

Supporting Information

A Solar Multifield-Driven Hybrid Chemical System for Purification of Organic Wastewater by Focused on a Nano-Carbon/TiO₂/Ti Central Electrode

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1. Preparation of 2-step TiO₂ NTs

The 2-step TiO₂ NTs were fabricated by a two-step anodization process (Scheme 1). Prior to anodization, the Ti foils were first ultrasonically cleaned with ethanol and room-temperature distilled water, followed by drying in N₂ gas. The anodization was carried out using a conventional two-electrode system with the Ti foil as an anode and a Pt gauze (Aldrich, 100 mesh) as a cathode respectively. All electrolytes consisted of 0.5 wt% NH₄F in EG solution with 2 vol% water. All the anodization experiments were carried out at room temperature. In the first-step anodization, the Ti foil was anodized at 50 V for 30 min, then the as-grown nanotube layer was ultrasonically removed in deionized water, leaving a compact two-dimensional hexagonal pattern on the surface of the Ti foil alone. The patterned Ti foil then underwent the second anodization at 20 V for 30 min, in which the hexagonal pattern formed top-porous structure and subjective NTs grew below the top-porous layer. After second-step anodization, the prepared TiO₂ NTs sample was cleaned with distilled water and dried off with N₂ gas. The as-anodized TiO₂ NTs were annealed in air at 450 °C for 1 h with a heating rate of 5 °C min⁻¹.

2. The experimental apparatus of thermo-photo-electrochemistic nitrobenzene degradation

The activity of nano-carbon / TiO₂ NTs / Ti electrode was evaluated by degradation of nitrobenzene in a self-built three-field experimental setup shown as Fig. S1. The experimental apparatus is an In-situ thermo-photo-electrochemical microreactor-analyzer (in-situ TPEC-MRA) for measurements of the nitrobenzene oxidation. The experimental apparatus was set up by combining with three ports of photoelectric, photothermal and electrochemical units (Thermo-Electro-Reactor) for the treatment of the wastewater containing NB.

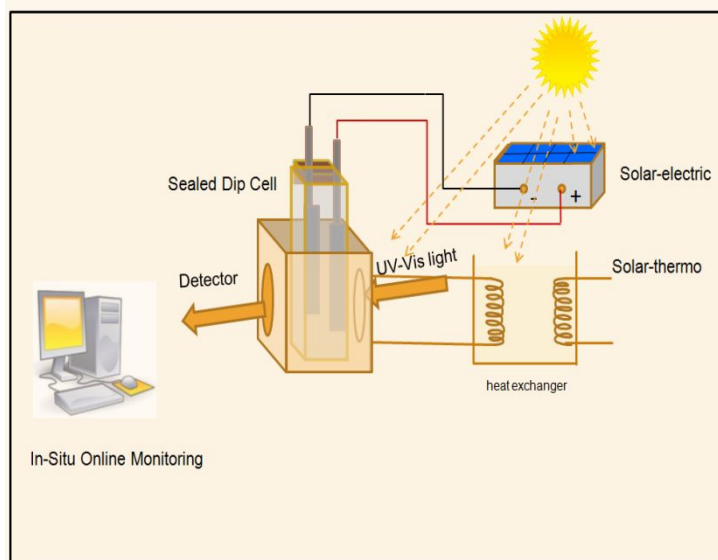
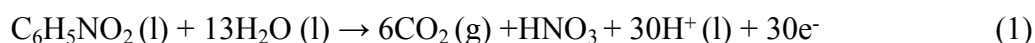


Fig. S1 Setup of In-situ thermo-photo-electrochemical microreactor-analyzer (in-situ TPEC-MRA) for measurements of the nitrobenzene oxidation

The in-situ TPEC-MRA built in a visible-UV spectrophotometer (Shimadzu, Japan, UV-1700) was explored and exploited for serving as a reactor and an analyzer by a variation of the incident light, temperature, potential and time during. The concentration of NB was 20 mg/L. A digital multimeter with PC interface was applied to measure the current change with the time. The in-situ TPEC-MRA, equipped with a thermo-photo-electrochemical micro quartz dip cell (12.5*12.5*45mm, Optical path 10mm) as a reactor, was built in a visible-UV spectrophotometer. It was explored and exploited for serving as both a reactor and an analyzer by the measurement of the light absorption with the variation of many parametrs. Pt sheets (9 mm × 15 mm) were used as both working electrode and counter electrode in the TPEC-MRA. Both the photo-, thermo- and electro-energy for the requirement of the system were fully supplied by the solar energy as shown in the figure. The degradation was real-timely monitored in progressing by the TPEC-MRA. Before the experimentation, the electrode was immersion in the aqueous nitrobenzene solution for 60 s under dark to achieve the adsorption-desorption equilibrium.

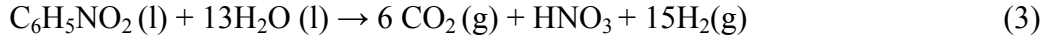
3. Theoretical calculation

The electrochemical oxidation of nitrobenzene can occur directly through electron transfer between the anode and nitrobenzene. Eqs.1-3 summarize the electrode reaction of nitrobenzene treatment by STEP, electrochemical oxidation of nitrobenzene to carbon dioxide in anode (1) and hydrogen evolution in cathode (2),





Full cell reaction:



By the calculation of the degradation potential, solar thermal can reduce the energy required for the electrolysis process. These processes can be determined using the data for available entropy S , enthalpy H , and free-energy G , and they are identified by a negative isothermal temperature coefficient of the cell potential [16]. Isothermal coefficient $(dE/dT)_{\text{isoth}}$ can be derived from the electric potential for constant temperature battery:

$$(dE/dT)_{\text{isoth}} = \Delta S/nF = (\Delta H - \Delta G)/nFT \quad (4)$$

At any electrolysis temperature of T_{STEP} , and at the unit activity, the electrolytic reaction has an electrochemical potential of E°_T . The calculation process can be obtained by using the fixed thermodynamic data, as:

$$E^\circ_T = -\Delta G^\circ(T=T_{\text{STEP}})/nF; E^\circ_{\text{ambient}} = E^\circ_T(T_{\text{ambient}}) \quad (5)$$

$$\text{Here, } T_{\text{ambient}} = 298.15\text{K, and} \quad (6)$$

In Eq. (5), E°_T is the standard electrode potential of the electrochemical reaction. By the standard electrode potential can judge an electrochemical reaction can occur spontaneously, $E^\circ_T > 0$, the reaction can occur spontaneously, without external electric field; if $E^\circ_T < 0$ reaction is a non spontaneous reaction.

Calculation of E°_T , ΔG° can also be achieved through the Gibbs-Helmholtz equation, the equation is as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

For a non ΔH standard condition, it needs to be calculated:

$$\Delta H^\circ = \Delta H^\circ_{298} + \int_{298}^T \Delta C_p \Delta dT \quad (8)$$

$$\Delta S^\circ = \Delta S^\circ_{298} + \int_{298}^T \frac{\Delta C_p}{T} dT \quad (9)$$

$$\text{Here, } \Delta C_p = \sum n_i \Delta C_{pi} \quad (10)$$

The 298K data of the products and reactants and on the type, get the integral constant value of ΔH°_{298} , so to at any temperature ΔH° , they get at any temperature ΔG° , finally obtained under arbitrary temperature standard electrode potential E°_T . According to $E_T = -E^\circ_T$, electrolytic cell reaction to obtain potentially.

According to the electrochemical degradation of nitrobenzene complete cell reaction, by referring to the reaction in the material under the different temperature thermodynamic data can be obtained (Table S1), using these data can be calculated to get the cell reaction ΔH° and ΔG° , so as to obtain the theory of electrode potential.

The variation of the nitrobenzene electrolysis potential with temperature is calculated with Eq. (5) and presented in Fig. S2. The nitrobenzene oxidation potential decreases with the increasing of temperature, which means that the STEP process can be applied to nitrobenzene electro-oxidation. For example, from 25 °C to the H₂O boiling point of 100 °C, the nitrobenzene electrolysis potential in the aqueous phase decreases from 1.2414V to 1.1850V. This decrease provides a theoretical basis of the STEP process for effective and efficient removal of nitrobenzene from wastewater.

Table S1. Thermodynamic data and calculation results of each material in photoelectric unit

T (K)	Cp,m(J/mol)				ΔC_p (KJ/mol)	$\Delta_r H_m^\circ$ (KJ/mol)	$\Delta_r S_m^\circ$ (KJ/mol·K)	$\Delta_r G_m^\circ$ (KJ/mol)	E_T (V)
	NB	H ₂ O	CO ₂	HNO ₃					
298	110.56	66.33	37.28	110.06	-0.6391	4268.8	2.2646	3593.95	1.2414
313	114.90	67.74	37.8	109.79	-0.6584	4258.92	2.2323	3560.21	1.2298
328	119.17	69.23	38.47	109.60	-0.6788	4248.43	2.1995	3527.00	1.2183
343	123.39	70.82	39.04	109.49	-0.7004	4237.28	2.1661	3494.31	1.2070
353	126.17	71.93	39.42	109.45	-0.7153	4229.46	2.1434	3472.84	1.1996
373	131.65	74.27	40.16	109.49	-0.7467	4212.80	2.097	3430.62	1.1850

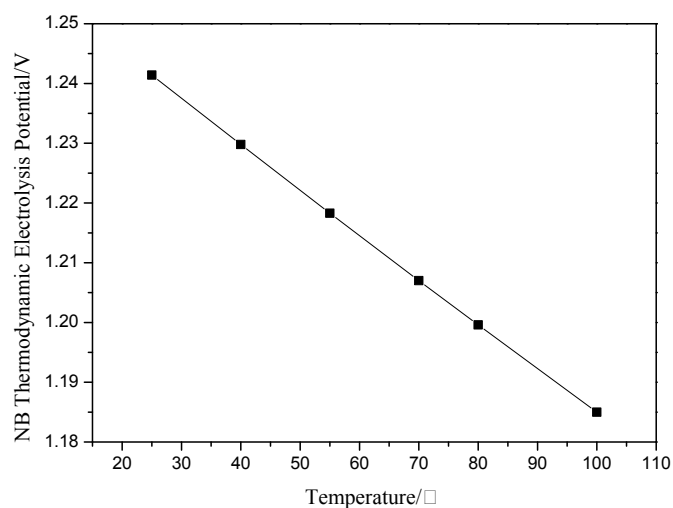


Fig. S2. Theoretical, thermodynamic calculation of the electrochemical potential of nitrobenzene oxidation

3. Morphology of nano-carbon / TiO₂ NTs / Ti electrode

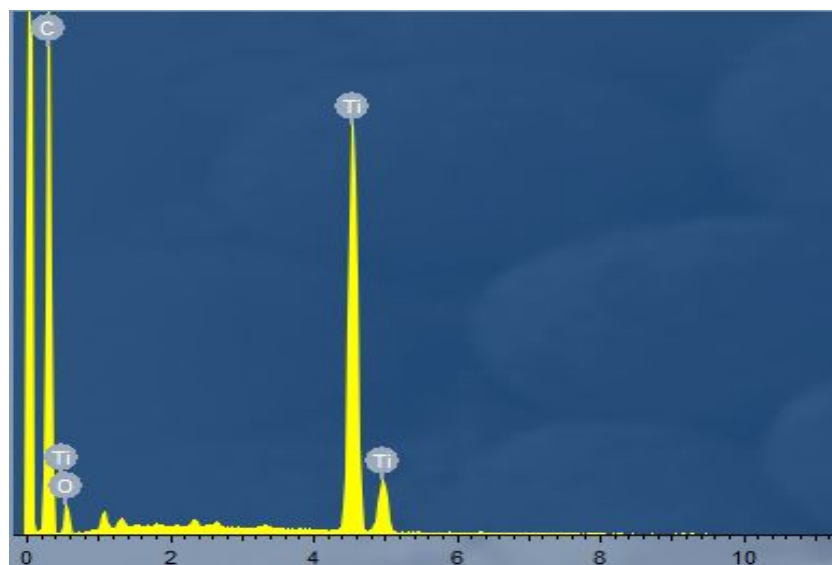


Fig.S3 EDS of nano-carbon/TiO₂/Ti

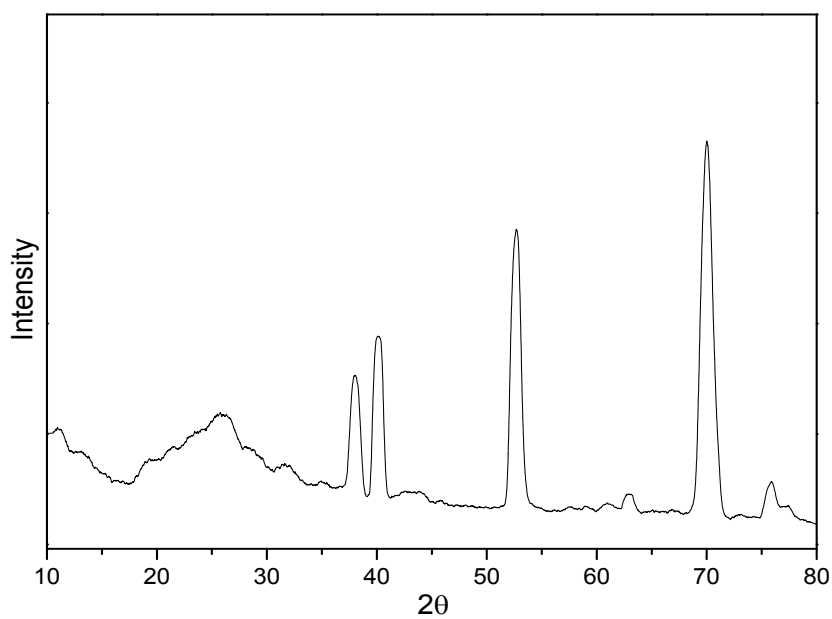


Fig. S4 XRD of nano-carbon/TiO₂/Ti

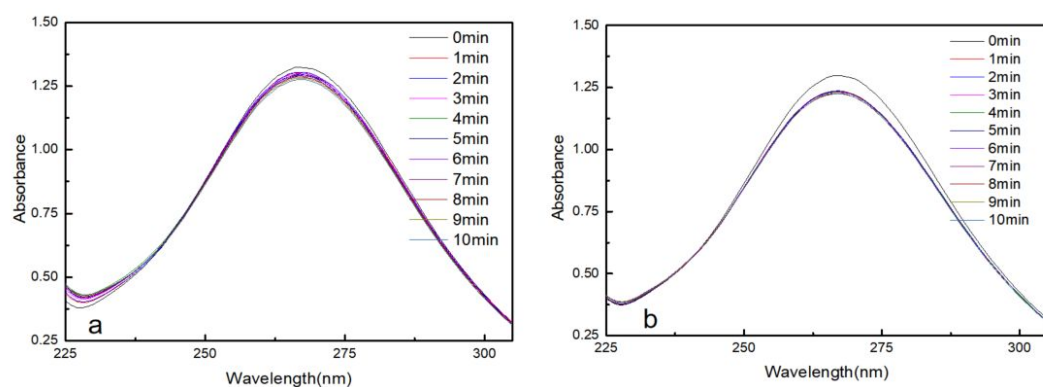


Fig. S5 UV-Vis of 2-step TiO_2 NTs/Ti (a) and nano-carbon/ TiO_2 NTs/Ti (b) in nitrobenzene solution in the dark;

4. Calculation of the Energy

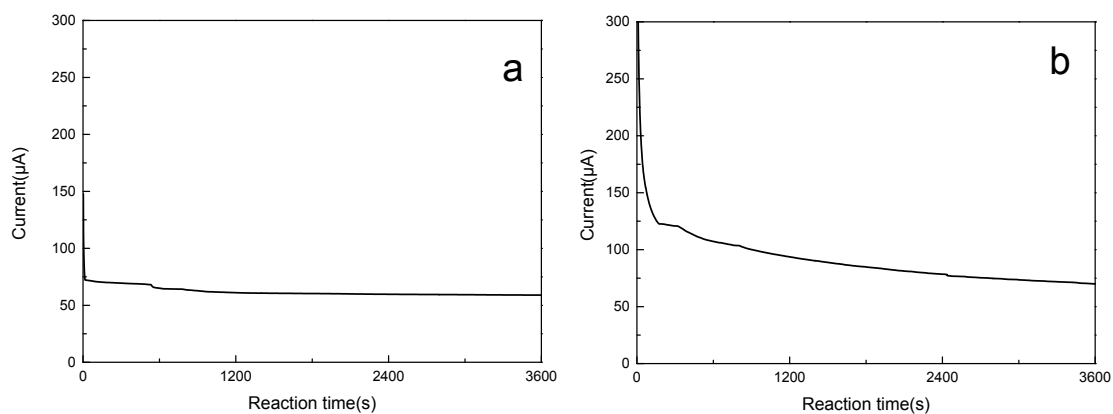


Fig. S6. Current-time curves in 1.2V with 2-step TiO_2 NTs/Ti (a) and nano-carbon/ TiO_2 NTs/Ti (b) at 30°C

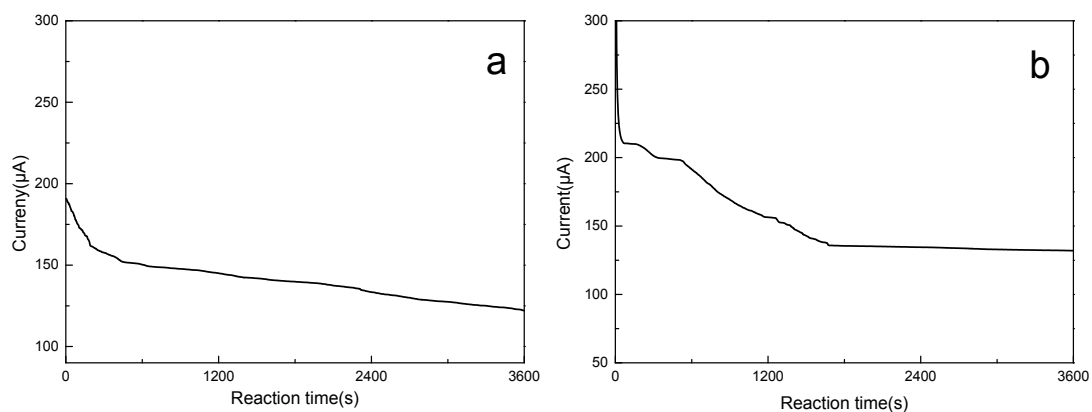


Fig. S7. Current-time curves in 1.2V with 2-step TiO_2 NTs/Ti (a) and nano-carbon/ TiO_2 NTs/Ti (b) at 60°C

W (1.2V, 30°C, 2-step TiO₂ NTs / Ti)= UIt =1.2v×430324.85*10⁻⁶A·s=0.52 J

W (1.2V, 30°C, nano-carbon / TiO₂ NTs / Ti)= UIt =1.2v×570604.51*10⁻⁶A·s= 0.69 J

W (1.2V, 60°C, 2-step TiO₂ NTs / Ti)= UIt =1.2v×902502*10⁻⁶A·s= 1.08 J

W (1.2V, 60°C, nano-carbon / TiO₂ NTs / Ti)= UIt =1.2v×1011656.29*10⁻⁶A·s= 1.21 J

5. Photocatalytic Mechanism

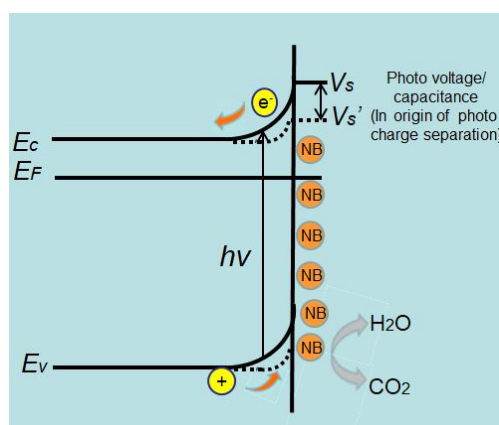


Fig. S8 The electronic band structure of nano-carbon/TiO₂ NTs/Ti. The change in band bending is represented by dashed lines. The redistribution of generated charges is indicated by the arrows.

For nano-carbon/TiO₂ NTs/Ti, the growth of nano-carbon nanotubes onto the TiO₂ NTs efficiently separated the photogenerated electron-hole pairs, yielding high decomposition efficiency. Upon light irradiation of the composite photocatalyst, electron (e_{CB}^-)–hole (h_{VB}^+) pairs were produced. It is believed that nano -carbon could act as an electron trap; thus, some of the photo-produced electrons in the CB of the TiO₂ NT were quickly transferred to the nano-carbon and the photogenerated charge carriers (holes and electrons) were effectively separated. Consequently, the electrons were transferred to the surface, where they react with adsorbed or dissolved oxygen to produce highly reactive super oxide radical anions ¹, while the holes oxidized H₂O or -OH ion into •OH radicals.

The electronic band structure of n-type semiconductors such as TiO₂ is characterized by upward band bending at the semiconductor–conductor interface, leading to a Schottky-type barrier as seen in Fig. S8. The surface localized electron states induce charge transfer between the surface and the semiconductor in order to establish thermodynamic equilibrium. This transfer leads to a non-neutral region of surface space-charge near the surface. This, in turn, results in a built-in electric field, V_s , commonly referred to as the surface potential barrier. When the photocatalyst was irradiated by light with a photon energy content greater than the bandgap, free charges

are generated by band-to-band transitions induced by the incident photons. The generated charges redistribute within the surface and/or the bulk as a result of the built-in electric field. Thus, the surface potential barrier will be altered after illumination. Exactly, this difference between the surface potential barrier in the dark (V_s) and the one under illumination (V_s'), is defined as the photo voltage/capacitance and is used to characterize the photocatalyst. The photo voltage/capacitance is the origin of photocharge separation because when more electrons are trapped at the surface of the photocatalyst, more holes move in the opposite direction to oxidize the NB to CO_2 and H_2O completely. Thus, NB can undergo thorough mineralization and the contamination caused by NB can be effectively controlled.

Reference

1. Vijayan, B. K.; Dimitrijevic, N. M.; Finkelstein-Shapiro, D.; Wu, J.; Gray, K. A., Coupling titania nanotubes and carbon nanotubes to create photocatalytic nanocomposites. *Acs Catalysis* **2012**, 2 (2), 223-229.