Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Core-Shell Structured CaS:Eu^{2+}@CaZnOS via Inward Erosion Growth to Realize a Super Stable Chalcogenide Red Phosphor

Xiaofang Wang,[†a] Zhongxian Qiu,[†a] Yanmei Li,[a] Qinghua Mi,[b] Wenli Zhou,[a] Shiyun Ai,[b] Jing Xu,[b] Yongfu Liu,[c] Shixun Lian[*a]

[a] Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Key Laboratory of Sustainable Resources Processing and Advanced Materials of Hunan Province, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China.

[b] College of Chemistry and Material Science, Shandong Agricultural University, Tai’an, Shandong, 271018, P. R. China.

[c] Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences (CAS), Ningbo, 315201, China

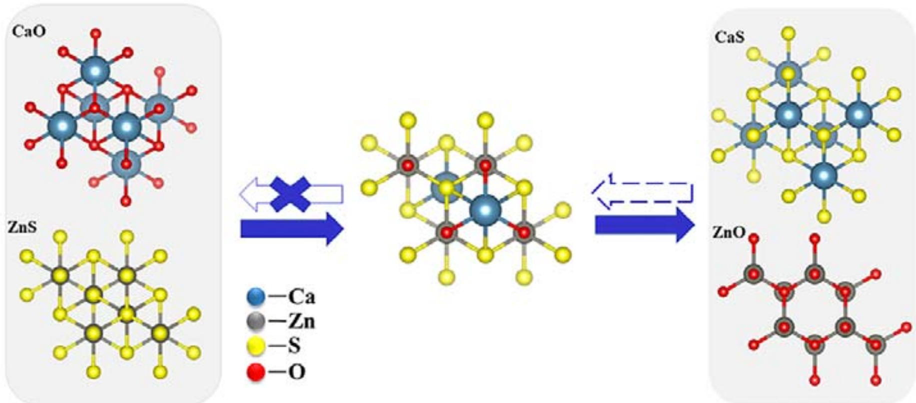

Figure S1. Schematic diagram of the crystal structures of the oxysulfide CaZnOS and the corresponding oxide/sulfide reactant counterparts. The arrows imply the combination or decomposition reactions based on ion-exchange crystal growth process. Solid arrows represent completely spontaneous reactions, the dotted arrow represents incomplete ion exchange, and the hollow arrow with a cross corresponds to an impossible process.

Especially, the similar local cationic symmetric structures in hexagonal ZnS (ZnS_4 tetrahedral coordination) and hexagonal CaZnOS (parallel ZnS_3O tetrahedra connected by CaO layer) guarantee an easy formation of this oxysulfide from the precursors of ZnS and CaO. By contrast, the remarkable difference of the cationic local structures between ZnO/CaS counterparts and CaZnOS leads to incomplete ion exchange between the reactants. Furthermore, upon heating above 1000 ℃, CaZnOS will gradually decompose into CaS and ZnO. As a result, the solid state reaction between CaS and

ZnO always results in CaZnOS/CaS/ZnO mixture instead of pure CaZnOS, which lays a foundation for the formation of CaZnOS coating layer on CaS micro-particles using ZnO nano-powders.

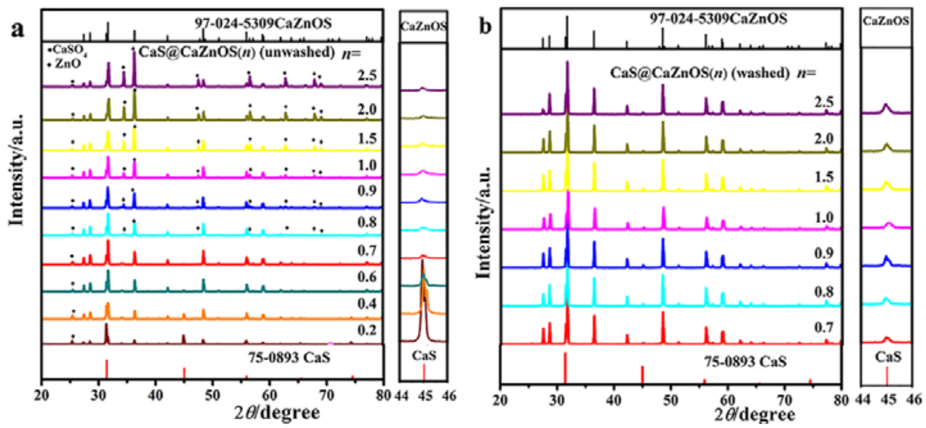

Figure S2. XRD patterns of CaS@CaZnOS(*n*) before (a) and after (b) washing. *n* refers to the ratios of starting reactants, i.e., CaS : *n*ZnO.

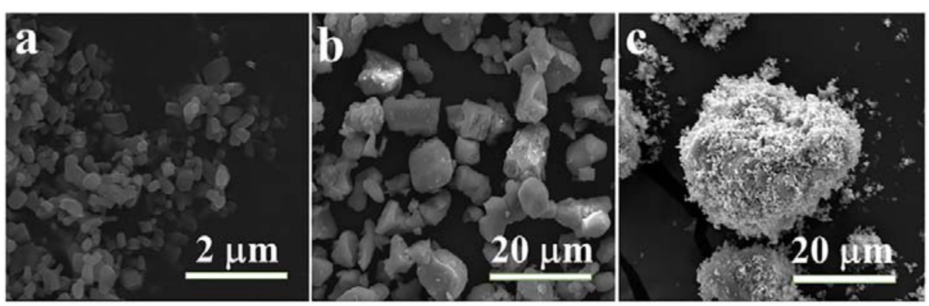

Figure S3. SEM images of the starting materials ZnO (a), CaS:Eu^{2+} (b) and the reactant mixture (c).

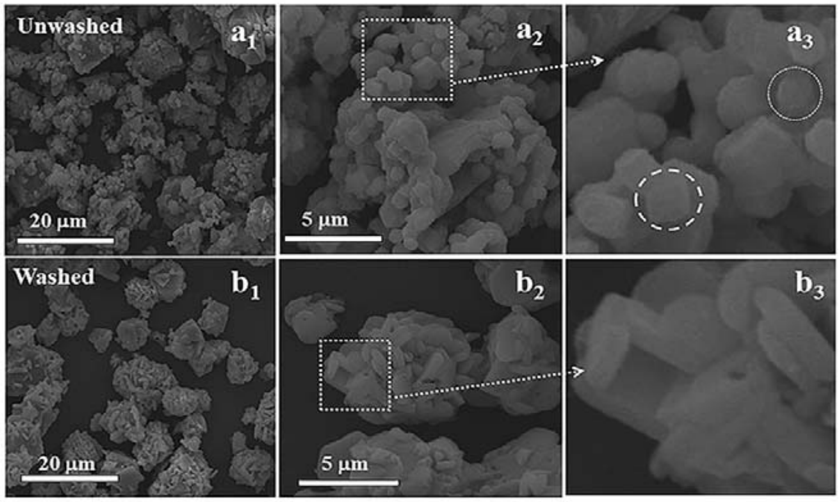

Figure S4. SEM images of the unwashed (a_{1-3}) and washed (b_{1-3}) CaS@CaZnOS(0.9).

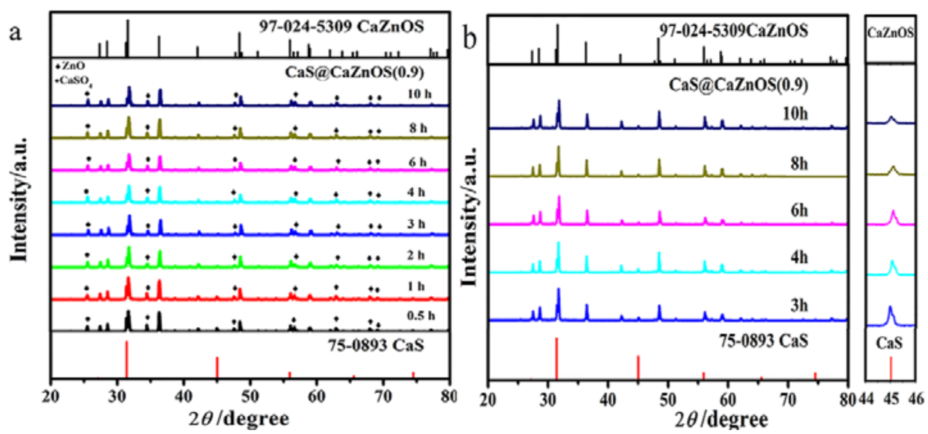

Figure S5. XRD patterns of CaS@CaZnOS(0.9) phosphors with different sintering time before (a) and after (b) washing.

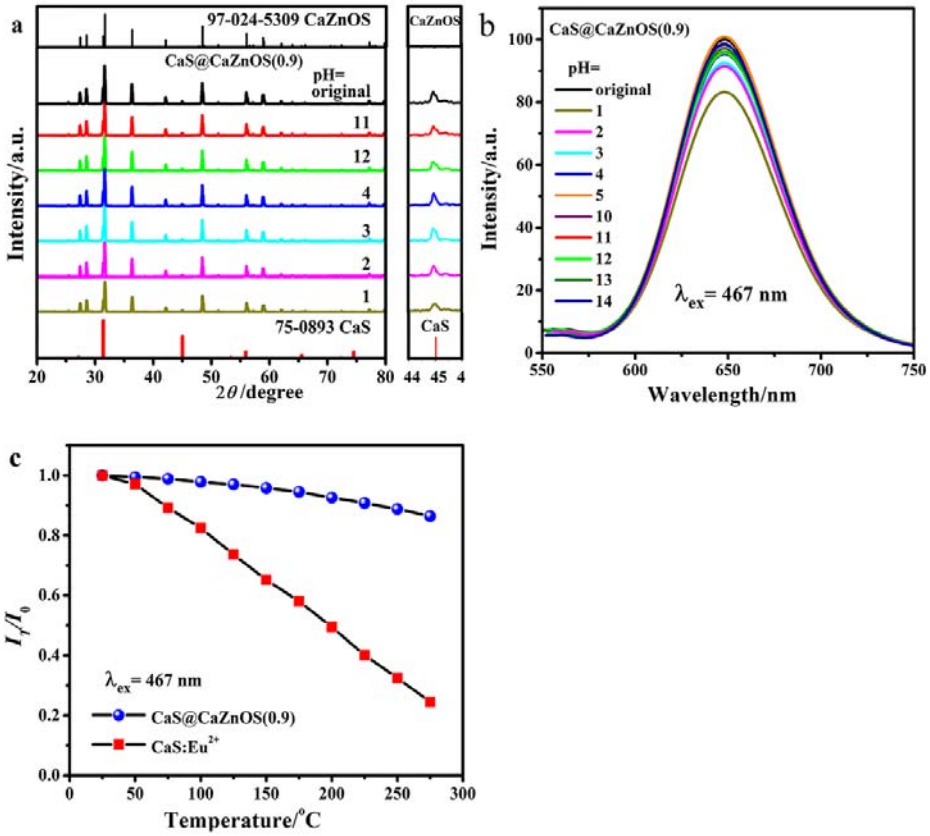

Figure S6. The representative XRD patterns (a) and emission spectra (b) of CaS@CaZnOS(0.9) phosphors after further washing treatment with water or HCl/NaOH solutions with various pH = 1-14, (c) The dependency of emission intensities of CaS:Eu^{2+} and CaS@CaZnOS(0.9) as functions of temperatures.