Supporting information

Electronic delocalization engineering of bismuth-based materials for catalytic electrochemical CO_2 and N_2 Conversion

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Table S1 Typical performance parameters of Bi-based materials for CO_2RR

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% l 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 c m^{-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_2SO_4	2600 μmol h^{-1} c m^{-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
$Bi_2O_2CO_3$ 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	~180mA 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 N_2RR

Material	Preparation method	NH_3 production rate	FE	Reference
2D mosaic bismuth nanosheets	electrochemical reduction	2.54 ± 0.16 μg cm^{-2} h^{-1} (~13.23 μg mg_{cat}^{-1} h^{-1})	10.46 ± 1.45% at -0.8 V vs RHE in 0.1 M Na_2SO_4	88
Bi nanodendrites	electrodeposition	25.86 μg h^{-1} mg^{-1}_{cat} 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 ± 1.3 μg h^{-1} mg_{cat}^{-1}	19.8 ± 1.1% at -0.4 V vs RHE in 0.1 M Na_2SO_4	193
bismuth particle	polyol reduction method	404.9 μg h^{-1} mg_{cat}^{-1}	62.37% at -0.50 V vs RHE in 0.5 M K_2SO_4	194
amorphous BiNi alloy	reduction method	17.5 μg h^{-1} mg_{cat}^{-1}	13.8% at -0.6 V vs RHE in 0.1 M Na_2SO_4	197
nanoporous Pd_3Bi	electrochemical dealloying	59 μg h^{-1} mg_{cat}^{-1}	21.5% at -0.2 V vs RHE in 0.05 M H_2SO_4	198
V_O-$Bi_4O_5I_2$-OH	solvothermal approach	20.44 μg h mg^{-1}_{cat}	32.4% at -0.1 V vs RHE in 0.1 M Na_2SO_4	201
$Bi_2S_{3-x}/Ti_3C_2T_x$	Microwave-assisted solvothermal method	68.3 μg $h^{-1}mg^{-1}$ 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_2SO_4 (pH 2.5)	~30 % at -0.6 V vs RHE in 0.5 M K_2SO_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_2SO_4 (pH = 4)	214