GE

reagent (Qiagen) for genomic DNA removal. cDNA was generated from total RNA with reverse transcriptase (Invitrogen) in duplicate. A QuantiTect SYBR Green PCR Kit (Qiagen) and the ABI ViiA 7 Real Time PCR System were used to amplify and quantify PCR products.

Western blotting. Briefly, protein concentrations were measured with the bicinchoninic acid (BCA) assay (Micro BCA protein assay kit; Thermo Scientific). 50-mg of total protein from different electrodes was fractionated by SDS-PAGE using 12.5% Tris-tricine polyacrylamide gel (Amresco, Solon, OH, USA), and transferred to polyvinylidene difluoride (PVDF) membranes (Bio-Rad, Hercules, CA, USA). The blotting membrane was treated with anti-pilA rabbit polyclonal antibody and anti-rabbit secondary antibody conjuncated with horseradish peroxidase (Sangon Biotech, Shanghai, China) sequentially. The PilA band was visualized by the chemiluminescence System (ChemiScope 3300, Clinx Science Instruments Co., Ltd., China). All of the experiments were repeated at least three times.

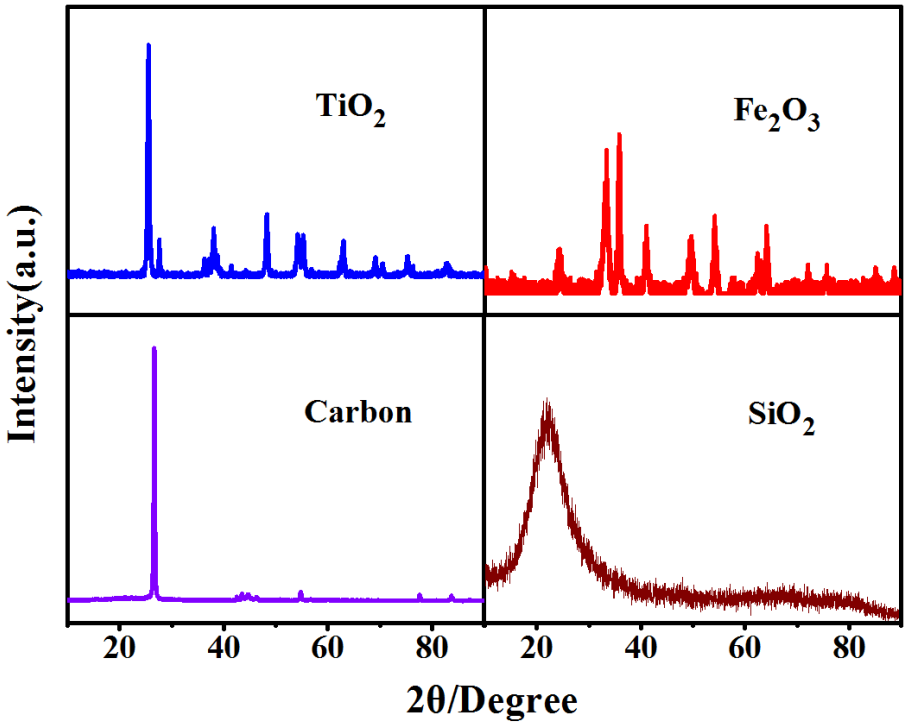

Figure S1 XRD patterns of NPs on the surface of ITO electrodes. The XRD were recorded on an Empyrean diffractometer at room temperature, operating at 40 kV and 40 mA, using a Cu Kα radiation (λ = 0.15418 nm).

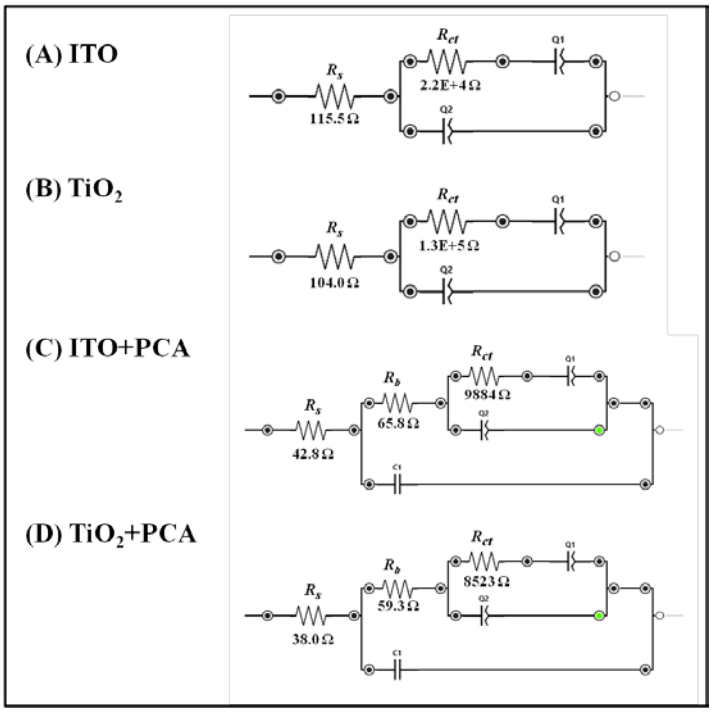

Figure S2 The equivalent circuits used for fitting the EIS spectra for bare ITO (A) bare TiO_2 NPs-coated ITO (B), biofilm-attached ITO (C), and biofilm-attached TiO_2-coated ITO (D), where the element R_s represents solution resistance (ohmic resistance), R_{ct} represents the activation (charge transfer) resistance, and R_b represents the biofilm resistance. The values obtained by fitting the EIS spectra were shown below each element.

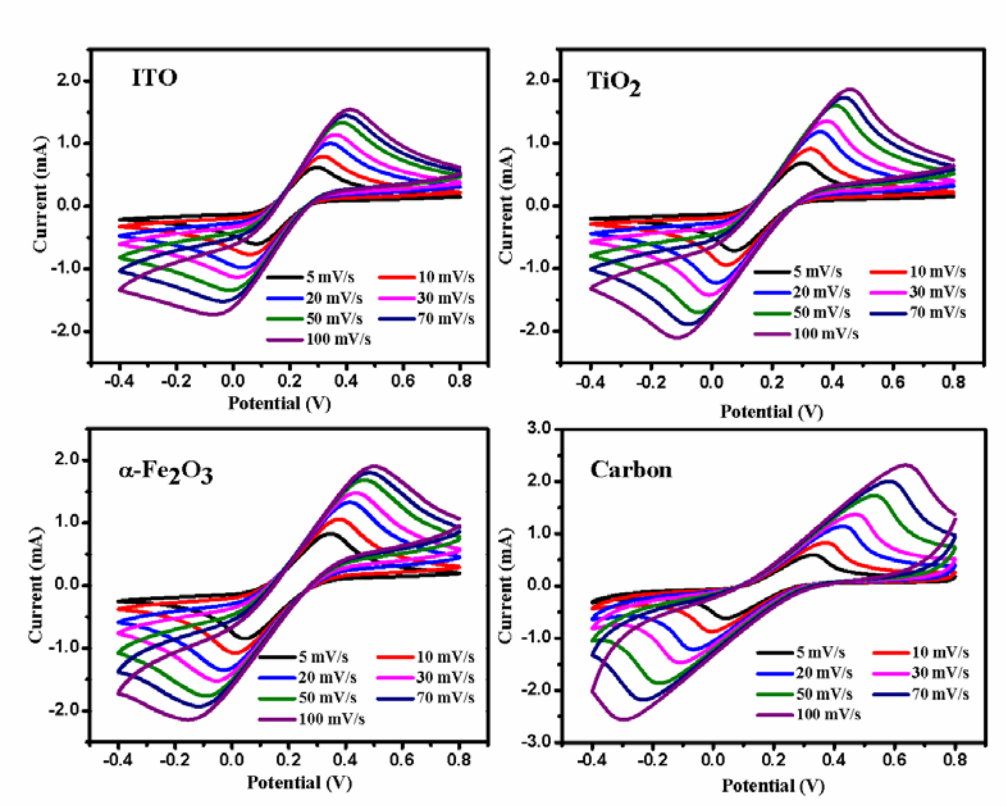

Figure S3 Determination of the EASA using CVs conducted in 0.1 M KNO_3 containing 0.1 M $K_4Fe(CN)_6$ at different scan rates of 5, 10, 20, 30, 50, 70, 100 mV/s

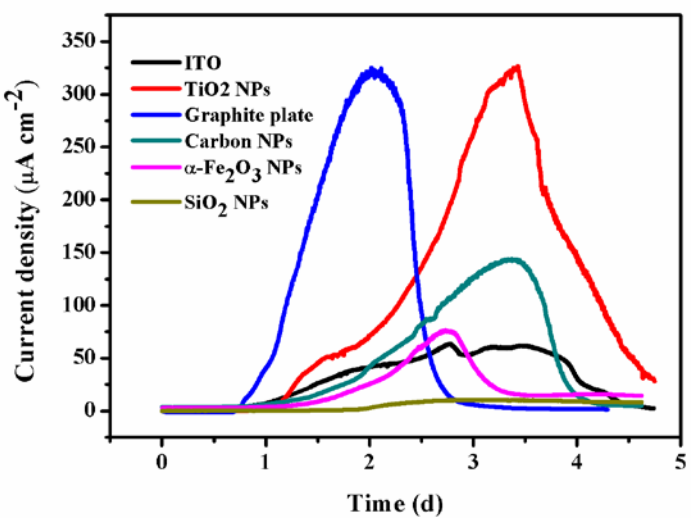

Figure S4 Amperometric i-t curves for strain PCA grown on graphite plate and on ITO electrode coated with different NPs. The current densities produced were calculated normalized with the anode areas (Table S1).

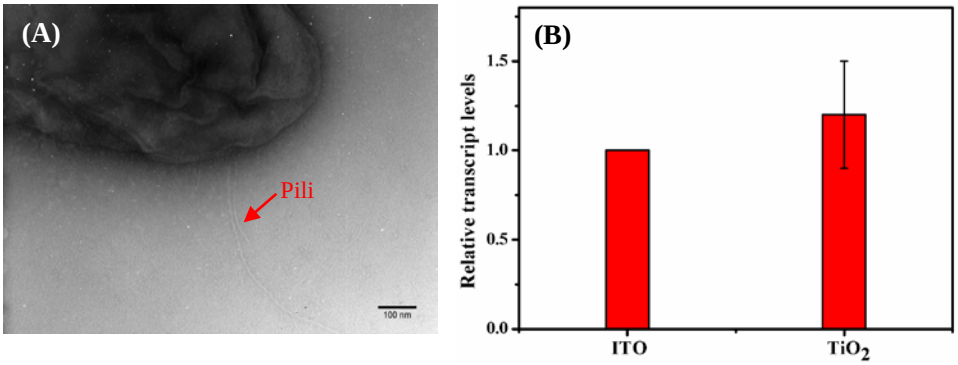

Figure S5 TEM images (A) and RT-qPCR analysis (B) of *pilA* gene showing the pili production in Δ*omcS Geobacter* cells was not enhanced by TiO_2 NPs.

Table S1 Characterization of various electrodes used in this study

Electrodes	Surface electrical conductivity (S/cm)	Anode area (cm^2)
ITO	0.25	1.21*
TiO_2-coated ITO	0.16	1.52*
α-Fe_2O_3-coated ITO	0.084	1.39*
Carbon-coated ITO	0.52	2.18*
SiO_2-coated ITO	-	1.33§
Graphite electrode	4.00	1.33§

*The EASA determined using Randles-Sevcik plots. §The surface area calculated based on the electrode size. -, exceeded the acceptable range of the meter.

Table S2 Primers used for RT-qPCR analyses.

Gene	Primer name	Primer sequence (5'-3')
pilA	*pilA*-F	ATCGGTATTCTCGCTGCAAT
	pilA-R	AATGCGGACTCAAGAGCAGT
omcS	*omcS*- F	TGGTTGGCGAAGGCATAGG
	omcS- R	CCATCAAGAACAGCGGTTCC
omcZ	*omcZ*- F	AAGGTTGCTGACCTTGTTGG
	omcZ- R	CCACCTATCAGCCCACTGTT
recA	*recA*- F	CACCGGCATAATCTCCAAGT
	recA- R	ATCTTGCGGATATCGAGACG
omcT	*omcT*- F	GGCTTCTGCGGTACTGATGT
	omcT- R	CCAGCAGATGAACAACGCTA