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Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts

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Electrocatalysis Hot Paper

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MoP Nanoparticles Supported on Indium-Doped Porous Carbon: Outstanding Catalysts for Highly Efficient CO_2 Electroreduction

*Xiaofu Sun, Lu Lu, Qinggong Zhu, Congyi Wu, Dexin Yang, Chunjun Chen, and Buxing Han**

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Ambient Aqueous Synthesis of Ultrasmall PEGylated $Cu_{2-x}Se$ Nanoparticles as a Multifunctional Theranostic Agent for Multimodal Imaging Guided Photothermal Therapy of Cancer

*Shaohua Zhang, Caixia Sun, Jianfeng Zeng, Qiao Sun, Guanglin Wang, Yong Wang, Yan Wu, Shixue Dou, Mingyuan Gao, and Zhen Li**

Electrochemical reduction of CO_2 to methanol using various electrodes and electrolytes

Electrode/ electrocatalysts	Electrode potential (V)	Electrolyte	j_{tot}^{a} (mA cm^{-2})	$FE^{b}_{methanol}$ (%)
$Cu_{1.63}Se$(1/3)	-2.1 V vs. Ag/Ag^+	[Bmim]PF_6 (30 wt%)/CH_3CN/H_2O (5 wt%)	41.5	77.6±2.0
[PYD]@Pd composite	-0.6 V vs. SCE	0.5 M KCl (aq)	~45	35
Pd/SnO_2	-0.24 vs. RHE	0.1M $NaHCO_3$	~1.5	54.8
[PYD]@Cu-Pt[c]	-0.6 V vs. SCE	0.5 MKCl	-	37
Pd or Pt/pyridinium	-	0.5 M KCl (aq)	0.05	22 ± 2
$Pd_{83}Cu_{17}$	-2.1 V vs. Ag/Ag^+	25 mol% [Bmim]BF_4 and 75 mol% water	31.8	80
	-0.55 V vs.	10 mM pyridoxine, 0.1 M		

Introduction

- A facile solvothermal synthesis of $Cu_{2-x}Se(y)$ nanocatalysts in diethylenetriamine and H_2O binary solution, where y represents the volume ratio of DETA and water (V_{DETA}/V_{H2O}).

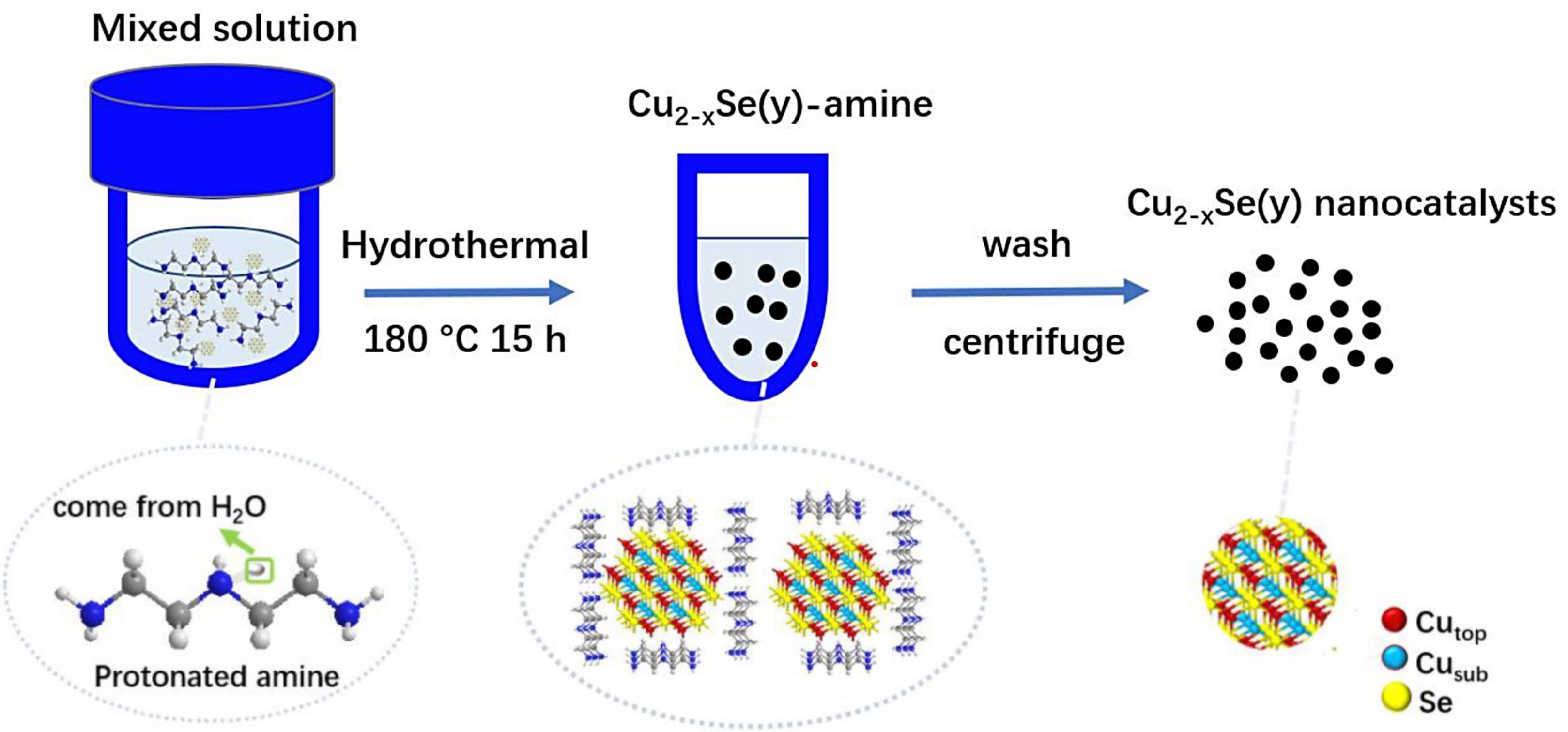
- The value of x is in the range of 0.3 to 0.4, depending on the atom ratio of Cu and Se in the catalysts.

- The properties of the catalysts, such as size and morphology, are solvent-dependent.

- The catalysts synthesized in the mixed solvent with V_{DETA}/V_{H2O} of 1:3 can convert CO_2 into methanol with a current density of 41.5 mA cm^{-2} at FE of 77.6%.

- The current density is higher than those reported up to date with very high methanol selectivity.

Synthesis of $Cu_{2-x}Se(y)$



$CuCl_2.2H_2O$
Na_2SeO_3
NH_2OH

$HN(CH_2CH_2NH_2)_2$
H_2O

Thermogravimetry curve of $Cu_{2-x}Se(y)$

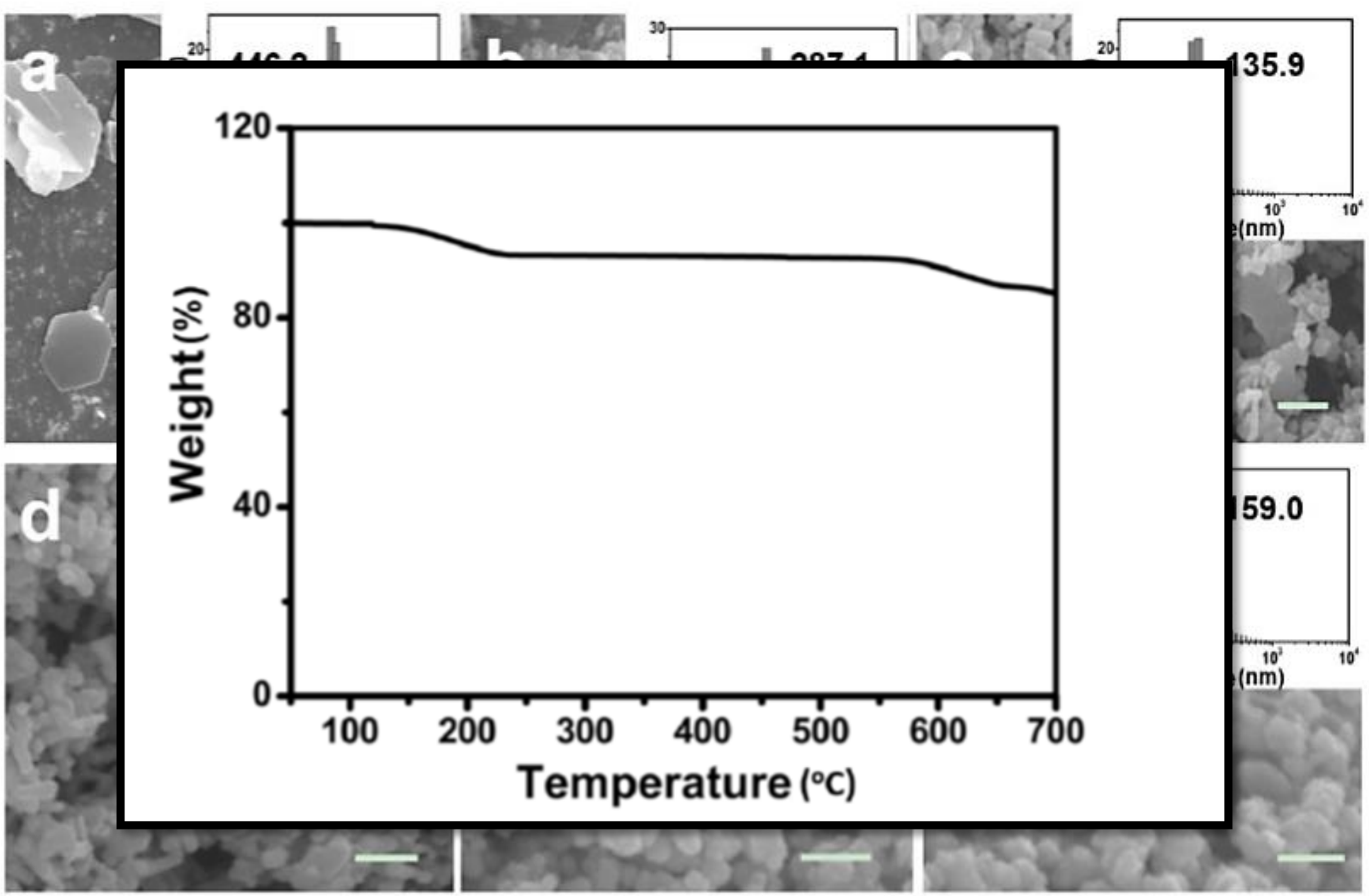


Fig: SEM and DLS images of various $Cu_{2-x}Se(y)$ nanocatalysts. (a) $Cu_{1.61}Se(1/0)$; (b) $Cu_{1.60}Se(3/1)$; (c) $Cu_{1.63}Se(1/1)$; (d) $Cu_{1.63}Se(1/3)$; (e) $Cu_{1.62}Se(1/5)$; (f) $Cu_{1.64}Se(0/1)$. Scale bar = 200 nm.

Characterization of $Cu_{1.63}Se(1/3)$

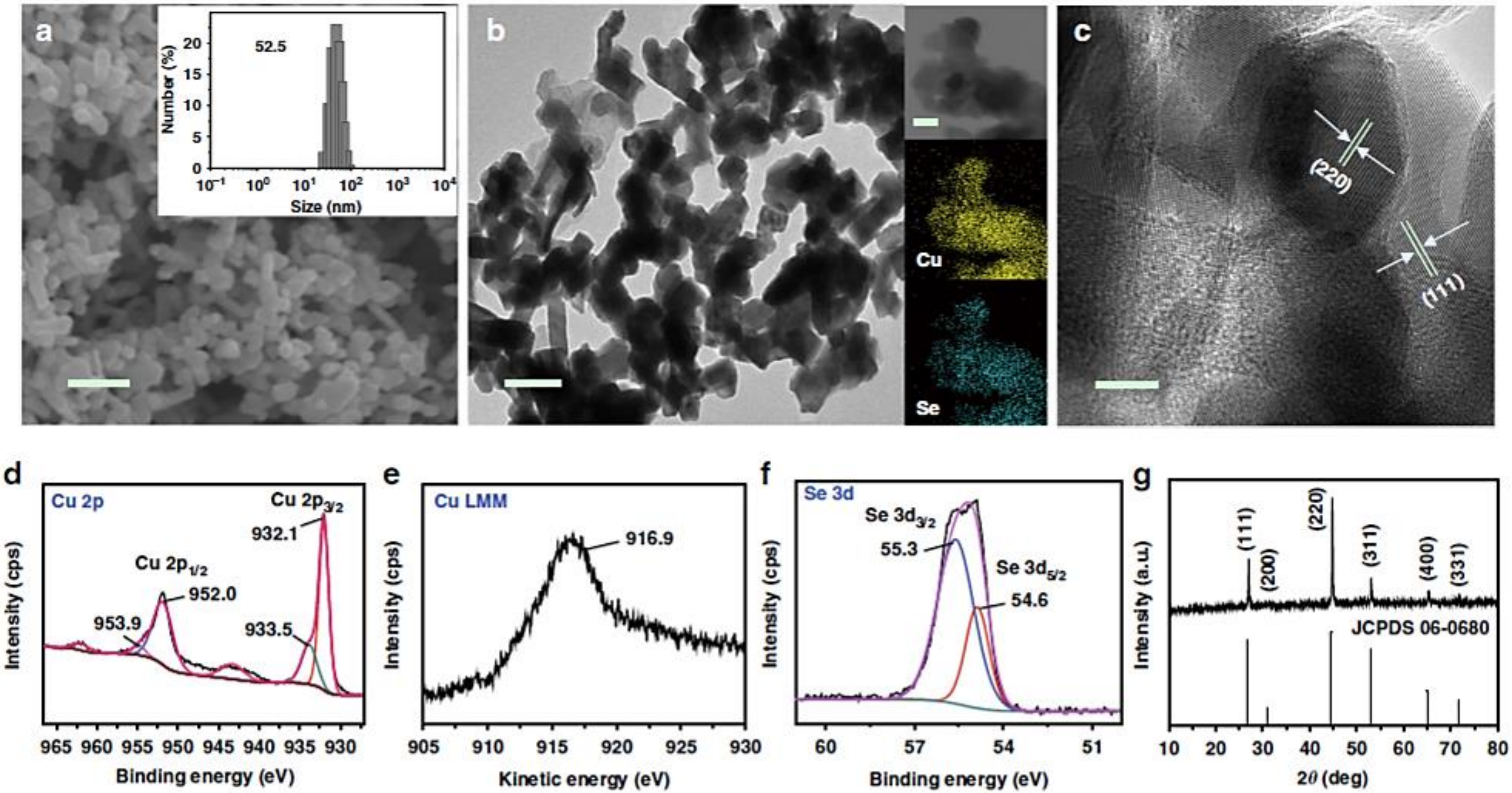


Fig. 1 Characterization of $Cu_{1.63}Se(1/3)$ nanocatalysts. **a** SEM image of the $Cu_{1.63}Se(1/3)$ nanocatalysts and the inset is size distribution determined by DLS, scale bar =200 nm; **b** TEM image of the $Cu_{1.63}Se(1/3)$ nanocatalysts and the inset is the corresponding elemental mappings, scale bar = 100 nm; **c** HRTEM image of the $Cu_{1.63}Se(1/3)$ nanocatalysts, scale bar = 10 nm; XPS spectra of the $Cu_{1.63}Se(1/3)$ nanocatalysts: **d** Cu 2p, **e** Cu LMM, and **f** Se 3d; **g** XRD patterns of the $Cu_{1.63}Se(1/3)$ nanocatalysts

Electrochemical studies

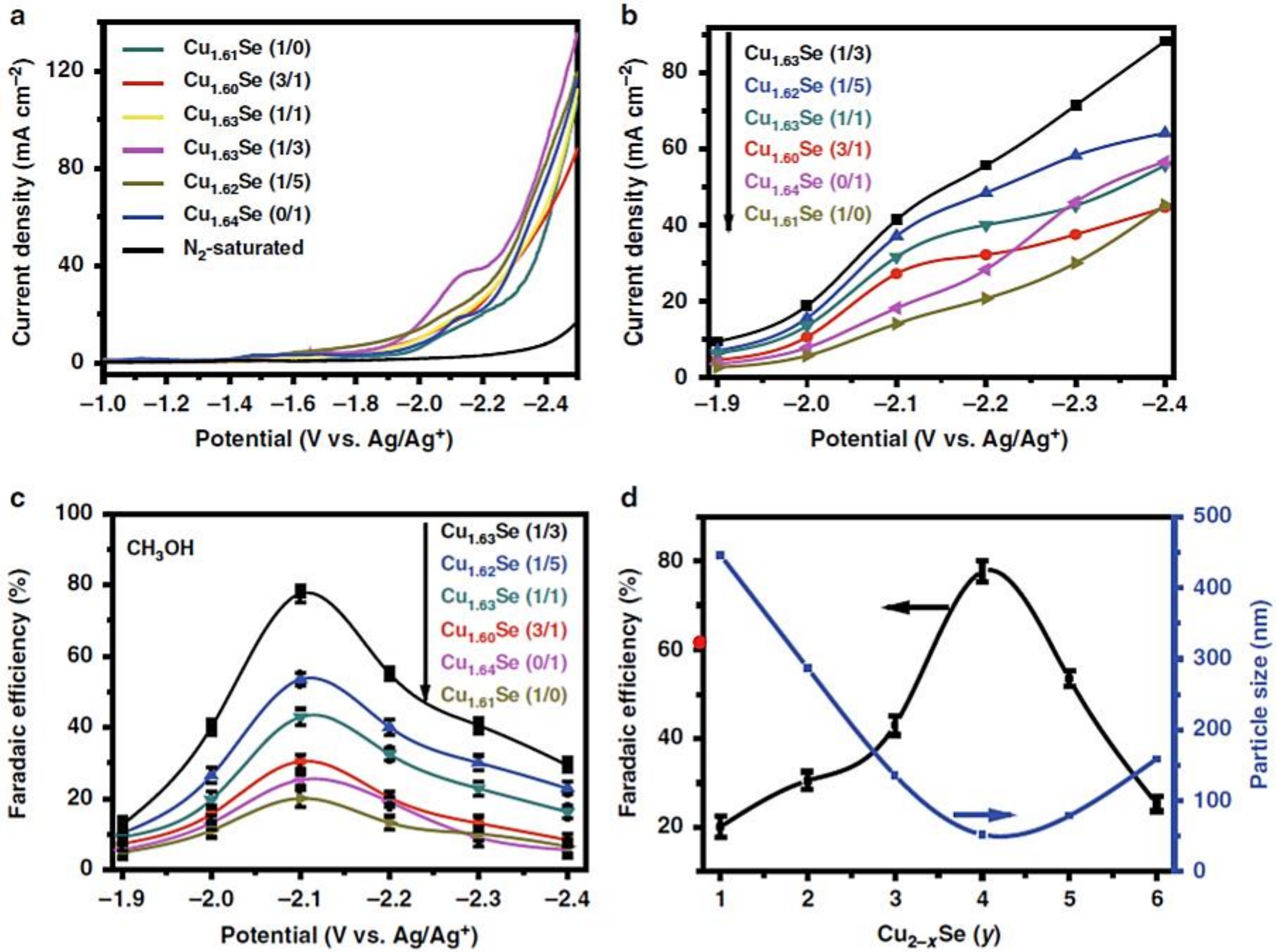


Fig. 2 CO_2 reduction performance on $Cu_{2-x}Se(y)$ nanocatalysts. **a** LSV traces on different electrodes in CO_2-saturated or N_2-saturated electrolyte at scan rate of 20 mV s^{-1}; **b** Total current density and **c** FE over $Cu_{1.63}Se(1/3)$ catalyst at different applied potentials; **d** Plots of particle size vs. FE of methanol on different catalysts (1) $Cu_{1.61}Se(1/0)$; (2) $Cu_{1.60}Se(3/1)$; (3) $Cu_{1.63}Se(1/1)$; (4) $Cu_{1.63}Se(1/3)$; (5) $Cu_{1.62}Se(1/5)$; (6) $Cu_{1.64}Se(0/1)$.

Electrochemical studies

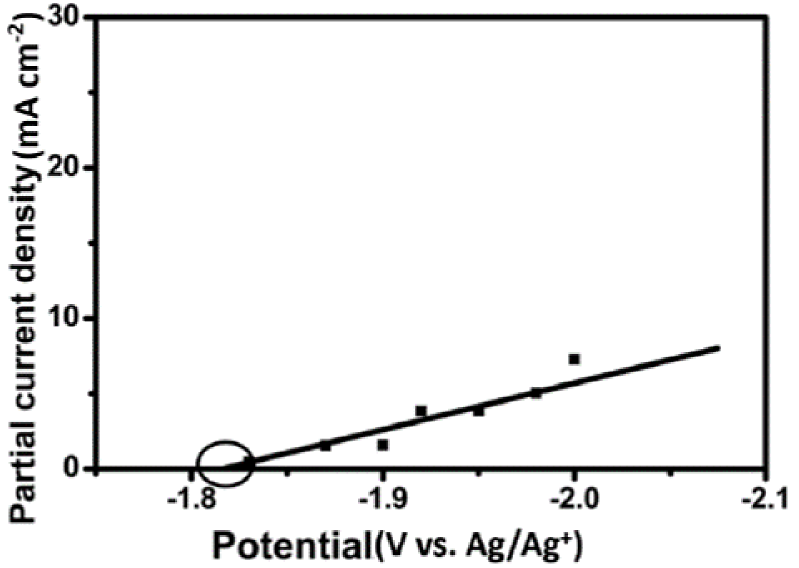


Fig: Partial current densities of methanol under different potentials.

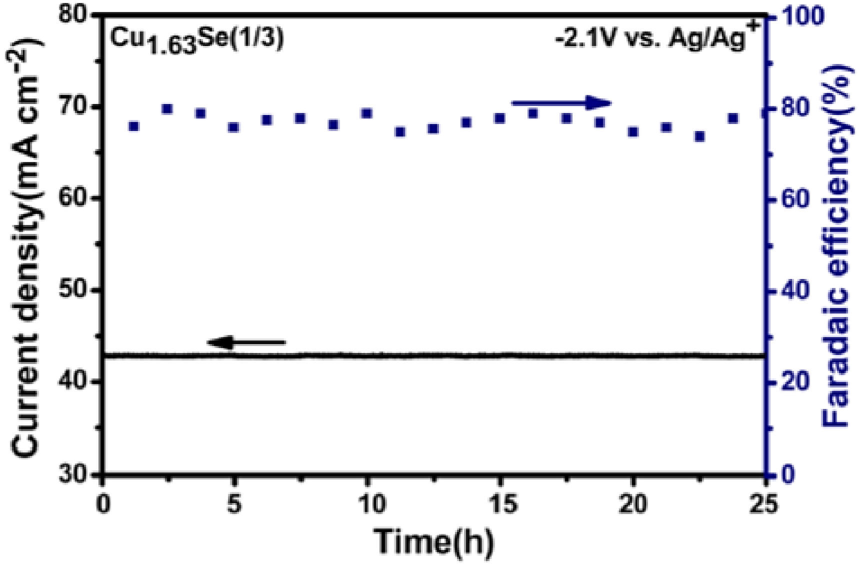


Fig: The long-term stability of the $Cu_{1.63}Se(1/3)$ catalyst at the applied potentials of −2.1 V vs. Ag/Ag+

Cell potential = 2.67 V (2.2-3.7 V)

Reported

Electrochemical studies

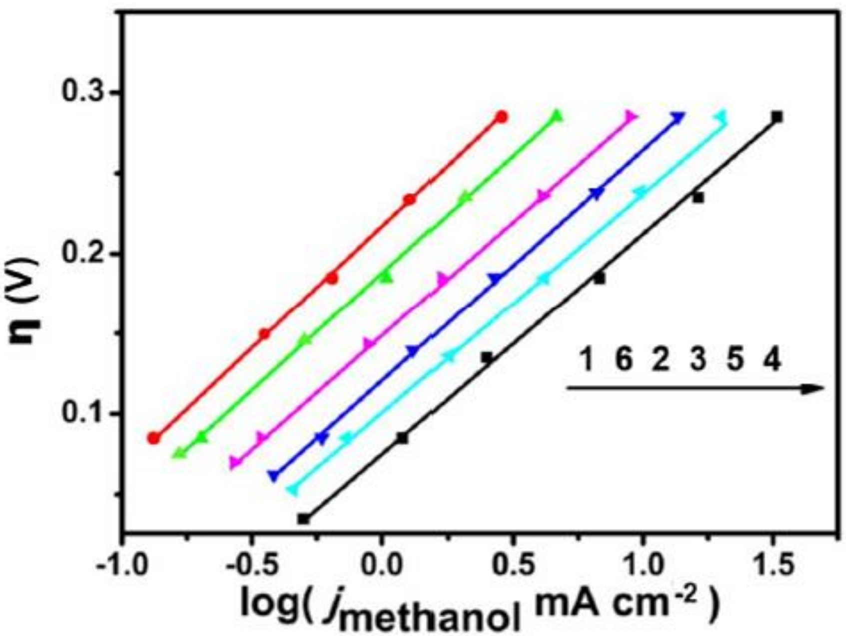


Fig: Tafel plot for CH_3OH production over various $Cu_{2-x}Se(y)$ nanocatalysts: **1)** $Cu_{1.61}Se(1/0)$; **2)** $Cu_{1.60}Se(3/1)$; **3)** $Cu_{1.63}Se(1/1)$; **4)** $Cu_{1.63}Se(1/3)$; **5)** $Cu_{1.62}Se(1/5)$ and **6)** $Cu_{1.64}Se(0/1)$.

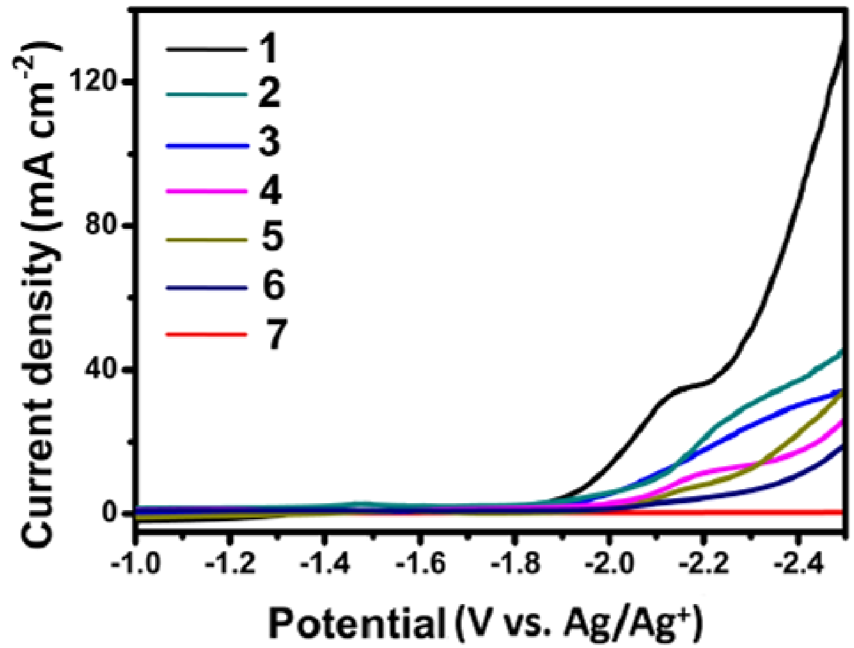


Fig: LSV traces recorded using $Cu_{1.63}Se(1/3)$ electrodes in various electrolytes. **(1)** $[Bmim]PF_6$ (30 wt%)/CH_3CN/H_2O (5 wt%); **(2)** $[Bmim]TF_2N$ (30 wt%)/CH_3CN/H_2O (5 wt%); **(3)** $[Bmim]BF_4$ (30 wt%)/CH_3CN/H_2O (5 wt%); **(4)** [Bmim]OAc (30 wt%)/CH_3CN/H_2O (5 wt%); **(5)** $[Bmim]NO_3$ (30 wt%)/CH_3CN/H_2O (5 wt%); **(6)** $[Bmim]ClO_4$ (30 wt%)/CH_3CN/H_2O (5 wt%) and **(7)** 0.5 M $TEAPF_6$ in the CH_3CN (92.86 wt%) and H_2O (7.14 wt%) mixture solution

Catalytic activity of various Cu-based catalysts

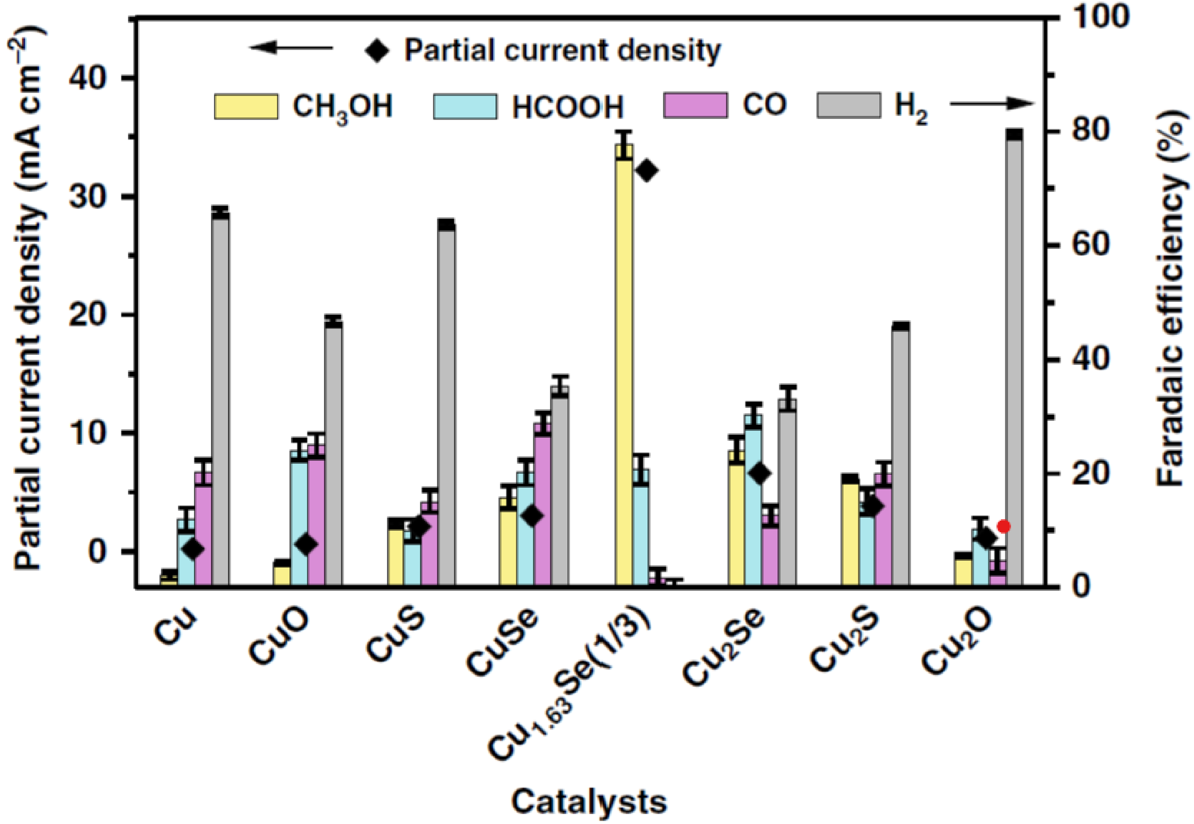


Fig. 3 Partial current density and FE of methanol over various catalysts at −2.1 V vs. Ag/Ag+.

Mechanism study of CO_2 reduction to methanol

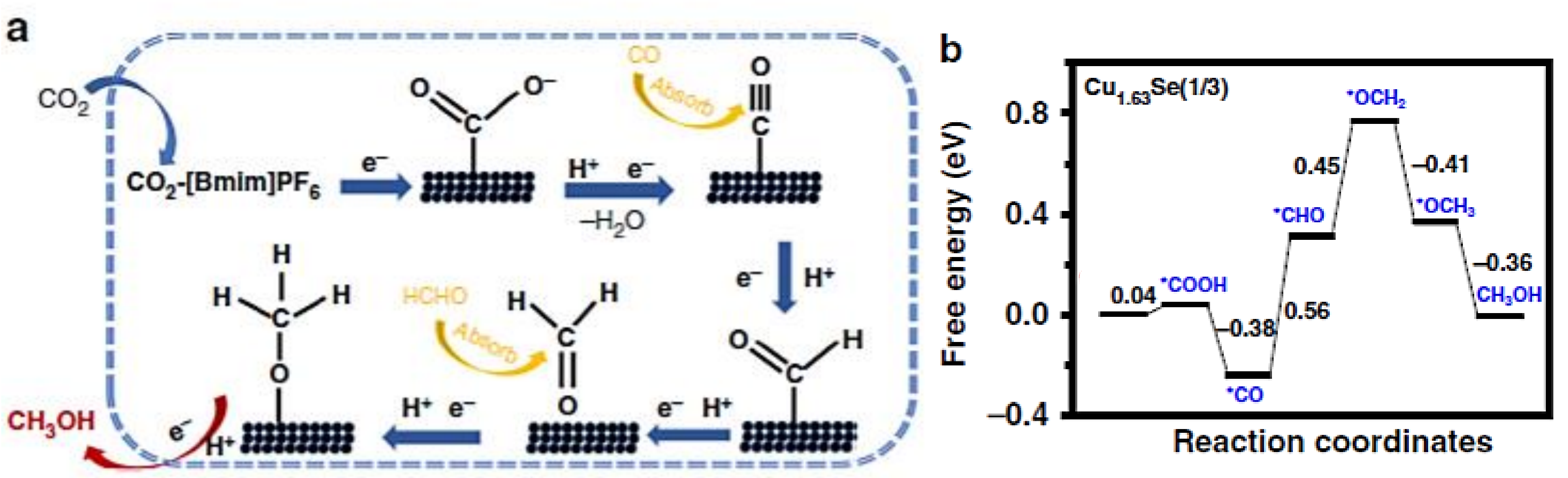


Fig: a Proposed mechanism on $Cu_{2-x}Se(y)$ electrode; **b** free energy diagrams on $Cu_{1.63}Se(1/3)$ electrode

Conclusion

- A series of $Cu_{2-x}Se(y)$ nanocatalysts were synthesized for selective electroreduction of CO_2 to methanol.

- The Cu and Se in the catalysts had excellent cooperative effect for catalysing the reaction. The size and morphology were crucial for the performance of the catalysts, which could be controlled by the V_{DETA}/V_{H2O} ratios.

- The $Cu_{1.63}Se(1/3)$ nanocatalysts yielded outstanding current density of 41.5 mA cm^{-2} with FE of 77.6% at −2.1 V vs. Ag/Ag+.

- Some other transition metal selenides can be designed as efficient electrocatalysts for CO_2 reduction.