

AgInS₂/In₂S₃ Heterostructure Sensitization of *Escherichia coli* for Sustainable Hydrogen Production

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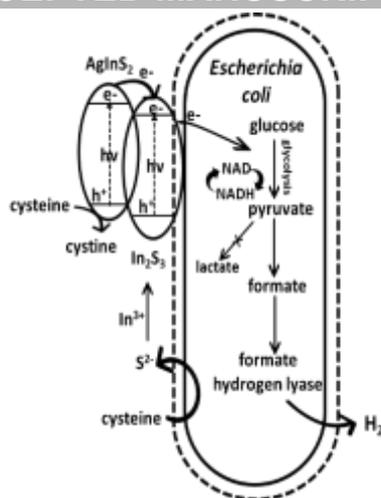
Abstract: Solar-to-chemical production by photosynthetic biohybrid systems does not only take advantage of the broadband light efficiency of semiconductor but also utilize highly specific biological catalytic power in living organism. Herein, we demonstrate a tandem inorganic-biological hybrid by combining AgInS₂/In₂S₃ and a facultative anaerobic bacterium, *Escherichia coli*, for biological H₂ production. The AgInS₂/In₂S₃@*E. coli* hybrid system harvests light energy and makes use of anaerobically synthesized bacterial endogenous [Ni-Fe]-hydrogenase and photo-generated electrons from AgInS₂/In₂S₃ hybrid for enhanced H₂ evolution efficiency. A highly quantum efficiency (QE) of 3.3% at 720 nm for H₂ production is achieved from the hybrid system, exceeding those of many reported photoheterotrophic bacteria. This biomimetic approach may provide a guidance for the interfacing of hybrid semiconductors with living organisms for solar-to-chemical production.

Keywords: AgInS₂/In₂S₃, *Escherichia coli*, biohybrid system, hydrogen production

The utilization of renewable and ecologically friendly solar energy is highly desired due to the depletion of energy resources and environment problems.^[1-3] Solar-driven hydrogen (H₂) evolution has attracted great attention because it provides an ideal strategy by using this clean energy to solve the problem of shortage of finite fossil fuels. Recently, photosynthetic biohybrid systems, which consist of excellent light-absorbing efficiency of inorganic semiconductors and high H₂-forming microorganisms, have attracted great attention. Some photosynthetic biohybrid systems for H₂ evolution have been exploited where purified hydrogenase and/or genetically engineered microorganisms are employed as biocatalysts.^[4] For example, Brown et al.^[5] reported a complex of CdS nanorods with purified [Fe-Fe]-hydrogenase, purified from *Clostridium acetobutylicum*, showed good photochemical activity for H₂ production. Honda et al.^[6] demonstrated that recombinant *E. coli* strain expressed both [Fe-Fe]-hydrogenase and relevant maturases of *C. acetobutylicum* enabled whole cell of bacteria photocatalytically produced H₂ with TiO₂ in the presence of methyl viologen (MV²⁺) as an electron transfer agent. Nevertheless, the usage of purified hydrogenases from specific microbes, genetic engineered microorganisms and/or MV²⁺ will increase the cost of the strategy, thus may limit its widespread application. An alternative approach for sustainable solar-to-chemical production scheme by photosynthetic biohybrid system is the use of whole bacterial cell without any genetic modification and enzyme purification. Recently, a significant breakthrough work has been accomplished by Sakimoto et al.^[7] Their study indicated that bio-precipitation of CdS nanoparticles onto the surface of acetogenic bacterium *Moorella thermoacetica* can facilitate its photoreductive capability of CO₂ to acetic acid. In their following work,^[8] they proved the inorganic semiconductor-to-bacterium electrons transfer mechanism using spectroscopic elucidation. Their results demonstrated that photoexcited electron transfer can promote the bacterial hydrogenase enzyme activity to generate H₂. Inspired by these pioneering studies, we believe that the following two aspects are very important in the construction of photosynthetic biohybrid systems for practical application in the field of solar-to-chemical production: 1) the photo-generated charge carriers should be easily separated, and photo-generated

electrons can quickly transfer to the microorganism without the help of electron transfer agents;^[7] and 2) the microorganism used should be genetic modification free, popular, and can synthesize hydrogenase.

We thus selected an ideal inorganic/whole-cell biohybrid photocatalytic H₂ production system consisting the following two parts: 1) the most well-studied bacterium, *E. coli*, which grows rapidly on a wide range of carbon sources, and 2) a solid-state heterojunction incorporating AgInS₂ with In₂S₃ nanoparticles. *E. coli* can anaerobically synthesize endogenous [Ni-Fe]-hydrogenase without any genetic engineering manipulation,^[9] and can produce H₂ by dark fermentation. Moreover, it is reported that *E. coli* can produce sulfide to precipitate metal ions and form sulfide complexes on the cell surface under aerobic condition.^[10] As an excellent light absorber, the AgInS₂/In₂S₃ junction can afford faster electrical conduction than that of In₂S₃. In this work, In₂S₃ nanoparticles were biologically grown on the surface of *E. coli* by the addition of suitable amount of In³⁺ and cysteine,^[11,12] and AgInS₂ nanoparticles were anchored on the surface of In₂S₃ via an *in-situ* ion exchange method under a mild condition (Supporting Information-experimental section and Figure S1). When the hybrid system was irradiated, both AgInS₂ and In₂S₃ could produce photo-generated electrons and holes. The photogenerated electrons on the conduction band (CB) of AgInS₂ would quickly transfer to the CB of In₂S₃, and finally transfer to *E. coli* to carry out microbial H₂ production (Figure 1). Meanwhile, the photogenerated holes on the valence band (VB) of In₂S₃ would transfer to the VB of AgInS₂, and then oxidize cysteine to cystine (Figure 1) due to the matched band structure between AgInS₂ and In₂S₃ (Supporting Information, Figure S3).^[13-15] This system can enhance the utilization of photo-generated electrons to participate in the microbial H₂ production by suppressing the recombination of photo-generated electrons and holes.



Scheme 1. Schematic pathway diagram for the AgInS₂/In₂S₃@*E. coli* system.

High angle annular dark field (HAADF) scanning transmission microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS) mapping and X-ray photoelectron spectroscopy (XPS) were performed to investigate the surface chemical composition and chemical state of the AgInS₂/In₂S₃@*E. coli* hybrid system. From Figure 1A and B, high densities of bright spots are uniformly dispersed on the surface of *E. coli*. No scattered nanoparticles are observed from the outside of the cell, suggesting the high level interaction between nanoparticles and *E. coli*. High magnification TEM image (Figure S2) indicates that the average size precipitated nanoparticles is about 15-20 nm. The EDS mapping reveals that the bright spots are composed of In, Ag and S (Figure 1C-F). Elements of C and N (Figure 1G and H) are originated from *E. coli* itself. The HAADF-STEM images of thin-sectioned sample indicate that most of the precipitated nanoparticles are located across the periplasmic space of the bacterial cells. The delicate structure perfectly combines the biological and inorganic system, which can effectively facilitate the electron-transfer within the hybrid system. The full scan survey XPS spectrum of the biohybrid system further confirms the presence of In, Ag, S, O, C, P and N elements (Figure 1K). The peaks in the high resolution XPS of In 3d (Figure 1L) at around 444.6 and 451.9 eV correspond to the In 3d_{5/2} and In 3d_{3/2}, respectively, demonstrating the presence of In³⁺ in the AgInS₂/In₂S₃ hybrid system.^[16,17] The Ag 3d spectrum (Figure 1M) consists of two individual peaks at around 368.6 and 374.3 eV,

corresponding to Ag 3d_{5/2} and Ag 3d_{3/2} binding energies, respectively, which can be attributed to Ag⁺.^[18] Furthermore, the minor peak of S 2p XPS (Figure 1N) located at 162.9 eV can be assigned to the sulfur-indium bond, and other peaks may refer to the sulfur present on the *E. coli* cell surface.^[17] XPS results also indicates that the atom ratio of Ag/In is 1/3. As such, all of the above results suggest the successful formation of AgInS₂/In₂S₃ junction.

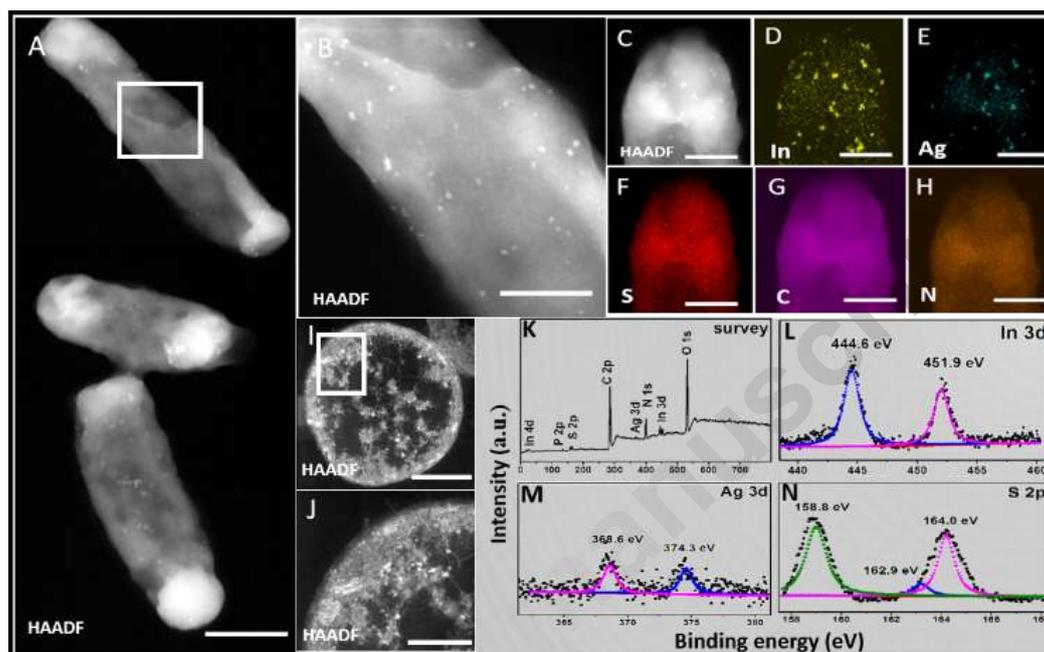


Figure 1. HAADF-STEM images (A, B) of AgInS₂/In₂S₃@*E. coli* hybrid, HAADF image (C) and EDS mapping (D-H) showing the In, Ag, S, C, N, HAADF images (I, J) of the thin-sectioned AgInS₂/In₂S₃@*E. coli* hybrid, full (K) and high resolution XPS spectra of In 3d (L), Ag 3d (M), S 2p (N) for AgInS₂/In₂S₃@*E. coli* hybrid. Scale bars in (A) 500 nm, in (B-I) 200 nm, in (J) 100 nm.

To demonstrate the applicability of the AgInS₂/In₂S₃@*E. coli* hybrid system, photocatalytic H₂ production experiments were carried out (Supporting Information-Experimental Section). From Figure 2A, H₂ produced from the In₂S₃@*E. coli* hybrid system under visible light (> 420 nm, 1400 W m⁻²) irradiation is 1460 μmol, which is much higher than that produced by *E. coli* alone. After the formation of AgInS₂/In₂S₃ on the cell surface of *E. coli* (AgInS₂/In₂S₃@*E. coli*), the H₂ evolution amount (1660 μmol) further increases, which is equivalent to an increase of ~30% as

compared to the untreated *E. coli* culture. During the dark reaction process, it is found that both of $\text{In}_2\text{S}_3@E. coli$ and $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$ systems show similar amount of H_2 produced by *E. coli* alone (the amount of H_2 production by *E. coli* alone in the dark and visible light irradiation are similar), suggesting the extra H_2 produced is ascribed to the effect of precipitated metal sulfide. All these phenomena indicate that the increased H_2 production amount by the as-prepared $\text{In}_2\text{S}_3@E. coli$ and $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$ hybrid systems is related to the photocatalytic enhancement by the biologically precipitated single In_2S_3 nanoparticles and $\text{AgInS}_2/\text{In}_2\text{S}_3$ inorganic hybrid. According to the previous studies concerning on the heterojunctions,^[19,20] we may consider the enhanced H_2 evolution activity can be attributed the heterojunction electric field between AgInS_2 and In_2S_3 , which promotes the photogenerated electron transfer efficiency. The detailed analysis and explanation will be discussed in photochemical section (Figure 3). As reported by Korinenko et al.,^[8] upon photoexcitation, the conduction band electrons of the inorganic semiconductor would transfer to membrane-bound protein of microorganism. In order to investigate electron generation and transduction in our system, a series of control experiments were carried out (Figure 2B, Supporting Information) in which 1) *E. coli* was systematically removed from $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$; 2) equal amount of isolated $\text{AgInS}_2/\text{In}_2\text{S}_3$ hybrid was mixed with *E. coli* (separation study); 3) electron scavenger, Cr(VI) was added (electron-scavenger study). In the absence of *E. coli*, negligible H_2 is detected from $\text{AgInS}_2/\text{In}_2\text{S}_3$ (the heat-treated hybrid system), indicating that the additional H_2 is not directly produced from water splitting by the surface $\text{AgInS}_2/\text{In}_2\text{S}_3$ nanoparticles. No obvious improvement is observed in the H_2 production from the separation study in comparison with that produced from *E. coli* alone, suggests that the close interfacial interaction between the $\text{AgInS}_2/\text{In}_2\text{S}_3$ hybrid and *E. coli* is indispensable for the electron transduction. This result is proved by the electron-scavenger study, which shows that the amount of extra H_2 decreases after the addition of Cr(VI) to the reaction system. As a result, we can conclude that the semiconductor-to-bacterial cell electron transfer mechanism also works on our system. Specifically, when the biohybrid system is irradiated, the photo-generated electrons on the CB of AgInS_2 will

first transfer to the CB of In_2S_3 , then the accumulated electrons on the CB of In_2S_3 will transfer to membrane-bound protein and finally participated in the H_2 evolution process.^[8] QE of the $\text{AgInS}_2/\text{In}_2\text{S}_3$ hybrid was also investigated (Figure 2C, Table S1). The QE of hydrogen production matches well with the UV-Vis absorption spectrum of the $\text{AgInS}_2/\text{In}_2\text{S}_3$, suggesting that the reaction is driven by light irradiation. We are also delighted to find out that the QE at 720 nm can reach 3.3%, which is higher than many reported photoheterotrophic bacteria.²¹ In addition, the H_2 evolution without noticeable deactivation was observed even after five cycle tests (Figure 2D), implying that $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$ biohybrid has excellent photo-stability. The cell viability, membrane integrity and genomic DNA content before and after the H_2 production process were investigated. No significant stimulation or inhibition of cell viability is observed during the photocatalytic process (Figure 3A). In fluorescent microscopic study, after staining with a dye mixture, no obvious red fluorescent dye-stained cells can be detected after H_2 evolution, further indicating the integrity of the cell membrane (Figure 3B and C). In addition, from the HAADF image of inset in Figure 3C, *E. coli* cell maintains its original structure after the reaction. Moreover, the $\text{AgInS}_2/\text{In}_2\text{S}_3$ nanoparticles still deposit on the surface of *E. coli* without falling off. It is also found that malondialdehyde (MDA),^[22] a typical lipid membrane peroxidation indicator, does not increase in the solution under aerobic condition (Figure 3A). Furthermore, the leakage and decomposition of genomic DNA are not observed from fluorescent intensity of the DNA bands.^[23] Also, the DNA concentration remains unchanged during the reaction (Figure 3D and E). All of the above results suggest that the biohybrid system is relatively active and stable during the H_2 production process under the anaerobic condition.

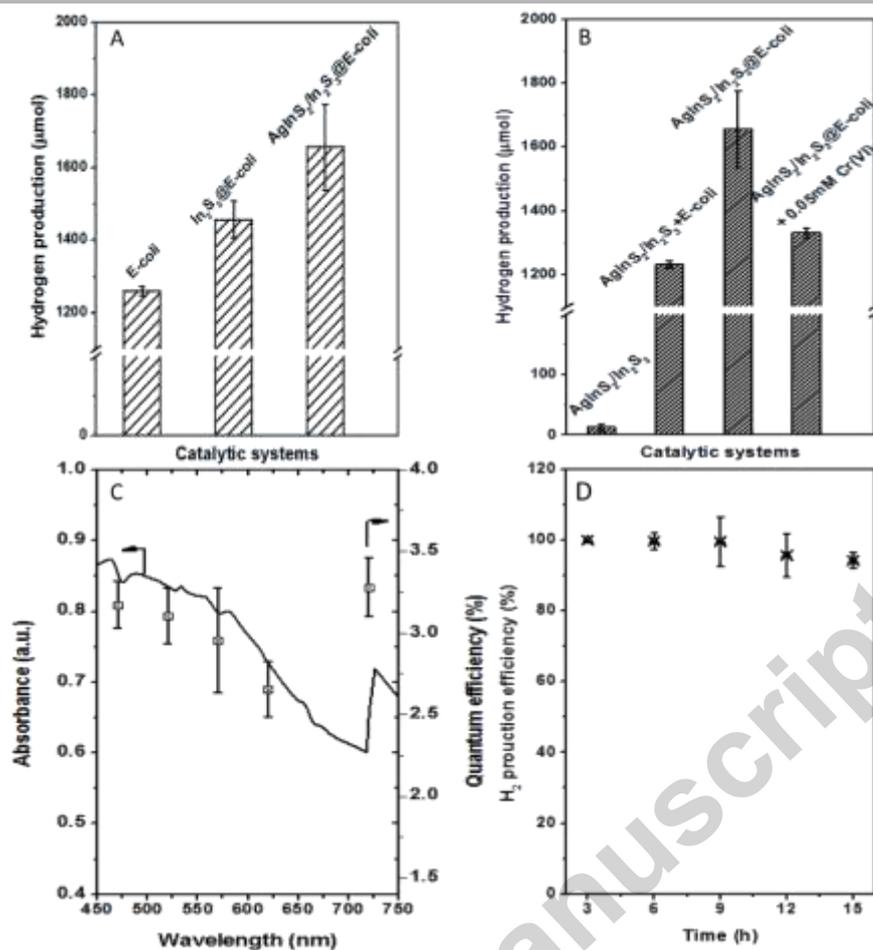


Figure 2. H₂ production (A) of *E. coli*, In₂S₃@*E. coli* and AgInS₂/In₂S₃@*E. coli* from equal volume of the hybrid system under visible light (> 420 nm, 1400 W m⁻²) irradiation for 3 h, electron-scavenger and separation studies (B) under the irradiation visible light (> 420 nm, 1400 W m⁻²) for 3 h, quantum efficiency and absorbance spectrum of the precipitated photocatalyst (C), the possibility of recycling ability (D) of AgInS₂/In₂S₃@*E. coli* hybrid system.

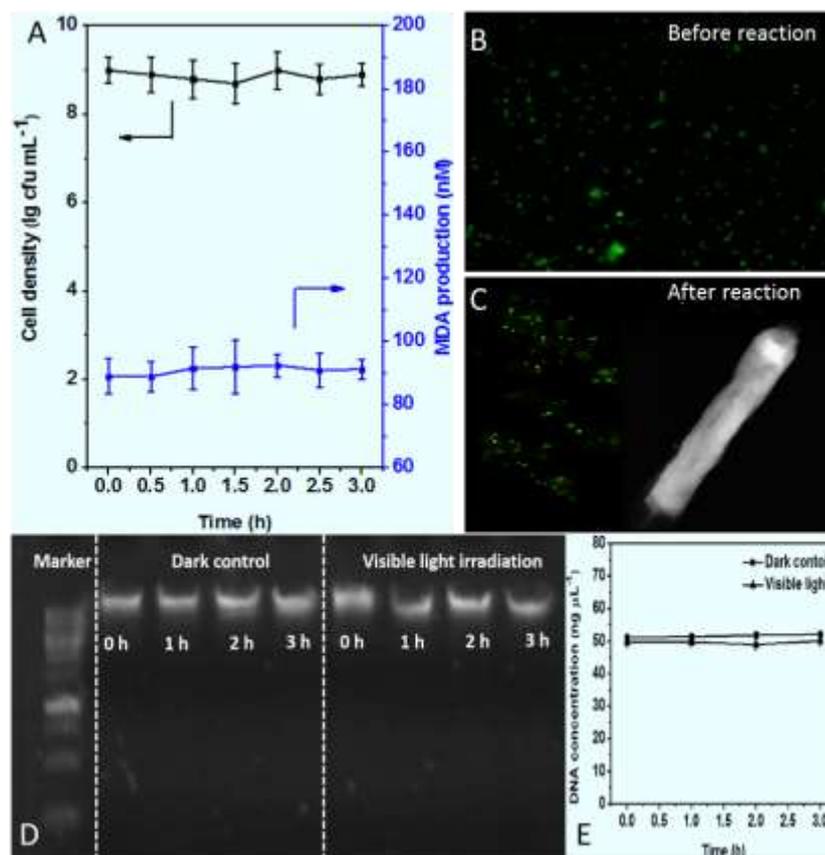


Figure 3. Cell viability and MDA production (A) during the H₂ production process, fluorescence microscopic images (B and C, inset: HAADF image of the hybrid after reaction) of *E. coli* before and after reaction, investigation of leakage and destruction of bacterial genomic DNA extracted from harvested cells during H₂ evolution process by means of agarose gel electrophoresis (D) and NanoDrop™ spectrophotometers (E).

As aforementioned, the separation-recombination rate of the photogenerated electron-hole pairs is a key factor affecting the efficiency of electron transduction from semiconductor to bacterial because the higher separation rate can enable more electrons to participate in biological H₂ production.^[24] To investigate the separation properties of photogenerated electron-hole pairs, a series of photoelectrochemical tests were carried out. As a photocathode, the photocurrent density of AgInS₂/In₂S₃ hybrid is consistently higher than that of In₂S₃ (Figure 4A). Nyquist plot (Figure 4B) obtained from AgInS₂/In₂S₃ hybrid exhibits a smaller arc radius as compared with In₂S₃, confirming the higher electronic conductivity of AgInS₂/In₂S₃ hybrid due to the effective electron transfer between AgInS₂ and In₂S₃. This result demonstrates the charge transfer at the interface between

AgInS₂ and In₂S₃ is significantly accelerated. In addition, when the surfaces of In₂S₃ and AgInS₂/In₂S₃ hybrid are irradiated with visible light, the arc radiuses are decreased, indicating that the electronic conductivities increased under light irradiation. The surface recombination rate was further studied using the decay profile of open circuit potential (V_{oc}) (Figure 4C). The average recombination rate can be calculated by the following equation: $(V - V_{light}) / (V_{dark} - V_{light}) = 1 - \exp(-kt)$, where V , V_{dark} , and V_{light} are the V_{oc} at any time, in the dark and under light irradiation; k is the pseudo-first order recombination rate constant.^[25] AgInS₂/In₂S₃ (0.084 s⁻¹) shows slower decay kinetic in comparison with In₂S₃ (0.097 s⁻¹) after turn-off the light, demonstrating that the surface recombination rate of AgInS₂/In₂S₃ is effectively suppressed as compared with In₂S₃. Moreover, AgInS₂/In₂S₃ hybrid also shows significantly reduced PL intensity, relative to In₂S₃, indicating a more efficient electron-hole separation on the as-prepared hybrid (Figure 4D).

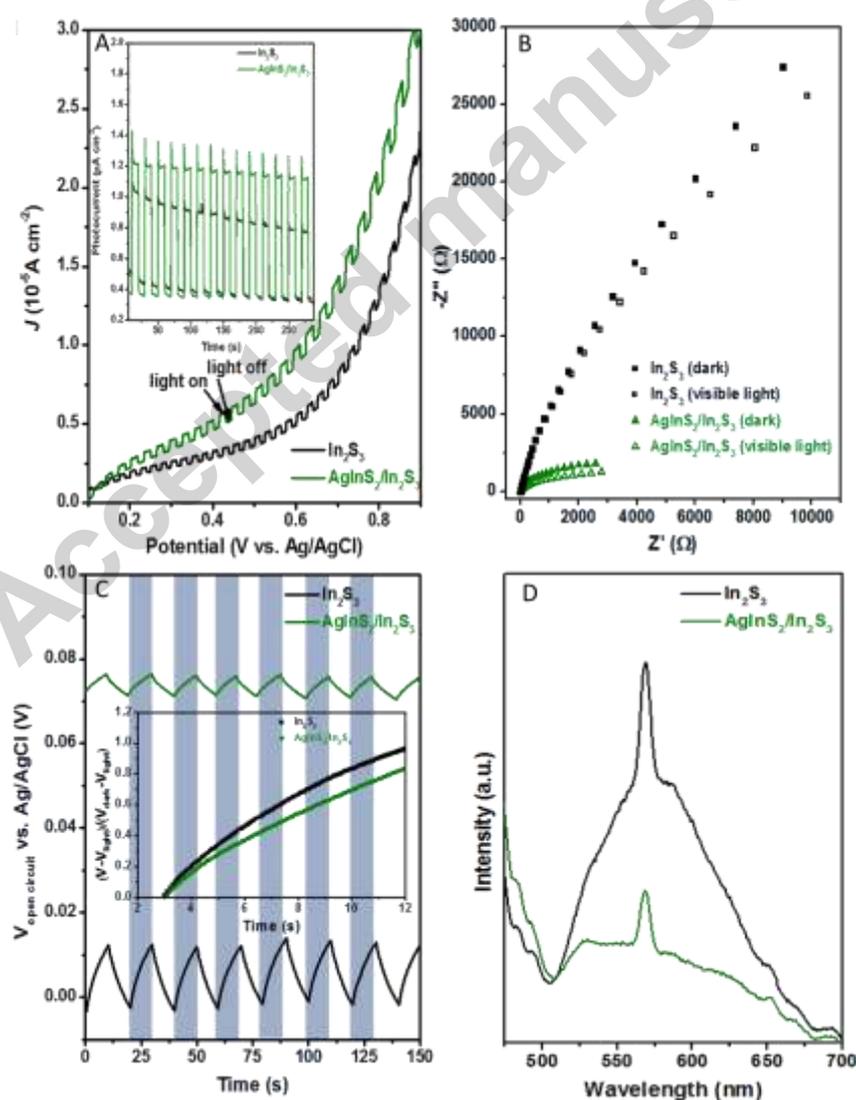


Figure 4. Linear sweeps voltammograms (A) of In_2S_3 and $\text{AgInS}_2/\text{In}_2\text{S}_3$, (without *E. coli*) inset: transition photocurrent at 0.4 V versus Ag/AgCl, nyquist plots (B) of In_2S_3 and $\text{AgInS}_2/\text{In}_2\text{S}_3$ in 0.1 M Na_2SO_4 solution under dark and visible light, open circuit potential (C) of In_2S_3 and $\text{AgInS}_2/\text{In}_2\text{S}_3$, inset: normalized open-circuit potential decay curves, steady state photoluminescence (PL) spectra (D) of In_2S_3 and $\text{AgInS}_2/\text{In}_2\text{S}_3$ at excitation wavelength of 438 nm.

To investigate pivotal factors affecting H_2 production performance, a series of experiments were carried out. In the biological H_2 evolution process of $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$ system, the available intracellular glucose serves as the original energy source and electron donor. Glucose is quickly consumed within 1 h both for dark control and visible light irradiation (Figure 5A, and no obvious difference can be detected, suggesting that the glucose can be rapidly absorbed by *E. coli* and quickly involved in the glycolysis process. In addition, compared to the dark control group, a lower lactate fermentation activity is exhibited in the light irradiation group during the 3 h reaction (Figure 5B), indicating that the unfavourable pathway in fermentative H_2 production is inhibited by the photo-generated electrons, and more energy sources flowed into the formic acid and H_2 production pathway. In contrast, a significantly higher intracellular formate concentration in the light irradiated hybrid cells is observed (Figure 5C). The result illustrates that more substrates for H_2 generation are accumulated under visible light. In addition, the stimulating effect on the FDH activity by the photo-generated electrons is also remarkable (Figure 5D), resulting in a stronger catalytic power for H_2 production. Higher intracellular reduction potential under light irradiation is also detected from the NADH/NAD ratio test (Figure 5E), illustrating that the hybrid cells are under higher stress of reducing potential and have to dispense with excess reducing equivalents to maintain the redox balance. The more accumulated NADH in the irradiated group also corresponds to the inhibited lactate fermentation in this experiment. It is therefore reasonable that with the help from photogenerated electrons from cell surface $\text{AgInS}_2/\text{In}_2\text{S}_3$, the hybrid cells can obtain more energy and higher catalytic activity for the fermentative H_2 production pathway, which finally lead to the enhanced biological H_2 production.

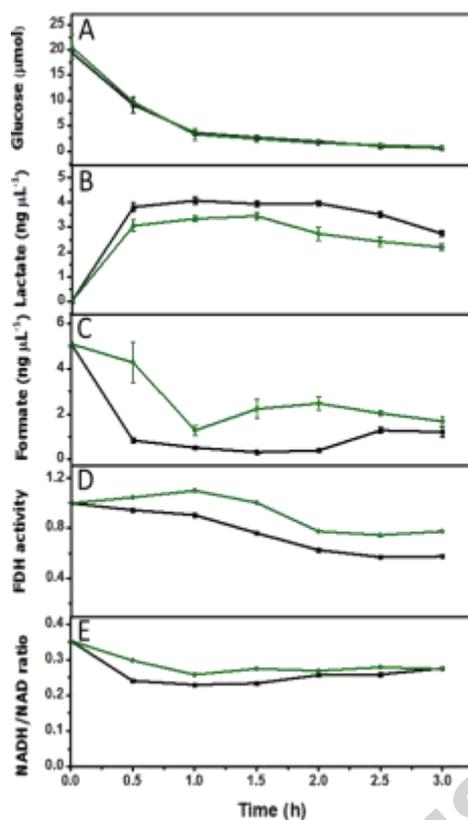


Figure 5. Mechanistic study of glucose utilization (A), lactate concentration (B), formate concentration (C), formate dehydrogenase activity (D), NADH/NAD ratio (E) of the $\text{AgInS}_2/\text{In}_2\text{S}_3@E. coli$ hybrid system in the dark (black line) and under visible light irradiation (green line).

To conclude, the H_2 production from solar-driven (bio)photocatalysis has great potential to be a green technology to address global energy shortage and environmental pollution problems. In our present work, we developed a biohybrid system containing the most well-studied bacterium, *E. coli* and its biologically precipitated $\text{AgInS}_2/\text{In}_2\text{S}_3$ hybrid. This system has the advantages of genetic manipulation free, using no electron transfer agents and high efficient electronic transmission. This is also the first report to make use of $\text{AgInS}_2/\text{In}_2\text{S}_3$ hybrid in the biohybrid system for conducting H_2 production. This strategy could be expanded to other metal sulfide hybrids as inorganic light harvesters to construct biohybrid system for utilization of solar energy.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/>

References

- [1] K. Sakimoto, N. Kornienko, P. Yang, *Acc. Chem. Res.* 50 (2017) 476-481.
- [2] R. Blankenship, D. Tiede, J. Barber, G. Brudvig, G. Fleming, M. Ghirardi, M. Gunner, W. Junge, D. Kramer, A. Melis, T. Moore, C. Moser, D. Nocera, A. Nozik, D. Ort, W. Parson, R. Prince, R. Sayre, *Science* 332 (2011) 805-809.
- [3] D. Kim, K. Sakimoto, D. Hong, P. Yang, *Angew. Chim. Int. Ed.* 54 (2015) 3259-3266.
- [4] C. Caputo, L. Wang, R. Beranek, E. Reisner, *Chem. Sci.* 6 (2015) 5690-5694.
- [5] K. Brown, M. Wilker, M. Boehm, G. Dukovic, P. King, *J. Am. Chem. Soc.* 134 (2012) 5627-5636.
- [6] Y. Honda, H. Hagiwara, S. Ida, T. Ishihara, *Angew. Chim., Int. Ed.* 2016, 55, 8045-8048; *Angew. Chim.* 128 (2016) 8177-8180.
- [7] K. Sakimoto, A. Wong, P. Yang, *Science* 351 (2016) 74-77.

- [8] N. Kornienko, K. Sakimoto, D. Herlihy, S. Nguyen, A. Alivisatos, C. Harris, A. Schwartzberg, P. Yang, *Proc. Natl. Acad. Sci. USA* 113 (2016) 11750-11755.
- [9] M. Lacasse, C. Douglas, D. Zamble, *Biochemistry* 55 (2016) 6821-6831.
- [10] C. Wang, A. Lum, S. Ozuna, D. Clark, J. Keasling, *Appl. Microbiol. Biotechnol.* 56 (2001) 425-430.
- [11] D. Cunningham, L. Lundie Jr. *Appl. Environ. Microbiol.* 59 (1993) 7-14.
- [12] B. Wang, C. Zeng, K. H. Chu, D. Wu, H. Y. Yip, L. Ye, P. K. Wong, *Adv. Energy Mater.* (2017) 1700611-1700620.
- [13] W. Huang, L. Gan, H. Yang, N. Zhou, R. Wang, W. Wu, H. Li, Y. Ma, H. Zeng, T. Zhai, *Adv. Funct. Mater.* 27 (2017) 1702448-1702456.
- [14] J. Zhou, G. Tian, Y. Chen, Y. Shi, C. Tian, K. Pan, H. Fu, *Sci. Rep.* 4 (2014) 4027.
- [15] Z. Liu, K. Guo, J. Han, Y. Li, T. Cui, B. Wang, J. Ya, C. Zhou, *Small* 10 (2014) 3153-3161.
- [16] F. Liu, Y. Jiang, J. Yang, M. Hao, Z. Tong, L. Jiang, Z. Wu, *Chem. Commun.* 52 (2016) 1867-1870.
- [17] Z. Jiang, D. Jiang, Z. Yan, D. Liu, K. Qian, J. Xie, *Appl. Catal. B: Environ.* 170-171 (2015) 195-205.
- [18] Y. Choi, H. Kim, G. Moon, S. Jo, W. Choi, *ACS Catal.* 6 (2016) 821-828.
- [19] T Di, B Zhu, B Cheng, J Yu, J Xu, *J. Catal.* 352 (2017) 532-541.
- [20] M. Tsai, M. Li, J. Retamal, K. Lam, Y. Lin, K. Suenaga, L. Chen, G. Liang, L. Li, J. He, *Adv. Mater.* 29 (2017) 1701168-1701174.
- [21] I. Akkerman, M. Janssen, J. Rocha, R. H. Wijffels, *Int. J. Hydrogen Energy* 27 (2002) 1195-1208.
- [22] O. Dalrymple, W. Isaacs, E. Stefanakos, M. Trotz, D. Goswami, *J. Photochem. Photobiol. A: Chem.* 221 (2011) 64-70.
- [23] S. Zhang, C. Ye, H. Lin, L. Lv, X. Yu, *Environ. Sci. Technol.*, 49 (2015) 1721-1728.
- [24] S. Cao, J. Low, J. Yu, M. Jaroniec. *Adv. Mater.* 27 (2015) 2150-2176.

[25] Z. Hu, Z. Shen, J. C. Yu. Chem. Mater. 28 (2016) 564-572.

Curriculum Vitae



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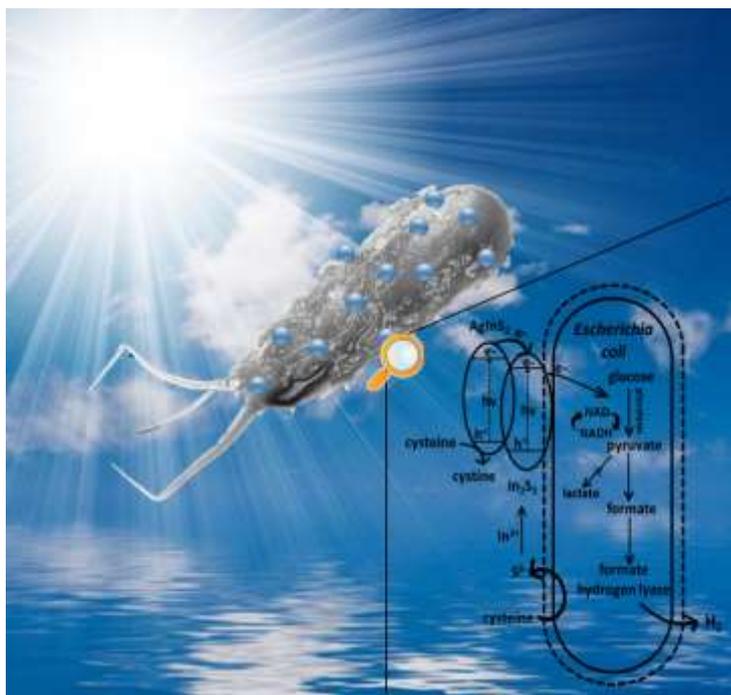
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Po Keung Wong has 40 years research experience on environmental science and technology. He received his B.Sc. and M.Phil. degrees from The Chinese University of Hong Kong (CUHK) and Ph.D. degree from University of California, Davis. He returned to CUHK to start his professorial career in 1986. Currently he is a professor in School of Life Sciences and the Associate Director of Environmental Science Programme. He also is visiting professor for Nankai University, South China University of Technology, Central China Normal University and Guangdong University of Technology in China. His current research focuses on photocatalytic water purification and energy production.

Accepted manuscript

Graphical Abstract



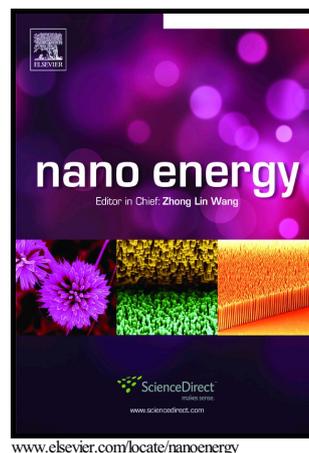
Research Highlights

- A tandem inorganic-biological hybrid is obtained for biological H₂ production.
- AgInS₂/In₂S₃ hybrid harvests light energy to enhance H₂ production by *E. coli*.
- *E. coli* makes use of [Ni-Fe]-hydrogenase and electrons for enhanced H₂ evolution.
- A highly quantum efficiency of 3.3% at 720 nm for H₂ production is achieved.

Author's Accepted Manuscript

AgInS₂/In₂S₃ Heterostructure Sensitization of *Escherichia coli* for Sustainable Hydrogen Production

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