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Supporting Information

Efficient plasmonic photocatalytic activity on silver-nanoparticle-decorated $AgVO_3$ nanoribbons

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1 Experimental method

1.1 Preparation of $AgVO_3$ nanoribbons

The $AgVO_3$ nanoribbon was synthesized using a hydrothermal process. Specifically, $AgNO_3$ (1.25 mmol) and NH_4VO_3 (1.25 mmol) were mixed in 60 mL of deionized water and subjected to ultrasonication for 30 min. The mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 180°C for 24 h. The mixture was allowed to cool down to room temperature, filtrated using filter paper. The solid fractions were washed with deionized water (100 mL) four times and absolute ethanol (50 mL) four times, then dried under vacuum at 80 °C. Thus, the chemical reaction involved in the hydrothermal synthesis can be briefly described by equation: $Ag^+ + VO_3^- = AgVO_3$.

1.2 Preparation of $Ag/AgVO_3$ nanoribbons

The $Ag/AgVO_3$ plasmonic photocatalyst was synthesized via an in-situ reduction of $AgVO_3$ by $NaBH_4$ solution at room temperature. The as-prepared $AgVO_3$ (0.05 g) was dispersed in 25 mL aqueous solution, Then 25 mL $NaBH_4$ solution (0.05 mmol/L) was added dropwise under vigorous stirring. The dispersion became deep red after reacting for 10 min, indicating the formation of Ag nanoparticles on the surfaces of $AgVO_3$. Finally, the obtained product was recovered by centrifugation.

2 Characterization and calculation

X-ray diffraction (XRD) was performed at room temperature using an X'Pert-ProMPD (Holand) D/max-γA X-ray diffractometer. X-ray photo-electron spectroscopy (XPS) was used to identify surface chemical composition and chemical states of the catalysts on a PHI5000 Versa Probe electron spectrometer (ULVAC-PHI, Japan). The field emission scanning electron microscopy (FESEM) images were taken on a FEI-quanta 200F scanning electron microscope with an acceleration voltage of 20 kV. Transmission electron micrographs (TEMs) were taken on a FEI-Tecnai F20 (200 kV) transmission electron microscope (FEI). Fluorescence emission spectra were recorded on a FluoroMax 4 type fluorescence spectrophotometer with an excitation wavelength at 350 nm. The photocurrent experiments were measured using an electrochemical station (CHI660D, Shanghai Chenhua Limited, China) in a conventional three-electrode configuration. The electrolyte was 0.01 M Na_2SO_4 aqueous solution. The light source was a high pressure xenon short arc lamp (CHF-XM35-150W, Beijing Changtuo Co.). UV-vis absorption spectra were performed using a Lambda 750 (PerkinElmer) spectrophotometer at a wavelength range of 200-800 nm.

The density functional calculations were performed using the plane-wave pseudopotential method, as implemented in the CASTEP code. Three-dimensional periodic boundary conditions were used to approximate an infinite solid. The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerh (PBE) functional form was applied, along with ultrasoft pseudopotentials. Three dimensional finite difference time domain (FDTD) simulations were performed to theoretically model near field distribution of the $Ag/AgVO_3$. In the simulations, we assumed that the Ag nanoparticles were uniformly distributed in the x-y plane of the cross section of $AgVO_3$ nanoribbon and embedded in a background medium of water. Illumination of the $Ag/AgVO_3$ was simulated with a linearly polarized plane wave, propagating in the +Y direction.

The band edge positions of both the conduction band and the valence band can be determined using a simple approach [1]. The conduction band edge (E^0_{CB}) of a semiconductor at the point of zero charge (pH_{ZPC}) can be predicted using the following equation: $E^0_{CB} = X-E^e-0.5E_g$. Where X is the absolute electronegativity of the semiconductor, E^e is the energy of free electrons on the hydrogen scale (4.5 eV), and E_g is the band gap of the semiconductor. The DFT calculation results show the band gap energy of $Ag/AgVO_3$ was ~1.5 eV. The X value for $AgVO_3$ was 5.86 eV. Consequently, the E_{CB} value of $AgVO_3$ was calculated to be 0.61 eV, and the E_{VB} value was estimated to be 2.11 eV.

3 Photoreaction procedures

The photocatalytic activities of as-synthesized photocatalysts were evaluated by decomposing CV under visible light irradiation in a photoreaction apparatus. Visible light was generated by using 500 W Xe lamp irradiation with a 420 nm cut-off filter to remove light of $\lambda < 420$ nm. For photodegradation of the dyes, 0.05 g of photocatalyst was put into 50 mL (10 mg/L) CV solutions. Prior to irradiation, the suspensions were magnetically stirred for 1 h to reach adsorption–desorption equilibrium in the dark. At given time intervals of visible light irradiation, about 3 mL aliquots were collected from the reaction suspension, centrifuged at 8,000 rpm for 10 min and filtered through a 0.22 μm Millipore filter to remove the particles. The filtrate was subsequently analyzed by UV–vis spectroscopy at its maximum absorption wavelength. To ensure the reproducibility of the results, duplicate runs were performed for each condition for averaging the results. The reference experiments including the photolysis of CV without photocatalyst and the dark adsorption of CV by the samples were also carried out. The results showed that there was no obvious photocatalytic degradation of CV in the absence of photocatalyst. The dark adsorption experiment showed that the adsorption amount on the surface of photocatalyst was low, and there was a little effect on the degradation efficiency. However, we calculated the degradation efficiency of the sample with considering the effect of adsorption.

The detection of the reactive species is similar to the process used for the photodegradation experiment. Various scavengers were introduced into the CV solution before the addition of the photocatalyst. The dosages of these scavengers are referred to previous studies [2, 3]. Benzoquinone (BQ), ammonium oxalate (AO) and isopropanol (IPA) are the scavengers of $\bullet O_2^-$, h^+ and $\bullet OH$, respectively.

References

1 H. Xu, H. Li, C. Wu, J. Chu, Y. Yan, H. Shu, Z. Gu, *J. Hazard. Mater.*, 2008, **153,** 877.

2 G. T. Li, K. H. Wong, X. W. Zhang, C. Hu, J. C. Yu, R. C.Y. Chan, P. K. Wong, *Chemosphere*, 2009, **76,** 1185.

3 N. Zhang, S. Q. Liu, X. Z. Fu, Y. J. Xu, *J. Phys. Chem. C*, 2011, **115**, 9136.

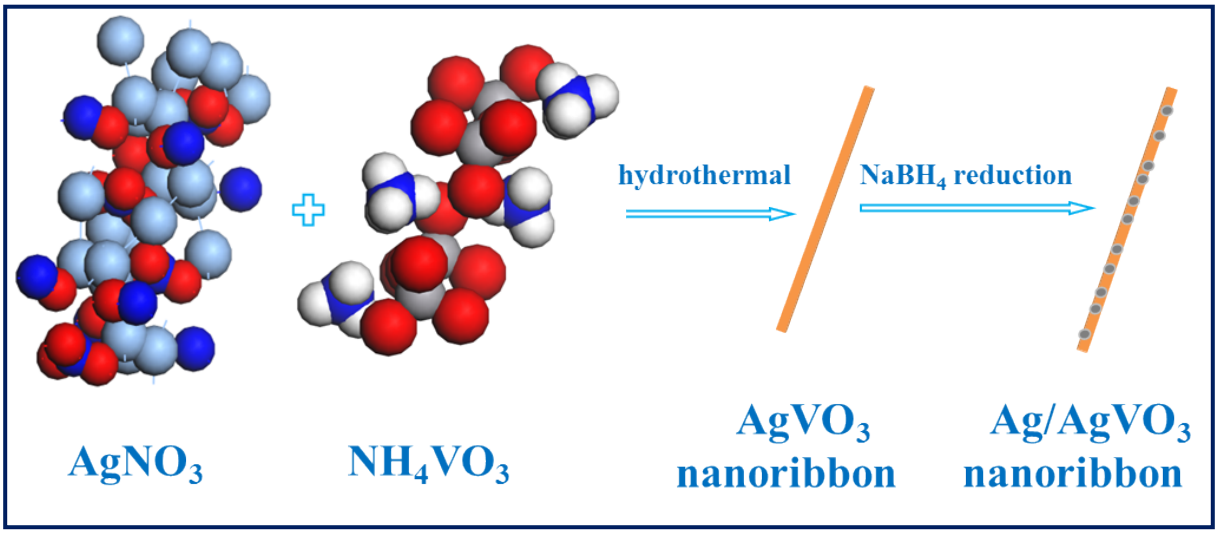

Fig. S1 Schematic illustration of the synthesis of Ag/$AgVO_3$ nanoribbons.

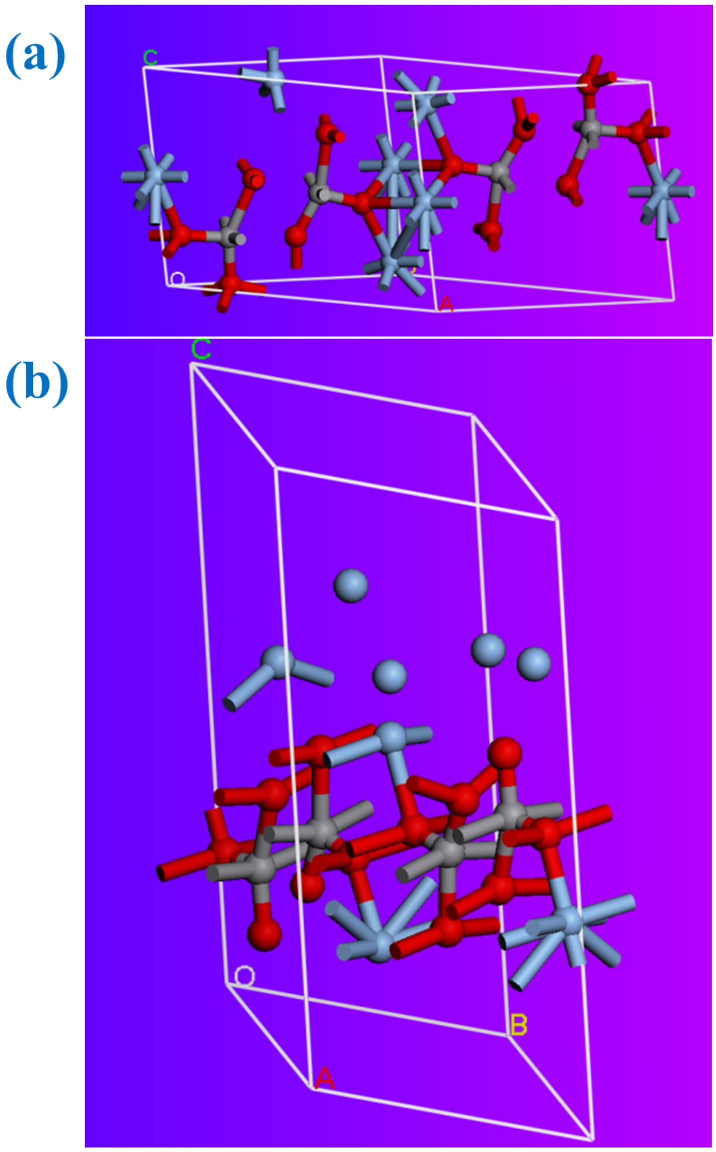

Fig. S2 (a) Crystal structures of $AgVO_3$ and (b) $Ag/AgVO_3$,

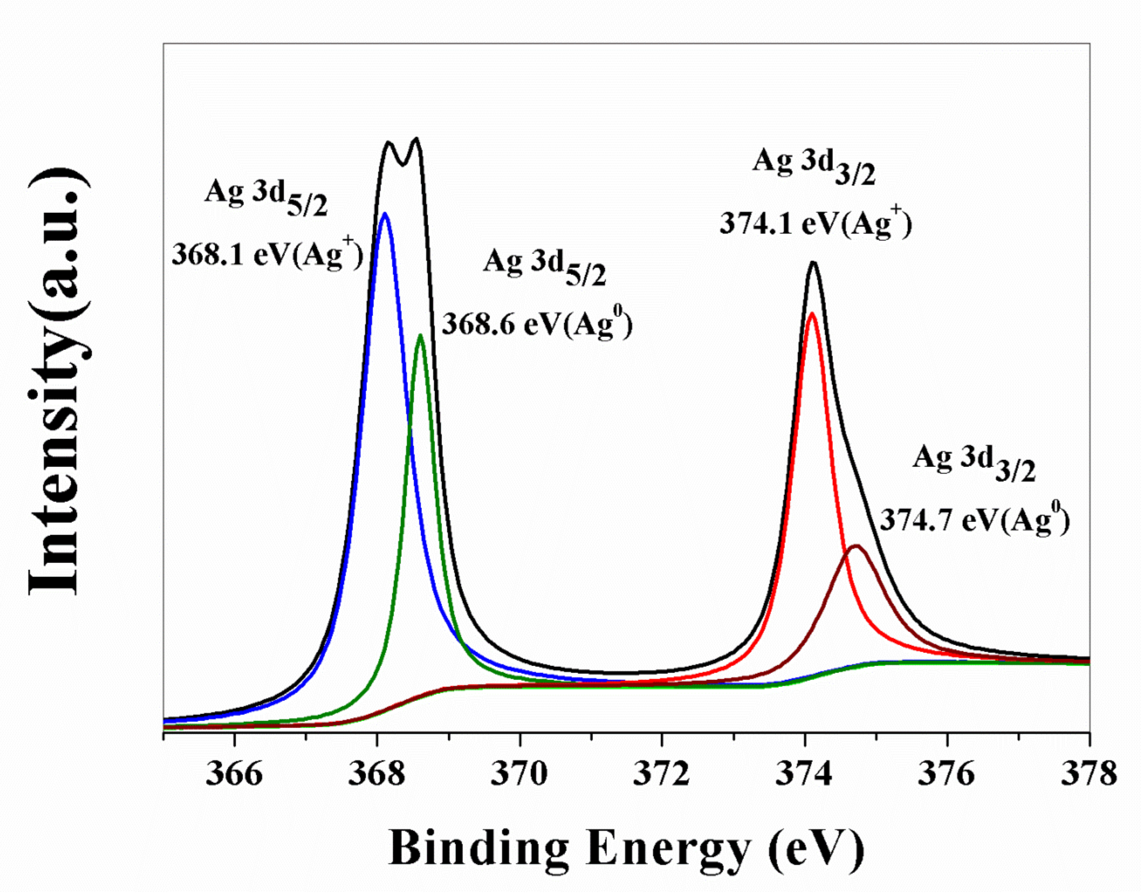

Fig. S3 The high resolution scanning XPS spectra of Ag/AgVO$_3$.

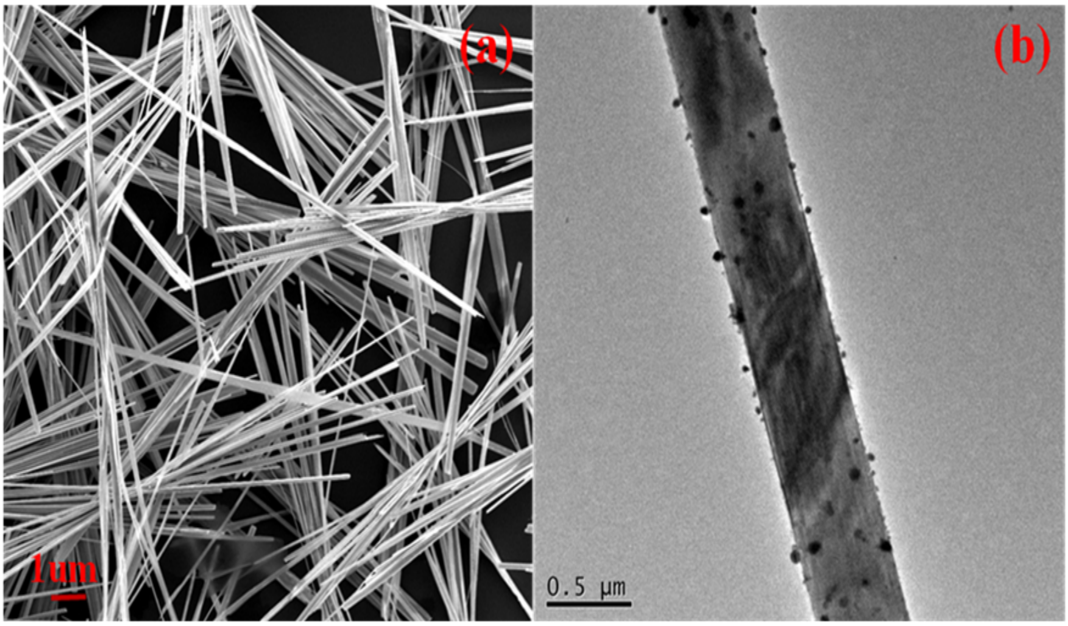

Fig. S4 (a) FESEM image of AgVO$_3$. (b) TEM image of Ag/AgVO$_3$.

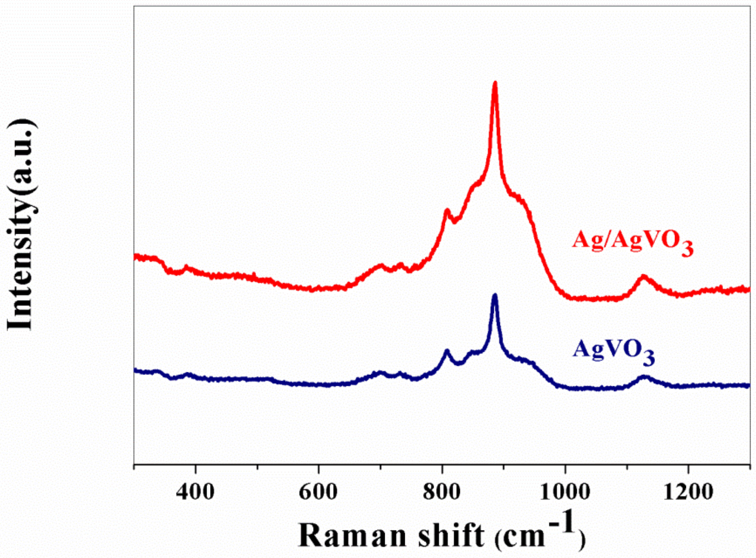

Fig. S5 Raman spectra of the samples.