Supporting information

In vivo synthesis of semiconductor nanoparticles in *Azotobacter vinelandii* for light-driven ammonia production

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Fig. S1 Photographs of *A. vienlandii* only (left) and *A. vinelandii* cultured in a medium containing 0.1 mM CdCl₂ and 1.0 mM cysteine (cys) (right). The images illustrate the coloration differences in response to the presence of the biosynthesis precursors



Fig. S2 Relative expression level of *icsS* gene of *A. vinelandii* cell with varying cysteine concentrations of the culture condition.



Fig. S3 Photographs of the culture media containing 0.1 mM CdCl₂ and various sulfur precursors—cysteine (Cys), sodium sulfide (Na₂S), cysteamine (CA), and 3-mercaptopropionic acid (MPA)—after the cultivation condition (24 h, 30 °C) in (a) the absence and (b) the presence of *A. vinelandii*. The characteristic yellow color represents the synthesized CdS nanoparticles. Absorption spectra of the corresponding culture media in (c) the absence and (d) the presence of *A. vinelandii*.



Fig. S4 Absorbance of *A. vinelandii* cultured for 24 h at 30 °C in (a) a medium with NP biosynthesis precursors and (b) a medium without precursors. (c) Absorbance difference between of *A. vinelandii* when cultured in a medium with nanoparticle biosynthesis precursors versus a control medium. (d) Tauc plot for determining the band gap of CdS nanoparticles synthesized within the *A. vinelandii*. Red squares represent the x-intercepts of corresponding tangents (dashed line) for estimating band gaps of nanoparticles.



Fig. S5 NADH/NAD ratio of *A. vinelandii* (Cys + CdCl₂) biohybrid under light irradiation.



Fig. S6 TEM image of CdS nanoparticle with the (111), (200) lattice fringe of CdS cubic structure.

Bacteria species	Photosensitizer	Light source	Strategy	Productivity (mol NH4 ⁺ /mol cells)	Ref.
A. vinelandii (DJ995)	CdS/ZnS, CdSe/ZnS, InP/ZnS, Cu₂ZnSn₅4/ZnS QDs	400 nm LED	Mixing cell and QDs	4 x 10 ⁷	1
<i>A. vinelandii</i> (DJ995)	Au nanoclusters	400 nm LED	Mixing cell and Au nanoclusters	1 x 10 ⁸	2
A. vinelandii (KCTC2426)	InP/ZnSe QDs	400 nm LED	Cell co-culture with QD during growth phase	1.4 x 10 ⁸	3
A. vinelandii (KCTC2426)	CdS nanoparticles	400 nm LED	Intracellular NP <i>in vivo</i> biosynthesis	1.8 x 10 ⁸	This work

Table S1. Comparative table of inorganic-bacteria biohybrid for light-driven ammonia production with N₂ fixation

Reference

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- 2 J. R. Bertram, Y. Ding and P. Nagpal, *Nanoscale Adv.*, 2020, **2**, 2363–2370.
- 3 S. Koh, Y. Choi, I. Lee, G.-M. Kim, J. Kim, Y.-S. Park, S. Y. Lee and D. C. Lee, J. Am. Chem. Soc., 2022, 144, 10798–10808.