Supplementary Information (SI) for CrystEngComm.

Supporting Information

Cu nanosheets with exposed (111) crystal facets for highly efficient electrocatalytic CO_2 reduction reaction toward methanol production

Yuyuan Chen,[a] Yachang Huang,[a] Xia Hu,[b] Sijie Lin[a] and De-Kun Ma *[a]

[a] Zhejiang Key Laboratory of Alternative Technologies for Fine Chemicals Process, Shaoxing University, Shaoxing 312000, China

[b] School of Life and Environmental Sciences, Shaoxing University, Shaoxing 312000, China

Details of computation

The 1 × 1 ×1 Gamma-centered k-points mesh was adopted for the supercell model with 64 total atoms. Cu(111) and Cu(200) surface was chosen for DFT calculations to be inconsistent with the HRTEM results. During the reduction of CO_2 to produce CH_3OH, the bottom two layers of Cu atoms are fixed, while the top two layers and the adsorbed atoms are allowed to move freely. To consider van der Waals, the DFT-D3 method of Grimme was used. The overall calculation accuracy and the electronic optimization algorithm were set to normal. The self-consistent iteration convergence criterion is 10^{-7}. Wave functions were expanded using a plane-wave basis set with a kinetic energy cutoff of 500 eV and the geometries were fully relaxed until the residual force on each atom was less 0.02 eV/Å.

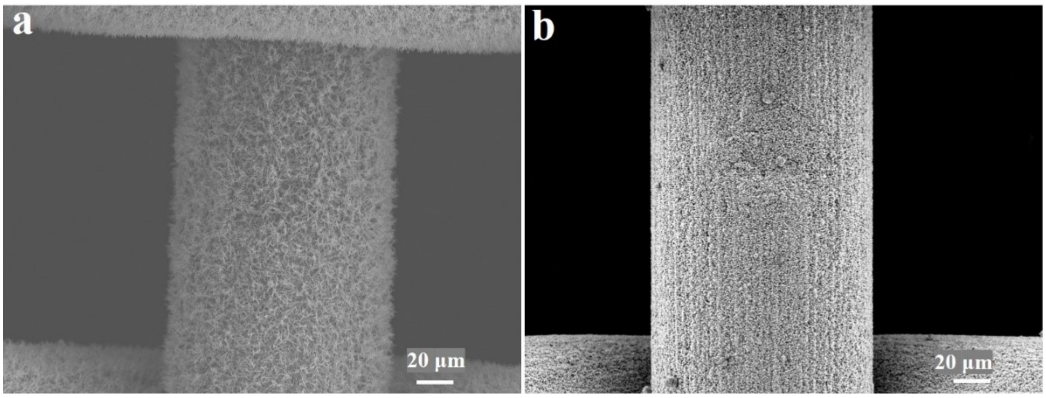

Fig. S1 FE-SEM images of Cu NRs and Cu NSs at low magnification.

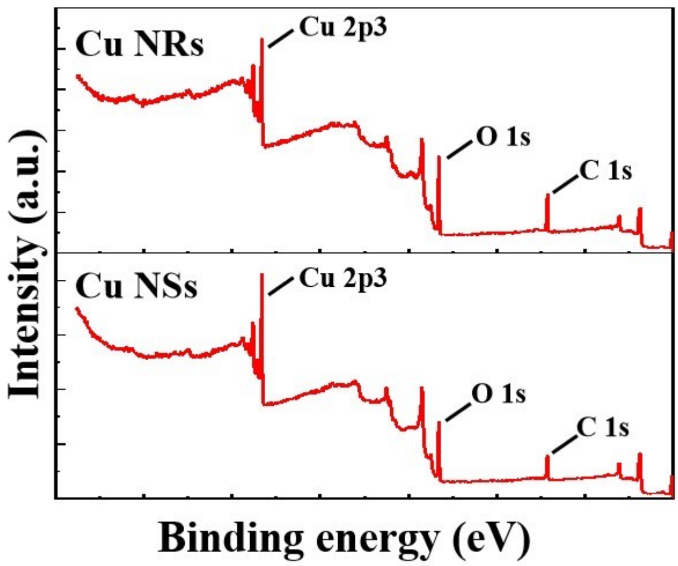

Fig. S2 XPS survey spectra of Cu NRs and Cu NSs.

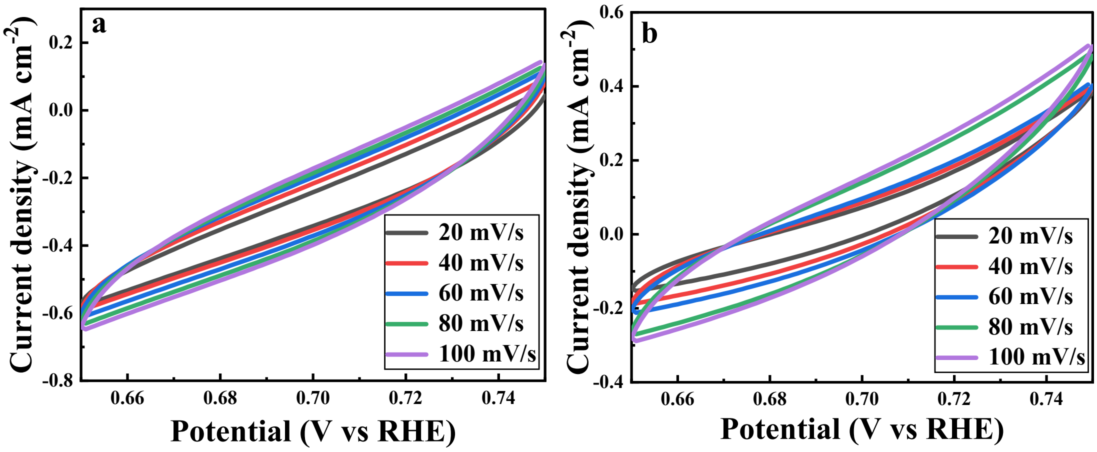

Fig. S3 CV curves obtained at different scan rates (from 20 to 100 mV S^{-1}) for Cu NSs (a) and Cu NRs (b).

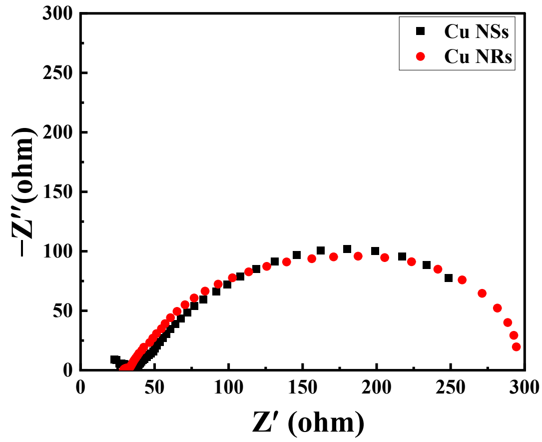

Fig. S4 Electrochemical impedance spectra of Cu NSs and Cu NRs.

Fig. S5 Digital photo of experimental equipment for electrocatalytic CO_2RR.

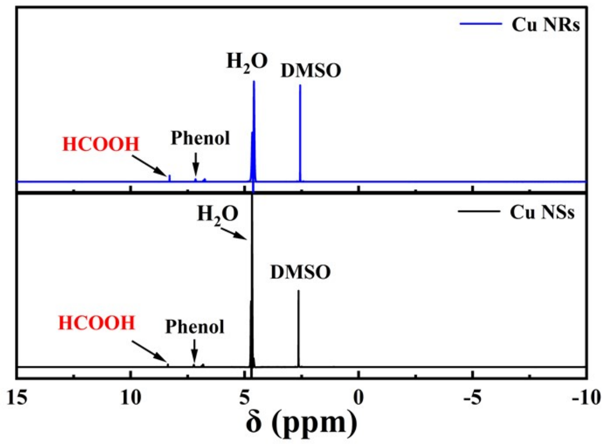

Fig. S6 ^1H NMR spectra of the products obtained over Cu NSs and Cu NRs in the presence of HCOOH. Phenol was used as internal standard substance.

Table S1 Comparison of representative electrocatalysts for CO_2RR toward CH_3OH

Catalyst	electrolyzer	electrolyte	FE (%)	Potential (vs RHE)	Ref.
Cu NSs	H-cell	$KHCO_3$	68	-0.6 V	This work
Cu_2O	H-cell	$KHCO_3$	47.5	-2.0 V	[1]
$Cu_{1.63}Se(1/3)$	H-cell	[Bmim][PF_6]/MeCN/ H_2O (5%)	77.6	-2.1 V	[2]
$Pd_{83}Cu_{17}$ bimetallic aerogels	H-cell	[Bmim][BF_4]:H_2O (1:3)	80	-2.1 V	[3]
C-Py-Sn-Zn	H-cell	0.1M $KHCO_3$	59.9	-0.5 V	[4]
CoO/CN/Ni	H-cell	0.5 M $KHCO_3$	70.7	-0.7 V	[5]
Ag,S-Cu_2O/Cu	H-cell	($BMImBF_4$):H_2O = 1:3	67.4	-1.18 V	[6]
CuSAs/TCNFs	H-cell	0.1 M $KHCO_3$	44	-0.9 V	[7]
Cu sandwich	H-cell	0.1M $KHCO_3$	24	-0.5 V	[8]
Cu_2O/CuO	H-cell	0.5 M $KHCO_3$ + 10 mM of pyridine + HCl	6.46	-0.81 V	[9]
RuOM-CNTs	H-cell	0.5 M $NaHCO_3$	65	-1.35 V	[10]
Pt	H-cell	10 mM PN, 0.1 M KCl	5	-0.06 V	[11]
BBD	H-cell	1 M ammonia water	24.3	-0.64 V	[12]

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