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Formation of Hierarchical FeCoS₂-CoS₂ Double-Shelled Nanotubes with Enhanced Performance for Photocatalytic Reduction of CO₂

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Abstract

Hierarchical FeCoS₂-CoS₂ double-shelled nanotubes have been rationally designed and constructed for efficient photocatalytic CO₂ reduction under visible light. The synthetic strategy, engaging the two-step cation-exchange reactions, precisely integrates two metal sulfides into a double-shelled tubular heterostructure with both of the shells assembled from ultrathin two-dimensional (2D) nanosheets. Benefiting from the distinctive structure and composition, the FeCoS₂-CoS₂ hybrid can reduce bulk-to-surface diffusion length of photoexcited charge carriers to facilitate their separation. Furthermore, this hybrid structure can expose abundant active sites for enhancing CO₂ adsorption and surface-dependent redox reactions, and harvest incident solar irradiation more efficiently by light scattering in the complex interior. As a result, these hierarchical FeCoS₂-CoS₂ double-shelled nanotubes exhibit superior activity and high stability for photosensitized deoxygenative CO₂ reduction, affording a high CO-generating rate of 28.1 $\mu\text{mol h}^{-1}$ (per 0.5 mg of catalyst).

Keywords: CO₂ reduction; heterostructure; hollow; metal sulfides; photocatalysis

The fixation of CO₂ into energy-rich low-carbon products by photocatalysis is one promising strategy to mitigate global warming by lowering the greenhouse gas concentration, and simultaneously to pursue renewable energy alternatives by storing the solar energy into chemical bonds.^[1-3] In recent years, researchers have indeed made some impressive progresses in the studies of exploring catalytic materials and constructing reaction systems for CO₂ conversion powered by the sun.^[4-10] Nevertheless, the current efficiency of photocatalytic CO₂ reduction does not meet the criteria for practical utilization. This is mainly restricted by the great energy barriers of CO₂ reduction in both thermodynamics and kinetics,^[3, 11] and the low efficiency of multiple physiochemical processes during photocatalysis.^[1, 12] Therefore, to realize the ultimate objective of CO₂ photoreduction for sustained solar fuel production, it is desirable to develop new catalysts to selectively operate the reaction with high efficiency.

Metal sulfide semiconductors have attracted enormous interest in photocatalysis for CO₂ reduction, owing to their suitable band structures, rich redox functions and tunable electronic and optical properties.^[13-19] In particular, the coupling of matched metal sulfides forming heterostructures is deemed as an effective method to strengthen their photocatalytic activity,^[16, 20] because the potential gradient between the interfaces can powerfully boost charge separation and migration. Meanwhile, metal sulfide hybrids typically possess improved photo-stability and extended optical harvesting compared with the individual counterparts.^[21-22] Apart from designing the composition, delicate engineering of favorable structures for the materials is also of significant importance to enhance their photocatalytic performance.

Due to the apparent structural virtues, hierarchical hollow heterostructures composed of 2D nanosheets are being actively employed as photocatalysts for solar-to-chemical energy conversion, such as CO₂ reduction and water splitting.^[17, 23-27] To be specific, hierarchical materials hold readily accessible and interconnected porous networks, which can promote the transport of guest species to promote reaction dynamics.^[28-29] Besides, hollow scaffolds with interior cavities can work as a trap-

well to render scattering/reflection of incident light,^[30-32] and this photo-trapping effect would be further reinforced if the hollow structures are multi-shelled.^[33] Moreover, the nanosheet-constructed hierarchical hollow architectures possess shortened diffusion pathway of charges, large surface area and high content of exposed active sites, which will inhibit recombination of electron-hole pairs, improve CO₂ capture/adsorption, and support kinetics of photoredox reactions.^[26, 34-35] Based on the above considerations, it is motivated to fabricate hierarchical metal sulfide heterostructures with multi-shells and nanosheet substructures for efficient CO₂ photoreduction.

We herein demonstrate a facile metal-organic framework (MOF)-assisted synthesis method to construct hierarchical FeCoS₂-CoS₂ double-shelled nanotubes (DSNTs) with both of the shells assembled from 2D nanosheet subunits. As schematically elucidated in **Figure 1**, starting with the Fe-based MOF (MIL-88A, MIL=Materials of Institut Lavoisier) hexagonal prisms, MIL-88A@Fe-Co hydroxide yolk-shell nanotubes (YSNTs) are produced *via* the cation-exchange reaction between MIL-88A and Co²⁺ ions in a mixture of water and ethanol (step i). Following that, Fe-Co hydroxide DSNTs are formed by further etching the MOF cores through the second cation-exchange reaction (step ii). Finally, the Fe-Co hydroxide DSNTs are subjected to a sulfidation treatment by annealing with sulfur powder at 400°C in N₂ atmosphere (step iii), producing the hierarchical FeCoS₂-CoS₂ DSNTs. Thanks to the unique compositional and structural merits, the FeCoS₂-CoS₂ hybrid can effectively enhance CO₂ adsorption and surface redox catalysis, promote separation and movement of photo-formed charges, and increase utilization of incident light irradiation. Consequently, the FeCoS₂-CoS₂ hybrid can catalyze the CO₂-to-CO conversion reaction with remarkable activity and high stability in a photosensitized system under visible light irradiation, giving a superior CO production rate of 28.1 μmol h⁻¹ (per 0.5 mg of catalyst).

Dispersed MIL-88A nanorods with high uniformity are synthesized through a modified hydrothermal method (Figure S1a, Supporting Information). The field-emission scanning electron microscopy (FESEM) image and transmission electron microscopy (TEM) image show the smooth

surface and solid nature of the hexagonal prisms with an average diameter of about 500 nm (Figure S1b,c, Supporting Information). The X-ray diffraction (XRD) pattern confirms the formation of MIL-88A (Figure S2a, Supporting Information),^[36-37] and energy-dispersive X-ray (EDX) analysis verifies its chemical composition of C, O and Fe elements (Figure S2b, Supporting Information). After the first cation-exchange reaction, the produced MIL-88A@Fe-Co hydroxide YSNTs remain the overall nanorods structure (**Figure 2a**, and Figure S3a, Supporting Information). The high-magnification FESEM images show the hierarchical surface of the nanorods with 2D nanosheet subunits on the surface (Figure S3b,c, Supporting Information). In this process, the MIL-88A prisms are steadily etched by the protons generated from hydrolysis of Co^{2+} ions, releasing Fe^{3+} ions outward to react with Co^{2+} ions and OH^- ions forming Fe-Co hydroxide nanosheets. Because the dissolution of MIL-88A is kinetically faster than the formation of the hydroxide nanosheets, a gap between the MOF core and the hydroxide shell emerges, thus forming the yolk-shell structure for MIL-88A@Fe-Co hydroxide, which can be clearly discerned from the TEM images (Figure 2b,c). The XRD pattern of MIL-88A@Fe-Co hydroxide YSNTs gives distinct diffraction signals attributed to that of MIL-88A, suggesting the MOF core is not etched completely (Figure S4a, Supporting Information). The EDX spectrum of MIL-88A@Fe-Co hydroxide YSNTs indicates the presence of Fe, Co and O elements with the Fe to Co atomic ratio of about 1:2.3, reflecting the formation of the Fe-Co hydroxides (Figure S4b, Supporting Information).

Then, the MIL-88A@Fe-Co hydroxide YSNTs are transferred into Fe-Co hydroxide DSNTs through the second cation-exchange reaction. The FESEM images show the intact structure and hierarchical surface of Fe-Co hydroxide DSNTs constructed by hydroxide nanosheets with a larger size than those of MIL-88A@Fe-Co hydroxide YSNTs (Figure 2d-f). The hierarchical double-shelled configuration of Fe-Co hydroxide DSNTs is clearly revealed by the TEM images (Figure 2g,h). There is not any solid core remained in Fe-Co hydroxide DSNTs, suggesting the complete removal of the MIL-88A precursor. This is further supported by the disappearance of strong diffraction peaks of

MIL-88A in the XRD pattern (Figure S5a, Supporting Information). The high-magnification TEM image shows that both shells of Fe-Co hydroxide DSNTs are consisted of randomly assembled nanosheets (Figure 2i). Formation of Fe-Co hydroxide DSNTs is also supported by the EDX spectrum (Figure S5b, Supporting Information), which shows strong signals of Fe, Co and O elements with an increased Co/Fe ratio.

The FeCoS₂-CoS₂ DSNTs are finally obtained by annealing the Fe-Co hydroxide DSNTs with sulfur powder at 400°C in N₂ as indicated by XRD and EDX analyses (Figure S6, Supporting Information). The FESEM images show the well preserved hierarchical structure of FeCoS₂-CoS₂ DSNTs without obvious aggregation (**Figure 3a,b**). The cross-sectional image of an individual FeCoS₂-CoS₂ DSNT displays the nanosheet-assembled hierarchical surfaces of both the outer and inner shells (inset, Figure 3b). The magnified FESEM image shows that the thickness of the metal sulfide nanosheets is about 20 nm (Figure 3c). The morphological feature of the FeCoS₂-CoS₂ DSNTs is also observed from TEM (Figure 3d). The closer TEM analysis discloses the presence of numerous pores on the metal sulfide nanosheets (Figure 3e). EDX analysis further confirms the gap between the two shells by delineating the relative elemental compositions of Fe, Co, and S along the line scan across the longitudinal direction of a single nanotube (Figure 3f). In the high-resolution TEM (HRTEM) image (Figure S7, Supporting Information), two distinct lattice fringes with d-spacings of 0.28 and 0.25 nm can be clearly discerned, which can be indexed to the (220) and (101) crystal planes of CoS₂ and FeCoS₂, respectively. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping images demonstrate the distribution of Fe, Co and S elements in the FeCoS₂-CoS₂ DSNTs (Figure 3g). As can be seen, in the outermost region of the nanotube, the signal intensity of Fe is weaker than that of Co, indicating that the outer shell should contain a higher content of CoS₂ than the inner shell. This can be easily understood by the relatively insufficient supply of Fe³⁺ ions in forming Fe-Co hydroxide during the first-step ion-exchange reaction, leading to the generation of more cobalt hydroxide on the outer

surface. To study the chemical states of elements in the FeCoS₂-CoS₂ nanotubes, X-ray photoelectron spectroscopy (XPS) characterizations are performed and the results further support the successful formation of the FeCoS₂-CoS₂ DSNTs (Figure S8, Supporting Information).

To investigate the influence of compositions and structures of metal sulfide hybrids on catalytic performance, three control samples, namely FeS_x-CoS₂ nanotubes (Figure S9, Supporting Information), FeCoS₂-CoS_{1.97} nanotubes (Figure S10, Supporting Information) and FeCoS₂-Co₉S₈ nanotubes (Figure S11, Supporting Information), are also synthesized by annealing the Fe-Co hydroxide DSNTs at 300, 500 and 600°C, respectively, under otherwise the same conditions. Also, the FeCoS₂ and CoS₂ materials are prepared for comparison (Figure S12, Supporting Information).

The textural properties of the FeCoS₂-CoS₂ DSNTs are investigated by N₂ sorption measurements. The result indicates that the material has a high Brunauer-Emmett-Teller (BET) surface area of 41.8 m² g⁻¹ (Figure S13, Supporting Information). The hysteresis loop in the N₂ sorption isotherm curve demonstrates the existence of mesopores that are mainly stemmed from the porous walls and nanosheets. The porous structure and high surface area of the FeCoS₂-CoS₂ nanotubes are favorable for enhancing CO₂ capture and concentration, as revealed by CO₂ adsorption tests. The CO₂ sorption isotherms show that the FeCoS₂-CoS₂ nanotubes can afford a CO₂ uptake of about 8 cm³ g⁻¹ at 0°C and 1 atm (Figure S14, Supporting Information). Meanwhile, the room-temperature steady-state photoluminescence (PL) analysis is performed to estimate the separation-recombination rate of the photogenerated charges in the CO₂ photoreduction system (Figure S15, Supporting Information). The PL intensity declines dramatically in the presence of the catalyst, indicating the largely inhibited recombination of photoinduced charges. These characterizations reveal that the hierarchical FeCoS₂-CoS₂ DSNTs own the merits of promoting charge separation and transport. On the other hand, the flat-band potential of the FeCoS₂-CoS₂ hybrid is calculated to be -0.67 V (vs. normal hydrogen electrode, NHE, pH = 7.0) derived by the Mott-Schottky plots (Figure S16, Supporting Information), which is sufficient to drive the CO₂-to-CO conversion reaction.

Besides, the redox potential of $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+$ (i.e., -1.09 V vs. NHE, bpy = 2,2'-bipyridine) is more negative than the flat-band potential of the $\text{FeCoS}_2\text{-CoS}_2$ hybrids. These results indicate that the $\text{FeCoS}_2\text{-CoS}_2$ catalysts are thermodynamically capable of receiving the photoexcited electrons from the reduced photosensitizer for reducing the adsorbed CO_2 molecules to generate CO.

Based on the above discussions, photocatalytic CO_2 conversion performance of the hierarchical $\text{FeCoS}_2\text{-CoS}_2$ DSNTs is tested in a mixed medium of acetonitrile and H_2O under simulated solar irradiation ($\lambda \geq 400$ nm), with $\text{Ru}(\text{bpy})_3^{2+}$ (abbreviated as **Ru**) as the photosensitizer and triethanolamine (TOEA) as the electron donor. As shown in **Figure 4a** (column 1), the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs exhibit high CO_2 photoreduction activity with a CO generation rate of $28.1 \mu\text{mol h}^{-1}$. Such a photocatalytic CO_2 -to-CO conversion rate is much higher than that of reported works in similar systems (Table S1, Supporting Information), suggesting the outstanding performance of the $\text{FeCoS}_2\text{-CoS}_2$ catalyst. Obviously, the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs have a superior performance than the Fe-Co hydroxide DSNTs (column 2), indicating the virtues of metal sulfides to the reaction. However, the CO_2 reduction reaction is almost stopped, when the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs are absent in the system (column 3), which highlights that the catalyst is responsible for the exceptional CO_2 photoreduction efficiency achieved. On the other hand, the individuals of FeCoS_2 and CoS_2 and their physical mixture manifest much inferior performance compared with the $\text{FeCoS}_2\text{-CoS}_2$ catalyst (column 4-6). This suggests that the tight interfacial contacts in the hybrids is essential to the reaction for effectively boosting the separation and transfer of photoinduced charges.

To understand the critical importance of the composition and structure of the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs, other metal sulfide catalysts are also employed to run the CO_2 photoreduction reaction for comparison. As presented in Figure 4b, the $\text{FeS}_x\text{-CoS}_2$ nanotubes show a CO generation rate of $17.7 \mu\text{mol h}^{-1}$, much lower than that of the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs, possibly due to the lack of hexagonal FeCoS_2 phase in the former. As expected, the $\text{FeCoS}_2\text{-CoS}_{1.97}$ and $\text{FeCoS}_2\text{-Co}_9\text{S}_8$ nanotubes exhibit poor CO_2 reduction performance compared with the $\text{FeCoS}_2\text{-CoS}_2$ DSNTs, which is primarily

attributed to their damaged double-shelled structure, although they have enhanced crystallinity that is typically favorable for photocatalysis. Such findings reveal that both chemical composition and spatial architecture of the FeCoS₂-CoS₂ DSNTs contribute largely to the superb photocatalytic CO₂ performance.

The ¹³C-enriched CO₂ is used as a feedstock for the reaction and the yielded CO is analyzed by gas chromatography-mass spectrometry (GC-MS) analysis. The results reveal that only ¹³CO with m/z value of 29 is detected (Figure 4c), proving that the CO product originates from the CO₂ gas. Besides, when conducting the CO₂ photoreduction reaction in Ar atmosphere, no formation of CO is observed (Figure 4a, column 7). This result further supports that the CO₂ feedstock is the carbon source of the CO product obtained. To check the stability of the FeCoS₂-CoS₂ DSNTs, after each reaction, the catalyst is collected and utilized to re-start the CO₂ reduction reaction for five cycles. No significant drop in the CO/H₂ generation rate is observed during the stability tests (Figure 4d), which reflects the high durability of the catalyst for the photocatalytic CO₂ reduction catalysis. Besides, FESEM and TEM characterizations of the FeCoS₂-CoS₂ DSNTs sample after the photocatalytic CO₂ reduction also verify the high structural stability of the photocatalyst (Figure S17, Supporting Information). The long-term performance evaluation indicates that the FeCoS₂-CoS₂ catalyst exhibits high CO-releasing activity in the first hour but thereafter the CO yield rate gradually drops (Figure 4e), which is mainly induced by photobleaching of the **Ru** photosensitizer as reported in such CO₂ reduction systems.^[38-40]

The control experiments demonstrate that the FeCoS₂-CoS₂ catalyst is inactive for producing any CO or H₂ in the absence of TEOA (Figure S18, Supporting Information), indicating the electron donor is indispensable to the reaction, which is consistent with previous works.^[41-42] Besides, the CO₂-to-CO conversion is completely terminated when the reaction is conducted without the introduction of visible light or **Ru**, implying photocatalytic nature of the reaction. Moreover, the activity of the FeCoS₂-CoS₂ catalyst is also examined under different wavelength illumination (Figure

4f). The trend of Co/H₂ generation is consistent with optical absorption intensity of **Ru**, not that of the catalyst (Figure S19, Supporting Information), which confirms that the CO₂ reduction reaction is a photosensitized process.

In summary, hierarchical FeCoS₂-CoS₂ double-shelled nanotubes are designed and fabricated for high-efficiency photocatalytic CO₂ reduction with visible light. The multistep synthesis route is beneficial to make the FeCoS₂-CoS₂ hybrids with tunable architecture and composition to tailor the catalytic performance. The nanosheet-assembled hierarchical double-shelled hollow structure could reduce diffusion distance of photoinduced charges, offer profuse catalytically active sites and utilize incident photoirradiation more efficiently. As a result, the metal sulfide hybrids manifest outstanding CO₂ reduction activity and high stability in a photosensitized tandem system. This work may inspire further development of metal sulfide semiconductors with desirable spatial nanostructures for artificial solar fuel production through visible light CO₂ reduction.

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Figures and Captions

Figure 1. Illustration of the synthetic process of hierarchical FeCoS₂-CoS₂ DSNTs. (i): ion-exchange reaction to form MIL-88A@Fe-Co hydroxide YSNTs, (ii): conversion to Fe-Co hydroxide DSNTs through a second ion-exchange reaction, and (iii): sulfidation reaction and thermal annealing in N₂.

Figure 2. (a) FESEM images and (b,c) TEM images of MIL-88A@Fe-Co hydroxide YSNTs; (d-f) FESEM images and (g-i) TEM images of Fe-Co hydroxide DSNTs.

Figure 3. (a-c) FESEM images, (d,e) TEM images and (f) line scan spectrum of one FeCoS₂-CoS₂ DSNT. (g) HAADF-STEM and elemental mapping images of one FeCoS₂-CoS₂ DSNT. (Inset in b shows the cross-sectional FESEM image of one FeCoS₂-CoS₂ DSNT).

Figure 4. (a) Photoreduction of CO₂ under various reaction conditions. (b) CO₂ photoreduction performance of different samples. (c) Results of GC-MS analysis for CO generated from the ¹³CO₂ isotope experiment. (d) Stability tests of the FeCoS₂-CoS₂ DSNTs catalyst for five cycles. (e) Time-yield plots of the products. (f) Wavelength-dependent CO/H₂ generation and the light absorption spectrum of **Ru** (blue line).

TOC image

Hierarchical FeCoS₂-CoS₂ double-shelled nanotubes are constructed by ultrathin nanosheets for efficient CO₂ photoreduction. The unique structure can sufficiently inhibit recombination of electrons and holes by shortening diffusion length, exploit incident visible light by enhancing scattering in the cavity, and expose abundant active sites for redox reactions. Benefiting from these advantages, the obtained FeCoS₂-CoS₂ hybrid exhibits outstanding performance for CO₂-to-CO conversion powered by solar light.