

Electronic Supplementary Information

Low-cost valence-rich copper–iron–sulfur–oxygen porous nanocluster driving an exceptional energy-saving carbonyl oxidation reaction in alkali and near-neutral electrolyte

Yanqing Wang^a, Yuemeng Li^b, Liping Ding^{a,*}, Yanfeng Tang^{a,*}, Jun Ding^{b,*}

^a School of Chemistry and Chemical Engineering, Nantong University, Nantong 226007, China

^b Department of Materials Science & Engineering, National University of Singapore, 117575,

Singapore

Experimental Section

Materials

Highly conductive Cu foam(CF) support was bought from Latech Scientific Supply Pte. Ltd. $(\text{NH}_4)_2\text{Fe}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, ethyl alcohol, KOH, and H_2SO_4 (95-98wt%), carbohydrazide were purchased from Sigma-Aldrich Chemical Reagent Co.

Fabrication of Cu-Fe-S-O porous nanocluster (Cu-Fe-S-O PN) coating

Cu-Fe-S-O porous nanocluster (Cu-Fe-S-O PN) coating was prepared as follows. In a typical synthesis, to remove the oil on the surface of CF, a piece of CF was immersed into ethyl alcohol at room temperature for 2 min. Then CF was dipped into 5 volume% H_2SO_4 for 2min at room temperature to remove the copper oxide of the surface of CF. Finally, CF was immersed into wet chemical bath synthesis (CBS) solution for 4h at room temperature. The CBS solution contains 130g/L $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 35g/L $(\text{NH}_4)_2\text{Fe}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Notably, we used deionized water to clean CF for a few times among the above two processes to avoid the effect from the remain solution of every process. The mass loading of Cu-Fe-S-O PN catalyst is about $0.85\text{mg}/\text{cm}^2$.

Characterizations

ZEISS SEM Supra 40 (attached EDS from Oxford Instrument) was employed to observe the microstructure of varied samples and test chemical composition of samples. XRD patterns were determined by Bruker D8 Advanced Diffractometer

System. The element analysis of surface layer of samples was investigated by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD).

Electrochemical measurements

The carbohydrazide oxidization reaction (COR) process was determined by using the typical three-electrode cell connected to a Bio-logic VMP 3. In this cell, the Cu-Fe-S-O PN coating/CF, Hg/HgO and Pt were employed as the working electrode (WE) ($1 \times 1 \text{ cm}^2$), a reference electrode (RE) and a counter electrode (CE), respectively. The electrolyte solution contains 1M KOH and 0.5M carbohydrazide and the pH value of electrolyte is 14. According to the equation $E(\text{RHE}) = E_{\text{Hg/HgO}} + 0.059\text{pH} + 0.098 \text{ V}$, we convert all the measured potential values to reversible hydrogen electrodes (RHE) standard. LSV curves were measured with the scan rates of 1mV/s without special statement. Tafel slopes were calculated by analyzing LSV curves. Moreover, all the electrochemical datas in this paper were presented after 100% IR compensation without special statement.

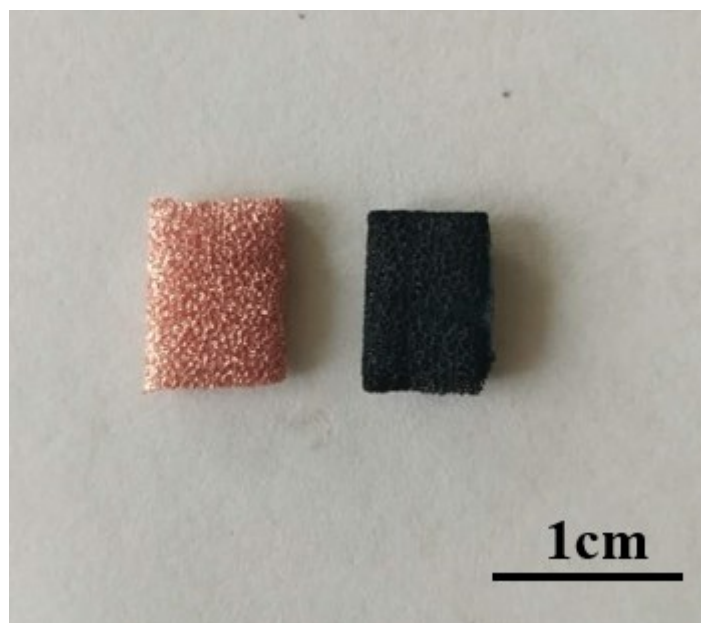


Figure S1 the digital photos of Cu foam (left) and Cu-Fe-S-O PN coating (right)

Table S1 The element atomic content of the surface layer of Cu-Fe-S-O PN coating by XPS analysis.

Element	Atomic/%
Cu K	25.5
Fe K	19.1
S K	1.4
O K	54.0
Total	100.00

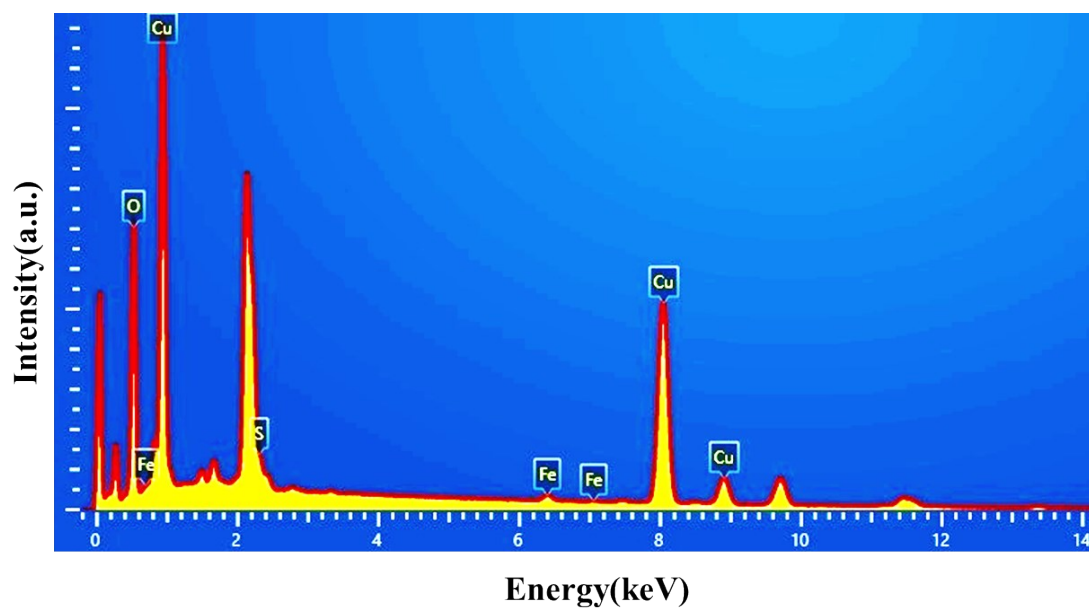


Figure S2 The EDS test results of Cu-Fe-S-O PN coating

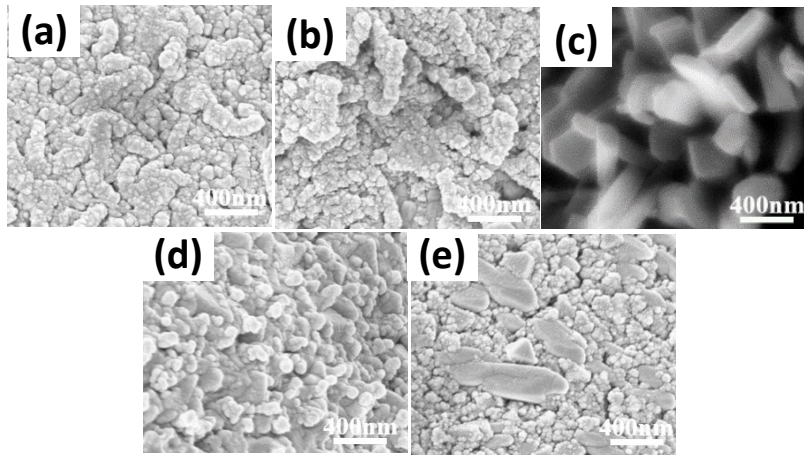


Figure S3 The influence of different reaction time on the microstructure of Cu-Fe-S-O PN coating

(a) 1h (b) 2h (c) 4h (d) 8h (e) 16h

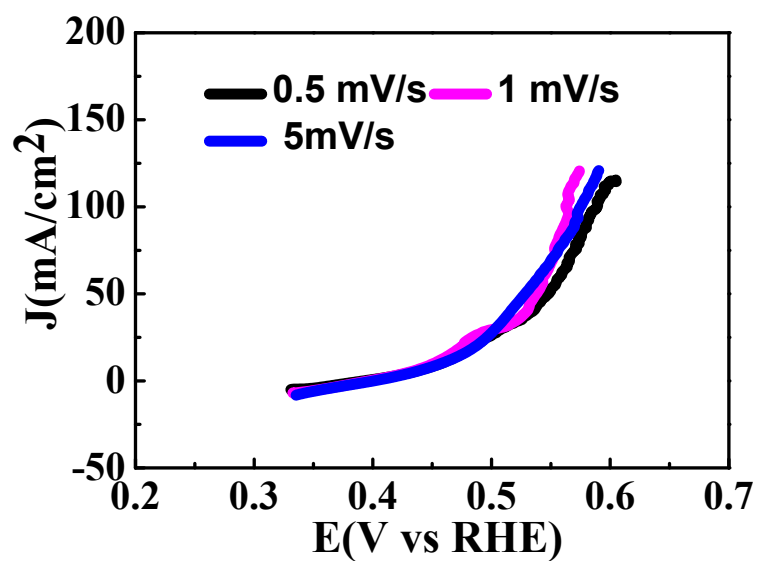


Figure S4 LSV performance for COR of Cu-Fe-S-O PN coating under different scanning rates in alkali electrolyte

(a)



(b)

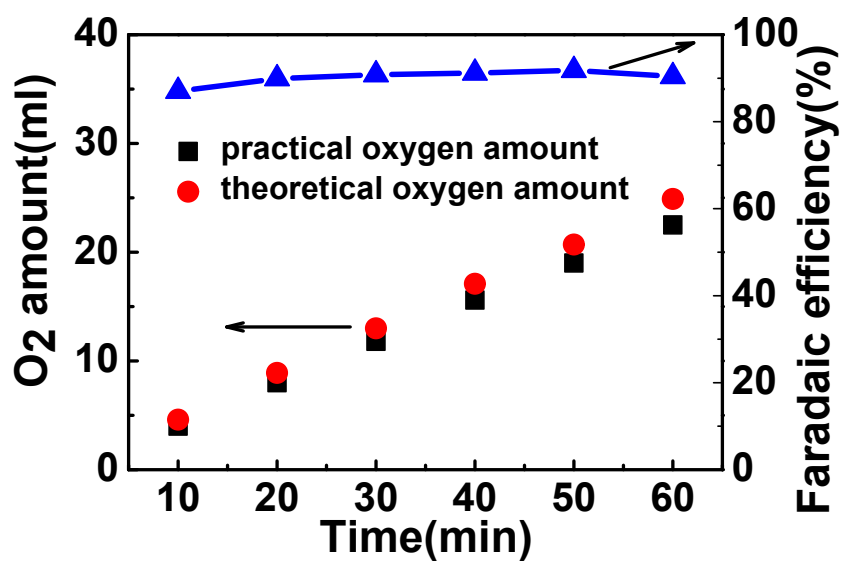


Figure S5 The observation and calculation of faradaic efficiency of OER process (a) the experimental phenomenon scheme of three electrodes system for OER test at potential 1.60V(VS RHE) (b) the oxygen evolution amount and faradaic efficiency at about 100mA/cm² for different electrolysis time.

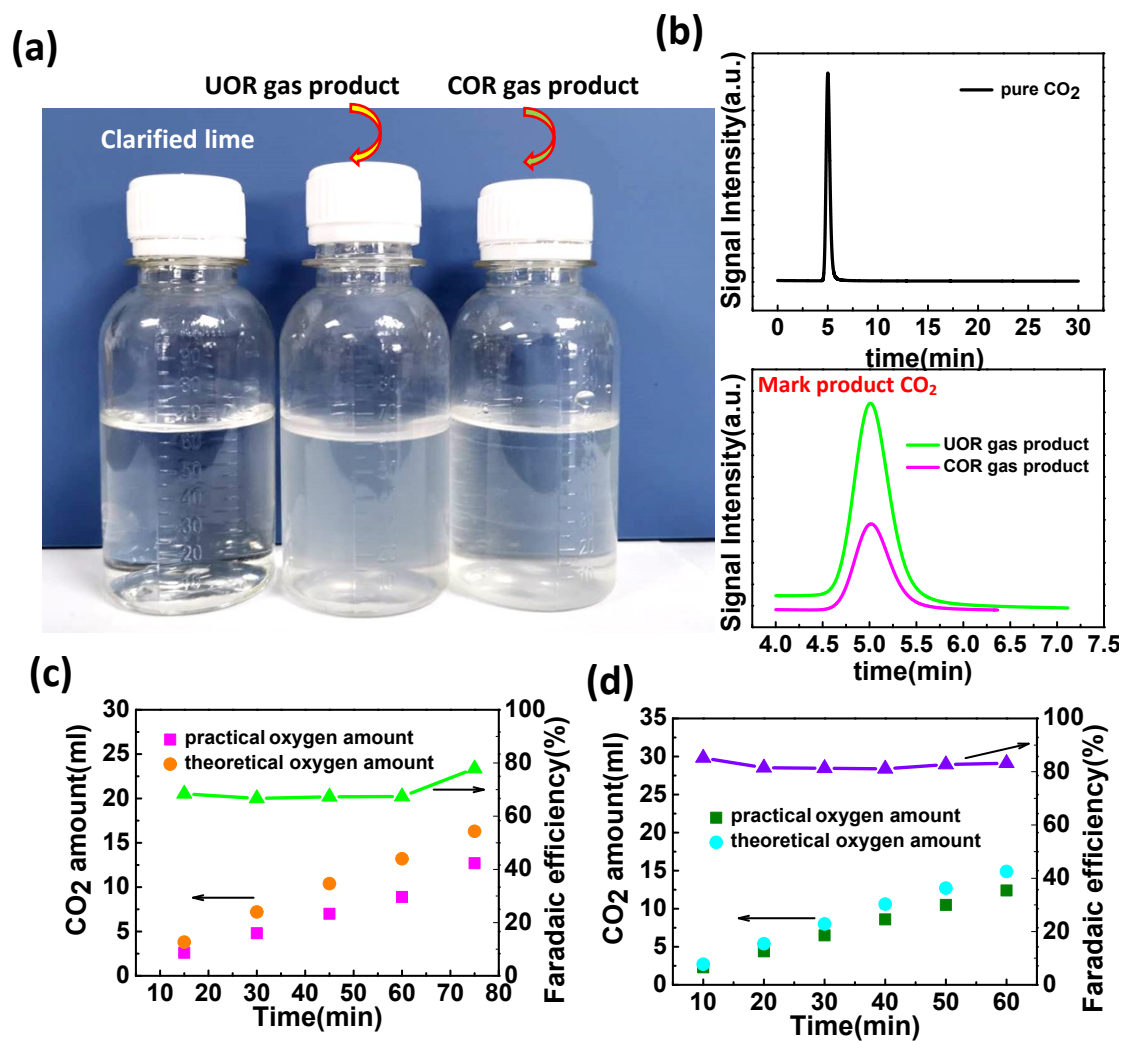


Figure S6 The verification and calculation of faradaic efficiency of UOR and COR process (a) lime water experiment for detecting the mark product CO₂ of UOR and COR (b) Specific carbon dioxide gas chromatography (GC) experiment for detecting the mark product CO₂ of UOR and COR (c) the CO₂ amount and faradaic efficiency at about 100mA/cm² for different urea electrolysis time (d) the CO₂ amount and faradaic efficiency at about 100mA/cm² for different carbohydrazide electrolysis time

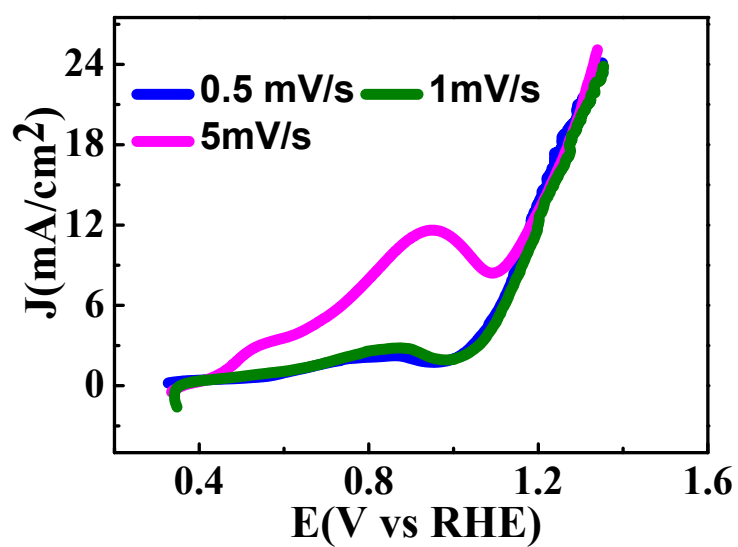


Figure S7 LSV performance for COR of Cu-Fe-S-O PN coating under different scanning rates in near-neutral electrolyte

Supplementary METHODS

Calculation of electrochemically active surface area (*ECSA*)

The electrochemical double-layer capacitance C_{dl} of electrode is calculated according to the below equation:

$$C_{dl} = J_c \div v \quad (1)$$

The CV curves in the non-Faradaic capacitance current range are presented in **Fig 2e**.

The charge current J_c and the scan rate v can be obtained from **Fig 2f**.

After calculation, as shown in Fig 2f, C_{dl} value of Cu-Fe-S-O PN/CF electrode is 34.8mF.

The electrochemically active surface area *ECSA* of electrode is calculated as the below equation on the basis of the previous published articles:

$$ECSA = C_{dl} \div C_s \quad (2)$$

According to the as-reported literatures, the specific capacitance value of the sample

C_s is 0.040 mF/cm², as such, the *ECSA* of Cu-Fe-S-O PN/CF electrode is 870cm².

Table S2. The comparison of the anode oxidization potential between Cu-Fe-S-O PN coating COR catalysis system and other environmental-friendly energy-saving electrolysis systems

Catalyst	j [mA /cm ²]	potential (vs RHE)[V] @ j	Electrolyte composition	Ref																																													
Cu-Fe-S-O PN	10	0.45	1MKOH +0.5M carbohydrazide	This work																																													
	100	0.56			Ni ₂ P NPA/NF	10	1.35	1MKOH +10mM HMF	<i>Angew. Chem.</i> 2016, 128, 1	100	1.38	Co ₃ O ₄ NS/CP	10	1.445	1MKOH +1M ethanol	<i>ACS Cent. Sci.</i> 2016, 2, 8, 538	100	1.59	Co ₃ FeP _x @NF	10	1.24	1MKOH +0.1M carbohydrate substrates	<i>Appl Catal B-Environ,</i> 2020,263, 118109	100	1.36	CoS ₂ -MoS ₂	10	1.29	1MKOH+0.5Murea	<i>Adv. Energy Mater.</i> 2018, 8, 1801775	100	1.33	Ni ₃ S ₂ /NF	100	1.40	1MKOH+10mM benzyl alcohol	<i>J. Am. Chem. Soc.</i> 2016, 138, 13639	Ni ₃ S ₂ /NF	100	1.41	1MKOH+10mM furfural	<i>J. Am. Chem. Soc.</i> 2016, 138, 13639	Ni ₃ S ₂ /NF	100	1.40	1MKOH+10mM furfuryl alcohol	<i>J. Am. Chem. Soc.</i> 2016, 138, 13639	Fe ₂ P/SSM	100
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Table S3. The comparison of the anode oxidization potential between Cu-Fe-S-O PN coating COR catalysis system and other reported highly efficient catalysts in neutral or near-neutral electrolyte

Catalyst	j [mA /cm ²]	potential (vs RHE)[V @ j]	Electrolyte composition	Ref
Cu-Fe-S-O PN	10	1.01	0.1M sodium borate +0.5M carbohydrazide	This work
Ni(S0.5Se0.5)2	10	1.731	1MPBS	<i>J. Mater. Chem. A</i> , 2019, 7, 16793
Li-IrSe2	10	1.545	1MPBS	<i>Angew. Chem. Int. Ed.</i> 2019, 58, 14764.
v-NiFe LDH	10	1.50	1MPBS	<i>ACS Energy Lett.</i> 2019, 4, 1412
CoFe- Bi@CoFe-LDH NA/M	10	1.648	0.1M K-Bi	<i>ACS Sustainable Chem.</i> <i>Eng.</i> 2018, 6, 2, 1527
Ni3N@Ni-Bi NS/Ti	10	1.635	0.1M K-Bi	<i>J. Mater. Chem. A</i> , 2017,5, 7806
NiCo2Te4/PTC DA	10	1.35	1MPBS	<i>Appl Catal B-Environ</i> 2019,254, 424
CoO/Co4N/NF	10	1.628	1MPBS	<i>J. Mater. Chem. A</i> , 2018, 6,24767
Co-Bi-Pi@CoP	10	1.64	0.1MK-Bi	<i>ChemSusChem</i> 2017, 10, 1370.
CoP	10	1.336	1MPBS	<i>J. Am. Chem. Soc.</i> 2014, 136, 21, 7587
NiFe HCH	10	1.619	1MNaHCO3	<i>Inorg. Chem.</i> 2019, 58, 1895
CoO/CoSe2	10	1.567	0.5MPBS	<i>Adv. Sci.</i> , 3: 1500426
MoS2@CoO	10	1.555	1MPBS	<i>J. Phys. Chem. C</i> 2019, 123, 5833
δMnO2/FTO	10	1.83	0.5MNa2SO4	<i>J. Am. Chem. Soc.</i> 2012, 134, 1519.
Ni-Bi/RGO	10	1.582	0.1MK-Bi	<i>ChemCatChem</i> 2018, 10, 2826.
Mn-Co-Bi/CC	10	1.596	0.5MK-Bi	<i>J. Mater. Chem. A</i> 2017, 5, 12091.

Table S4. The comparison of the anode oxidization potential between Cu-Fe-S-O PN coating COR catalysis system and other reported Cu-based or Fe-based catalysts in neutral or near-neutral electrolyte

Catalyst	j [mA /cm ²]	potential (vs RHE)[V] @ j	Electrolyte composition	Ref
Cu-Fe-S-O PN	10	1.01	0.1M sodium borate +0.5M carbohydrazide	This work
Fe (II)-acetate buffer	1	1.71	0.1M acetate buffer solution	<i>Angew. Chem., Int. Ed.</i> 2015,54, 4870.
Fe-Ci	10	1.79	0.2 M HCO ₃ ⁻ /CO ₃ ²⁻ - solution	<i>Chem. Commun.</i> 2016, 52, 5753.
N-Fe ₂ PO _{5-x}	10	1.545	1MPBS	<i>Adv. Funct.</i> <i>Mater.</i> 2018, 28, 1801397.
Iron oxyhydroxide thin films (A- Fe)	1	1.72	0.5 M borate buffer	<i>J. Mater. Chem. A</i> 2016, 4, 3655.
FeOOH nanorods	0.88	1.52	0.1M Na ₂ SO ₄	<i>Nanoscale</i> 2017, 9, 4751.
Fe-Pi-Bi/CC	10	1.664	0.1MK-Bi	<i>Inorg. Chem.</i> 2017, 56, 3131.
Cu ₄ O ₄ core complex	10	1.96	0.1MPBS	<i>Dalton Trans.</i> 2016, 45, 12685.
[Cu ₂ (BPMAN)(m-OH)] ³⁺	10	2.03	1MNaHCO ₃	<i>Angew. Chem., Int. Ed.</i> 2015, 54, 4909.
Cu(II)-CO ₃ ²⁻	23	1.68	1M Na ₂ CO ₃	<i>Angew. Chem.</i> 2013, 125, 728.
1D heterogeneous Cu (II) coordination polymer	1	1.793	0.1MK-Bi	<i>ChemElectroChem</i> 2017, 4, 75.
Cu/CuO	1	1.715	1M Na ₂ CO ₃	<i>Angew. Chem., Int. Ed.</i> 2015, 54, 2073.
Cu ₂ Se- Cu ₂ O/TF	10	1.695	0.2 M carbonate buffer	<i>Chem. Commun.</i> 2018, 54, 4979.

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