Supporting Information for

Core-Shell Structured Ce_2S_3@ZnO and Their Potential as Pigment

Wen-Xin Mao [a,b], Wei Zhang [b], Zi-Xiang Chi [b], Rong-Wen Lu [*a], An-Min Cao [*b], and Li-Jun Wan [*b]

E-mail address: lurw@dlut.edu.cn, anmin_cao@iccas.ac.cn, wanlijun@iccas.ac.cn

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China.*

[b] *Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China.*

Experimental Section

Chemicals

Ce_2S_3 (Alfa Aesar), Zinc acetate ($ZnAc_2 \cdot 2H_2O$, Alfa Aesar), Hexamethylenetetramine (HMTA, Alfa Aesar), Ascorbic acid (AA, Alfa Aesar), ethanol (Alfa Aesar). All chemicals were used without further purification and all solutions were prepared using ultrapure water (resistance >18 MΩ cm^{-1}).

Preparation Ce_2S_3@ZnO Core−Shell particles.

First, a calculated amount of $Zn(Ac)_2 \cdot 2H_2O$ and Ascorbic acid (10 mM $Zn(Ac)_2 \cdot 2H_2O$ and 2 mM AA) was added to 50 ml water and this step is targeted to make Zn^{2+} interact with AA to form a Zn^{2+}-AA complexion which plays a key role in the formation of Ce_2S_3@ZnO.[1] Because of the size of Ce_2S_3 particles is large (average diameter is 1 μm) and to make sure that every core particle can be coated with a uniform ZnO layer, 0.5-2.0 molar ration of Zn^{2+}/Ce_2S_3 is effective to form well dispersed Ce_2S_3@ZnO particles. Finally, 20 mM HMTA was then added to cause ZnO formation. Because HMTA can hydrolyze in water to give NH_3,[2, 3] so that the basicity of the solution was

changing slowly, which can ensure the reacting environment suitable for controlled hydrolysis and this is critical in the synthesis process. After sealing and vortexing for 30 s, the reaction mixture was incubated at 90 ℃ for 3 h.

To isolate the Ce_2S_3@ZnO core-shell particles, the reaction mixture was centrifuged at 7500 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water and ethanol 2 times each, then were collected at the bottom of the Eppendorf tubes.

Characterization

The morphology of the final products was observed y SEM (JEOL 6701F, operating at 10kV). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2100F (JEOL) operated at 200kV. X-ray diffraction (XRD) measurement was carried out using a Rigaku D/max2500 diffractometer with filtered Cu Kα radiation, and the data were collected from 10° to 80°. The compositional analysis is done with inductively coupled plasma atomic emission spectroscopy (ICP-AES). The color performance was carried out by a Color-Eye 7000A. H_2S absorption measurement was performed by a NS-4003 series gas-sensing measurement system. 5 g of each pigment powders was put into a 10 L sealed container. With temperature increasing, the volume of H_2S released by pigment was increasing and the sensitivity reflected the concentration of H_2S.[4, 5]

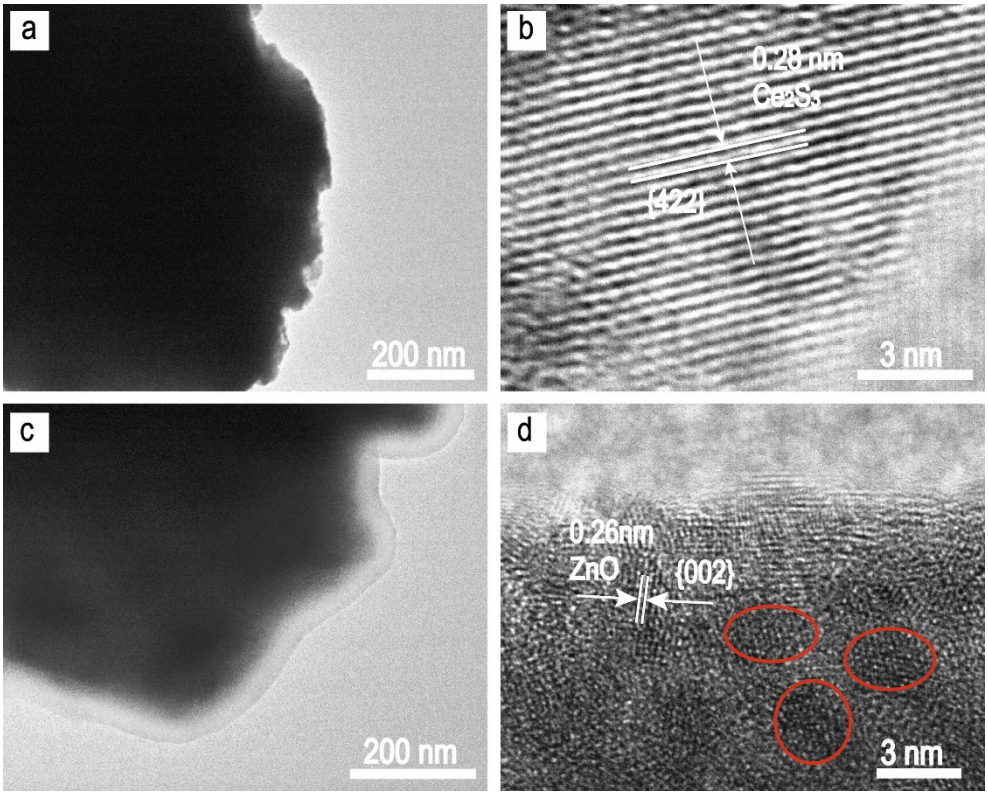

Figure. S1 TEM images of (a) Ce_2S_3 and (b) HRTEM image of crystal lattice of Ce_2S_3. (c) TEM image of Ce_2S_3 with a uniform ZnO layer and (d) HRTEM image of ZnO layer with a huge number of small and randomly oriented nanocrystallines.

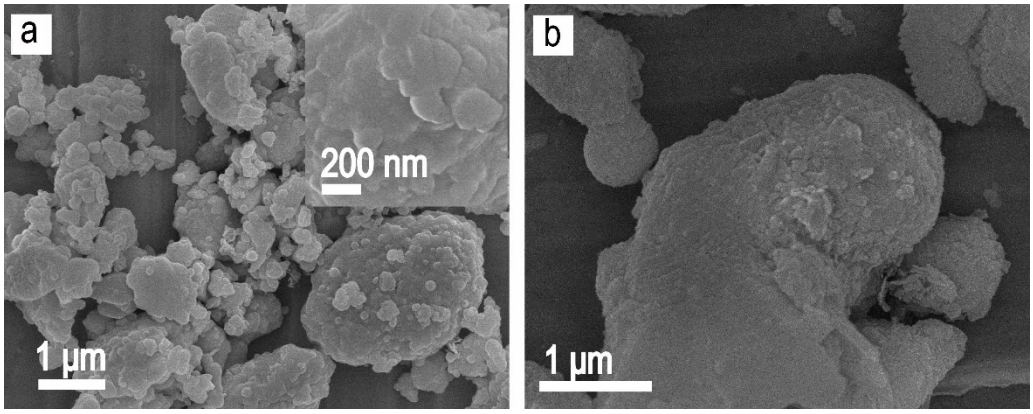

Figure. S2 SEM images of Ce_2S_3 with 12 nm ZnO nanoshell

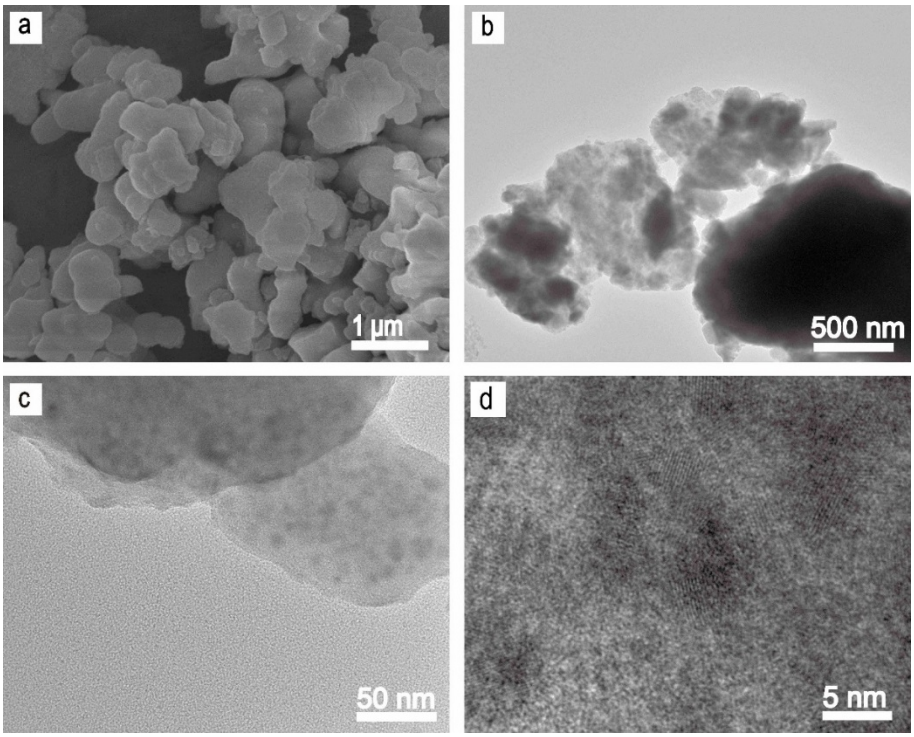

Figure. S3 Commercial sample of Ce_2S_3-ZnO

References

1. H. A. Tajmir-Riahi, *J. Inorg. Biochem.*, 1991, **42**, 47-55.

2. S. Xu and Z. L. Wang, *Nano Res.*, 2011, **4**, 1013-1098.

3. H. Sun, J. T. He, J. Y. Wang, S. Y. Zhang, C. C. Liu, T. Sritharan, S. Mhaisalkar, M. Y. Han, D. Wang and H. Y. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 9099-9110.

4. L. Mei, J. Deng, X. Yin, M. Zhang, Q. Li, E. Zhang, Z. Xu, L. Chen and T. Wang, *Sens. Actuators, B*, 2012, **166–167**, 7-11.

5. E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan and Z. L. Wang, *Appl. Phys. Lett.*, 2002, **81**, 1869-1871.