Electronic Supplementary Information

High-Performance Natural-Sunlight-Driven Ag/AgCl Photocatalysts with a Cube-

Like Morphology and Blunt Edges via a Bola-Type Surfactant-Assisted Synthesis

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Fig. S1 The EDX elemental analysis of the samples fabricated *via* our bola-type surfactantassisted method, which is conducted under ambient conditions (A) and in a strictly darkened room (B). The EDX results of the samples (C) fabricated by a modified tadpole surfactant-assisted synthesis, wherein single-head single-tail cationic CTAC surfactant of chloride counteranions is employed as chlorine source and template.



Fig. S2 The TEM image (A) of our cube-like Ag/AgCl captured soon after the focusing, wherein the structures are destroyed rapidly by the electron beam of TEM. The HRTEM image (B) of the electron beam-destroyed samples.



Fig. S3 The UV-visible diffuse reflectance spectra of the samples fabricated *via* our bolatype surfactant-assisted method, which is conducted in a strictly darkened room. Inset: a photograph of the as-fabricated samples.



Fig. S4 The Cl 2p (A) and Ag 3d (B) XPS spectra, and the PXRD pattern (C) of the samples synthesized *via* our bola-type surfactant-assisted method, which is conducted in a strictly darkened room. It can be seen from these XPS results that negligible binding energy peaks attributing to the metallic Ag^0 species could be deconvoluted. Moreover, as indicated by the inset of panel C, different from the corresponding PXRD pattern of the samples fabricated under ambient conditions, wherein diffraction peak ascribing to the {111} facet of cubic phase metallic Ag^0 could be detected around 38.2° , (Fig. 2C of the main context), negligible $Ag\{111\}$ peaks could be observed in the present case.



Fig. S5 The typical SEM images of the cube-like Ag/AgCl structures with blunt edges fabricated *via* our bola-type HBTMC surfactant-assisted synthesis, wherein HBTMC solutions of 5 times diluted (4×10^{-4} M, panel A), and 5 (1×10^{-2} M, panel B) and 10 (2×10^{-2} M, panel C) times concentrated concentration were used.



Fig. S6 The low-magnification (A) and high-magnification (B) SEM images of the spherelike Ag/AgCl structures fabricated by a modified tadpole surfactant-assisted synthesis, wherein single-head single-tail cationic CTAC surfactant of chloride counteranions is employed as chlorine source and template.



Fig. S7 The Cl 2p (A) and Ag 3d (B) XPS spectra of the sphere-like Ag/AgCl structures fabricated by a modified tadpole surfactant-assisted synthesis, wherein single-head single-tail cationic CTAC surfactant of chloride counteranions is employed as chlorine source and template.



Fig. S8 The PXRD pattern (A) and UV-visible diffuse reflectance spectra (B) of the spherelike Ag/AgCl structures fabricated by a modified tadpole surfactant-assisted synthesis, wherein single-head single-tail cationic CTAC surfactant of chloride counteranions is employed as chlorine source and template. The diffraction peak ascribing to the {111} facet of cubic phase metallic Ag⁰ is shown in the inset of panel A, as marked with \blacktriangle . Inset in panel B: a photograph of thus-fabricated samples.



Fig. S9 The real-time absorption spectra of MO (A-D) and 4-CP (E-H) during the visiblelight-driven photodegradation process, wherein no catalysts (A, E), P25-TiO₂ (B, F), our sphere-like (C, G) and cube-like (D, H) Ag/AgCl structures are presented in the reaction systems.



Fig. S10 The real-time absorption spectra of MO during the visible-light-driven photodegradation process over our cube-like (A-C) and sphere-like (D-F) Ag/AgCl structures, wherein EDTA-2Na (A, D), TBA (B, E) and BQ (C, F) are presented in the reaction systems.



Fig. S11 The real-time absorption spectra of 4-CP during the visible-light-driven photodegradation process over our cube-like (A, B) and sphere-like (C, D) Ag/AgCl structures, wherein EDTA-2Na (A, C) and TBA (B, D) are presented in the reaction systems.



Fig. S12 The real-time absorption spectra of MO (A-C) and 4-CP (D-F) during the naturalsunlight-driven photodegradation process, wherein no catalysts (A, D), our sphere-like (B, E) and cube-like (C, F) Ag/AgCl structures are presented in the reaction systems.



Fig. S13 The projected density of states (PDOS) and the charge density of VBM and CBM of AgCl.



Fig. S14 The SEM images of our cube-like (A) and sphere-like (B) Ag/AgCl structures after the photocatalytic degradation of MO dye under visible-light irradiation.



Fig. S15 The PXRD pattern of our cube-like (A) and sphere-like (B) Ag/AgCl structures after the photocatalytic degradation of MO dye under visible-light irradiation.



Fig. S16 The XPS spectra of our cube-like (A, B) and sphere-like (C, D) Ag/AgCl structures after the photocatalytic degradation of MO dye under visible-light irradiation.



Fig. S17 The unit cell of the cubic phase AgCl. Gray and green balls represent Ag and Cl, respectively.