Robust Interaction of ZnO and TiO_2 Nanoparticles with Layered Graphitic Carbon Nitride for Enhanced Photocatalytic Oxidative Desulfurization of Fuel Oil: Mechanism, Performance and Stability

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1. Chemical

Titanium isopropoxide (TIP, 97%, Sigma-Aldrich), Zinc chloride hexahydrate ($ZnCl_2.6H_2O$, 98%, Sigma-Aldrich), Dibenzothiophene ($C_{12}H_8S$, 98%, Sigma-Aldrich), benzoquinone (p-BQ, 99%,

Sigma-Aldrich), tert-butanol (TBA, 99%, Sigma-Aldrich), potassium dichromate ($K_2Cr_2O_7$, 99%, Sigma-Aldrich), acetonitrile (99%, China), acetic acid (CH_3COOH, 98%, China), n-octane (98%, China), ethanol (C_2H_5OH, 98%, China), Hydrogen peroxide (H_2O_2, 30% in H_2O, China), Ammonium chloride (NH_4Cl, 98%, China).

2. Characterization techniques

Phase structure, surface valence state, elemental composition, specific surface area, morphology and optical properties of ZnO, TiO_2, OCN and 20%ZnO-TiO_2/OCN material samples analyzed by X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany), X-ray photoelectron spectroscopy (XPS, Thermo VG Multilab 2000), Energy Dispersive X-ray Spectroscopy (EDS, JED-2300), transmission electron microscopy (TEM, Leica IEO 906E), photoluminescence (PL, Varian), Mott-Schottky (MS, Biologic SP 300), electrochemical impedance spectroscopy (EIS, AUTOLAB, Metrohm, Netherland), gas chromatography–mass spectrometry (GC-MS, ISQ 7000 GC-MS system by Thermo Scientific), and UV-Vis diffuse reflectance spectra (UV-Vis DRS, UV-2600, Shimadzu) methods.

The product of the oxidative desulfurization process is determined on the ISQ 7000 GC-MS system by Thermo Scientific. The system includes Trace 1310 gas chromatography, ISO 7000 ExtractaBrite ion source mass spectrometer, Lumin gas purifier and trap, CombiPAL CTC Analytics AG automatic sample injector with headspace sampling, and TraceGOLD TG-5MS chromatography column by Thermo Scientific: column height 30 m, inner diameter 0.25 mm, stationary phase thickness 0.25 µm.

First, 1 mL of the sample is placed in a 1.8 mL vial and heated to 250 ^oC. The gas chromatography column is heated to 50 ^oC for 1 minute; then heated from 50 ^oC to 100 ^oC and held for 2 minutes; then heated to 270 ^oC and held for 20 minutes, and finally heated to 300 ^oC. The gas chromatography column heating process is performed at a rate of 50 ^oC/minute. Then, helium gas is used at a rate of 1 mL/minute to transfer the product from the GC to the open MS at 280 ^oC. The ion source temperature is 250 °C, and the ionization mode is electron impact (EI). The product of the oxidative desulfurization process is processed using the Chromeleon™ chromatography data system (CDS) software.

3. Additional information and results

Table S1. The content of $ZnCl_2.6H_2O$ and titanium isopropoxide used in the synthesis of ZnO-TiO_2/OCN samples

Samples	OCN (g)	Titanium(IV) Isopropoxide (mL)	$ZnCl_2.6H_2O$ (g)
10%ZnO-TiO_2/OCN	0.5	1.52	0.30
20%ZnO-TiO_2/OCN	0.5	1.14	0.60
30%ZnO-TiO_2/OCN	0.5	0.76	0.91

Table S2. Binding energies of the bonds in the ZnO, TiO_2, OCN and 20%ZnO-TiO_2/OCN samples

		ZnO	TiO_2	OCN	20%ZnO-TiO_2/OCN	20%ZnO-TiO_2/OCN after 5 cycles
Zn2p	Zn $2p_{1/2}$	1022.60	-	-	1022.72	1022.81
	Zn $2p_{3/2}$	1045.75	-	-	1045.81	1022.83
Ti2p	Ti^{3+}	-	-	-	457.47	458.64
		-	-	-	462.96	463.17
	Ti^{4+}	-	458.52	-	458.79	459.72
		-	464.17	-	464.46	465.53
	Ti-N	-	-	-	460.28	461.36
		-	-	-	465.91	466.77
C1s	sp^2 C–C	-	-	284.87	284.73	284.85
	C–O	-	-	287.80	287.51	287.59
	N–C=N	-	-	288.53	288.03	288.37
	Ti- N	-	-	-	396.63	396.81

N1s	C–N=C	-	-	398.77	398.59	398.80
	sp^3N	-	-	400.41	399.92	400.00
	C_2–NH	-	-	401.74	401.31	401.43
O1s	N–C–O	-	-	530.64	530.48	530.99
	Ti-O or Zn-O	532.09	532.00	-	532.29	532.77
	–OH groups	533.91	533.88	533.93	533.97	534.55

Table S3. Element composition (wt%) of OCN and ZnO-TiO_2/OCN samples

Samples	C	N	O	Ti	Zn	Total
OCN	43.60	51.66	4.74	-	-	100
10%ZnO-TiO_2/OCN	22.04	26.12	20.34	23.63	7.87	100
20%ZnO-TiO_2/OCN	21.94	26.07	18.69	16.94	16.36	100
30%ZnO-TiO_2/OCN	21.92	26.47	15.18	12.9	23.53	100

Table S4. The benchmark of the as-synthesized 20%ZnO-TiO_2/OCN sample

Materials	Reaction conditions	Light source	Photocatalytic performance	Ref.
ZnO/FSM-16	[DBT] = 200 mg L^{-1} $m_{catalyst}$ = 0.3 g L^{-1}	Hg lamp (60 W, UV)	95% in 550 min	[1]
TiO_2/g-C_3N_4	[DBT] = 500 mg L^{-1} $m_{catalyst}$ = 10.0 g L^{-1}	250 W high-pressure Hg lamp (UV light)	98.9% in 120 min	[2]
Ti_3C_2/g-C_3N_4	[TH] = 140 mg L^{-1} $m_{catalyst}$ = 2.5 g L L^{-1}	300 W xenon lamp	73.6 % in 180 min	[3]
Ag@AgBr/Al-SBA-15	[DBT] = 500 mg L^{-1} $m_{catalyst}$ = 1.0 g L^{-1}	Sunlight irradiation	98.66% in 300 min	[4]
Ti-SBA-15	[DBT] = 500 mg L^{-1} $m_{catalyst}$ = 2.5 g L^{-1}	35 W UV light	92.68% in 360 min	[5]

Ag_3PO_4/d-C_3N_4	[DBT] = 200 mg L^{-1} $m_{catalyst}$ = 2.5 g L^{-1}	300 W xenon lamp	92.5 % in 180 min	[6]
AgCl/$PbMoO_4$	[DBT] = 200 mg L^{-1} $m_{catalyst}$ = 1.5 g L^{-1}	Not mentioned	97.0% in 120 min	[7]
Ni-WO_3@g-C_3N_4	[DBT] = 100 mg L^{-1} $m_{catalyst}$ = 2.0 g L^{-1}	Not mentioned	97.0% in 180 min	[8]
WO_3/g-C_3N_4	[DBT] = 500 mg L^{-1} $m_{catalyst}$ = 2.0 g L^{-1}	Not mentioned	91.2% in 180 min	[9]
CeO_2/ATP/g-C_3N_4	[DBT] = 200 mg L^{-1}	300 W xenon lamp	98 % in 180 min	[10]
ZnO-TiO_2/OCN	[DBT] = 300 mg L^{-1} $m_{catalyst}$ = 1.5 g L^{-1}	300 W xenon lamp	99.19% in 120 min	This work

Table S5. Calculated optical properties of the $(TiO_2)_7$, $(ZnO)_6$, $(TiO_2)_7(ZnO)_6$, OCN and ZnO-TiO_2/OCN samples

System	**$(TiO_2)_7$**	**$(ZnO)_6$**	**$(TiO_2)_7(ZnO)_6$**	**OCN**	**ZnO-TiO_2/OCN**
Bandgap (eV)	5.00	4.28	3.97	4.17	3.44
Peak (UV, eV)	3.89	3.26	3.27	3.66	2.83

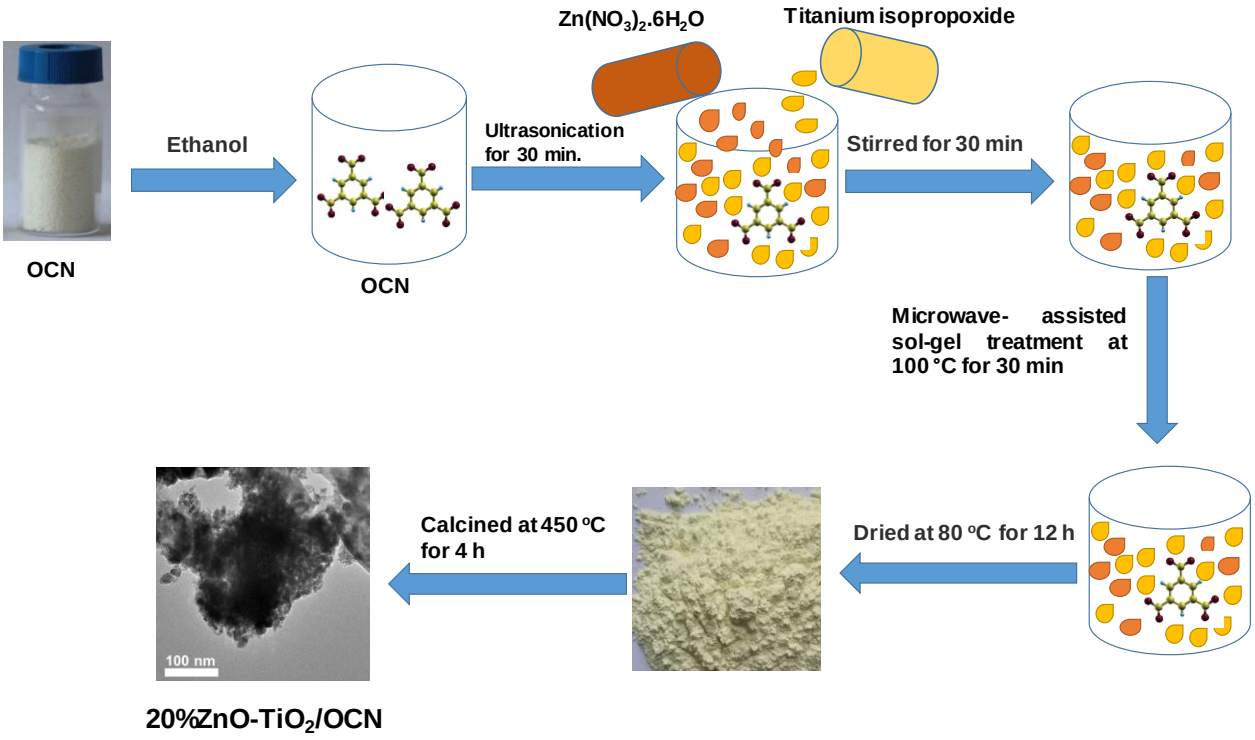
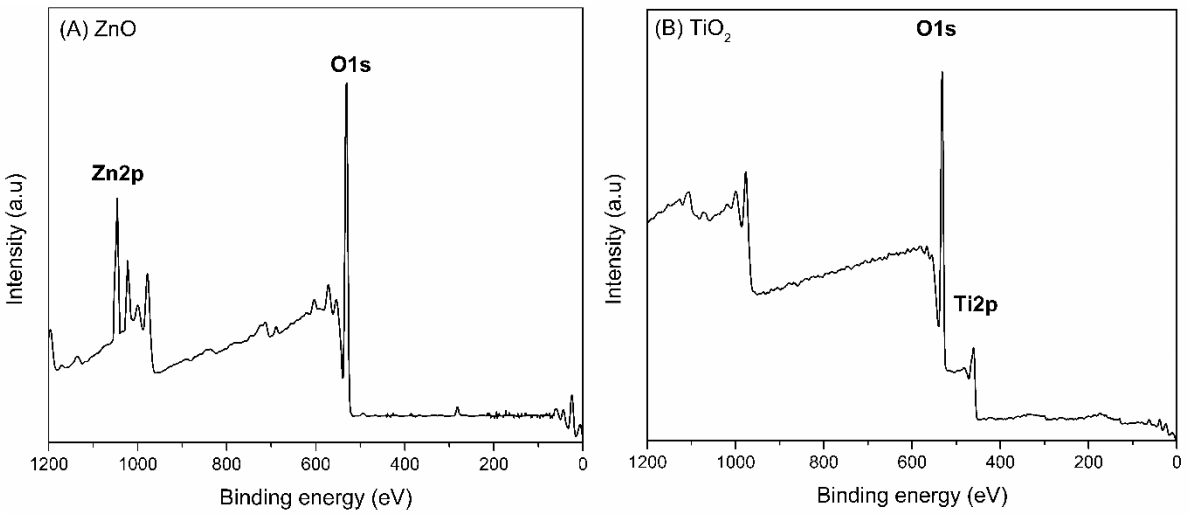


Figure S1. Schematic synthesis of ZnO-TiO_2/OCN materials by microwave-assisted sol-gel method



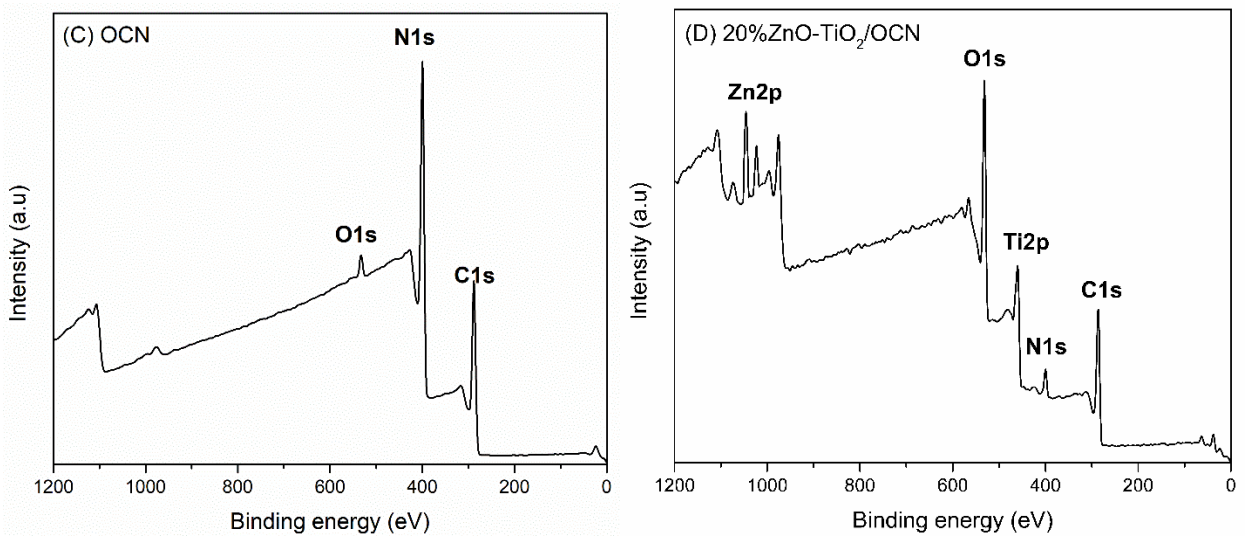


Figure S2. Survey XPS spectra of ZnO (A), TiO_2 (B), OCN (C) and 20%ZnO-TiO_2/OCN (D) samples

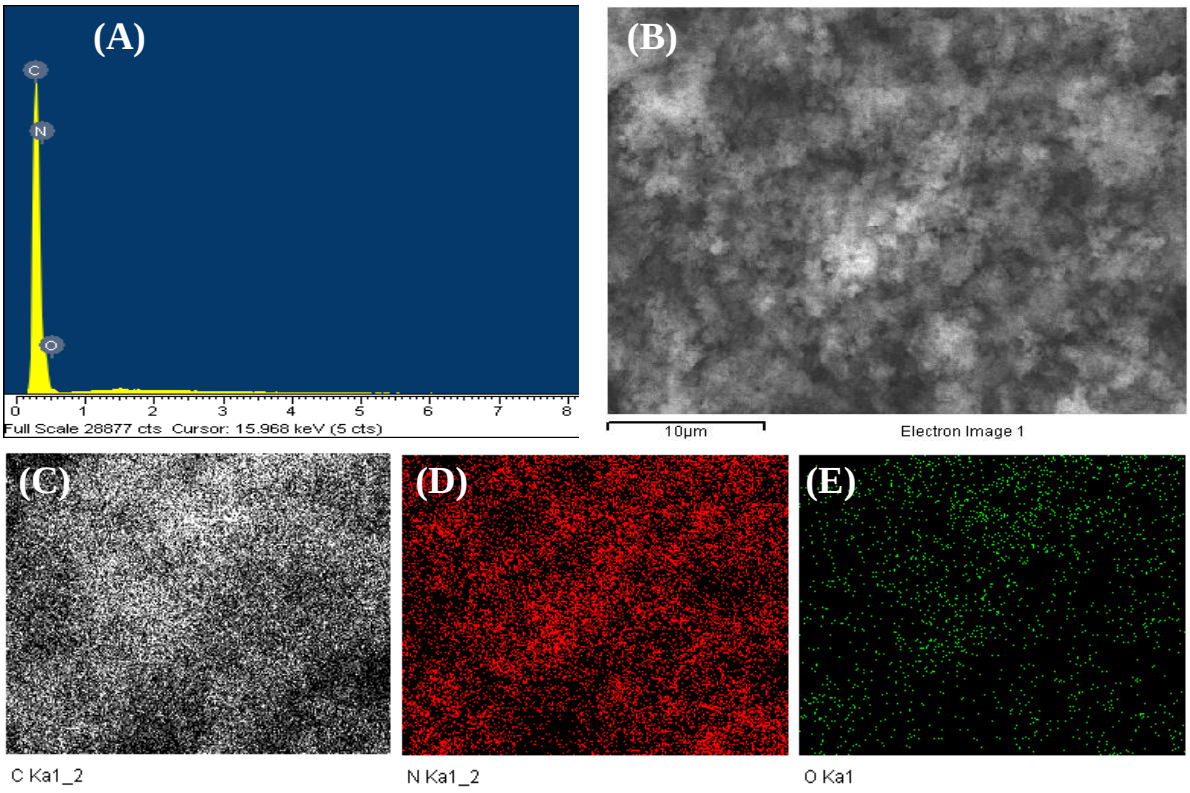


Figure S3. EDS spectrum (A), EDS element layered image (B), EDS element mapping images of C (C), N (D) and O (E) of OCN sample.

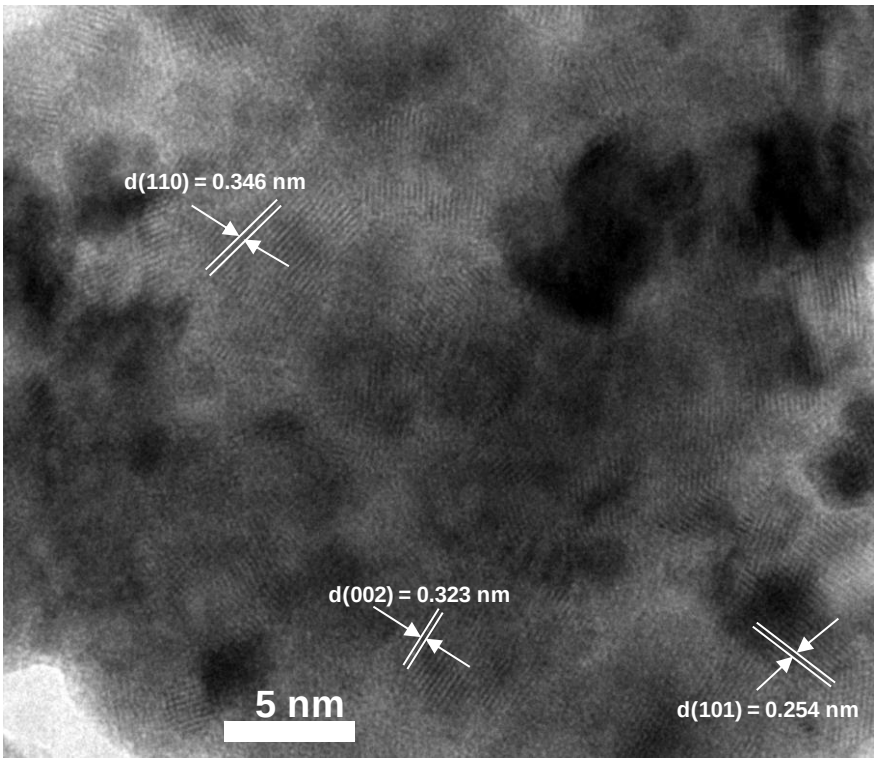


Figure S4. HRTEM image of 20%ZnO-TiO_2/OCN sample

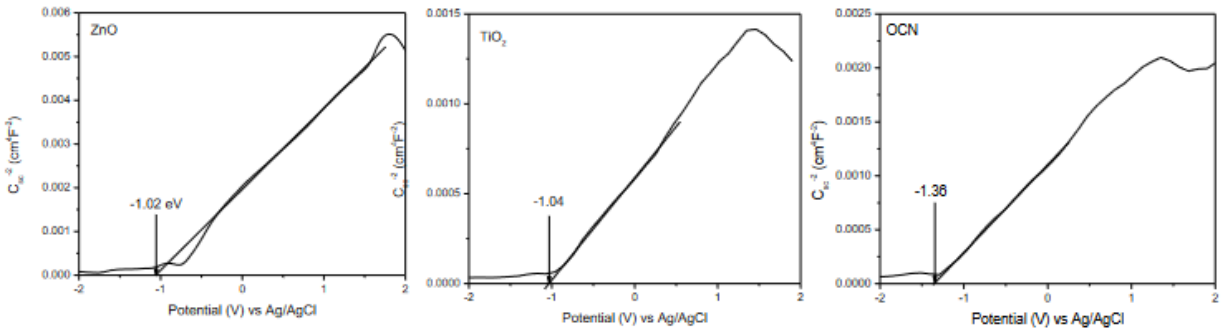


Figure S5. Mott–Schottky (MS) plot of ZnO, TiO_2 and OCN samples

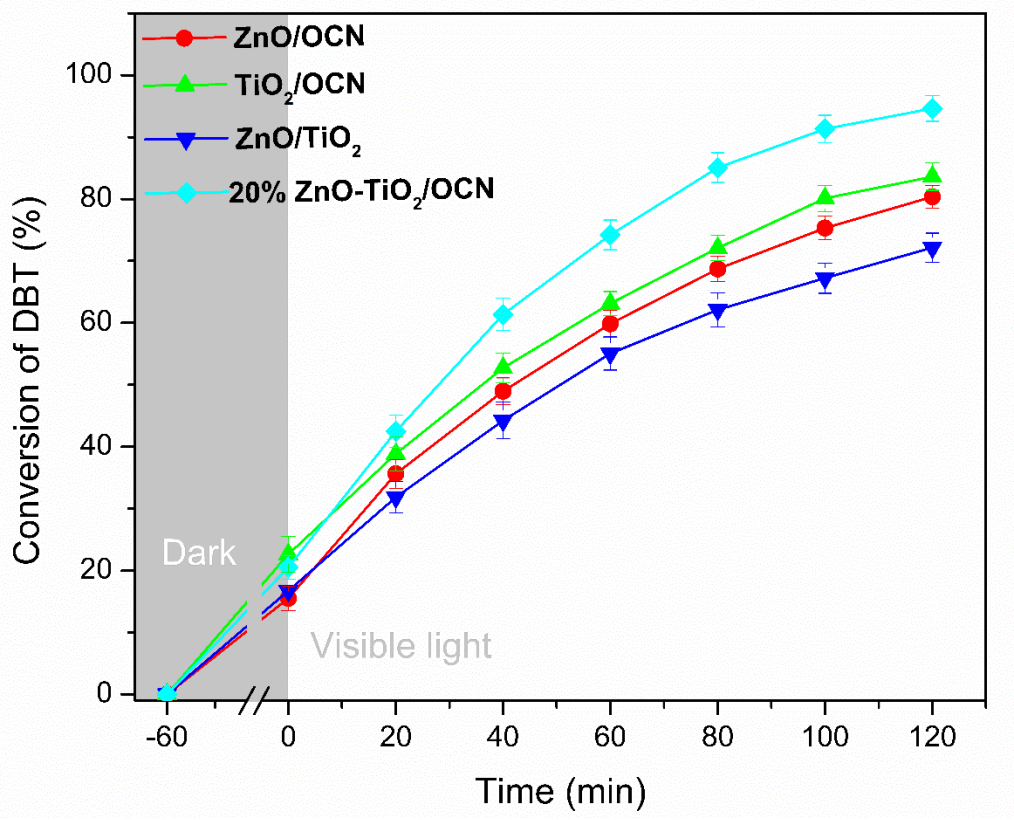


Figure S6. DBT conversion using ZnO/OCN, TiO_2/OCN, ZnO-TiO_2 and ZnO-TiO_2/OCN samples

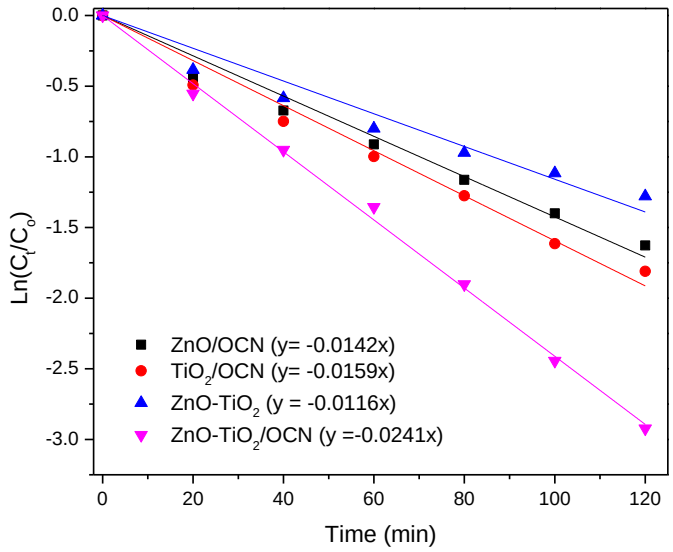
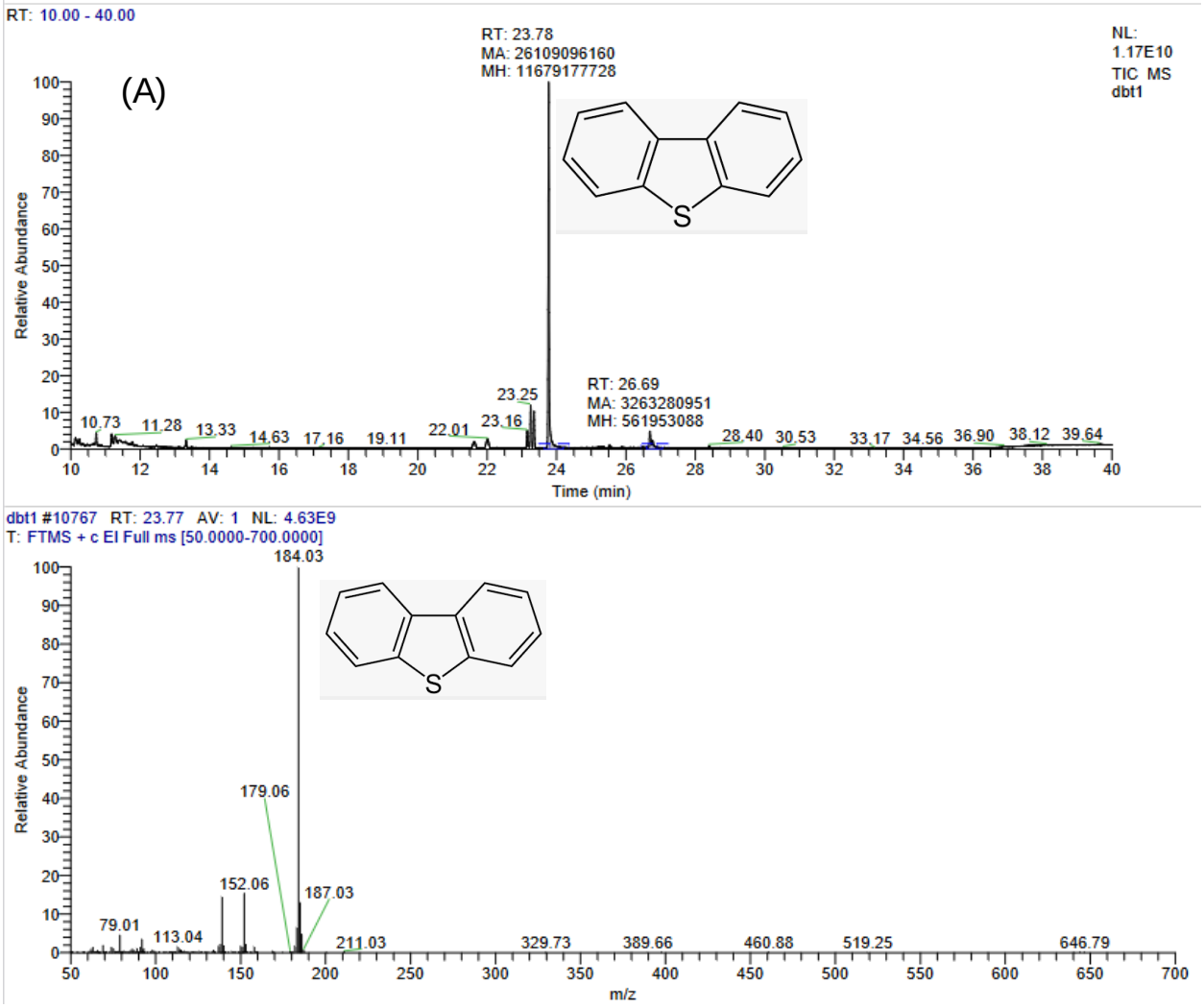


Figure S7. First-order reaction kinetics of ZnO/OCN, TiO_2/OCN, ZnO-TiO_2, and ZnO-TiO_2/OCN samples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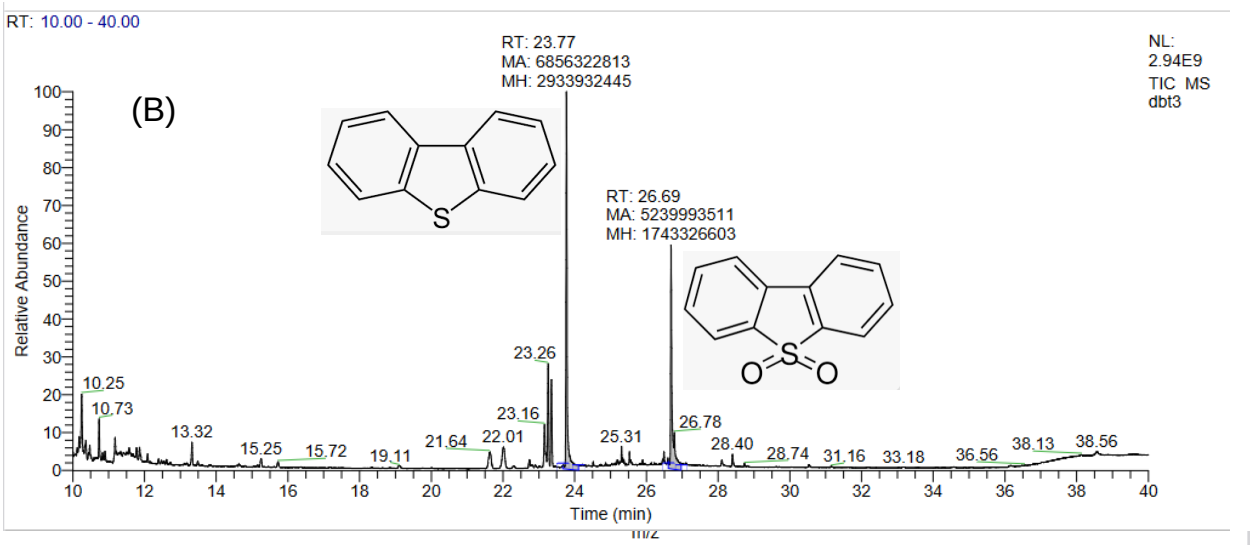
(A)
RT: 23.78
MA: 26109096160
MH: 11679177728
NL:
1.17E10
TIC MS
dbt1
Relative Abundance
Time (min)
RT: 26.69
MA: 3263280951
MH: 561953088
10.73
11.28
13.33
14.63
17.16
19.11
22.01
23.16
23.25
28.40
30.53
33.17
34.56
36.90
38.12
39.64
dbt1 #10767 RT: 23.77 AV: 1 NL: 4.63E9
T: FTMS + c EI Full ms [50.0000-700.0000]
184.03
179.06
152.06
187.03
79.01
113.04
211.03
329.73
389.66
460.88
519.25
646.79
Relative Abundance
m/z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(B)
RT: 23.77
MA: 6856322813
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RT: 26.69
MA: 5239993511
MH: 1743326603
NL:
2.94E9
TIC MS
dbt3
Relative Abundance
Time (min)
10.25
10.73
13.32
15.25
15.72
19.11
21.64
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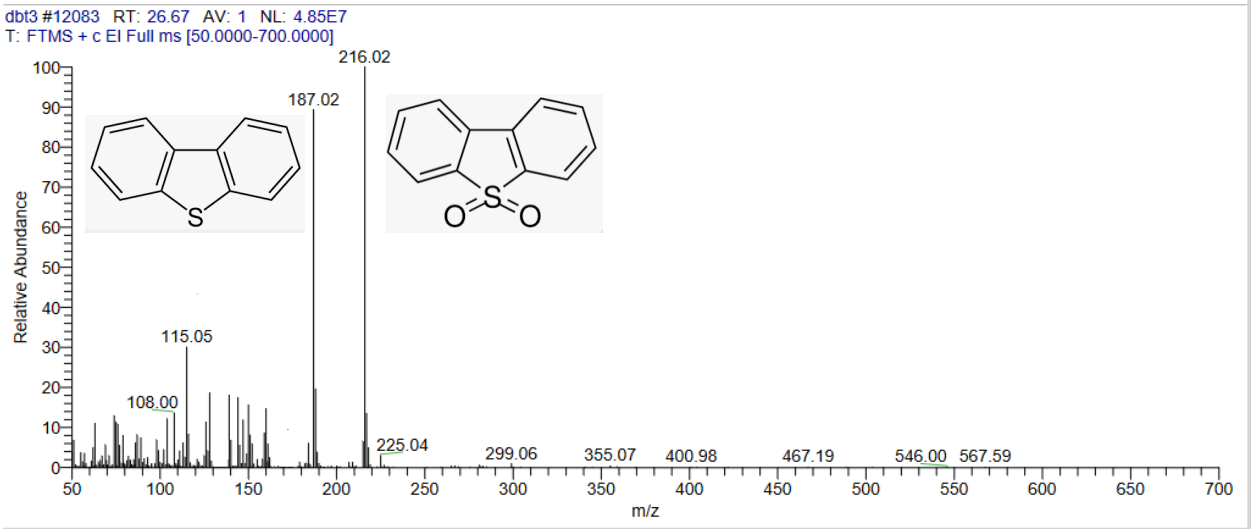
28.74
31.16
33.18
36.56
38.13
38.56


dbt3 #12083 RT: 26.67 AV: 1 NL: 4.85E7
T: FTMS + c EI Full ms [50.0000-700.0000]
Relative Abundance
m/z
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187.02
115.05
108.00
225.04
299.06
355.07
400.98
467.19
546.00
567.59

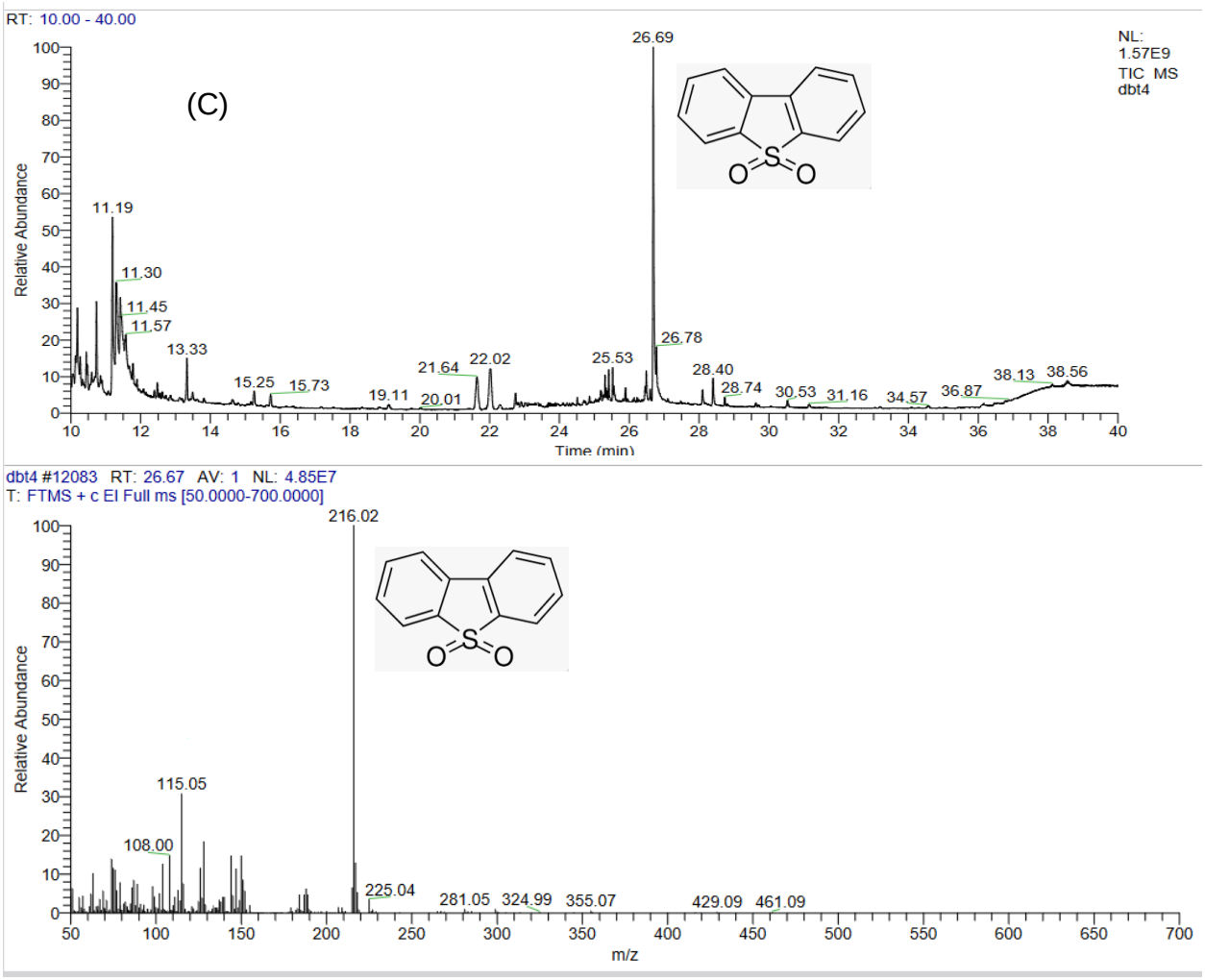

Figure S8. GC-MS of DBT (A) GC-MS spectra of the products in the desulfurization of DBT over 20%ZnO-TiO_2/OCN photocatalyst after 20 min (B) and 120 min (C)

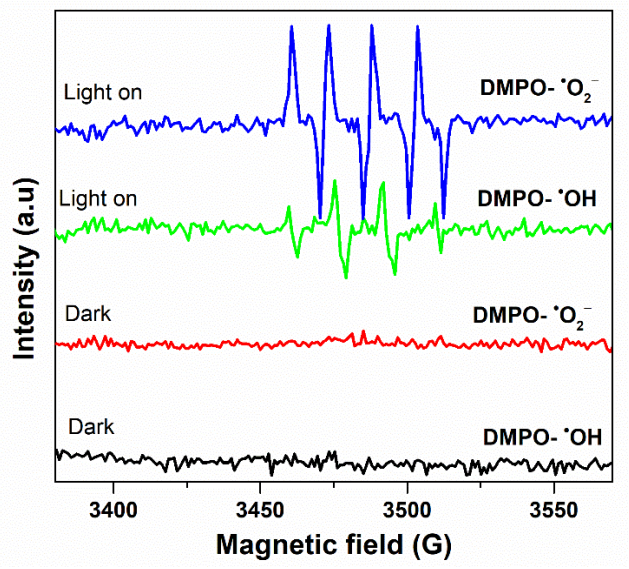

Figure S9. ESR spectra of 20%ZnO-TiO_2/OCN in the presence DMPO to detect ˙OH and $˙O_2^-$.

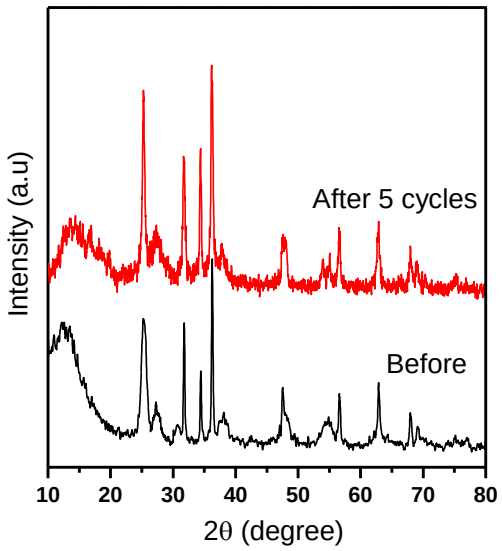

Figure S10. XRD patterns of 20%ZnO-TiO_2/OCN sample before and after reaction

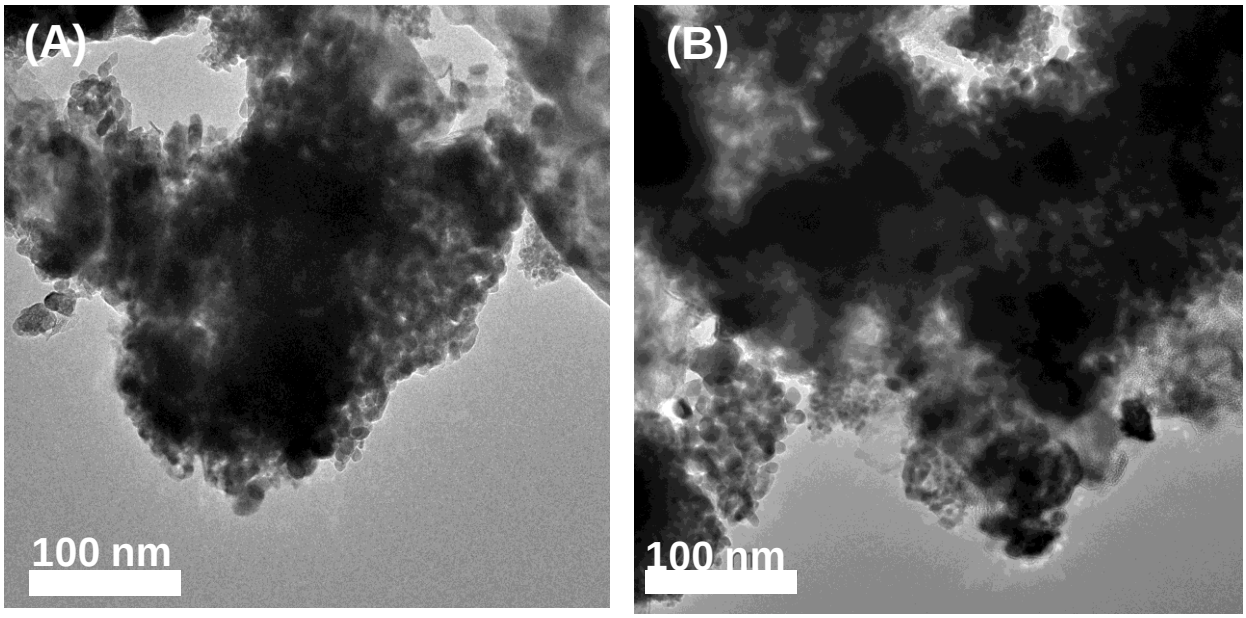

Figure S11. TEM image of 20%ZnO-TiO_2/OCN sample before and after the reaction.

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