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Supporting Information

Highly Active and Stable AuNi Dendrite as Electrocatalyst for Oxygen Reduction

Reaction in Alkaline Media

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Parameters optimization

To achieve high-performance Au_xNi_y catalyst, firstly, the parameters during the electrodeposition process, such as applied electrodeposition potentials and the precursor feeding ratios, were optimized. The comparative ORR curves of as-prepared Au_xNi_y catalysts at various parameters are presented in Fig. S1[†]. Clearly, the as-prepared Au_1Ni_2 deposited at -0.6 V vs. SCE exhibits the highest ORR activity under our experimental conditions. The specific values of these as-prepared catalysts for ORR activities, such as onset potential (E_{onset}), half-wave potential ($E_{1/2}$) and diffusion-limiting current density, are all summarized in Table S1[†]. The morphologies and components of these as-prepared Au_xNi_y catalysts were examined by SEM and EDX, respectively. As shown in Fig. S3a, c and e[†], the morphologies of the as-prepared Au_1Ni_2 catalysts change from dendrites to "flowers" with the variation of electrodeposition potentials from -0.5 to -0.7 V vs. SCE. On the other hand, with the increasing of Ni²⁺ contents in precursors, the pronounced 3D nanosponge morphology (Fig. S3f[†]) is developed (Au_1Ni_3 , 15 mM HAuCl₄ + 45 mM NiSO₄). The "flowers" and "sponge" Au_xNi_y catalysts have lower porosity and less active sites, which may have a negative effect on the catalytic activities of Au_xNi_y catalysts.

Fig. S4[†] displays the corresponding EDX results of these as-prepared Au_xNi_y catalysts. The EDX analysis indicates that the Ni contents in the nanostructures evidently increase with the electrodeposition potentials moving negatively. The Ni atoms in Au₁Ni₂ catalysts increase from 1.13 at % at -0.5 V to 51.8 at % at -0.7 V vs. SCE. Similarly, Ni contents in the Au_xNi_y catalysts deposited at -0.6 V vs SCE also show the increased trend with the decrease of the mole ratios of metallic precursor (HAuCl₄ : NiSO₄). The Ni contents change from 2.44 at % for Au₁Ni₁ to 21.35 at % for Au₁Ni₃. Pure Ni has no catalytic activity toward oxygen reduction reaction,¹ thus, superfluous Ni atoms in Au_xNi_y catalysts probably block the active sites of Au atoms, leading to the degradation of the catalytic activity.

Based on the standard potentials of Au(III) and Ni(II) (Au³⁺/Au, +1.50 V vs. SHE (standard hydrogen electrode) and Ni²⁺/Ni, -0.25 V vs. SHE), we can expect that Ni atoms in as-prepared Au_xNi_y catalysts can be easily removed by electrochemical dealloying in acid solution, which will induce to form highly porous structure and definitely further enhance the catalytic activities of Au_xNi_y catalysts for ORR.² Apparently, as shown in the Fig. S2[†], the improvements of ORR activities are observed in all the AuNi catalysts after dealloying. More interestingly, the Au₁Ni₂ catalyst deposited at -0.6 V vs. SCE still shows the most excellent catalytic activity after dealloying.



Fig. S1 ORR polarization curves of as-prepared Au_xNi_y catalysts recorded in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. (a) As-prepared Au_1Ni_2 catalysts deposited at different potentials: -0.5 V, -0.6 V, -0.7 V vs. SCE. (b) As-prepared Au_xNi_y catalysts deposited at -0.6 V vs. SCE with different initial concentrations of metallic precursor: 15 mM HAuCl₄ + 15 mM NiSO₄ (Au₁Ni₁), 15 mM HAuCl₄ + 30 mM NiSO₄ (Au₁Ni₂) and 15 mM HAuCl₄ + 45 mM NiSO₄ (Au₁Ni₃).



Fig. S2 ORR polarization curves of as-prepared (dashed line) and dealloyed (solid line) Au_xNi_y catalysts recorded in oxygen-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. (a) Au_1Ni_2 catalysts deposited at different potentials: -0.5 V, -0.6 V, -0.7 V vs. SCE. (b) Au_xNi_y catalysts deposited at -0.6 V vs. SCE with different initial concentrations of metallic precursor: 15 mM HAuCl₄ + 15 mM NiSO₄ (Au_1Ni_1), 15 mM HAuCl₄ + 30 mM NiSO₄ (Au_1Ni_2) and 15 mM HAuCl₄ + 45 mM NiSO₄ (Au_1Ni_3).



Fig. S3 SEM images of as-prepared Au₁Ni₂ catalysts at different deposition potentials: (a) -0.5 V, (c) -0.6 V, (e) -0.7 V vs. SCE, and Au_xNi_y catalysts deposited at -0.6 V vs. SCE with the various initial precursor solutions: (b) 15 mM HAuCl₄ + 15 mM NiSO₄ (Au₁Ni₁), (d) 15 mM HAuCl₄ + 30 mM NiSO₄ (Notably, image (d) shows the morphology of the dealloyed Au₁Ni₂), (f) 15 mM HAuCl₄ + 45 mM NiSO₄ (Au₁Ni₃).



Fig. S4 EDX profiles for the as-prepared Au_xNi_y catalysts at varied deposition potentials (a, c, e), and with different concentrations of metallic precursor (b, d, f). Notably, profile (d) gives the compositional information about the dealloyed Au_1Ni_2 catalyst deposited at -0.6 V vs SCE.

Supplementary results



Fig. S5 ORR curves (1600 rpm) for (a) dealloyed AuNi, (b) as-prepared AuNi, (c) commercial Pt/C and (d) pure Au catalysts obtained by performing the ORR measurements on separately prepared samples (from #1 to #4). Insets show the corresponding regional comparison in $E_{1/2}$. It can be seen that each sample provides a reproducible ORR curve under the same experimental conditions.



Fig. S6 The rotation-rate-dependent ORR polarization curves of (a) commercial Pt/C and (c) pure Au catalysts in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹. The Koutecky-Levich plots (j⁻¹ vs. $\omega^{-1/2}$) of (b) commercial Pt/C and (d) pure Au catalysts at different potentials.



Fig. S7 Electron transfer numbers of pure Au, commercial Pt/C, as-prepared AuNi and dealloyed AuNi catalysts at various potentials, the error bars are also included.



Fig. S8 The rotation-rate-dependent ORR polarization curves of the various Au_xNi_y catalysts in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹. The corresponding Koutecky-Levich plots (j⁻¹ vs. $\omega^{-1/2}$) of each electrocatalyst were also shown.



Fig. S9 TEM images of dealloyed AuNi catalyst (a) before and (b) after 5,000 potential cycles.

Samples of as- prepared Au _x Ni _y	Metal precursor HAuCl ₄ : NiSO ₄ (in mM)	Deposition potential (V vs. SCE)	E_{onset} (V vs. RHE) \pm SD	$E_{1/2}$ (V vs. RHE) ± SD	Diffusion- limiting current density (mA cm ⁻²) ± SD
Au ₁ Ni ₁	15:15	-0.6 V	0.93 ± 0.002	0.839 ± 0.001	4.14±0.015
Au_1Ni_2	15:30	-0.6 V	1.00 ± 0.002	0.869 ± 0.002	4.86±0.010
Au ₁ Ni ₃	15:45	-0.6 V	0.95 ± 0.003	0.852 ± 0.002	4.65 ± 0.020
Au_1Ni_2	15:30	-0.5 V	0.93 ± 0.002	0.843 ± 0.003	3.54 ± 0.026
Au_1Ni_2	15:30	-0.7 V	0.89 ± 0.003	0.647 ± 0.003	4.47±0.023

Table S1 Summary of the electrochemical analysis for as-prepared Au_xNi_y catalysts deposited at different parameters. Standard deviation (SD).

Table S2 Summary of the initial concentrations of metallic precursor (mM), applied electrodeposition potential (V vs. SCE), and gold and nickel atomic concentrations (at %) obtained by EDX analysis.

Samples of as-	Metal precursor HAuCl₄ : NiSO₄	Deposition potential	Composition of as-prepared Au _x Ni _y		
prepared Au _x Ni _y	(in mM)	(V vs. SCE)	Au (at %)	Ni (at %)	
Au ₁ Ni ₁	15:15	-0.6 V	97.56	2.44	
Au_1Ni_2	15:30	-0.6 V	86.25	13.75	
Au ₁ Ni ₃	15:45	-0.6 V	78.65	21.35	
Au_1Ni_2	15:30	-0.5 V	98.87	1.13	
Au_1Ni_2	15:30	-0.7 V	48.2	51.8	

Table S3 Comparison of the ORR activities of our best-performing AuNi catalysts with those of previously reported electrocatalysts. $\Delta E_{1/2}$ indicates the difference of half-wave potential ($E_{1/2}$) between the reported catalysts and the commercial Pt/C catalysts. The positive value represents the improvement in $E_{1/2}$ with respect to Pt/C, the minus value represents the opposite trend; SA: specific activity; IF: defined as the ratio of specific activity of the proposed catalyst divided by that of the identically synthesized commercial Pt/C, measured at the same voltage.

Catalyst	E _{onset} (V)	<i>E</i> _{1/2} (V)	$\frac{\Delta E_{1/2}}{(\mathrm{mV})}$	SA (mA cm ⁻ ²)	Measured at (V)	IF	Temp.	Electrolyte	Ref.
Dealloyed AuNi	1.030	0.896	67	0.500	0.80	2.8	RT	0.1 M KOH	this work
AuNi	1.000	0.869	40	0.430	0.80	2.4	RT	0.1 M KOH	this work
Au	0.900	0.810	-19	0.150	0.80	-	RT	0.1 M KOH	this work
Dealloyed AuNi@pTBA*	-	0.884	40	0.590	0.75	2.1	RT	0.1 M NaOH	3
AuNi@pTBA*	-	0.824	-20	0.290	0.75	1.0	RT	0.1 M NaOH	3
AuAg	0.917	-	-	-	-	-	RT	0.1 M NaOH	4
Au/rGO	-	0.610	-20	-	-	-	RT	0.1 M KOH	5
$Au_{0.9}Pd_{0.1}/C**$	0.958	0.858	-12	-	-	-	RT	0.1 M NaOH	6
Au _{0.8} Pd _{0.2} /C**	1.043	0.911	41	-	-	-	RT	0.1 M NaOH	6
Au _{0.7} Pd _{0.3} /C**	0.993	0.872	2	-	-	-	RT	0.1 M NaOH	6
Au(100)	0.960	0.800	-	-	-	-	RT	0.1 M KOH	7, 8
Au(110)	0.840	0.700	-	-	-	-	RT	0.1 M KOH	7, 8
Au(111)	0.840	0.670	-	-	-	-	RT	0.1 M KOH	7, 8
Dealloyed Pt ₆ Ni ₁	-	0.916	50	1.230	0.90	6.2	30°C	0.1 M HClO ₄	9
Dealloyed Pt ₁ Ni ₁	-	0.897	31	0.670	0.90	3.4	30°C	0.1 M HClO ₄	9
Dealloyed Pt ₁₅ Cu ₈₅	-	0.890	30	0.450	0.90	3.0	RT	0.1 M HClO ₄	10
Dealloyed PtFe ₅	-	-	-	0.383	0.90	2.3	25°C	0.1 M HClO ₄	11
Dealloyed PdCu	-	0.840	15	0.150	0.80	1.5	RT	0.1 M HClO ₄	12
Dealloyed PdNi	-	-	-	0.210	0.90	1.3	RT	0.1 M HClO ₄	13

All of the potentials in this table were referred to RHE. * represents that the V_{RHE} was converted from Ag/AgCl saturated KCl, $E_{vs. RHE} = E_{vs. Ag/AgCl} + 0.197 \text{ V} + 0.059 \times \text{PH}$. ** represents that the V_{RHE} was converted from saturated calomel electrode, $E_{vs. RHE} = E_{vs. SCE} + 0.241 \text{ V} + 0.059 \times \text{PH}$.

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