

Electronic Supplementary Information (ESI)

Synthesis of Ag nanoparticles encapsulated in hollow silica spheres for efficient and selective removal of low-concentrated sulfur compounds

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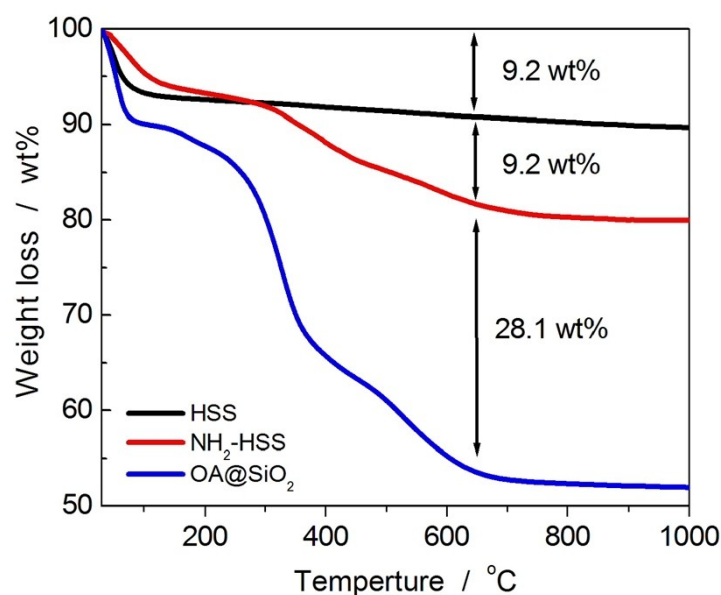


Fig. S1 Weight loss curves of HSS, NH₂-HSS and OA@SiO₂ in a flow of air. The weight loss of HSS seen at 100 °C < T (corresponding to 9.2 wt%) is due to the removal of absorbed water. The NH₂-HSS showed the additional weight loss seen at T < 650 °C (corresponding to 9.2 wt%) which is attributed to the breakdown of the amine groups and the alkyl groups of APTES. The OA@SiO₂ shows the further weight loss seen at T < 650 °C (corresponding to 21.7 wt%) which is due to combustion of the oleic acid. From these results, it is confirmed that the prepared NH₂-HSS retained the amine groups while the oleic acid was removed.

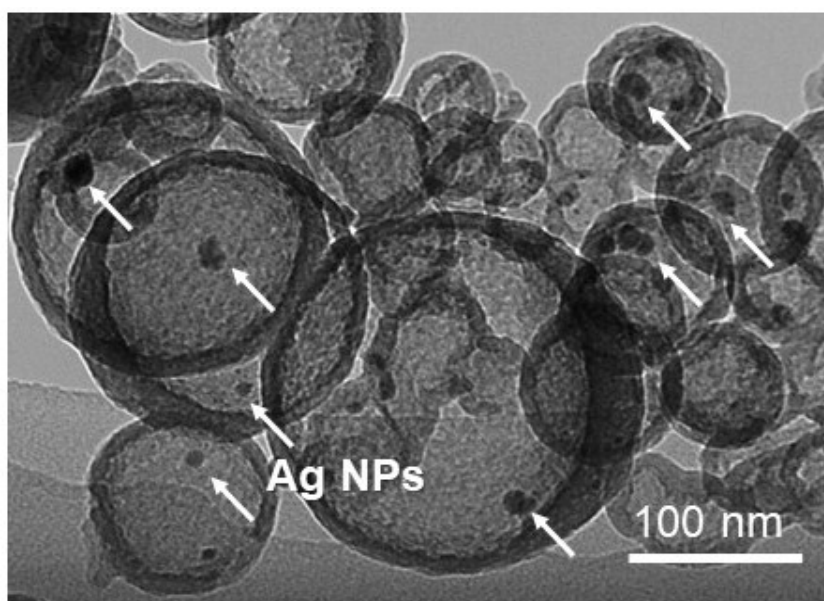


Fig. S2 TEM image of Ag@HSS (wide region).

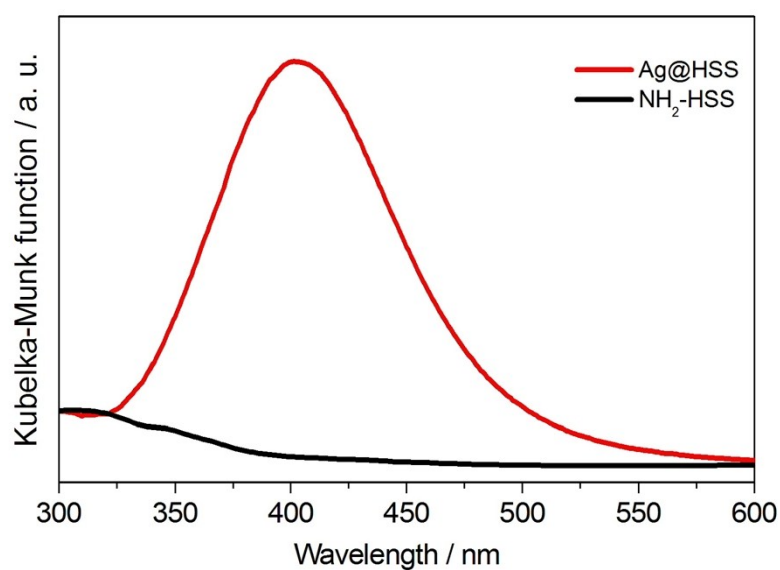


Fig. S3 UV-vis spectra of $\text{NH}_2\text{-HSS}$ and Ag@HSS . The spectra of Ag@HSS showed the peak at 400 nm derived from AgNPs.

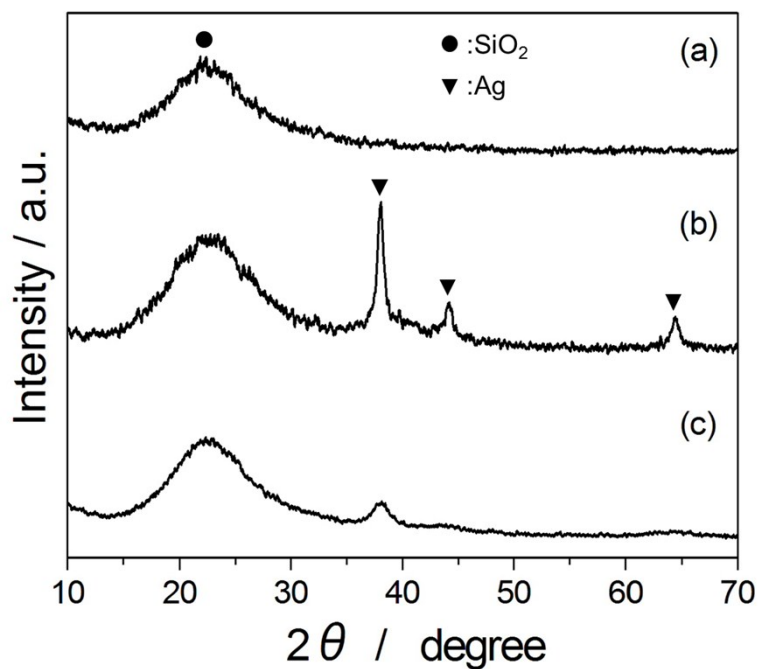


Fig. S4 XRD patterns of (a) $\text{NH}_2\text{-HSS}$, (b) Ag/SiO_2 and (c) Ag@HSS . The broad peak seen at $2\theta = 15\text{--}30^\circ$ is associated with amorphous nature of silica.

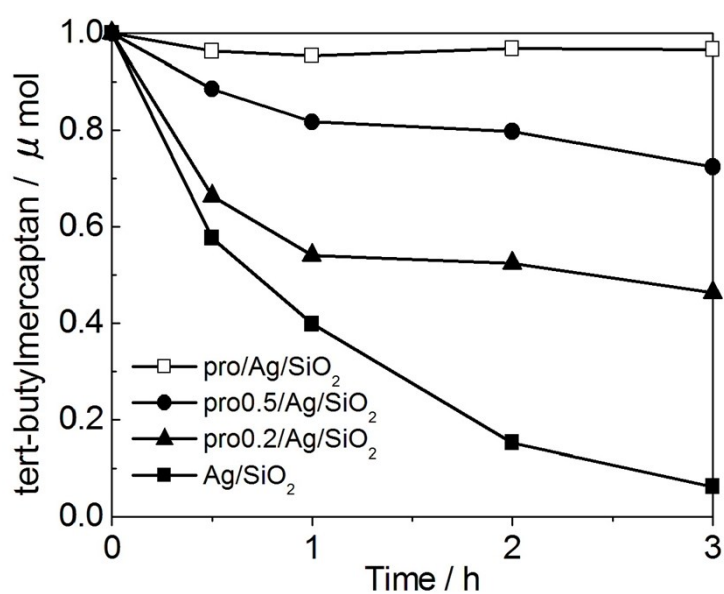


Fig. S5 Adsorption kinetics of TBM (*tert*-buthylmercaptan) over Ag/SiO₂ and protein adsorbed Ag/SiO₂. The amount of adsorbed protein to the surface of 10 mg of Ag/SiO₂ were 2 mg (pro0.2/Ag/SiO₂), 5 mg (pro0.5/Ag/SiO₂) and 10 mg (pro/Ag/SiO₂).

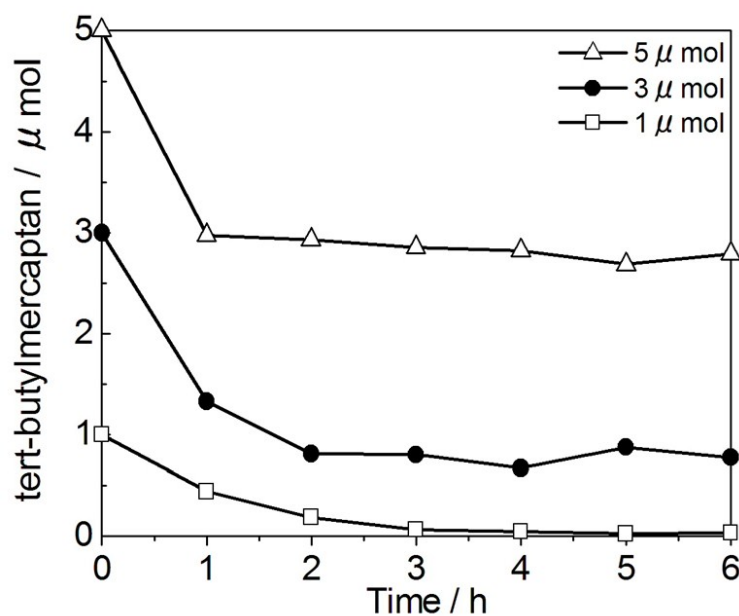


Fig. S6 Adsorption kinetics of 1 μmol, 3 μmol and 5 μmol of TBM (*tert*-buthylmercaptan) over Ag@HSS.

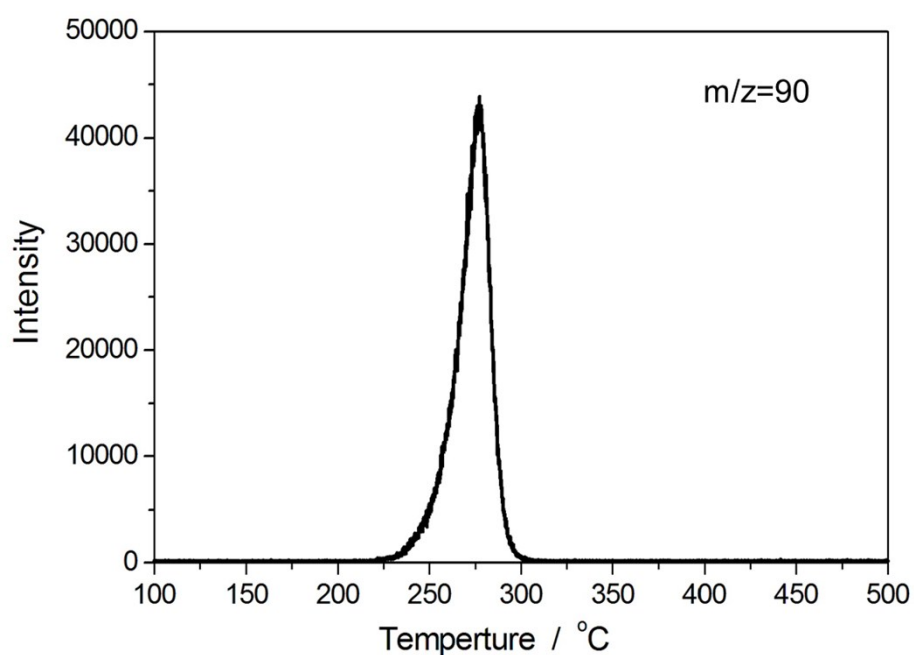


Fig. S7 EGA profile ($m/z=90$) obtained from TBM (*tert*-buthylmercaptan) adsorbed Ag@HSS. The peak caused by the desorption of TBM is observed around 220-310 °C, confirming that the adsorbed TBM is completely desorbed from Ag/@HSS by heat treatment at 500 °C.

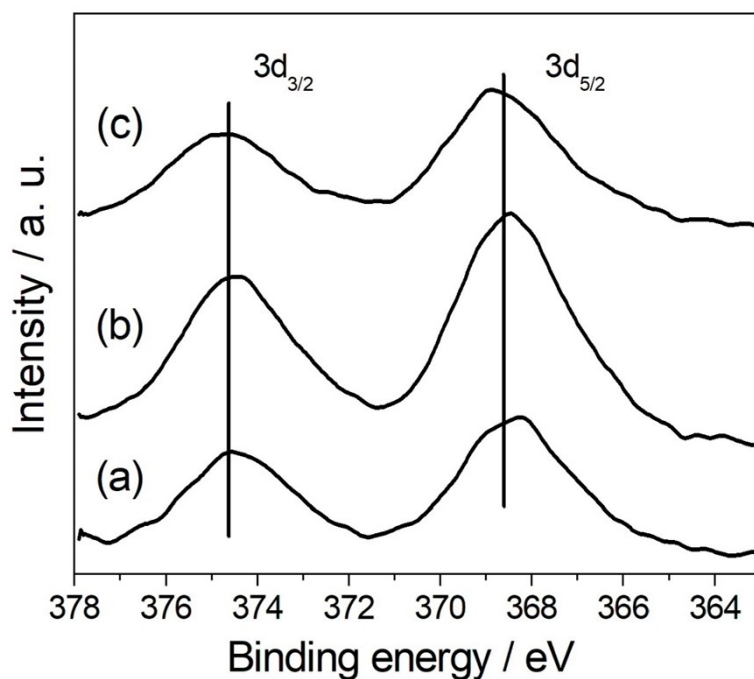


Fig. S8 Ag 3d XPS spectra of Ag@HSS (a) as-synthesized, (b) after adsorption of TBM (*tert*-buthylmercaptan), (c) after regeneration for 2 h at 500 °C.

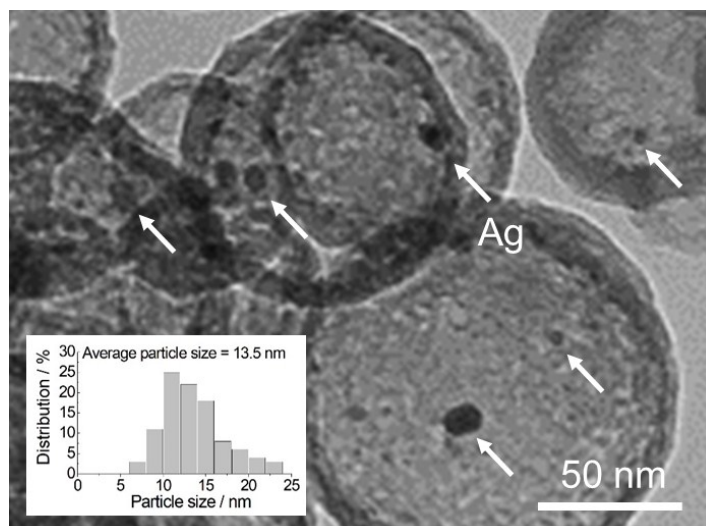


Fig. S9 TEM image of Ag@HSS after regeneration treatment for 2 h at 500 °C. The inset shows the particle size distribution diagram of AgNPs.

Table S1 Adsorption capacities of Ag@HSS and reported samples toward sulfur compounds.

Sample	Adsorbate ^a	Support	Adsorption capacity [mol-S / mol-Ag]	Ref.
Ag@HSS	TBM	Hollow silica sphere	0.48	This study
AgNa-Y	TBM	Y-zeolite	0.34	1
AgNa-Y	TBM	Y-zeolite	0.35	2
Ag-X	TBM	X-zeolite	0.62	3
AgSi	TBM	Amorphous silica	1.06	4
Ag-MSN	DBT	Mesoporous silica nanoparticles	0.21	5

^a TBM = *tert*-butylmercaptan, DBT = Dibenzothiophen

- [1] D. Lee, E. Y. Ko, H. C. Lee, S. Kim and E. D. Park, *Appl. Catal. A*, 2008, **334**, 129-136.
- [2] S. Satokawa, Y. Kobayashi and H. Fujiki, *Appl. Catal. B*, 2005, **56**, 51-56.
- [3] R. Barzamini, C. Falamaki and R. Mahmoudi, *Fuel*, 2014, **130**, 46-53.
- [4] K. Shimizu, S. Komai, T. Kojima, S. Satokawa and A. Satsuma, *J. Phys. Chem. C*, 2007, **111**, 3480-3485.
- [5] J. M. Palomino, D. T. Tran, J. L. Hauser, H. Dong and S. R. J. Oliver, *J. Mater. Chem. A*, 2014, **2**, 14890-14895.