Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Facile preparation of a polyoxometalate nanoparticle via solid-state chemical reaction for aerobic oxidation desulfurization catalysis

Hang Yu, Wenwen Bu, Zijia Wang, Zhuoyue Zhao, Mehwish Jadoon and Xiaohong Wang*

Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China, Tel.: 0086-431-85098531; Fax: 0086-431-85099759, E-mail address: wangxh665@nenu.edu.cn

Figure Caption

Materials

All chemicals and solvents used in this work were AR grade or better without further purification. For oxidation desulfurization, thiophene, DBT, BT and 4,6-DMDBT were prepared from the stock solution.

Physical measurements

IR spectra (4000-400 cm^{-1}) were recorded in KBr disks on a Nicolet Magna 560 IR spectrometer. UV-Vis spectra (200-800 nm) were recorded on a Cary 500 UV-Vis-NIR spectrophotometer. DR-UV-Vis spectra (200-800 nm) were obtained on a UV-2600 UV-Vis spectrophotometer (Shimadzu). The UV-visible spectra were recorded on T1810. XPS were recorded on an Escalab-MK II photoelectronic spectrometer with Al Kα (1200 eV). Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDAX) spectroscopy were performed using a XL30 ESEM FEG at 25 kV (PhilipsXL-30). EDAX was performed to take into account of the P, V, Mo, C, N, Ag and O elements. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. The XRD patterns of the samples were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). The Cyclic voltammetry curve was performed using Shanghai Chenhua Instrument Co., Ltd. CHI600E electrochemical Workstation. The particle-size distribution was to use Zetasizer Nano ZSE test analysis. The BET surface area was carried out using American Mike ASAP2020M gas adsorption analyzer and AUTOSORB-IQ-MPXR gas adsorption analyzer. The ^{31}P MAS NMR spectrum of $(NH_4)_5H_6PMo_4V_8O_{40}$, $AgPMo_4V_8$ powder and $AgPMo_4V_8$ nanoparticle were obtained using a Bruker AVANCE Ⅲ spectrometer at 400 MHz. The identification and quantification of DBT, 4,6-

DMDBT, BT and thiophene in decalin were performed by Gas Chromatography (GC). The sulfur content in real diesel was tested by ICP-AES (ICAP 6300).

Table S1 The comparison between various POM catalysts under aerobic conditions.

Catalyst and usage	Solvent	Substrate	Oxidant	T (℃)	Reaction time (h)	Con. (%)
$[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$ 40 mg	Decalin	DBT	O_2	97	7	100
$M_2(PcTN)_2$/W-HZSM-5 (M = Fe, Co, Ni, Cu, Zn and Mn) 100 mg	-	T BT DBT	O_2	60	3	> 85
$[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ 11 mg	Decalin	4,6-DMDBT DBT BT	O_2	80	5 7 12	100 100 65
$[C_8H_{17}N(CH_3)_3]_3HIV_9O_{28}$ 40 mg	Decalin	DBT 4,6-DMDBT	O_2	90 90	6 7	100 100
$[Cu_2(BTC)_{4/3}(H_2O)_2]_6[H_5PV_2Mo_{10}O_{40}]$ 44 mg	Decalin	DBT	O_2	80	1.5	100
$(NH_4)_5H_6PV_8Mo_4O_{40}$ 20 mg	Decalin	DBT 4,6-DMDBT BT T	O_2	100	6 6 11 12	100 100 100 97
IMo_6@iPAF-1 10 mg	Decalin	DBT 4,6-DMDBT BT T	O_2	90	5 5 7 10	100 100 100 97.6
$[PyPS]_3Co(OH)_6Mo_6O_{18}$ and Benzenesulfonic acid and polyethylene glycol 20 mg	Decalin	DBT 4,6-DMDBT BT	O_2	60	4 6 8	100 100 100
$Na_3Fe(OH)_6Mo_6O_{18}$ and Benzenesulfonic acid and polyethylene glycol 20 mg	Decalin	DBT 4,6-DMDBT BT	O_2	60	3 3 6	99 99 95
$Na_3H_6CrMo_6O_{24}$ and PEG (polyethylene glycol)/SSA (5-sulfosalicylic acid) 20 mg	Decalin	DBT 4,6-DMDBT	O_2	60	2 3	100 100
$(NH_4)_3Co(OH)_6Mo_6O_{18}$ and p-toluenesulfonic acid 20 mg	Decalin	DBT	O_2	70	0.5	100
$Ag_6(NH_4)_5PMo_4V_8O_{40}$ 20 mg	Decalin	DBT 4,6-DMDBT BT T	O_2	100	3.5 2 6 8	100 100 100 97

Table S2 Results of elemental analysis of catalysts (theoretical calculated values in brackets).

Catalysts	Elementary results (calculated values in parenthesis)/%					
	Ag	N	H	P	Mo	V
$Ag_6(NH_4)_5PMo_4V_8O_{40}$ powder	29.43 (29.02)	3.18 (3.58)	0.92 (0.88)	1.41 (1.32)	17.45 (17.33)	18.53 (18.55)
$Ag_6(NH_4)_5PMo_4V_8O_{40}$ nanoparticle	29.42 (29.02)	3.17 (3.58)	0.91 (0.88)	1.42 (1.32)	17.54 (17.33)	18.53 (18.55)

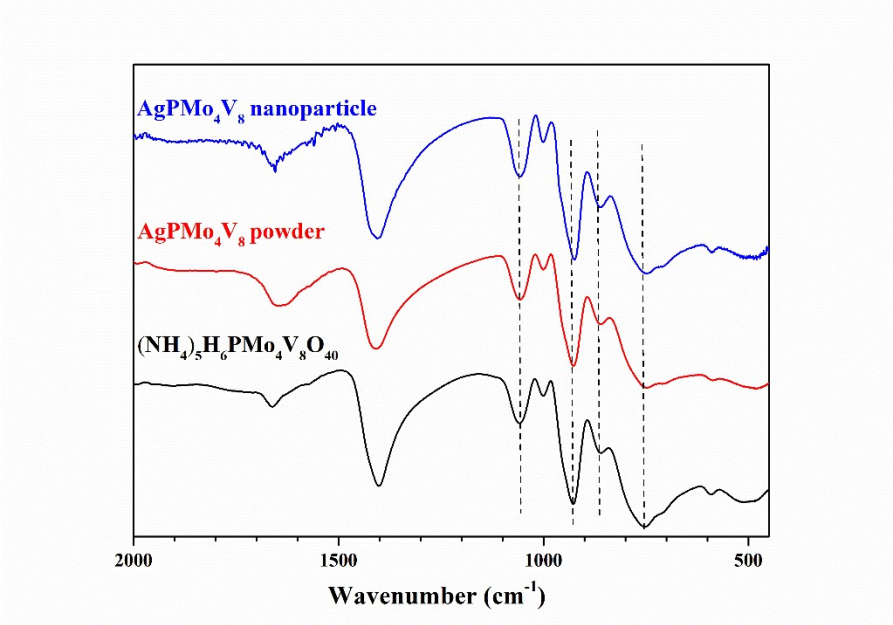

Fig. S1 FTIR spectra of $(NH_4)_5H_6PMo_4V_8O_{40}$, $AgPMo_4V_8$ powder and $AgPMo_4V_8$ nanoparticle.

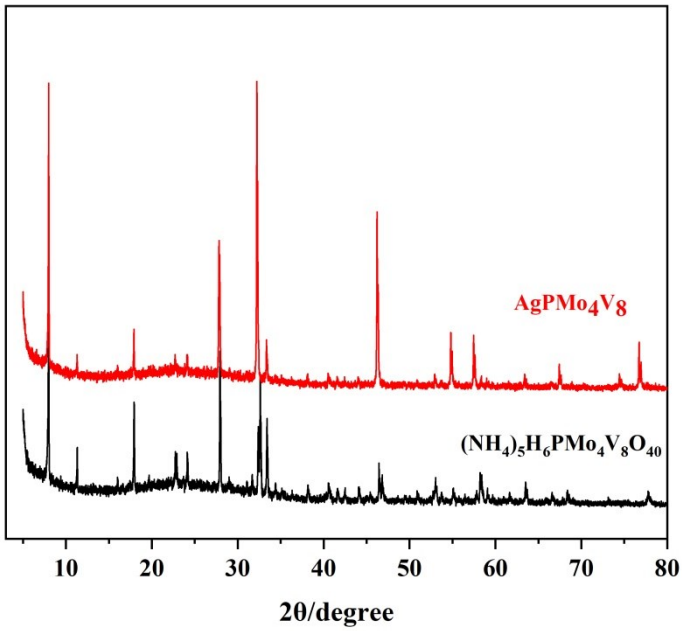

Fig. S2 The XRD patterns of $(NH_4)_5H_6PMo_4V_8O_{40}$ and $AgPMo_4V_8$ nanoparticle.

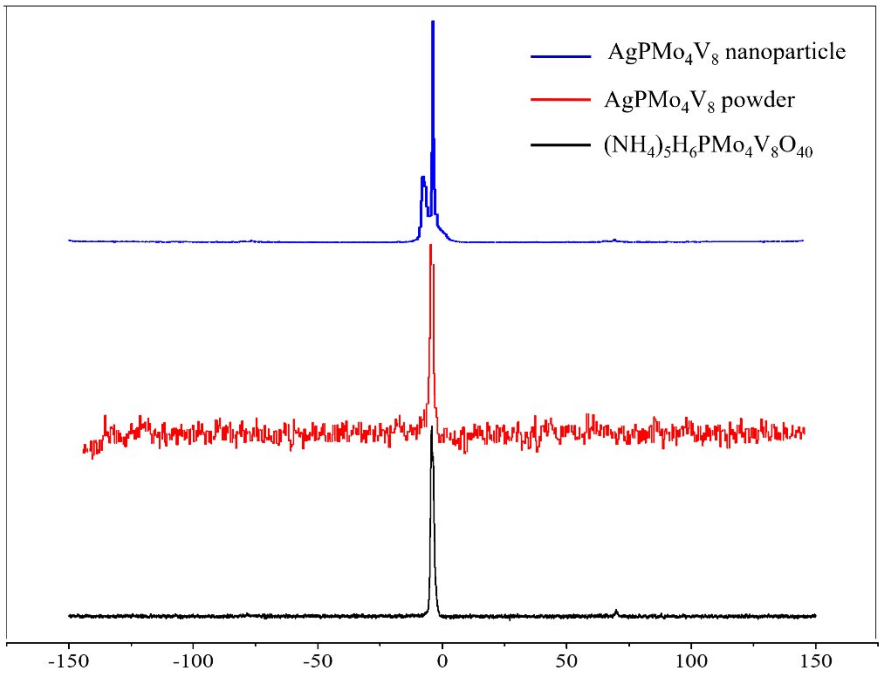

Fig. S3 The ^{31}P MAS NMR spectra of $(NH_4)_5H_6PMo_4V_8O_{40}$, $AgPMo_4V_8$ powder and $AgPMo_4V_8$ nanoparticle.

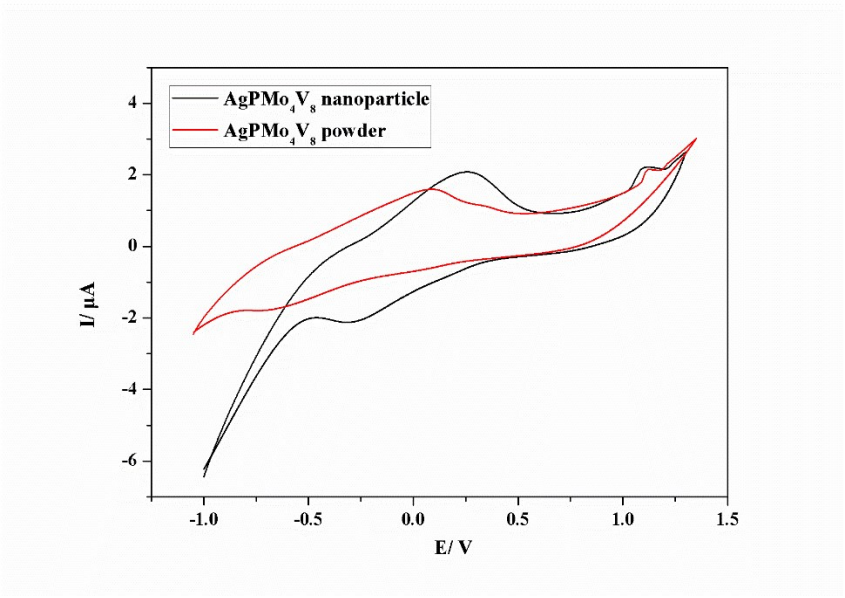

Fig. S4 Cyclic voltammograms of $AgPMo_4V_8$ nanoparticle and $AgPMo_4V_8$ powder.

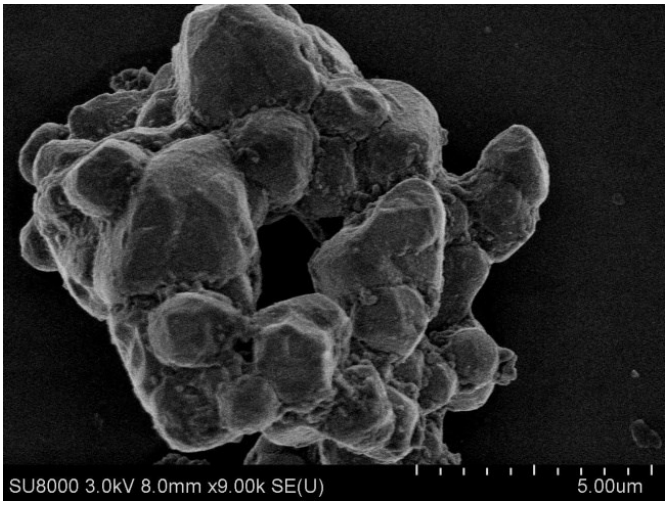

Fig. S5 The SEM image of $AgPMo_4V_8$ powder.

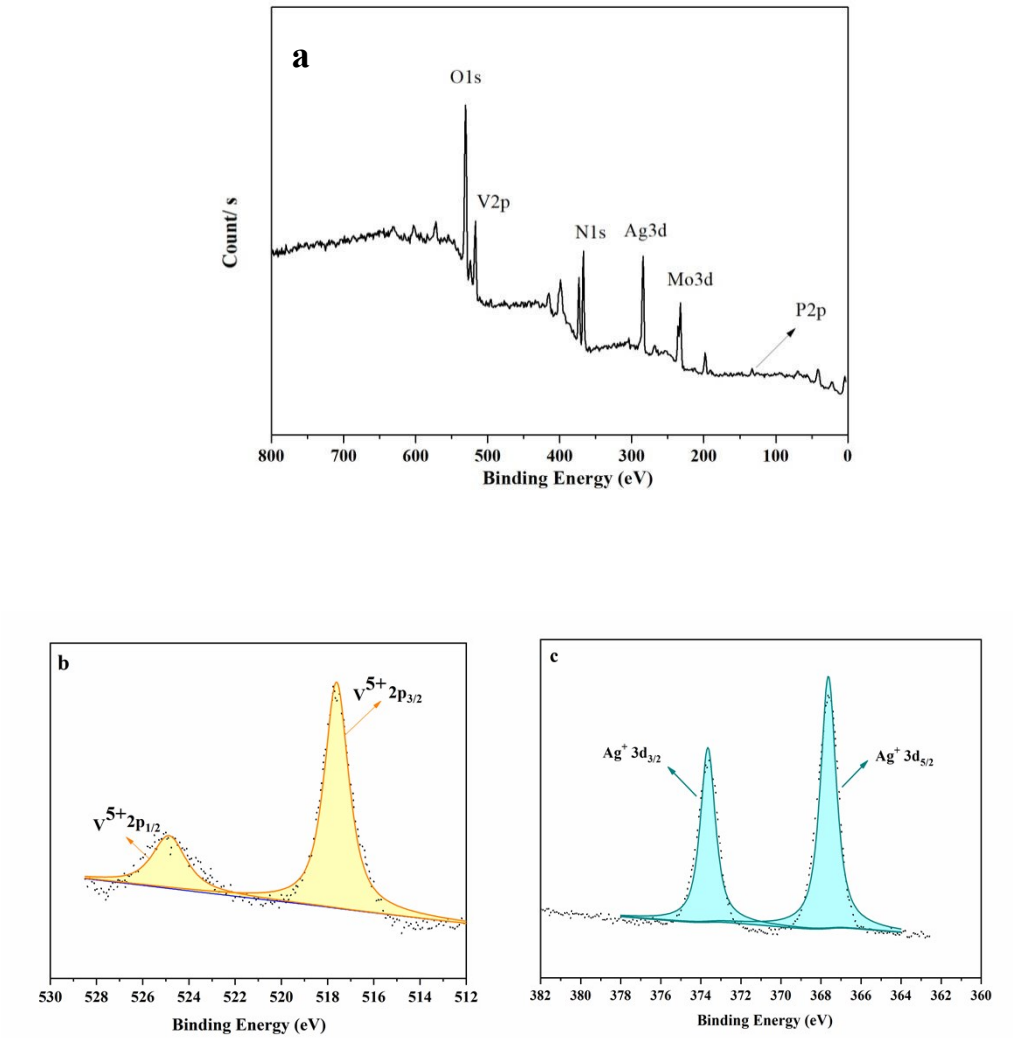

Fig. S6 XPS spectra of $AgPMo_4V_8$ powder **(a)**; spectra of V2p elements **(b)** and Ag3d elements **(c)** of $AgPMo_4V_8$ powder.

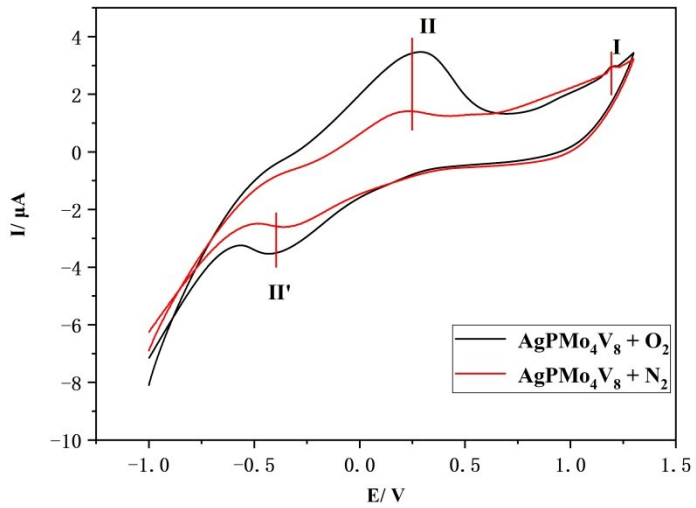

Fig. S7 Cyclic voltammograms of $AgPMo_4V_8$ nanoparticle in nitrogen and oxygen atmosphere.

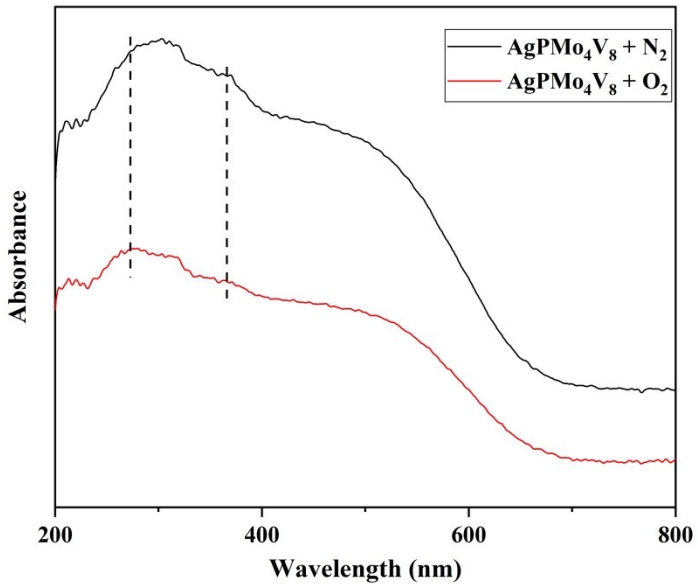

Fig. S8 DR-UV spectra of $AgPMo_4V_8$ nanoparticle in N_2 and in O_2.

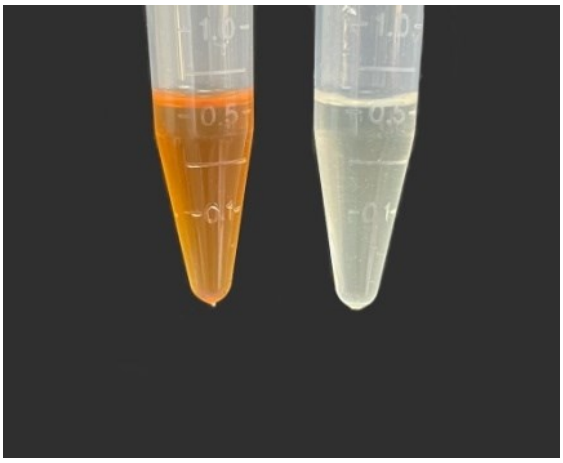

Fig. S9 The gasoline before the reaction (left) and after (right) treatment.

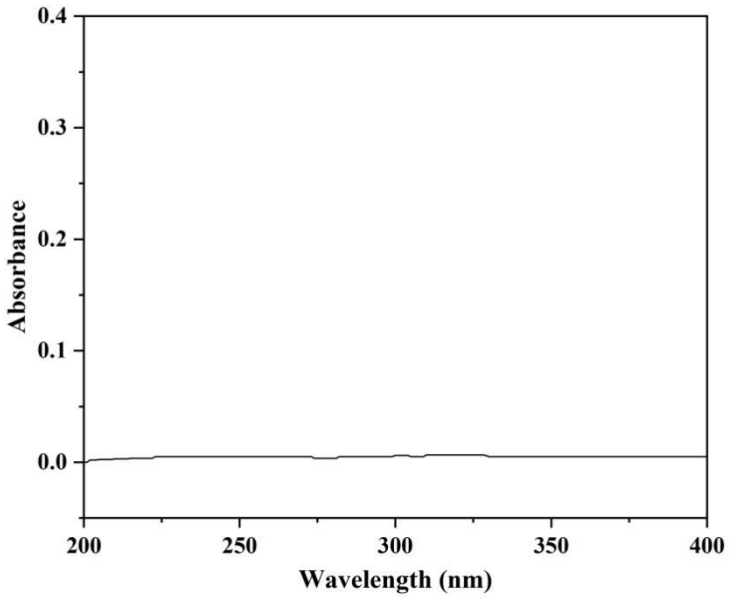

Fig. S10 Uv spectrum of reaction mixture after separating catalyst.

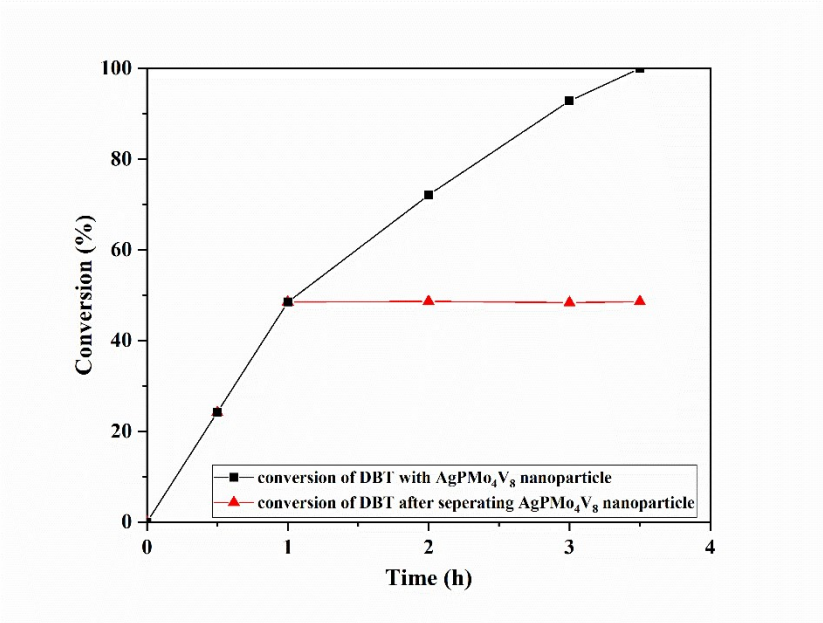

Fig. S11 The dissolving test of $AgPMo_4V_8$ nanoparticle in AODS of DBT.

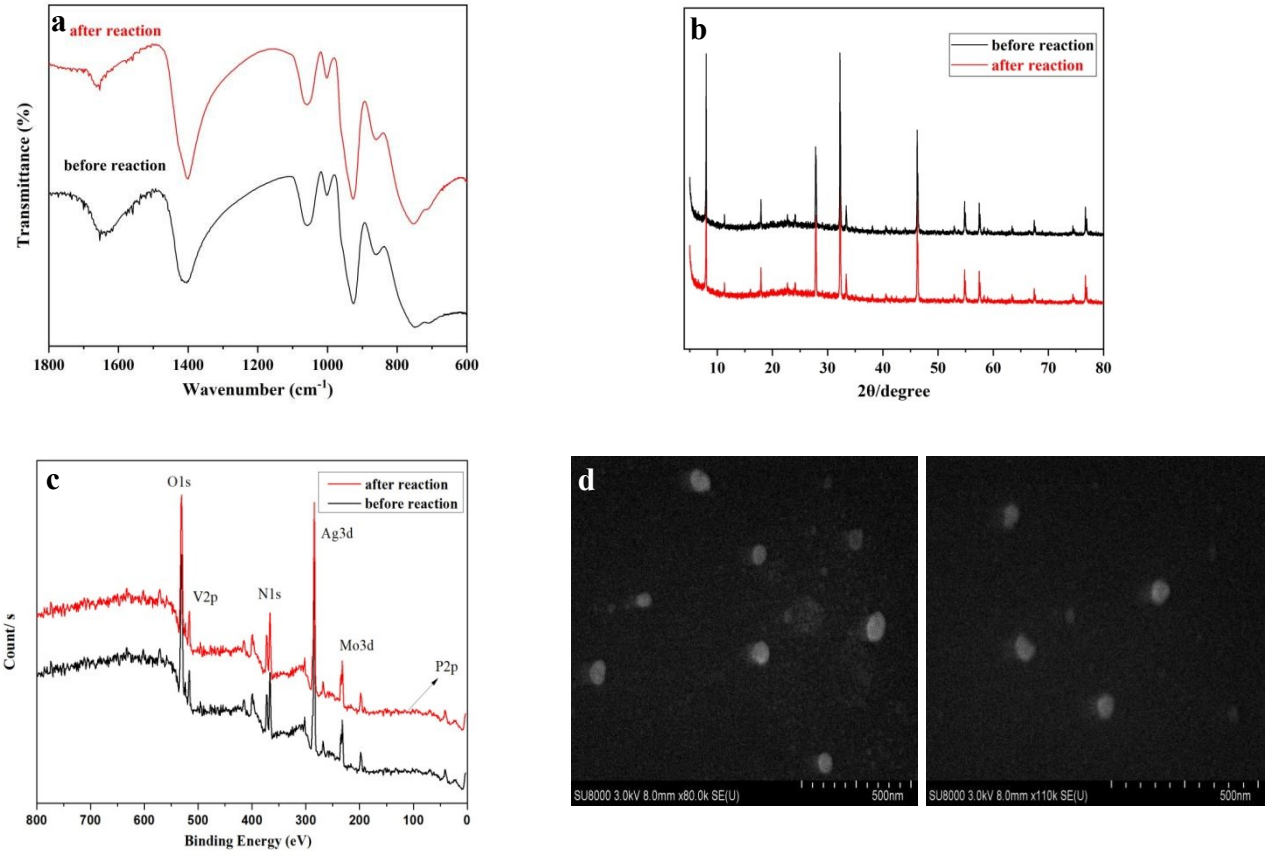

Fig. S12 The IR **(a)**, XRD **(b)**, XPS **(c)** and SEM **(d)** of $AgPMo_4V_8$ nanoparticle before and after the reaction.

Fig. S13 The precipitation of $DBTO_2$ after aerobic oxidative treatment.

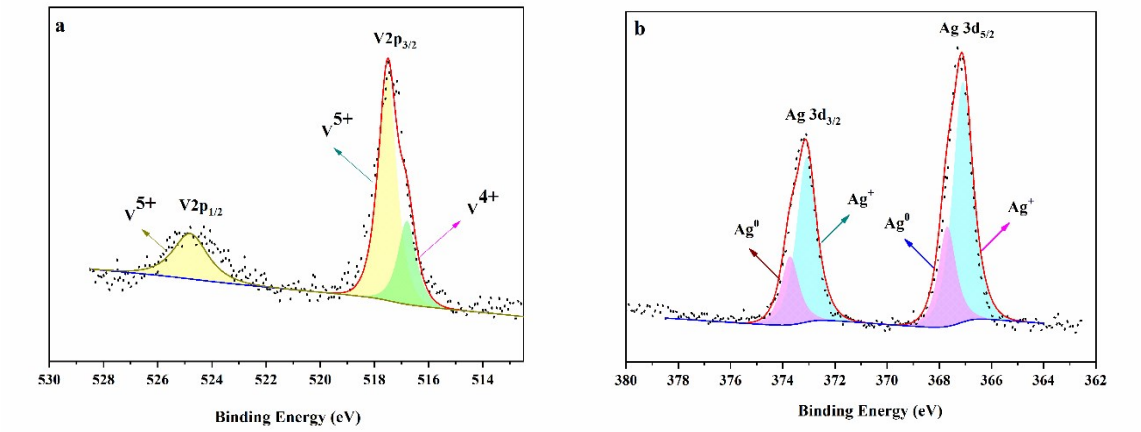

Fig. S14 XPS spectra of V2p elements **(a)** and Ag3d elements **(b)** of $AgPMo_4V_8$ nanoparticle after reaction.