

Noble-metal-free MOF Derived ZnS/CeO₂ Decorated with CuS Cocatalyst Photocatalyst with Efficient Photocatalytic Hydrogen Production Character

Xiao-li Wang,^[a] Yang Xiao,^[a] Hui Yu,^{*,[a]} Ying Yang,^[a] Xiang-ting Dong,^[a] and Long Xia^{*,[b]}

Inspired by the rich morphology of ZnO and cation-exchange technology, regular dodecahedron-like CeO₂/ZnO was obtained by the calcination of Ce doped ZIF-8 precursor in this study, and CeO₂/ZnS was obtained by the in-situ vulcanization of CeO₂/ZnO. This design not only maintained the morphology of ZIF-8, but also enhanced the oxidation-reduction capacity of the catalyst. When the Ce content was 10 wt%, 10-CeO₂/ZnS sample showed the best photocatalytic hydrogen production performance in all X-CeO₂/ZnS samples. Loading of co-catalysts can effectively enhance the surface hydrogen reduction in photocatalytic water splitting by introducing a positive Schottky

barrier. CuS was regarded as a promising cocatalyst to replace the noble metals due to its low cost and equivalent or even better performance. The in-situ cation exchange method was used to load co-catalyst CuS on the 10-CeO₂/ZnS composites to obtain the 10-CeO₂/ZnS-CuS composites which had the large specific surface area, regular dodecahedral structure and much excellent photolysis of water to produce hydrogen characters. This work provided a new strategy for the advantages combining of co-catalyst, p-n junction as well as the porous structure to enhance the photocatalytic characters.

1. Introduction

As a promising clean energy, hydrogen has become a research hot spot due to its non-pollutant and sustainability. There are many ways to produce hydrogen, electro-catalytic hydrogen production^[1–5] and photocatalytic hydrogen production have attracted more and more attentions, and the visible photocatalytic water decomposition to produce hydrogen is a promising technology.^[6–8] Among the reported photocatalysts until now, ZnS exhibits the excellent transmission properties, high electron mobility, non-toxicity, water insolubility and relative inexpensive which has been considered as an important photocatalyst for water photolysis and wastewater treatment. ZnS has been used to photocatalytic treatment wastewater which makes the difficult to oxidize and hydrolyze pollutants produce the nontoxic products easily.^[9–12] Compared with ZnO, ZnS has the stronger redox capacity which makes H⁺ more likely bond with electrons to form H₂. But, ZnO has the more abundant morphologies than ZnS. As we all know, the morphology of material has a great influence on the photocatalytic performance. Up to now, the various syntheses methods have been used to produce ZnS nanostructures with

different morphologies such as nanowire^[13] or nanorods,^[14] which required either the higher temperature or the higher pressure or both of them. In order to meet the practical requirement, it is necessary to explore a facile approach to prepare ZnS with both the more novel structure and the higher photocatalytic activity.

The porous structures can expose the more active sites to promote the reaction rate between the substrate and the catalyst by reducing the diffusion resistance, and the porous photocatalysts have the broader application prospects.^[15] Unique properties including exceptional porosity, structural diversity, high thermal stability, large specific surface area and chemical stability have made the MOFs materials become the ideal candidates for energy conversion and catalytic applications.^[16–20] Especially, the porous materials derived from MOFs precursor have aroused considerable interest in many applications which retain the original structural characteristics of MOFs, and obtain the porous structures with the large specific surface area and the more active sites.^[21] ZIF-8 (Zeolitic imidazolate framework-8) with the regular dodecahedron structure is the most common Zn-containing MOF material which has demonstrated its potentials in the fabrication of functional nanocomposites for a wide variety of applications such as CO₂ absorption and photocatalytic hydrogen production, etc.^[22–24]

ZnS only responds to UV light (~4% of the solar spectrum) due to its wide band gap (3.6–3.8 eV) which is one of the main restrictions in its actual applications and the most key barrier to further improve photocatalytic efficiency,^[25–26] and it is still a challenging to obtain the more high photocatalytic efficiency. In order to solve the problem, the numerous attempts have been made to extend the light absorption of ZnS into the visible light region for photocatalytic H₂ evolution, such as

[a] X.-l. Wang, Y. Xiao, Prof. H. Yu, Prof. Y. Yang, Prof. X.-t. Dong
School of Chemistry & Environmental Engineering
Changchun University of Science and Technology
Changchun 130022 (P. R. China)
E-mail: yuhui@cust.edu.cn

[b] Prof. L. Xia
School of Materials Science and Engineering
Harbin Institute of Technology (Weihai)
Weihai 264209 (P. R. China)
E-mail: xialong@hit.edu.cn

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doping^[27] and coupling with narrow bandgap semiconductors.^[28] Among various strategies, one of the most ideal strategies for the visible light response is to joint narrow band gap semiconductors onto the surfaces of wide band gap (E_g) semiconductors to form the heterojunction by which increases the light absorption range to the solar spectrum.^[29–30] CeO_2 is preferred candidate due to its unique superiorities such as high chemical stability and environmental friendliness, Ce (III) and Ce (IV) oxidation state conversion is easy which has a suitable valence band with ZnS.^[31,32]

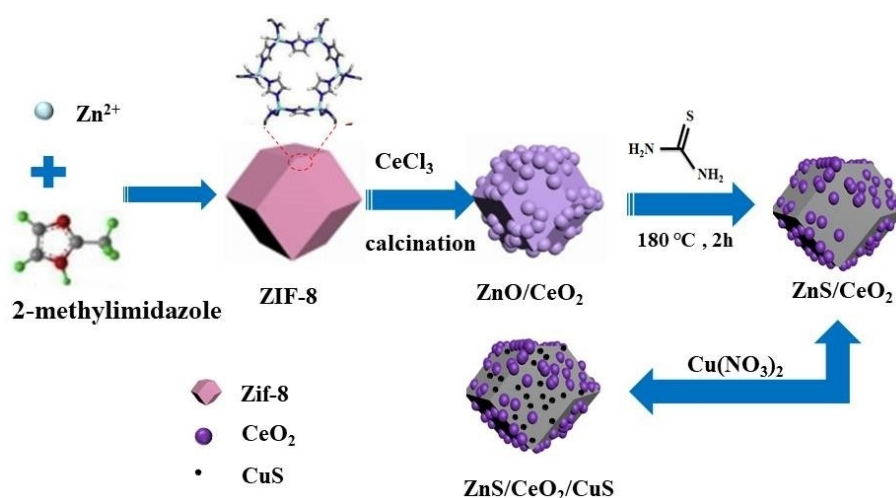
In addition, CeO_2 has the higher oxygen-storage/release capacity and can also response to visible light which has been widely researched in the photocatalysis, especially in the photocatalytic hydrogen production fields. Xiao et al.^[33] synthesized the ordered porous chrysanthemum-like CeO_2/ZnO composite by the hydrothermal template method, the Ce^{4+} was an electron acceptor which could easily capture electrons to form Ce^{3+} , and the trapped electrons could also be captured by the adsorbed O_2 for further reaction which was beneficial to the high-efficiency photocatalytic H_2 production. Dao^[34] et al synthesized $\text{Au@CeO}_2\text{-Pt}$ composite using a hydrothermal method, which showed the superior photocatalytic H_2 production performance due to its large BET surface area and an abundance of active sites. Liu et al.^[35] synthesized the $\text{CeO}_2/\text{g-C}_3\text{N}_4$ composite which exhibited the excellent photocatalytic H_2 production character under visible-light due to the stronger interfacial effects, the more visible-light absorbance and the faster electron transfer. However, the photocatalytic efficiency of ZnS/CeO_2 is still seriously limited by the fast recombination of charge carriers.^[36–38] Therefore, the exploring for the proper strategies to inhibit the recombination of photogenerated electrons-holes have become urgent in the ZnS/CeO_2 heterojunction structure.

It has been confirmed that the decoration of noble metals on semiconductor is a promising solution to promote the separation and migration of photogenerated electrons-holes due to the Schottky barrier.^[39,40] The decoration of noble metals

on ZnS/CeO_2 is a good choice to solve the trouble of charge recombination, it is mainly attributed to the plasma effect of noble metals which can promote the separation of electron-holes pairs by capture photoelectron.^[41,42] However, their applications are limited greatly due to the much higher price of noble metals in the photocatalysis field. Therefore, researchers mostly used some compounds with narrow band gap, such as Co_3O_4 ,^[43] NiS ,^[44] CuS ,^[45] etc. as co-catalysts to replace the noble metals.

Inspired by the rich morphology of ZnO and cation-exchange technology, regular dodecahedron structure ZnO was obtained by ZIF-8 precursor calcination, and ZnS was obtained by in-situ vulcanize on ZnO.

As Scheme 1, basis on the design idea, the present work designed a dodecahedron structure CeO_2/ZnO firstly by the calcination of the Ce doped ZIF-8 precursor. The activity of ZnO is much higher than that of CeO_2 , and ZnO is more easily vulcanized than CeO_2 . Therefore, when the prepared ZnO/CeO_2 samples were vulcanized, ZnO was preferentially vulcanized into ZnS, and CeO_2 was completely retained. This successful design not only maintained the morphology of ZIF-8, but also enhanced the oxidation-reduction capacity of the catalyst. Such, CeO_2/ZnS composite was obtained by the in-situ sulfide of CeO_2/ZnO under hydrothermal condition in this study. CuS was loaded on CeO_2/ZnS composite by cation replacement method. Due to its narrow band gap and metal-like characteristics, CuS could play a similar role with noble metals to promote the separation of photogenerated electron-hole pairs of CeO_2/ZnS composite under simulated sunlight. In addition, the influence of CeO_2 doped concentration was well explored. A series of characterization methods were used to evaluate the structure, morphology and photolysis water properties of the prepared material. The material had the larger specific surface area, the more active sites, the better light capture and the higher electron transfer efficiency. The photocatalytic mechanism and the role of CuS were discussed



Scheme 1. Schematic illustration for the synthetic route of CuS decorated regular dodecahedron ZnS/CeO_2 .

2. Results and Discussion

2.1. Phase structure and morphology characterizations

Figure 1a showed the XRD patterns of the Zif-8 and Ce^{3+} /Zif-8 samples. All diffraction peaks could be perfectly assigned to the standard diffraction data of Zif-8 (Simulate). The sharp diffraction peaks indicated that the prepared materials had much higher crystallinity, and the introduction of Ce^{3+} ions did not change the phase structure of Zif-8.

Figure 1b showed the XRD pattern of X- CeO_2 /ZnS-CuS samples with different Ce content. It could be seen that the diffraction peaks were gradually increased along with the increase of Ce content. The XRD diffraction patterns of the CeO_2 /ZnO and CeO_2 /ZnS samples were given in Figure 1c. In the XRD pattern of CeO_2 /ZnO, the diffraction peaks of Zif-8 disappeared completely, the strong diffraction peaks at 31.8° , 34.4° , 36.2° , 47.7° , 56.7° , 62.8° , 66.3° , 67.9° and 69.1° were corresponded to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes of ZnO (JCPDS No.36-1415), respectively, and a much weak diffraction peak at 28.8° could be assigned to the (111) crystal plane of CeO_2 (JCPDS No.43-1002). After in-situ vulcanization, the characteristic diffraction peaks of ZnO were disappeared, and all diffraction peaks were corresponded to CeO_2 or ZnS because the standard pattern of CeO_2 (JCPDS No.43-1002) was remarkably similar with ZnS

(JCPDS No.65-1691). But, the diffraction peaks were shown after vulcanization, which should mainly be corresponded to ZnS in Fig. 1b, and a small quantity of CeO_2 was also existed in the prepared materials according to the Figure 1c. Because the low content of CuS was obtained by cationic replacement method, and no diffraction peaks of CuS could be observed in the XRD pattern, the similar result was even reported in the reference.^[46] Compare Figure 1b and Figure 1c, the diffraction peaks at 33.6° were shown when Ce content were 10 wt% and 20 wt%, but the peak was not shown in Figure 1c (10- CeO_2 /ZnO sample). Such, it could be deduced that CuS (JCPDS No.78-2122) existed in the prepared 10- CeO_2 /ZnS-CuS and 20- CeO_2 /ZnS-CuS samples. The ZnS content would be reduced along with Ce content increase, and the diffraction peaks of CuS was shown, it could be proved that Cu mainly replaced the Zn in the in-situ cation exchange process.

In order to observe the effect of CeCl_3 on the morphology of ZIF-8, Figure 2 given the SEM images of the Zif-8 and Ce^{3+} /Zif-8 with different content of Ce samples. Along with the increase of Ce^{3+} content, the surfaces of Zif-8 gradually became rougher, but the regular dodecahedron structure of Zif-8 was basically maintained, and the rough surfaces provided the more active sites and contact areas with reactive molecules. When Ce^{3+} content was 20%, a large number of aggregates were accumulated on the surface of ZIF-8, and the agglomerations were adverse to the light absorption and utilization.

Figure 3 showed the SEM images of calcined Zif-8 and X- CeO_2 /ZnO samples. After calcination, the obtained samples still maintained the regular dodecahedron structure of Zif-8, and the particle size of samples was gradually refined with the increase of CeO_2 content. When the Ce content was 20%, a large amount of CeO_2 was agglomerated on the surface of ZnO, which was adverse to the photocatalytic process.

Figure 4a showed the SEM image of 10- CeO_2 /ZnS-CuS sample. It could be observed that the 10- CeO_2 /ZnS-CuS composite still maintained the regular dodecahedron of Zif-8, but its surface became more rough which could be attributed to the removal of organic skeleton to appear the porous structure and the distribution of CeO_2 and CuS small particles on the surface of the material. The rough porous surfaces were beneficial to the exposure of the active sites and the increase of the contact areas between the catalyst and the reactive molecules.

Figure 4b showed the TEM image of 10- CeO_2 /ZnS-CuS sample, the loose porous structure could be seen in the material, which was caused by the removal of organic framework after calcination of Zif-8. The SAED image of 10- CeO_2 /ZnS-CuS sample (Figure 4c) showed that the prepared material had multiple diffraction rings, it proved that the material had the polycrystalline structure. The distinct lattice fringe with a spacing of 0.32 nm, 0.17 nm, 0.27 nm and 0.31 nm could be clearly found in Figure 4d, which were corresponded to the (101) and (103) crystal planes of ZnS, (111) plane of CeO_2 and (111) plane of CuS, respectively.

Figure 4(e, f) were respectively the nitrogen absorption-desorption isotherms and pore size distribution curves (inset) of 10- CeO_2 /ZnS and 10- CeO_2 /ZnS-CuS samples which both showed

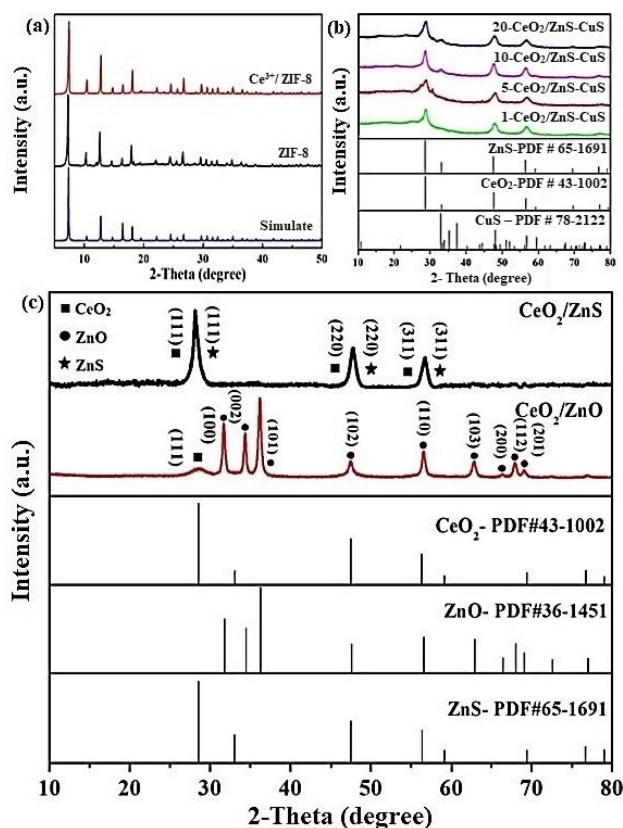


Figure 1. XRD patterns of (a) Zif-8 and Ce^{3+} /Zif-8 samples, (b) X- CeO_2 /ZnS-CuS samples and (c) 10- CeO_2 /ZnO and CeO_2 /ZnS samples

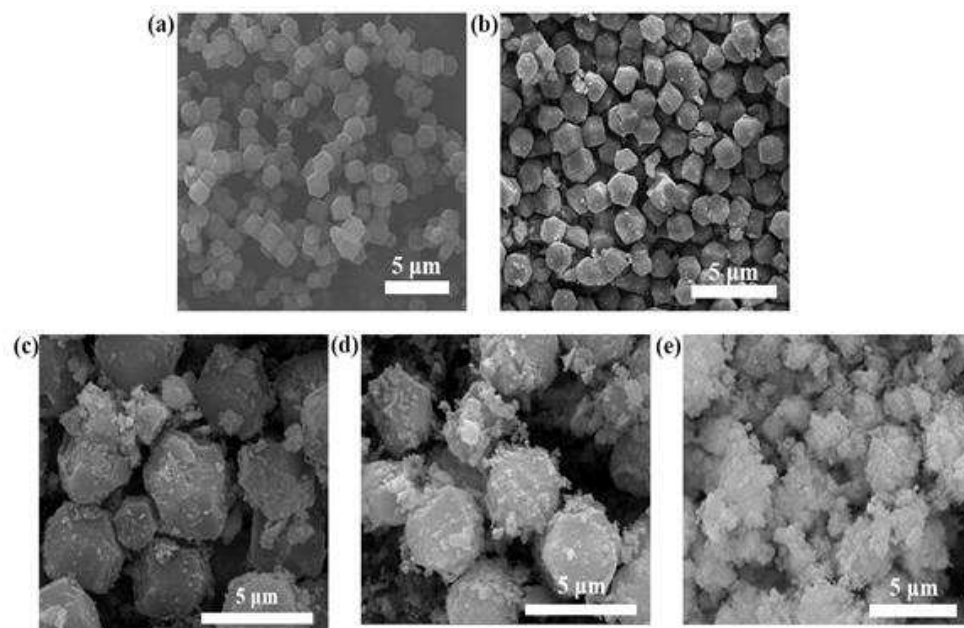


Figure 2. SEM images of (a) Zif-8, (b) 1%-Ce³⁺/Zif-8, (c) 5%-Ce³⁺/Zif-8, (d) 10%-Ce³⁺/Zif-8 and (e) 20%-Ce³⁺/Zif-8 samples.

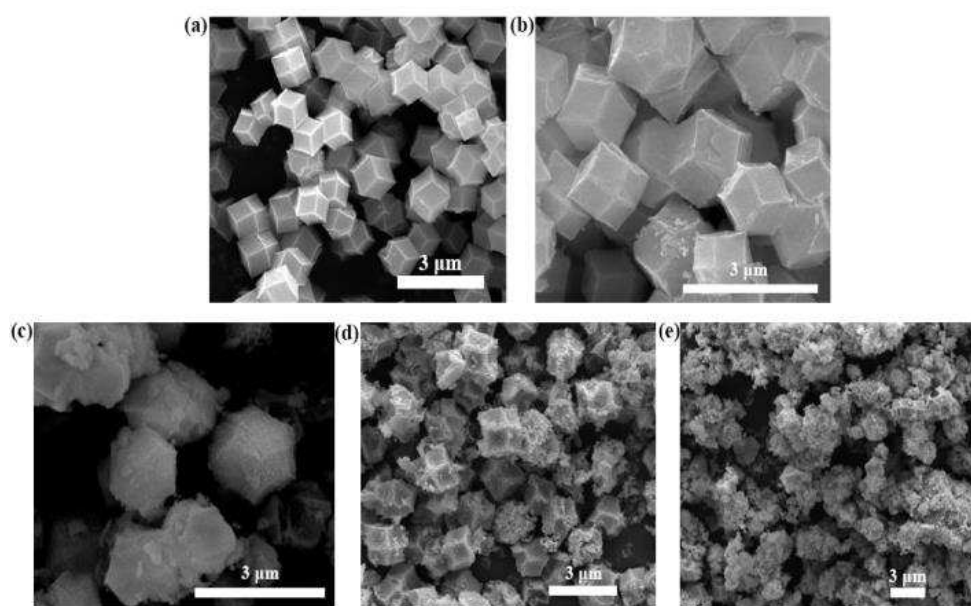


Figure 3. SEM images of (a) Calcined Zif-8, (b) 1-CeO₂/ZnO, (c) 5-CeO₂/ZnO, (d) 10-CeO₂/ZnO, (e) 20-CeO₂/ZnO samples.

the character of IV type isotherm with a H1 type hysteresis loop, it illustrated that the materials had the cylindrical pores. The specific surface areas, the pore volumes, the average pore sizes of the 10-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples were 133.074 m²g⁻¹ and 156.076 m²g⁻¹, 0.304559 cm³g⁻¹ and 0.446611 cm³g⁻¹, 2.53 nm and 2.72 nm. It could be found that the specific surface area and the pore size of the 10-CeO₂/ZnS-CuS were higher. When the cation enters the channel, it will occupy the internal surface. As we all know, the radius of Cu atom was smaller than that of Zn, Cu ions replaced Zn ions

during in-situ cation exchange, it necessarily led to the skeleton contraction of 10-CeO₂/ZnS sample which made the pore diameter increase, the pore volume was increased, and the specific surface area was also increased. But, the pore diameter, the pore volume and the specific surface would no longer increase when the Zn ions on the surface of the sample were completely replaced. The larger specific surface area was favorable for the exposure of the active site and the improvement of photocatalytic performance. At the same time, because the CuS was used as cocatalyst in this study, the doping content

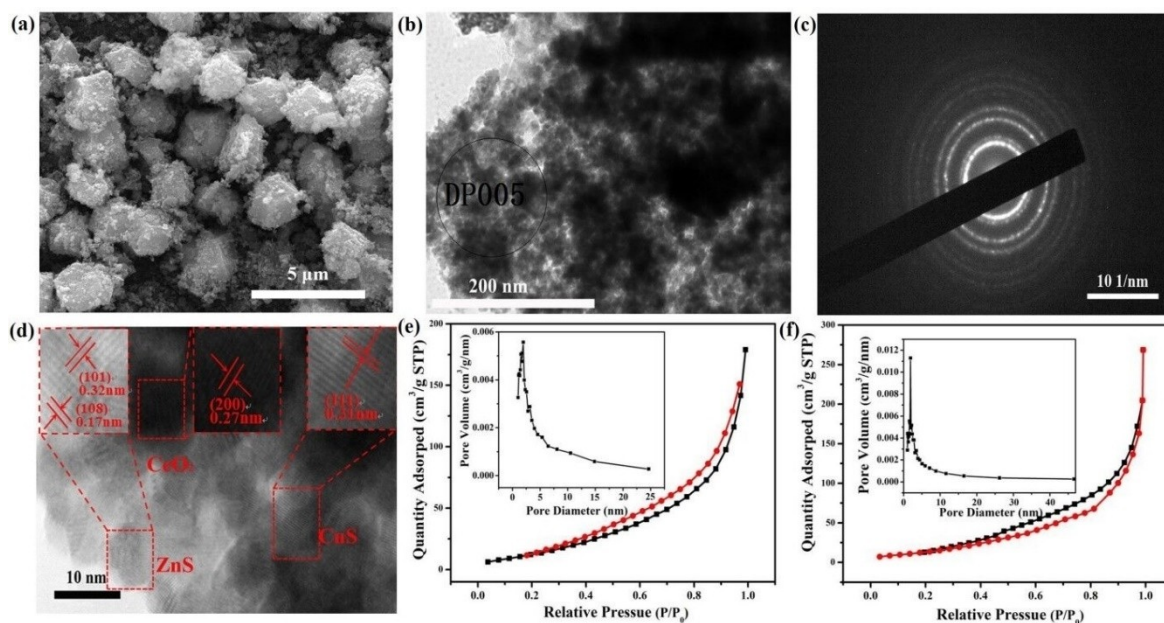


Figure 4. (a) SEM image, (b) TEM image, (c) SAED pattern, (d) HRTEM image of 10-CeO₂/ZnS-CuS sample, and Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of (e) 10-CeO₂/ZnS, (f) 10-CeO₂/ZnS-CuS samples.

of Cu could not too much, and it was the main reason that we chose the post cation exchange method. Therefore, loading CuS was the main factor for the further increase of specific surface area and photocatalytic performance.

2.2. Analysis of element morphology and distribution

The XPS technique was used to elucidate the elemental compositions and chemical present states in 10-CeO₂/ZnS-CuS sample. The total spectrum (Figure 5a) showed that the 10-CeO₂/ZnS-CuS sample comprised the Ce, Zn, S, Cu and O elements. From the Zn 2p spectrum in Figure 5b, two strong peaks could be seen at 1022.1 eV and 1045.5 eV which were attributed to Zn 2p_{3/2} and Zn 2p_{1/2}. Figure 5c showed the O 1s

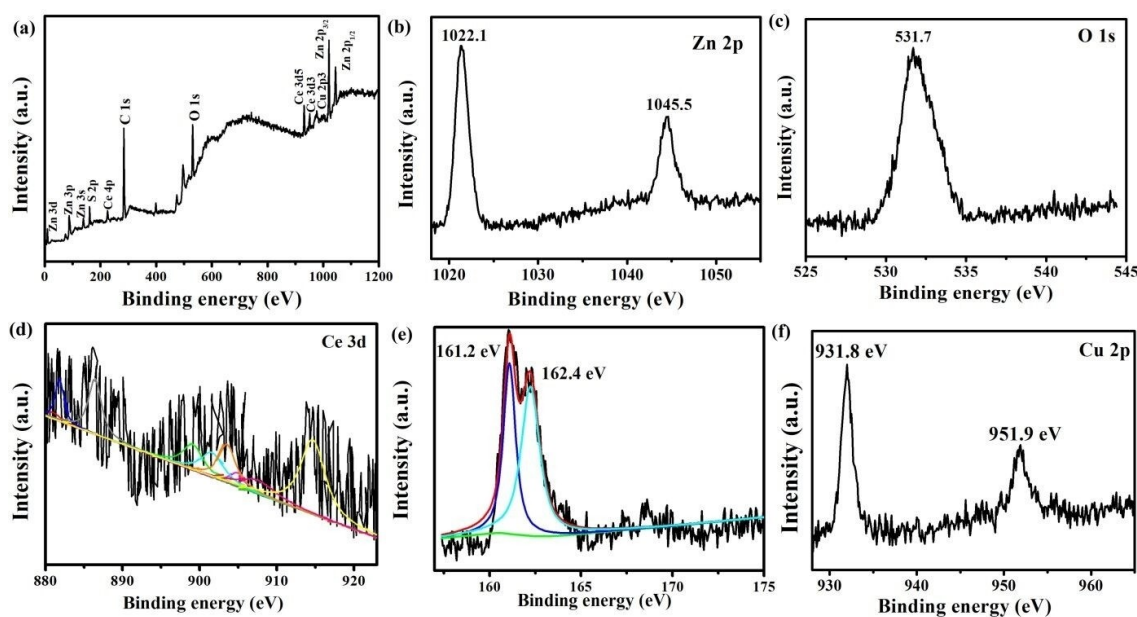


Figure 5. XPS spectra of the 10-CeO₂/ZnS-CuS sample: (a) survey, (b) Zn 2p, (c) O 1s, (d) Ce 3d, (e) S 2p, (f) Cu 2p spectra.

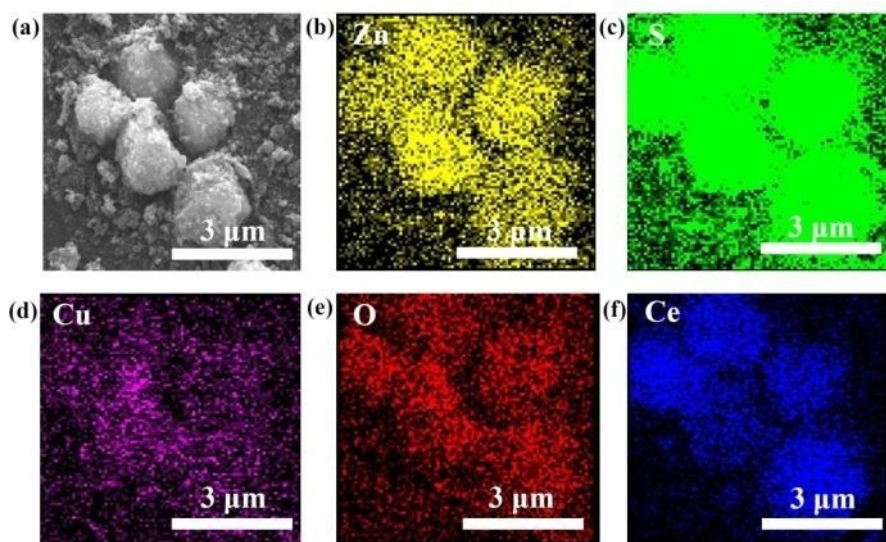


Figure 6. EDS elemental distributed images of 10-CeO₂/ZnS-CuS sample.

spectrum, and the signal peak of binding energy at 531.7 eV was belonged to O²⁻ in of CeO₂. The Ce 3d spectrum (Figure 5d) showed a single peak and two multiple peaks. Corroding to the gauss-lorenz function, the XPS spectrum of CeO₂ could be decomposed into ten peaks at 880.9 eV, 883 eV, 885.2 eV, 888.5 eV, 898.1 eV, 899.1 eV, 901.9 eV, 903.4 eV, 907 eV and 916.9 eV, respectively. Among them, the characteristic peak at 916.9 eV was the characteristic peak of Ce⁴⁺.^[47] The XPS spectra of S 2p was shown in Figure 5e which indicated the presence of S²⁻ in 10-CeO₂/ZnS-CuS sample. As Figure 5f, the characteristic peaks at 931.8 eV and 951.9 eV could be corresponded to Cu 2p_{3/2} and Cu 2p_{1/2}, it inferred that the Cu existed in the Cu²⁺ state.

In order to prove the element distribution of 10-CeO₂/ZnS-CuS sample, the surface element distribution was scanned in the 10-CeO₂/ZnS-CuS sample, and the test results were shown in Figure 6. It could be seen that Zn, S, Ce, O and Cu were evenly distributed on the surface of the prepared sample, which further prove 10-CeO₂/ZnS-CuS sample was successfully prepared.

Figure 7 was the EDS spectrum of 10-CeO₂/ZnS-CuS sample, the signal peaks of O, Ce, Zn, S and Cu elements were shown in the energy spectrum which was consistent with the EDS elemental distributed images of 10-CeO₂/ZnS-CuS sample in Figure 6. The contents of Zn, S, Ce, O and Cu were 19.51%, 30.79%, 14.3%, 26.3% and 9.10%.

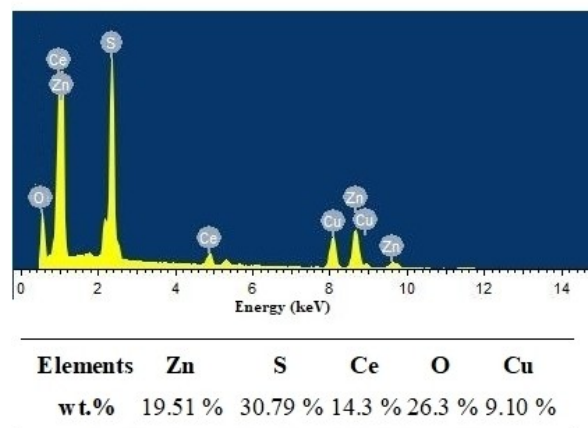


Figure 7. EDS spectrum and element percentages of 10-CeO₂/ZnS-CuS sample.

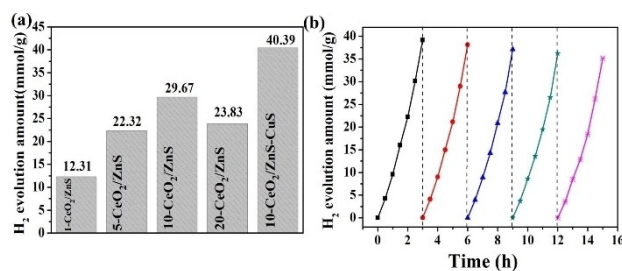


Figure 8. (a) Photocatalytic production hydrogen performance of X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples (b) photocatalytic hydrogen evolution cyclic stability of 10-CeO₂/ZnS-CuS sample.

2.3. Performance of photocatalytic hydrogen production.

The performance of photocatalytic hydrogen production was used to evaluate the photocatalytic activity of the photocatalyst. Figure 8a showed the hydrogen production rate bar charts of the X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples. When the Ce content was 10 wt%, the 10-CeO₂/ZnS sample showed the best photocatalytic property whose hydrogen production

rate was 29.67 mmol g⁻¹ in 3 h, and the hydrogen production efficiency was 9.89 mmol g⁻¹ h⁻¹. When the 10-CeO₂/ZnS sample was loaded with CuS, it could be clearly seen that the

hydrogen production performance of 10-CeO₂/ZnS-CuS sample was significantly enhanced. The hydrogen production rate was 40.39 mmol g⁻¹ in 3 h, and the hydrogen production efficiency reached up to 13.47 mmol g⁻¹ h⁻¹ which was about 1.4 times of 10-CeO₂/ZnS. This result indicated that CuS cocatalyst could provide the more active sites to increase the photocatalytic capacity.

In order to determine the relative photocatalytic stability of the 10-CeO₂/ZnS-CuS sample, the catalyst was collected after each reaction and used in the next cycle photocatalytic hydrogen production experiments under the same conditions. The photocatalytic hydrogen production process were examined in five consecutive experimental cycles, the results were showed in Figure 8b, the catalyst still maintained the much better photocatalytic performance whose hydrogen production rate was 36.67 mmol g⁻¹ in 3 h after 5 time cycles, its conservation rate was about 91%. The phase structure and morphology of 10-CeO₂/ZnS-CuS sample had not significantly changes before and after photocatalytic experiments as the supporting information Figure S1. It indicated that the catalyst had much better cyclic stability and application prospect.

The average hydrogen production rate of photolysis water was also much higher than the most of the photocatalysts of the published works, the comparison results were shown in Table 1.

2.4. Photocatalytic mechanism of CeO₂/ZnS-CuS composite

As we all know, the photocatalytic properties of semiconductors are highly dependent on their optical absorption properties, which can be determined by UV-vis diffuse reflectance absorb spectra. Figure 9a showed the UV-vis absorption spectra of ZnS, CeO₂, X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples. For the X-

Table 1. Comparison of photocatalytic hydrogen production property of a series of similar work.		
Photocatalyst	H ₂ production rate	Ref.
Ni-P/DR-ZnS	3.45 mmol g ⁻¹ h ⁻¹	[11]
CdS-ZIF-8	12.65 mmol g ⁻¹ h ⁻¹	[22]
Zn-deficient ZnS	0.337 mmol g ⁻¹ h ⁻¹	[32]
CeO ₂ QDs/Carbon	0.582 mmol g ⁻¹ h ⁻¹	[37]
FeNi@NGC/g-C ₃ N ₄	2.696 mmol g ⁻¹ h ⁻¹	[48]
CeO ₂ /ZnS-CuS	13.47 mmol g ⁻¹ h ⁻¹	This work

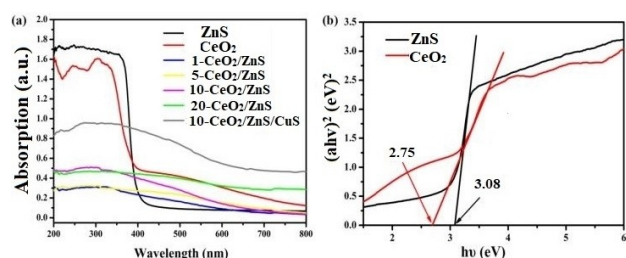


Figure 9. (a) UV-Vis diffuse reflectance absorb spectra of samples; (b) graphical of band gaps evaluation of ZnS and CeO₂.

CeO₂/ZnS samples, the absorption edges of samples were extended to visible light region, and the absorbing abilities to visible light were gradually increased with the increase of Ce content which reached the biggest for 10-CeO₂/ZnS sample. After loaded CuS, the 10-CeO₂/ZnS-CuS sample showed the strongest visible light absorption and the broadest visible light absorption region. The band gaps curves of ZnS and CeO₂ were shown in Figure 9b, and the band gap energy of the materials could be determined according to the diffuse reflection pattern combined with the following formula [Eq. (1)]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

Where α , h , ν , A and E_g represented the absorption coefficient, Planck's constant, optical frequency, constant, and band gap, respectively. Band gap of ZnS and CeO₂ were 3.08 and 2.75 eV, respectively.

In general, photoluminescence (PL) spectra can validate the photogenerated carriers recombination rate of the sample. According to the principle of PL spectra, the stronger PL intensity indicates that the higher electron-hole recombination efficiency happens, and the higher separation efficiency of the electron-hole is corresponded with the higher photocatalytic efficiency. The PL spectra of X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples were shown in Figure 10a, the 10-CeO₂/ZnS-CuS sample showed the weakest PL intensity, it should has the highest separation efficiency of photogenerated electron-hole and the best photocatalytic performance which was consistent with the photocatalytic test results. It also illustrated that cocatalyst CuS significantly could improve the separation efficiency and migration rate of photogenerated carriers to improve the photocatalytic performance of the material.

In order to further verify the photogenerated electronic-hole recombination efficiency of samples, the X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples were carried out the test of EIS and Tafel, and the test results were shown in Figure 10b and Figure 10c. The EIS diagrams can reflect the charge transfer

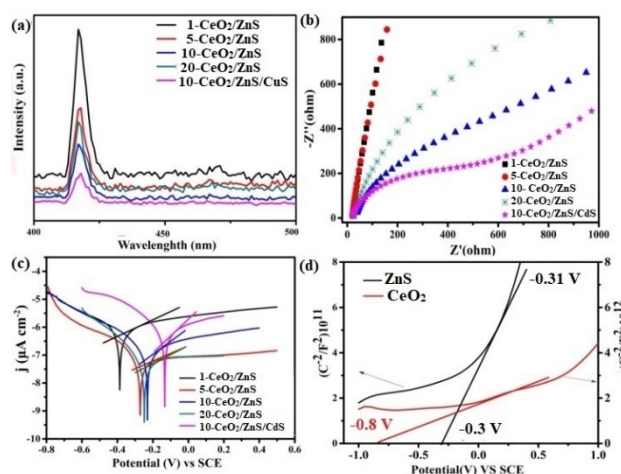


Figure 10. (a) PL spectra, (b) EIS Nyquist plots, (c) Tafel polarization curves in 0.1 M Na₂SO₄ solution of X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples and (d) Mott – Schottky curve of ZnS and CeO₂.

ability of samples, the sample with the smaller arc radius and impedance will have the stronger electronic-hole separation ability. From the EIS diagrams in Figure 10b, the 10-CeO₂/ZnS-CuS sample had the smallest arc radius, it indicated that the impedance of 10-ZnS/CeO₂ sample was significantly reduced by the decorated CuS cocatalyst, the carrier transfer efficiency was enhanced, and the 10-CeO₂/ZnS-CuS sample had the strongest electronic-hole separation ability.

Figure 10c showed the Tafel curve of the X-CeO₂/ZnS and 10-CeO₂/ZnS-CuS samples, the anodic Tafel slope of the 10-CeO₂/ZnS-CuS sample was the largest, the 10-CeO₂/ZnS-CuS sample should have the fastest electron transfer and the highest photocatalytic activity.^[49] These electrochemical test results were consistent with the PL spectra and hydrogen production performance tests.

The conduction band (CB) and valence band (VB) edge potentials of the semiconductor catalyst are the important parameters to evaluate the formation and transfer of photoelectrons-holes. In order to further explain the production of active species, the band potentials of ZnS and CeO₂ were measured and calculated as Figure 10d. The Mott-Schottky (MS) plots of ZnS and CeO₂ showed a positive slope, it indicated that the ZnS and CeO₂ were n-type semiconductor.^[50] The flat band potential was derived from the intersection of the tangent line and the x-coordinate of the curve.^[51–52] Flat band potentials of ZnS and CeO₂ were 0.3 V and 0.8 V, and they were −0.06 V and −0.56 V relative to the standard hydrogen electrode (NHE) band potentials. The conduction band potential (E_{CB}) of n-type semiconductor is more negative about 0.1 V than the flat-band potential.^[53] Therefore, the E_{CB} of ZnS and CeO₂ were ca. −0.16 V and −0.66 V vs NHE, respectively. The valence band potential can be calculated according to the formulas [Eqs. (2)–(3)]:

$$E \text{ (vs NHE)} = E \text{ (vs SCE)} + 0.24 \quad (2)$$

$$E_{vb} = E_g + E_{cb} \quad (3)$$

Where, E_{vb} is the valence band potential, E_{cb} is the conduction band potential, E_g is the band gap of the semiconductor. The E_{vb} of ZnS and CeO₂ were 2.82 eV and 1.09 eV, respectively.

Figure 11 showed the photocatalytic mechanism diagram of the composite material. The CeO₂/ZnS II type heterostructure is favorable for the transfer of photoelectron-hole to promote the photocatalytic hydrogen production capacity of the sample. Because the CB position of CeO₂ is more negative than the CB position of ZnS, the electrons on the CB of CeO₂ are transferred to ZnS when sunlight illuminates, the cocatalyst CuS captures the electrons on the CB of ZnS, and the electrons react with H⁺ to form H₂. Because the VB of ZnS is lower than the VB of CeO₂, the holes are transferred to the VB of CeO₂ through the interface, and MeOH is used as the holes catcher to capture holes in the VB of CeO₂ which achieves the effective separation of photoelectron-hole and improves photocatalytic performance.

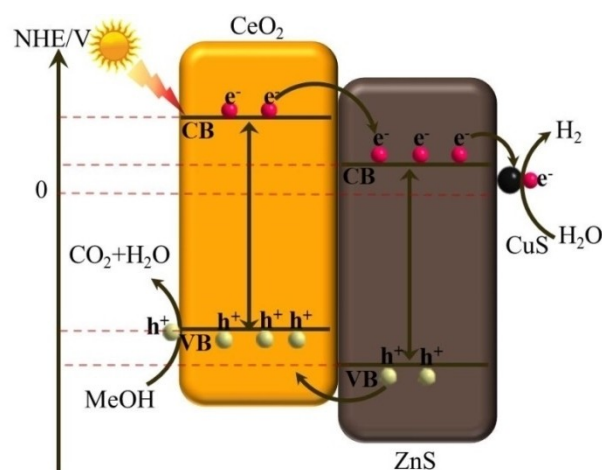


Figure 11. Photocatalytic hydrogen production mechanism schematic diagram of the CeO₂/ZnS-CuS.

3. Conclusions

In this work, metal organic frame material Zif-8 was used as the precursor, CeCl₃ was used as the Ce source, and CeO₂/ZnS composite material was obtained after calcining and vulcanizing. When the content of Ce was 10 wt%, 10-CeO₂/ZnS sample showed the best photocatalytic hydrogen production performance in all X-CeO₂/ZnS samples. At the same time, in-situ cation exchange method was used to load cocatalyst CuS on the 10-CeO₂/ZnS composite to obtain 10-CeO₂/ZnS-CuS composite which had the larger specific surface area and regular dodecahedral structure. The hydrogen production efficiency of the 10-CeO₂/ZnS-CuS sample reached about 13.47 mmol.g^{−1}.h^{−1} which was about 1.4 times of 10-CeO₂/ZnS. It could be attributed to the loading cocatalyst CuS to form the ternary system, and the regular porous dodecahedral structure provided the larger specific area, the more active sites and the more efficient electronic transmission.

Experiment Section

Chemicals

Cerium trichloride (CeCl₃·7H₂O, A.R., Shanghai yuanye biotechnology Co., Ltd. China), Ethanol (A.R., Beijing Chemical Works), Zinc nitrate (Zn(NO₃)₂·6H₂O, A.R., Tianjin guangfu technology development Co., Ltd. China), 2-methyl imidazole (C₄H₆N₂, A.R., Shanghai alighting biochemical technology Co. Ltd. China), Thioacetamide (C₂H₅NS, A.R., Shanghai McLean biochemical technology Co., Ltd. China), Copper nitrate (Cu(NO₃)₂·3H₂O, A.R., Tianjin guangfu technology development Co. Ltd. China). Deionized water was used in all experiments as solvent.

Preparation of metal-organic frameworks material Zif-8

The metal organic framework material Zif-8 was prepared according to the method of reference [54]. The specific experimental steps were as follows:

3.645 g of 2-methylimidazole was dissolved into 450 mL methanol to get solution A. 3.34 g $\text{Zn}(\text{NO}_3)_2$ was dissolved into methanol to get solution B. The solution A and solution B were mixed quickly and stirred for 24 h. The final solution was filtered, washed with deionized water for three times and dried at 70 °C to get Zif-8.

Preparation of CeO_2/ZnO composites

100 mg of Zif-8 was evenly distributed into 10 mL deionized water by ultrasound to obtain solution A. A certain amount of CeCl_3 was dissolved into deionized water to get solution B. Solution B was added into solution A drop by drop which was stirred for 2 h under room temperature. The precipitate was centrifuged, washed multiple times with deionized water and anhydrous ethanol, and dried at 60 °C for 12 h. The power sample was heat-treated at 350 °C for 3 h with the 2 °C per minute heating rate.

Preparation of $\text{CuS-CeO}_2/\text{ZnS}$ composites

50 mg of $\text{C}_2\text{H}_5\text{NS}$ was dissolved into 20 mL deionized water, 50 mg of CeO_2/ZnO sample was added into the solution which was ultrasound for 20 min. The turbid liquid was transferred into 50 mL hydrothermal reactor at 180 °C for 2 h, the obtained power was dried at 60 °C for 12 h, and CeO_2/ZnS sample was obtained. The composite material was signed as $\text{X-CeO}_2/\text{ZnS}$, where X represented the content of Ce.

100 mg of CeO_2/ZnS was distributed in 10 mL deionized water under ultrasound for 30 min, 1.97 mol % $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into the solution which was stirred for 2 h. The power sample was washed multiple times with deionized water and anhydrous ethanol, and dried at 60 °C for 12 h to get the composites material.

The above synthesis steps were shown in the Scheme 2.

Characterization

The phase structure was examined by powder X-ray diffraction (XRD) pattern which was collected on a Siemens D5005 diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$ and operating at 30 kV and 20 mA). X-ray photoelectron spectroscopy (XPS, Versa Probe PHI 5000) was employed to determine the surface electronic states. Surface morphologies were observed by the scanning

electron microscope (SEM, JEOL JSM-5600 L) and transmission electron microscopy (TEM, JEOL 2010). The specific surface areas of the samples were measured by nitrogen adsorption-desorption isotherms at 77 K according to the Brunauer-Emmett-Teller analysis (BET, ASAP 2020, Micromeritics, USA). A desorption isotherm was used to determine the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. The UV-Vis diffuser reflectance spectra (DRS) were recorded on a UV-vis spectrophotometer (UV-3010, Hitachi, Japan) using BaSO_4 as a reference, and converted from reflection to absorbance by the Kubelka-Munk method. All electrochemical analysis (electrochemical impedance spectroscopy (EIS) and the Tafel analysis) were obtained from a CH-660D (China) electrochemical work station using platinum carbon as the counter electrode, saturated calomel electrode (SCE) as the reference electrode. 5 mg of as-prepared sample was distributed in 500 μL distilled water, 500 μL ethyl alcohol and 20 μL membrane solution with ultrasound for 30 min and then evenly coated on working electrodes to prepare the working electrodes. 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte. Simulated sunlight was used as the light source (300 W, light intensity 200 mW/cm^2), and the distance between the lamp and the electrode was about 16 cm.

Photocatalytic H_2 - production activity test

In a typical reaction, 100 mg of photocatalyst was dispersed into 25 mL MeOH (As sacrificial agent) and 75 mL deionized water mixed solution which was transferred into a glass vessel reactor. In order to rid dissolved oxygen in the reactor, N_2 was aerated before light illumination. Then, the reactor was irradiated with Xe-lamp (300 W, light intensity 200 mW/cm^2), and stirred magnetically. Finally, the H_2 evolution was analyzed by an online gas chromatograph (Techcomp, GC7900; TCD detector, 5 $\text{\AA}$ molecular sieve column) every one hour.

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Scheme 2. Synthesized flow chart of $\text{CeO}_2/\text{ZnS-CuS}$ composites.

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Conflict of Interest

The authors declare no conflict of interest.

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