

Supporting information

Electronic delocalization engineering of bismuth-based materials for catalytic electrochemical CO₂ and N₂ Conversion

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Table S1 Typical performance parameters of Bi-based materials for CO₂RR

Material	Preparation method	Partial current density	Stability (h)	HCOOH production rate	FE	Energy efficiency	Reference
single-crystalline Bi rhombic dodecahedron	solvent thermal reduction	290.1 mA cm ⁻² @-0.78V vs RHE	20 h @ at -0.68 V vs RHE in 1.0 M KOH	2.88 mmol cm ⁻² h ⁻¹	> 92.2% from 9.8 to 290.1 mA cm ⁻²	69.5%	70
angular-shaped Bi microparticles	electrodeposition	271.7 mA cm ⁻² @-1.1 V vs RHE in 1 M KOH	10 h@-1.1 V vs RHE	5.0688 mmol cm ⁻² h ⁻¹ @-1.1 V vs RHE	> 95% from -0.6 to -1.1 V vs RHE	76.4% @-0.6 V vs RHE	129
Cu-doped Bi	electrochemical reconstruction	-1.1 A cm ⁻² (Total) at -0.86 V vs RHE	100 h at -400 mA cm ⁻²	21.0 mmol h ⁻¹ cm ⁻² at -0.86 V vs RHE in 1 M KOH	> 96%	/	137
nanoporous Sb-Bi alloys	dealloying	734 mA cm ⁻² at -1.0 V vs RHE in 1 M KOH	12 h @ -0.8 V vs RHE in 0.5 M KHCO ₃	13.6 mmol h ⁻¹ cm ⁻² at -1.0 V vs RHE	95.8 % at -0.9 V vs RHE	64.8 % at -0.8 V vs RHE	139
Bi/CeOx	electrochemical reduction	137 mA cm ⁻² at -1.3 V vs RHE	34 h @ at -1.2 V in 0.2 M Na ₂ SO ₄	2600 μmol h ⁻¹ cm ⁻² at -1.3 V vs RHE	98 % at -1.2 V	/	146

Bi nanoribbons/Bi-O edge sites	H ₂ thermal reduction	46.4 mA/cm ² at -1.2 V vs RHE in 0.5 M KHCO ₃	> 100 h in 0.5 M KHCO ₃	/	> 95% in wide range	/	151
Sn-doped Bi/BiOx	dealloying	~100 mA cm ⁻² at -0.7 V vs RHE	20 h @ at -0.7 V vs RHE in 1.0 M KOH	/	> 92% in wide range	/	154
Bi ₂ O ₂ CO ₃ nanosheet	electrically driven conversion	930 mA cm ⁻² at -1.55 V vs RHE	12 h @ at -0.9 V vs RHE in 0.5 M KHCO ₃	/	93% at -1.55 V vs RHE	/	161
Bi nanodendrites	galvanic-cell deposition	~180 mA cm ⁻² at -1.25 V vs RHE	80 h @ at -0.88 V vs RHE in 0.5 M KHCO ₃	3.4 mmol h ⁻¹ cm ⁻² at -1.25 V vs RHE in 1 M KOH	96.7% at -0.92 V vs RHE in 1 M KOH	/	165
V-Bi single atom alloy	in situ electrochemical reduction	77.7 mA cm ⁻² at -1.3 V vs RHE	90 h @ at -0.88 V vs RHE in 1 M KHCO ₃	/	96.2% at -0.9 V vs RHE in 1 M KOH	/	172
Bi nanosheets	electrochemical reconstruction	~308 mA cm ⁻² at -1.4 V vs RHE	110 h @200 mA cm ⁻²	/	> 95% @-0.98 V vs RHE in 1 M KOH	/	183
O-Bi-ene	electrochemical transformation	/	12 h @-0.9 V vs RHE in 0.5 M KHCO ₃	/	> 90% @ -0.8 ~ -1.1 V vs RHE	64.9% at 1.9 V in 1 M KOH	188

Table S2 Typical performance parameters of Bi-based materials for N₂RR

Material	Preparation method	NH ₃ production rate	FE	Reference
2D mosaic bismuth nanosheets	electrochemical reduction	$2.54 \pm 0.16 \mu\text{g cm}^{-2} \text{h}^{-1}$ ($\sim 13.23 \mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$)	$10.46 \pm 1.45\%$ at -0.8 V vs RHE in $0.1 \text{ M Na}_2\text{SO}_4$	88
Bi nanodendrites	electrodeposition	$25.86 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ at -0.60 V vs RHE	10.8% at -0.55 V vs RHE in 0.1 M HCl	192
Bi hollow nanospheres	one-pot solvothermal method	$23.4 \pm 1.3 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	$19.8 \pm 1.1\%$ at -0.4 V vs RHE in $0.1 \text{ M Na}_2\text{SO}_4$	193
bismuth particle	polyol reduction method	$404.9 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	62.37% at -0.50 V vs RHE in $0.5 \text{ M K}_2\text{SO}_4$	194
amorphous BiNi alloy	reduction method	$17.5 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	13.8% at -0.6 V vs RHE in $0.1 \text{ M Na}_2\text{SO}_4$	197
nanoporous Pd ₃ Bi	electrochemical dealloying	$59 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	21.5% at -0.2 V vs RHE in $0.05 \text{ M H}_2\text{SO}_4$	198
V _O -Bi ₄ O ₅ I ₂ -OH	solvothermal approach	$20.44 \mu\text{g h} \text{mg}_{\text{cat}}^{-1}$	32.4% at -0.1 V vs RHE in $0.1 \text{ M Na}_2\text{SO}_4$	201
Bi ₂ S _{3-x} /Ti ₃ C ₂ T _x	Microwave-assisted solvothermal method	$68.3 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ at -0.6 V vs RHE	22.5% at -0.4 V vs RHE in 0.5 M LiClO_4	206

Bi clusters in amorphous BiO _x	Electrochemical reconstruction	~113 μg h ⁻¹ mg _{cat} ⁻¹ at -0.8 V vs RHE in 0.5 M K ₂ SO ₄ (pH 2.5)	~30 % at -0.6 V vs RHE in 0.5 M K ₂ SO ₄ (pH 2.5)	207
Lithium/bismuth co-functionalized phosphotungstic acid	impregnation approach	61 ± 1 μg h ⁻¹ mg _{cat} ⁻¹	85% ± 2% at -0.1 V vs RHE in 0.1 M Li ₂ SO ₄ (pH = 4)	214