

## Supporting Information

### Enhanced Charge Separation of TiO<sub>2</sub> Nanotubes Photoelectrode for Efficient Conversion of CO<sub>2</sub>

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## **Supplementary Note**

### **Materials and methods**

#### **Reagents**

The chemical reagents used in this work were AR grade and bought from the company of Sinopharm Chemical Reagent Co. Ltd including fluorinated ammonia ( $\text{NH}_4\text{F}$ ), propanetriol ( $\text{C}_3\text{H}_8\text{O}_3$ ), oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), glacial acetic acid ( $\text{CH}_3\text{COOH}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium hydrogen carbonate ( $\text{KHCO}_3$ ) and palladium chloride ( $\text{PdCl}_2$ ). The water utilized throughout this study was deionized water.

#### **Fabrication of $\text{TiO}_2$ nanotubes (TNTs) photoelectrode**

An anodization process was used to construct the  $\text{TiO}_2$  nanotubes (TNTs) photoelectrodes. Before anodization, Ti foils were pretreated with oxalic acid for 2 h under the temperature of 98 °C to remove oil stains on the surface of Ti foils. After pretreatment, deionized water was used to wash away the oxalic acid on the surface of Ti foils. Finally, the Ti foils were kept in alcohol solution at room temperature before use. The anodization of the Ti foils was conducted in a 100 ml plastic beaker in which the anode and cathode were Ti foil and Pt foil, respectively. The electrolyte was fluorinated ammonia and propanetriol in deionized water, and a direct-current power

was used to supply the applied voltage. The applied voltage was 20 V and the anodization process lasted for 2 h. When the anodization process was over, the amorphous TiO<sub>2</sub> photoelectrodes were dried in an oven with a temperature of 70 °C for 4 h and then calcined at 500 °C for 2 h. Finally, the TiO<sub>2</sub> nanotubes photoelectrode regarded as TNTs were obtained.

Fabrication of TNTs photoelectrodes decorated with MnO<sub>x</sub> (Mn/TNTs).

TNTs were decorated with MnO<sub>x</sub> by a simple impregnation method. First, 0.4 g, 0.6 g, 0.8 g or 1.0 g of KMnO<sub>4</sub> were put into 200 mL of deionized water, and the solution was stirred continuously for half an hour. Next, 20 mL of acetic acid (1.0 M) was poured into the KMnO<sub>4</sub> aqueous solution, and the mixture solution containing acetic acid and KMnO<sub>4</sub> was stirred continuously for half an hour. Finally, TNTs were placed into the mixture solution for 2 h in a vacuum oven, and then dried with the temperature of 70 °C for 6 h in the vacuum oven, calcined at the temperature of 400 °C for two hours (N<sub>2</sub>). The heating rate was set as 5 °C min<sup>-1</sup>. The TNTs photoelectrodes decorated with MnO<sub>x</sub> were referred to as XMn/TNTs, where X stands for the different amount of KMnO<sub>4</sub> used.

Fabrication of TNTs photoelectrodes decorated with Pd (Pd/TNTs)

Pd was electrodeposited onto the TNTs photoelectrodes through application of a constant potential (−0.8 V) in a three-cell configuration with an electrolyte consisting of a mixture of PdCl<sub>2</sub> (1 mM) and NaSO<sub>4</sub> (0.5 M). The cathode was the synthetic TNTs photoelectrode, anode was a Pt foil and the reference electrode was a standard calomel electrode. To control the amount of the deposition of Pd, the

electrodeposition time was varied for 3, 5, 7, 10, 15 min. After electrodeposition, the photoelectrodes were washed repeatedly with deionized water, and then dried at 70 °C for four hours in a vacuum oven. The TNTs photoelectrodes decorated with Pd were referred to as YPd/TNTs, where Y indicates the electrodeposited time.

Preparation of TNTs photoelectrodes co-decorated with MnO<sub>x</sub> and Pd (Pd/Mn/TNTs)

To codecorate TNTs photoelectrodes with Pd and MnO<sub>x</sub>, Pd was electrodeposited onto the Mn/TNTs photoelectrodes through application of a constant potential (−0.8 V) in a three-cell configuration. The cathode was the Mn/TNT photoelectrode, the anode was Pt, and the reference electrode was a saturated calomel electrode, in a PdCl<sub>2</sub> solution (1 mM) and a NaSO<sub>4</sub> (0.5 M) electrolyte. To control the amount of the deposition of Pd, the electrodeposition time was varied for 3, 5, 7, 10, and 15 min. After treatment, the photoelectrodes were repeatedly washed using deionized water, and then dried at 70 °C for four hours in a vacuum oven. The TNTs photoelectrodes codecorated with MnO<sub>x</sub> and Pd were referred to as YPd/XMn/TNTs, where Y indicated the electrodeposition time. All of the photoelectrodes were prepared in duplicate.

### **Characterization of materials.**

A diffractometer (Rigaku D/MAX III-3B) with accelerating voltage of 40 kV, applied current of 30 mA and radiation of Cu Ka was used to measure the crystal phase composition of the synthetic photoelectrodes. Ultraviolet-vis diffuse reflectance spectroscopy of different photoelectrodes was obtained using a spectrophotometer (model UV-2550, Shimadzu), and BaSO<sub>4</sub> was used as the reference material. The

XPS measurement was performed on a PHI-5700 ESCA instrument with Al k X-ray source. The C1s peak of the surface adventitious carbon located at the binding energy of 284.6 eV was used as standard to calibrate all of other binding energies. The surface morphology of an electrode was observed by a field-emission scanning electron microscope (SEM, FEI Quanta 200F). Transmission electron microscopy (TEM) was obtained by using a JEM-3010 electron microscope (JEOL, Japan), with an applied acceleration voltage of 300 kV. The surface photovoltage spectra with an N<sub>2</sub> atmosphere was measured using combined equipment. The light derived from a 500 W xenon lamp (CHFXQ500W, Global Xenon Lamp Power, China) was passed through a double-prism monochromator (Hilger and Watts D 300, England) to get the monochromatic light. A lock-in amplifier (SR830, USA) isochronous with a light chopper (SR540, USA) was applied to collect the photovoltage data. The photoelectrode was placed between a mica sheet and an ITO glass and then the prepared samples were placed in a vessel in which a quartz window was set to make the light transmitted.

### **Photoelectrochemical tests**

The photoelectrochemical properties of the synthetic photoelectrodes were tested using a potentiostat (Princeton Applied Research, Versa STAT3) with the synthetic photoelectrodes as working electrodes, Pt foil (99.9%) as the counter electrode, and a standard calomel reference electrode. The electrolyte was 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution with a concentration of 0.1 M. The nitrogen with a high purity (99.999%) was sparged into electrolyte before and during the experiments. Electrochemical impedance spectra

(EIS) were obtained with the same potentiostat and solution. The frequency was set from 0.01 Hz to 100000 Hz, the amplitude was 10 mV (RMS). The illumination source was a 150 W xenon (GY-10A, Tuopu Co. Ltd., China) and light intensity was 100 mW cm<sup>-2</sup>.

### **Measurement of produced •OH concentrations**

The concentration of •OH produced was measured based on the fluorescence signal of 2-hydroxyterephthalic acid (TAOH), which resulted from the reaction of •OH with terephthalic acid (TA). The photoelectrodes were immersed in TA solutions ( $5 \times 10^{-4}$  M) and irradiated with a xenon lamp. Before the photoelectrode was exposed to light, the solution was continuously stirred using a magnetic stirrer for half an hour. A volume of 5 mL solution was removed at 15 min intervals for measurement of fluorescence (FP-6500 fluorescence spectrometer, Jasco Co.). The excitation wavelength was 315 nm and emission peak wavelength was 425 nm.

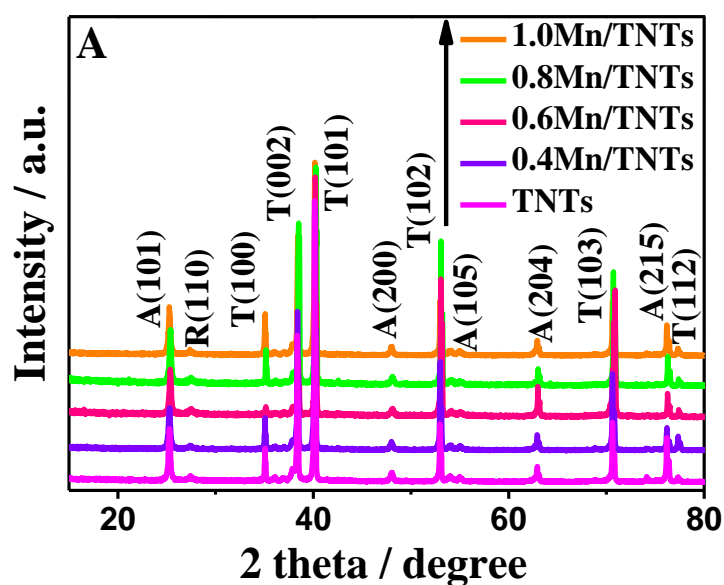
### **Photocatalytic CO<sub>2</sub> conversion**

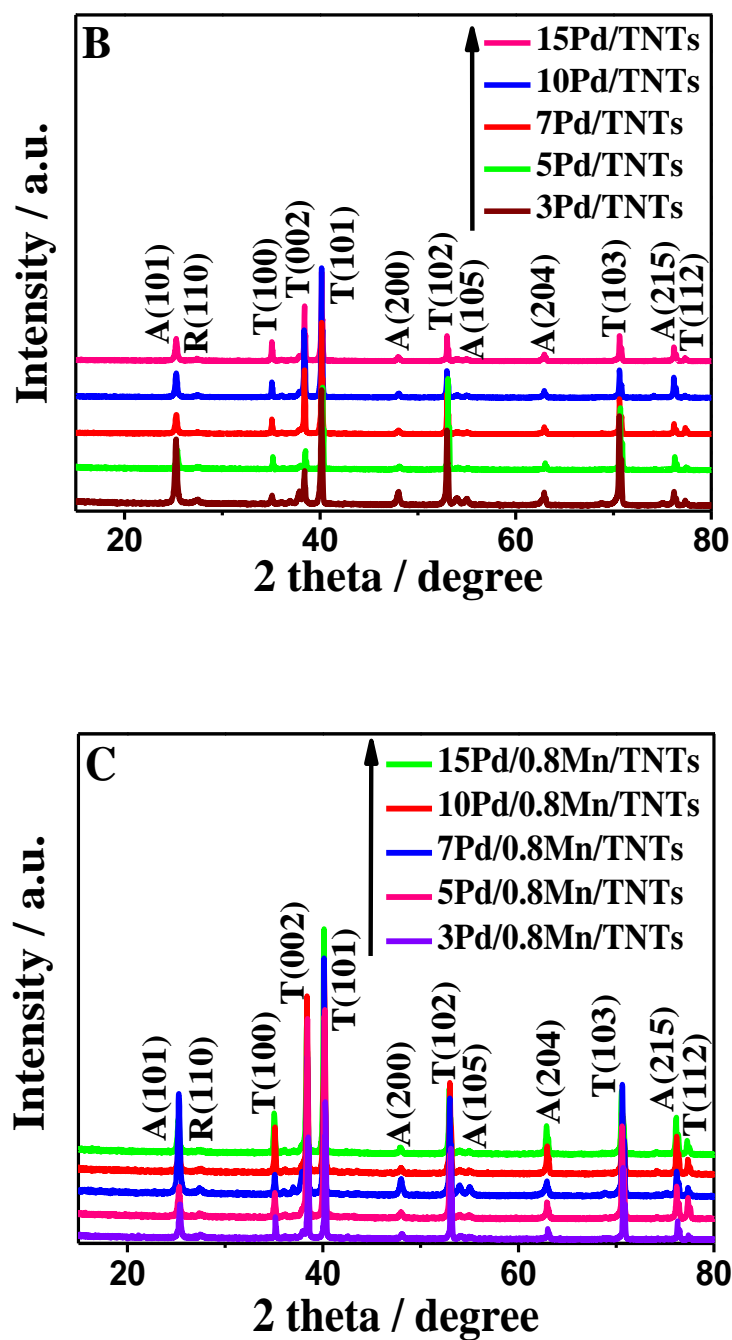
To evaluate the photocatalytic performance of CO<sub>2</sub> conversion, the synthetic TNTs photoelectrodes were placed in a reactor consisted of two column chambers made of glass and a quartz window on one chamber for light penetration. The electrolyte was 0.1 M KHCO<sub>3</sub>, and a 150 W xenon lamp was used as the light source. Before irradiation, carbon dioxide gas with a high purity was sparged into the solution until it was saturated. After a period of irradiation with light, 1.0 mL samples were taken to measure the chemical concentrations. Methanol was analyzed using a gas chromatograph (Agilent GC 7890A, USA), with a flame ionization detector (FID) and

a HP-Innowax 19095 N-123 column. Before analysis, formic acid with a volume of 50  $\mu\text{L}$  was added into 1 mL of the liquid samples to make the pH below 2. Formic acid and acetic acid concentrations were analysed using an ion chromatograph (IC 6100, Wanyi, AnHui, China). Before analysis, the liquid samples were diluted 100 times and filtered through a 0.22  $\mu\text{m}$  pore diameter membrane.

### Supplementary Figures and Tables:

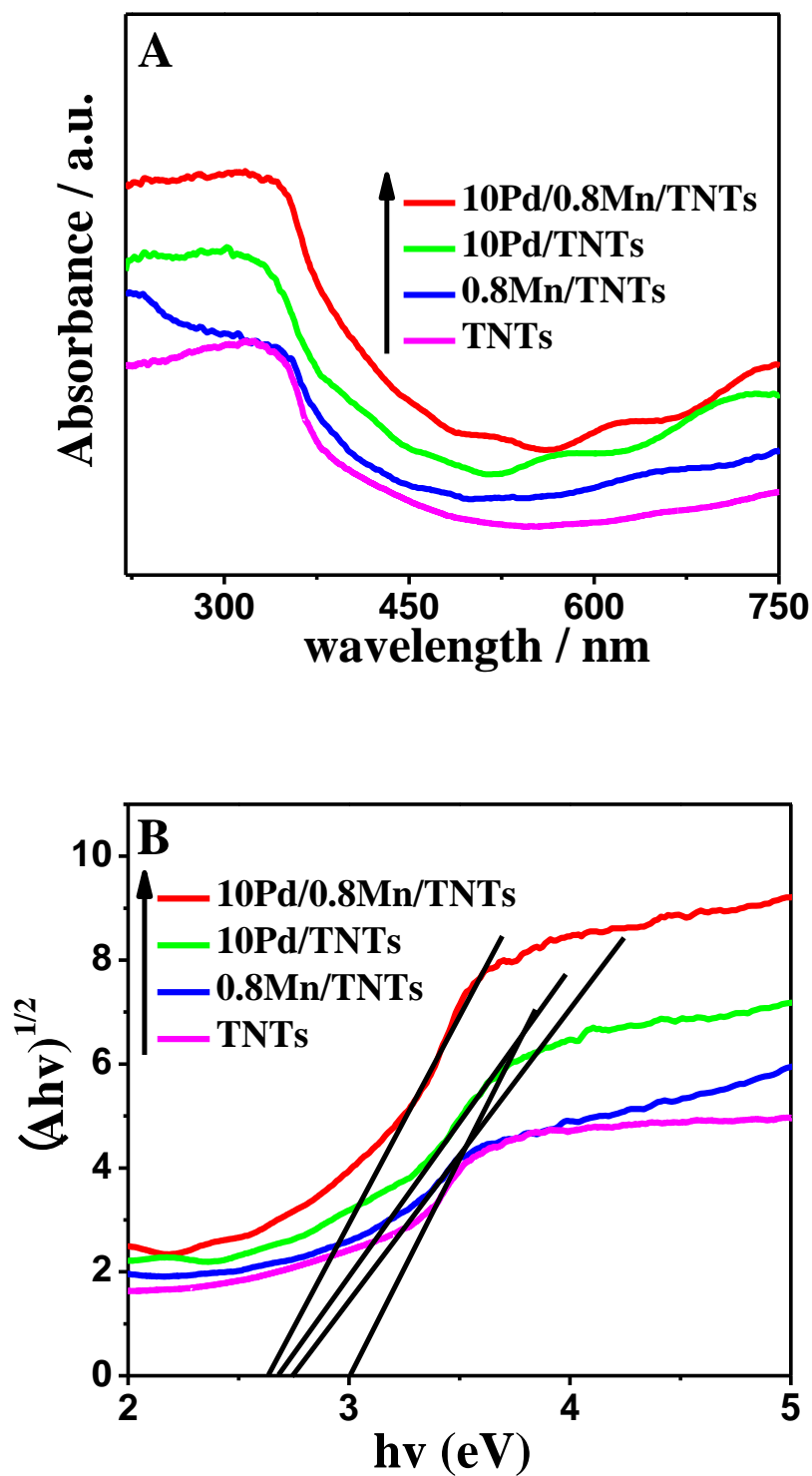
**Figure S1.** XRD patterns of different photoelectrodes. (A) Bare TNTs and  $\text{MnO}_x$  decorated TNTs. The numbers 0.4, 0.6, 0.8 and 1.0 stand for the used mass of  $\text{KMnO}_4$ . (B) Pd decorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element. (C)  $\text{MnO}_x$  and Pd codecorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element.



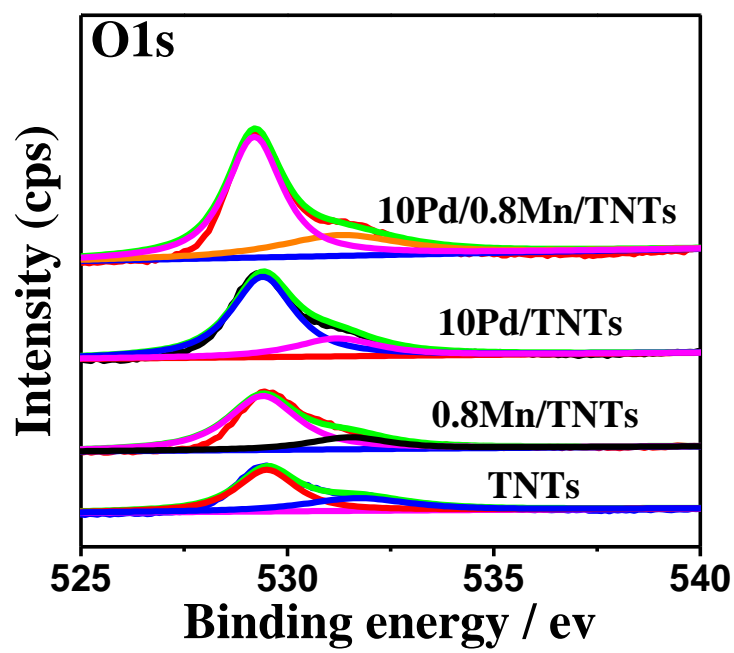
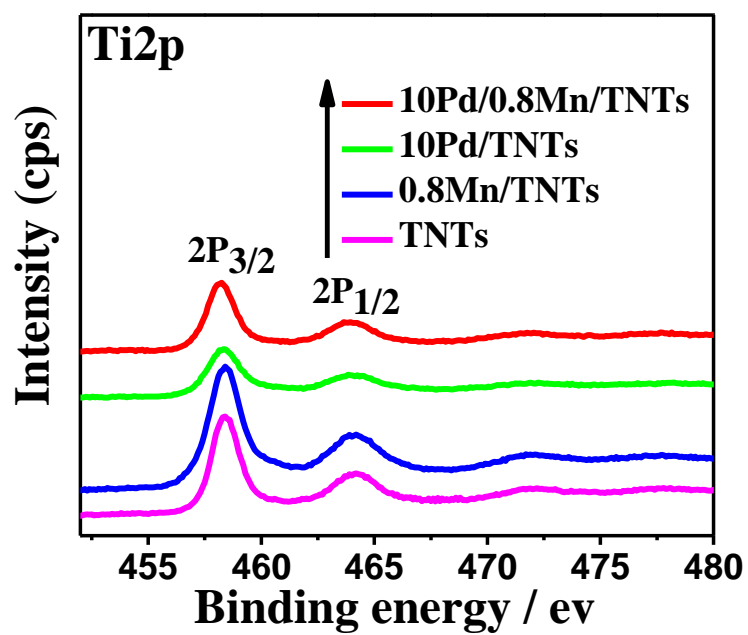


**Figure S2.** (A) UV–Vis absorption reflectance spectra (B) Tauc plots of transformed Kubelka–Munk function  $[F(R) \cdot hv]^{1/2}$  versus  $hv$  for different photoelectrodes. TNTs stands for bare  $\text{TiO}_2$  nanotubes. 0.8Mn/TNTs stands for  $\text{MnO}_x$  decorated TNTs. The number 0.8 means the used mass of  $\text{KMnO}_4$ . 10Pd/TNTs stands for Pd decorated TNTs. The number 10 means the electrochemical deposition time of Pd element. 10Pd/0.8Mn/TNTs stands for  $\text{MnO}_x$  and Pd codecorated TNTs.

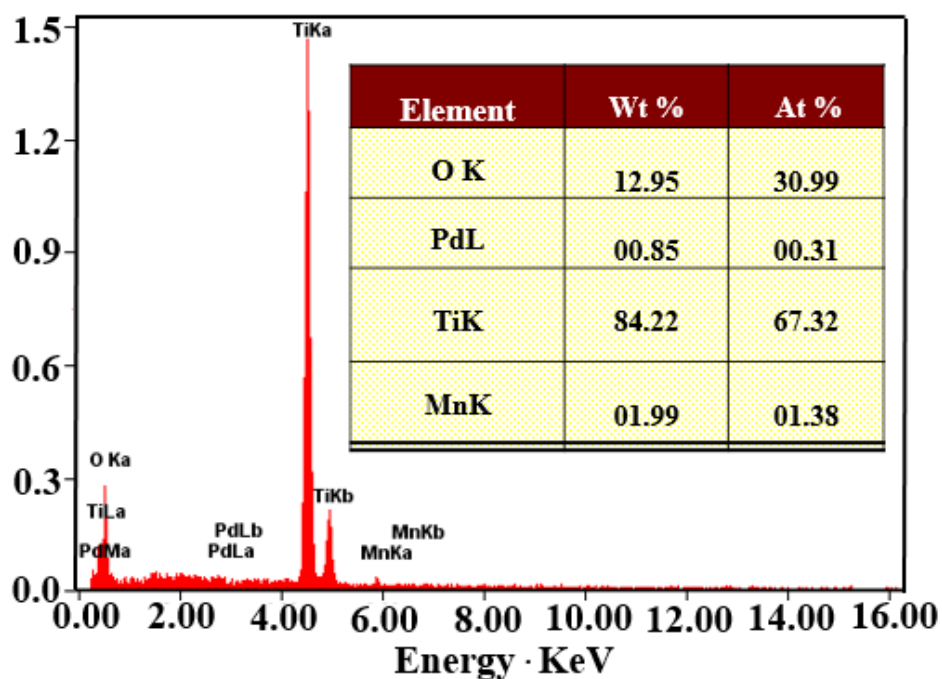




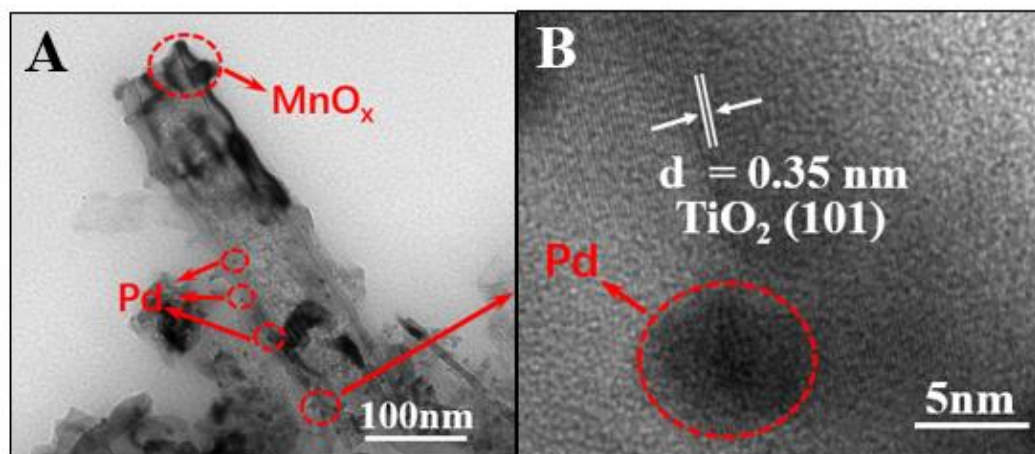
**Figure S3.** XPS spectra of different photoelectrodes. Ti2p and O1s spectra of 10Pd/0.8Mn/TNTs, 0.8Mn/TNTs, 10Pd/TNTs and TNTs photoelectrodes. The number 0.8 in 10Pd/0.8Mn/TNTs and 0.8Mn/TNTs stands for the used mass of  $\text{KMnO}_4$ . The number 10 in 10Pd/TNTs and 10Pd/0.8Mn/TNTs stand for the electrochemical deposition time of Pd element.



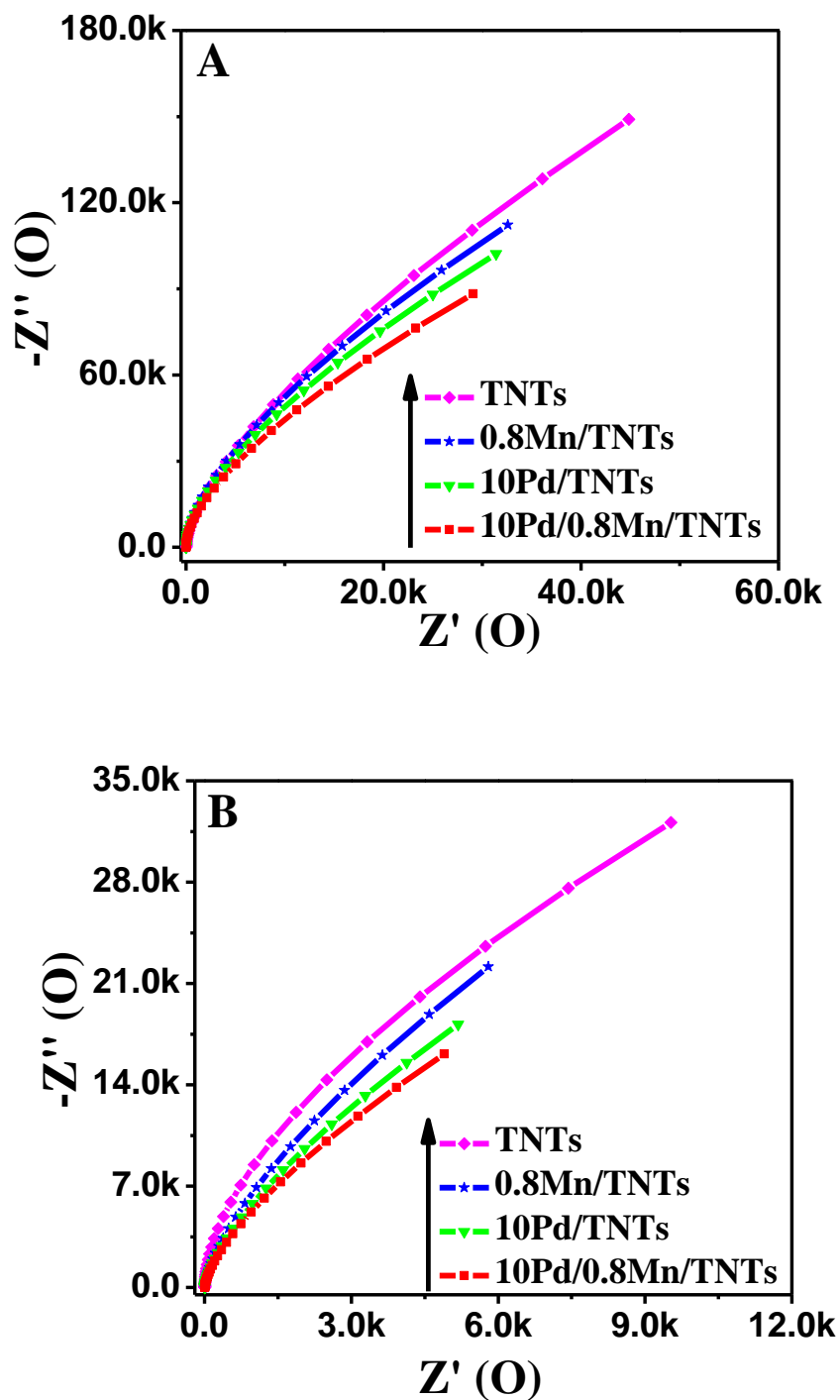
**Figure S4.** EDX spectroscopy of 10Pd/0.8Mn/TNTs photoelectrode.

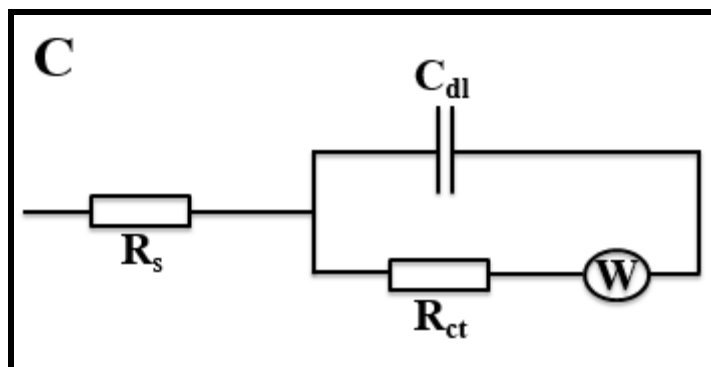


**Figure S5.** TEM and HRTEM images of 10Pd/0.8Mn/TNTs photoelectrode.



**Figure S6.** Equivalent circuit of Nyquist plots for electrochemical impedance spectra (A) in dark and (B) under light irradiation on different photoelectrodes. (C) Equivalent circuit model of  $R_s(Cdl(R_{ct}W))$ .

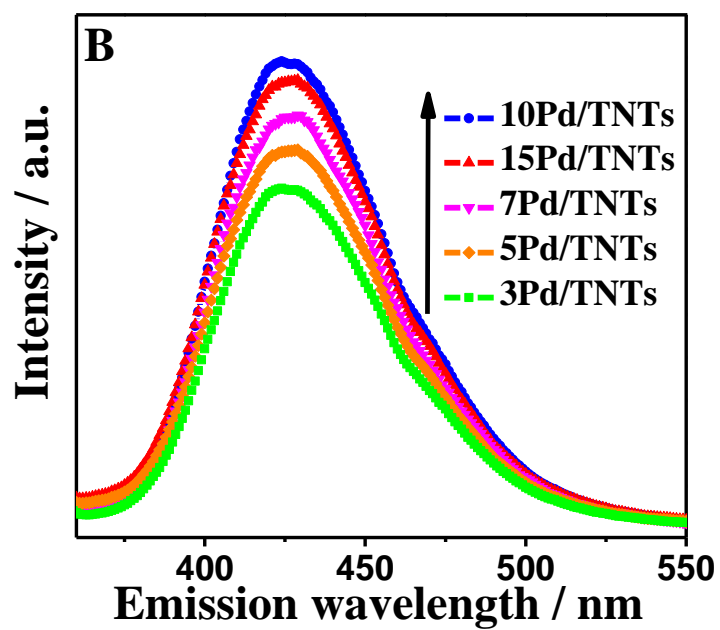
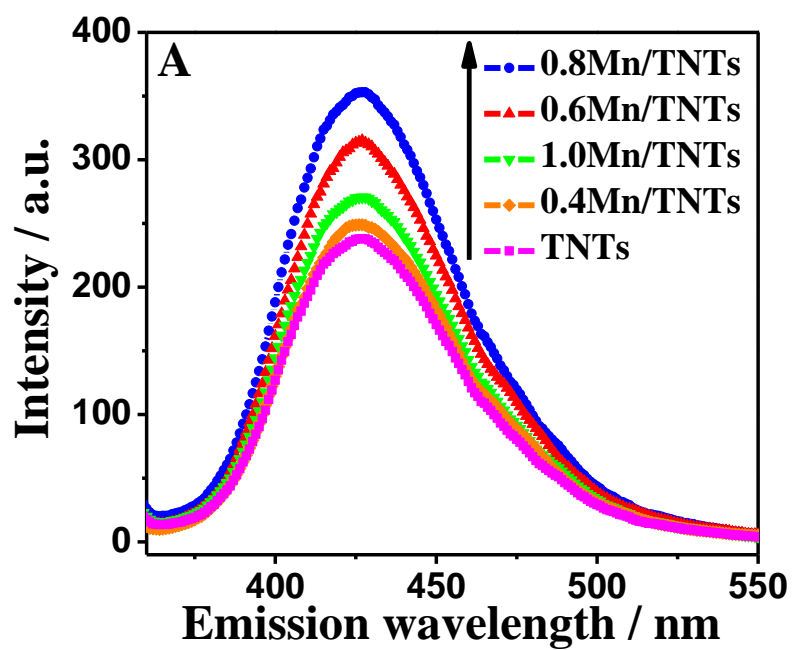


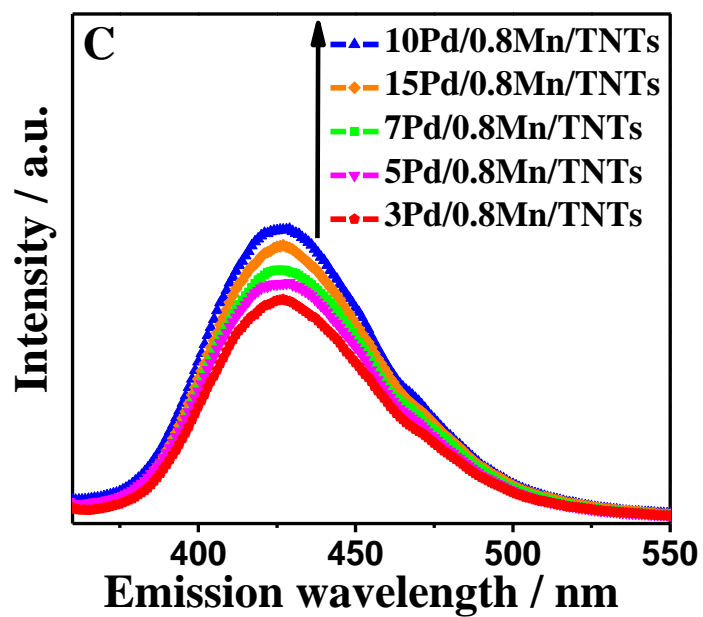


**Table. S1** Equivalent circuit model analysis of  $R_s(C_{dl}(R_{ct}W))$  which is obtained from different photoelectrodes.

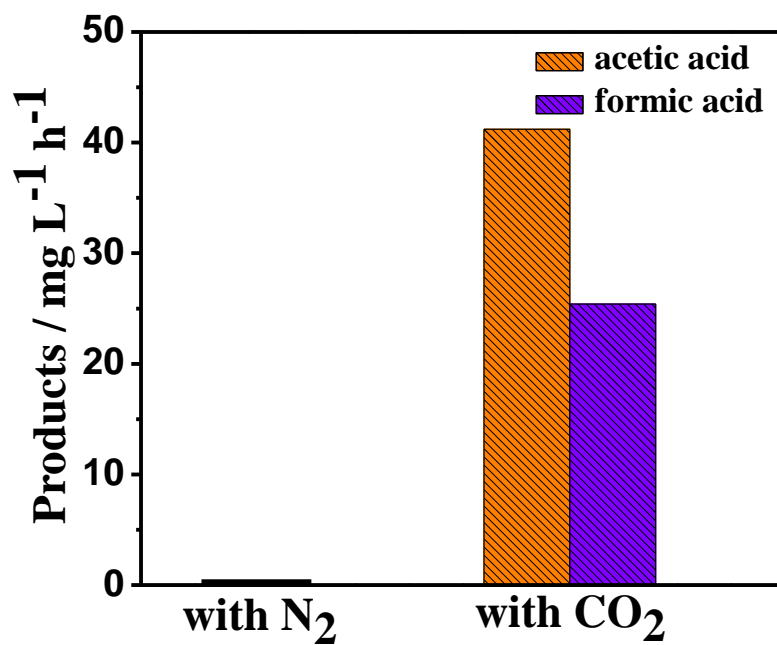
	Under dark		Under illumination	
photoelectrode	$R_s/\Omega$	$R_{ct}/\Omega$	$R_s/\Omega$	$R_{ct}/\Omega$
TNTs	5.633	$1.174 \times 10^5$	4.121	$4.124 \times 10^4$
0.8Mn/TNTs	4.395	$8.518 \times 10^4$	3.759	117.1
10Pd/TNTs	4.205	$7.742 \times 10^4$	3.664	30.47
10Pd/0.8Mn/TNTs	3.944	$6.594 \times 10^4$	3.629	1.803

**Figure S7.** Fluorescence spectra related to hydroxyl radicals on different photoelectrodes after irradiation for 1 h by the widely-used terephthalic acid fluorescent method. (A) Bare TNTs and  $MnO_x$  decorated TNTs. The numbers 0.4, 0.6, 0.8 and 1.0 stand for the used mass of  $KMnO_4$ . (B) Pd decorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element. (C)  $MnO_x$  and Pd codecorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element.

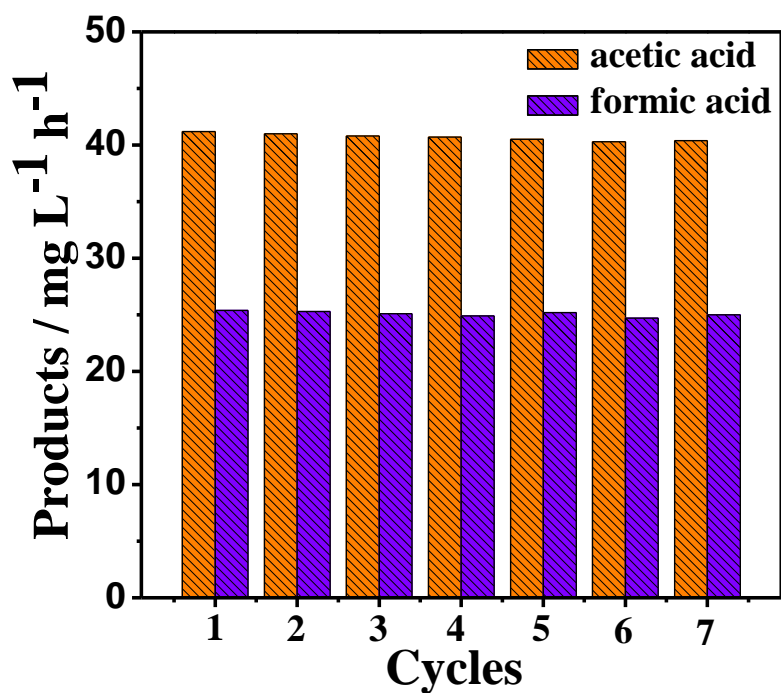




**Figure S8.** Photocatalytic activities test in  $\text{KHCO}_3$  aqueous solution (0.1 M) on 10Pd/0.8Mn/TNTs photoelectrode with  $\text{N}_2$  and  $\text{CO}_2$  under xenon lamp irradiation for 1 h.



**Figure S9.** The stability tests of photocatalytic  $\text{CO}_2$  conversion on 10Pd/0.8Mn/TNTs photoelectrode for 7-run recyclable experiments.



**Figure S10.** SPS response of bare and decorated TNTs photoelectrodes in N<sub>2</sub>. (A) MnO<sub>x</sub> decorated TNTs. The numbers 0.4, 0.6, 0.8 and 1.0 stand for the used mass of KMnO<sub>4</sub>. (B) Pd decorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element. (C) MnO<sub>x</sub> and Pd codecorated TNTs. The numbers 3, 5, 7, 10, 15 stand for the electrochemical deposition time of Pd element.

