

Supporting information

A Dispersive Scattering Centers-based Strategy for Dramatically Enhancing the Photocatalytic Efficiency of Photocatalysts in Liquid-Phase Photochemical Processes: A Case of Ag nanosheets

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1. Experimental Section

Chemicals: poly(vinyl pyrrolidone) (PVP, $M_w \approx 30000$ g/mol), cetyltrimethyl ammonium bromide (CTAB, 99%), silver nitrate (AgNO_3 , 90%), chloroauric acid (HAuCl_4 , 99%), ascorbic acid (AA, 99%), methanol (CH_3OH , 99.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%), toluene (C_7H_8 , 99.5%), n-pentanol ($\text{C}_5\text{H}_{11}\text{OH}$, 99.5%), cyclohexane (C_6H_{12} , 99%) and methylene orange (MO, analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ferrocene ($(\text{C}_5\text{H}_5)_2\text{Fe}$, 98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.95%) were purchased from Alfar Aesar. Degussa P25 was purchased from Shanghai Haiyi Co. All reagents were used as received without further purification.

Syntheses and characterization of Ag nanoparticles. In our study, three kinds of Ag nanoparticles (*i.e.* Ag NSs, Ag MSs, and Ag NPs) were chosen as scattering centers for comparison. Ag NSs, which possess a triangle outline with the side length of 200 ± 50 nm and the thickness of 15 ± 10 nm, were prepared according to the conventional method reported by Xia's group.¹ In a typical synthesis, PVP (0.546 g) was dissolved in 8.0 mL of water in a 20 mL vial and heated to 60 °C in air under magnetic stirring. After the above aqueous solution had been heated to 60 °C, an aqueous AgNO_3 solution (3.0 mL, 188 mM) was rapidly added into the vial and the reaction mixture was heated at 60 °C in air for 21 h.

Ag MSs, which are irregular sheets with 1 μm in size and 30 nm in thickness, were synthesized via a simple liquid-liquid assisted wet chemical route reported in our previous study.² In a typical synthesis, an aqueous PVP solution (1 mL, 4 mM) and ethanol (5mL) was sequentially added into a 25 mL beaker

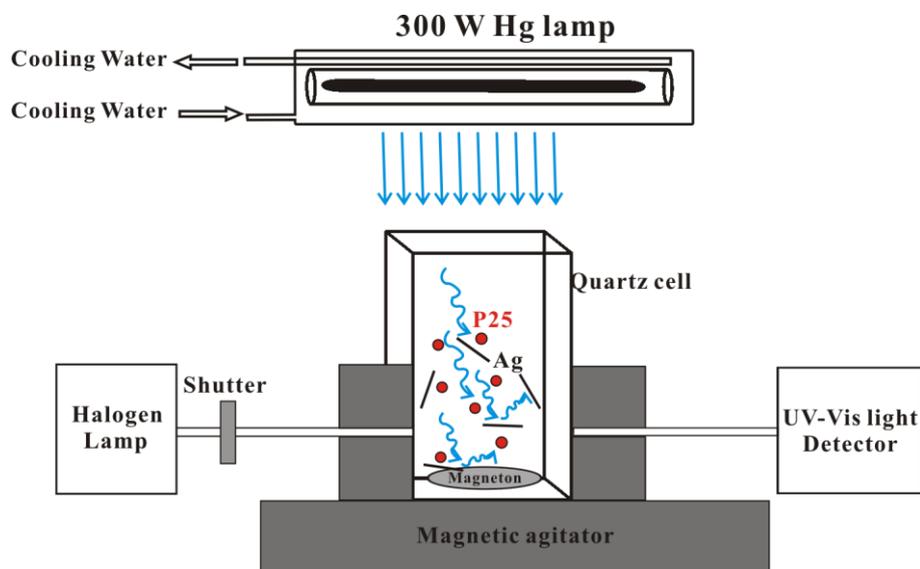
containing an aqueous AgNO_3 solution (5 mL, 6 mM) under magnetically stirring to form a homogeneous phase. Then 12 mg of ferrocene was dissolved into a toluene and n-pentanol mixed solvent (2 mL, v/v of 1:1), and then added into the beaker as the organic phase. After the reaction for 30 min under stirring, some gray powders were precipitated in the aqueous phase.

Ag NPs, which are irregular particles of 100 nm in size, were synthesized by a simple chemical reduction method using PVP as capping reagent and AA as reducing reagent. In a typical synthesis, PVP (0.3 g) was dissolved in a 100 mL beaker containing an aqueous AgNO_3 solution (10 mL, 5 mM) at room temperature under magnetic stirring for 15 min. Then an aqueous AA solution (10 mL, 10 mM) was sequentially added into the above mixture solution and keep magnetic stirring for 60 min.

Syntheses Au nanoparticles. Like synthesizing Ag NPs, CTAB (0.1 g) was dissolved in a 100 mL beaker containing an aqueous HAuCl_4 solution (10 mL, 5 mM) at room temperature under magnetic stirring for 15 min. Then an aqueous AA solution (10 mL, 100 mM) was sequentially added into the above mixture solution and keep magnetic stirring for 30 min.

It should be indicated that PVP was used as protection reagent in all synthetic processes. To remove excess PVP, all of samples were washed with water and ethanol several times before the characterization and photocatalytic experiments.

The morphology of all products were monitored by scanning electron microscopy (SEM, Hitachi S4800) with an accelerating voltage of 15 kV, and transmission electron microscopy (TEM, JEM-2100) with an acceleration voltage of 200 kV.



Scheme S1. Schematic diagram of the system used to evaluate the scattering abilities of Ag nanoparticles.

Evaluation of light-scattering ability of Ag nanoparticles. The light-scattering measurement system is composed of a high-pressure Hg lamp (cooled by water) for illuminating, a quartz cell (1 cm × 1 cm × 4.5 cm), a magnetic stirrer for stirring, and a fiber optical spectrometer (USB2000 spectrometer, ocean optic

company) equipped with high-performance 2048-element linear CCD-array detector, as shown in Scheme S1. The Hg lamp is set on the top of the quartz cell with a distance of 10 cm, and the output powder is 300 W. The USB2000 optic fiber spectrometer is used for on-line detection of the adsorption/scattering behavior of light in the solution. It should be in particular pointed out that there is a shutter between the light source (halogen lamp) of the spectrometer and the quartz cell. This shutter must be closed to eliminate the influence of halogen lamp on scattering of the Hg lamp light when evaluating light scattering abilities of Ag nanoparticles.

For the evaluation of light scattering ability of Ag nanoparticles, a suspension (3 mL, 0.02 g/L) containing Ag nanoparticles (*i.e.*, Ag NSs, Ag MSs, or Ag NPs) was added in the quartz cell by a micro-injector under continuous stirring. Under the irradiation of the Hg lamp, the detector of the spectrometer recorded the signals of the light scattered by Ag nanoparticles suspended in the solution, the intensity of which reflected the scattering ability of Ag nanoparticles. In this experiment, the shutter between the light source of the spectrometer and the quartz cell should be closed. For comparison, a blank experiment without adding any Ag nanoparticles was further carried out.

Photocatalytic production of H₂ by splitting water. The photocatalytic H₂ production experiments were carried out in a homemade top-irradiation vessel connected to a stainless steel closed gas circulation system. Typically, the commercially photocatalysts Degussa P25 (50 mg) were well dispersed in a mixed solution of deionized water (80 mL) and methanol (20 mL) under magnetically stirring. After that, 2 mg Ag nanoparticles was dispersed in the above solution under magnetically stirring to form Ag suspension (0.02 g/L). The reaction temperature was maintained at room-temperature by a cooling water circulation. A 300 W Xe lamp (PLS-SXE-300UV, Beijing Trusttech Co. Ltd) with the wavelength of 220~770 nm was employed as light source. Before irradiation, the system was pumped to remove the air, and then Ar gas (99.999%) was inlet as carrier gas until the system reached the atmospheric pressure. The amount of the H₂ evolved was determined by using a gas chromatography (GC 2060) with a thermal conductivity detector. For the Pt-modified TiO₂ samples, Pt nanoparticles (1 wt%) were deposited as co-catalyst on P25 by photoreduction before the H₂ evolution measurement. Typically, an H₂PtCl₆ aqueous solution (1.282 mL, 1 mM) was impregnated into 100 mL of methanol/water solution containing 50 mg P25, and irradiated under a 300 W Xe lamp for 1 h at room temperature.

Photocatalytic degradation of MO. Typically, P25 (10 mg) was dispersed in a 40 mL of aqueous solution containing methyl orange (MO) aqueous solution (4×10^{-5} M) and Ag nanoparticle suspension (0.02 g/L) under ultrasonic to form a suspension, and the suspension was magnetically stirred for 30 min in the dark. After irradiated under 300 W Xe lamp, a 4 mL of dispersion was sampled every definite min and centrifuged to remove the photocatalyst. The photodegradation efficiency was monitored by measuring the absorbance of the centrifuged solutions at the maximum absorption wavelength of MO (465 nm) with UV-vis spectroscopy (SHIMADZU, UV-2550) at room temperature. To test the reuse of the catalyst and

the Ag nanosheet, the powder samples were collected by centrifugation after the first photocatalytic degradation measurement, and then re-dispersed into the fresh MO aqueous solution for the following measurement. To investigate the influence of Ag nanoparticles on the photocatalytic degradation ability of TiO₂, a contrast test without any Ag nanoparticles added in the solution was further carried out. All the tests were carried out at room temperature.

2. Supplementary Results

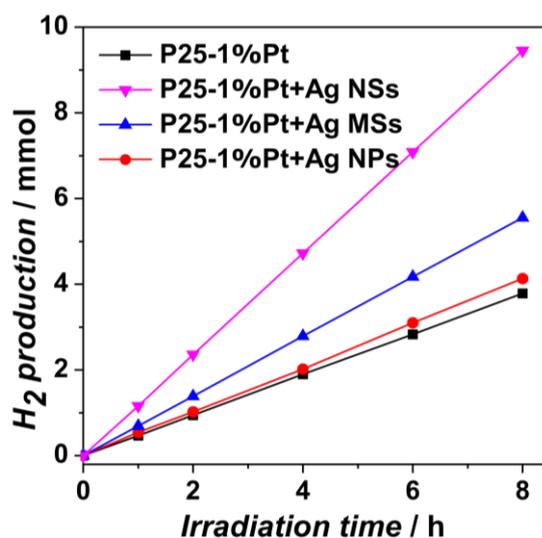


Fig. S1 H₂ evolution curves over P25 loaded with 1% Pt nanoparticles in the absence and presence of different Ag nanoparticles as scattering centers (0.02 g/L) under irradiation of 300 W Xe lamp.

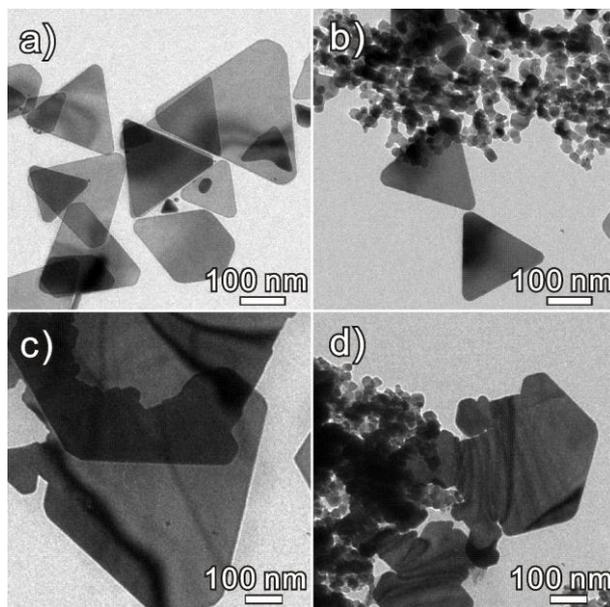


Fig. S2 TEM images of Ag NSs and Ag MSs (a,c) before and (b,d) after photocatalytic degradation reaction.

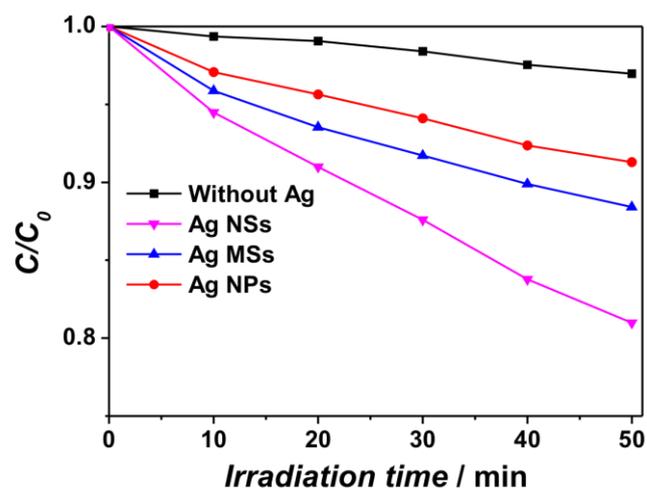


Fig. S3 Photodegradation curves of MO in the absence of P25 with different Ag nanoparticles as scattering centers (0.02 g/L) under irradiation of 300 W Hg lamp.

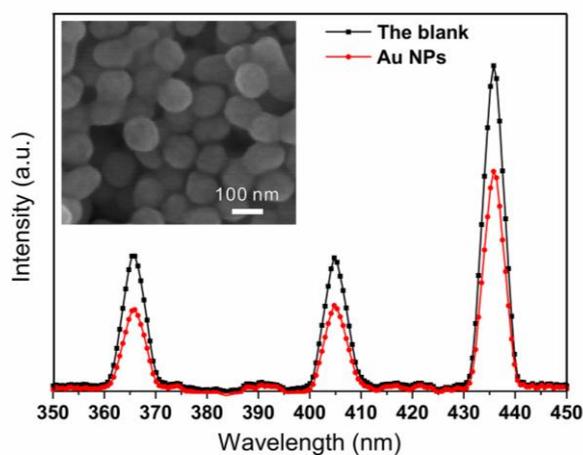


Fig. S4 Scattering spectra of the Hg lamp light using without and with Au nanoparticles as dispersive scattering centers (0.02 g/L). Insets are SEM image of Au NPs.

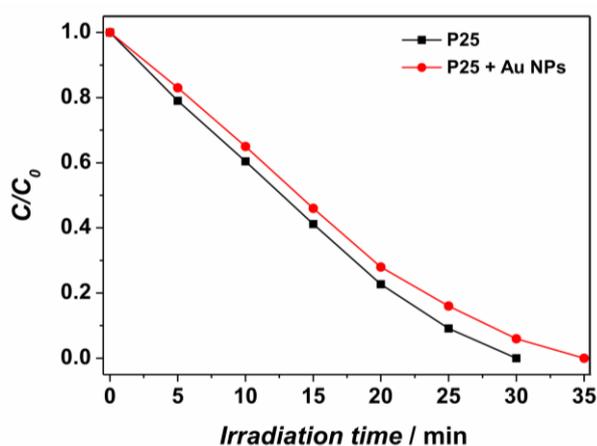


Fig. S5 MO degradation curves over P25 in the absence or presence of Au nanoparticles as scattering centers. The concentration of Au nanoparticles is 0.02 g/L.

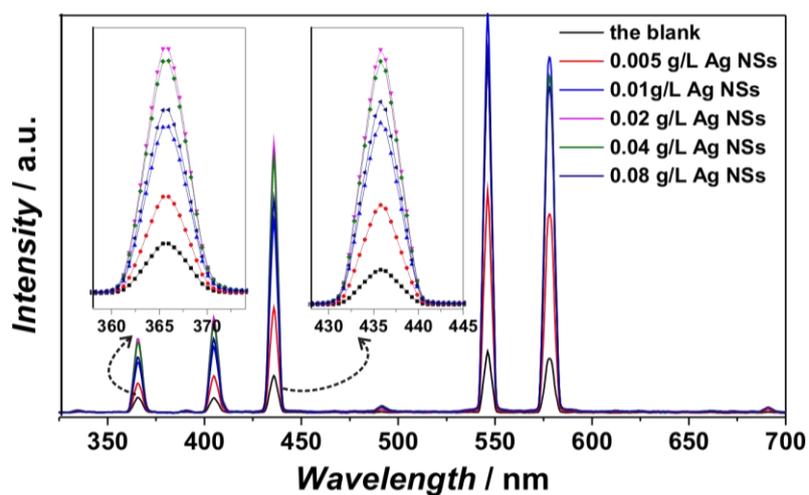


Fig. S6 Scattering spectra of the Hg lamp light in the presence of Ag NSs with different concentrations.

3. References

1. I. Washio, Y. Xiong, Y. Yin and Y. Xia, *Adv. Mater.*, 2006, **18**, 1745.
2. M.-S. Jin, Q. Kuang, X.-G. Han, S.-F. Xie, Z.-X. Xie and L.-S. Zheng, *J. Solid State Chem.*, 2010, **183**, 1354.