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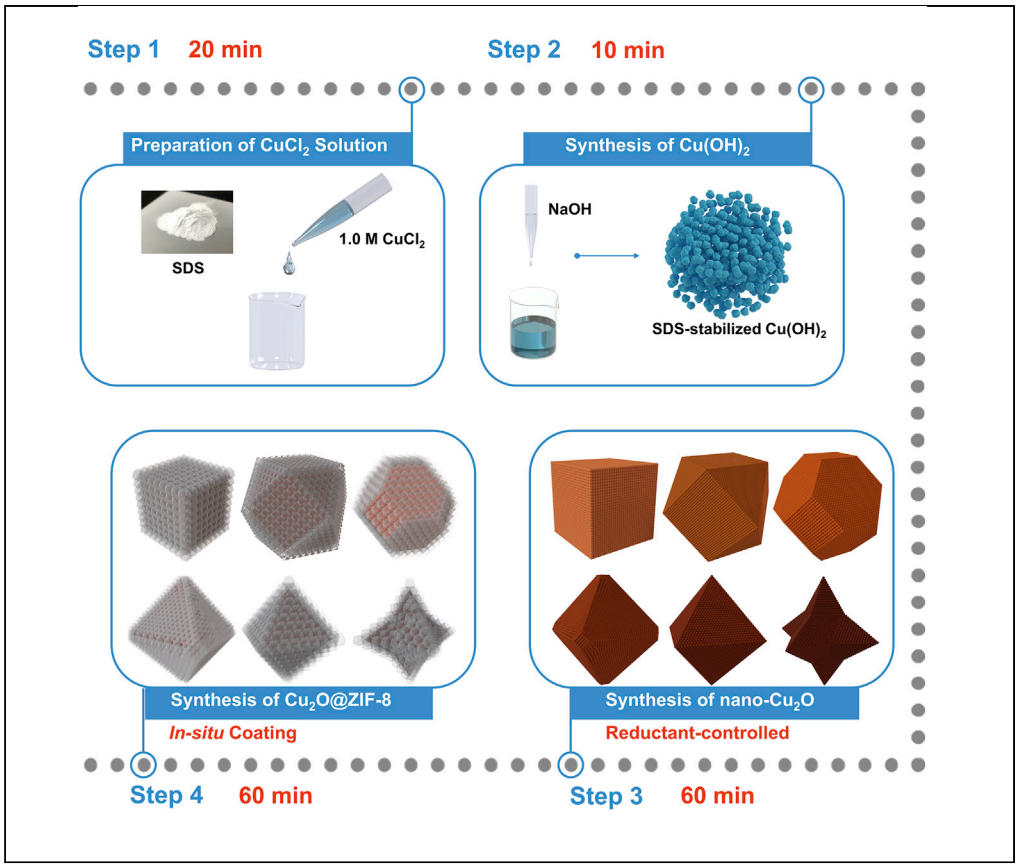
Protocol to modify the surface of nano-Cu_2O using facet controlling and MOF shell coating



The morphology of nano-Cu_2O profoundly determines its catalytic performance. Here, we provide two universal and reliable techniques to modify the surface of nano-Cu_2O. First, we detail steps for the systematic tuning of the exposed facets of nano-Cu_2O ranging from low index to high index using reductant-controlled technique in the presence of sodium dodecyl sulfate. Second, we describe steps for facet-directed precipitation in which the morphology-dependent ZIF-8 (a type of zeolitic imidazolate frameworks) shells on different nano-Cu_2O are well introduced.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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Highlights

Reductant-controlled technique to tune the exposed facets of nano-Cu_2O

Construct nano-Cu_2O with exposed "terrace and step" {332} facets

Introduce facet-directed ZIF-8 shell on nano-Cu_2O with morphology dependence

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Protocol to modify the surface of nano-Cu_2O using facet controlling and MOF shell coating

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SUMMARY

The morphology of nano-Cu_2O profoundly determines its catalytic performance. Here, we provide two universal and reliable techniques to modify the surface of nano-Cu_2O. First, we detail steps for the systematic tuning of the exposed facets of nano-Cu_2O ranging from low index to high index using reductant-controlled technique in the presence of sodium dodecyl sulfate. Second, we describe steps for facet-directed precipitation in which the morphology-dependent ZIF-8 (a type of zeolitic imidazolate frameworks) shells on different nano-Cu_2O are well introduced.

For complete details on the use and execution of this protocol, please refer to Luo et al. (2022).

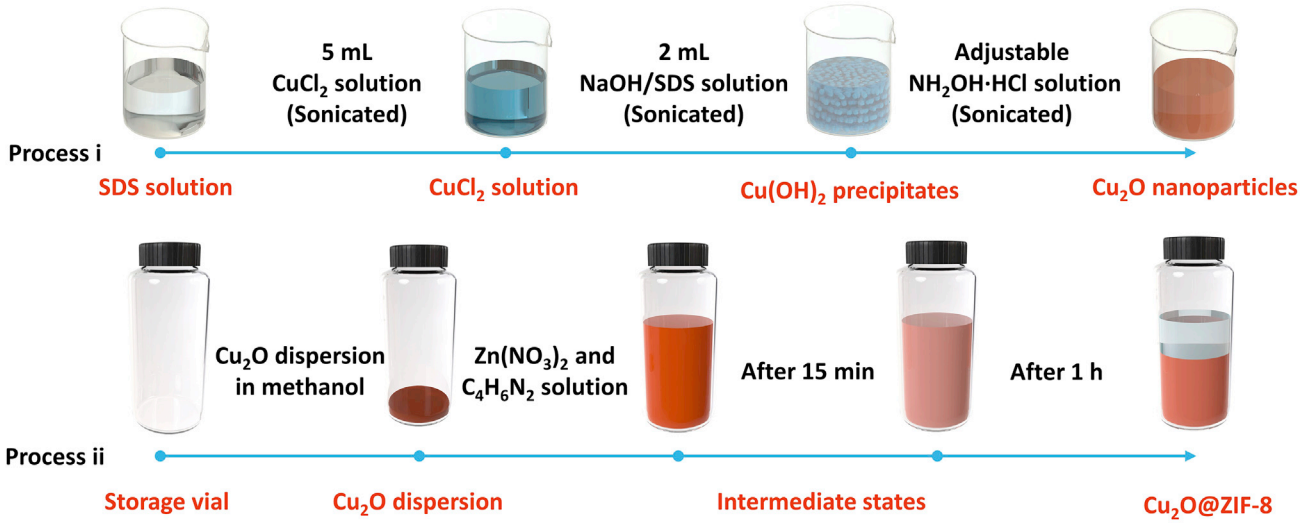
BEFORE YOU BEGIN

Materials with specific nanoscopic or microscopic morphologies have extensive perspective of application, especially in heterogeneous catalysis, optical devices, and batteries (Lai et al., 2019; Liu et al., 2022; Diehl et al., 2022; Joshi et al., 2021). As an outstanding semiconductor material, Cu_2O has been widely investigated in photo or electrocatalysis, due to its relatively low cost, abundance of Cu on earth and promising selectivity of specific product, whose surface morphology will profoundly influence its catalytic performance (Ma et al., 2021; Wu et al., 2019; Liu et al., 2021; Gao et al., 2020). In the past research, Cu_2O nanomaterials with low index facets such as {100}, {110} and {111}, have been well-studied, both in synthesis and applications (Huang et al., 2012; Aran-Ais et al., 2020; Hua et al., 2014). Further, systematical synthesis of nano-Cu_2O from low index facets to high index facets, and universal surface coating approach with stable metal organic framework material were proposed in our previous work (Luo et al., 2022).

Herein, the protocol describes those two strategies to modify the surface of nano-Cu_2O (Scheme 1). For process i, Cu_2O nanoparticles with different morphologies are successfully synthesized through sonicating by tuning the usage of reductant in the presence sodium dodecyl sulfate (SDS), which is beneficial for the formation of concave (Wang et al., 2013). For process ii, facet-directed precipitation method is carried out to *in-situ* coat ZIF-8 (2-Methylimidazole zinc salt, a type of zeolitic imidazolate frameworks) shell on Cu_2O nanoparticles under low oxygen condition. Before synthesis, the following preparations should be made.

Preparation of the reagents and equipment

A complete list of reagents and equipment can be found in the "key resources table".



Scheme 1. Synthetic procedure for Nano-Cu_2O and Cu_2O@ZIF-8
Reproduced with permission (Luo et al., 2022).

Preparation of stock solution

Timing: 30 min

1. Preparation of stock solutions during process i in Scheme 1.
   a. Add 0.3410 g $CuCl_2·2H_2O$ into 20.00 mL distilled water to prepare 0.1 M $CuCl_2$ solution. Store the stock solution at 20°C.
   b. Add 1.6000 g NaOH and 0.0029 g SDS into 20.00 mL distilled water to prepare 2.0 M NaOH/0.5 mM SDS solution. Store the stock solution at 20°C.
   c. Add 1.3898 g $NH_2OH·HCl$ into 20.00 mL distilled water to prepare 1.0 M $NH_2OH·HCl$ solution. Store the stock solution at 4°C.
2. Preparation of stock solutions during process ii in Scheme 1.
   a. Add 0.7139 g $Zn(NO_3)_2$ into 20.00 mL methanol to prepare 0.12 M $Zn(NO_3)_2$ solution. Store the stock solution at 20°C and saturate with N_2 before use.
   b. Add 0.7882 g $C_4H_6N_2$ into 20.00 mL methanol to prepare 0.48 M 2-methylimidazole solution. Store the stock solution at 20°C and saturate with N_2 before use.

⚠ CRITICAL: Zinc nitrate hexahydrate is a corrosive chemical; thus, it should be handled in the fume hood and avoid direct skin contact.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Copper(II) chloride dihydrate ($CuCl_2·2H_2O$) (AR)	Aladdin (Shanghai, China)	CAS: 10125-13-0
Hydroxylammonium chloride ($NH_2OH·HCl$) (99.99%)	Aladdin (Shanghai, China)	CAS: 5470-11-1
Sodium hydroxide (NaOH) (AR)	Aladdin (Shanghai, China)	CAS: 1310-73-2
2-Methylimidazole ($C_4H_6N_2$) (AR)	Aladdin (Shanghai, China)	CAS: 693-98-1
Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$) (AR)	Acros Organics (USA)	CAS: 10196-18-6
Ethanol (CH_3CH_2OH) (AR)	Concord (Tianjin, China)	CAS: 64-17-5
Methanol (CH_3OH) (AR)	Concord (Tianjin, China)	CAS: 67-56-1

(*Continued on next page*)

Continued		
REAGENT or RESOURCE	SOURCE	IDENTIFIER
Polyvinyl pyrrolidone (PVP) (M_w = 10000) (AR)	Aladdin (Shanghai, China)	CAS: 9003-39-8
Sodium dodecyl sulfate (SDS) (Approx. 95%)	Solarbio (Beijing, China)	CAS: 151-21-3
Distilled water (H_2O) (AR)	Concord (Tianjin, China)	CAS: 7732-18-5
Nitrogen (N_2) (>99.999%)	Liufang (Tianjin, China)	CAS: 7727-37-9
Other		
Beaker (200 mL) (Thick wall)	Synthware Glass Co., Ltd	N/A
Storage vial (20 mL, 27.5 × 57 mm)	ALWSCI	C0000057
PTFE hose (3 mm)	N/A	N/A
Ultrasonic cleaner (37 kHz)	Elma Schmidbauer GmbH	Elmasonic S 100 H
Mass flow controller (0.1–100 sccm)	HORIBA	S48 32/HMT
Vacuum drying oven	Marvel Technology Co., Ltd	DZF-2AS
Centrifuge (1.744–4360 RCF (× g))	N/A	N/A
Pipette (1000–5000 μL)	Lichen Bangxi Co., Ltd	Discovery-H
Analytical balance (MAX = 120 g, d = 0.1 mg)	Sartorius	BSA124S-CW
Measuring cylinder (20 mL, 50 mL)	Synthware Glass Co., Ltd	N/A
PLA Models	N/A	N/A
Scanning electron microscope (SEM)	ZEISS	MERLIN Compact
Transmission electron microscope (TEM)	Thermo Scientific	Talos F200X G2
Polysilicon wafer (2 × 2 mm)	N/A	N/A

MATERIALS AND EQUIPMENT

PLA models

During the sonicated process, we build a 3D printed PLA model to prevent the beaker from moving in the ultrasonic cleaner (Details see Figure 1A).

Alternatives: Any tool that can prevent the beaker from moving casually during sonicating will do.

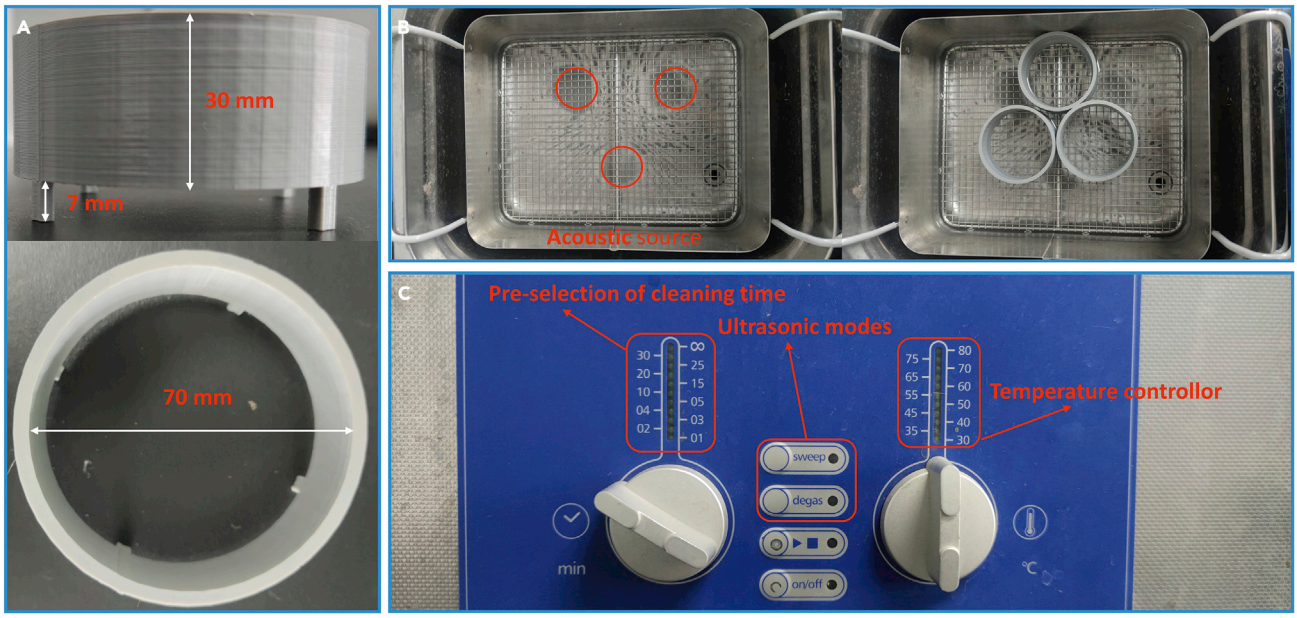


Figure 1. Ultrasonic cleaner equipment

(A) Dimensions of PLA Model. The inner diameter of PLA model should be larger than the outer diameter of beaker.

(B) The position of acoustic source and the PLA Models are put between each two acoustic sources.

(C) Control panel of Ultrasonic cleaner.

Ultrasonic cleaner

During the preparation of each stock solution, we choose degas-mode (150 W, 37 kHz) for sonicating the mixture to be fully dissolved. When it comes to the reaction time, 2.8 L water is recommended to be added into the tank, and sweep-mode (150 W, 37 kHz) is chosen to form even sound field distribution in the ultrasonic bath. The beakers should be put into the PLA Models to avoid moving during reaction process, and the temperature controller is just used to monitor the real-time temperature of reaction surroundings (Details see Figures 1B and 1C).

Note: Those two ultrasonic modes have the same power and frequency, but different sound field distributions.

Stock solution of 0.1 M $CuCl_2$ solution (Storage: 20°C)		
Reagent	Final concentration	Amount
$CuCl_2 \cdot 2H_2O$	0.1 M	0.3410 g
Distilled water	N/A	20.00 mL
Total	**N/A**	**20.00 mL**

Note: The 0.1 M $CuCl_2$ solution can be stored at 20°C for two weeks.

Stock solution of 2.0 M NaOH/0.5 mM SDS solution (Storage: 20°C)		
Reagent	Final concentration	Amount
NaOH	2.0 M	1.6000 g
SDS	0.5 mM	0.0029 g
Distilled water	N/A	20.00 mL
Total	**N/A**	**20.00 mL**

Note: The 2.0 M NaOH/0.5 mM SDS solution can be stored at 20°C for one day.

Stock solution of 1.0 M $NH_2OH \cdot HCl$ solution (Storage: 4°C)		
Reagent	Final concentration	Amount
$NH_2OH \cdot HCl$	1.0 M	1.3898 g
Distilled water	N/A	20.00 mL
Total	**N/A**	**20.00 mL**

Note: The 1.0 M $NH_2OH \cdot HCl$ solution can be stored at 4°C for one day.

Stock solution of 0.12 M $Zn(NO_3)_2$ solution (Storage: 20°C)		
Reagent	Final concentration	Amount
$Zn(NO_3)_2$	0.12 M	0.7139 g
Methanol	N/A	20.00 mL
Total	**N/A**	**20.00 mL**

Stock solution of 0.48 M $C_4H_6N_2$ solution (Storage: 20°C)		
Reagent	Final concentration	Amount
2-Methylimidazole	0.48 M	0.7882 g
Methanol	N/A	20.00 mL
Total	**N/A**	**20.00 mL**

Note: The 0.12 M $Zn(NO_3)_2$ solution and 0.48 M $C_4H_6N_2$ can be stored at 20°C for two weeks.

⚠ CRITICAL: SDS has an irritating effect on mucous membranes and upper respiratory tract. Be sure to wear masks when using it.

Alternatives: In our experiments, we use beakers and storage vials for the synthesis of nano-Cu_2O and Cu_2O@ZIF-8 composites. However, alternative containers such as conical flasks with plug can also be used.

Optional: The resources listed above were only based on our experience. The chemicals and resources obtained from reliable commercial sources are feasible.

STEP-BY-STEP METHOD DETAILS

Synthesis of Nano-Cu_2O

Timing: 14 h

The initial step for the synthesis of nano-Cu_2O (Process i in Scheme 1) is the SDS-stabilized $Cu(OH)_2$ synthesis. Subsequently, $NH_2OH{\cdot}HCl$ act as both reductant and morphology control agent to modify the exposed facets of nano-Cu_2O.

1. Weigh 0.8650 g (3 mmol) SDS powder to a 200 mL beaker.
2. Add 92.75 mL distilled water to the beaker.

Note: We fabricated nano-Cu_2O with six different morphologies by controlling the usage of $NH_2OH{\cdot}HCl$ solution, according to which, the usage of distilled water should be adjusted. In short, the total solvent volume should be controlled at 100 mL.

3. Sonicate for 10 min until the SDS is fully dissolved.
4. Add 5 mL 0.1 M $CuCl_2$ solution into above SDS solution and sonicate for another 10 min to form homogenous solution.
5. Add 2 mL 2.0 M NaOH/0.5 mM SDS solution into $CuCl_2$/SDS solution dropwise (1 drop every 2 s) with shaking the beaker (see Methods video S1).
6. Sonicate for another 10 min to form blue SDS-stabilized $Cu(OH)_2$ flocs at 25°C–40°C.

Note: The subsequent reductant-controlled experiment is operated following this step.

⚠ CRITICAL: The NaOH/SDS solution is strong alkaline and corrosive. Avoid dripping on hands!

7. Add 0.25 mL 1.0 M $NH_2OH{\cdot}HCl$ solution dropwise with shaking the beaker (see Methods video S2), and the flocs will turn from blue to green.

Note: We modified the exposed facets of nano-Cu_2O by adjusting the usage of $NH_2OH{\cdot}HCl$. In this step, 0.25 mL 1.0 M $NH_2OH{\cdot}HCl$ will help in forming cubic Cu_2O nanoparticles (Figures 2A1, 2B1 and 2C1). By increasing the usage of 1.0 M $NH_2OH{\cdot}HCl$ solution to 0.50 mL, 0.75 mL, 1.00 mL, 1.25 mL and 2.00 mL, the morphology of nano-Cu_2O will turn to corner-cut cube, corner-cut octahedron, truncated octahedron, octahedron, and concave octahedron, respectively (see Figures A2-A6, B2-B6 and C2-C6). Table 1 shows the exact amount of each reagent in the synthesis of different Cu_2O nanoparticles.

Table 1. Exact amount of each reagent in the synthesis of nano-Cu_2O

Reagent	A-Cu_2O	B-Cu_2O	C-Cu_2O	D-Cu_2O	E-Cu_2O	F-Cu_2O
SDS	0.8650 g	0.8650 g	0.8650 g	0.8650 g	0.8650 g	0.8650 g
0.1 M $CuCl_2$	5 mL	5 mL	5 mL	5 mL	5 mL	5 mL
Distilled water	92.75 mL	92.50 mL	92.25 mL	92.00 mL	91.75 mL	91.00 mL
2.0 M NaOH/0.5 mM SDS	2 mL	2 mL	2 mL	2 mL	2 mL	2 mL
1.0 M $NH_2OH{\cdot}HCl$	0.25 mL	0.50 mL	0.75 mL	1.00 mL	1.25 mL	2.00 mL

8. Sonicate for 1 h at 30°C–40°C. The green flocs will disappear forming uniform dispersion, and the color will turn from green to orange or brown gradually (see Methods video S3).

   Note: No more than 3 experimental groups that are carried out simultaneously. During the sonicating process, ice cubes can be added into ultrasonic cleaner tank to avoid overheating.

9. Collect the precipitates by centrifuging at (2791 RCF (× g) for 3 min.
10. Wash the obtained brown precipitates with ethanol (50 mL × 3) and distilled water (50 mL × 1) by sonicating and followed centrifuging at 2791 RCF (× g) for 3 min to remove the residual SDS and reactants.
11. Wash the precipitates with ethanol (50 mL), eventually.
12. Transfer the precipitates to oven, vacuum drying for 12 h at 65°C.

Characterization of nano-Cu_2O

Timing: 6 h

After the successful preparation of nano-Cu_2O with six morphologies, scanning electron microscopy (SEM) and transmission electron microscope (TEM) characterizations are adopted to evaluate the surface conformation of nano-Cu_2O.

13. Disperse 1 mg Cu_2O nanoparticles into 1 mL ethanol and sonicate 5 min to form homogeneous dispersion.
14. Drop 10 μL nano-Cu_2O dispersion on the polysilicon wafer, then transfer the polysilicon wafer to oven, vacuum drying for 2 h at 65°C for further SEM characterization.

   Note: SEM characterization, TEM sample preparation and TEM characterization are operated by professional engineer.

Synthesis of Cu_2O@ZIF-8

Timing: 14 h

In this process, PVP (M_w = 10,000) is used as an armor to protect nano-Cu_2O from being etched, and as a surfactant to help ZIF-8 crystal *in-situ* coating on nano-Cu_2O to form Cu_2O@ZIF-8 core-shell composites. All of the six morphological Cu_2O nanoparticles can be coated with ZIF-8 shell through this method (Figures 3 and 4).

15. Weigh 5 mg Cu_2O nanoparticles, 200 mg PVP (M_w = 10,000) to a 20 mL vial. Add 1.0 mL methanol and sonicate for 10 min with degas mode until all the mixture dissolve.
16. Pump N_2 to Cu_2O/PVP dispersion for 10 min.

   Note: Pumping N_2 into the dispersion through a PTFE hose with the gas flow rate being controlled to 20 sccm by a Mass flow controller (Figure 5). Notably, N_2 is just used to remove

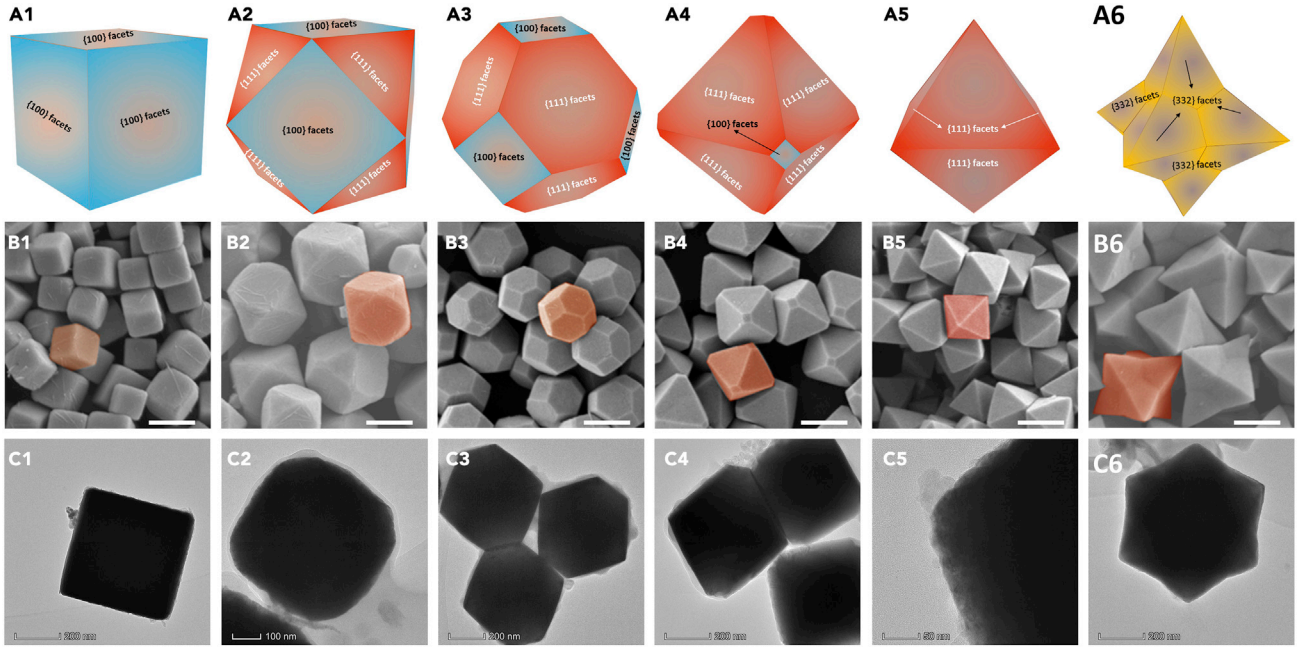


Figure 2. Six types of nano-Cu_2O with different exposed facets

Reproduced with permission (Luo et al., 2022).

(A) 3D models of nano-Cu_2O, **1**: Cube, **2**: Corner-cut cube, **3**: Corner-cut octahedron, **4**: Truncated octahedron, **5**: Octahedron, **6**: Concave octahedron, labelled as **A-** to **F-Cu_2O** respectively.

(B) SEM patterns of different nano-Cu_2O. Scale bar: 500 nm.

(C) TEM patterns of different nano-Cu_2O.

the dissolved oxygen in the solvent, and the strict oxygen-free condition is not required. The same is true for subsequent N_2-saturate operations.

17. Pump N_2 to the prepared 0.12 M $Zn(NO_3)_2$ solution and 0.48 M $C_4H_6N_2$ solution for 20 min.
18. Add 5 mL N_2-saturated 0.12 M $Zn(NO_3)_2$ solution and 5 mL N_2-saturated 0.48 M $C_4H_6N_2$ solution into Cu_2O/PVP dispersion.
19. Shake storage vial with the lid on for 10 s, and then set quietly for 1 h at around 25°C.
20. After 1 h, the supernatant should be colorless transparent.
21. Pour off the supernatant. Centrifuge at 697.6 RCF (× g)for 3 min to collect the precipitates and wash with methanol (50 mL × 3).
22. Vacuum drying for 12 h at 65°C in oven.

Characterization of Cu_2O@ZIF-8

Timing: 6 h

After the successful preparation of six types of Cu_2O@ZIF-8 composites, scanning electron microscopy (SEM), transmission electron microscope (TEM) and elemental mapping are carried to characterize the morphology of Cu_2O@ZIF-8 (Figures 3 and 4).

23. Disperse 1 mg Cu_2O@ZIF-8 composites into 1 mL ethanol and sonicate 5 min to form homogeneous dispersion.
24. Drop 10 μL Cu_2O@ZIF-8 dispersion on the polysilicon wafer, then transfer the polysilicon wafer to oven, vacuum drying for 2 h at 65°C for further SEM characterization.

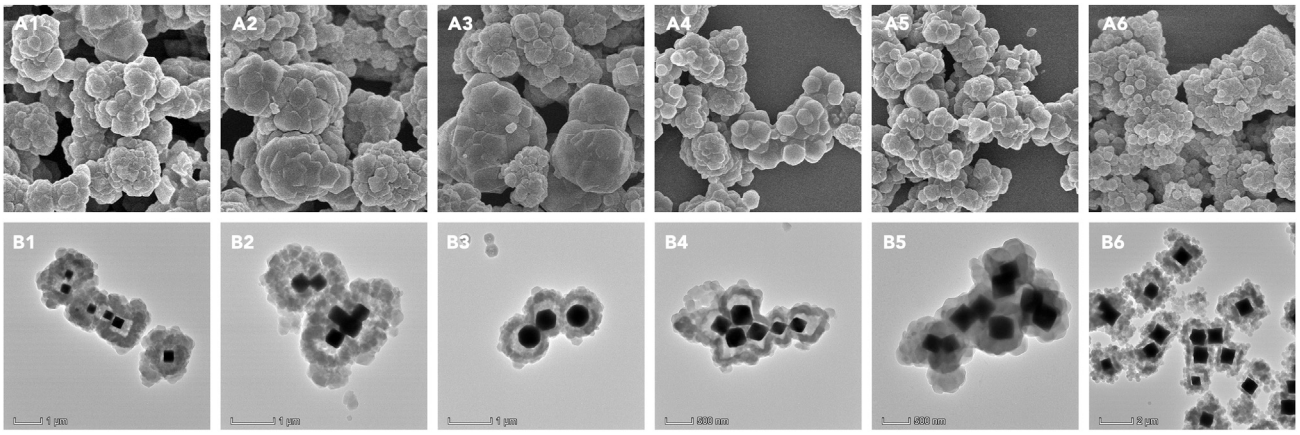


Figure 3. Morphology characterization of Cu_2O@ZIF-8 composites

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(A and B) (A) SEM and (B) TEM patterns of **A-** to **F-Cu_2O@**ZIF-8 composites, respectively.

Note: Similarly, SEM characterization, TEM sample preparation and TEM characterization are operated by professional engineer.

EXPECTED OUTCOMES

This protocol provides systematic strategies for modifying the surface conformation of nano-Cu_2O with reductant-controlled and facet-directed precipitation methods. By adjusting the usage of reductant, Cu_2O nanoparticles with different exposed facets ranging from low index to high index were synthesized, and with the molar ratio of the usage of $NH_2OH{\cdot}HCl$ to $CuCl_2$ increasing to 4:1, nano-Cu_2O with high index facets {332} (a "terraces and steps" structure) (Wang et al., 2013) was fabricated (Figure 2B). Furthermore, the ZIF-8 shell was *in-situ* introduced on each nano-Cu_2O under stationary condition with PVP as both protector and surfactant, and the contour profiles of ZIF-8 shell were highly dependent on the morphologies of nano-Cu_2O.

LIMITATIONS

For the reductant-controlled methods to modify, only nano-Cu_2O was chosen as an example to construct different exposed facets, whether it is suitable for other metal oxide or not, is still requiring further research. The slow growth rate of alkaline metal oxides in weak acid reduction surroundings, might contribute to form high index facets (Ng and Fan, 2006). Besides, ZIF-8 has high crystallinity, high stability and importantly, mild synthesis condition, in which Cu_2O can be stable for a long time. In this case, MOFs prepared under high temperature and strong acid conditions may not be suitable for this method.

TROUBLESHOOTING

Problem 1

The prepared SDS-stabilized $Cu(OH)_2$ flocs is dark green (step 6 in "synthesis of Nano-Cu_2O").

Potential solution

Prepare new NaOH/SDS solution. Control the temperature below 40°C and the reaction time no more than 10 min. The newly prepared NaOH/SDS solution is clear and transparent (Figure 6A), while the overdue NaOH/SDS solution contains white suspended matters (Figure 6B). The eligible SDS-stabilized $Cu(OH)_2$ flocs is blue (Figure 6C).

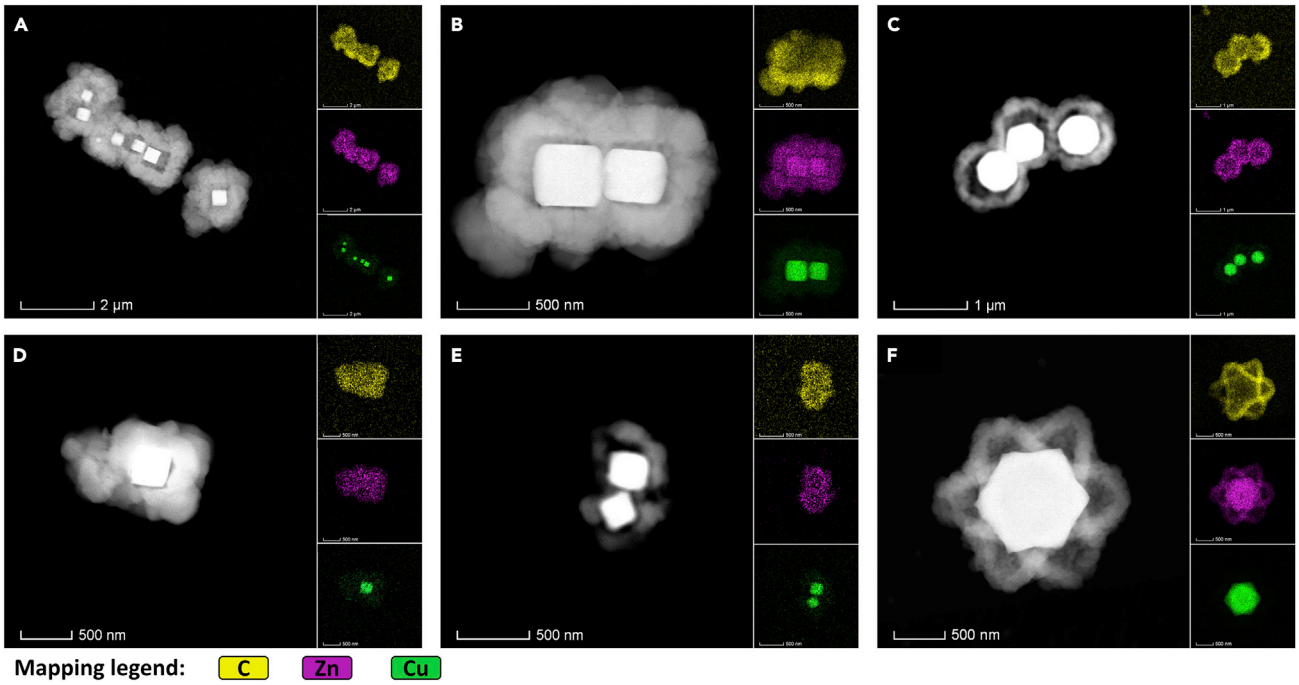

Figure 4. HAADF-STEM patterns and elemental mapping of Cu_2O@ZIF-8 composites

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(A–F) The labels (A) to (F) are correspond to **A-** to **F-Cu_2O**@ZIF-8, respectively.

Problem 2

After adding $NH_2OH \cdot HCl$, the color of the dispersion changes lightly, and when sonication reaction is performed, precipitates can be seen obviously which can't be dispersed (steps 7 and 8 in "synthesis of Nano-Cu_2O").

Potential solution

Prepare new 1.0 M $NH_2OH \cdot HCl$ solution or purchase new $NH_2OH \cdot HCl$ reagent. Additionally, the color of the synthesized nano-Cu_2O distinguish with each other, ranging from orange to dark brown in the sort from **A-** to **F-Cu_2O** (Figure 7).

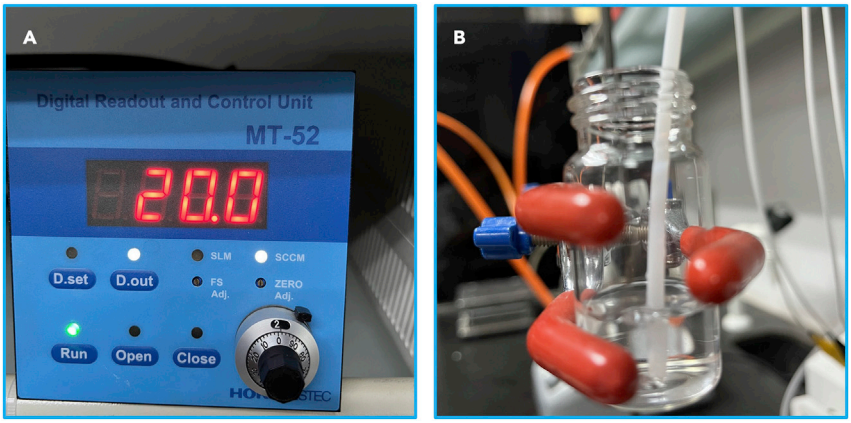

Figure 5. Photographs of N_2-saturate operation

(A) Control pane of Mass flow controller.

(B) N_2-saturate operation image.

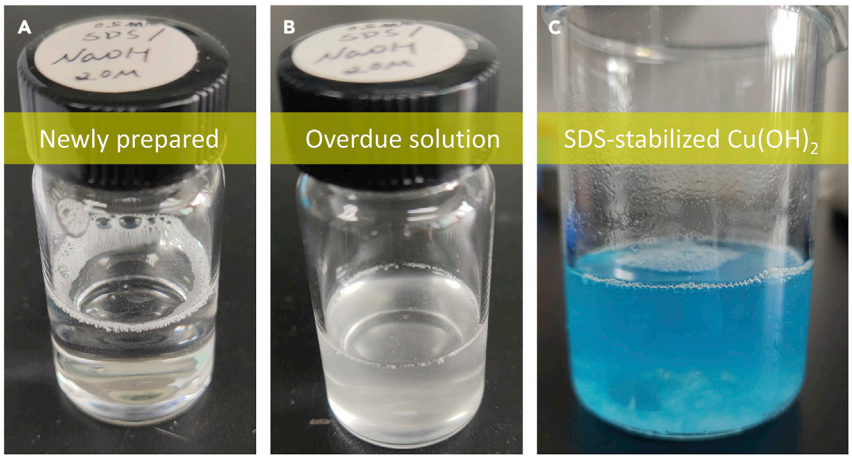

Figure 6. Photographs of stock solutions and products
(A) Newly prepared 2.0 M NaOH/0.5 mM SDS solution.
(B) Overdue 2.0 M NaOH/0.5 mM SDS solution.
(C) Eligible SDS-stabilized $Cu(OH)_2$ flocs.

Problem 3
The as-prepared **F-Cu_2O** nanoparticles are not in concave octahedral shape.

Potential solution
In step 7 in "synthesis of Nano-Cu_2O", the dropping speed of 1.0 M $NH_2OH \cdot HCl$ solution is significant. Try to ensure that the last drop is fully dispersed by shaking before adding the next drop.

Problem 4
The supernatant is light blue after 1 h during the synthesis of Cu_2O@ZIF-8 composites (step 20 in "synthesis of Cu2O@ZIF-8").

Potential solution
Keep the reaction temperature lower than 25°C, and saturate stock solutions with N_2.

Problem 5
The nano-Cu_2O core in Cu_2O@ZIF-8 composites are etched (Figure 8) after synthesis (steps 19 and 20 in "synthesis of Cu2O@ZIF-8").

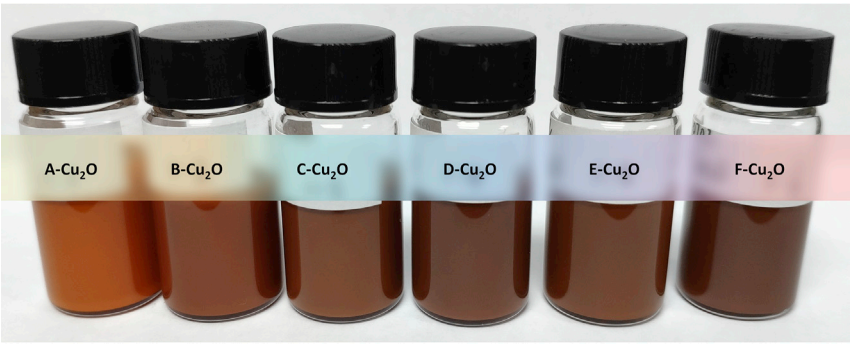

Figure 7. The digital photographs of A- to F-Cu_2O
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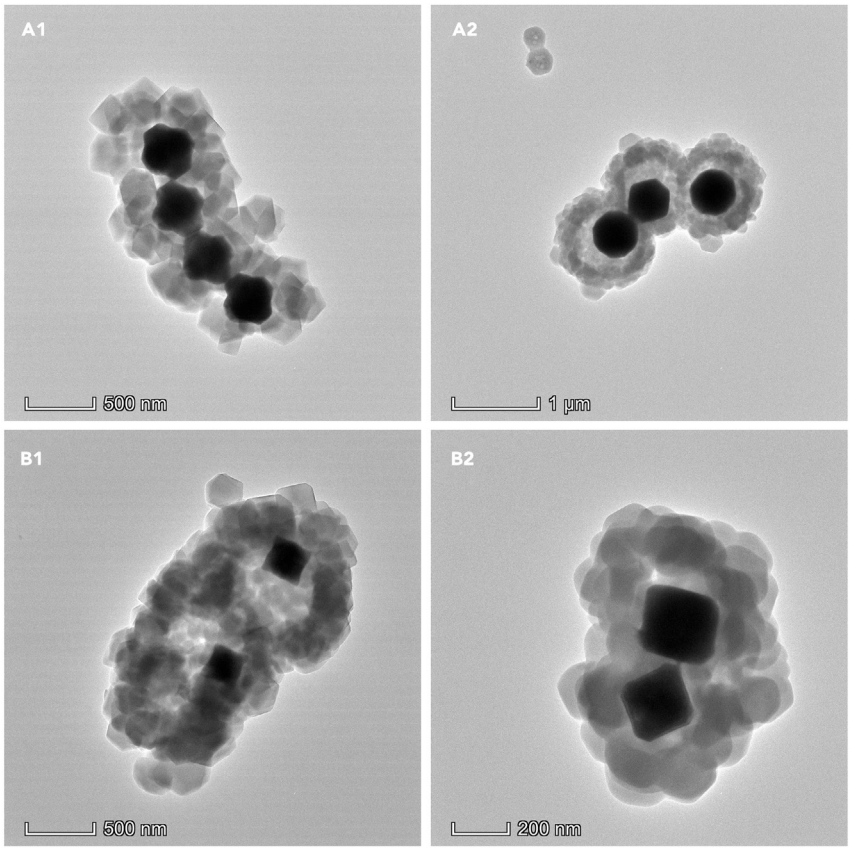

Figure 8. TEM images of Cu_2O@ZIF-8 composites
(A) Core-etched (A1) and normal (A2) **C-Cu_2O**@ZIF-8.
(B) Core-etched (B1) and normal (B2) D-Cu_2O@ZIF-8.

Potential solution

Remove O_2 gas in $Zn(NO_3)_2$ and $C_4H_6N_2$ methanol solutions with N_2 pumping for at least 20 min before use.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Jian-Gong Ma (mvbasten@nankai.edu.cn).

Materials availability

All reagents generated in this study are available from the lead contact.

Data and code availability

The published article includes all datasets/code generated or analyzed during this study. Original data have been deposited to Mendeley Data: https://onlinelibrary.wiley.com/doi/10.1002/anie.202116736.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xpro.2022.101792.

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AUTHOR CONTRIBUTIONS

H.Q.L. discovered the reaction and completed the experiments. J.-G.M. and C.P. directed the project. H.Q.L., B.L., and J.-G.M. wrote the manuscript with input from all authors. All authors analyzed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no conflict of interest.

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