Supporting Information

Highly Durable AgO_x Clusters/Mesoporous TiO₂ Photocatalyst with Synergistic

Effects Induced Superior H₂ Evolution and CO₂ Reduction

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Experimental Details

Chemicals

Chemicals used in the material preparation were all reagent grade from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) including titanium butoxide (97%), acetonitrile, butan-1-ol, ammonia (28%), ethanol, sodium hydroxide, nitric acid (68%), silver nitrate, chloroplatinic acid, polyvinylidene fluoride (PVDF, 8 wt%), N-methyl-2-pyrrolidone (NMP, 99 %) and methanol. Degussa P25 TiO₂ nanoparticles from Evonik were used in the control experiments. Milli-Q water (resistivity of 18.2 m Ω .cm) was used throughout this work.

Materials synthesis

Amorphous titania spheres were prepared using the following approach.¹ In a typical process, 7.16 mL of titanium butoxide (TBO) was added dropwise to a solvent mixture of acetonitrile and butan-1-ol (volume ratio of 1:1, 200 mL) under moderate stirring until a clear solution was obtained. A second solution containing the same solvent mixture of 200 mL and distilled water (3.6 mL) and ammonia (2.7 mL) was quickly added to the TBO solution under moderate stirring. A white precipitate formed within a few seconds. After constant stirring for 2 h, the white precipitate was collected by centrifugation and washed with ethanol 3 times before being dried under vacuum. The product was calcined at 400 °C for 1h using a ramp rate of 2 °C/min to form titania spheres.

0.5 g of the titania spheres were dispersed in 30 mL of 5 M sodium hydroxide solution before being transferred into a Teflon-lined stainless-steel autoclave (50 mL in capacity) for hydrothermal treatment at 140 °C for 10 h. The products were washed with water and collected by centrifugation several times to remove residual sodium hydroxide. The obtained sodium titanate spheres were simply redispersed in 500 mL of 0.1 M nitric acid solution before being collected by centrifugation and washed with water 3 times to obtain hydrogen titanate. Dilute aqueous silver nitrate solutions (50 mL) of various concentration (to give a Ag/TiO₂ ratio of 0.5, 1.0, 2.0, 3.0 and 5.0 wt%) were used to simply redisperse the hydrogen titanate, before washing with water and ethanol several times then drying at room temperature. Calcination in a muffle furnace at 450 °C for 1 h in air using a ramp rate of 2 °C/min from room temperature (ca. 20 °C) produced the AgO_x cluster/TiO₂ composites (ACTs). The resulting samples were labelled ACT0.5, ACT1, ACT2, ACT3 and ACT5 corresponding to the amount of Ag/TiO₂ weight ratio used during the synthesis. The sample obtained without soaking in the silver nitrate solution gave TiO₂ mesoporous spheres. R-ACT2 corresponds to the retrieved ACT2 after 90 min HER. Composites based on other metals, MCT2 (M = Co, Fe and Ni), were prepared by soaking the hydrogen titanate in dilute metal nitrate solution of an M/TiO₂ weight ratio of 2.0.

Control samples were based on Degussa P25 TiO₂ nanoparticles and prepared by immersion in the same amount of silver nitrate as for the synthesis of ACTs. P25 TiO₂ nanoparticles (0.5 g) were dispersed in silver nitrate aqueous solutions of various concentrations under magnetic stirring. The suspension was slowly dried at 60 °C under moderate stirring. The resulted powder was calcined using the same process as the ACTs, to obtain $AgO_x/P25$ TiO₂. The samples were labelled as A0.5, A1, A2, A3 and A5, respectively. A Pt/TiO₂ control sample was prepared through the same process where chloroplatinic acid was used instead of silver nitrate with the same amount of metal loading in the ACT2 and A2 during syntheses.

Characterisation

A Spectra 300S/TEM, ThermoFisher spherical aberration corrected transmission electron microscope (STEM/TEM) was used to investigate the morphology and conduct elemental mapping of the samples. X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer (Ultima IV) using

Cu Ka irradiation under a 40 kV working voltage were used to determine the crystal phases of the obtained samples. Raman spectra were acquired on a HORIBA Lab-RAM HR-Evolution Raman spectrometer with laser excitation at 532 nm. The UV/Vis diffuse reflectance spectra (UV/Vis DRS) were obtained with a UV/Vis/NIR spectrophotometer (UH4150, Hitachi, Japan) in the wavelength range 300-800 nm. The photoluminescence spectra were recorded on a fluorescence spectrophotometer (F-280-Laser-NIR, Gangdong Science and Technology Development Co., LTD. Tianjin) with an excitation wavelength of 460 nm. X-ray photoemission spectra were collected using a Thermo Escalab 250xi analyzer. Ag 3d and Ti 2p binding energies were recorded using Al Ka (1486.6 eV) as the excitation source and a pass energy of 23.5 eV. The position of the XPS peaks of the corresponding element is referenced to the C1s peak of carbonaceous contamination.

Photocatalytic hydrogen generation

Photocatalytic hydrogen evolution reactions were carried out using a vacuum sealed reaction system. 10 mg of the powdered photocatalyst was ultrasonically dispersed in a 50 mL methanol aqueous solution (volume ratio of 1:10) in a reactor of 350 mL with a surrounding water jacket to eliminate the thermal effect from illumination. The reaction temperature was controlled at 20 ± 1 °C by a cooling water system. The top quartz window of the reactor was illuminated with a 300 W Xe lamp (Perfect Light, PLS-SXE300D). Gas evolution was determined by an online gas chromatograph (GC-7860, Ar carrier gas).

Apparent quantum efficiency (AQE) measurement

Measurement of AQE followed the same procedure as the photocatalytic HER test under monochromatic light obtained by using bandpass filters with different wavelengths (350, 365, 475, 500 and 520 nm). The light intensity of monochromatic light was measured by a photometer (Perfectlight, PL-MW2000). The AQE can be obtained by the following equation:

$$AQE = \frac{2 \times N_A \times n_{H_2}}{N_{incident}} \times 100\%$$

where N_A and $n(H_2)$ represents the Avogadro constant (6.022 × 10²³ mol⁻¹) and amount of produced H₂ molecules, respectively. N_{incident} is the number of incident protons, which can be calculation from:

$$N_{incident} = \frac{Pt}{hv} = \frac{ISt\lambda}{hc}$$

where *P* is the light power (W), *t* is the reaction time (s), *h* is the Planck constant (6.626 × 10⁻³⁴ J s), *v* is the frequency of light (Hz), *I* is the light intensity (W cm⁻²), *S* is the illuminated area (cm⁻²), λ is the wavelength of monochromatic light (m), and *c* is the speed of light in vacuum (3 × 10⁸ m s⁻¹).

Photoelectrochemical measurement

Photoelectrochemical tests were measured using a (CHI 760E Electrochemical Workstation) with a three-electrode system. A platinum plate $(1 \times 1 \text{ cm}^2)$, a saturated Ag/AgCl electrode and films of the sample on a fluorine doped tin oxide (FTO) coated glass plate $(1 \times 1 \text{ cm}^2)$ were used as the counter, reference and working electrode, respectively.

The working electrode was prepared as follows. A mixture of 300 mg of the synthesised sample, 2.7 g PVDF and 1 mL NMP was moderately stirred overnight. Thin films on FTO glass were prepared by blade coating the slurry mixture before drying and calcining at 400 °C for 1 h.

Computational details

The first-principle calculations were performed within the density functional theory (DFT) planewave pseudopotential method, as implemented in the Vienna Ab-initio Simulation Package (VASP code).^{2, 3} The exchange-correlation energy and the core electrons were considered using the generalized gradient approximation (GGA) by the Perdew-Burke-Ernzerhof (PBE) functional and the projector augmented wave (PAW) pseudopotentials, ^{4, 5} respectively. A plane-wave cutoff energy of 450 eV was used. A 3×3×1 Monkhorst-Pack special k-point grid is used for Brillouin zone. Convergence criteria employed for both the electronic self-consistent relaxation and ionic relaxation are set to be 10⁻⁴ and 0.05 eV/Å for energy and force, respectively. The vdW interaction is treated using the DFT-D3 method proposed by Grimme.

A cluster model with 13 metal atoms was used. A relative comparison among the M/TiO_2 (M = Ni, Co and Fe) composites enabled identification of trends and suggested explanations for the observed findings. To properly accommodate the metal cluster, a relatively large supercell of anatase (101) surface was used, that is a (2×3) four-Ti-layer slab (48 Ti and 96 O atoms) with a vacuum thickness of 16 Å. The experimental bulk lattice parameters (a=3.786 Å, c=9.514 Å) of TiO₂ were used for the (101) surface calculations throughout the present work.⁶ To produce electronic structure properties more accurately, the DFT+U method was used, where the onsite Coulomb correction was set on Ti 3d orbitals with an effective U value of 4.2 eV as suggested in literature works.^{7,8} The extra photoelectron in systems was simulated by adding an excess electron into the supercell as common practice. The localization of an electron on a particular Ti site of TiO2 can be initially configured and followed by DFT+U electronic structure optimization. Site-projected magnetic moments are calculated to ensure the localization of the electron, while the spin density is visualized by the isodensity surface. To determine the structures of M/TiO₂ composites, AIMD simulation was performed to search for the optimal structures of metal clusters on the TiO₂ slab. The simulation was performed in the canonical (NVT) ensemble employing Nosé-Hoover thermostats. The temperature was set at 450 K with the time step 2 fs. More than 8 ps AIMD simulation was performed, and all the simulations reach the equilibrium plateau after ~4 ps. The final structural configuration is then fully optimized until all forces

diminish.

The proton-promoted electron-transfer (PPET) energy is defined by the energy change of moving an excess electron from TiO₂ bulk to supported metal particles with the adsorption of proton. The adsorption energy of the hydrogen atom (E_{ad}) is defined as the energy difference after and before the adsorption with respect to the gas phase H₂ molecule according to $E_{ad}=E_{total}-E_{surface}-1/2E_{H2}$, where $E_{surface}$, E_{H2} and E_{total} are the energies for the clean surface, H₂ molecule in the gas phase, and hydrogen atom adsorbed on the surface, respectively. The hydrogen absorption free energy, ΔG_{H} , is obtained by adopting the entropy correction proposed by Norskov *et al.* according to $\Delta G_{H}=E_{ad}+0.24$ eV.⁹



Figure S1. (a) Elemental mapping image with corresponding Ti, O and Ag mapping images and a line scan element analysis; and (b) nitrogen sorption isotherm and pore size distribution of ACT2. (c) High resolution elemental mapping of Ti, Ag and O, and a corresponding line scan of an AgO_x cluster.



Figure S2. (a) XRD and (b) Raman spectra of ACTs and TiO₂ mesoporous spheres.

The strong E_g mode at ~144 cm⁻¹ demonstrates the well-crystalline anatase TiO₂ after annealing at 450 °C. The small peak at ~198 cm⁻¹ might be ascribed to some titanate remaining in the samples.^{10, 11}

Sample	Surface hydroxyl group (%)	Surface Ag (at%) by XPS	Ag (wt%) by ICP- MS
Mesoporous TiO ₂ spheres	19.8	-	
ACT0.5	14.1	0.20	0.19
ACT1	12.7	0.27	0.36
ACT2	12.3	0.52	0.82
ACT3	12.2	0.78	1.26
ACT5	11.4	1.30	2.13

Table S1. Surface hydroxyl groups and Ag loadings estimated by XPS, and Ag loading determined by ICP-MS for the mesoporous TiO_2 spheres and ACTs.



Figure S3. (a) Overall XPS spectrum and high-resolution XPS spectra of (b) Ti 2p, (c) Ag 3d and (d) O1s of ACT0.5.



Figure S4. (a) Overall XPS spectrum and high-resolution XPS spectra of (b) Ti 2p, (c) Ag 3d and (d) O1s of ACT1.



Figure S5. (a) Overall XPS spectrum and high-resolution XPS spectra of (b) Ti 2p, (c) Ag 3d and (d) O1s of ACT2.



Figure S6. (a) Overall XPS spectrum and high-resolution XPS spectra of (b) Ti 2p, (c) Ag 3d and (d) O1s of ACT3.



Figure S7. (a) Overall XPS spectrum and high-resolution XPS spectra of (b) Ti 2p, (c) Ag 3d and (d) O1s of ACT5.



Figure S8. The H_2 evolution of ACTs. All experiments were carried out after pre-illumination for 90 min.

Photocatalyst	Scavenger	Light	HER (mmol·g ⁻¹ ·h ⁻¹)	Reference	
ACT2	10 vol%300 W Xemethanol(full spectrur		22.8	This work	
		300 W Xe (> 420 nm)	0.38		
Ag-rGO-TiO ₂	20 vol% methanol	300 W Xe (420-780 nm)	5.3×10 ⁻⁴	12	
Ag/TiO ₂ with SCN-	10vol% methanol	300 W Xe (> 320 nm)	0.04	13	
Ag/TiO ₂	10 vol% lactic acid	23 mW cm ⁻² (365 nm)	0.6	14	
Ag/TiO ₂	5 vol% glycorel	300 W Xe (full spectrum)	1.5	15	
Ag/a-TiO ₂	20 vol% methanol	300 W Xe (full spectrum)	25.5	16	
Ag@C@TiO ₂	20 vol% methanol	500 W Xe (> 420 nm)	0.07	17	

Table S2. Hydrogen evolution rates for Ag-based TiO_2 composites from the literature.

Photocatalyst	Concentration (mg/mL)	Scavenger	Light	HER (mmol·g ⁻¹ ·h ⁻¹)	Reference
ACT2	0.2	10 vol% methanol	300 W Xe	22.8	This work
Ag/TiO ₂	2	5 vol% glycorel	300 W Xe	1.5	15
Ag/a-TiO ₂	0.5	20 vol% methanol	300 W Xe	12.7	16
Cu/TiO ₂	0.06	25 vol% methanol	300 W Xe	16.6	18
Co-TiO ₂	0.1	10 vol% methanol	300 W Xe	21.5	19
TiO ₂ /Au@NiS ₁₊ x	0.6	25 vol% methanol	300 W Xe	9.6	20
Pt ₁ /SnO ₂ /UiO- 66-NH ₂	1	10 vol% triethanolamine	300 W Xe	2.2	21
Pt ₁ /TiO ₂	0.2	10 vol% triethanolamine	300 W Xe	17.2	22
Cu-Cu ₂ O/TiO ₂	0.1	5 vol% glycerol	100 W Xe	15.1	23
Ni SA/TiO ₂ ª	0.5	20 vol% methanol	280 W Xe	2.9	24

Table S3. Hydrogen evolution rates for relevant composites with corresponding test conditions from the literature.

^aSA, single atom.



Figure S9. The HER efficiency of the P25 based control samples (A0.5-A5) with the same Ag loading as the ACTs.



Figure S10. Two HR-TEM images of ACT5.

Photocatalyst	Concentration (mg/mL)	Reaction medium	Light	Products	Efficiency (µmol·g ⁻¹ ·h ⁻¹)	Ref.
ACT2	0.2	H ₂ O/triethano lamine	300 W Xe (full spectrum)	CO CH ₄	72.1 32.6	This work
Ag_2Pd_1/TiO_2	0.2	H ₂ O/ triethanolami ne	300 W Xe (full spectrum)	CH ₄	79.0	23
Ag@TiO ₂ core-shell	1	H ₂ O vapor	300 W Xe (full spectrum)	CH_4	10.9	24
Ag/TiO ₂	5	H ₂ O vapor	47.23 W m ⁻² (365 nm)	CO CH ₄	0.7 5.8	25
Ag-TiO ₂	0.5	H ₂ O	300 W Xe (<400 nm)	CO CH ₄	23.9 14.5	26
CODH/AgNCs -PMAA/TiO ₂ ª	0.5	H ₂ O/ triethanolami ne	300 W Xe (>420 nm)	СО	36.2	27
Ag/TiO ₂	1	H ₂ O/NaHCO ₃	100 W Me (full spectrum)	СО	5.2	28
Cu/CN	5	H ₂ O	300 W Xe (full spectrum)	СО	11.2	18
Cu/CeO _{2-x}	5	H ₂ O	300 W Xe (full spectrum)	СО	1.7	29
Cu/TiO ₂	2	H ₂ O	300 W Xe (full spectrum)	СО	5.6	30
Au/TiO ₂	2	H ₂ O	300 W Xe (full spectrum)	СО	56.8	30
Nanorattle Au@PtAg-ZIF-8	3	H ₂ O	300 W Xe (full spectrum)	СО	14.5	31
Pt SA/ZrO ₂	0.33	H ₂ O	300 W Xe (full spectrum)	CO CH ₄	14.0	34
Zn-Al LDH nanosheet ^b	2	H ₂ O	300 W Xe (full spectrum)	СО	8	35

Table S4. Photocatalytic CO_2 reduction on Ag-based TiO_2 composites with corresponding test conditions from the literature.

^aCODH, carbon monoxide dehydrogenase; PMMA, polymethacrylic acid.

^bLDH, layered double hydroxide



Figure S11. (a) UV-vis absorption spectra and (b) corresponding Tauc plots of mesoporous TiO_2 spheres and ACTs, (c) UV-vis absorption spectra of R-ACTs.



Figure S12. The HER efficiency of ACT2 under different wavelength light.



Figure S13. The HER efficiency of ACTs under visible light (> 420 nm) irradiation.



Figure S14. The (a) Mott-Schottky plots and (b) photoluminescence spectra of mesoporous TiO_2 and ACTs (excitation wavelength 365 nm).



Figure S15. The Gibbs adsorption energies of H atom on the typical sites of M_{13}/TiO_2 systems.



Figure S16. The Gibbs adsorption energies of a H atom on the $TiO_2(101)$ surface and $Ag_2O(111)$ surface.



Figure S17. The Gibbs adsorption energies of H atom on the different sites of the Ag_{13}/Ag_2O system.



Figure S18. Spin density plots (at the iso-value of $0.02 |e|/Bohr^3$) evidencing the electron transfer in a Ni₁₃/TiO₂ composite with the adsorption of a proton. Energy of 0.03 eV is needed for an excess electron to move from a Ti³⁺ site in the TiO₂ bulk to the Ni₁₃ cluster.



Figure S19. Spin density plots (at the iso-value of $0.02|e|/Bohr^3$) for Fe₁₃/TiO₂ and Co₁₃/TiO₂. Upon the adsorption of Fe₁₃ and Co₁₃ clusters, electrons will transfer from the metals to TiO₂ and cause the reduction of Ti⁴⁺ to Ti³⁺ at the interface, indicating that the reverse process (electron transfer from TiO₂ to the metal) is difficult.



Figure S20. The Gibbs adsorption energies of H atom on the different sites of the Ag_5/Ag_2O and Ag_{19}/Ag_2O systems.

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