Supporting Information for:

**One-Step Electrochemical Dealloying of 3D bi-continuous Micro-nano Porous Bismuth Electrodes and CO2RR performance**

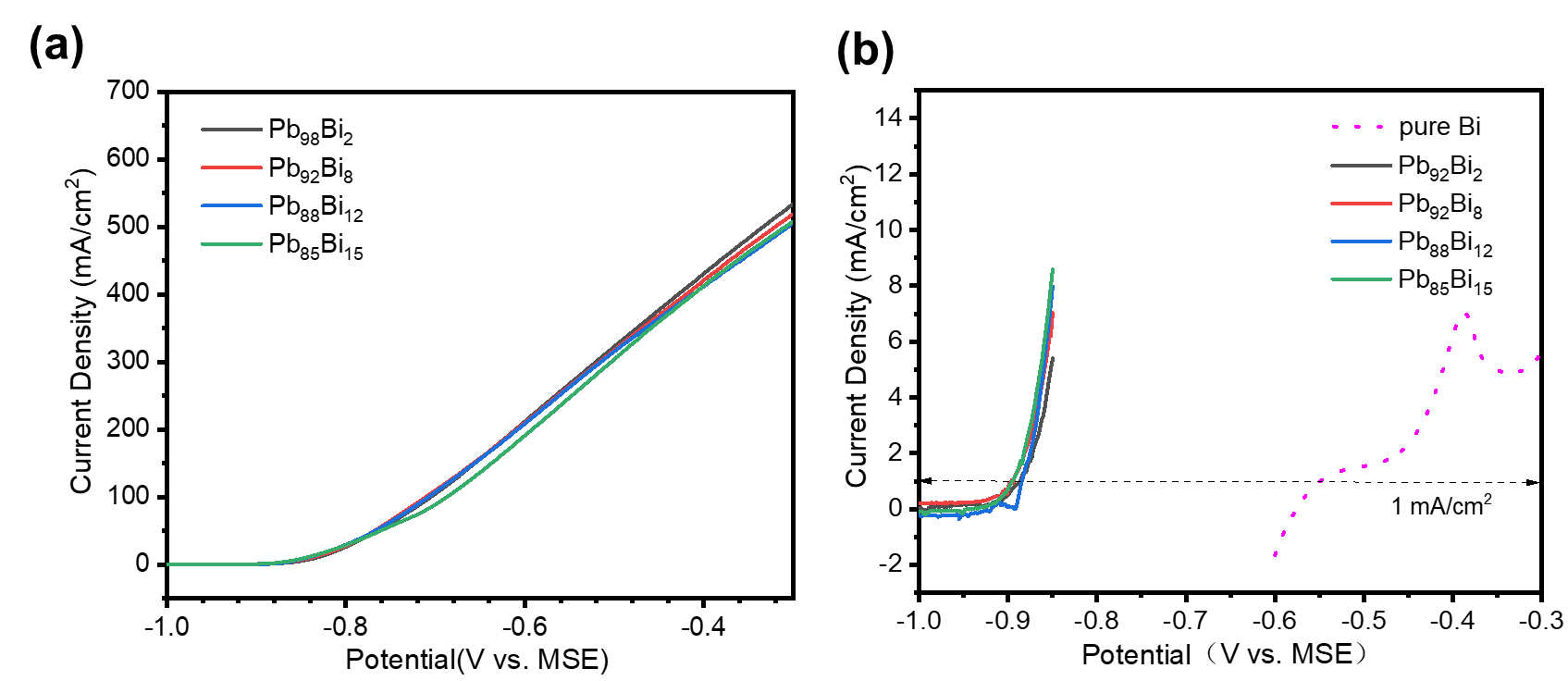
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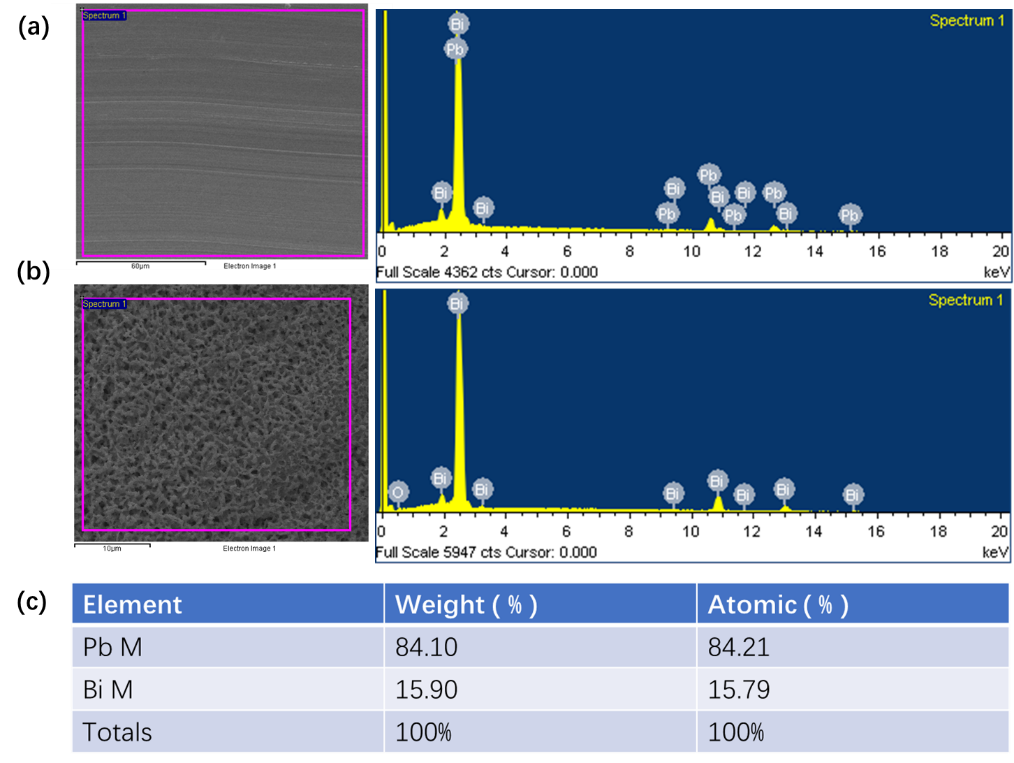
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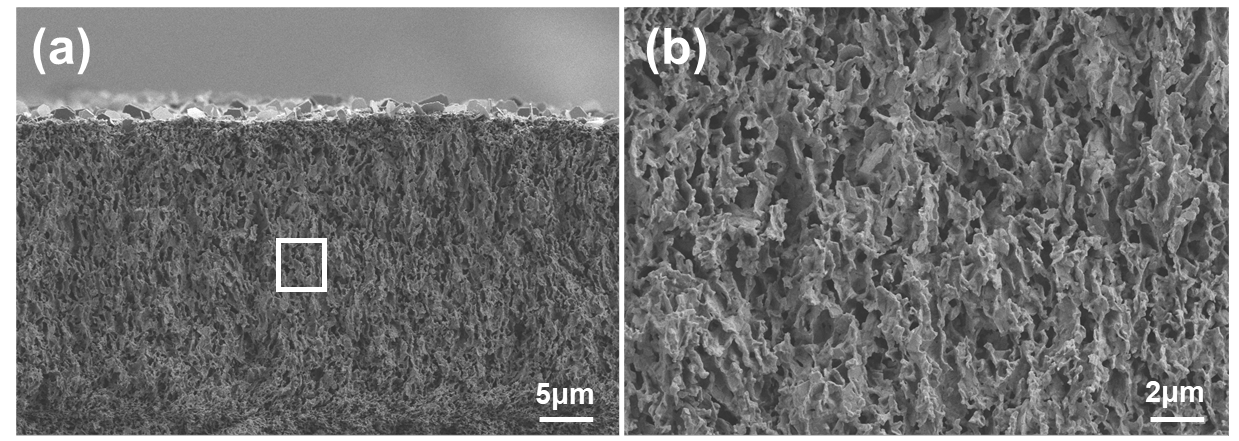
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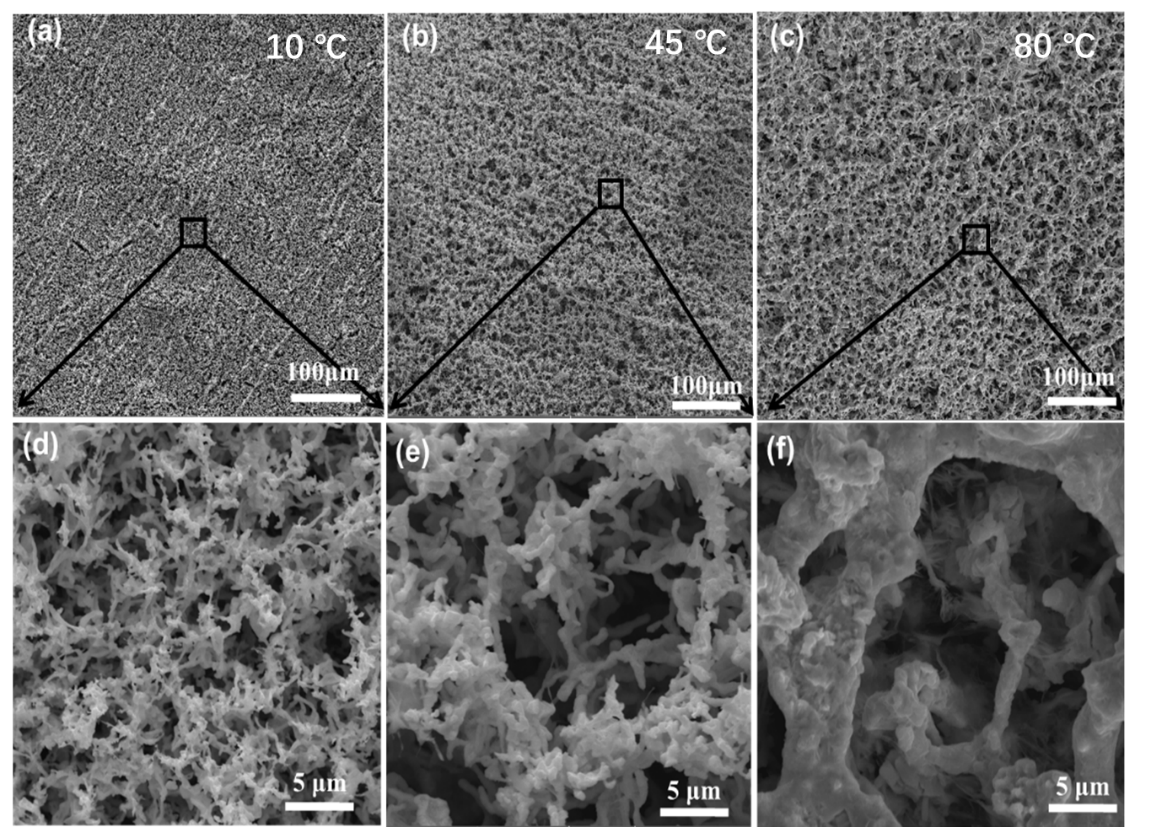
**Fig S1** (a)Linear sweep voltammetry curves of Pb98Bi2、Pb92Bi8、Pb88Bi12、Pb85Bi15 alloy in 0.5 M HNO3 aqueous solution at 25℃. The scan rate is 5.0 mV/s. (b) Comparison of details of Pb-Bi alloy and pure Bismuth sample in LSV curves.

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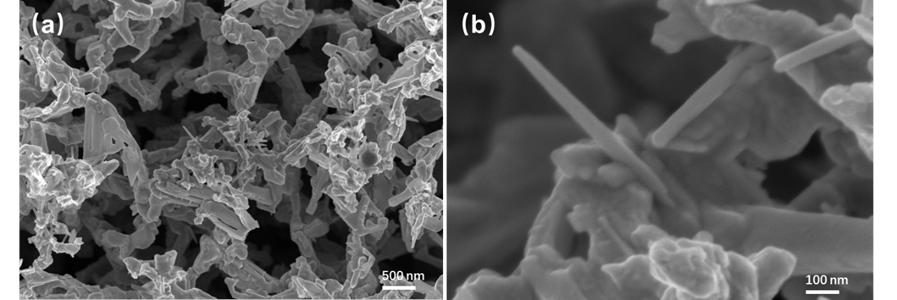
**Fig S2** EDS analyses of Pb98Bi15 alloy before (a) and after (b) and (c)element qualitative analysis. the potentiostatic dealloying with electric potential of -0.55 V vs. MSE in 0.5 M HNO3 aqueous solution at 10℃, 3600s.



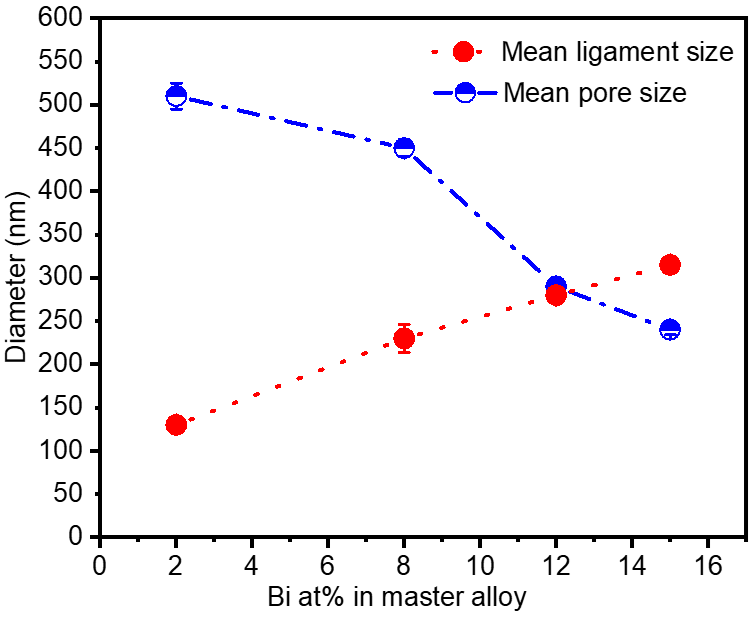
**Fig S3** (a,b)cross-section SEM images of np-Bi12 sample. dealloying with electric potential of -0.55 V vs. MSE in 0.5 M HNO3 aqueous solution at 10℃,1200s.

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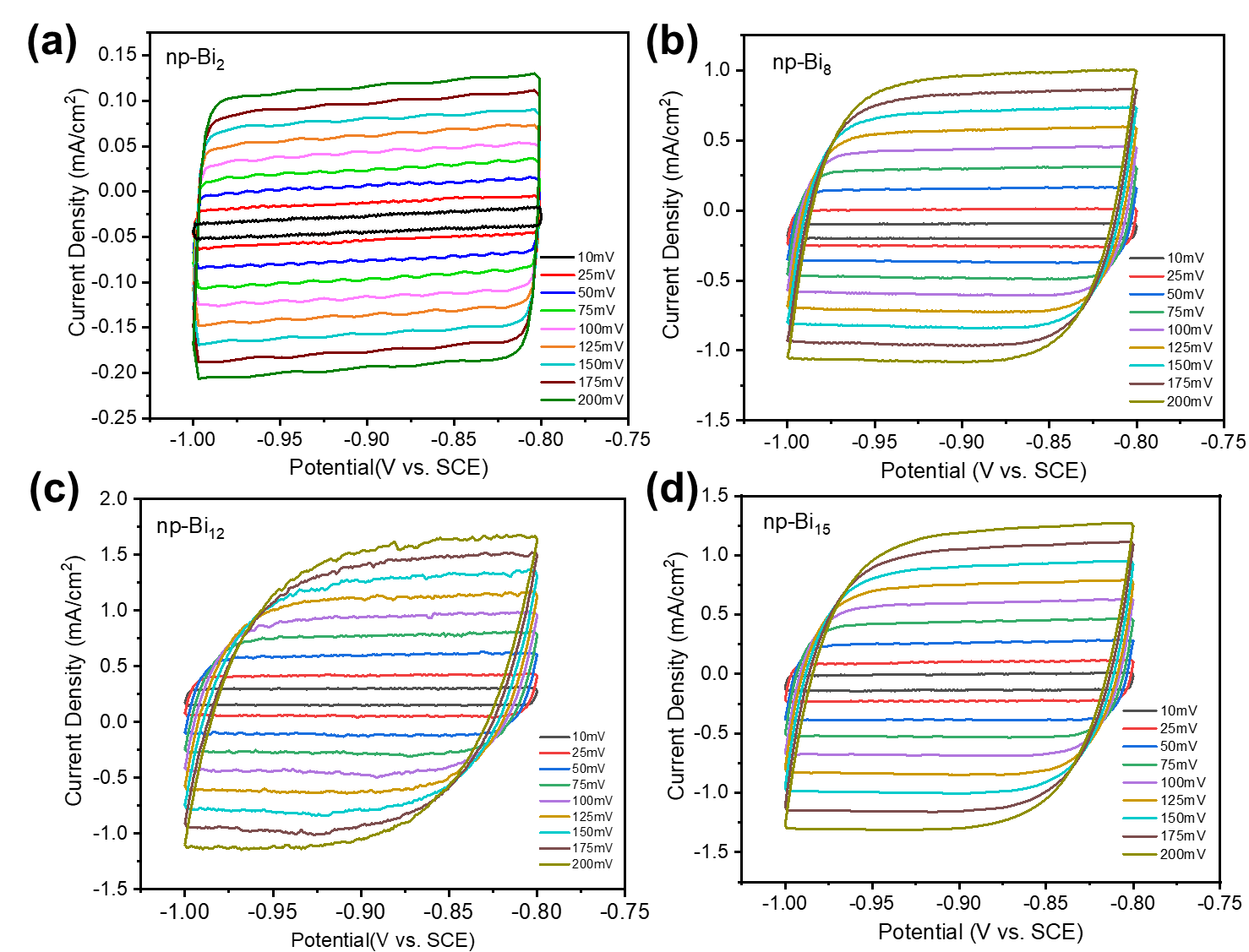
**Fig S4** Top-view SEM images of Pb98Bi2 alloy after the potentiostatic dealloying at 10℃ (a,d)、45℃ (b,e) and 80℃ (c,f).

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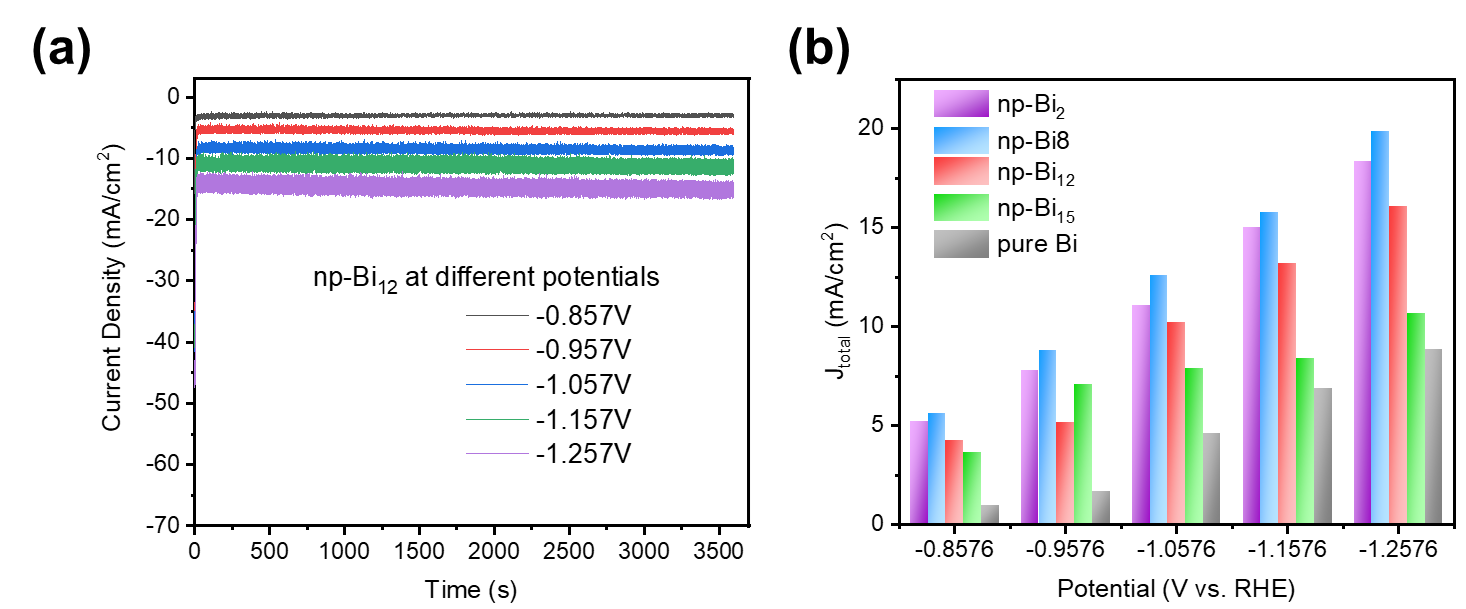
**Fig S5** High-resolution scanning electron micrograph of np-Bi2 sample.

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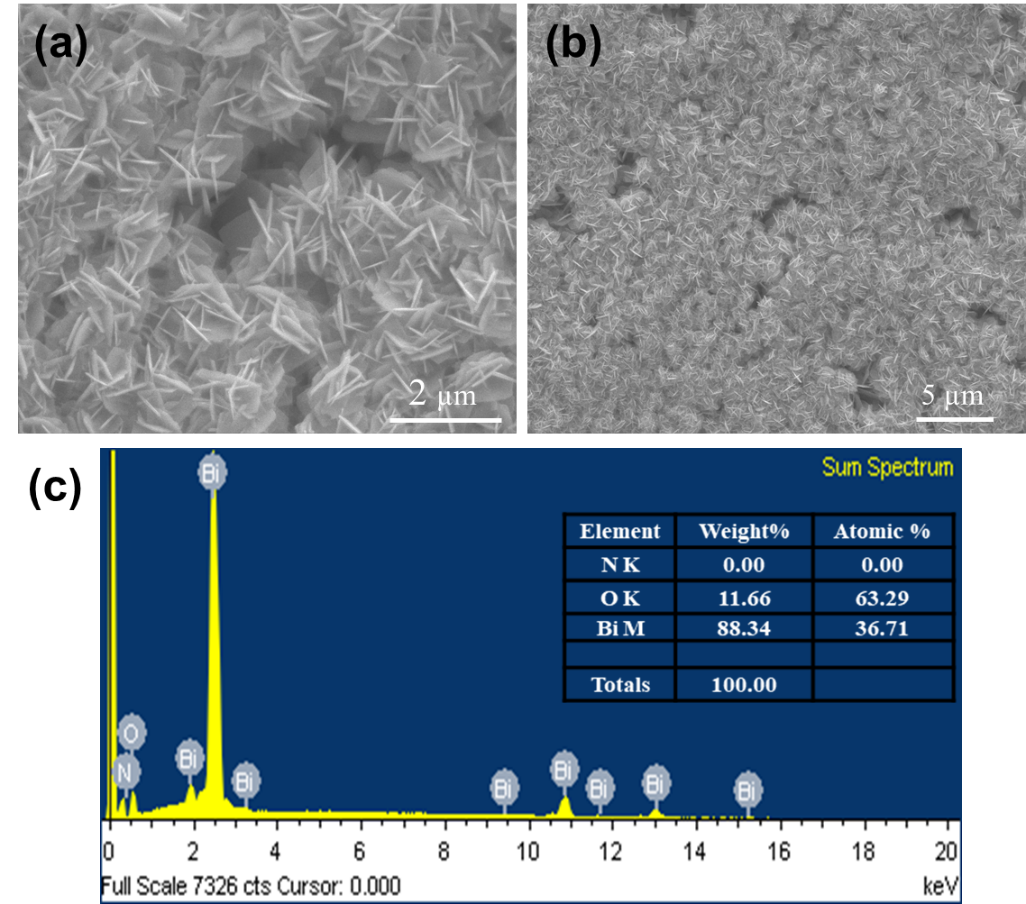
**Fig S6** Distribution diagram of the average pore size and ligament size of nano-porous Bi samples as a function of composition. Applied potential is -0.55 V vs. MSE. Electrolyte is 0.5 M HNO3 aqueous solution, dealloying temperature is 10℃.

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**Fig.S7** Cyclic voltammetry (CV) curves of （a）np-Bi2 , （b）np-Bi8，（c）np-Bi12,（d）np-Bi15 at different scanning speeds in a 0.1 M KHCO3 aqueous solution saturated with N2.

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**Fig S8** (a) Time-dependent current density curves of np-Bi12 at different potentials. (b) The calculated total current density (Jtotal) values of four nanoporous electrodes under 1hour electrochemical catalysis.

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**Fig S9** Low (a) and high (b) magnification SEM images of np-Bi12 electrodes after 24h of long-term electrolysis test. (c) EDS analysis of the oxidized np-Bi12 electrodes.

**Table S1** The relationship between the size of four nanoporous Bi samples with different morphologies and the Faraday efficiency of formic acid.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample Name | Mean pore size（nm） | Mean ligament size（nm） | FEHCOOH（%） |
| Bi2-10 | **510** | **130** | **76.7** |
| Bi8-10 | **450** | **230** | **74.5** |
| Bi12-10 | **290** | **280** | **92.2** |
| Bi15-10 | **240** | **315** | **88.8** |