Macro-/micro-coupling regulation of nanoporous metals *via* vapor phase alloying-dealloying

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ABSTRACT Nanoporous metals with bicontinuous ligament-channel structure are of great importance in catalysis, electro-catalysis, actuation and energy storage and conversion. However, the intrinsic brittleness of nanoporous metals has always been the “Achilles heel” that impedes their practical applications. Utilizing the vapor pressure difference of metals, herein we propose a flexible and general vapor phase alloying (VPA)-dealloying strategy to fabricate nanoporous layers supported on the substrates with the same element. By adjusting the VPA time and temperature, the thickness and microstructure control over nanoporous layers can be realized by combining with diverse dealloying methods. Besides, various metals including Ag, Au, Cu, Co and Ni with different macro sizes and shapes can be fabricated into nanoporous structures through this method. More importantly, the greatly improved tensile ductility owing to the nanoporous layer-substrate structure and well enhanced catalytic performance for hydrogen evolution reaction of the as-fabricated nanoporous metals signify great potentials of the VPA-dealloying strategy for practical applications.

Keywords: nanoporous metals, vapor phase alloying-dealloying, macro and micro regulation of nanostructure, dealloying mechanism, mechanical properties

INTRODUCTION

Nanoporous metals have recently aroused great interests because they not only maintain the features of bulk metals such as excellent thermal/electrical conductivity but also gain numerous intriguing properties of nanostructures including large specific surface area, novel size effect, fast mass transport, highly efficient catalytic activity and significantly enhanced kinetics [1,2]. Numerous nanoporous metals such as Au, Pd, Pt, Ag, Cu, Co, Ni [3–11] and their alloys [12–16] have been fabricated by dealloying and show tremendous potentials in electrocatalysis [17–19],

actuation [20,21], surface-enhanced Raman scattering [22], supercapacitors [23] and energy storage and conversion [24]. Dealloying is an important route to fabricate nanoporous metals, which involves the selective dissolution of non-noble element(s) and diffusion/re-organization of noble metal atoms. Several dealloying methods have been developed, including conventional chemical/electrochemical dealloying [3,25–28], liquid metal dealloying [29–31], electrolytic dealloying in non-aqueous electrolytes [23,32] and vapor phase dealloying (VPD) [5,33]. These dealloying techniques are all effective and have their respective advantages, which extend the range of nanoporous metals from noble metals to transition metals and even refractory metals.

Freestanding nanoporous metals always show no tensile plasticity and cannot be bent flexibly [34,35]. Consequently, the intrinsic brittleness becomes the “Achilles heel” of nanoporous metals that enormously impedes their structural and functional applications, and thus improving the ductility of nanoporous metals becomes an enormous challenge and central science issue [36,37]. To address this issue, a strategy was proposed by Wang and Weissmüller [38] to impregnate the nanoporous metal with a polymer, which indeed improved the ductility of nanoporous gold as manifested by three-point bending. Unfortunately, this approach was also accompanied with the partial loss of structural and functional properties of nanoporous metals. It is worth noting that in a film-substrate system, a polymer substrate (for example, polyimide) can significantly improve the ductility of metal films which have good adhesion with the substrate by delocalizing deformation in the film [39]. Moreover, through enhancing the adhesion between the film and substrate, adhesion layers could further retard the strain localization and the metal films on polymer substrates could be stretched beyond 50% [40]. When directly ap-

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plied to gradient nano-grained films, the above principle remarkably improves the yield strength and tensile ductility of nano-grained metal that is intrinsically brittle [41]. Taking advantage of the ductility enhancement principle of the film-substrate system, formation of a nanoporous layer on a ductile metal substrate will be a feasible solution to solve the intrinsic brittleness issue of nanoporous metals. However, under the precondition of ensuring the strong interfacial adhesion, it remains a great challenge to fabricate the nanoporous layer on the surface of the metal substrate and realize the thickness control of the nanoporous layer simultaneously.

In this work, utilizing the vapor pressure difference of metals, we developed a vapor phase alloying (VPA)-dealloying strategy to fabricate nanoporous metals, during which the precursors were synthesized at the saturated vapor of the metals with low evaporation temperatures (here, Zn). Because of the great flowability and reactivity of metallic vapor, the thickness and microstructure control over nanoporous layers with arbitrary shapes supported on the metal substrates can be realized combining with diverse dealloying methods. The same element of nanoporous layer and substrate can guarantee the strong interfacial adhesion and good modulus match, which are two key factors to achieve the constraint of the substrate to the nanoporous layer and improve the ductility of nanoporous metals. In addition, the VPA-dealloying strategy is a flexible and universal method to fabricate nanoporous metals with different macro sizes and shapes. More importantly, the good tensile mechanical properties and the greatly enhanced catalytic activity of the obtained nanoporous metals manifest their potentials in practical applications.

EXPERIMENTAL SECTION

Sample preparation

To realize surface alloying of metals, Zn powder (purity: 99.9 wt%) was chosen as the sacrificing metal because of its lower evaporation temperature than those of most metals and earth abundance. Before the VPA, commercial Ag foil (purity: 99.99 wt%; thickness: 50 or 200 μm), Co foil (purity: 99.99 wt%; thickness: 200 μm), Ni foil (purity: 99.99 wt%; thickness: 100 μm), Cu foil (purity: 99.99 wt%; thickness: 200 μm), Ag wire (purity: 99.99 wt%; diameter: 200 μm), Ag bulk (purity: 99.99 wt%; size: $5 \times 5 \times 2 \text{ mm}^3$), Au wire (purity: 99.99 wt%; diameter: 50 μm) and Ni foam (purity: 99.9 wt%) were rinsed by acetone, alcohol and dried in vacuum to remove the contamination on the surface. Here the fabrication of Ag-Zn surface

alloys was chosen as an example to illustrate the VPA process. The Zn powder with a mass of 1 g was first put into the bottom of a quartz tube to make sure the Zn powder was sufficient for the VPA process and Ag foil was fixed at the middle of the quartz tube without directly touching with Zn powder. Then, the quartz tube was purged by Ar and pumped to vacuum repeatedly for at least 5 times, and sealed by hydrogen flame. Finally, the quartz tube was heated in a resistance furnace at a series of temperatures for different times to proceed the VPA.

To obtain nanoporous metals, various dealloying methods were adopted. Electrochemical dealloying was performed in a $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution on a CHI760E potentiostat in a standard three-electrode cell at ambient temperature. Saturated calomel electrode (SCE), graphite rod and precursor alloys served as the reference electrode, counter electrode and working electrode, respectively. Before electrochemical dealloying, linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s^{-1} to determine the dealloying potential. Then the potentiostatic dealloying was performed until the current density decreased abruptly. Nanoporous metals were also obtained by chemical dealloying or VPD. The detailed dealloying procedures are given in the Supplementary information.

Microstructural characterization

X-ray diffraction (XRD) measurements of all samples were performed on an XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) with $\text{Cu K}\alpha$ radiation. The microstructures and chemical compositions were characterized by a scanning electron microscope (SEM, ZEISS SIGMA300) equipped with an energy dispersive X-ray (EDX) analyzer. The ligament size of nanoporous metals was evaluated using the Nano Measure software by manually measuring at least 200 ligaments in SEM images. In addition, a home-made sample holder with flowing corrosion solutions was adopted for *in-situ* XRD of dealloying.

Mechanical and electrocatalytic measurements

The hardness and elastic modulus of nanoporous Ag were tested by the TriboIndenter (TI980) with a calibrated Berkovich diamond tip. During the experiments, the loading rate was set as $200 \mu\text{N s}^{-1}$ and the maximum load was $1000 \mu\text{N}$. And the holding time and loading/unloading time were 2 and 5 s, respectively. The distance between indents was at least three times larger than the size of indents. For each sample, at least three load-displacement curves were repeatedly conducted to ensure

the accuracy of data. The tensile tests were performed on an electronic universal testing machine (CMT6103) at a constant strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. For hydrogen evolution reaction (HER), LSV was recorded in a N_2 -saturated 1 mol L^{-1} KOH solution in the three-electrode cell with pristine Ni foam or nanoporous Ni foam as the working electrode at a scan rate of 5 mV s^{-1} . An Ag/AgCl electrode (in a saturated KCl solution) and graphite rod were used as the reference electrode and counter electrode, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic illustration for the fabrication processes of nanoporous metals through the VPA-dealloying strategy. In a vacuum environment, when heated to the temperature above the evaporation temperature of N-metal while below M-metal, the N-metal will transform to vapor while the M-metal can keep stable. As a result, an alloy layer forms on the M-metal surface because of the gas-solid reaction induced by the diffusion between the two kinds of metals. Noticeably, the shape of

M-metal is flexible and not only limited to foils. The thicknesses and phase compositions of the alloy layer can be controlled by adjusting the temperature and time of VPA. After alloying, chemical or electrochemical dealloying can be conducted to obtain nanoporous M utilizing the difference of chemical/electrochemical activity of metals. For some refractory metals or transition metals that are prone to be oxidized, nanoporous M can also be fabricated by VPD. Eventually, the nanoporous layers supported on the metal substrates with different shapes such as foil, wire, bulk and even foam can be obtained after the VPA-dealloying processes. From the perspective of improving mechanical properties (especially ductility) of nanoporous metals, this strategy could guarantee good modulus match between the nanoporous layer and substrate (the same metal) and nice interfacial adhesion (*in-situ* surface alloying-dealloying).

In order to explore the growth mechanism of the alloy layer during VPA, we take the Ag-Zn system as an example due to the following reasons. First, because of the large difference in saturated vapor pressures of Zn and Ag

Figure 1 The schematic illustration showing the fabrication strategy of nanoporous metals supported on the metal substrates by the combination of VPA with subsequent dealloying.

Figure 2 (a) The temperature dependence of the saturated vapor pressures of Zn and Ag. (b) The typical XRD pattern of the AgZn alloy layer after VPA at 923 K for 15 min. (c) The optical microscope photograph of the alloy layer after VPA at 923 K for 15 min. (d) SEM image of the cross-section and the line-scan result of the sample corresponding to (c). (e) Plot of $\ln \Delta x$ versus $\ln t$ for VPA at different temperatures. (f) Plot of $\ln k$ versus the reciprocal temperature to determine the activation energy for the AgZn layer growth.

(Fig. 2a) [42], there is a wide temperature range and vacuum condition where Zn powder can be sublimated into vapor while Ag foil is stable and keeps its original shape. Second, the interface between the alloy layer and pristine Ag substrate is optically evident so that the thickness of the alloy layer can be measured by optical microscopy [43]. Third, nanoporous Ag is an ideal catalyst for various energy conversion reactions after dealloying [44–46]. Here, the Ag foil with a thickness of 200 μm was chosen as the substrate for VPA. Consistent with the Ag–Zn phase diagram (Fig. S1) [47], the typical pattern in Fig. 2b illustrates the AgZn phase (PDF # 29-1156) first forms on the surface of the Ag foil at the early stage of VPA. After

VPA at 923 K for 15 min, the thickness of the AgZn layer is $104 \pm 8 \mu\text{m}$, and there is a fairly obvious interface between the alloy layer and the Ag substrate (Fig. 2c). The SEM image and the line-scan result in Fig. 2d further illustrate that the Zn and Ag contents show an abrupt variation in the interfacial zone, but keep stable in the AgZn alloy layer. With the VPA time extending to 30, 35 and 45 min, the thicknesses of the alloy layers increase to 156 ± 9 , 222 ± 12 and $343 \pm 12 \mu\text{m}$, respectively (Fig. S2a). Moreover, the contents of Zn and Ag are constant throughout the whole cross-section of the as-alloyed sample after VPA for 45 min (Fig. S2b). The present results demonstrate that AgZn is the single alloy

phase at the early stage of VPA and only after the whole Ag foil transforms to AgZn, other alloy phases with higher Zn content such as Ag₅Zn₈ or AgZn₃ can appear. For further analyzing the rule of thickness variation, the VPA between the Ag foil and Zn powder was conducted at the lower temperatures of 773, 823 and 873 K. As shown in Fig. S3, the thicknesses of AgZn layers increase with the extension of time at 773 K. Nevertheless, the growth rate of the alloy layer is much slower than that at 923 K, and more than 16 h is necessary for the Ag foil to completely react with the Zn vapor to form AgZn. This scenario matches well with the Fick's law of diffusion and illustrates that the thickness of alloy layer can be facily modulated by optimizing the VPA temperature and time.

It is known that the relationship between the thickness of reaction layer (Δx) and diffusion time (t) can be described by the following equations [48,49]:

$$\Delta x = kt^n, \quad (1)$$

$$\ln \Delta x = n \ln t + \ln k, \quad (2)$$

where k is the rate constant and n is the kinetic exponent. The average thickness variations of AgZn layers at 773 and 923 K were measured and summarized in Tables S1 and S2. Clearly, a good linear relationship between $\ln \Delta x$ and $\ln t$ can be obtained at different alloying temperatures in Fig. 2e. The n values were calculated to be 1.01 and 1.02 at 773 and 923 K, respectively. The growth mechanisms of intermetallic compounds can be classified into two types, reaction-controlled ($n = 1$) and diffusion-controlled ($n = 0.5$) [50–52]. Therefore, the growth of AgZn layer is governed by the reaction-controlled mechanism. This result is consistent with the reaction-controlled process of Ti–Al system [50,52], but different from the diffusion-controlled formation of intermetallic compounds in the Ag–Zn couple at 573–623 K [43]. The activation energy (Q) for the reaction-controlled growth process can be assumed to follow an Arrhenius relation at different temperatures (T),

$$k = k_0 \exp\left(-\frac{Q}{RT}\right), \quad (3)$$

$$\ln k = \ln k_0 - \frac{Q}{RT}, \quad (4)$$

where k_0 is a temperature-independent constant, and R is the gas constant. The values of $\ln k$ and T are listed in Table S3. According to Equation (4), $\ln k$ is plotted *versus* reciprocal temperature in Fig. 2f, which follows a good linear correlation. The slope of the line represents $-Q/R$, so the activation energy was calculated as 124.8 kJ mol^{−1}, which is much higher than 58.1 kJ mol^{−1} in the Ag–Zn system for a diffusion-controlled process at temperatures

between 573 and 623 K [43]. The different growth mechanisms (reaction-controlled *versus* diffusion-controlled) and reaction types (vapor-solid *versus* solid-solid) account for the discrepancy in the activation energy.

As mentioned above, the thickness of Ag–Zn alloy layer can be controlled by modulating the VPA time and/or temperature. Thus, nanoporous Ag supported on the Ag substrate can be fabricated by dealloying the Ag–Zn layer, and its thickness could be effectively regulated (Fig. 3). With prolonging VPA time, the thickness of the porous Ag layer increases (Fig. 3a–f). Furthermore, the nanoporous structure runs across the entire section of the foil for the VPA time of 16 h (Fig. 3c). The XRD and EDX results in Fig. S4 illustrate that almost all Zn atoms in the AgZn layer were leached away. The thickness of the nanoporous layer is about 75, 120 and 280 μm at 773 K for the VPA time of 4, 9 and 16 h, respectively, corresponding well with that of the alloy layer in Fig. S3. Additionally, the average ligament size of nanoporous Ag is determined to be 0.56 ± 0.12 μm for the VPA time of 4 h (Fig. 3d, g), but decreases to 0.36 ± 0.08 and 0.30 ± 0.06 μm with the VPA time prolonging to 9 and 16 h, respectively (Fig. 3h, i). Notably, the nanoporous structure becomes more open and uniform with increasing VPA time, which is probably associated with the higher Zn content in the alloy layer for the longer VPA time owing to the non-stoichiometric nature of AgZn phase (Fig. S1).

According to the phase diagram (Fig. S1), several intermetallic compounds (β–AgZn, γ–Ag₅Zn₈, and ε–AgZn₃) exist in the Ag–Zn system. The Ag foils (50 μm in thickness) were used to investigate the VPA-induced phase evolution in the Ag–Zn system. Only the AgZn phase can be identified after VPA for 4 and 9 h at 773 K (Fig. S5). Ag₅Zn₈ and AgZn₃ appear in turn after prolonging the alloying time to 16 and 25 h, which suggests that the phase compositions can be precisely controlled by modulating the VPA time. Nanoporous Ag foils were thus obtained by potentiostatic dealloying of these Ag–Zn precursors with different phase compositions (Fig. 4a–c, Figs S6a and S7). For the nanoporous Ag dealloyed from AgZn, the ligaments show good connection, but the connecting degree of ligaments decreases with increasing Zn content in the Ag–Zn precursors. And loose connection is observed in the sample dealloyed from AgZn₃ (Fig. 4c). Accordingly, the porosity in nanoporous Ag obviously improves with the increase of Zn in the Ag–Zn precursors (Fig. S7). Fig. S6b and Fig. 4d–f show the size distributions of ligaments in the obtained nanoporous Ag, and the average ligament size shows a

Figure 3 Cross-sectional SEM images showing the microstructures of nanoporous Ag fabricated through potentiostatic dealloying of the AgZn alloy phase at 773 K for different VPA times of (a, d) 4, (b, e) 9 and (c, f) 16 h (the pristine thickness of Ag foil is 200 μm). The columnar plots in (g, h and i) show the characteristic length scales of nanoporous Ag corresponding to (d, e, and f), respectively.

downtrend with the phase evolution in the Ag-Zn precursors (Fig. 4g). In addition, the typical XRD pattern verifies that the as-dealloyed sample is composed of the single face-centered cubic (fcc) Ag phase, and the obtained nanoporous Ag foil maintains a good self-supporting property (Fig. 4h and inset). Through the VPA-directed phase engineering in the Ag-Zn system, the microstructures of nanoporous Ag including the connecting degree of ligaments, the porosity and the average ligament size could be effectively regulated, which are crucial factors influencing mechanical properties of nanoporous metals [37,53,54].

Thanks to the effect of temperature and time on VPA, we also synthesized the AgZn_3 precursors from the Ag foil of 50 μm in thickness at different temperatures (773 K for 25 h, 823 K for 16 h, 873 K for 4 h and 923 K for 50 min), Fig. 4i. After potentiostatic dealloying, the obtained nanoporous Ag foils exhibit a similar bicontinuous ligament-channel structure (Fig. S8). Fig. 4i shows the average ligament size of these nanoporous Ag foils, as well as the temperature dependence of VPA time to form

AgZn_3 . As temperature increases, the VPA time to obtain AgZn_3 gradually decreases owing to the accelerating diffusion of both Ag and Zn at higher temperatures. The average ligament size is 0.15 ± 0.03 , 0.14 ± 0.02 , 0.20 ± 0.04 and 0.21 ± 0.04 μm for nanoporous Ag fabricated by dealloying of the AgZn_3 precursors obtained at 773, 823, 873 and 923 K, respectively, which shows a slight change with the VPA temperature. Obviously, VPA at higher temperatures could lead to rapid formation of desired precursors, without sacrificing the large porosity and small ligaments of the nanoporous structure after dealloying.

In-situ XRD was further conducted to explore the dealloying mechanism and the chemical dealloying of AgZn_3 at a constant flow of 4 mol L^{-1} HNO_3 was taken as an example (Fig. 5a, b). Before the dealloying, all the peaks are well indexed to AgZn_3 . At the early stage of dealloying, the peak intensity of AgZn_3 weakens as time increases, without other peaks being observed. While after 200 min, the peaks of Ag located at 38.12° , 44.28° , 64.43° , 77.47° and 81.54° appear and strengthen con-

Figure 4 Cross-sectional SEM images showing the microstructures of nanoporous Ag fabricated by potentiostatic dealloying of the AgZn, Ag₅Zn₈ and AgZn₃ precursors obtained through VPA at 773 K for (a) 9, (b) 16 and (c) 25 h (the pristine thickness of Ag foil is 50 μm). (Inset of a) Corresponding low-magnification SEM image. (d–f) The characteristic length scales of nanoporous Ag corresponding to (a–c), respectively. (g) The average ligament size *versus* the VPA time/alloy phases. (h) The typical XRD pattern of nanoporous Ag dealloyed from AgZn precursor after VPA for 4 h at 773 K. (Inset of h) Optical photograph of the nanoporous Ag foil. (i) The VPA time needed to form AgZn₃ at different temperatures and the corresponding average ligament size of nanoporous Ag after dealloying.

stantly, which are accompanied by gradually decreasing and vanishing AgZn₃ peaks. Eventually, only the Ag peaks can be detected, indicating the absolute dissolution of Zn atoms and formation of nanoporous Ag. Noticeably, the transformation from AgZn₃ to Ag is straightforward without the occurrence of other phases such as Ag₅Zn₈, AgZn or Ag(Zn) whose compositions are within the range of Ag and AgZn₃. Furthermore, the peak positions of Ag (220) and AgZn₃ (110) almost keep invariable during the whole dealloying process (Fig. 5c), which robustly supports no solid solution forming.

In order to reveal the ligament coarsening mechanism, AgZn₃ foil was immersed in 4 mol L⁻¹ HNO₃ for different times under free corrosion condition at room temperature. The morphologies of nanoporous Ag show little variation but the ligaments coarsen obviously with increasing dealloying time (Fig. S9). Similar to the iso-

thermal grain growth in polycrystalline materials, the relationship between the average ligament size and dealloying time can be described as follows [5,55,56]:

$$d(\tau)^{n'} = k_0' \tau \exp\left(-\frac{Q'}{RT}\right) = K\tau D_s, \quad (5)$$

$$D_s = D_0 \exp\left(-\frac{Q'}{RT}\right), \quad (6)$$

where $d(\tau)$ is the average ligament size at time τ , D_s is the diffusivity, k_0' , K and D_0 are constants, R is the gas constant, T is the dealloying temperature, and Q' is the activation energy. n' is the coarsening component and related to the mechanism that dominates the coarsening process. A value of $n' = 3$ standards for bulk diffusion while $n' = 4$ signifies surface diffusion. The relationship between $\ln[d(\tau)]$ and $\ln\tau$ is plotted in Fig. 5d, and the coarsening exponent is calculated to be about 4 according

Figure 5 (a) Contour plot and (b) line plot of the *in-situ* XRD results revealing the chemical dealloying process of AgZn₃ from the Ag foil of 50 μm (VPA at 773 K for 25 h) at a constant flow of 4 mol L⁻¹ HNO₃. (c) The relationship between the peak positions and the dealloying time of Ag (220) and AgZn₃ (110). (d) The average ligament sizes of nanoporous Ag *versus* the dealloying time in a logarithmic scale. (e) The SEM image of the interfacial zone of nanoporous Ag and AgZn₃ alloy and the line-scan results after chemical dealloying of AgZn₃ alloy in 4 mol L⁻¹ HNO₃ after 100 min. (f) Schematic illustration of the dealloying process.

to the slope of the fitting line (0.25), which implies that surface diffusion plays a leading role in the dealloying process [7,57]. Additionally, the line-scan results reveal that on the boundary between the undealloyed alloy and nanoporous layer, the contents of Ag and Zn show an abrupt variation within a small distance of 1 μm (Fig. 5e and Fig. S10), illustrating that the dissolution of Zn is restricted in a small range and the dealloying proceeds

almost layer by layer.

Based on the above results and analyses, the dealloying mechanism can be summarized as follows (Fig. 5f). During the early stage of dealloying, the active Zn atoms dissolve from the surface of the alloy and leave many vacancies dispersed, and thus Ag atoms that remain at the low-coordination sites will diffuse and aggregate toward more stable sites to form islands to minimize the inter-

facial energy [58]. As the dealloying proceeds, Zn atoms dissolve constantly from AgZn_3 with the electrolyte penetrating the pores and attacking the next layer. During this process, the remaining Ag atoms agglomerate and rearrange to form nanoporous structure simultaneously, leaving an obvious boundary to distinguish the nanoporous Ag and the AgZn_3 alloy. Particularly, the ligaments on the top layer have already coarsened with increasing dealloying time, compared with the newly formed ligaments at the boundary. Finally, nanoporous Ag with a bicontinuous ligament-channel structure forms. Movie S1 vividly illustrates the whole dealloying process.

Taking advantage of the large vapor pressure difference between Zn and other metals such as Ni, Co, Cu and Au (Fig. S11) [42], the VPA-dealloying strategy can also be utilized to synthesize a series of nanoporous metals and offers the ability to work with irregular shaped surfaces. As for Ni, $\text{Ni}_2\text{Zn}_{11}$ (PDF # 65-5310) forms on the surface of the pristine Ni foil after VPA for 4 h with slight surface change (Fig. 6a, b). After VPD, only the Ni phase (PDF # 65-0380) can be identified and almost no Zn is left in the as-dealloyed sample (Fig. 6c and Fig. S12c). The SEM images in Fig. 6d, Fig. S12a and b demonstrate the formation of nanoporous Ni with an average ligament size of $0.30 \pm 0.06 \mu\text{m}$. Through a similar VPA-VPD procedure, the foil-supported nanoporous Co was successfully fabricated (Fig. 6e and Fig. S13). In addition, nanoporous Cu with an average ligament size of 100 nm was obtained through chemical dealloying of the Cu foil-supported CuZn layer formed by VPA (Fig. 6f and Fig. S14). Besides foils, metallic wires are also suitable for VPA. Here, Ag and Au wires with different diameters were subjected to VPA. After dealloying, nanoporous Ag and Au wires with distinct length scales were obtained (Fig. 6g, h, Figs S15 and S16), which further reveals the flexibility of the present strategy. Apparently, by tuning the VPA temperature and time to control the thickness of the alloy layer, self-supporting and flexible nanoporous metal wires can be acquired after dealloying. Bulk nanoporous metals show great potentials in actuation [59,60] and are also model materials to explore mechanical properties of three-dimensional porous materials [61]. Notably, bulk porous Ag can be fabricated by the VPA-dealloying strategy, with a homogeneous ligament-channel structure throughout the entire section (Fig. 6i and Fig. S17).

Because metal vapor can permeate into any space, the VPA-dealloying strategy is applicable to metals with more complicated and irregular shapes like foams. Ni foam is a kind of technologically important engineering material

(Fig. S18), and has extensive applications in electrocatalysis and batteries [62,63]. After the VPA-dealloying treatment, nanoporous structure is formed on the surface of skeletons of Ni foam (Fig. 6j–l). Encouragingly, the integrity of Ni foam can be maintained without collapsing, which signifies its potential for practical applications. As summarized in Fig. 6m, various metals (Ag, Au, Cu, Co and Ni) with kinds of shapes (foils, wires, bulks and even foams) and different macro sizes (from $50 \mu\text{m}$ of Au wire to 2 mm of Ag bulk) can be manufactured into nanoporous structures through the VPA-dealloying strategy. The insets are corresponding photographs, demonstrating their good self-supporting characteristics. More importantly, the microscopic length scale of nanoporous metals can be well regulated with a range from tens of nanometer to submicron. All these examples convincingly manifest the feasibility and generalizability of the VPA-dealloying strategy, which paves a new way to fabricate the nanoporous structure supported on the metal substrate.

To better show the potential applications of above nanoporous metals, mechanical and electrocatalytic properties were also investigated. Fig. 7a shows the load-displacement curves of nanoporous and pristine Ag foils through nanoindentation tests. Compared with the pristine Ag foil, the shift toward higher displacement of nanoporous Ag indicates its strength degradation. The hardness of nanoporous Ag decreases to 0.63 GPa (Fig. 7b) compared with the pristine Ag foil (0.96 GPa), which is consistent with previous reports for nanoporous metals such as Au [64,65]. Moreover, the elastic modulus of nanoporous Ag (42 GPa) is about half of that of the pristine Ag foil (83 GPa), indicating its good elastic match which is a key parameter controlling the confinement from the substrate for ‘film-substrate’ materials [39–41]. It is known that freestanding nanoporous metals almost show no tensile ductility [34,35]. Surprisingly, the substrate-supported nanoporous Ag samples could be subjected to tensile tests and show noticeable ductility (Fig. 7c, d). The substrate-supported Ag with a nanoporous layer of $15 \mu\text{m}$ exhibits an average elongation of $59.6\% \pm 3.5\%$, comparable to that of pristine Ag foil ($64.3\% \pm 6.5\%$), implying that the nanoporous layer could synergistically deform with the substrate. With increasing nanoporous layer thickness, the elongation of the substrate-supported nanoporous Ag obviously decreases. However, the elongation could reach up to $16.1\% \pm 3.8\%$ even for the Ag foil with the nanoporous layer of $120 \mu\text{m}$. Moreover, the substrate-supported Ag with nanoporous layers of different thicknesses can be bent freely and re-

Figure 6 (a–c) XRD patterns of pristine Ni foil, $\text{Ni}_{11}\text{Zn}_{11}$ alloy foil after VPA at 773 K for 4 h and nanoporous Ni foil after VPD at 923 K for 1 h. The insets of (a, b) are the corresponding optical photographs. (d–i) The SEM images showing the microstructures of nanoporous metals with different shapes fabricated by the VPA-dealloying strategy. The optical photograph (j) and SEM images (k, l) of nanoporous Ni foam at different magnifications. (m) The average ligament sizes and macro sizes of different nanoporous metals with photographs as the insets.

peatedly without rupture (inset of Fig. 7d), and the nanoporous layer is well bonded to the Ag substrate after the tensile test (Fig. S19). The above results demonstrate that the tensile ductility of the substrate-supported na-

noporous metals is much superior to those without substrates, which could be attributed to the good modulus match and excellent adhesion between the nanoporous layer and the substrate with the same element.

Figure 7 (a) Load-displacement curves and (b) nanomechanical properties of pristine and nanoporous Ag foils. (c) The tensile stress-strain curves of the substrate-supported Ag with nanoporous layers of different thicknesses (15, 37 and 120 μm). (d) The elongation of the substrate-supported Ag versus the thickness of nanoporous layer. The inset of (d) is the optical photograph of the substrate-supported Ag with the nanoporous layer of 37 μm after bending.

Fig. S20a displays the polarization curves of pristine and nanoporous Ni foams towards HER in 1 mol L⁻¹ KOH at 5 mV s⁻¹. The nanoporous Ni foam exhibits an overpotential of 190 mV at 10 mA cm⁻², much lower than that of the pristine Ni foam (289 mV). Furthermore, the nanoporous Ni foam presents a smaller Tafel slope of 100 mV dec⁻¹ (Fig. S20b), exhibiting a superior catalytic activity than the pristine Ni foam (112 mV dec⁻¹). The remarkable HER performance of the nanoporous Ni foam is associated with the unique hierarchical structure containing macro- and nano-sized pores, which can promote the mass transport and provide more active sites.

CONCLUSIONS

In summary, we report a universal and flexible VPA-dealloying strategy to fabricate nanoporous layers supported on the metal substrates with the same element. Selecting the Ag-Zn system as an example, by tuning the VPA time and temperature, the thickness and microstructure control over nanoporous layers can be realized combining with subsequent dealloying. In particular, the growth of AgZn during VPA is controlled by the reaction-controlled mechanism, and the chemical dealloying of AgZn₃ to form nanoporous Ag is straightforward without the occurrence of intermediate/metastable phases and governed by surface diffusion. Additionally, various

metals with different macro sizes and shapes (here Ag foil, Ag wire, Ag bulk, Ni foil, Co foil, Cu foil, Au wire and Ni foam) can be fabricated into nanoporous structures with good self-supporting properties by the VPA-dealloying strategy. More importantly, the good modulus match and the excellent interfacial adhesion between the nanoporous layer and the substrate account for the noticeable tensile ductility of the substrate-supported nanoporous Ag, which will greatly push forward practical applications of nanoporous metals. Apart from Zn, it can be anticipated that other metals with high vapor pressures such as Mg and Cd can also be applied as sacrificing elements in this strategy to further extend the range of nanoporous metals.

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Author contributions Zhang Z conceived the idea and designed the experiments. Shi Y prepared the samples, analyzed the data, performed the measurements and wrote the manuscript. Zhang Y performed the SEM characterizations. Qin J took part in the data analysis.

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过气相合金化-脱合金化实现对纳米多孔金属宏观/微观结构的耦合调控

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摘要 具有双连续韧带-孔隙结构的纳米多孔金属在催化、电催化、驱动、能源储存和转化领域起着越来越重要的作用。然而, 纳米多孔金属的本征脆性一直是制约其实际应用的“阿喀琉斯之踵”。针对这个问题, 本文利用不同金属的蒸气压差, 提出了一种具有普适性的气相合金化(VPA)-脱合金策略来制备同种金属基底支撑的纳米多孔层。通过调节VPA的时间和温度, 结合不同的脱合金方式, 可以实现对纳米多孔层宏观厚度和微观结构的调控。此外, 具有不同宏观尺寸和形状的金属, 如 Ag, Au, Cu, Co和Ni, 均可以通过此策略制备成纳米多孔结构。更重要的是, 由于基底对纳米多孔层的支撑作用, 其拉伸塑性得到了大幅度的提高; 获得的纳米多孔金属应用于析氢反应时也表现出良好的催化性能。本文研究结果表明气相合金化-脱合金策略在实际应用中具有极大的潜力。