Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information:

Ultra small subnano TiO_x cluster as an excellent co-catalyst for photocatalytic degradation of tetracycline on plasmonic Ag/AgCl

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This file includes:

Fig. S1 (a) XRD patterns of TiO_x@Ag/AgCl loaded with different concentrations of TiO_x from 0.1 to 5 times of the as-prepared fresh sample and the pristine sample; (b) XRD patterns of the as-prepared fresh TiO_x@Ag/AgCl and the used TiO_x@AgCl after 10 cycles.

Fig. S2 PL spectra of the as-prepared TiO_x@Ag/AgCl, 0.1TiO_x@Ag/AgCl and the synthesized Ag/AgCl.

Fig. S3. FTIR spectra of the as-prepared TiO_x@Ag/AgCl and the synthesized Ag/AgCl

Fig. S4 EIS nyquist plots of Ag/AgCl and TiO_x@Ag/AgCl

Fig. S5 Absorption spectrums of the degradation of TC with the presence of TiO_x@Ag/AgCl.

Fig. S6 Dependence of the TC adsorption efficiency on the TiO_x@Ag/AgCl in the dark

Fig. S7 HAADF images of TiO_x@Ag/AgCl exposed under different time of electron beam irradiation a) 0 s; b) 10 s; c) 20 s; d) 30 s; e) 40 s; f) 50 s.

Fig. S8 Effect of different scavengers on photocatalytic degradation

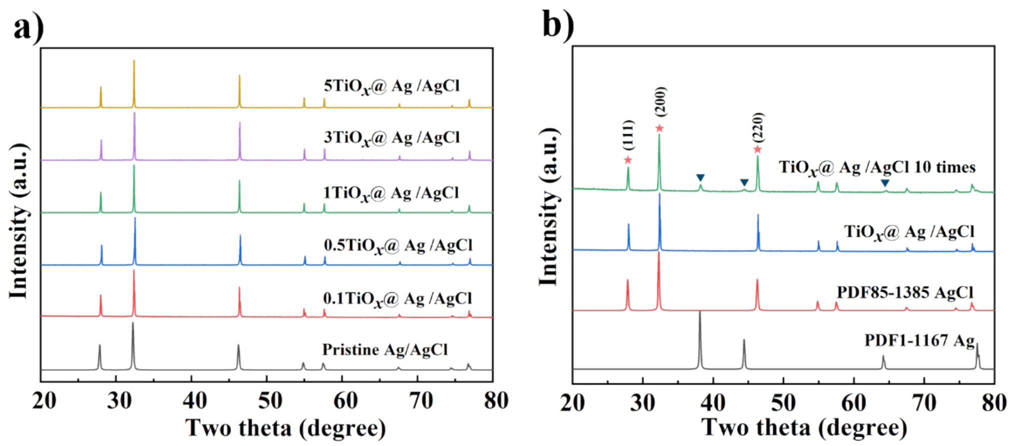
Fig. S9. Effect of different scavengers on photocatalytic degradation ESR signals of DMPO-$O_2^{\bullet -}$ and DMPO-HO• of TiO_x@Ag/AgCl. scavengers on photocatalytic degradation.

Fig. S10. LC-MS analysis of TC and its intermediates in the photodegradation reaction

Fig. S11. Proposed possible pathways of photocatalytic degradation of TC

Table. S1 EDX result of TiO_x@Ag/AgCl

Table. S2 Corresponding reaction rate constant k of TC of various catalyst



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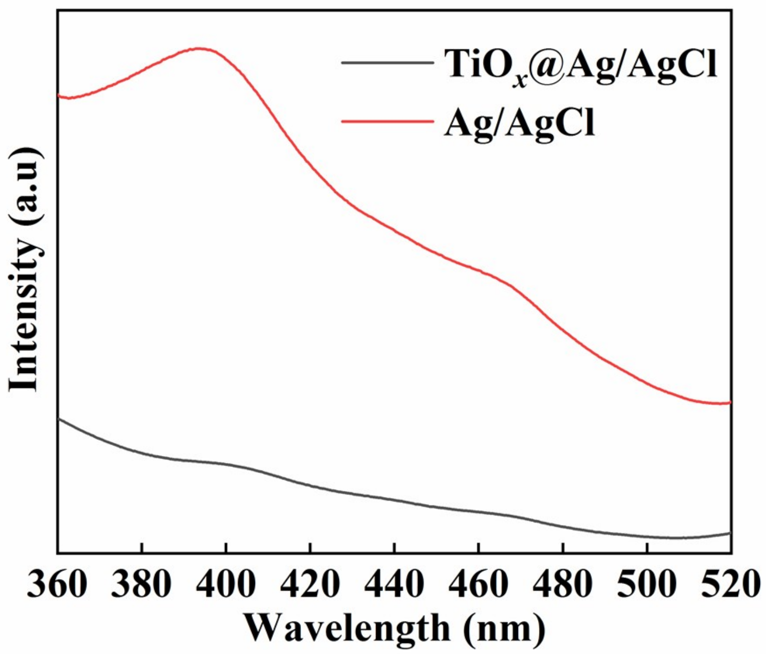


Fig. S2. PL spectra of TiO_x@Ag/AgCl and the synthesized Ag/AgCl.

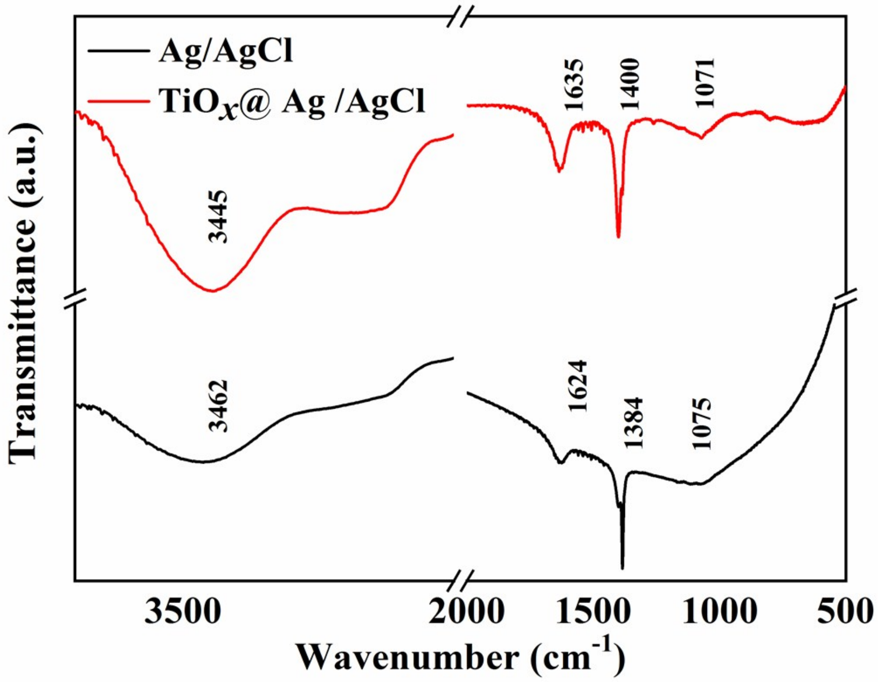


Fig. S3. FTIR spectra of the as-prepared TiO_x@Ag/AgCl and the synthesized Ag/AgCl.

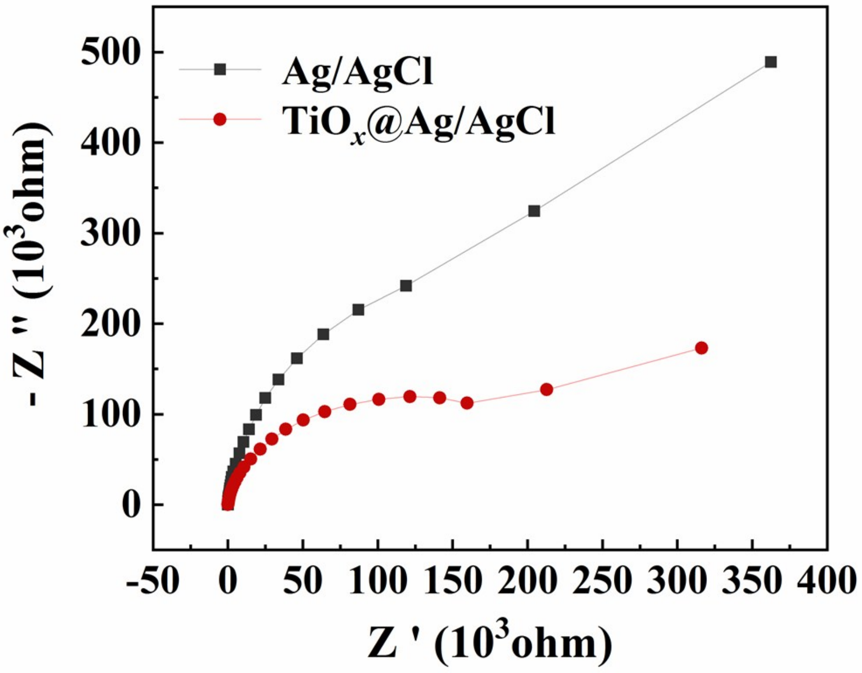


Fig. S4. EIS nyquist plots of Ag/AgCl and TiO_x@Ag/AgCl in 0.5 M Na_2SO_4 aqueous solution in the dark.

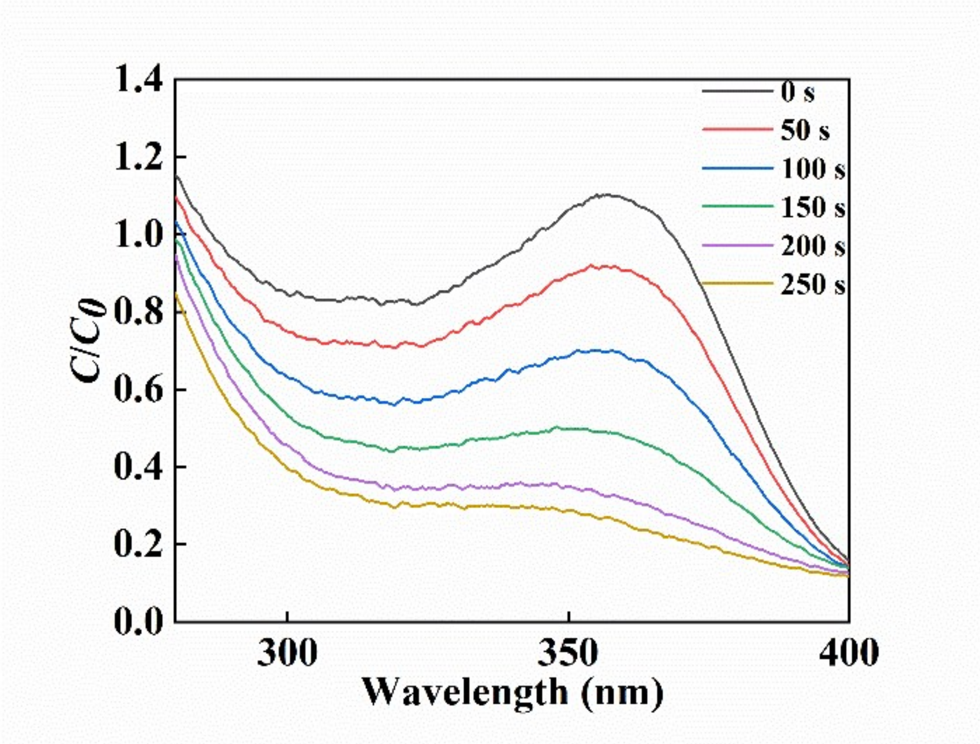


Fig. S5. Absorption spectrums of the degradation of TC with the presence of TiO_x@Ag/AgCl.

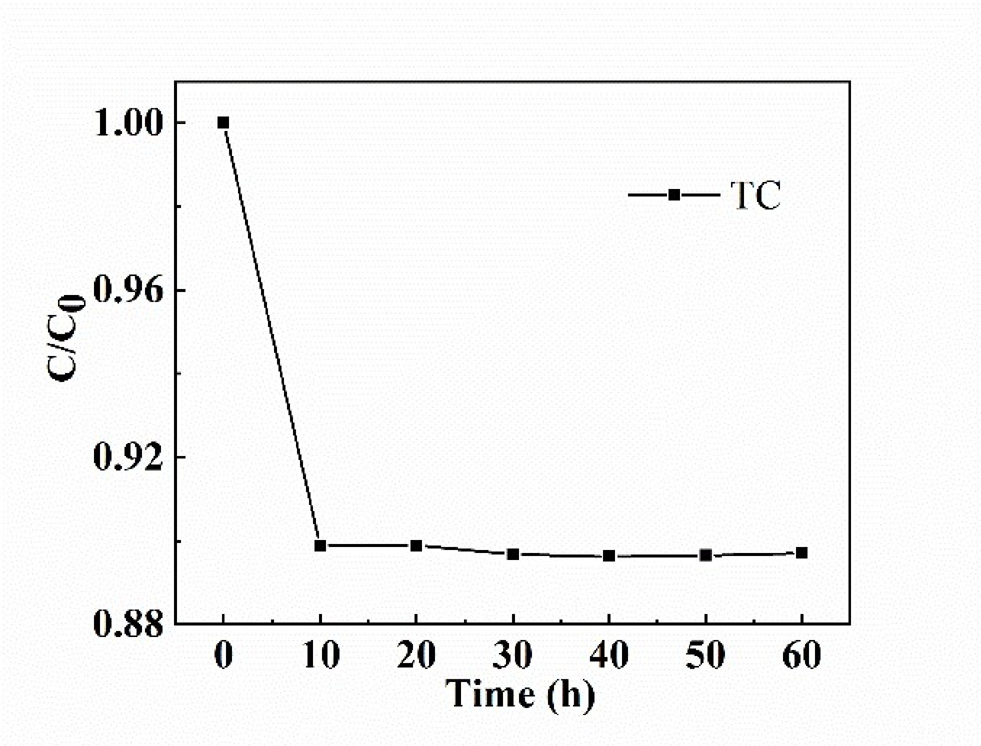
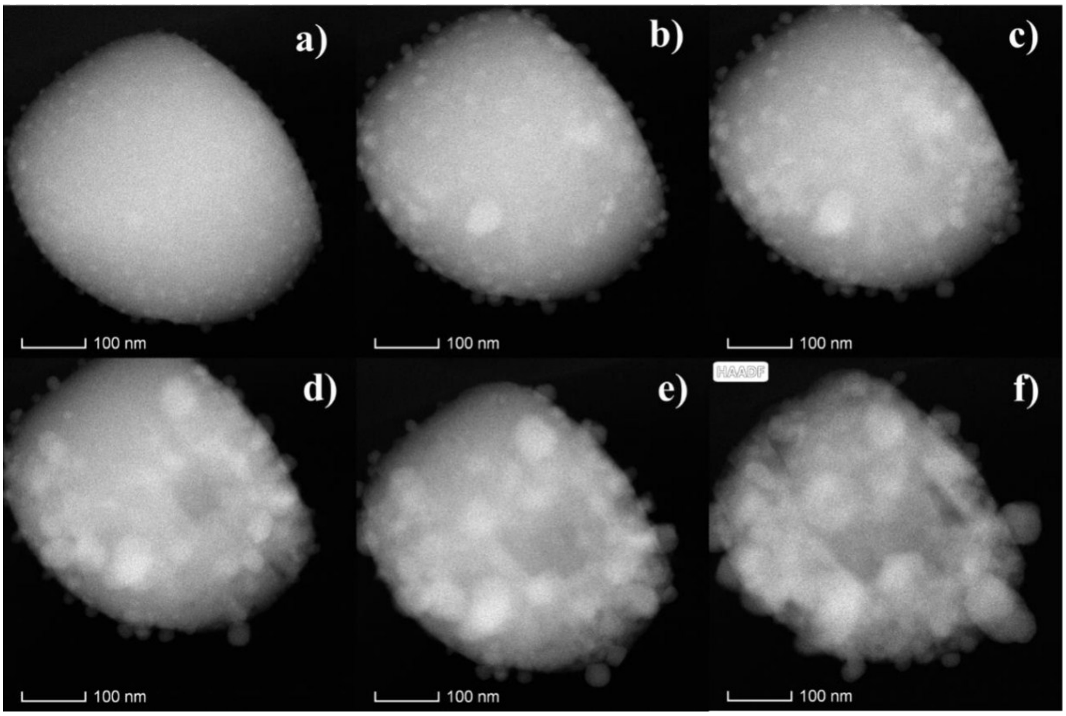


Fig. S6. Dependence of the TC adsorption efficiency on the TiO_x@Ag/AgCl in the dark



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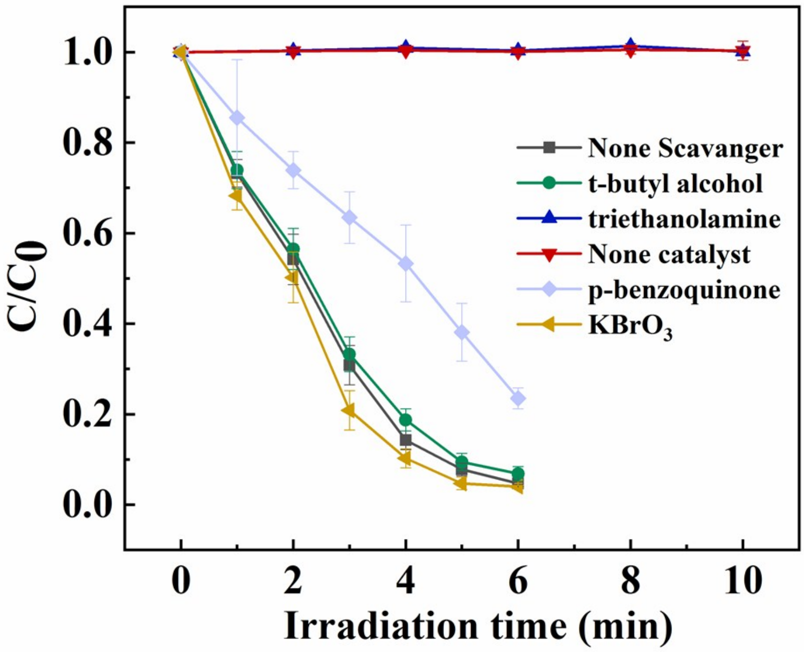

Fig. S8. Effect of different scavengers on photocatalytic degradation.

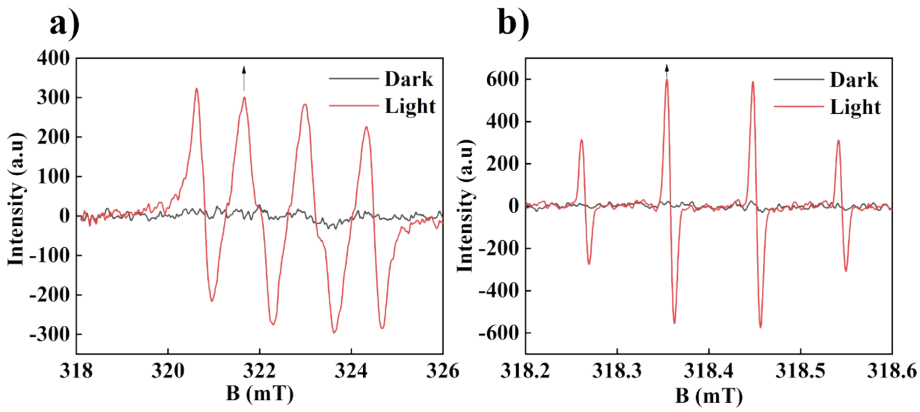

Fig. S9. ESR signals of DMPO-$O_2{\bullet}^-$ and DMPO-HO• of TiO_x@Ag/AgCl.

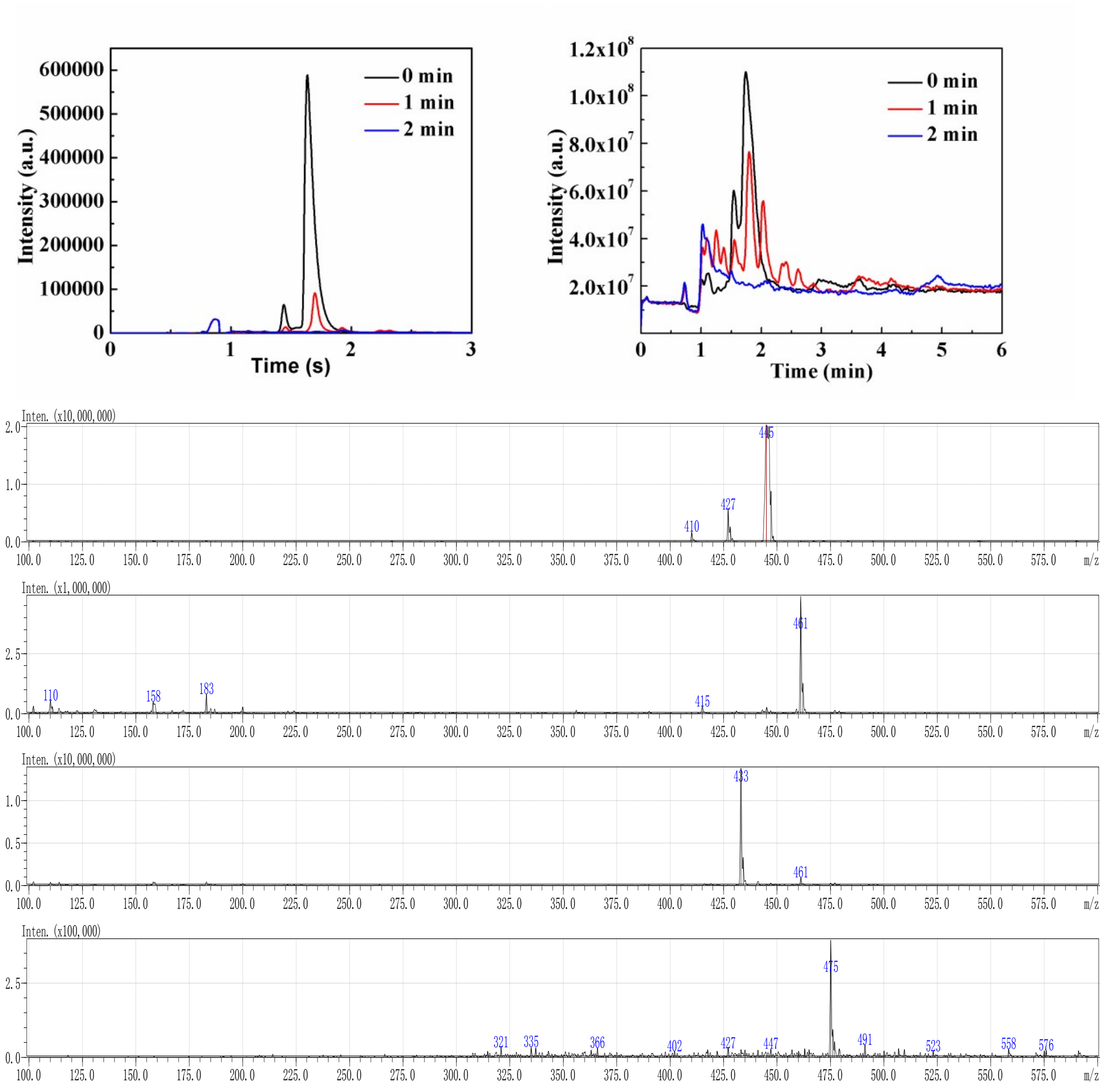

Fig. S10. LC-MS analysis of TC and its intermediates in the photodegradation reaction

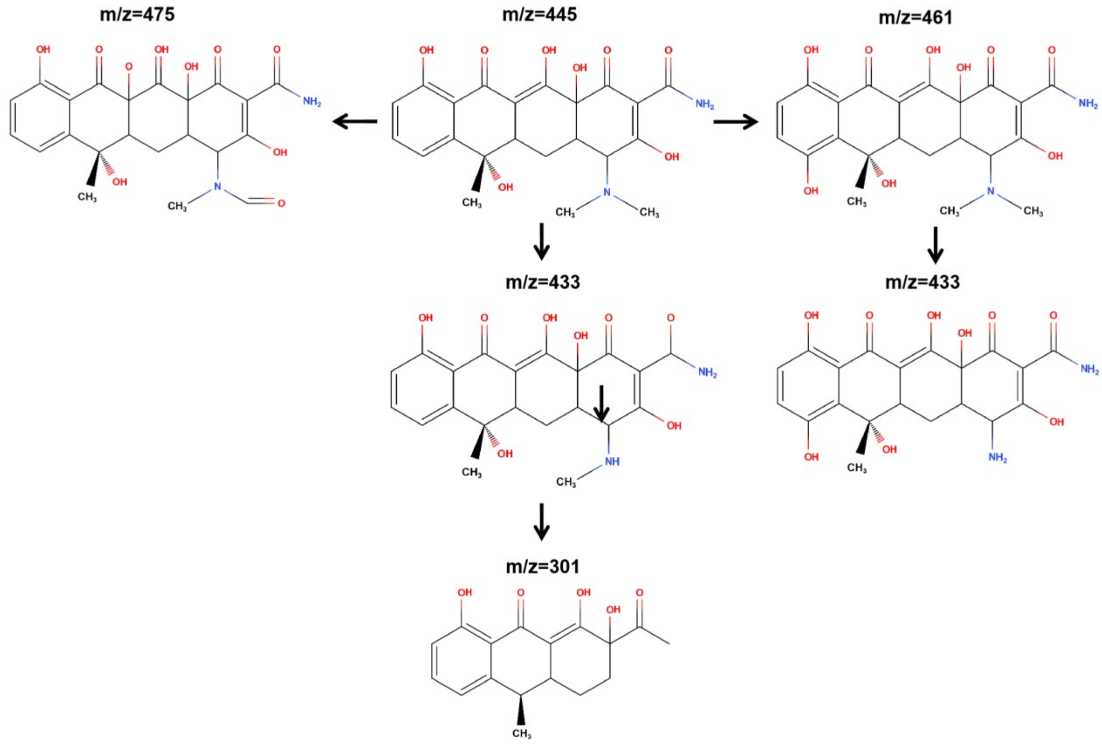

Fig. S11. Proposed possible pathways of photocatalytic degradation of TC

Table S1 EDX result of TiO_x@Ag/AgCl

Element	Atomic Fraction (%)	Mass Fraction (%)
Ag (L)	49.51	24.89
Cl (K)	50.09	0.27
Ti (K)	0.41	74.84

Table S2 Corresponding reaction rate constant (k) of TC and MO of various catalyst

Material structure	Light source	Light condition	Organic pollutants	Degradation rate
TiOx@Ag/AgCl (This work)	300 W Xe lamp	AM 1.5G	tetracycline	0.49247 min^{-1}
N-doped $BiOIO_3$ [1]	LED light	357 nm	tetracycline	0.04025 min^{-1}
$BiVO_4$ (0 4 0)-Ag@CdS [2]	300W Xe lamp	≥420 nm	tetracycline	0.0875 min^{-1}
Cu/Cl-g-C_3N_4 [3]	300W Xe lamp	≥400 nm	tetracycline	0.0271 min^{-1}
AgI/Bi_2WO6 [4]	300W Xe lamp	≥420 nm	tetracycline	0.075 min^{-1}
CoO/g-C_3N_4 [5]	300W Xe lamp	≥400 nm	tetracycline	0.0173 min^{-1}
LDH-Ag_2O/Ag [6]	300W Xe lamp	≥420 nm	tetracycline	0.0184 min^{-1}
α-Fe_2O_3@g-C_3N_4 [7]	100W LED lamp	420 nm	tetracycline	0.042 min^{-1}
Fe-doped surface-alkalinized g-C_3N_4 [8]	300W Xe lamp	≥420 nm	tetracycline	0.0164 min^{-1}
Nitrogen modified titania /strontium ferrite/diatomite (N-TSD) [9]	150W Xe lamp	≥400 nm	tetracycline	0.0165 min^{-1}
Bi_2WO_6/$CuBi_2O_4$ [10]	300W Xe lamp	≥400 nm	tetracycline	0.0393 min^{-1}
$NiFe_2O_4$/C yolk–shell nanospheres [11]	800W Xe lamp	≥420 nm	tetracycline	0.44295 min^{-1}
CQDs/ZnO@HNTs [12]	500W Xe lamp	≥420 nm	tetracycline	0.0275 min^{-1}
carbon-doped Bi_2MoO_6 [13]	300W Xe lamp	≥420 nm	tetracycline	0.0399 min^{-1}
(Mo,C)-TiO_2/FTO [14]	500W Xe lamp	≥420 nm	tetracycline	0.0221 min^{-1}
Poly (triazine imide) hollow tube (PTI)/ZnO heterojunction [15]	300W Xe lamp	≥420 nm	tetracycline	0.034 min^{-1}
CNT/$LaVO_4$ [16]	300W Xe lamp	≥420 nm	tetracycline	0.0098 min^{-1}
Bi_2S_3 @Bi_2WO_6 /WO_3 [17]	400W Xe lamp	≥420 nm	tetracycline	0.0168 min^{-1}

Bi-CNNS [18]	300W Xe lamp	≥420 nm	tetracycline	0.09458 min^{-1}
PoPD/AgCl-35/CN [19]	250W Xe lamp	≥420 nm	tetracycline	0.0375 min^{-1}
MCU-C_3N_4 [20]	300W Xe lamp	≥420 nm	tetracycline	0.022 min^{-1}
WO_3/$Bi1_2O_{17}Cl_2$ [21]	300W Xe lamp	≥420 nm	tetracycline	0.0046 min^{-1}
QDs/BiOCl/BiOBr [22]	250W Xe lamp	≥400 nm	tetracycline	0.0133 min^{-1}
Bi_2MoO_6/$NiTiO_3$ [23]	300W Xe lamp	≥400 nm	tetracycline	0.0243 min^{-1}
$BiVO_4$/N-CQDs/Ag_3PO_4 [24]	300W Xe lamp	≥420 nm	tetracycline	0.07097 min^{-1}
$Bi_2Zr_2O_7$ [25]	Xe lamp	Simulated sunlight	tetracycline	0.00868 min^{-1}
Eu-CN@$BiVO_4$ [26]	300W Xe lamp	≥420 nm	tetracycline	0.06528 min^{-1}
Ag^0(NP)/TiO_2 [27]	UV-A lamp	= 360 nm	tetracycline	0.0112 min^{-1}
C-doped TiO_2 [28]	25W flexible white visLED light	= 450 nm	tetracycline	0.0099 min^{-1}
NiS and MoS_2 nanosheet comodified graphitic C_3N_4 [29]	Xe lamp	≥400 nm	tetracycline	0.0254 min^{-1}
AgBr/CuBi2O4 [30]	300W Xe lamp	≥420 nm	tetracycline	0.03511 min^{-1}
$FeNi_3$/SiO_2/CuS [31]	18W UV lamp	= 254 nm	tetracycline	0.0257 min^{-1}
α-Bi_2O_3/g-C_3N_4 [32]	300W Xe lamp	≥400 nm	tetracycline	0.01223 min^{-1}
β-Bi_2O_3@g-C_3N_4 [33]	250W Xe lamp	≥420 nm	tetracycline	0.0311min^{-1}
CdS/SnO_2 [34]	300W Xe lamp	≥420 nm	tetracycline	0.0143min^{-1}
CdS/Bi_3O_4Cl [34]	250W Xe lamp	≥420 nm	tetracycline	0.0643min^{-1}
BiOBr/CTF-3D [35]	500W Xe lamp	≥420 nm	tetracycline	0.04122 min^{-1}

RGO-ZnTe [36]	solar simulator	AM 1.5G	tetracycline	0.033 min^{-1}
potassium (K)-doped porous ultrathin g-C3N4 [37]	300W Xe lamp	≥300 nm	tetracycline	0.0282 min^{-1}
$In_2S_3/BiPO_4$ [38]	350W Xe lamp	≥400 nm	tetracycline	0.0145 min^{-1}
carbon dots/$NiCo_2O_4$ [39]	300W Xe lamp	≥420 nm	tetracycline	0.02134 min^{-1}
In_2O_3 [39]	250W Xe lamp	≥420 nm	tetracycline	0.0073 min^{-1}
Bi_2WO_6/Ag_2O/CQDs [40]	500W Xe lamp	≥400 nm	tetracycline	0.035 min^{-1}

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