Support Information

Charge-Transfer Dynamics at Ag/Ni-MOF/Cu₂O

Heterostructure in Photoelectrochemical NH₃ production

Ying Liu,^{a†} Jianmin Lu,^{b†} Qianxiao Zhang,^a Yajie Bai,^a Xuliang Pang,^a Song Wang,^{c*} Hongye Bai^{a*} and Weiqiang Fan^{a*}

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China.
^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, PR China.
^c Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang, 441053, PR China.
[†] These authors contributed equally to this work. *E*-mail addresses: wangsong1984@126.com, bhy198412@163.com, fwq4993329@yahoo.com

Materials

DL-Lactic acid (C₃H₆O₃, \geq 85.0% purity), Sodium hydroxide (NaOH, \geq 96.0% purity), Methanol (CH₃OH, \geq 99.7% purity), Nickel (II) nitrate hexahydrate (Ni(NO₃)·6H₂O, \geq 98.0% purity), Silver nitrate (AgNO₃, \geq 99.8% purity), N,N-Dimethylformamidel (C₃H₇NO, DMF, \geq 99.0% purity), Sodium borohydride (NaBH₄, \geq 98.0% purity), Polyvinyl pyrrolidone (C₆H₉NO)_n, PVP), Potassium bromide (KBr, \geq 99.0% purity). The above pharmaceutical reagents are from Sinopharm Chemical ReagentCo., Ltd. Co. Copper (II) sulfate pentahydrate (CuSO₄·5H₂O, 99.99% purity), Lithium sulfate monohydrate (Li₂SO₄·H₂O, \geq 99.0 purity) and p-Phthalic acid (C₈H₆O₄, PTA, \geq 99.0 purity) was offered by Aladdin Bio-Chem Technology Co., LTD. p-Dimethylaminobenzaldehyde (*p*-C9H11NO, \geq 99.0 purity) is from Shanghai Macklin Biochemical Co., Ltd.

Characterization

The image of all catalyzer was examined by scanning electron microscopy (SEM, Hitachi S-4800 25.0 kV 7.5mm×40.0 SE(U)) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin electron microscope (FEI Co.)). The composition and crystal patterns of catalyst were recorded on a Powder X-ray diffraction (XRD, Bruker D8 ADVANCE). The valence, functional group and composition of catalyst were detected by X-ray photoelectron spectroscopy (XPS, Thermos Fisher Scientific, Escalab 250Xi, Al Ka). The existence of organic group of Ag/Ni-MOF/Cu₂O heterostructure and NH₃ was discovered by FTIR spectra (Nicolet Nexus 470). The temperature programmed desorption (TPD) was measured by Micromeritics Autochem II chemisorption analyser.

Preparation

Synthesis of Cu₂O: Cu₂O was synthesized by the electrodeposition method, Firstly, 5.8 g DL-Lactic acid and 2 g CuSO₄ were dissolved in 20 mL deionized water to form an electrolyte (pH=10.5 adjusted by 4 M NaOH). Next, the electrodeposition potential and temperature were controlled at -0.4 V and 60 °C for 5 minutes (Electrodeposition system consist of Ag/AgCl reference electrode, Pt counter electrode and FTO working electrode.). After the deposition, the Cu₂O/FTO was washed by ethanol and deionized water for three times, respectively, and then dried in a vacuum at 60 °C.

Synthesis of Ni-MOF-x/Cu₂O: Ni-MOF-xh/Cu₂O was synthesized using the hydrothermal method. Firstly, 0.166 g PTA and 0.096 g Ni(NO₃)₂·6H₂O were dissolved in 20 mL DMF. Then, 2 mL 0.4 M NaOH solution was slowly added to the above solution. After full dissolution, the mixture solution was transferred to a Teflon-lined stainless steel autoclave containing Cu₂O. The autoclave was transferred into oven (100 °C) and reacted for x h (x=0.5, 1,1.5 and 2). The Ni-MOF-xh/Cu₂O was washed by ethanol and DMF for three times, respectively, and dried in a nature condition.

Synthesis of Ag/Ni-MOF/Cu₂O: Firstly, 41 mg PVP and 117 mg KBr were dissolved in 75 mL CH₃OH. Then, 1 mL AgNO₃ diluted solution (10 mg AgNO₃ dissolved in 10 mL deionized water) was slowly added to above mixture solution. After complete dissolution, the as-prepared solution was transferred to a roundbottom flask and the Ni-MOF/Cu₂O catalyst was suspended in round-bottom flask, and heated at 80 °C for 30 min. Then, 10 mL NaBH₄ solution was injected into the above solution dropwise. The resulted Ag/Ni-MOF/Cu₂O was washed by deionized water for three times.

Synthesis of BiVO₄: Firstly, Bi(NO₃)₃·5H₂O (0.04 M) and KI (0.4 M) were dissolved in 50 mL deionized water (pH=1.7 adjusted by HNO₃). Meanwhile, 20 mL ethanol with 0.23M p-benzoquinone was added into above solution and stirred. The obtained solution was transferred into the three-electrode system. Then, the electrodeposition (0.5 V vs. RHE, 5 min) was carried out at room temperature. The prepared BiOI film was washed with deionized water, and 0.2 mL DMSO solution containing 0.2 mol/L VO(acac)₂ was dripped. Then, the sample was annealed in a muffle furnace at 450 °C for 2 h (2 °C/min). Afterwards, the V₂O₅ in sample was removed by 1 M NaOH solution, and BiVO₄ were finally obtained.

PEC Measurements

A three-electrode H-type sealed cell (1 cm² Ag/Ni-MOF/Cu₂O as cathode, Ag/AgCl as reference electrode and 1 cm² BiVO₄ as anode) was implemented for PEC NRR system with illumination of solar light (AM 1.5G, 100 mW/cm²). 50 mL aqueous Li₂SO₄ (0.01 M) was set as the electrolyte. PEC measurements were conducted with a CHI 852 electrochemical workstation with illumination at room temperature. The NRR activity was evaluated with controlled potential electrolysis and reaction time in the electrolyte. During each test, the electrolyte was continuously bubbled with N₂ at a flow rate of 2 sccm. Before NRR, N₂ was passed through the electrolyte for 1 hour to remove O₂. Then, the whole PEC NRR process was reacted under light conditions (full spectrum) for 2 hours. The correlative Ag/AgCl electrode was converted to reversible hydrogen electrode (RHE) according to the following relationship:

$$E(RHE) = E(Ag/AgCl) + 0.197 V + 0.0593 pH:$$

Mott-Schottky plots were calculated based on the following equations:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_d} \left(E - E_{fb} - \frac{KT}{e} \right)$$
(1)
$$\mathbf{f} d \left(\frac{1}{\varepsilon} \right) \mathbf{I}$$

$$N_d = \frac{2}{e\varepsilon_0 \varepsilon A^2} \left[\frac{d \left(\overline{c^2} \right)}{dE} \right]^{-1}$$
(2)

Where *c* represents the capacitance of space charge layer, ε_0 represents the vacuum dielectric constant, *K* refers to Bohr Zimmer constant, *A* corresponds to the area of photoelectrode, *T* corresponds the absolute temperature, *e* is the electron charge, ε refers to dielectric constant, *E* is the applied voltage.

The determination of NH₃

The concentration of synthesis NH₃ was detected by Nessler reagent colorimetric method. In detail, 25 mL electrolyte was removed from cathode reaction chamber, followed by mixing with 0.5 mL KNaC4H4O₆ aqueous solution (1.8 M) and 0.5 mL Nessler reagent. The absorbance of electrolyte was detected three times with UV-Vis spectrophotometer (Agilent Technologies Cary 8454 UV-Vis) at 425 nm. The NH₃ yield rate was calculated by the following formula: $v_{\text{NH3}} = (c_{\text{NH3}} \times V)/(t \times S)$, where c_{NH3} is the concentration of NH₃, V is the volume of electrolyte, t is the NRR time and S is the electrode area of the catalyst. The Faradaic efficiency (FE) can be calculated as follows: $FE = 3F \times c_{NH3} \times V/(17 \times Q)$, where *F* is the Faraday constant (96485 C mol⁻¹), *Q* is the total quantity of charges.

¹⁵N and ¹⁴N isotope labeling experiment:

¹⁵N₂ with the ¹⁵N pureness of 99% (from Aladdin) was used to carry out the isotopic labeling experiment in 0.01 M Li₂SO₄ electrolyte. The reactor was sealed, degassed, and injected with Ar for several times, and finally filled with ¹⁵N₂. Then, 0.1 mL reaction solution was thoroughly mixed with 0.6 mL dimethyl sulphoxide-D6 (99.9% D, from Adamas) for the ¹H nuclear magnetic resonance (NMR) measurement on a BRUKER AVANCE III 400 M NMR spectrometer. For comparison, ¹⁴N₂ experiment was also operated in the same way.

Determination of hydrazine hydrate (N₂H₄)

The presence of N_2H_4 in the electrolyte was detected by Watt and Chrisp method. A mixture of para-(dimethylamino) benzaldehyde, 30 mL HCl and 300 mL C₂H₅OH was used as color reagent. 5 mL electrolyte was removed from the cathode reaction chamber. After reaction for 10 min under ambient temperature, the absorbance of electrolyte was detected at 460 nm. We discovered that the UV-Vis curves of the resulting electrolyte estimated by the Watt and Chrisp method in our system are almost the same as that of the blank solution, thus demonstrating that there was no formation of N_2H_4 .

DFT calculations

We have employed the Vienna Ab Initio Package (VASP)^[1,2] to perform all the spin-polarized density functional theory (DFT) calculations within the generalized

gradient approximation (GGA) using the PBE ^[3] formulation. We have chosen the projected augmented wave (PAW) potentials ^[4,5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the residual force was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology ^[6] was used to describe the dispersion interactions.

The equilibrium lattice constants of triclinic Ni-BDC unit cell were optimized, when using a 2×3×4 Monkhorst-Pack k-point grid for Brillouin zone sampling, to be a=10.022 Å, b=7.675 Å, c=6.142 Å, $a=98.4^{\circ}$, $\beta=95.9^{\circ}$, $\gamma=114.8^{\circ}$. This unit cell was used to construct a (010) surface model with p (2×1) periodicity in the x and ydirections and 1 stoichiometric layer in the z direction seperated by a vacuum layer in the depth of 15 Å in order to separate the slab from its periodic duplicates. This surface model contains 6 Ni, 28 H, 32 C and 24 O atoms. During structural optimizations, the Γ point in the Brillouin zone was used for k-point sampling, and the bottom half stoichiometric layer was fixed while the top half was allowed to fully relax.



Fig. S1 Material comparison picture (1: Cu₂O. 2: Ni-MOF/Cu₂O. 3: Ag/Ni-MOF/Cu₂O).



Fig. S2 (a) XRD patterns. (b) FTIR spectra. (c) Raman spectra.



Fig. S3 The XRD simulation patterns of Cu_2O , Ni-MOF and FTO.



Fig. S4 EDS spectra of the Ag/Ni-MOF/Cu₂O heterostructure on FTO glass.



Fig. S5 XPS spectra of Ag/Ni-MOF/Cu₂O heterostructure.

The crystallographic structures of $BiVO_4$ was studied by X-ray diffraction (XRD), the peaks at 29.3° and 31.1° can respond to diffractions from (1 2 1) and (0 4 0) planes of monoclinic scheelite $BiVO_4$ (JCPDS No. 14-0688). Other diffraction peaks of $BiVO_4$ can also be found in the XRD patterns, indicating that $BiVO_4$ has been successfully synthesized.



Fig. S6 XRD pattern of BiVO₄.



Fig. S7 NRR behavior of Ag/Ni-MOF/Cu₂O electrodes.



Fig. S8 (a) LSV in 0.1 M N₂ or Ar saturated Li₂SO₄ solution. (b) UV-vis absorption spectra. (c) Transient photocurrent curves at 1.23 V vs. RHE under 100 mW/cm² illumination. (d-f) Mott–Schottky plots measured at room temperature. (g) EIS spectra. (h) Randles circuit corresponding to EIS. (i) The FTIR spectra of NH_4^+ .

Photocathode	<i>R</i> s (Ω cm ²)	Rct (Ω cm ²)
Cu ₂ O	68.01	4269
Ni-MOF/Cu ₂ O	89.01	2017
Ag/Ni-MOF/Cu ₂ O	1054	1114

Table S1 Corresponding fitted parameters of EIS data using the equivalent circuit inFig.S7h.



Fig. S9 (a) The standard curve of NH_4^+ and (b) corresponding absorbance curve.



Fig. S10 (a) NH_3 yield rate of different samples. (b) Color reaction of different solutions. (c) UV-vis absorption curves and corresponding absorbance values at 425 nm of the 0.1 M Li_2SO_4 electrolyte. (d) Chronoamperometry results of different potentials. (e) NH_3 yield rates and Faradaic efficiencies at different potentials (all quantitative experiments were repeated more than three times to obtain the most

accurate NH_3 yield rate range, and the corresponding error interval is indexed in the graph.). (f) NH_3 yield rates of Ni-MOF-xh/Cu₂O (x=0.5, 1, 1.5 and 2).

Catalyst ^[Ref.]	electrolyte	Conditions	NH ₃ yield rate	Faradaic effciency
Pt ^[7]	6 M KOH	30 °C	$0.191 \ \mu g \ h^{-1} \ cm^{-2}$	0.01 %
Au/TiO ₂ ^[8]	0.1 M KOH	RT	21.4 $\mu g \ h^{-1} \ mg^{-1}$	8.11 %
PEBCD/C ^[9]	0.5 M Li ₂ SO ₄	40°C	$4.33 \ \mu g \ h^{-1} \ cm^{-2}$	4.87 %
N-doped carbon ^[10]	0.05 M H ₂ SO ₄	RT	$11.76 \ \mu g \ h^{-1} \ cm^{-2}$	1.42 %
g-C ₃ N ₅ /BiOBr ^[11]	0.05 M HCl +Na2SO4 Solution	25	$29.4 \ \mu g \ h^{-1} \ m g^{-1}$	11.0 %
Au-PTFE/TS ^[12]	0.05 M H ₂ SO ₄	RT	$18.9 \ \mu g \ h^{-1} \ cm^{-2}$	37.8 %
Fe_2O_3 -CNT ^[13]	2.0 m NaHCO ₃	RT	$0.22 \ \mu g \ h^{-1} \ cm^{-2}$	0.15 %
Au NPs coated Nb- SrTiO ₃ /Zr/ZrO _x ^[14]	HCl aqueous solution	RT	$6.5 \text{ nmol } h^{-1} \text{ cm}^{-2}$	23.3%
Ag/Ni-MOF/Cu ₂ O This work	0.1 Li ₂ SO ₄	RT	$4.63 \ \mu g \ h^{-1} \ cm^{-2}$	24.3 %

 Table S2 Summary of the representative reports on artificially NRR.



Fig. S11 (a) Hydrogen evolution rate. (b) The rate ratio of NH_3/H_2 production.



Fig. S12 Color reaction of (a) Cu₂O and (b) Ni-MOF/Cu₂O.



Fig. S13 The absorbance values of different bias voltages.



Fig. S14 (a) The standard curve of N_2H_4 and (b) corresponding absorbance curve.



Fig. S15 The absorbance curves of N_2H_4 with different bias voltages.



Fig. S16 (a) Curve of NH_3 yields reaction time at 0.5 V vs. RHE over Ag/Ni-MOF/Cu₂O. (b) Time dependent current density curve for Ag/Ni-MOF/Cu₂O at 0.5 V vs. RHE.

Compared with the photocathodes not involved in the reaction, no significant change can be observed for Ag/Ni-MOF/Cu₂O structures according to XRD patterns and Cu 2p XPS spectra. Therefore, the results indicate that the introduction of Ag/Ni-MOF on surface of Cu₂O could effectively protect Cu₂O from oxidation.



Fig. S17 (a) XRD and (b) XPS of Ag/Ni-MOF/Cu₂O after reaction PEC NRR (2 h).

References

- [1] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15–50.
- [2] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169–11186.
- [3] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865-3868.
- [4] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758-1775.
- [5] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953–17979.
- [6] S. Grimme, J. Antony, S. Ehrlich, H. J. Krieg, Chem. Phys. 2010, 132, 154104.
- [7] B. L. Sheets, G. G. Botte, Chem. Commun. 2018, 54, 4250.
- [8] M. M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan, Q. Jiang, Adv. Mater. 2017, 29, 6.
- [9] G. F. Chen, X. R. Cao, S. Q. Wu, X. Y. Zeng, L. X. Ding, M. Zhu, H. H. Wang, J. Am. Chem. Soc. 2017, 139, 9771.
- [10] Y. M. Liu, Y. Su, X. Quan, X. F. Fan, S. Chen, H. T. Yu, H. M. Zhao, Y. B. Zhang, J. J. Zhao, ACS Catal. 2018, 8, 1186.
- [11] M. X. Li, Q. J. Lu, M. L. Liu, P. Yin, C. Y. Wu, H. T. Li, Y. Y. Zhang, S. Z. Yao, ACS Appl. Mater. Interfaces 2020, 12, 38266.
- [12] J. Y. Zheng, Y. H. Lyu, M. Qiao, R. L. Wang, Y. Y. Zhou, H. Li, C. Chen, Y. F.
- Li, H. J. Zhou, S. P. Jiang, S. Y. Wang, Chem 2019, 5, 617.
- [13] S. M. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. S. Su, G. Centi, ACS Sustain. Chem. Eng. 2017, 5, 7393.
- [14] D. N. Liu, J. H. Wang, S. Bian, Q. Liu, Y. H. Gao, X. Wang, P. K. Chu, X. F.,Yu, *Adv. Funct. Mater.* 2020, **30**, 7.