

Bubble-Promoted Assembly of Hierarchical, Porous Ag₂S Nanoparticle Membranes

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Supplementary Information:

- 1. Figure S1. Structural characterization of Ag₂S nanoparticles.**
- 2. Figure S2. Dense Ag₂S films obtained by the self-assembly process using clean nanoparticles (without oleylamine).**
- 3. Figure S3. Contact angle measurements on the porous Ag₂S membrane.**
- 4. Figure S4. SEM image of the cross-section of the porous Ag₂S membrane showing three layers of pores..**
- 5. Figure S5. Photocatalytic applications of porous Ag₂S membranes.**

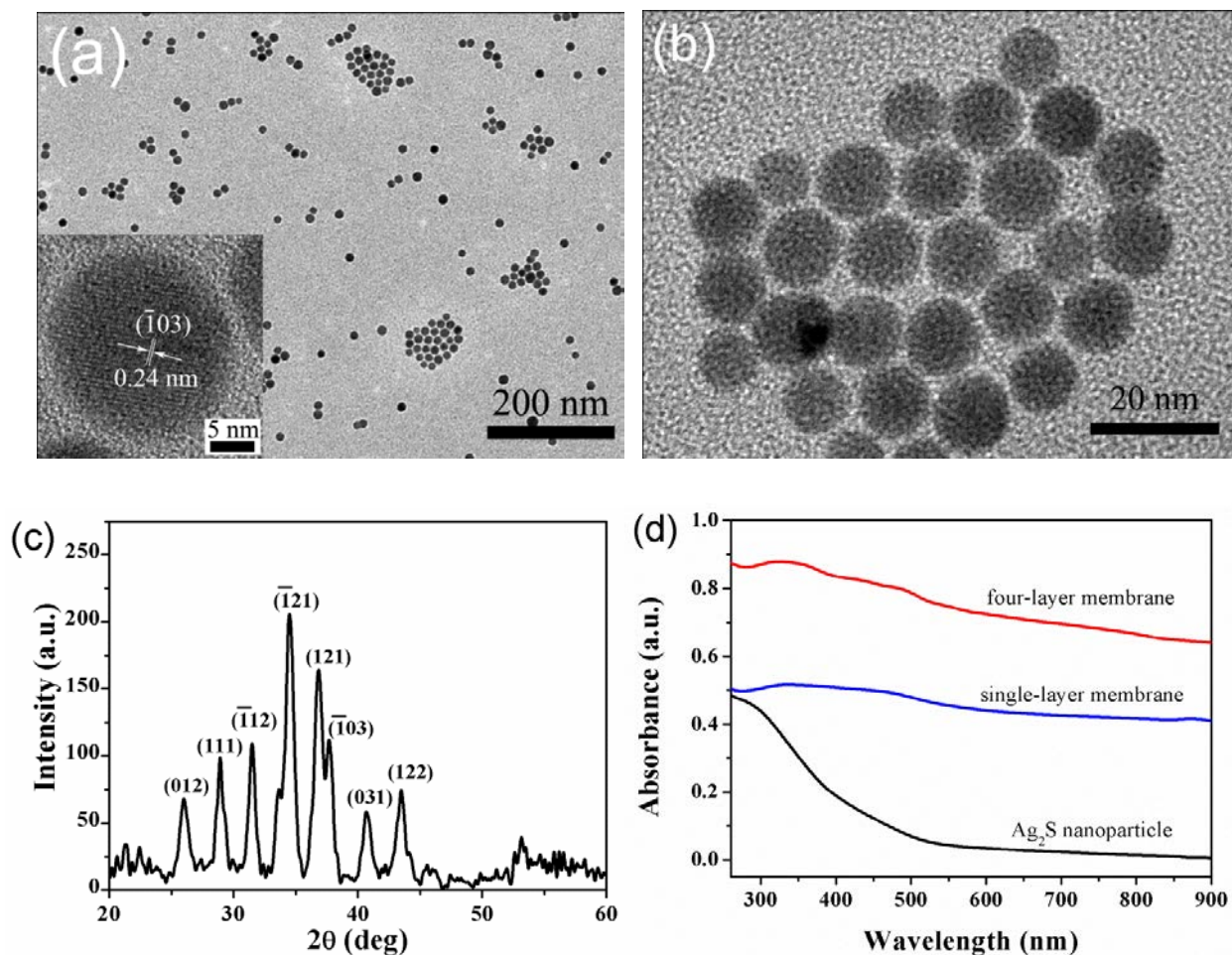


Figure S1. Structural characterization of Ag_2S nanoparticles. (a) and (b) TEM images of the purified Ag_2S nanoparticles in different magnifications. Inset in (a), HRTEM image of a single-crystalline nanoparticle in which the plane $(\bar{1}03)$ and lattice distance (0.24 nm) are indicated. (c) XRD pattern of the assembled solid Ag_2S nanoparticle membrane. The diffraction peaks are indexed as a monoclinic α -phase Ag_2S (JCPDS No.14-0072). (d) UV-visible absorption spectra of a Ag_2S nanoparticle suspension in hexane, a thin single-layer porous membrane and a thick four-layer porous membrane. It seems that the onset of absorption in the membrane spectrum is less defined compared to nanoparticles, and we suppose that the presence of sub- μm pores in the membrane might contribute to a wider light absorption range and move the onset to longer wavelength.

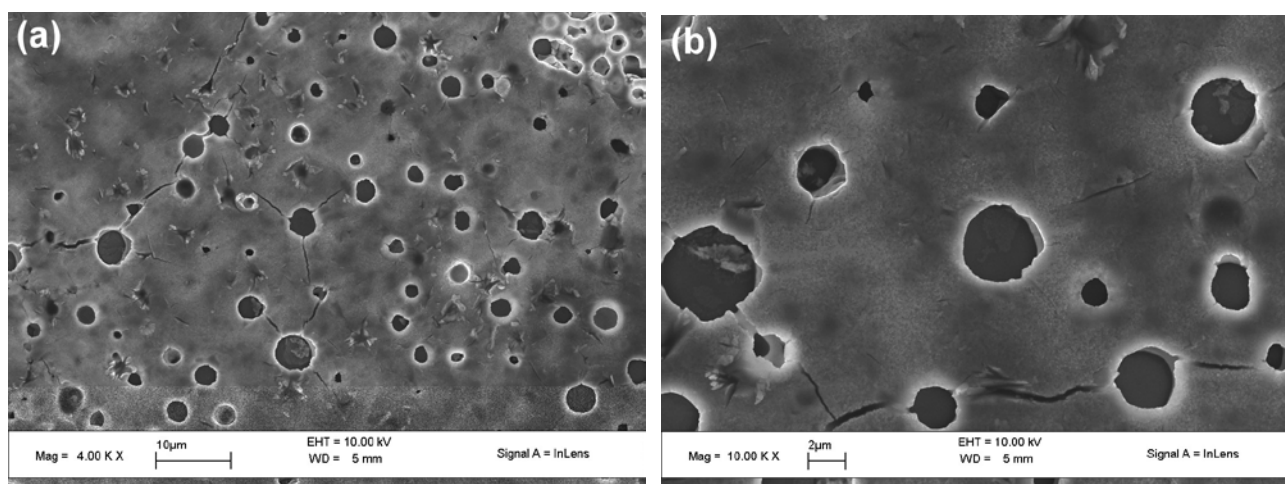


Figure S2. Dense Ag₂S films embedded with irregular pores obtained by the same self-assembly process but using thoroughly washed clean surface Ag₂S nanoparticles (without oleylamine).

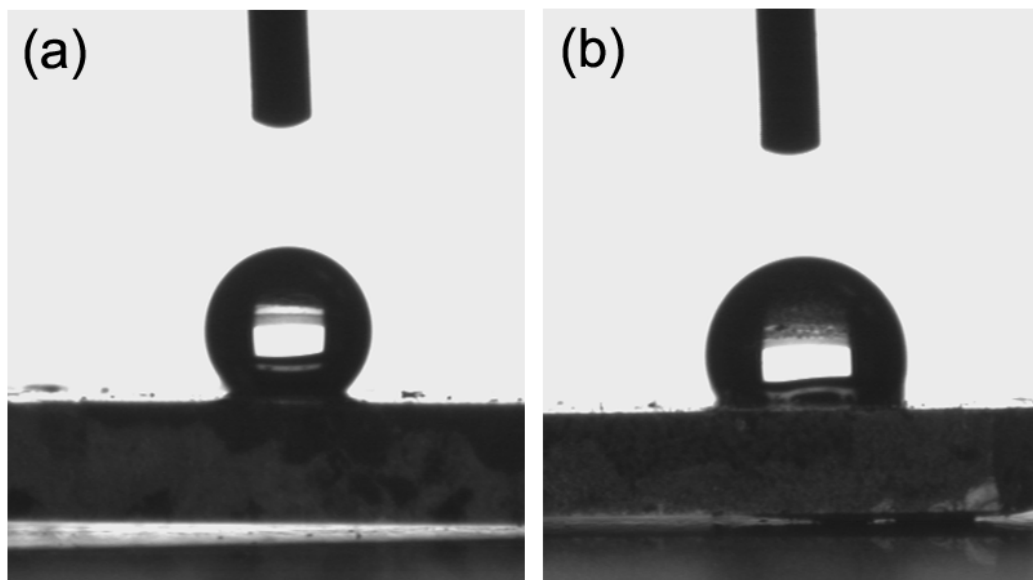


Figure S3. Contact angle measurements on the porous Ag₂S membrane. (a) A water droplet sitting on top of a four-layer membrane, resulting in a contact angle of about 147°. (b) Water contact angle to a single-layer membrane is about 117°.

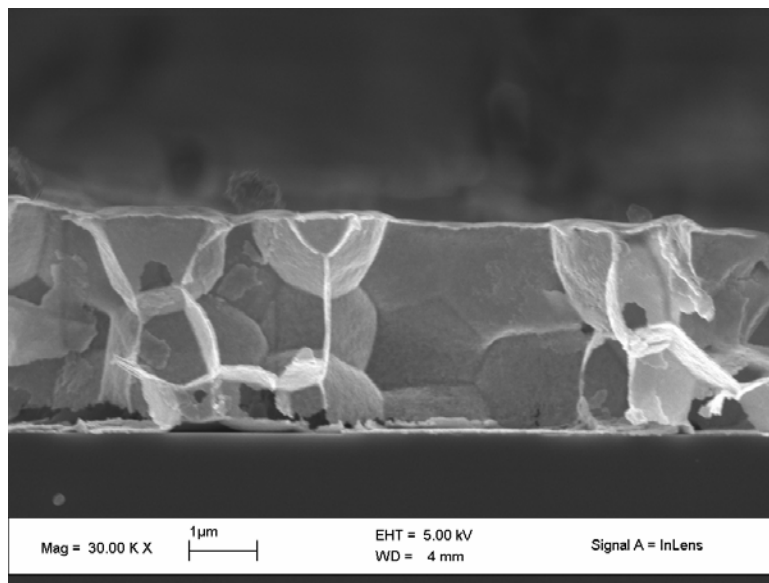


Figure S4. SEM image of the cross-section of the porous Ag_2S membrane showing three layers of pores.

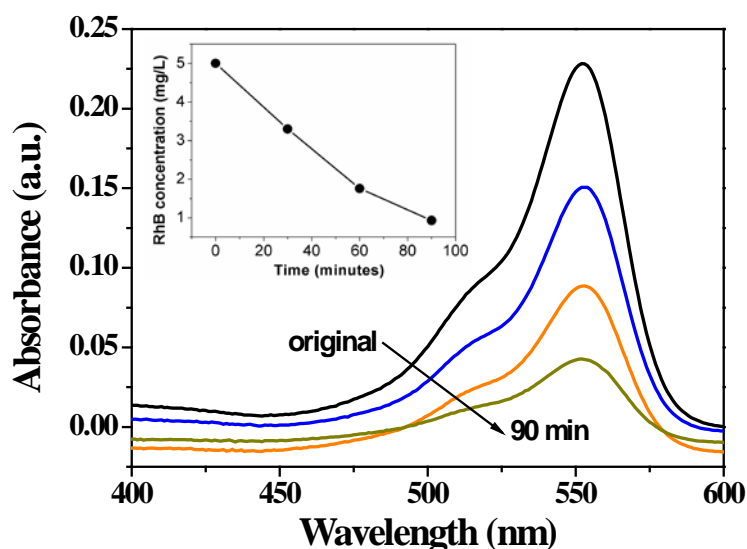


Figure S5. Photocatalytic applications of porous Ag_2S membranes. The semiconducting Ag_2S membrane can be used as a photocatalytic substrate for decomposition of dye molecules in water. About 5 mL RhB aqueous solution with a dye concentration of 5 mg/L was contained in a small glass well (diameter of 40 mm). Two assembled Ag_2S membranes (a few μm thick) with sizes of about $1 \times 1 \text{ cm}^2$ were transferred onto a quartz plate and then immersed at the bottom of RhB solution with the porous membrane facing upward to receive the incident light. The solution was irradiated by visible light coming from a Xe lamp for a certain period (30, 60 and 90 minutes), and its concentration was monitored by UV-Vis spectroscopy. The intensity of characteristic RhB absorption band at 510 nm gradually diminishes with longer time, and the RhB concentration drops to 0.93 mg/L after 90 minutes irradiation, less than 20% of initial concentration (Fig. S4). Decomposition of organic molecules is due to the photo-excitation of Ag_2S nanoparticles and production of free charge carriers (holes) which oxidize dye molecules. The porous structure is favorable for maximum dye adsorption inside the pores and subsequent photocatalysis process. Over the period, the decrease of RhB concentration shows a linear relationship with time (inset of Fig. S4).