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$_x$@Ag/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$_2$• 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
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 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$_2$SO$_4$ 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
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. ESR signals of DMPO-$\text{O}_2^\cdot$ and DMPO-HO$^\cdot$ 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (%)</th>
<th>Mass Fraction (%)</th>
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</thead>
<tbody>
<tr>
<td>Ag (L)</td>
<td>49.51</td>
<td>24.89</td>
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<tr>
<td>Cl (K)</td>
<td>50.09</td>
<td>0.27</td>
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<tr>
<td>Ti (K)</td>
<td>0.41</td>
<td>74.84</td>
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Table S2 Corresponding reaction rate constant (k) of TC and MO of various catalyst

<table>
<thead>
<tr>
<th>Material structure</th>
<th>Light source</th>
<th>Light condition</th>
<th>Organic pollutants</th>
<th>Degradation rate</th>
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<tbody>
<tr>
<td>TiOx@Ag/AgCl (This work)</td>
<td>300 W Xe lamp</td>
<td>AM 1.5G</td>
<td>tetracycline</td>
<td>0.49247 min⁻¹</td>
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<tr>
<td>N-doped BiOIO₃</td>
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<td>357 nm</td>
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<td>0.04025 min⁻¹</td>
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<tr>
<td>BiVO₄ (0 4 0)-Ag@CdS</td>
<td>300W Xe lamp</td>
<td>≥420 nm</td>
<td>tetracycline</td>
<td>0.0875 min⁻¹</td>
</tr>
<tr>
<td>Cu/Cl-g-C₃N₄</td>
<td>300W Xe lamp</td>
<td>≥400 nm</td>
<td>tetracycline</td>
<td>0.0271 min⁻¹</td>
</tr>
<tr>
<td>AgI/Bi₂WO₆</td>
<td>300W Xe lamp</td>
<td>≥420 nm</td>
<td>tetracycline</td>
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<tr>
<td>CoO/g-C₃N₄</td>
<td>300W Xe lamp</td>
<td>≥400 nm</td>
<td>tetracycline</td>
<td>0.0173 min⁻¹</td>
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<td>LDH-Ag₂O/Ag</td>
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<td>≥420 nm</td>
<td>tetracycline</td>
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<tr>
<td>α-Fe₂O₃@g-C₃N₄</td>
<td>100W LED lamp</td>
<td>420 nm</td>
<td>tetracycline</td>
<td>0.042 min⁻¹</td>
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<tr>
<td>Fe-doped surface-alkalinized g-</td>
<td>300W Xe lamp</td>
<td>≥420 nm</td>
<td>tetracycline</td>
<td>0.0164 min⁻¹</td>
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<td>C₃N₄/strontium ferrite/diatomite (N-TSD)</td>
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<td>tetracycline</td>
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<tr>
<td>Bi₂WO₆/CuBi₂O₄</td>
<td>300W Xe lamp</td>
<td>≥400 nm</td>
<td>tetracycline</td>
<td>0.0393 min⁻¹</td>
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<td>800W Xe lamp</td>
<td>≥420 nm</td>
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<td>(Mo,C)-TiO₂/FTO</td>
<td>500W Xe lamp</td>
<td>≥420 nm</td>
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<tr>
<td>Poly (triazine imide) hollow tube (PTI)/ZnO heterojunction</td>
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<td>≥420 nm</td>
<td>tetracycline</td>
<td>0.0168 min⁻¹</td>
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<tr>
<td>Material</td>
<td>Light Source</td>
<td>Wavelength (nm)</td>
<td>Incident Light</td>
<td>Time Constant (min⁻¹)</td>
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<td>--------------------------------</td>
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<td>Bi-CNNS</td>
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<td>MCU-C$_2$N$_4$</td>
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<td>≥420</td>
<td>tetracycline</td>
<td>0.022</td>
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<td>WO$_3$/Bi$_2$O$_3$/Cl$_2$</td>
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<td>300W Xe lamp</td>
<td>≥400</td>
<td>tetracycline</td>
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<td>BiVO$_4$/N-CQDs/Ag$_3$PO$_4$</td>
<td>300W Xe lamp</td>
<td>≥420</td>
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<td>Bi$_2$Zr$_2$O$_7$</td>
<td>Xe lamp</td>
<td>Simulated sunlight</td>
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<td>Eu-CN@BiVO$_4$</td>
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<td>tetracycline</td>
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<td>Ag$_0$(NP)/TiO$_2$</td>
<td>UV-A lamp</td>
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<tr>
<td>C-doped TiO$_2$</td>
<td>25W flexible white visLED light</td>
<td>= 450</td>
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<td>NiS and MoS$_2$ nanosheet comodified graphitic C$_3$N$_4$</td>
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<td>0.0254</td>
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<td>AgBr/CuBi$_2$O$_4$</td>
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<td>Material</td>
<td>Light Source</td>
<td>Wavelength</td>
<td>Tetracycline (min⁻¹)</td>
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<td>RGO-ZnTe</td>
<td>Solar simulator</td>
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<td>potassium (K)-doped porous ultrathin g-C3N4</td>
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<td>500W Xe lamp</td>
<td>≥400 nm</td>
<td>0.035</td>
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</table>

References


