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The morphology of nano-Cu$_2$O profoundly determines its catalytic performance. Here, we provide two universal and reliable techniques to modify the surface of nano-Cu$_2$O. First, we detail steps for the systematic tuning of the exposed facets of nano-Cu$_2$O 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$_2$O 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$_2$O
Construct nano-Cu$_2$O with exposed “terrace and step” (332) facets
Introduce facet-directed ZIF-8 shell on nano-Cu$_2$O with morphology dependence

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Protocol to modify the surface of nano-Cu$_2$O using facet controlling and MOF shell coating

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SUMMARY

The morphology of nano-Cu$_2$O profoundly determines its catalytic performance. Here, we provide two universal and reliable techniques to modify the surface of nano-Cu$_2$O. First, we detail steps for the systematic tuning of the exposed facets of nano-Cu$_2$O 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$_2$O 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$_2$O 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$_2$O 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$_2$O 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$_2$O (Scheme 1). For process i, Cu$_2$O 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$_2$O 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”.

(Protocol continues on the next page)
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$_2$O 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$_2$OH·HCl into 20.00 mL distilled water to prepare 1.0 M NH$_2$OH·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$_4$H$_6$N$_2$ 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     |
|-----------------------------------------|-------------------------|----------------|
| Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O) (AR) | Aladdin (Shanghai, China) | CAS: 10125-13-0 |
| Hydroxylammonium chloride (NH$_2$OH·HCl) (99.99%) | Aladdin (Shanghai, China) | CAS: S470-11-1 |
| Sodium hydroxide (NaOH) (AR)            | Aladdin (Shanghai, China) | CAS: 1310-73-2 |
| 2-Methylimidazole (C$_4$H$_6$N$_2$) (AR) | Aladdin (Shanghai, China) | CAS: 693-98-1  |
| Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (AR) | Acros Organics (USA)    | CAS: 10196-18-6 |
| Ethanol (CH$_3$CH$_2$OH) (AR)           | Concord (Tianjin, China) | CAS: 64-17-5   |
| Methanol (CH$_3$OH) (AR)                | Concord (Tianjin, China) | CAS: 67-56-1   |

(Continued on next page)
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.

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**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.

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| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Polyvinyl pyrrolidone (PVP) (Mw = 10000) (AR) | Aladdin (Shanghai, China) | CAS: 9003-39-8 |
| Sodium dodecyl sulfate (SDS) (Approx. 95%) | Solarbio (Beijing, China) | CAS: 151-21-3 |
| Distilled water (H2O) (AR) | Concord (Tianjin, China) | CAS: 7732-18-5 |
| Nitrogen (N2) (>99.999%) | LiuJang (Tianjin, China) | CAS: 7727-37-9 |
| Beaker (200 mL) (Thick wall) | Synthware Glass Co., Ltd | N/A |
| Storage vial (20 mL, 27.5 x 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 (1744–4360 RCF (x g)) | N/A | N/A |
| Pipette (1000–5000 μL) | Licheng 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 x 2 mm) | N/A | N/A |
**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.

| Reagent              | Final concentration | Amount   |
|----------------------|---------------------|----------|
| CuCl$_2$·2H$_2$O     | 0.1 M               | 0.3410 g |
| Distilled water      | N/A                 | 20.00 mL |
| **Total**            |                     | 20.00 mL |

*Note:* The 0.1 M CuCl$_2$ solution can be stored at 20°C for two weeks.

| 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**            |                     | 20.00 mL |

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

| Reagent              | Final concentration | Amount   |
|----------------------|---------------------|----------|
| NH$_2$OH·HCl         | 1.0 M               | 1.3898 g |
| Distilled water      | N/A                 | 20.00 mL |
| **Total**            |                     | 20.00 mL |

*Note:* The 1.0 M NH$_2$OH·HCl solution can be stored at 4°C for one day.

| Reagent              | Final concentration | Amount   |
|----------------------|---------------------|----------|
| Zn(NO$_3$)$_2$       | 0.12 M              | 0.7139 g |
| Methanol             | N/A                 | 20.00 mL |
| **Total**            |                     | 20.00 mL |

| Reagent              | Final concentration | Amount   |
|----------------------|---------------------|----------|
| 2-Methylimidazole    | 0.48 M              | 0.7882 g |
| Methanol             | N/A                 | 20.00 mL |
| **Total**            |                     | 20.00 mL |
Note: The 0.12 M Zn(NO₃)₂ solution and 0.48 M C₄H₆N₂ 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-Cu₂O and Cu₂O@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-Cu₂O

△ Timing: 14 h

The initial step for the synthesis of nano-Cu₂O (Process i in Scheme 1) is the SDS-stabilized Cu(OH)₂ synthesis. Subsequently, NH₂OH·HCl act as both reductant and morphology control agent to modify the exposed facets of nano-Cu₂O.

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-Cu₂O with six different morphologies by controlling the usage of NH₂OH·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 CuCl₂ 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 CuCl₂/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 NH₂OH·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-Cu₂O by adjusting the usage of NH₂OH·HCl. In this step, 0.25 mL 1.0 M NH₂OH·HCl will help in forming cubic Cu₂O nanoparticles (Figures 2A1, 2B1 and 2C1). By increasing the usage of 1.0 M NH₂OH·HCl solution to 0.50 mL, 0.75 mL, 1.00 mL, 1.25 mL and 2.00 mL, the morphology of nano-Cu₂O 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 Cu₂O nanoparticles.
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 (x g) for 3 min.
10. Wash the obtained brown precipitates with ethanol (50 mL x 3) and distilled water (50 mL x 1) by sonicating and followed centrifuging at 2791 RCF (x 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-Cu2O**

- **Timing:** 6 h

After the successful preparation of nano-Cu2O with six morphologies, scanning electron microscopy (SEM) and transmission electron microscope (TEM) characterizations are adopted to evaluate the surface conformation of nano-Cu2O.

13. Disperse 1 mg Cu2O nanoparticles into 1 mL ethanol and sonicate 5 min to form homogeneous dispersion.
14. Drop 10 µL nano-Cu2O 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 Cu2O@ZIF-8**

- **Timing:** 14 h

In this process, PVP ($M_w = 10,000$) is used as an armor to protect nano-Cu2O from being etched, and as a surfactant to help ZIF-8 crystal in-situ coating on nano-Cu2O to form Cu2O@ZIF-8 core-shell composites. All of the six morphological Cu2O nanoparticles can be coated with ZIF-8 shell through this method (Figures 3 and 4).

15. Weigh 5 mg Cu2O 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 N2 to Cu2O/PVP dispersion for 10 min.

**Note:** Pumping N2 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, N2 is just used to remove
the dissolved oxygen in the solvent, and the strict oxygen-free condition is not required. The same is true for subsequent N2-saturate operations.

17. Pump N2 to the prepared 0.12 M Zn(NO3)2 solution and 0.48 M C4H6N2 solution for 20 min.
18. Add 5 mL N2-saturated 0.12 M Zn(NO3)2 solution and 5 mL N2-saturated 0.48 M C4H6N2 solution into Cu2O/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 Cu2O@ZIF-8

Timing: 6 h

After the successful preparation of six types of Cu2O@ZIF-8 composites, scanning electron microscopy (SEM), transmission electron microscope (TEM) and elemental mapping are carried to characterize the morphology of Cu2O@ZIF-8 (Figures 3 and 4).

23. Disperse 1 mg Cu2O@ZIF-8 composites into 1 mL ethanol and sonicate 5 min to form homogeneous dispersion.
24. Drop 10 μL Cu2O@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.
EXPECTED OUTCOMES

This protocol provides systematic strategies for modifying the surface conformation of nano-Cu$_2$O with reductant-controlled and facet-directed precipitation methods. By adjusting the usage of reductant, Cu$_2$O nanoparticles with different exposed facets ranging from low index to high index were synthesized, and with the molar ratio of the usage of NH$_2$OH·HCl to CuCl$_2$ increasing to 4:1, nano-Cu$_2$O 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$_2$O 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$_2$O.

LIMITATIONS

For the reductant-controlled methods to modify, only nano-Cu$_2$O 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$_2$O 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$_2$O").

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).
Problem 2
After adding NH$_2$OH-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$_2$O”).

Potential solution
Prepare new 1.0 M NH$_2$OH-HCl solution or purchase new NH$_2$OH-HCl reagent. Additionally, the color of the synthesized nano-Cu$_2$O distinguish with each other, ranging from orange to dark brown in the sort from A- to F-Cu$_2$O (Figure 7).

Figure 4. HAADF-STEM patterns and elemental mapping of Cu$_2$O@ZIF-8 composites
Reproduced with permission (Luo et al., 2022).
(A–F) The labels (A) to (F) are correspond to A- to F-Cu$_2$O@ZIF-8, respectively.

Figure 5. Photographs of N$_2$-saturate operation
(A) Control pane of Mass flow controller.
(B) N$_2$-saturate operation image.
Problem 3
The as-prepared F-Cu₂O nanoparticles are not in concave octahedral shape.

Potential solution
In step 7 in “synthesis of Nano-Cu₂O”, the dropping speed of 1.0 M NH₂OH·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 Cu₂O@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 N₂.

Problem 5
The nano-Cu₂O core in Cu₂O@ZIF-8 composites are etched (Figure 8) after synthesis (steps 19 and 20 in “synthesis of Cu₂O@ZIF-8”).
Potential solution
Remove O₂ gas in Zn(NO₃)₂ and C₄H₆N₂ methanol solutions with N₂ 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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