Electronic supplementary information (ESI) for Chemical Communications

A photoelectrochemical methanol fuel cell based on aligned TiO_2 nanorods decorated graphene photoanode

Xinyuan Li,[a] *Guowen Wang,*[b] *Lin Jing,* [a] *Wei Ni,* [a] *Huan Yan,* [a] *Chao Chen,* [a]

*Yi-Ming Yan**[a]

a: Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing, 100081, People's Republic of China

b: Beijing Aerospace Propulsion Institute, Beijing, 10076, People's Republic of China

*Corresponding Author.

Email: bityanyiming@163.com

Tel (Fax): +86-10-68918696

Experimental

Preparation of G-TNRs: Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummer's method. G-TNRs were synthesized by a modified hydrothermal method according to a previous report [1]. Briefly, 0.02 g of GO was dispersed into 20 mL of absolute ethanol, and the mixture was processed by ultrasound for 1 h to obtain a clear suspension. Then 0.022 mL of tetrabutyl titanate (TBOT) was slowly added into the suspension and then the mixture was stirred for 1h. Subsequently, the mixture was centrifuged and dried at 60 ˚C to obtain a brown powder. After the brown power was annealed at 500 ˚C for 2 h under Ar atmosphere, the RGO sheets decorated with TiO_2 nanocrystal seeds were prepared. Subsequently, 40 mL of deionized (DI) water, 40 mL of concentrated HCl (37.5%), and 2.83 mL of TBOT were mixed with magnetic stirring, and then the RGO sheets decorated with TiO_2 nanocrystal seeds were added into the mixture with a further 5 min agitation. The mixture was then transferred into a 100 mL teflon-lined stainless steel autoclave, and heated at 150˚C for 4 h. After cooling to room temperature, the precipitate was then separated by centrifugation at 4200 rpm, washed with DI water and ethanol several times to remove residuum. The obtained product was dried in vacuum at 60 ˚C overnight.

Preparation of pure TNRs: Indium-tin oxide (ITO) was heated to 500 ℃ in air for 1 h, and then transfered into a 50 mL teflon-lined stainless steel autoclave with the mixture of 20 mL of DI water, 20 mL of concentrated HCl (37.5%), and 1.42 mL of TBOT. The mixture was kept at 150℃ for 4 h followed by naturally cooling to room temperature. After the as-obtained product was peeled from ITO, it was washed with DI water and ethanol several times to remove residuum. Finally, the prepared product was dried in vacuum at 60 ˚C overnight.

Structural and morphological characterization: The morphology structure of the synthesized powders was observed by scanning electron microscopy (SEM, QUANTA FEG 250) and transmission electron microscopy (TEM, FEI Tecnai, Model

G2T30). Raman spectra was obtained by a Micro-Raman spectrometer system (Renishaw RM 2000). X-ray diffraction (XRD) patterns of the powders were performed through a diffractometer (D8 Focus, Bruker instrument, Germany) with Cu Kα radiation (λ =1.5406 Å) to determine the crystal structure. UV-vis spectra of the powders were measured by a UV-vis spectroscopy (PE Lambda-35, Perkins Elmer) with a wavelength range of 300-800 nm. X-ray photoelectron spectroscopy measurements were performed with a Kratos HSi spectrometer with a hemi-spherical analyzer. FTIR measurements were performed with a Perkin Elmer FT-IR spectrophotometer in the spectral range 500-4000 cm^{-1}.

Electrochemical and photoelectrochemical measurements and PECFC assembly: ITO was processed by ultrasound for 15 min in soapy water, DI water, acetone and ethanol, respectively, before used. The photocatalytic electrode was prepared as follows: 4 mg of the G-TNRs and 4 mg of TNRs were dispersed in 1 mL of ethanol respectively, ultrasound dispersed evenly. Then, the samples were loaded onto the ITO electrodes (1×1 cm squares) drop by drop at 60°C, respectively. Herein, the TNRs electrode was prepared for comparison. The photocatalytic performance were performed with a CHI 660 electrochemical workstation (Chenhua, Shanghai, China). And the measurements were completed in a 0.5 M Na_2SO_4 electrolyte solution (pH 7), using the three-electrode setup (particles coated ITO electrode as the working electrode, a Pt wire as the counter electrode, and saturated calomel electrode (SEC) as the reference electrode). The photocurrent was recorded under a bias voltage of 0.2 V with a photo resource 500 W Xe lamp with tunable cut-off filter (71SW30, Saifa, Beijing, China). The input power density of the light is 0.5 $mW \cdot cm^{-2}$. The relationship between light wavelength and photocurrent on different modified electrodes was studied in the light wavelength range of 280 to 420 nm. The photocurrent was also measured for each switch on/off event under monochromatic light 360 nm irradiation. Linear sweep voltammetry (LSV) was recorded with a sweeping rate of 1 $mV \cdot s^{-1}$ under illumination of solar simulator (PLS-SXE300C, Bofeilai, Beijing, China) or darkness. The preparation of ORR electrode was similar to photocatalytic electrode. Briefly, 5 mg of the GN-CNT was dispersed in 5 mL of ethanol, after ultrasonic for

10 minutes, the obtained homogeneous suspension was loaded onto the pretreated ITO electrode (1×1 cm squares) drop by drop at 60°C. And electrochemical experiments were performed with a CHI 660 electrochemical workstation and conducted in a oxygen-saturated 0.5 M Na_2SO_4 electrolyte solution (pH 7), using the three-electrode setup (GN-CNT as the working electrode, SEC as the reference electrode, and a Pt wire as the counter electrode).

To confirm the feasibility of the PEC fuel cell, we constructed a PEC fuel cell using a two-compartment quartz with a Nafion membrane as the separator. The electrode materials of photoanode and cathode were G-TNRs and GN-CNT, respectively. Polarization curves of the PEC fuel cell were performed with a CHI 660 electrochemical workstation combining with a solar simulator. For comparison, we also examined the performance of PEC fuel cell based on TNRs photoanode.

Mechanism for the photocatalytic oxidation of methanol:

The mechanism has been proposed in previous reports [2, 3] for the photocatalytic oxidation of methanol. Here, the process of the photocatalytic degradation of methanol can be described as follow. The UV irradiation activates TiO_2 to generate strongly oxidative holes (h_{VB}^+) in valence band and the h_{VB}^+ react with H_2O to generate a free radical ·OH. The free radical ·OH could oxidize the methanol to form formaldehyde and formic acid, and further oxidize to CO_2 and H_2O (eqs 1, 2, 3)."

$$TiO_2 \xrightarrow{hv} e_{CB}^- + h_{VB}^+ \qquad (1)$$

$$h_{VB}^+ + H_2O \rightarrow \cdot OH + H^+ \qquad (2)$$

$$CH_3OH \xrightarrow{\cdot OH} HCHO \xrightarrow{\cdot OH} HCOOH \xrightarrow{\cdot OH} CO_2 + H_2O \qquad (3)$$

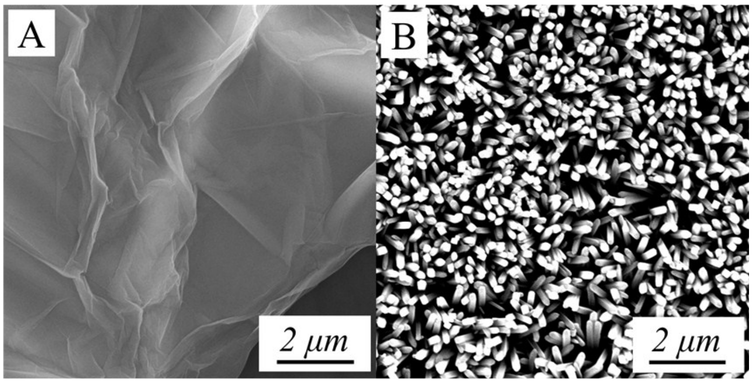

Fig.S1 SEM images of GO (A) and TNRs (B).

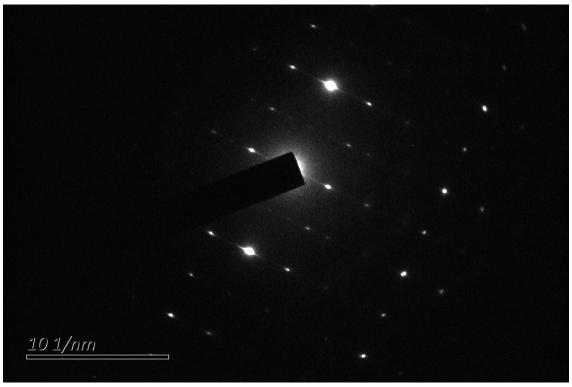

Fig.S2 highly symmetric selected area electron diffraction pattern of G-TNRs.

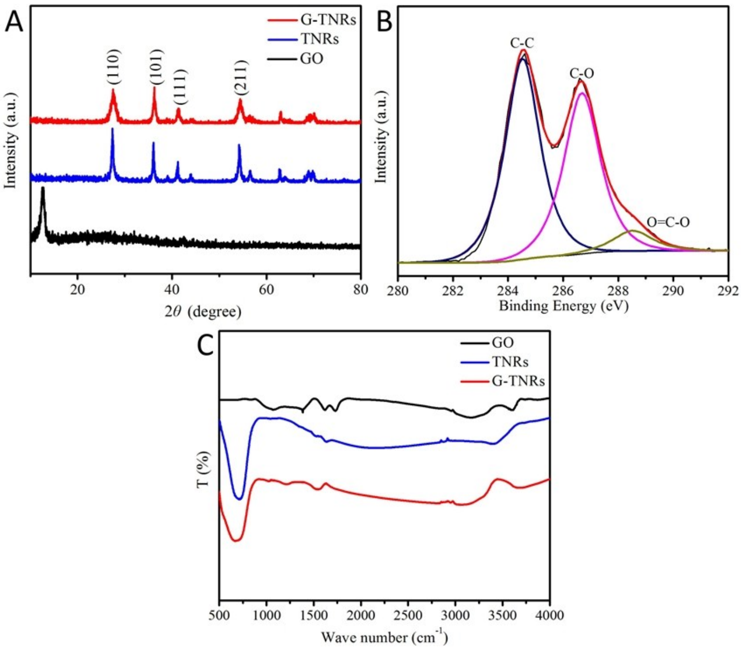

Fig.S3 XRD images (A) and FTIR spectra (C) of G-TNRs, TNRs, GO, respectively. (B) High-resolution XPS spectra of C1s for GO.

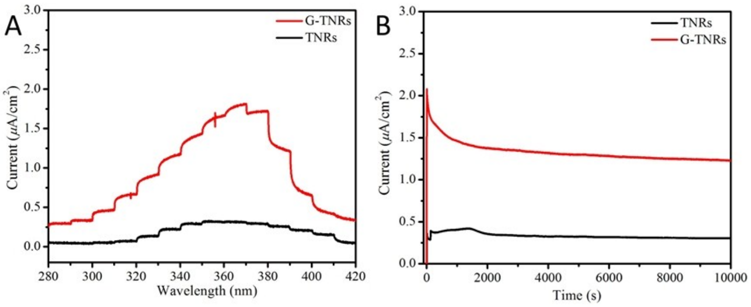

Fig.S4 (A) The photocurrent-wavelength curves obtained from TNRs and G-TNRs modified ITO electrodes in the electrolyte of 0.5M Na_2SO_4 and 1 M methanol with a bias voltage of 0.2 V. (B) The stability of the PEC methanol oxidation reaction on the TNRs and G-TNRs electrodes.

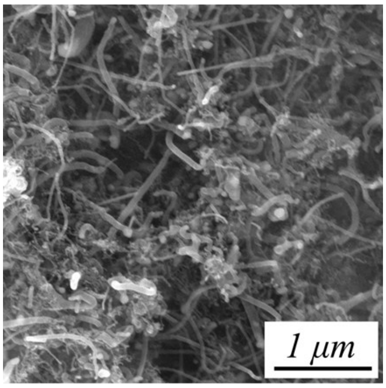

Fig.S5 SEM images of GN-CNT.

Notes and references

1. R. Zou, Z. Zhang, L. Yu, Q. Tian, Z. Chen, J. Hu, Chemistry-A European Journal, 2011，17，13912-13917.
2. R. Wang, G. Jiang, Y. Ding, Y. Wang, X. Sun, X. Wang and W. Chen, ACS applied materials & interfaces, 2011, 3, 4154-4158.
3. J. Schneider and D. W. Bahnemann, The Journal of Physical Chemistry Letters, 2013, 4, 3479-3483.