

Preprints are preliminary reports that have not undergone peer review. They should not be considered conclusive, used to inform clinical practice, or referenced by the media as validated information.

Cu1.94S Nanocrystal Superstructure for Photocatalytic Hydrogen Evolution

Lian Zhu Sun Yat-sen University **Jin Liu** Sun Yat-sen University Liguang Wang Wenzhou University Alvin Dai Argonne National Laboratory Huile Jin Wenzhou University Hsiu-Yi Chao Sun Yat-sen University Long Jiang Sun Yat-sen University **Tianpin Wu** Argonne National Laboratory Zheng-Ping Qiao (<a>cesqzp@mail.sysu.edu.cn) Sun Yat-sen University

Research Article

Keywords: nonstoichiometric, nanocrystal superstructure, photocatalytic hydrogen evolution

Posted Date: August 26th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-800301/v1

License: (c) This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Abstract

Ordered nonstoichiometric $Cu_{1.94}S$ nano superstructure are constructed and provide notably improved catalytic H₂ evolution reaction performance at 2482.00 µmol g⁻¹ h⁻¹. Careful selection of metal organic framework precursors with long range metal ion alignments impact performance, as well-ordered superstructures give rise to uniform electromagnetic fields and organized interparticle interactions that facilitate charge carrier transport. These close packed nanoparticles with negatively charged carboxylate surfaces inhibit large [Ru(bpy)₃]Cl₂ and triethanolamine transport outwards, but allow smaller H₂O particles to enter superstructure interiors. In this case, separation happens not only between electrons and holes but also between reduction and oxidation zones. Abundant dangling bonds also form from the complex nonstoichiometric $Cu_{1.94}S$ structure and bulk aggregation of close packed $Cu_{1.94}S$, up to hundreds of nanometers, provides abundant catalytic active sites.

Introduction

In photocatalysis, the fundamental steps are understood to include light absorption, electron-hole pair generation, charge separation, and transport¹.Enhancing any steps can promote photocatalysis performance. In terms of improving charge carrier transport, mitigating electronic resistance is crucial in photocatalysts, especially for nano-powders. Efforts should be made to control catalyst morphology as excessive grain boundaries will impede carrier movement. Interestingly, facile electronic transport has been observed in ordered thylakoid stacks found in chloroplasts used for photosynthesis². Inspired by these findings, we seek to construct ordered superstructures in catalyst materials. In principle, uniform electromagnetic fields and organized interparticle interactions found in these structures facilitate efficient charge carrier transport^{3–8}.

However, it is still a great challenge to understand the relationship between fine structure and photocatalytic property. In this paper, the ordered superstructure was further shed light on, contributing to the formation of surface dangling bonds on particles.

Synthesis methods to construct ordered superstructures have been seldom explored in the field^{9–12}. Despite this, studies on self-assembly using intermolecular forces have seen promising results^{13–15}. However, reaction conditions are usually limited to specific use cases and synthesis requires precise control¹⁶. Metal organic frameworks on the other hand show long range metal ion alignment and provide the possibility for topological control in ordered superstructures. Therefore a well-studied benchmark MOFs, $Cu_3(BTC)_2$ (BTC = 1, 3, 5-benzenetricarboxylate, $[C_6H_3(COO)]^{3-}$) (known as HKUST-1), was selected as a copper source for the $Cu_{1.94}$ S superstructure. This method may also be extended to construct other superstructure designs based on the abundance of MOFs sources.

Nonstoichiometric compound nanocrystals are notable for use as catalysts because they exhibit abundant surface dangling bonds and defect-induced active sites^{17–21}. Copper chalcogenides in

particular, are selected as candidates in our work since they observe various stable nonstoichiometric phases. Cu_{1.94}S is used as the model copper chalcogenide due to its remarkable lattice structure complex that provides abundant active sites.

Results And Discussion

Cu_{1.94}S synthesis steps areprovided in the method section. All of the reagents were purchased commercially and used without further purification. The sulfur source was 1-dodecanethiol and the copper source was Cu(CH₃COO)₂ or Cu₃(BTC)₂ sol prepared followingreferences in literature 22.PXRD (Fig. 1a) and FTIR spectra (Fig. 1b) were used to analyze the powder material phase and to investigate the presence of organic cappingagentson particle surfaces, respectively. It is observable that bothcatalysts prepared by either Cu(CH₃COO)₂ (upper) or Cu₃(BTC)₂ sol (below) display similar PXRD peaks. All of the diffraction peaks can be indexed as djurleite Cu_{1.94}S (PDF#23–0959). As for FTIR spectra, there are stretching vibration absorption peaks indicating Cu–O (726 cm⁻¹), C-H (2857 and 2927 cm⁻¹) caused by 1-dodecanethiol, and C = O present in carboxyl groups (1467 and 1645 cm⁻¹) from CH₃COO⁻ (upper) or BTC³⁻ (below).

 $Cu_{1.94}S$ morphologies were characterized using TEM. $Cu(CH_3COO)_2$ and $Cu_3(BTC)_2$ prepared $Cu_{1.94}S$ aggregate as randomly distributed nanoparticles with diameters of 6.1 ± 0.9 nm (Fig. 2a-c, denoted as **RA**) and $Cu_{1.94}S$ ordered superstructure with diameters of 5.1 ± 0.4 nm (Fig. 2d-i, denoted as **SS**), respectively. The inset FFT pattern in Fig. 2e shows high stacking order, six-fold axes, and confirms a HCP superstructure(Figure S1)¹⁰. Ordering also occurs in **SS** over hundreds of nanometers (Fig. 2g). Small angle XRD of **SS** shows equidistance's of 7.98 nm, which is coincidental with the periodicity found in ordered structure (Fig. 2h) images. Single particle HRTEM images of **SS** (Fig. 2i) shows good crystallinity and the lattice fringe can be indexed to the (804) plane, which corresponds to the strongest XRD diffraction peak found at a 2 θ of 37.62° (Fig. 1a).

Photocatalytic hydrogen evolution experiments were conducted to characterize catalyst performance. Tris(2,2'-bipyridine)ruthenium(ii) complex $[Ru(bpy)_3]Cl_2$, was added as visible-light harvesting agent. An exact description of the catalyst system (denoted as $[Ru(bpy)_3]Cl_2$, **Ru-RA**, or **Ru-SS**) is provided in the experimental section. UV-vis spectra (Fig. 3a) show that orange $[Ru(bpy)_3]Cl_2$, **Ru-RA**, and **Ru-SS** absorb visible light intensely, while black copper sulfides exhibit weak absorption. This result also shows that $[Ru(bpy)_3]Cl_2$ is the strongest photosensitizer. Photoluminescence (PL) spectra (Fig. 3b) were used to investigate photo-induced electron and hole recombination. Obvious fluorescence quenching occurred in **Ru-SS**, which indicates effective inhibition of recombination.

Capacitance measurements were conducted to obtain a Mott-Schottky plot (Figure S2), from which one can see that **SS** is a p-type semiconductor with a flat band potential of 1.68 V and a top valence band of 1.78 V. Solid UV-vis absorption spectra (Figure S3) shows that the bottom conduction band (CB) of **SS** is -0.22 V, which is lower than $E(H_2O/H_2)$. This CB is more positive than the HOMO of $[Ru(bpy)_3]Cl_2$ (-0.88

V)[23] and permits electron transfer from $[Ru(bpy)_3]Cl_2$ to **SS** (Fig.3c). Theadaptive band structure enable **Ru-SS** to photo-catalyze hydrogen evolution.

Photocatalytic H₂ evolution reactions (HER) were also carried out under visible light irradiation as a model reaction. H₂ evolution rates found in **Ru-SS** were 2482.00 µmol g⁻¹ h⁻¹ and about five times greater than that of **Ru-RA** (520.29 µmol g⁻¹ h⁻¹). The Cu_{1.94}S-**SS** system in this paper shows high H₂ evolution rates. As shown in Table 1, this rate was even found to be higher than those of some other metal sulfide nanocomposites²⁷⁻³³.

Catalyst	H ₂ evolution rate	Reference
	µmol g ⁻¹ h ⁻¹	
Ru-SS	2482.00	this work
Ru-RA	520.29	this work
SS	20.46	this work
[Ru(bpy) ₃]Cl ₂	0	this work
Cu _{1.94} S	34.038	24
Cu _{1.94} S	20	25
Cu _{1.94} S	11	26

Table 1 Comparison of **Ru-SS** with nano-copper sulfides for photocatalysis of H_2 evolution reactions

Photoelectrochemistry, photophysics, and electrical performance were further studied to elucidate this markedly improved catalysis. Conditions for photoelectrochemical measurement are described in the experimental section. Both **Ru-RA** and **Ru-SS** show fast photocurrent response, as shown in Fig. 4a. **Ru-SS** exhibits higher photocurrent density, which indicates faster charge separation. Time-resolved fluorescence decay spectra (Fig. 4b) show that the average fluorescence lifetimes for [Ru(bpy)₃]Cl₂, **Ru-RA**, and **Ru-SS** are 148.95, 155.22, and 162.88 ns, respectively. **Ru-SS** shows the longest lifetime, which indicates the best electron-hole pair separation or lowest electron-hole recombination rates. Nyquist plot were used to measure the electrical conductivity of **RA** and **SS**. Smaller Nyquist arc radii seen in **SS** (Figure S4) show higher electrical conductivity, which suggests faster interparticle charge transfer. Therefore, **SS** related samples provide relatively fast photo response, low electron-hole recombination rates, and fast interparticle charge transfer. These properties collectively enable significantly improved photocatalytic performance.

Fine structure investigation is one of the challenges inhibiting deep understanding and rational design of catalysts. **RA** and **SS** exhibit distinguished catalytic activity but show only stacking pattern differences according to TEM. Thus X-ray Absorption Fine Structure (XAFS) was used for further characterization and results are shown in Fig. 5 and Table S1. Figure 5c shows EXAFS peaks of curves in R space that are characterized as Cu–S bonds. According to local structure fitting (Table S1), the Cu–S average coordination number (CN) is 1.5 and 3.1 for **SS** Cu_{1.94}S and **RA** Cu_{1.94}S, respectively. This is much lower than that of bulk Cu_{1.94}S, as shown in its lattice structure (Figure S5), but is reasonable for nanomaterials with large quantities of unsaturated surface coordinate ions. Here the unsaturated coordinate ions are copper. Closed packed structures in **SS** can provide extra stability for abundant dangling bonds upon the CN difference of **SS** and **RA**. Cu–O bonds are present in incomplete Cu²⁺–BTC^{3−} (**SS**) or Cu²⁺–CH₃COO[−] (**RA**), which is deduced from IR spectra (Fig. 1b) and confirmed by EXAFS calculation. The lower Cu–O CN in **SS** (1.2) than that in **RA** (2.6) indicates that the amount of BTC^{3−} (**SS**) is less than that of CH₃COO[−] (**RA**) on the nanoparticle surfaces. Relative anion amounts were also identified using zeta potentials, which are – 10.07 mV and –18.35 mV for **SS** and **RA**, respectively. Less negative zeta potentials present in **SS** indicate less negatively charged carboxylate and thus more unsaturated copper.

Normalized Cu K-edge X-ray absorption near edge structures (XANES) of **SS** and **RA** are shown in Fig. 5b. The lower absorption edge of **SS** shows that the oxidation number of copper in **SS** is lower than that in **RA**. This may be due to a less abundance of Cu^{2+} from incompletely broken $Cu^{2+}-BTC^{3-}$ than that from incompletely broken $Cu^{2+}-CH_3COO^{-}$.

More surface dangling bonds, lower Cu–O CN, and lower oxidation number indicate that **SS** has less BTC³⁻ on nanoparticle surfaces. This is potentially due to close-packed ordered arrangements. In addition, the steric hindrance of BTC³⁻ is greater than that of CH₃COO⁻. When considering molecular structures, it can be deduced that the close packed ordered superstructure, as well as residue BTC³⁻, block efficient transport of large [Ru(bpy)₃]Cl₂ (1.329 nm·1.329 nm·1.329 nm) and triethanolamine (TEOA, 1.150 nm·1.070 nm) (Figure S6) outwards but allow small H₂O to enter the interior of **SS**.

This process and key factors for remarkably enhanced catalytic performance found in **SS** photocatalyst is summarized in Scheme 1. First, incident visible light induces metal-to-ligand charge transfer and generates electron-hole pairs in $[Ru(bpy)_3]Cl_2$. Afterwards, electrons move to $Cu_{1.94}S$ due to their adaptive band structure. Then, 1-dodecanethiol and carboxylate on particle surfaces, along with the close packed structure, block large $[Ru(bpy)_3]Cl_2$ and TEOA transport outwards but allow small H₂O to enter the interior of $Cu_{1.94}S$ aggregates. Electrons are used to reduce H₂O to H₂, while holes are sacrificed by TEOA around $[Ru(bpy)_3]Cl_2$. The catalytic region is divided into reduction zones (interior) and oxidation zones (outside) for **SS**. In comparison with **RA**, **SS** prepared by MOFs exhibit ordered superstructure and show relatively higher electron conductivity caused by uniform electromagnetic fields and interparticle interactions. **SS** has also more surface dangling bonds and offers more catalytic active sites. Therefore, catalysts containing **SS** provide more efficient separation of electrons and holes. Close packed **SS** with more steric hindrance provided by BTC^{3-} also block $[Ru(bpy)_3]Cl_2$ and TEOA more efficiently.

In summary, we constructed $Cu_{1.94}S$ nanocrystal ordered superstructure and clearly show that the materials have beneficial properties distinct from single and randomly aggregated counterparts. The close-packed ordered nanoparticles were simply prepared by careful selecting MOFs as metal sources that simultaneously endow materials with more catalytic active sites and more efficient redox. Therefore, as prepared model $Cu_{1.94}S$ exhibits greatly improved HER catalytic performance of 2482.00 µmol g⁻¹ h⁻¹ and provides guidelines to inform future catalyst design.

Methods

Characterization

Powder X-ray diffraction (XRD) analysis was performed using a Rigaku Dmax-2000 diffractometer equipped with Cu Ka (λ = 0.15406 nm) radiation. FTIR analysis of nanocrystal surfaces was performed on a Nicolet AVATAR 330 Fourier Transform Infrared Spectrometer in the range of 400–4000 cm⁻¹. Catalyst morphologies were observed with transmission electron microscopy (TEM, JEOL JEM-2100F) and operated at 200 kV. UV-visible absorption (UV-vis ABS) was conducted on a Perkin Elmer UV-Vis-NIR Spectrophotometer Lambda 950 at room temperature. Steady photoluminescence spectra were measured on Combined Fluorescence Lifetime and Steady State Spectrometers (Edinburgh FLS920) at an excitation wavelength of 406 nm. Time resolved photoluminescence spectra were conducted by Edinburgh FLS920 equipped with a picosecond pulsed light emitting diode (Edinburgh EPLED-405). The excitation and emission wavelength were 406 nm and 610 nm, respectively. Samples were prepared by ultrasonic dispersion of 5mg RA or SS in 5 mL 0.05 mg/mL [Ru(bpy)₃]Cl₂ for 30 min, denoted as Ru-RA and Ru-SS. Sample that contained only 5 mL 0.05 mg/mL [Ru(bpy)₃]Cl₂ was denoted as [Ru(bpy)₃]Cl₂. Photocurrent density, Nyquist plots, and Mott-Schottky plot measurements were obtained using CHI 760D electrochemical workstations (CHI, Shanghai). X-ray absorption spectra were collected at the 9-BM-C beamline (Advanced Photon Source (APS) at Argonne National Laboratory (ANL)) in the transmission mode at Cu K-edge. The spectra were normalized and analyzed using Athena software. EXAFS raw data were background-subtracted, normalized, and Fourier transformed using standard procedures in the IFEFFIT package. Generated hydrogen gas was tested and analyzed using a gas chromatograph equipped with FID (GC 9790) and nitrogen acted as the carrier gas. Zeta potentials were measured on the Brookhaven High Sensitive Zeta Potential and Particle Size Analyzer 90Plus PALS. The solvent was acetonitrile.

Preparation of Cu₃(BTC)₂

 $Cu_3(BTC)_2$ sol (BTC = 1, 3, 5-benzenetricarboxylate) was synthesized by the following steps: 1,3,5benzentricarboxylic acid/anhydrous ethanol solution (0.02 mol L⁻¹, 10 mL) was dripped slowly (1 mL min⁻¹) into $Cu(CH_3COO)_2$ /anhydrous ethanol solution (0.01 mol L⁻¹, 10 mL) under ultra-sonication at 25 °C and then kept for an additional 2 min. After centrifugation, the upper liquid was discarded and the lower sediment was washed with ethanol three times. This step was repeated 6 times in total. The lower sediment was collected and washed by 30 mL 1-octadecene 3 times. After centrifugation the upper liquid was discarded and the lower sediment was discarded and the lower Cu₃(BTC)₂ sol was ready for further use.

Preparation of SS Cu_{1.94}S

In an optimized experiment, pre-obtained $Cu_3(BTC)_2$ sol (copper source) and 1-dodecanethiol (750 µL, AR, sulfur source) were successively added into 1-octadecene (29.25 mL, AR) in a three-necked flask. The mixture was then heated to 220 °C for 30 minutes under N₂, and cooled to room temperature. Products were precipitated by introducing ethanol (20 mL) and centrifugated at 16500 rpm for 3 min. Precipitates were then washed with ethanol three times and dried under vacuum at 80 °C for 12 h.

Preparation of RA Cu_{1.94}S

The process is similar to that for SS $Cu_{1.94}$ S except that the copper source is $Cu(CH_3COO)_2$ (0.2 g, AR).

Catalysis experiments

In an optimized experiment, catalytic systems were prepared as followed. $[Ru(bpy)_3]Cl_2 \times 6H_2O$ (bpy = 2', 2bipyridine) (2 mg, AR), $Cu_{1.94}S$ (5 mg, RA or SS), and deionized water (100 µL) were dispersed into a solution of triethanolamine (TEOA) (1 mL) and acetonitrile (4 mL). This catalytic system was denoted as Ru-RA or Ru-SS. Comparative catalytic solution without $Cu_{1.94}S$ was denoted as $[Ru(bpy)_3]Cl_2$ and that without $[Ru(bpy)_3]Cl_2$ was denoted as SS ($Cu_{1.94}S$). Catalytic systems with nanopowders were ultrasonicated for 15 min to enhance dispersion and stirred vigorously during photocatalysis. The light source was a 300 W Xe lamp with a 400 nm cut-off filter. After illumination for 1 h, the produced gases were analyzed and quantified by gas chromatography.

Declarations

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare no competing interests.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21571193) and the Open Funds of the State Key Laboratory of Rare Earth Resource Utilization RERU2013012. This research used the beamline 9-BM at the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Author contributions

L.Z., J.L.: Conceptualization, Methodology, Investigation, Writing - original draft, Project administration; L.W., A.D., H.J., T.W.: Data Investigation, Review; H.C., L.J.: Review; Z.Q.: Data Investigation, Review, Project administration, Supervision.

References

- Wang, Q. & Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev*, **120**, 919–985 https://doi.org/10.1021/acs.chemrev.9b00201 (2020).
- Tang, S., Qiu, W., Xiao, S., Tong, Y. & Yang, S. Harnessing hierarchical architectures to trap light for efficient photoelectrochemical cells. *Energ. Environ. Sci*, **13**, 660–684 https://doi.org/10.1039/c9ee02986a (2020).
- Bian, Z., Tachikawa, T. & Majima, T. Superstructure of TiO2 Crystalline Nanoparticles Yields Effective Conduction Pathways for Photogenerated Charges. *J. Phys. Chem. Lett*, 3, 1422–1427 https://doi.org/10.1021/jz3005128 (2012).
- He, L. *et al.* Spatial Separation of Charge Carriers in In2O3 x(OH)y Nanocrystal Superstructures for Enhanced Gas-Phase Photocatalytic Activity. *ACS Nano*, **10**, 5578–5586 https://doi.org/10.1021/acsnano.6b02346 (2016).
- 5. Lin, J. *et al.* Ultrasensitive SERS Detection by Defect Engineering on Single Cu20 Superstructure Particle. *Adv. Mater*, **29**, 1604797 https://doi.org/10.1002/adma.201604797 (2017).
- Luo, D. *et al.* Ordered Superparticles with an Enhanced Photoelectric Effect by Sub-Nanometer Interparticle Distance. *Adv. Funct. Mater*, **27**, 1701982 https://doi.org/10.1002/adfm.201701982 (2017).
- 7. Wang, L., Cai, M., Sun, W., He, L. & Zhang, X. Promoting Charge Separation in Semiconductor Nanocrystal Superstructures for Enhanced Photocatalytic Activity. *Adv. Mater. Inter*, **5**, 1701694

https://doi.org/10.1002/admi.201701694 (2018).

- 8. Zhou, C. *et al.* Spatial separation of charge carriers in Nb2O5 nanorod superstructures for enhanced photocatalytic H2 production activity. *Mater. Today Chem*, **10**, 259–263 https://doi.org/10.1016/j.mtchem.2018.09.005 (2018).
- 9. Wang, P. P., Qiao, Q., Zhu, Y. & Ouyang, M. Colloidal Binary Supracrystals with Tunable Structural Lattices. *J. Am. Chem. Soc*, **140**, 9095–9098 https://doi.org/10.1021/jacs.8b05643 (2018).
- Zhuang, Z., Peng, Q., Zhang, B. & Li, Y. Controllable synthesis of Cu2S nanocrystals and their assembly into a superlattice. *J. Am. Chem. Soc*, **130**, 10482–10483 https://doi.org/10.1021/ja803644g (2008).
- 11. Hou, K., Han, J. & Tang, Z. Formation of Supraparticles and Their Application in Catalysis. *ACS Mater. Lett*, **2**, 95–106 https://doi.org/10.1021/acsmaterialslett.9b00446 (2019).
- Zhang, H. T., Chen, X. H. & Gang Wu & Large-Scale Synthesis and Self-Assembly of Monodisperse Hexagon Cu2S Nanoplates., 21, 4281–4282 (2005).
- 13. de Silveira, Q. G. et al. Supraparticle Nanoassemblies with Enzymes. *Chem. Mater*, **31**, 7493–7500 https://doi.org/10.1021/acs.chemmater.9b02216 (2019).
- Deng, D. *et al.* Template-Free Hierarchical Self-Assembly of Iron Diselenide Nanoparticles into Mesoscale Hedgehogs. *J. Am. Chem. Soc*, **139**, 16630–16639 https://doi.org/10.1021/jacs.7b07838 (2017).
- 15. Miszta, K. *et al.* Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures. *Nat. Mater*, **10**, 872–876 https://doi.org/10.1038/nmat3121 (2011).
- 16. Brittman, S. *et al.* Binary Superlattices of Infrared Plasmonic and Excitonic Nanocrystals. *ACS Appl. Mater. Inter*, **12**, 24271–24280 https://doi.org/10.1021/acsami.0c03805 (2020).
- Feng, C. *et al.* Maintaining stable LSPR performance of W18049 by protecting its oxygen vacancy: A novel strategy for achieving durable sunlight driven photocatalysis. *Appl. Catal. B-Environ*, **276**, 119167 https://doi.org/10.1016/j.apcatb.2020.119167 (2020).
- Long, M. *et al.* Efficient visible light photocatalytic heterostructure of nonstoichiometric bismuth oxyiodide and iodine intercalated Bi202CO3. *Appl. Catal. B-Environ*, **184**, 20–27 https://doi.org/10.1016/j.apcatb.2015.11.025 (2016).
- Murali, A., Lan, Y. P. & Sohn, H. Y. Effect of oxygen vacancies in non-stoichiometric ceria on its photocatalytic properties. *Nano-Structures & Nano-Objects*, **18**, 100257 https://doi.org/10.1016/j.nanoso.2019.100257 (2019).
- Valeeva, A. A. *et al.* Influence of calcination on photocatalytic properties of nonstoichiometric titanium dioxide nanotubes. *J. Alloy Compd*, **796**, 293–299 https://doi.org/10.1016/j.jallcom.2019.04.342 (2019).
- Wei, W. *et al.* Oxygen defect-induced localized surface plasmon resonance at the WO3 x quantum dot/silver nanowire interface: SERS and photocatalysis. *Nanoscale*, **11**, 5535–5547 https://doi.org/10.1039/c9nr01059a (2019).

- 22. Qi, Y. *et al.* Mild metal-organic-gel route for synthesis of stable sub-5-nm metal-organic framework nanocrystals. *Nano Res*, **10**, 3621–3628 https://doi.org/10.1007/s12274-017-1539-x (2017).
- Yang, X., Huang, T., Gao, S. & Cao, R. Boosting photocatalytic oxidative coupling of amines by a Rucomplex-sensitized metal-organic framework. *J. Catal*, **378**, 248–255 https://doi.org/10.1016/j.jcat.2019.08.038 (2019).
- Li, L., Xu, J., Ma, J., Liu, Z. & Li, Y. A bimetallic sulfide CuCo2S4 with good synergistic effect was constructed to drive high performance photocatalytic hydrogen evolution. *J. Colloid Interface Sci*, 552, 17–26 https://doi.org/10.1016/j.jcis.2019.05.036 (2019).
- 25. Zhu, D. *et al.* Seed-mediated growth of heterostructured Cu1.94S-MS (M = Zn, Cd, Mn) and alloyed CuNS2 (N = In, Ga) nanocrystals for use in structure- and composition-dependent photocatalytic hydrogen evolution. *Nanoscale*, **12**, 6111–6120 https://doi.org/10.1039/c9nr10004k (2020).
- 26. Han, S. K. *et al.* Precursor Triggering Synthesis of Self-Coupled Sulfide Polymorphs with Enhanced Photoelectrochemical Properties. *J. Am. Chem. Soc*, **138**, 12913–12919 https://doi.org/10.1021/jacs.6b06609 (2016).
- Li, X., Xie, K., Song, L., Zhao, M. & Zhang, Z. Enhanced Photocarrier Separation in Hierarchical Graphitic-C3N4-Supported CuInS2 for Noble-Metal-Free Z-Scheme Photocatalytic Water Splitting. ACS Appl. Mater. Inter, 9, 24577–24583 https://doi.org/10.1021/acsami.7b06030 (2017).
- 28. Qiu, B. *et al.* Efficient Solar Light Harvesting CdS/Co9 S8 Hollow Cubes for Z-Scheme Photocatalytic Water Splitting. *Angew. Chem*, **56**, 2684–2688 https://doi.org/10.1002/anie.201612551 (2017).
- 29. Liu, Y. *et al.* In-situ construction of hierarchical CdS/MoS2 microboxes for enhanced visible-light photocatalytic H2 production. *Chem. Eng. J*, **339**, 117–124 https://doi.org/10.1016/j.cej.2018.01.124 (2018).
- Wei, R. B. *et al.* Dual-cocatalysts decorated rimous CdS spheres advancing highly-efficient visiblelight photocatalytic hydrogen production. *Appl. Catal. B-Environ*, **231**, 101–107 https://doi.org/10.1016/j.apcatb.2018.03.014 (2018).
- 31. Khan, S. *et al.* Self-assembled heterojunction of metal sulfides for improved photocatalysis. *Chem. Eng. J*, **395**, 125092 https://doi.org/10.1016/j.cej.2020.125092 (2020).
- Zhang, X. *et al.* Copper phosphosulfides as a highly active and stable photocatalyst for hydrogen evolution reaction. *Appl. Catal. B-Environ*, **273**, 118927 https://doi.org/10.1016/j.apcatb.2020.118927 (2020).
- Zhang, Y. *et al.* Visible light driven hydrogen evolution using external and confined CdS: Effect of chitosan on carriers separation. *Appl. Catal. B-Environ*, **277**, 119152 https://doi.org/10.1016/j.apcatb.2020.119152 (2020).

Figures





PXRD (a) and FTIR spectra (b) of as-prepared Cu1.94S.



Figure 2

(a-c) Morphology schematic, TEM images, and Histograms of diameter distributions in RA; (d-f) Morphology schematic, TEM images, and Histograms of diameter distribution in SS; (the insets in e: corresponding FFT patterns), (g) TEM images with low magnification of SS; (h) SAXRD patterns of SS (the insets: corresponding zoom-in pictures of e). (i) HRTEM of a single nanocrystal in SS.





(a) UV-vis of [Ru(bpy)3]Cl2, Ru-RA, and Ru-SS; (b) PL of [Ru(bpy)3]Cl2, Ru-RA, and Ru-SS (c) Schematic illustration for band-energy alignment in SS and [Ru(bpy)3]Cl2.



Figure 4

(a) Transient photocurrent density responses of Ru-SS, and Ru-RA; (b) Time resolved photoluminescence decay spectra of [Ru(bpy)3]Cl2, Ru-SS and Ru-RA.



Figure 5

(a) XAFS of Cu2S(black), RA Cu1.94S (blue), and SS Cu1.94S (red) (b) Normalized Cu K-edge XANES of RA Cu1.94S (blue) and SS Cu1.94S (red) (c) EXAFS in R space of RA Cu1.94S (blue) and SS Cu1.94S (red).



Figure 6

Scheme 1 Schematic Illustration of Carrier Transfer and Separation in Cu1.94S–[Ru(bpy)3]Cl2 photocatalytic system.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

• SupportingInformation.pdf