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Electronic Supplementary Information

Near-infrared Absorbance Properties of Cu_{2-x}S/SiO₂ Nanoparticles and

Their PDMS-based Composites

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Figure S1. XRD patterns of the $Cu_{2-x}S$ NPs prepared at ascorbic acid concentrations of (a) 0 M, (b) 0.1 M, (c) 0.3 M, and (d) 0.5 M. The bars are from the JCPDS standards for CuS (06-0464) and $Cu_{1.8}S$ (47-1748).



Figure S2. Size histograms of (a) CuS, (b) Cu_{1.8}S, (c) CuS/SiO₂, and (d) Cu_{1.8}S/SiO₂ NPs.



Figure S3. The absorbance spectra of the CuS and $Cu_{1.8}S$ NPs.



Figure S4. The FT-IR spectra of the (a) CuS, (b) CuS/SiO₂, (c) Cu_{1.8}S, and (d) Cu_{1.8}S/SiO₂ NPs.



Figure S5. The absorption spectra of the photocatalytic degradation of a methylene blue solution in the presence of (a) CuS and (b) CuS/SiO₂ NPs under lamp irradiation for 30 min.



Figure S6. (a) The photocatalytic activity and (b) kinetic rate of photo-degradation of methylene blue in the presence of CuS and CuS/SiO₂ NPs under lamp irradiation for 30 min.

Photocatalytic properties

Previous reports have shown that copper sulfide is a highly-effective photocatalyst due to its narrow band gap.¹⁻⁵ In the catalytic reaction over copper sulfide, H_2O_2 plays an important role because this reaction is similar to a Fenton reaction.³ Hydroxyl radicals, which are capable of degrading organic compounds, can be efficiently generated in the presence of H₂O₂.^{4,5} To demonstrate the photo-degradation ability of CuS NPs, we investigated the photocatalytic activity using methylene blue as an organic dye. Fig. S5 shows the time-dependent absorption spectra of a methylene blue solution with different photocatalysts under lamp irradiation. The concentration of MB was observed by measuring the absorbance at a wavelength of 665 nm, which is characteristic of MB. Indeed, the decrease of the absorbance at 665 nm indicates the photo-degradation efficiency of MB. It is clearly demonstrated that the maximum absorbance peak decreases over CuS and CuS/SiO2 NPs after 30 min of irradiation, as shown in Fig. S5. It should be noted that the CuS NPs led to complete photo-degradation after 30 min, as shown in Fig. S5 (a). Fig. S6 indicates the photocatalytic activity and kinetic rate of photo-degradation using the absorbance intensity at 665 nm. Remarkably, only 6.80 % of MB was degraded in 30 min when the silica-treated CuS NPs were used as a photocatalyst. The photo-degradation efficiency of the CuS/SiO₂ NPs is much less than that of CuS NPs. It is well known that the silica coating can reduce the photocatalytic activity by acting as a passivation layer. Thus, the silica layer prohibits the photo-degradation reaction of MB on the surface of CuS NPs.



Figure S7. UV-vis spectra of (a) CuS - PDMS and (b) CuS/SiO₂ - PDMS films with respect to the high-temperature and high-humidity test time (85 $^{\circ}$ C - 85% test) for 1 week.



Figure S8. Typical photographs of the CuS - PDMS film before and after the high-temperature and high-humidity test (85 °C - 85% test).



Figure S9. PL spectrum changes of 5 x 10^{-4} M basic solution of terephthalic acid with (a) CuS and (b) CuS/SiO₂ NPs during light irradiation.

Reference

- 1. W. Xu, S. Zhu, Y. Liang, Z. Li, Z. Cui, X. Yang and A. Inoue, Sci. Rep., 2015, 5.
- 2. J. Huang, Y. Wang, C. Gu and M. Zhai, Mater. Lett., 2013, 99, 31-34.
- 3. Z. Li, L. Mi, W. Chen, H. Hou, C. Liu, H. Wang, Z. Zheng and C. Shen, CrystEngComm, 2012, 14, 3965-3971.
- 4. M. Tanveer, C. Cao, Z. Ali, I. Aslam, F. Idrees, W. S. Khan, F. K. But, M. Tahir and N. Mahmood, *CrystEngComm*, 2014, **16**, 5290-5300.
- 5. J. Kundu and D. Pradhan, ACS Appl. Mater. Inter., 2014, 6, 1823-1834.