**Supporting Information**

# Photo-hydrogen production by *Rhodopseudomonas faecalis* RLD-53 immobilized on the surface modified activated carbon fibers

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## Experimental Section

### Bacterium and medium

The photo-fermentative bacteria used in this work was *Rhodopseudomonas faecalis* RLD-53, which was previously isolated from freshwater pond sludge.[1] Acetate was the sole carbon source in the medium for hydrogen production. The culture medium of strain RLD-53 consisted of (in g/l) acetate, 4.1; glutamate,1.69; $KH_2PO_4$, 0.5; $K_2HPO_4$,0.5; $MgSO_4{\cdot}4H_2O$, 0.2; EDTA-Na, 0.1; $CaCl_2$, 0.08; NaCl, 0.1; $FeSO_4{\cdot}7H_2O$, 0.012; L-cysteine, 0.5; trace element solution, 1ml; vitamin solution, 1ml. The trace element solution contained $CoCl_2.6H_2O$ 0.01 g, $FeCl_2.4H_2O$ 1.8 g, $CuCl_2.2H_2O$ 0.01 g, $ZnCl_2$ 0.1 g, $MnCl_2.4H_2O$ 0.7 g, $NaSeO_3.5H_2O$ 0.01 g, $H_3BO_3$ 0.5 g, dd$H_2O$ 1.0 L. The vitamin solution contained Biotin 0.1 g, p-Aminobenzo acid 0.2 g, Niacin 0.35 g, Thiamine dichloride 0.3 g, Vitamin $B_{12}$ 0.05 g, Ca-panthothenate 0.1 g, Pyridoxolium hydrochloride 0.1 g , dd$H_2O$ 1.0 L. The initial pH of the medium was adjusted to 7.0 by 0.1 N HCl or NaOH.

### Activated carbon fibers and surface modification

Activated carbon fibers (ACFs) were obtained from Sinocarb Carbon Fibers CO., LTD (Anshan,China) with specific surface areas of 1500 $m^2/g$. Before their modification, these commercial fibers were washed in the acetone with ultrasound to remove the surface contamination, and finally dried in a vacuum oven at 105 $^oC$. Surface modifications were conducted by $HNO_3$ oxidation followed by steam explosion. The ACFs (1 g) were added into aqueous $HNO_3$ (400 ml) with concentration of 0, 2, 4, 6 mol/l in a round bottom flask equipped with a condenser. The oxidations were carried out at the boiling temperature for 1 h. The oxidized fibers were repeatedly washed with distilled water until the pH was about 7.0 to remove residual acid. Fibers were then dried overnight in an oven at 105 $^oC$. Steam explosion modifications were performed using the oxidized fibers in a sealed bottle at 1.21 MPa steam for 15 min, and the pressure was then released. The samples were labeled as ACFS-0, ACFS-2, ACFS-4 and ACFS-6 according to the $HNO_3$ concentrations, respectively.

**Hydrogen production condition**

The hydrogen production experiments were conducted with 80 ml of the medium in 100 ml sealed reactors and filled with argon to keep anaerobic conditions. The reactors were autoclaved at 121 °C for 15 min. *R. faecalis* RLD-53 in the mid-exponential growth phase was inoculated into reactors. The reactors were stirred at 120 rpm at constant temperature of 35 °C. The light intensity on the outside surface of the reactors was maintained at 4000 lux by incandescent lamps (60 W).

**Scanning electron microscope (SEM) tests**

Surface morphology analysis of the ACFs was evaluated in a scanning electron microscope (SEM). The ACFs samples after immobilization were fixed with 2.5% glutaraldehyde and left for 1.5 h in a 4 °C refrigerator. The samples were gently washed with phosphate buffer solution and then dehydrated by successive passages through 50%, 70%, 80%, 90%, and 100% ethanol. Each rinsing and dehydrating step took 10 min. The samples were refreeze dried (Hitachi E-2030, Japan) for 4 h, subsequently coated with gold powder by Sputter Coater (Hitachi E-1010, Japan) and finally attached on to the microscope supports with silver glue. Scanning electron microscope images were taken at 5 kV using an SEM from Hitachi S-3400N, Japan.

**X-ray photoelectron spectroscopy (XPS) analysis**

X-ray photoelectron spectroscopy (XPS) was employed to determine the number and type of functional groups present on the surface of the ACFs samples. XPS was carried out on a PHI-5600 equipped with a monochromatic Al Kα source and data acquisition and processing were conducted using the PC Access ESCA version 7.2A program. The anode voltage and power were 12.5 kV and 250 W, respectively. The pressure in analysis chamber was maintained at $10^{-9}$ Torre during each measurement. All binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. Before each analysis, the carbon fibers samples were dried under vacuum at 105 °C. Spectra were analyzed using XPS Peak software (Version 4.1).

**Analytical method**

Biogas was sampled from the head space of the photobioreactor by using gas-tight glass syringes and hydrogen content was determined by using a gas chromatograph ((Agilent 4890D, Agilent Technologies, USA). The gas chromatograph column was Alltech Molesieve 5A 80/100. Argon was used as the carrier gas with a flow rate of 30 ml/min. Temperatures of the oven, injection, detector, and filament were 35 °C, 120 °C, 120 °C, 140 °C, respectively. Residual acetate in the effluent of culture broth were determined using a second GC(Agilent 7890 A, Agilent Technologies, USA) equipped with a flame ionization detector. The liquor samples were firstly centrifuged at 12,000 rpm for 5 min, and filtered through a 0.2 μm membrane before free acids were analyzed. The operational temperatures of the injection port, the column and the detector were 220, 190 and 220 °C, respectively. Nitrogen was used as carrier gas at flow rate of 50 ml/min.

## References

1. N. Q. Ren, B. F. Liu, J. Ding and G. J. Xie, *Bioresour. Technol.*, 2009, **100**, 484-487.