# Protein-Induced Structural Evolution of Silver Sulfide at Nanoscale: From Hollow Particles to Solid Spheres

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## Supporting Information

### Experiment Section

*Chemicals:* Bovine pancreatic RNase A was purchased from Sigma-Aldrich. Silver nitrate ($AgNO_3$) (≥99.8%, $M_w$ = 169.87 A.R.) and thioacetamide (TAA) (≥99.0%, $M_w$ =75.13) were purchased from Shanghai Chemical Reagents Company. Solutions were prepared by using purified water as the solvent with a resistivity of 18 m Ω .All chemicals were used as received without further purification.

*Synthesis $Ag_2S$ nanospheres*: $AgNO_3$ (5 mL, 50 mM) was introduced into 5 mL of 12.5 $mgmL^{-1}$ RNase A solution with vigorous stirring. The precursor solution was then kept at room temperature for pumping vacuum for 30 min. After that, freshly prepared TAA solution (5 mL, 50 mM) was injected. The as-prepared samples were stored in dark at 60°C.

*Characterization*: X-ray powder diffraction (XRD) measurements were performed on a Bruker D&Advance X-ray powder diffractometer with graphite monochromatized Cu Kα ( λ=0.15406 nm). Scanning electron microscopy (SEM) images were taken on a JSM-5600LV scanning electron microscope equipped with an X-ray energy dispersive spectroscopy (EDS) at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM), accompanied by selected-area electron diffraction (SAED), was carried out on a JEOL JEM 100CX-II transmission electron microscope; high resolution TEM (HRTEM) images were taken on a JEOL JEM-2010

transmission electron microscope. The UV–vis absorbance of the samples was measured on a Shimadzu UV-2450 UV–visible spectrophotometer. The FT-IR spectra were recorded on a Bio-Rad FTS-40 Fourier transform infrared spectrograph in the wavelength range of 4000~950 $cm^{-1}$. Circular dichroism (CD) spectra (190-260 nm) were recorded on a Jasco J-810 spectropolarimeter. The native polyacrylamide gel electrophoresis (PAGE) for RNase A and different stage $Ag_2S$ samples were both run in a 15% acrylamide gel at 130 V for 80 min. Atom force microscopy (AFM) imaging was performed using a Digital Instruments Multimode Scanning Probe Microscope equipped with a Nanoscope IIIA controller and a vertical engage J-scanner.

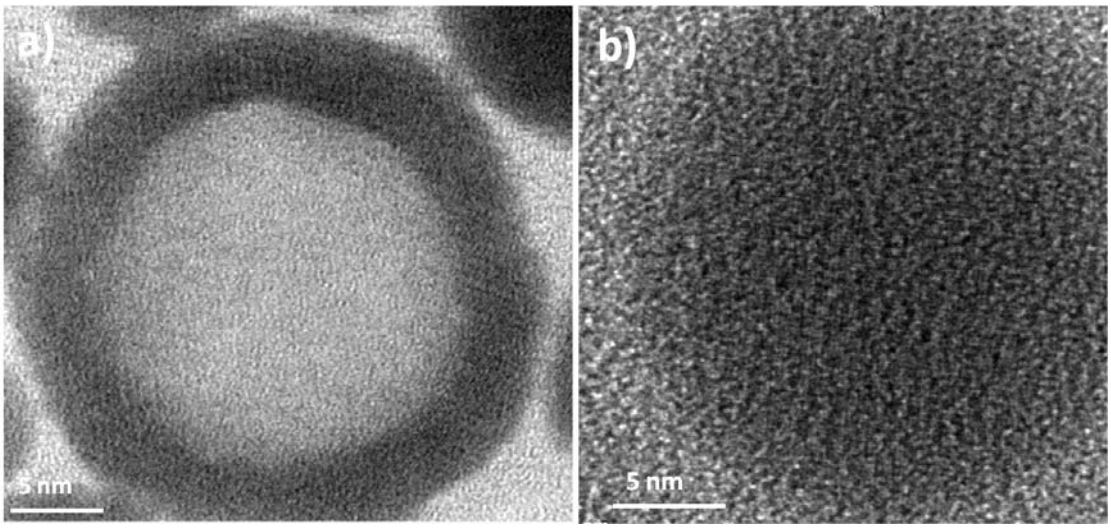


Fig.S1 HR-TEM images of a) hollow and b) solid $Ag_2S$ NPs.

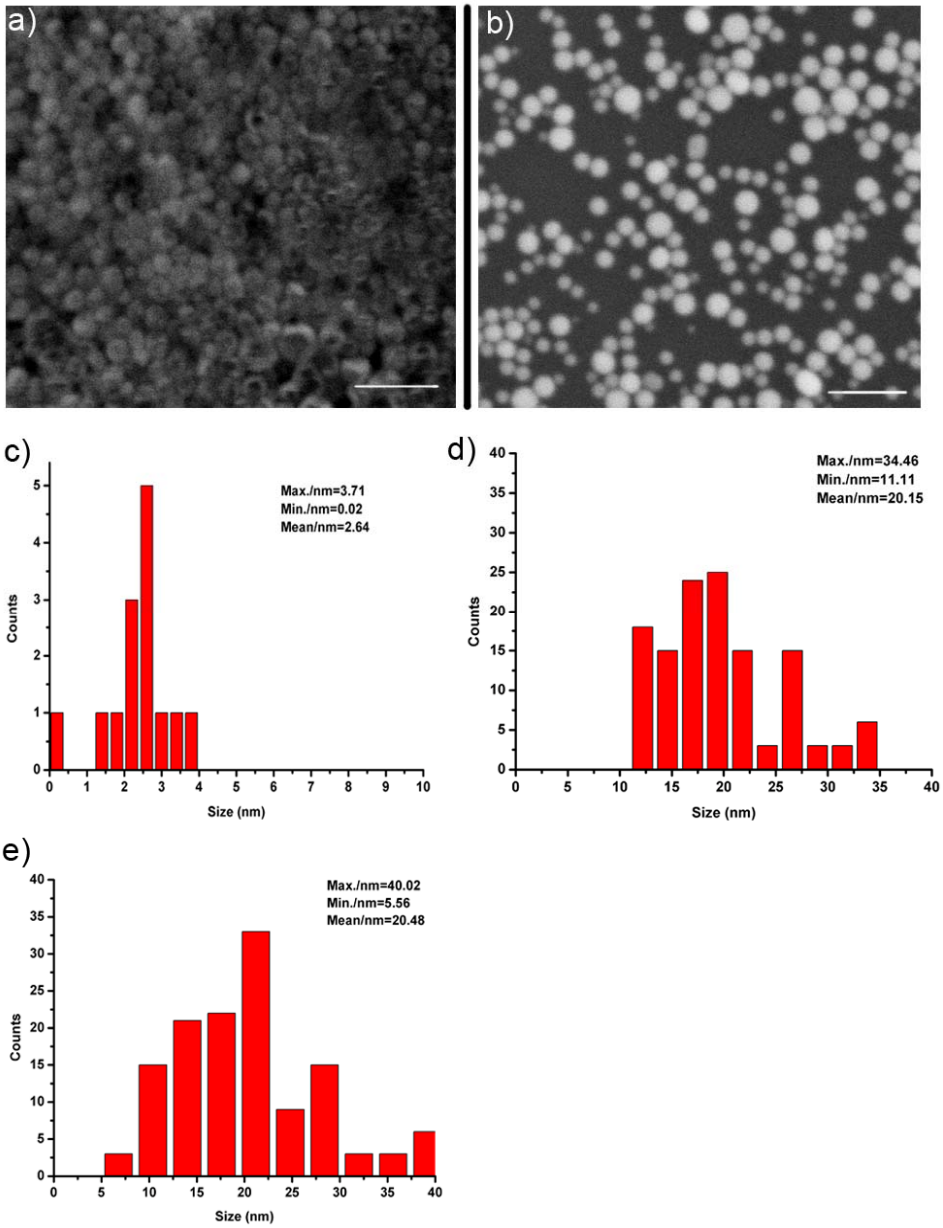


Fig.S2 SEM images of $Ag_2S$ NPs stored for a)20 days and b) 30 days. Scale bar is 100 nm. Size distribution of $Ag_2S$ NPs stored for c) 1 day, d) 20 days and e) 30 days.

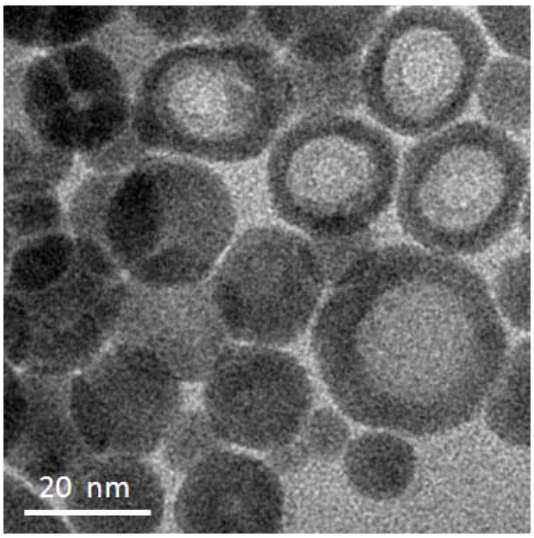


Fig.S3 TEM image of as-prepared $Ag_2S$ NPs stored for 20 days after centrifugation at 14000 rpm for 30 min.

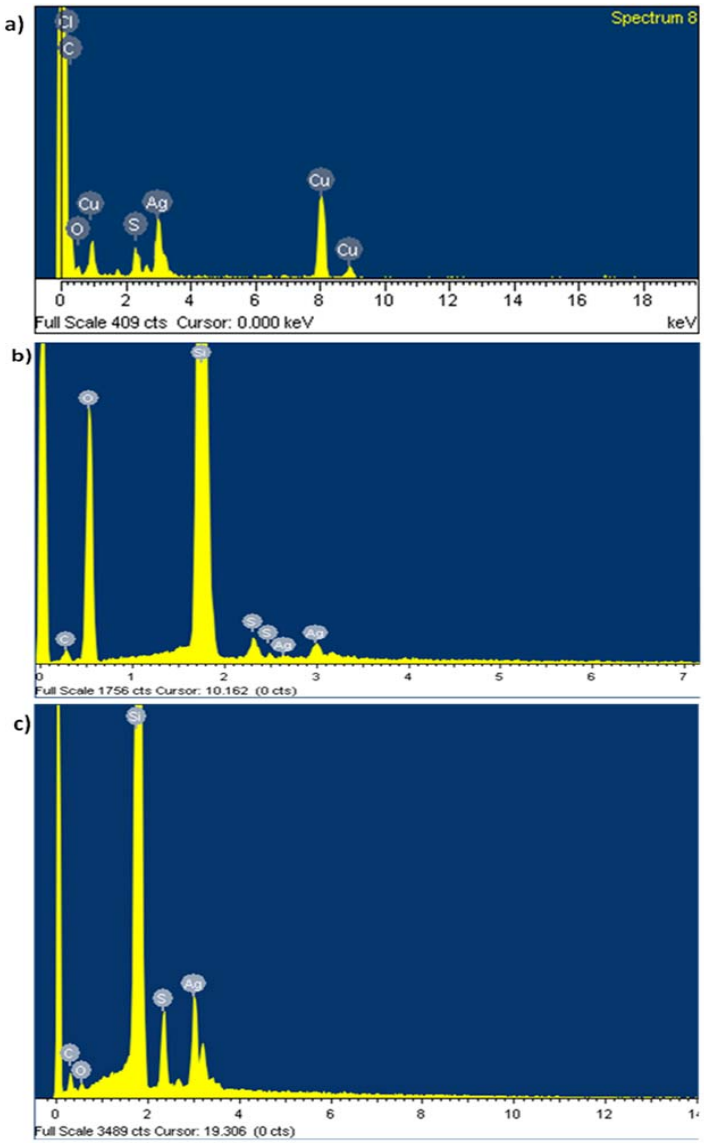


Fig.S4 EDS spectra of $Ag_2S$ NPs stored for a) 1 day, b) 20 days and c) 30 days.

Table S1. The main FT-IR peaks of pure RNase A, RNase A-Ag+ and RNase A-$Ag_2S$ (30 days).

| Assignments | -OH ($cm^{-1}$) | amide A ($cm^{-1}$) | amide Ⅰ ($cm^{-1}$) | amide Ⅱ ($cm^{-1}$) | $-NO_3^-$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| Pure RNase A | 3411 | 3150 | 1647 | 1539 | |
| RNase A-$Ag^+$ | 3273 | 3273 | 1636 | 1516 | 1369 |
| RNase A-$Ag_2S$ | 3423 | | 1624 | 1542 | 1317 |

Table S2. The percentages of the secondary structures of pure RNase A, RNase A-$Ag^+$ and RNase A-$Ag_2S$ (30 days) corresponding to the CD spectra.

| Assignments | α-helix (%) | β-sheet (%) | turn (%) | random (%) |
|---|---|---|---|---|
| Pure RNase A | 9.7 | 31.4 | 12.5 | 38.9 |
| RNase A-$Ag^+$ | 13.1 | 30.8 | 12.5 | 37.9 |
| RNase A-$Ag_2S$ | 20.8 | 25.8 | 12.5 | 39.5 |

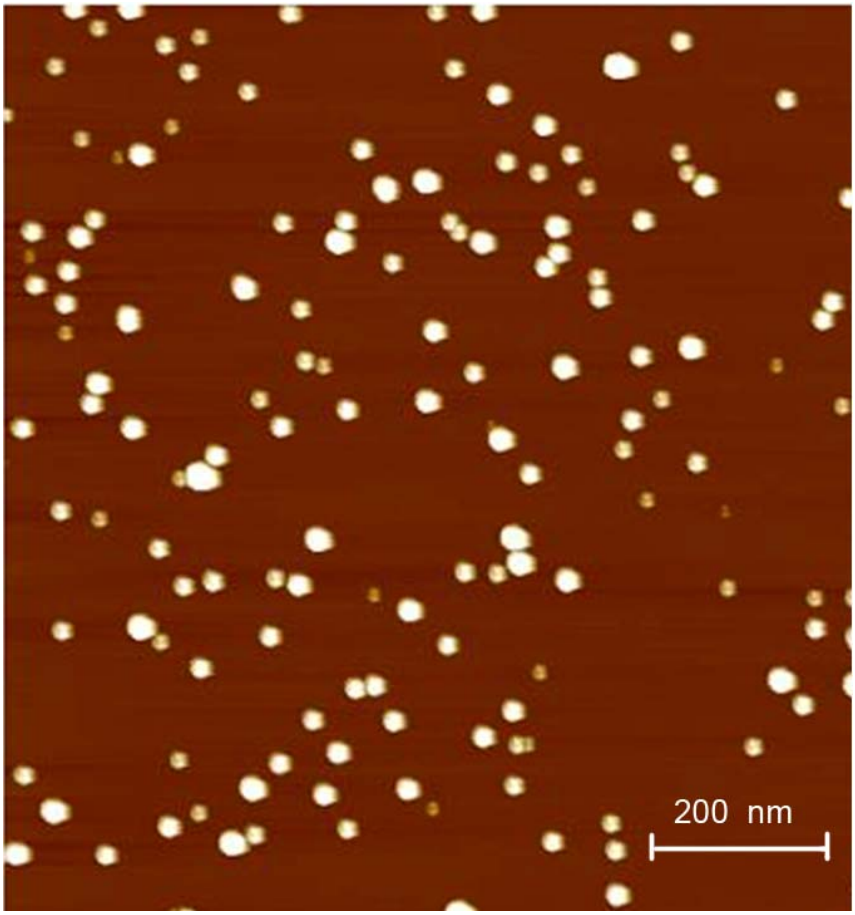


Fig.S5 AFM image of as-prepared $Ag_2S$ NPs stored for 30 days

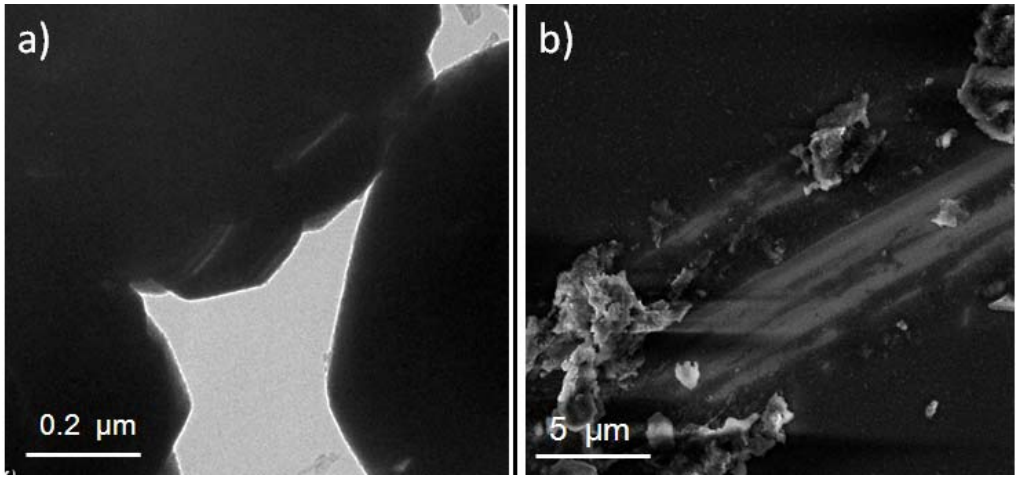


Fig.S6 a) TEM and b) SEM images of $Ag_2S$ precipitation without RNase A.

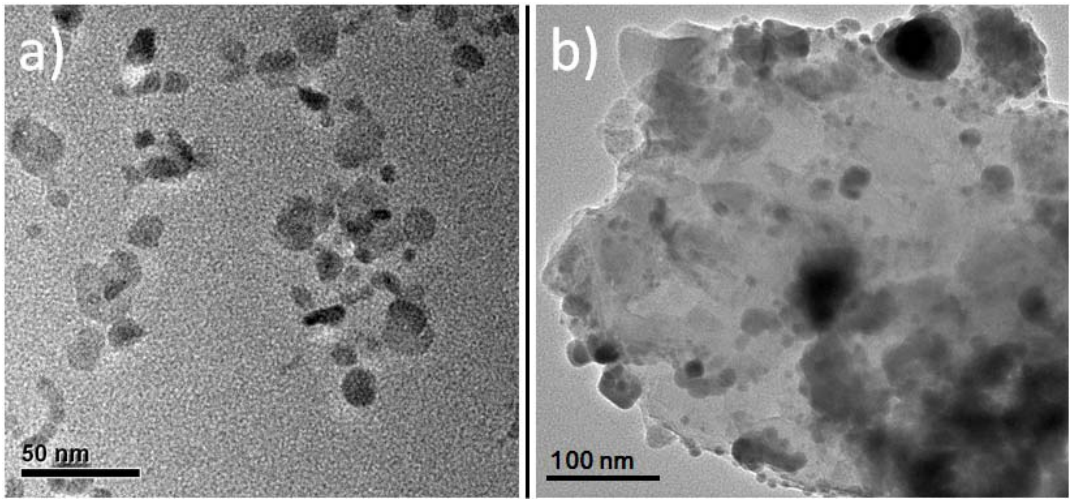


Fig.S7 a) TEM image of $Ag_2S$ NPs stored for 20 days at a) 40°C and b) 80°C.

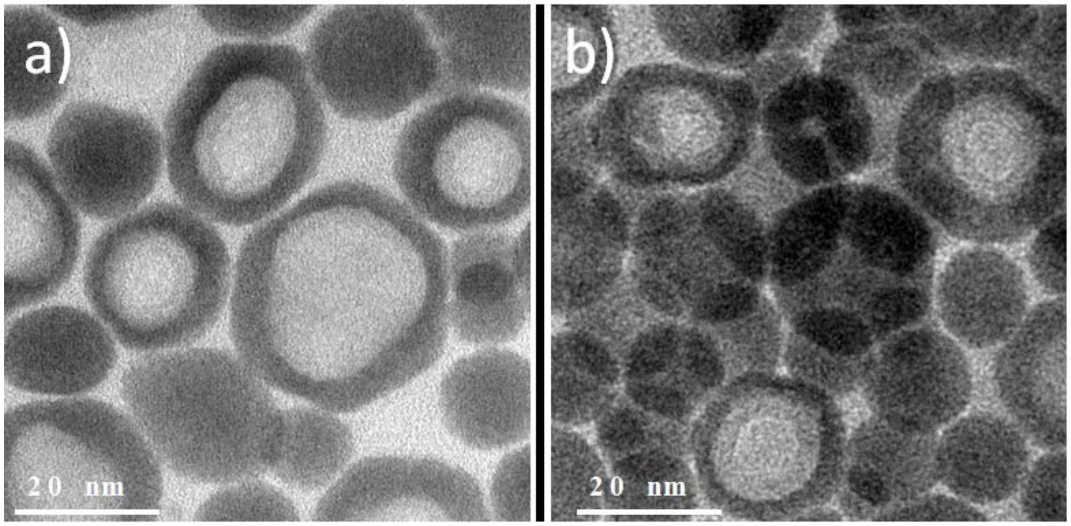


Fig. S8 TEM images of $Ag_2S$ NPs stored for a) 20 days and b) 25 days.