Supporting Information

Unique dendritic Bi_2S_3 with ultrathin nanosheets rich in S vacancy-defect toward promoting highly efficient photothermal CO_2 reduction into CO

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Table S1 Fitting result of XPS for Bi and S

Samples	Elements	Fitted area	Ratio of S/Bi
BS	Bi	1945.26	0.714
	S	1391.66	
Vs-BS1	Bi	4236.63	0.446
	S	1887.67	

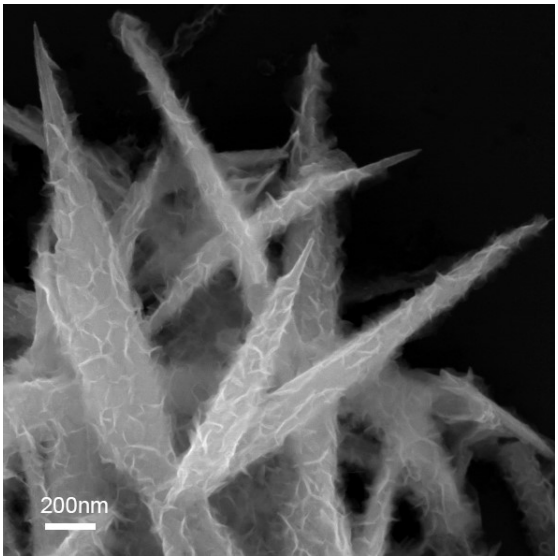


Fig. S1 SEM images of BS.

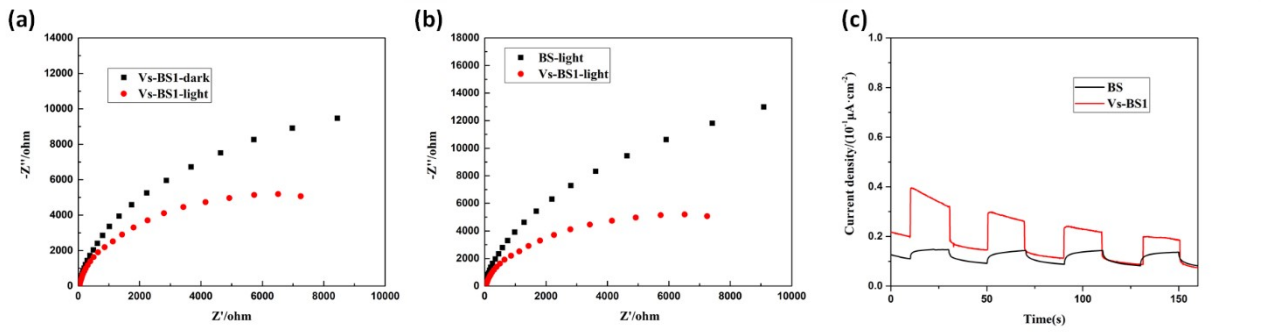


Fig. S2 (a) EIS Nyquist plots of the Vs-BS1 in the light and in the dark (b) EIS Nyquist plots of the BS and Vs-BS1 in the light (c) Transient photocurrent responses of BS and Vs-BS1.

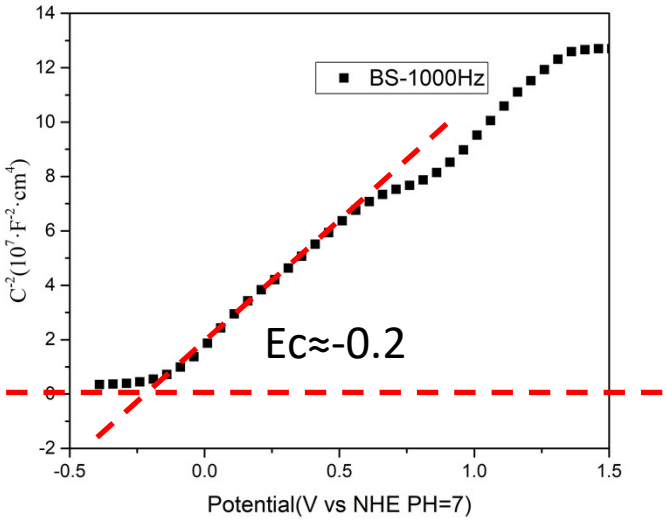


Fig. S3 Mott Schottky Curve of BS.

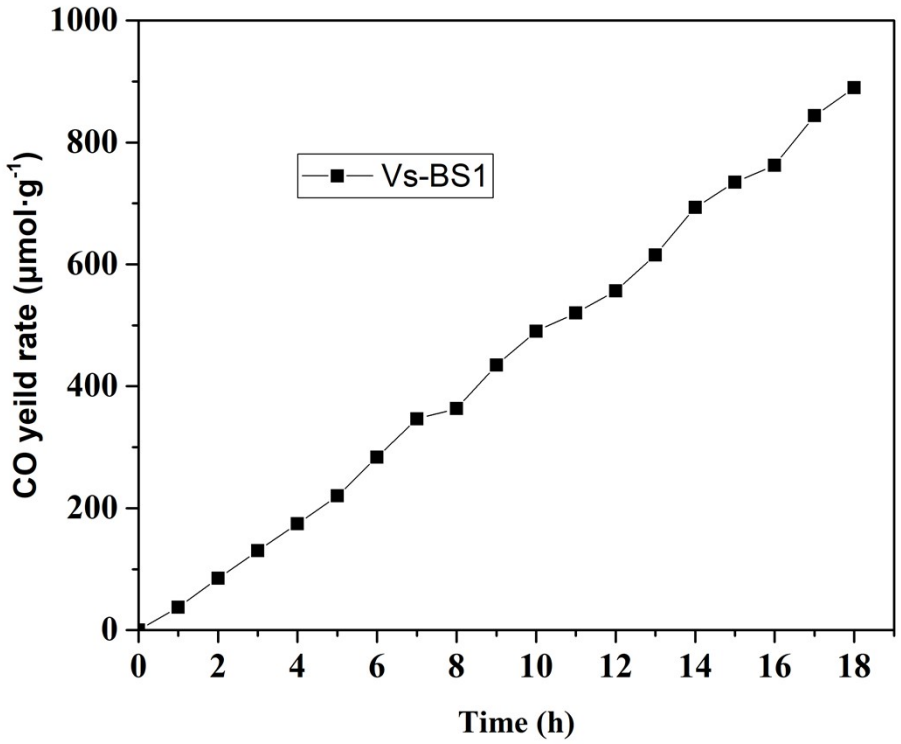


Fig. S4 The stability of photocatalytic performance of Vs-BS1 under the irradiation of a 300 W xenon lamp after 18 hours.

Computational details: Density functional calculations were performed by using the Vienna ab initio simulation package (VASP).[1, 2] The projector-augmented wave method was applied to consider electron-ion interactions.[3] The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was adopted for describing the exchange correlation.[4] The studied structures were relaxed by utilizing 450 eV as the cutoff energy for basis function. A 9×3×3 Monkhorst-Pack type of *k*-point sampling was used for bulk Bi_2S_3. The calculated lattice parameters are *a*=4.017 Å, *b*=11.170 Å, *c*=11.778 Å, which are in good agreement with experimental data. Three low-indexed surfaces are created by cleaving the relaxed bulk structure through the corresponding planes and the resultant structures are depicted in Figure S5. The lateral dimensions of slab models are 11.170 Å × 11.778 Å for (100) surface, 11.778 × 4.017 Å for (010) surface, and 4.017 × 11.170 Å for (001) surface. Monkhorst-Pack *k*-point meshes of 3×3×1, 3×9×1, and 9×3×1 are applied on structural and energetic calculations of (100), (010) and (001) surfaces, respectively. A vacuum region of 15 Å was added along the z-direction to avoid mirror interaction between adjacent supercells. Convergence thresholds of 10^{-5} eV for the energy and 0.01 eV $Å^{-1}$ for the forces were used for all optimizations.

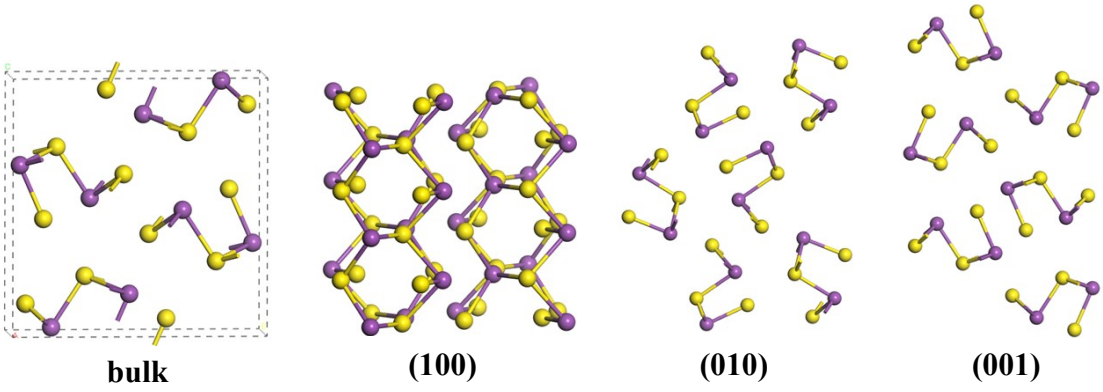


Fig. S5 Illustration of bulk and low-indexed surfaces of Bi_2S_3. The purple and yellow balls represent Bi and S atoms, respectively.

To estimate the relative stability of surfaces, the surface energy is calculated according to the following equation:

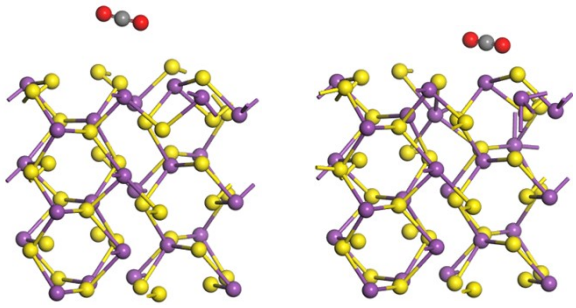
$$\gamma = (E_{\text{slab}} - \text{n}^{E_{Bi_2S_3}})/2A \qquad (1)$$

where E_{slab} is the energy of a slab model, n is the number of Bi_2S_3 bulk units in the slab, and $2A$ is the total exposed area of the two identical sides of the slab. The computed surface energies are 0.29 J/m^2 for (100) surface, 0.34 J/m^2 for (010) surface, 0.36 J/m^2 for (001) surface. The smaller the surface energy, the more stable the surface. The results suggest that (100) surface is more stable than (010) and (001), which is also consistent with the experimental observations. Therefore, we will only do further investigations on (100) surface.

Initially, we considered all possible active sites for CO_2 adsorption on the clean surface and the surface with a S vacancy in the top layer (V_s-Bi_2S_3). The adsorption energy (E_{ads}) of a CO_2 molecule on a surface is defined according to the following equation:

$$E_{ads} = E_{total} - E_{surface} - E_{CO_2} \qquad (2)$$

where E_{total} is the total energy of a CO_2 molecule supported on a surface, $E_{surface}$ is the energy of a clean surface, and E_{CO_2} is the energy of a CO_2 molecule in a supercell with the same size as the clean surface. According to the definition, a negative value of E_{ads} means a thermodynamically favorable adsorption process. The most stable structures are shown in Fig. S6. As shown in Fig. S6, the adsorption energies of a CO_2 molecule are -0.21 eV on the Bi_2S_3 surface and -0.33 eV on V_s-Bi_2S_3, which indicates that the CO_2 adsorption on the latter is more stable.



(a) E_{ads} = -0.21 eV **(b) E_{ads} = -0.33 eV**

Fig. S6 The optimized structures and the calculated adsorption energies of a CO_2 molecule supported on (a) the clean surface and (b) the surface with a S vacancy in the top layer.

To calculate the reaction free energy for each of the reaction steps, we follow Norskov's Computational Hydrogen Electrode (CHE) approach,[5]

$$\Delta G = \Delta E_{\text{ads}} + \Delta ZPE - T\Delta S \qquad (3)$$

where ΔE_{ads} refers to the density functional theory reaction energy, ΔZPE and ΔS are changes in zero-point energy and entropy, respectively. The values of ZPE are computed by vibration frequencies and ΔS are obtained from standard tables for gas-phase molecules.[6] We assume that S equals zero for the species adsorbed to the surface.

Reference

1 G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci*, 1996, **6**, 15-50.

2 G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B*, 1996, **54**, 11169-11186.

3 P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B*, 1994, **50**, 17953-17979.

4 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

5 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, Trends in the Exchange Current for Hydrogen Evolution, *J. Electrochem. Soc.*, 2005, **152**, J23.

6 D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC, Press, Boca Raton, FL, 84th Edn, 2003-2004.