Supporting Information

Facile and rapid growth of Ag_2S microrod arrays as efficient substrates for both SERS detection and photocatalytic degradation of organic dyes

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This file contains:

Experimental details;

Supporting figures S1 - S7.

Experimental details

Materials and chemicals. Silver foils (Ag, 3N, 0.1 mm thick), sulfur powder (S, 5N), crystal violet (CV, AR), rhodamine 6G (R6G, BR), Sudan I (SDI, BS), methyl orange (MO, Ind), methylene blue (MB, BS), acetone (≥ 99.5%), methanol (≥ 99.5%) and anhydrous ethanol (≥ 99.7%) were all purchased from Sinopharm Chemical Reagent Company and used just as received. For all experiments, highly pure water (Millipore) with resistivity greater than 18.0 MΩ·cm was used.

Growth of Ag_2S MRAs on Ag foil. The Ag foil was first cut into pieces (3 × 0.5 cm) and cleaned with acetone. Typically, the sulfur powder (0.01 g), Ag foil (one piece) and solvent methanol (37.5 - 38 mL) were directly added into a Teflon-lined stainless-steel autoclave (50 mL). The autoclave was then heated to 160°C, maintained for 1 h and then allowed to cool down to room temperature. The eventually obtained black foil was meticulously washed by ethanol for several times and dried naturally in air.

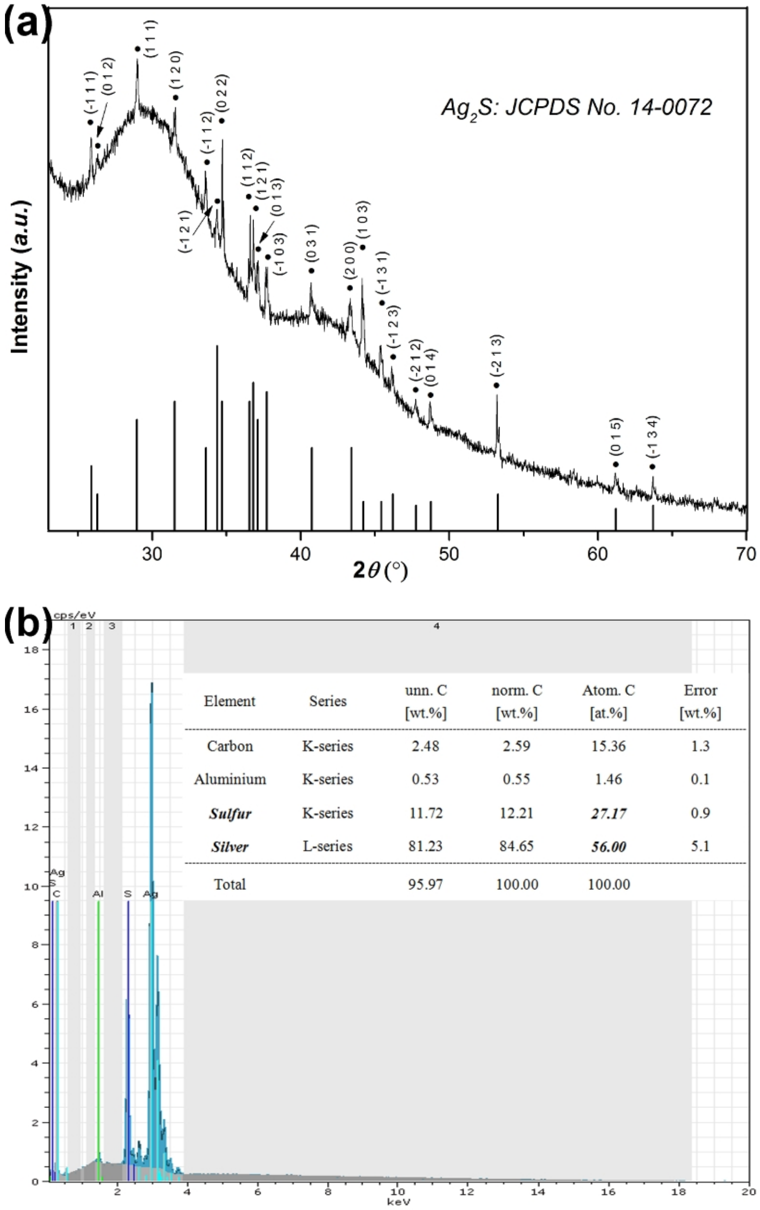
SERS measurements. 10^{-6} M aqueous solutions of MO, MB, CV and R6G as well as 10^{-6} M solution of SDI dissolved in 1 : 1 volume ratio of ethanol and water were first prepared. A little piece of the as-obtained MRA foil was immersed into the dye solution at room temperature and kept for 12 h in the dark so that the dye molecules could fully absorbed onto the surfaces of MRAs (a shorter time, for instance, 6 h or even 2 h, is also permissible). The little piece of MRA foil was afterward taken out and dried at 60°C for 1h. Particularly, the SERS signals on MRA substrates and corresponding Raman spectra of the as-purchased dye powders as well as the pristine solutions of MO and SDI were collected using a 633 nm laser as excitation source while for MB, CV and R6G, the 785 nm laser was utilized to avoid the photoluminescent signals of dye molecules.

Experiments of photocatalytic reaction. All measurements were conducted in quartz cuvettes (1 × 1 × 4 cm, Jingke Optical Instrument, Yixing). Typically, a whole piece (0.5 × 3 cm) of the as-obtained MRA foil was vertically put into 3 mL of the dye solution within a quartz cuvette. The quartz cuvette was then irradiated continuously with a 24 W UV lamp (365 nm, ZF-1A, Jihui Scientific Analysis Instrument, Shanghai) at room temperature. And the UV-vis absorbance spectra of the dye solutions were recorded simultaneously at 20 min interval.

Recyclability evaluation. The recyclability of Ag_2S MRA substrates were tested by conducting the SERS measurements as well as photocatalytic reactions of each one of the five different dyes for 5 cycles. Before entering a new photocatalytic reaction, the Ag_2S MRA foils were recycled and then rinsed by deionized water for several times. And meanwhile, the intensity of the strongest characteristic peak in SERS spectrum and the degradation efficiency recorded during the first cycle were regarded respectively as 100% in either the SERS or the photocatalysis part.

Characterization. SEM images, EDS spectra and the TEM as well as HRTEM images were obtained using a field-emission scanning electron microscope (S4800, Hitachi, Japan) equipped with an energy dispersive spectrometer (XFlash 5030, Bruker, Germany) and a field-emission transmission electron microscope (JEM-2100F, JEOL, Japan) working at 200 kV of acceleration voltage. Powder XRD measurements were carried out on a X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation (1.5406 Å). The

UV-vis-NIR absorbance spectra as well as diffuse reflectance spectra were recorded using a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu, Japan), and the Raman spectra were obtained with a laser confocal Raman micro-spectrometer (inVia reflex, Renishaw, UK).



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
Carbon	K-series	2.48	2.59	15.36	1.3
Aluminium	K-series	0.53	0.55	1.46	0.1
Sulfur	K-series	11.72	12.21	***27.17***	0.9
Silver	L-series	81.23	84.65	***56.00***	5.1
Total		95.97	100.00	100.00	

Fig. S1. Representative (a) XRD pattern and (b) EDS spectrum of as-obtained Ag$_2$S MRAs.

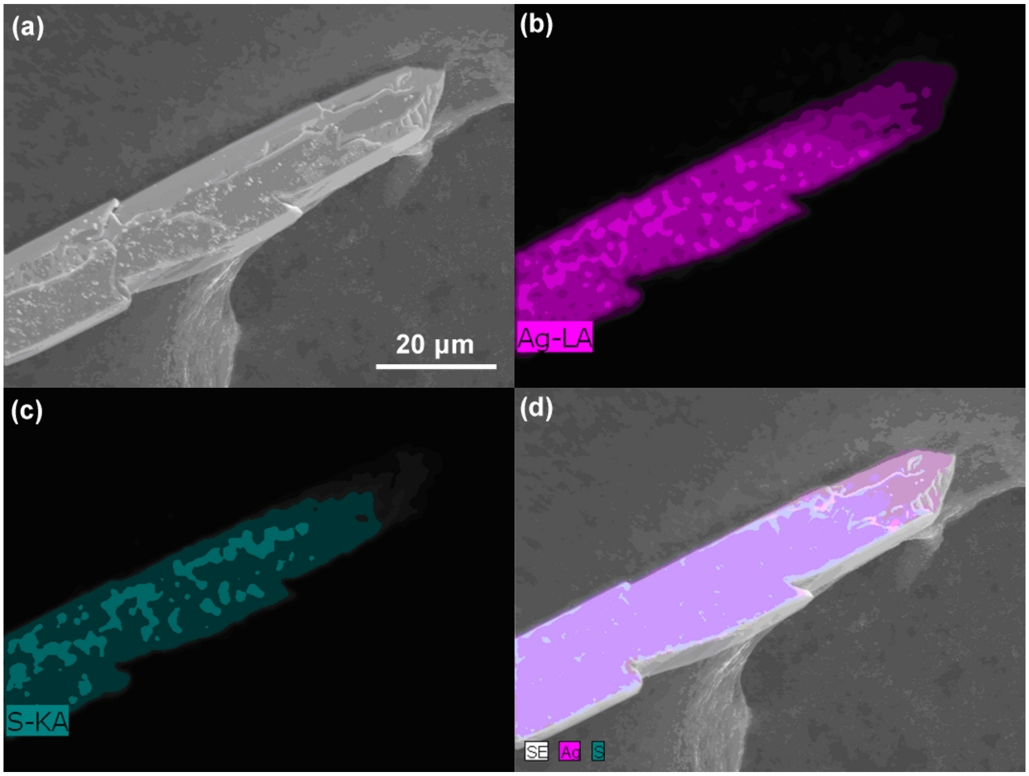


Fig. S2. (a) SEM image of a single Ag_2S microrod and the corresponding EDS element mapping of (b) silver, (c) sulfur and (d) an overlay.

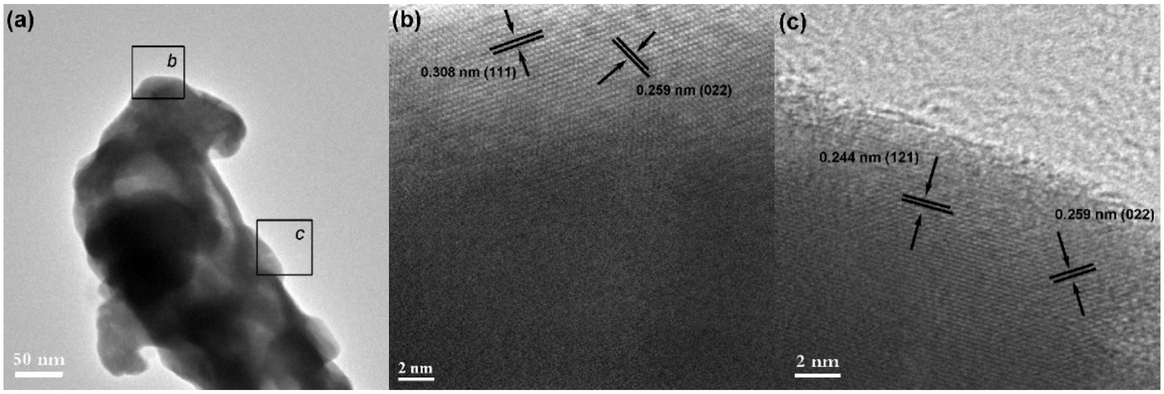


Fig. S3. (a) TEM image of a fragment of the obtained Ag_2S microrods and (b, c) the corresponding HRTEM images of the marked areas in (a).

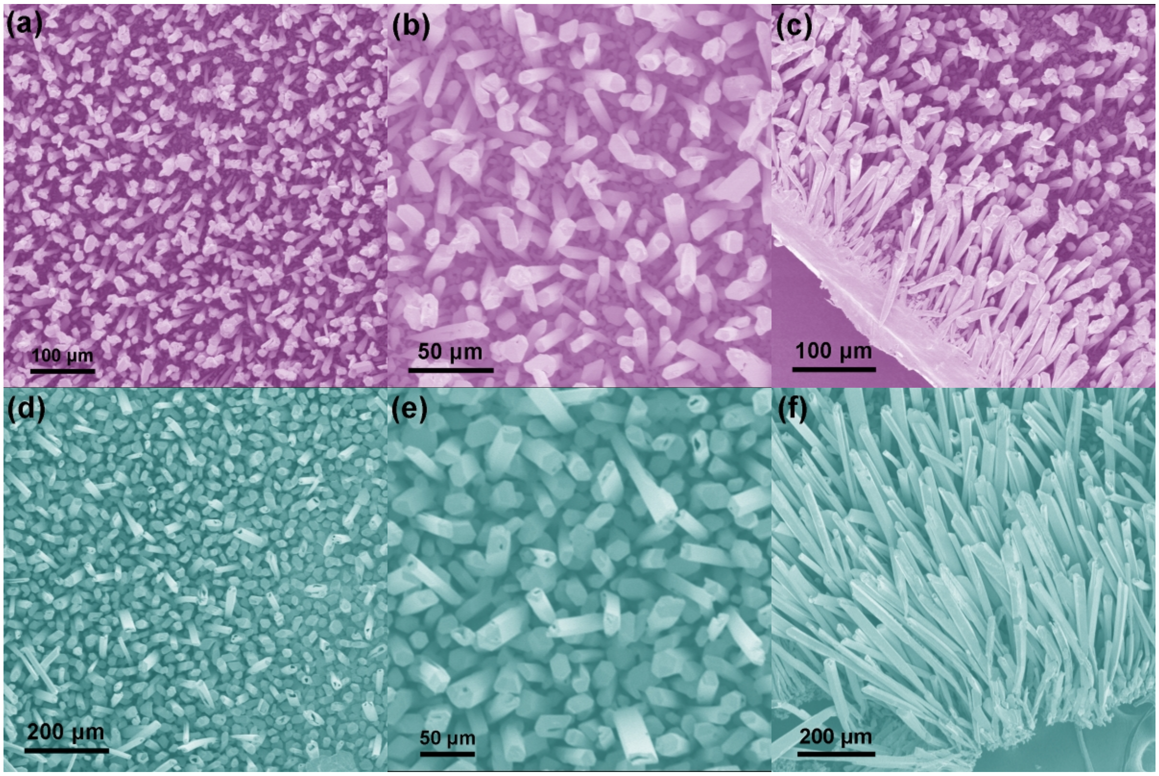


Fig. S4. (a-b, d-e) Top-view and (c, f) side-view SEM images of the as-obtained Ag_2S MRAs with 0.005 g (a-c) and 0.02 g (d-f) of the added amount of sulfur powder, respectively.

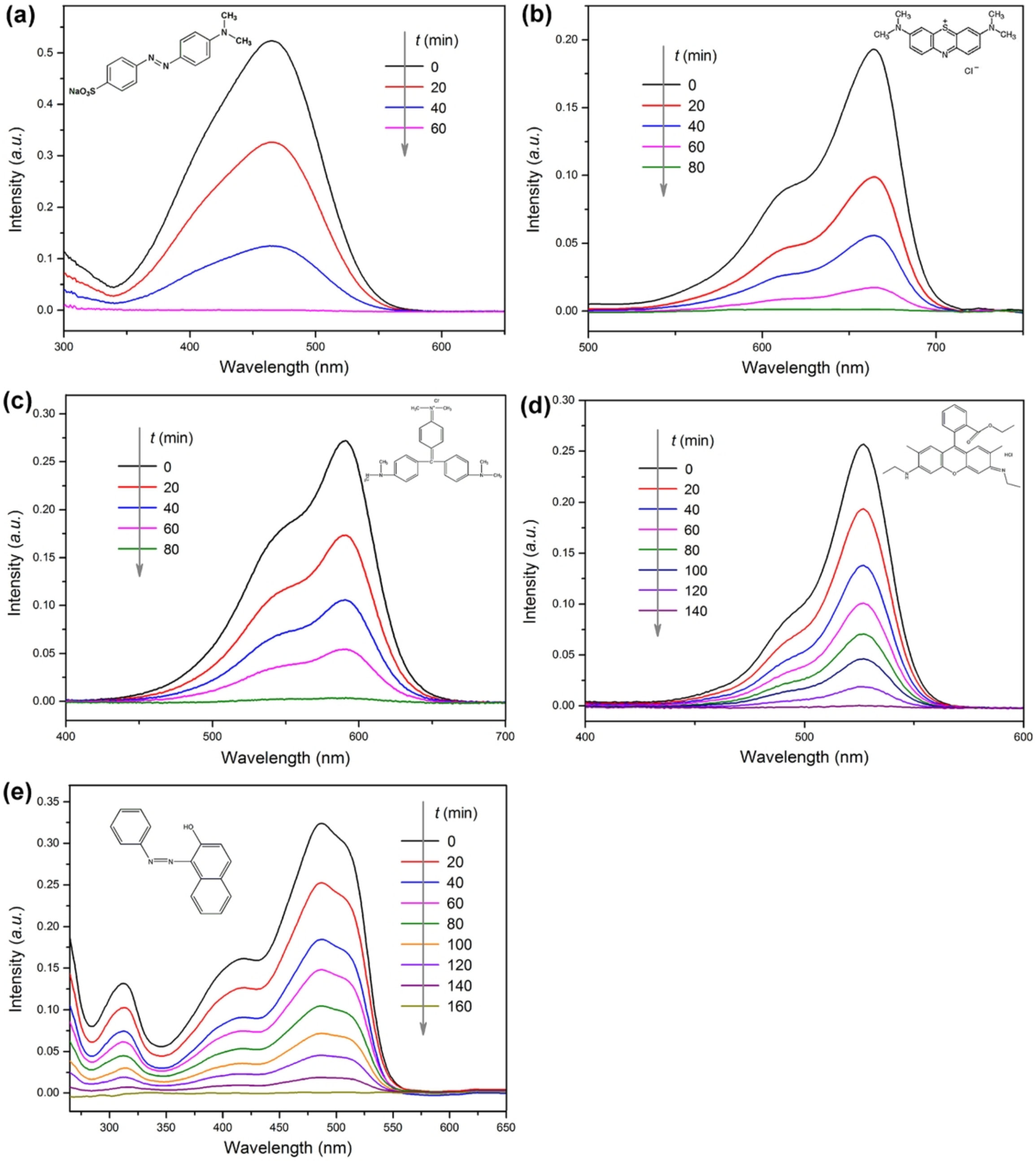


Fig. S5. The irradiation time-dependent absorbance spectra of 10^{-6} M aqueous solution of (a) MO, (b) MB, (c) CV, (d) R6G and (e) 10^{-6} M SDI solution dissolved in 1 : 1 volume ratio of ethanol and water in the presence of Ag_2S MRA substrates under UV light (365 nm, 24 W) irradiation.

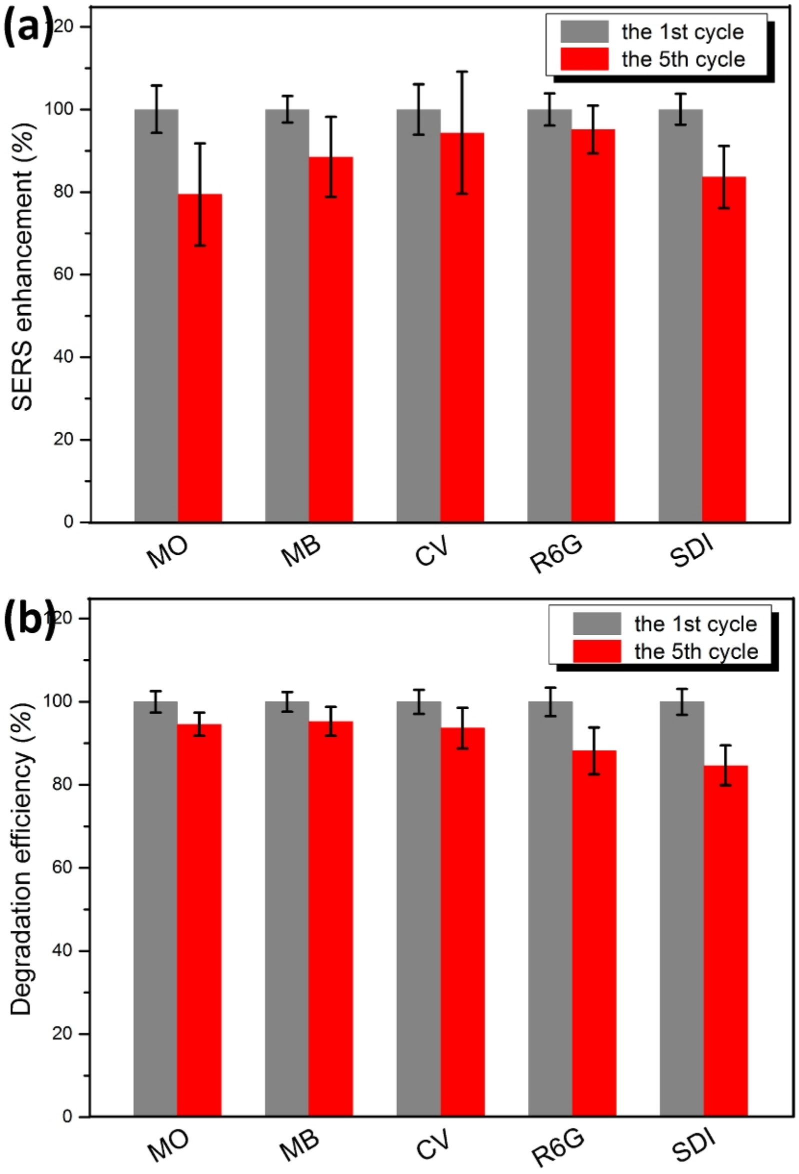


Fig. S6. The (a) SERS enhancement and (b) degradation efficiency of the five different dyes on the Ag_2S MRA substrates during the first cycle (the grey bars) and after recycling and reusing for five times (the red bars), respectively.

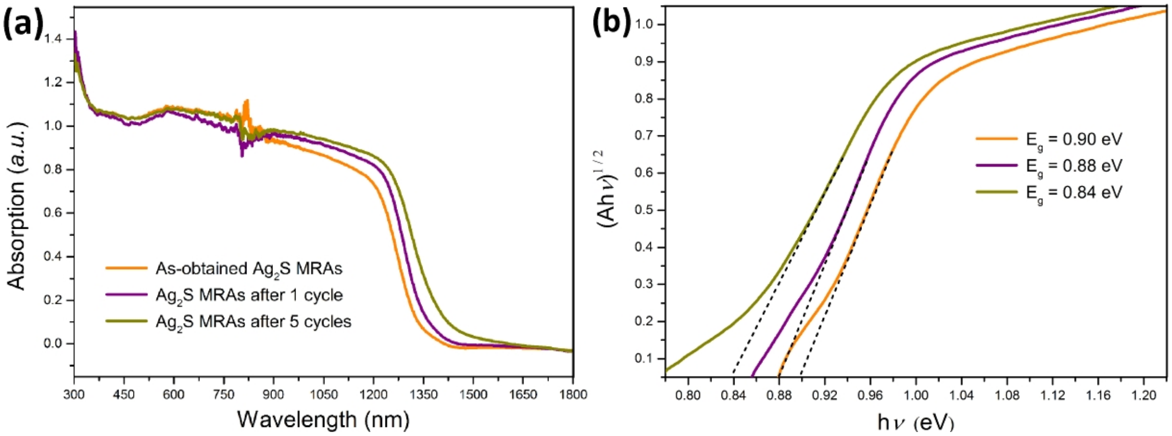


Fig. S7. (a) Representative UV-vis-NIR diffuse reflectance spectra of the as-obtained Ag_2S MRAs as well as the Ag_2S MRA substrates after 1 cycle or 5 cycles of the photocatalytic reaction; (b) the band-gaps calculated correspondingly from (a) using the plots of $(Ah\nu)^{1/2}$ *vs.* h*ν*.