Formation of hierarchical Co₉S₈@ZnIn₂S₄ heterostructured cages as an efficient photocatalyst for hydrogen evolution

Wang, Sibor; Guan, Bu Yuan; Wang, Xiao; Lou, David Xiong Wen

2018

Wang, S., Guan, B. Y., Wang, X., & Lou, D. X. W. (2018). Formation of hierarchical Co₉S₈@ZnIn₂S₄ heterostructured cages as an efficient photocatalyst for hydrogen evolution. *Journal of the American Chemical Society*, 140(45), 15145-15148.
doi:10.1021/jacs.8b07721

<https://hdl.handle.net/10356/138622>

<https://doi.org/10.1021/jacs.8b07721>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Journal of the American Chemical Society*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/jacs.8b07721>

Downloaded on 26 Apr 2023 23:11:09 SGT

Formation of Hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ Heterostructured Cages as An Efficient Photocatalyst for Hydrogen Evolution

Sibo Wang, Bu Yuan Guan, Xiao Wang, and Xiong Wen (David) Lou*

School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore

Supporting Information Placeholder

ABSTRACT: Here we demonstrate the delicate design and construction of hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cages as an efficient photocatalyst for hydrogen evolution with visible light. Two photoactive sulfide semiconductors are rationally integrated into a hierarchical hollow structure with strongly coupled heterogeneous shells and two-dimensional ultrathin subunits. The unique architecture can efficiently facilitate the separation and transfer of light-induced charges, offer large surface area, and expose rich active sites for photocatalytic redox reactions. Owing to the distinctive structural and compositional benefits, the hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ hollow heterostructures without using any cocatalysts show remarkable activity with a hydrogen-producing rate of $6250 \mu\text{mol h}^{-1} \text{g}^{-1}$ and high stability for photocatalytic water splitting.

The photocatalytic splitting of water with sunlight is an ideal approach to produce clean hydrogen (H_2) fuel in a sustainable manner.¹⁻³ So far, numerous semiconductor materials have been developed as photocatalysts for H_2 evolution, but the majority of them suffer from low photocatalytic activity.⁴⁻¹⁰ One main reason for the unsatisfactory efficiency of H_2 evolution is the inefficient separation and transport of light-stimulated charge carriers.

Metal sulfides (e.g., Co_9S_8 , ZnIn_2S_4) are attracting rising attention for water photosplitting because of their unique electronic and optical characteristics.¹¹⁻¹⁷ In particular, the rational coupling of metal sulfide semiconductors with proper band structures can effectively accelerate the separation and transfer of photoexcited charges due to the potential gradient between the heterogeneous interfaces.¹⁸⁻²⁰ Meanwhile, hybrid photocatalysts can also achieve improved photostability and optical harvesting.^{21,22} These advantages may render the heterostructures with reinforced photocatalytic performance. Besides the control in chemical composition, the realization of highly efficient photocatalytic reactions also strongly depends on the delicate design of the catalysts with appropriate structures.

Recently, hollow structured materials have been intensively studied as photocatalysts for solar energy conversion.²³⁻²⁷ The hollow architectures can not only shorten the bulk-to-surface distance to expedite the separation of photo-

generated charges, but also afford large surface area and abundant active sites to promote redox reactions.¹⁸ In addition, hollow particles, particularly polyhedral cages, can strengthen photoabsorption by internal multi-light scattering/reflection.^{14,25,27} Furthermore, the growth of two-dimensional (2D) semiconductor nanosheets on the polyhedral cages is highly favorable to reduce diffusion length for charges and enhance exposed catalytic active sites.²⁸ As a result, integration of all the considerations mentioned above may greatly contribute to the creation of new photocatalysts with high efficiency for solar-to-hydrogen energy conversion.

Figure 1. Schematic illustration of the synthetic process of hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cage: (I) sulfidation reaction and thermal treatment in argon atmosphere, and (II) growth of ZnIn_2S_4 NSs.

Herein, we demonstrate the rational design and construction of hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cages by growing ZnIn_2S_4 nanosheets (NSs) on the surface of Co_9S_8 dodecahedral cages as an efficient photocatalyst for H_2 evolution. The overall synthetic route for building the intricate hollow architectures is schematically illustrated in Figure 1. Starting with a zeolitic imidazolate framework-67 (ZIF-67) polyhedron as the precursor, a Co_9S_8 dodecahedral cage with high quality is produced via a sulfidation reaction and a subsequent thermal treatment (step I).²⁹ Afterward, the hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructure is produced by growing a layer of ZnIn_2S_4 NSs on the surface of the Co_9S_8 cage through a solvothermal process (step II). The complex $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ hollow architectures with hybrid shells and ultrathin NS subunits can promote the separation and transport of electron-hole pairs, offer large surface area, and disclose a lot of active sites for heterogeneous photoredox catalysis. Accordingly, the optimized $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ composites manifest superior activity and high stability for visible-light-splitting of water, affording a remarkable cocatalyst-free H_2 production rate of $6250 \mu\text{mol h}^{-1} \text{g}^{-1}$.

Uniform ZIF-67 dodecahedral particles are synthesized through a modified precipitation method (Figure S1).³⁰ Powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analyses confirm the formation of ZIF-67 (Figure S2). The as-obtained ZIF-67 is then converted to amorphous co-

balt sulfide (denoted as CoS_x) through a liquid phase sulfidation reaction (Figure S3).³¹ During the sulfidation process, the sulfide ions released from the decomposition of thioacetamide react with the cobalt ions on the surface of ZIF-67 and generate an outermost layer of CoS_x . Further reactions between the inward diffusing sulfide ions and the outward diffusing metal ions supply the growth of the CoS_x shell and finally lead to the formation of the CoS_x hollow structure.³² Field-emission scanning electron microscopy (FESEM) images show that the CoS_x particles well inherit the polyhedral morphology of their ZIF-67 precursors (Figure 2a and Figure S4a,b). Transmission electron microscopy (TEM) images validate the hollow structure of CoS_x particles (Figure 2b and Figure S4c). The amorphous nature of CoS_x is further confirmed by the selected area electron diffraction (SAED) pattern (Figure S4d). After an annealing treatment in argon atmosphere, the amorphous CoS_x is transformed to the Co_9S_8 phase (JCPDS card no.: 86-2273; Figure S5), and its dodecahedral morphology and hollow architecture are retained (Figure 2c-e and Figure S6a-c). Consistent with the XRD analysis, a set of distinct lattice fringes with spacing of 0.28 nm can be identified as the (222) planes of cubic Co_9S_8 (Figure 2f). The SAED pattern further indicates the polycrystalline nature of the Co_9S_8 material (Figure S6d). N_2 sorption measurements reveal that the Co_9S_8 particles possess a porous structure with a high Brunauer-Emmett-Teller (BET) surface area of about $81 \text{ m}^2 \text{ g}^{-1}$ (Figure S7).

Figure 2. (a,c) FESEM images and (b,d,e) TEM images of (a,b) CoS_x cages and (c-e) Co_9S_8 cages, and (f) HRTEM image of Co_9S_8 cage.

Subsequently, ultrathin ZnIn_2S_4 NSs are assembled on the surface of Co_9S_8 dodecahedral cages through a low-temperature solvothermal reaction (Figure S8). FESEM images reveal that the ZnIn_2S_4 NSs are homogeneously coated on the surface of Co_9S_8 cages (Figure 3a and Figure S9a), forming the hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cages. The magnified FESEM image presents the polyhedral shape of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ (Figure 3b), and its surface is composed of randomly assembled ZnIn_2S_4 NS subunits (Figure 3c). The hierarchical hollow configuration of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is further demonstrated by the TEM images (Figures 3d,e). The HRTEM image of the outmost ZnIn_2S_4 NSs displays clear lattice fringes with interlayer spacing of 0.32 nm assigned to the (102) crystal plane of hexagonal ZnIn_2S_4 (Figure 3f). The successful formation of the heterostructure of Co_9S_8 and ZnIn_2S_4 in nanodomains is revealed by SAED pattern, in which the two sets of diffraction fringes are indexed to Co_9S_8

and ZnIn_2S_4 , respectively (Figure S9b). The closer examinations on the shell of a $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ particle reveal that no noticeable inter-shell gap can be observed (Figure S9c,d), suggesting the tight heterogeneous coupling between the Co_9S_8 cage and ZnIn_2S_4 NS subunits. HRTEM image of the shell of a single $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cage also reveals the strong integration of the two sulfide semiconductors (Figure S9e). The valence states of the elements in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ are examined by X-ray photoelectron spectroscopy (XPS, Figure 3g and Figure S10). As can be seen, the binding energies of Co 2p shift from 778.3 and 793.6 eV in Co_9S_8 to 778.5 and 793.3 eV in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$. The results further demonstrate the existence of strong interaction between Co_9S_8 and ZnIn_2S_4 .^{14,33} The tight growth of ZnIn_2S_4 NSs on Co_9S_8 cages favors the formation of intimate interfacial contacts, which is highly favorable for efficient charge-separation/-transfer in the hybrids.³⁴ The N_2 sorption isotherms and the corresponding pore size distribution curve indicate the existence of mesopores in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ (Figure 3h, and Figure S11), which will facilitate the mass transfer for heterogeneous catalysis.³⁵

Figure 3. (a-c) FESEM images and (d,e) TEM images of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cages, (f) HRTEM image of ZnIn_2S_4 NS, (g) Co 2p XPS spectra of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ and Co_9S_8 , and (h) N_2 sorption isotherms of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$.

The time-dependent structural evolution of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is monitored by FESEM and TEM, and the results endorse a surface growth mechanism of ZnIn_2S_4 NSs on Co_9S_8 cages (Figure S12). Moreover, the mass ratio of Co_9S_8 to ZnIn_2S_4 in the heterostructures can also be controlled by adjusting the amount of Co_9S_8 particles added in the reaction system. 15%- $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ (Figures S13 and S14) and 30%- $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ (Figures S15 and S16) particles with different compositions are fabricated as two control samples (see Supporting Information for the detailed synthesis). The content of Co_9S_8 in the optimized $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructure is about 31% determined by EDX. In addition, ZnIn_2S_4 particles (Figures S17 and S18) and $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$

nanoparticles (NPs, Figures S19 and S20) are also synthesized for comparison under similar conditions.

UV-Vis diffuse reflectance spectra (DRS) indicate all the $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ hybrids manifest strong visible light absorption (Figure S21). The band gaps of Co_9S_8 and ZnIn_2S_4 are estimated to be about 0.97 and 2.12 eV, respectively (Figure S22).^{14,18} Besides, Mott-Schottky plots of the materials are collected to define their conduction band (CB) positions (Figure S23). The derived flat-band potentials of Co_9S_8 and ZnIn_2S_4 are about -0.75 and -0.95 V (vs. normal hydrogen electrode, NHE).^{14,18} Therefore, the band structures of Co_9S_8 and ZnIn_2S_4 are determined, which endows the proper redox ability of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ for H_2 production (Figure S24). All these observations suggest the potential of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ for visible-light redox catalysis (e.g., water photoreduction).

Figure 4. (a) Photocatalytic H_2 evolution performance of different samples. (b) Time-yield plots of H_2 . (c) H_2 generation rate in every four-hour-reaction for successive 5 cycles. (f) H_2 production under photoirradiation of different wavelengths.

Figure 4a depicts the photocatalytic water splitting performance of different samples under visible light irradiation ($\lambda \geq 400$ nm) with triethanolamine (TEOA) as the hole scavenger. The NS-assembled ZnIn_2S_4 particles are active to catalyze the splitting of water, giving a H_2 -evolving rate of 2160 $\mu\text{mol h}^{-1} \text{g}^{-1}$. Nonetheless, after assembling the ZnIn_2S_4 NSs on Co_9S_8 cages, the three $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ hollow composites manifest substantially improved activities with the highest H_2 formation rate of 6250 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which indicates that the mass ratio of the components in the heterostructure greatly affects the catalytic performance. Such a noble-metal-free H_2 generation rate is comparable to that of other works reported recently (Table S1). The solid $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ NPs with the optimized composition exhibit a H_2 production rate of 4650 $\mu\text{mol h}^{-1} \text{g}^{-1}$, inferior to that of the $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cages. This result demonstrates the advantage of hollow structure for the photocatalytic reaction. The bare Co_9S_8 sample is almost inactive, probably because of the high recombination rate of photoexcited charges. The $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ hybrid is found to be durable to release H_2 during the period of 6 h, while the H_2 -forming rate of ZnIn_2S_4 decreases obviously after photoreaction for 3 h (Figure 4b). These findings highlight the superior water photosplitting

performance of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$, which should benefit from the unique hierarchical hollow heterostructures enabling the efficient separation and transfer of photo-triggered charge carriers.

The stability of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is evaluated by operating the reaction for 20 h and the H_2 yielding rate in every four-hour-reaction is calculated. No apparent deactivation is observed in the successive 5 cycles (Figure 4c), suggesting the high stability of the composite photocatalyst. The stability of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is also supported by the XRD and FESEM characterizations of the sample after photocatalysis (Figure S25). Furthermore, the reaction system is further examined under light irradiation of different wavelengths. The results show that the H_2 generation activity of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is strongly dependent on the wavelength of incident light (Figure 4d), indicating the water splitting reaction is indeed initiated by light excitation of the photocatalyst.³⁶

To gain some insights into the high performance of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$, various photo-/electro-chemical characterizations are carried out. Time-resolved photoluminescence (TRPL) spectroscopy is utilized to probe the charge carrier dynamics of the materials (Figure 5a). The decay kinetics of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ exhibits longer average lifetime (5.43 ns) than that of ZnIn_2S_4 (3.88 ns), which indicates the former can effectively promote the separation of photoinduced electrons and holes. Moreover, steady-state PL quenching reveals the prohibited recombination of light-excited charges in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ (Figure 5b). On the other hand, electrochemical impedance spectra (EIS) show that $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ possesses a smaller high-frequency semicircle than the sole counterparts (Figure 5c), signifying a lower charge-transfer resistance in the hybrid that ensures the faster electron transfer. The accelerated charge transport kinetics in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is also reflected by the increased current response in transient photocurrent spectra (Figure 5d). These results of photo-/electro-chemical studies verify the improved separation and migration of light-generated charges in $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$, thus leading to the remarkable performance of photocatalytic H_2 evolution.

Figure 5. (a) TRPL spectra, (b) steady-state PL spectra, (c) EIS spectra, and (d) transient photocurrent spectra of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$, ZnIn_2S_4 and Co_9S_8 .

In summary, hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cages are synthesized by growing ultrathin ZnIn_2S_4 nanosheets on Co_9S_8 dodecahedral cages as an efficient photocatalyst for visible-light-driven water splitting. The synthetic approach can tailor the structure and composition of the hierarchical hybrid materials. These complex hollow architectures with strongly coupled heterogeneous shells and two-dimensional ultrathin subunits possess large surface area and rich reactive sites and can expedite the separation and transfer of light-induced charges. Consequently, the $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructures without the aid of any co-catalysts exhibit considerable activity and high stability for photocatalytic H_2 evolution.

ASSOCIATED CONTENT

Supporting Information

The experimental details, more FESEM/TEM images, XRD, EDX, DRS, XPS, and Mott-Schottky plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Email: xwlou@ntu.edu.sg

Notes

The authors declare no competing financial interests.

ACKNOWLEDGEMENTS

X. W. L. acknowledges the funding support from the National Research Foundation (NRF) of Singapore via the NRF investigatorship (NRF-NRFI2016-04).

REFERENCES

- Hisatomi, T.; Kubota, J.; Domen, K. *Chem. Soc. Rev.* **2014**, *43*, 7520.
- Maeda, K.; Higashi, M.; Lu, D.; Abe, R.; Domen, K. *J. Am. Chem. Soc.* **2010**, *132*, 5858.
- Xie, J.; Shevlin, S. A.; Ruan, Q.; Moniz, S. J. A.; Liu, Y.; Liu, X.; Li, Y.; Lau, C. C.; Guo, Z. X.; Tang, J. *Energy Environ. Sci.* **2018**, *11*, 1617.
- Banerjee, T.; Haase, F.; Savasci, G.; Gottschling, K.; Ochsenfeld, C.; Lotsch, B. V. *J. Am. Chem. Soc.* **2017**, *139*, 16228.
- Ran, J.; Guo, W.; Wang, H.; Zhu, B.; Yu, J.; Qiao, S. Z. *Adv. Mater.* **2018**, *30*, 1800128.
- Li, H.; Sun, Y.; Yuan, Z. Y.; Pei, Z. Y.; Ma, T. Y. *Angew. Chem. Int. Ed.* **2018**, *57*, 3222.
- Kuriki, R.; Ichibha, T.; Hongo, K.; Lu, D.; Maezono, R.; Kageyama, H.; Ishitani, O.; Oka, K.; Maeda, K. *J. Am. Chem. Soc.* **2018**, *140*, 6648.
- Zhu, M.; Kim, S.; Mao, L.; Fujitsuka, M.; Zhang, J.; Wang, X.; Majima, T. *J. Am. Chem. Soc.* **2017**, *139*, 13234.
- Meng, N.; Ren, J.; Liu, Y.; Huang, Y.; Petit, T.; Zhang, B. *Energy Environ. Sci.* **2018**, *11*, 566.
- Wang, K.; Yang, L. M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Jin, S.; Tan, B.; Cooper, A. *Angew. Chem. Int. Ed.* **2017**, *56*, 14149.
- Yang, W.; Zhang, L.; Xie, J.; Zhang, X.; Liu, Q.; Yao, T.; Wei, S.; Zhang, Q.; Xie, Y. *Angew. Chem. Int. Ed.* **2016**, *55*, 6716.
- Yang, M. Q.; Xu, Y. J.; Lu, W.; Zeng, K.; Zhu, H.; Xu, Q. H.; Ho, G. W. *Nat. Commun.* **2017**, *8*, 14224.
- Liu, M.; Chen, Y.; Su, J.; Shi, J.; Wang, X.; Guo, L. *Nat. Energy* **2016**, *1*, 16151.
- Qiu, B.; Zhu, Q.; Du, M.; Fan, L.; Xing, M.; Zhang, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 2684.
- Zhang, J.; Yu, J.; Zhang, Y.; Li, Q.; Gong, J. R. *Nano Lett.* **2011**, *11*, 4774.
- Shi, W.; Zhao, X.; Feng, J.; Liu, J.; Yang, G.; Wang, G.; Cheng, P. *Angew. Chem. Int. Ed.* **2018**, *57*, 9790.
- Cao, S.; Chen, Y.; Wang, H.; Chen, J.; Shi, X.; Li, H.; Cheng, P.; Liu, X.; Liu, M.; Piao, L. *Joule* **2018**, *2*, 549.
- Wang, S.; Guan, B. Y.; Lou, X. W. *J. Am. Chem. Soc.* **2018**, *140*, 5037.
- Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. *Chem. Soc. Rev.* **2014**, *43*, 5234.
- Tsuji, I.; Kato, H.; Kudo, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3565.
- Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A. *J. Am. Chem. Soc.* **2016**, *138*, 10260.
- Wang, S.; Guan, B. Y.; Lu, Y.; Lou, X. W. *J. Am. Chem. Soc.* **2017**, *139*, 17305.
- Zheng, D.; Cao, X. N.; Wang, X. *Angew. Chem. Int. Ed.* **2016**, *55*, 11512.
- Li, A.; Wang, T.; Chang, X.; Cai, W.; Zhang, P.; Zhang, J.; Gong, J. *Chem. Sci.* **2016**, *7*, 890.
- Wang, S.; Guan, B. Y.; Lou, X. W. *Energy Environ. Sci.* **2018**, *11*, 306.
- Zhu, T.; Wu, H. B.; Wang, Y.; Xu, R.; Lou, X. W. *Adv. Energy Mater.* **2012**, *2*, 1497.
- Sun, J.; Zhang, J.; Zhang, M.; Antonietti, M.; Fu, X.; Wang, X. *Nat. Commun.* **2012**, *3*, 1139.
- Zhang, M.; Wang, X. *Energy Environ. Sci.* **2014**, *7*, 1902.
- Zhang, H.; Nai, J.; Yu, L.; Lou, X. W. *Joule* **2017**, *1*, 77.
- Hu, H.; Han, L.; Yu, M.; Wang, Z.; Lou, X. W. *Energy Environ. Sci.* **2016**, *9*, 107.
- Yu, L.; Yang, J. F.; Lou, X. W. *Angew. Chem. Int. Ed.* **2016**, *55*, 13422.
- Shen, L.; Yu, L.; Wu, H. B.; Yu, X. Y.; Zhang, X.; Lou, X. W. *Nat. Commun.* **2015**, *6*, 6694.
- Zhu, H.; Zhang, J.; Yanzhang, R.; Du, M.; Wang, Q.; Gao, G.; Wu, J.; Wu, G.; Zhang, M.; Liu, B.; Yao, J.; Zhang, X. *Adv. Mater.* **2015**, *27*, 4752.
- Chen, Y.; Tian, G.; Ren, Z.; Pan, K.; Shi, Y.; Wang, J.; Fu, H. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13841.
- Wang, X.; Maeda, K.; Chen, X.; Takanabe, D.; Domen, K.; K.; Hou, Y.; Fu, X.; Antonietti, M. *J. Am. Chem. Soc.* **2009**, *131*, 1680.
- Ou, H.; Lin, L.; Zheng, Y.; Yang, P.; Fang, Y.; Wang, X. *Adv. Mater.* **2017**, *29*, 1700008.

TOC graphic

Hierarchical Co_9S_8 @ ZnIn_2S_4 Heterostructured Cages for H_2 Evolution