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Supporting Information:

Micro/nano-bubble assisted synthesis of Au/TiO₂@CNTs composite photocatalyst for

solar-light-driven photocatalytic degradation of gaseous styrene and its enhanced

catalytic mechanism

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Functionalization of carbon nanotubes (CNTs).

0.5 g of CNTs (95%, 8-15 nm, Beijing Boyu-Gaoke New Material Co., Ltd) were functionalized by a mixture of concentrated sulfuric acid (95%-98%, Guangzhou chemical reagent factory) and nitric acid (65%-68%, Guangzhou chemical reagent factory) with a volume ratio of 3:1 under the room temperature for 5 h. The above mixed dispersion was treated at 70 °C for 1 h and then 90 °C for 0.5 h. The obtained mixture was filtered and washed by mixed solution of water and EtOH (Volume ratio= 1:3). The final functional CNTs were treated by freeze-drying for 12 h and thermal treatment at 60 °C for 10 h.

Photoelectrochemistry measurement.

The photocurrent response of Au/TiO₂@CNTs nano-composites were conducted on a CHI650 electrochemical analysis instrument equipped with a three-electrode electrochemical setup, consisting of a working electrode, a platinum counter electrode and Ag/AgCl reference electrode. In this process, 30 mg of photocatalyst and 3 μ L of 0.05 g/mL nafion solution were dissolved in 1.0 mL of absolute ethanol and 100 μ L of ultrapure water to form a homogeneous suspension and coated onto FTO glass to form a uniform film, and then heated with the protection of N₂ gas at 200 °C for 2 hrs. The electrolyte was 0.1 M Na₂SO₄ aqueous solution degassed with N₂ and the illumination source was a 150 W xenon lamp with an ultraviolet cutoff filter (λ ≥420 nm). Electrochemical impedance spectroscopy (EIS) was also measured on CHI650 system using a three-electrode system in 0.1 M Na₂SO₄ solution under visible light.

Evaluation of photocatalytic activity.

The evaluation of photocatalytic activity of Au/TiO₂@CNTs composite photocatalyst was conducted on a photocatalytic reaction system. Thereinto, the gas distributing system (Beijing Zhongjiao-jinyuan Science and Technology Co. Ltd., China) provided the gaseous styrene with the initial concentration of 28±2 ppmv operating in a continuous flow mode. During photocatalytic process, 0.1 g of as-synthesized powders was filled in a custom-made cubic quartz glass reactor with the size of 1.5 cm×1.0 cm×0.1 cm, top of which was a xenon lamp (300 W) fixed vertically with distance of 9

cm. Before irradiation, gas–solid adsorption equilibrium was reached between gaseous styrene and photocatalyst. Gas samples were collected at given intervals using an auto-feeding device, and 1 mL of gas sample was injected into a gas chromatography (Shanghai Kechuang Chromatographic instrument Co. Ltd, China) with a capillary column (30 m × 0.32 mm × 0.5µm) for concentration determination. Simultaneously, the yield of carbon dioxide was detected by a GC900 gas chromatography (Shanghai Kechuang Chromatographic instrument Co. Ltd, China).

Identification of reactive oxidizing species.

For the 5,5-dimethyl-1-pyrroline N-oxide (DMPO, DOJINDO laboratories) spin trapping EPR experiments, 2 mg of the samples were suspended in 2 mL of de-ionized water for detection of hydroxyl radicals and 2 mg of the samples were suspended in 2 mL methanol for detection of superoxide radicals. 10 µL of the DMPO were mixed into above-mentioned suspended and irradiated for 5 min with a xenon lamp as light source, being then immediately transferred to the spectrometer cavity for EPR analysis.

Table S1. Variables and levels of central composite design for preparation of composites

Variable	Symbol	Levels				
	Symbol -	-2	-1(low)	0(center)	+1(high)	+2
Reaction temperature (°C)	А	25	40	55	70	85
Mass fraction of CNTs (%)	В	4	15	26	37	48
Reaction time (h)	С	4	8	12	16	20
Amount of HAuCl₄ (mmol)	D	0.004	0.011	0.018	0.025	0.032

Dura	Ir	ndepend	ent varia	bles	Degradation	Predicted	Mineralization	Predicted
Kun -	Α	В	С	D	Efficiency (%)	Value (%)	Efficiency (%)	Value (%)
1	55	15	12	0.025	17.0	20.9	18.9	19.7
2	55	15	16	0.025	20. 0	19.9	7.8	7.9
3	40	15	8	0.011	22.0	22.7	25.2	27.5
4	55	37	12	0.011	31.6	30.0	21.3	22.4
5	55	26	12	0.018	24.1	23.3	19.5	17.6
6	70	26	12	0.018	38.2	34.1	24.6	25.3
7	40	26	16	0.018	13.6	11.2	6.7	5.9
8	40	4	8	0.018	14.5	12.6	41.1	38.4
9	85	26	8	0.018	38.3	39.2	30.7	31.0
10	40	15	12	0.011	10.8	13.1	24.0	22.6
11	25	48	12	0.018	24.3	24.2	43.0	44.1
12	70	37	12	0.011	35.9	39.0	32.0	29.5
13	55	26	16	0.004	38.7	38.3	29.2	27.1
14	40	37	8	0.025	17.8	17.2	16.2	12.5
15	55	26	12	0.032	28.9	27.2	12.8	13.3
16	55	26	12	0.018	23.0	23.3	17.6	17.6
17	55	26	12	0.018	23.2	23.3	20.2	17.6
18	40	37	16	0.025	23.1	24.1	22.9	21.4
19	55	26	12	0.018	20.6	23.3	15.7	17.6
20	70	15	20	0.011	40.9	41.8	16.3	17.3
21	70	37	8	0.011	34.9	33.5	17.6	19.4
22	70	26	4	0.018	24.4	25.5	5.4	4.4
23	40	15	8	0.025	14.6	14.7	14.5	18.1
24	55	15	16	0.011	24.5	23.0	18.8	21.8
25	70	26	8	0.018	31.0	29.9	19.8	20.2
26	70	26	8	0.018	30.6	29.9	20.2	20.2
27	55	37	12	0.025	20.3	22.2	13.3	15.7
28	70	15	16	0.025	36.6	36.2	20.2	17.7
29	55	37	16	0.025	29.6	29.2	15.0	16.1
30	40	37	16	0.011	20.6	21.0	15.9	16.5

Table S3. ANOVA for response surface quadratic model for degradation of gaseous styrene

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value
Regression	1960.10	14	140.01	24.69
Residual	85.05	15	5.67	
Correction total	2045.15	29		

R² = 0.9584, adjusted R² = 0.9196.

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value
Regression	2057.76	14	146.98	21.75
Residual	101.36	15	6.76	
Correction total	2159.13	29		

 $R^2 = 0.9513$, adjusted $R^2 = 0.9092$.

Table S5. Degradation and mineralization efficiency of gaseous styrene catalyzed by TiO_2 , $TiO_2/CNTs$, Au/ TiO_2 and Au/ $TiO_2@CNTs$ composites

Туре	TiO ₂	TiO ₂ /CNTs	Au/TiO ₂	Au/TiO ₂ @CNTs
Degradation (%)	34.2	41.2	52.7	69.2
Mineralization (%)	8.2	12.9	27.5	52.5

Table S6. Specific surface area and pore size of TiO₂, TiO₂/CNTs, Au/TiO₂ and Au/TiO₂@CNTs composites

Туре	TiO ₂	TiO ₂ /CNTs	Au/TiO ₂	Au/TiO ₂ @CNTs
BET Surface Area (m ² /g)	61.4	78.7	90.0	104.4
Pore size (Å)	32.4	40.6	23.4	34.7



Fig. S1. TEM images of Au/TiO₂@CNTs. a, TEM images of Au/TiO₂ nanoparticles coupled with CNTs; b and c, High– resolution TEM images of Au/TiO₂@CNTs photocatalyst.



Fig. S2. XRD spectra of TiO₂ and Au/TiO₂@CNTs composites with different reaction temperature



Fig. S3. XPS spectra of Au/TiO₂@CNTs: a, whole pattern of XPS; b, O 1s; c, C 1s; d, Au 4f.



Fig. S4. XPS spectra of Au/TiO₂@CNTs: a,Ti2p; b, O 1s; c, C 1s; d, Au 4f.



Fig. S5. Correlation of the predicted and experimental degradation (a) and mineralization efficiencies (b) of gaseous styrene catalyzed by Au/TiO₂@CNTs composites.



Fig. S6. Residual plots for photocatalytic degradation (a, b) and mineralization (c, d) efficiency of styrene by Au/TiO₂@CNTs composites.



Fig. S7. Plots of degradation (a) and mineralization (b) of gaseous styrene catalyzed by TiO_2 , $TiO_2/CNTs$, Au/TiO₂ and Au/TiO₂/CNTs composites.



Fig. S8. XRD spectra of Au/TiO₂@CNTs composites before and after photocatalysis test.



Fig. S9. EPR spectra of: (a) TiO₂, (b) Au/TiO₂, (c) TiO₂/CNTs, and (d) Au/TiO₂@CNTs composites.



Fig. S10. O_2 -TPD profiles of Ti O_2 , Au/Ti O_2 and Au/Ti O_2 @CNTs composites.