Dual-phase nanostructuring as a route to flexible nanoporous metals with outstanding comprehensive mechanical properties

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ABSTRACT The mechanical properties of nanoporous metals (NPMs) are very important for their potential applications in flexible electronics. Here, the NP Cu@Zr-Cu-Al metallic glass (NP Cu@Zr-Cu-Al MG) composite with high strength, high hardness, and good flexibility is reported. The NP Cu@Zr-Cu-Al MG was synthesized by a two-step dealloying method. First, the flexible NP Zr-Cu-Al MG was prepared by selective etching the active Y-rich MG from the pseudobinary MG system ($\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG + $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG) of $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ alloy. The NP Cu@Zr-Cu-Al MG was then obtained by further etching the NP Zr-Cu-Al MG and the Cu layer was evenly covered on the MG matrix of ligaments. The NP Cu@Zr-Cu-Al MG demonstrated good flexibility due to its non-cracking structure and the existence of flexible Zr-Cu-Al MG. Additionally, the NP Cu@Zr-Cu-Al MG showed the highest tensile strength of 143.9 MPa and nanohardness of 0.79 GPa among all the reported NPMs. The Zr-Cu-Al MG strengthening phase weakened the rupture of Cu@Zr-Cu-Al ligaments, which could effectively restrain the crack initiation and propagation in the NP Cu@Zr-Cu-Al MG. Finally, it could improve the comprehensive mechanical properties. The NP Cu@Zr-Cu-Al MG was applied as an electrode for supercapacitors and glucose biosensors. The NP Cu@Zr-Cu-Al MG electrode displayed better conductivity and supercapacitor capacitance than the bare NP Zr-Cu-Al MG electrode.

Keywords: nanoporous metals, metallic glass, mechanical properties, nanoindentation, flexible electrodes

INTRODUCTION

Flexible electronics have acquired immense popularity since the rapid development of wearable equipment and biomedical devices, such as the roll-up displays, smart-watches, portable screen, artificial electronic skin, and implantable medical biosensors [1–3]. The flexible electrodes are the key parts of such devices; they could act as the power source units for bendable electronic screens and the biosensor components for wearable healthcare monitoring [4,5]. Therefore, one of the critical challenges for flexible electronics is to design and synthesize the reliable, flexible electrode materials with good electrochemical performance, robust flexibility, and with ultra-thin and lightweight characteristics [1,3,4].

In recent years, nanoporous metals (NPMs) such as NP Cu [6], Ni [7], Au [8], Ag [9], Pd [10], and Pt [11] have attracted attention for lithium-ion batteries, biosensors, and supercapacitors, owing to their excellent energy storage performance and electrocatalytic properties [6–11]. However, these NPMs usually possess macroscopic fragility, which can damage the physicochemical stability and reliability. The brittleness of NPMs also limits their potential applications in flexible electronics. Therefore, it is challenging to synthesize NPMs with good flexibility. Additionally, NPMs often exhibit relatively low tensile strength due to their irregular open-cell structures [12,13]. The NPMs usually show irregular distributions of ligament shape, size, and surface curvature. Hence, the tensile stress is concentrated on the weak ligaments of

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NPMs under an external force. Once the weakest ligaments are ruptured, the stress concentration quickly increases at their neighbouring ligaments, leading to the sequential rupturing and rapid propagation of micro-cracks [12,14]. Some reports investigated the mechanical properties of the NPMs using various techniques: compression and tension testing of millimeter-sized samples [15,16], micro-pillar compression [17], Vickers hardness, and nanoindentation measurements [18,19]. The studies on NP Au and Ag [20,21] demonstrated that the mechanical properties of NPMs could be related to the Gibson-Ashby (G-A) scaling laws [22], which were initially established for the conventional porous materials with low density and irregular open-cell structure on a millimetre or micrometre scale. However, Liu *et al.* [23] reported that the strength of NP Au predicted by G-A scaling laws was considerably larger than the actual values. It was attributed to imperfect connectivity within NP Au owing to noncontribution of the non-connected Au ligaments to the instant strength under the external load [21,23]. A modified G-A scaling equation has been constructed by introducing an effective relative density (φ_{eff}) [23]:

$$\sigma_{\text{nanoporous}} = 0.3\sigma_{\text{solid}}\phi_{\text{eff}}^{3/2}, \quad (1)$$

where $\sigma_{\text{nanoporous}}$ and σ_{solid} are the strengths of NPMs and the solid ligaments, respectively. The effective relative density (φ_{eff}) only denotes the volume fraction of interconnected solid ligaments that can sense and respond to the external load. According to modified G-A scaling equation, there are two methods for increasing the mechanical strength of NPMs: (1) optimising the connectivity of solid ligaments in NPMs to improve the value of φ_{eff} and (2) enhancing the intrinsic strength of the solid ligaments in NPMs to improve the value of σ_{solid} .

The precursor alloys with uniform dual phases are dealloyed to form the well-interconnected solid ligaments structure [21]. This is because nanopores are formed only *via* a simple excavation of extra phases of polycrystalline master alloys; they do not form *via* a complex atomic reconstruction process, which involves rebuilding an open-cell nanoporous structure through surface diffusion. In our previous work, the significantly continuous NP Ag metals with good ligament connectivity were fabricated by dealloying the bi-phased Cu-Ag-La alloy precursors [21]. The well-interconnected NP Ag samples exhibited a high φ_{eff} of 0.407, while the φ_{eff} of the ill-interconnected NPMs was as low as 0.147. Therefore, the NP Ag samples with good connectivity had large tensile strength of 68 MPa and nanohardness of 0.206 GPa, which are much

higher than those of reported NP Au and Ag materials with poor connectivity [21,23]. Additionally, the improvement of the intrinsic strength of the ligaments was also reported. Gwak *et al.* [20] fabricated the twinned NP Au with a tensile strength of 87.5 MPa, which was approximately three times greater than that of NP Au with rare twins. It indicated that internal defects and strengthening phases could act as effective barriers to obstruct dislocation motion, and further enhance the macroscopic strength [24–26]. Two important aspects should be considered to enhance the intrinsic strength of the ligaments: (1) type of reinforcements to be selected and (2) ways to embed the reinforcements in the ligaments.

Metallic glass (MG) is considered as appropriate reinforcement due to its superior high fracture toughness, high mechanical strength, and good elastic behaviour [27,28]. Many studies have focused on the Zr-Cu-based MG systems, such as Zr-Cu-Al, Zr-Al-Ni-Cu, Zr-Ti-Ni-Cu-Be and Zr-Cu-Al-Ag, due to their high glass-forming abilities and good mechanical properties [29,30]. Nevertheless, Zr-Cu-based MG generally displays lower electrical conductivity than its crystalline counterpart owing to its disordered structures [31]. On the other hand, plenty of Zr and Al elements in Zr-Cu-based MG can influence the electrochemical behaviors owing to their poor chemical activity. Therefore, combining the advantages of both MG and NPMs, the NPMs@MG composite is considered to have good comprehensive performance.

The flexible NP Cu@Zr-Cu-Al MG composite was prepared by a two-step chemical dealloying method. It was observed to have larger tensile strength and nanohardness than pure NP Cu. Moreover, it showed better electrical conductivity than pure NP Zr-Cu-Al MG alloy. Additionally, the composite exhibited good physicochemical properties and long-term stability. The flexible NP Cu@Zr-Cu-Al MG composite is a promising material for micro-electromechanical systems—wearable healthcare and flexible electronic devices.

EXPERIMENTAL SECTION

Synthesis method

The alloy ingots with the composition of $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ and $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ were prepared by arc-melting the mixtures of pure elements under argon atmosphere in a water-cooled Cu hearth. The master alloys were reversed and re-melted at least five times to ensure the uniformity of the alloy composition. The $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ ingots were prepared

by mixing $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ and $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ alloys with the weight ratio of 1:1.015 [27]. The MG ribbons were prepared by re-melting the ingots in a high-frequency induction furnace and rapidly ejecting them onto a rotating copper wheel with a linear velocity of 36.7 m s^{-1} . The as-formed $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ ribbon is a pseudobinary MG, which is composed of $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG and $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG components [27,32]. The $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ ribbon samples with a size of $1.5 \text{ mm} \times 25 \mu\text{m} \times 3 \text{ cm}$ (width $\times$ thickness $\times$ length) were immersed in the 0.1 mol L^{-1} HNO_3 solution at 298 K . The electrochemical etching of $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ ribbons were potentiostatically kept at 0.4 V (vs. Ag/AgCl), controlled by an electrochemical workstation (Gamry Interface 1000). The etching potential was determined by thermodynamic and kinetic considerations of two MG components [27]. The $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG is relatively inert compared with the $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG owing to its quite lower anodic current density at the applied potential of 0.4 V . Therefore, the $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG can be electrochemically dissolved while the relatively stable Zr-Cu-Al MG is retained as the skeletons of nanoporous structure (Fig. 1a). Thereafter, the NP Zr-Cu-Al MG ribbons were rinsed with deionized water five times, and then further dealloyed in the 0.2 mol L^{-1} HF acid solution at 298 K . Finally, the ribbons were well rinsed with deionized water and alcohol to remove the residual

HF solutions, and then dried in a vacuum chamber. The control sample of NP Cu was prepared by dealloying the $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG ribbons in the 0.05 mol L^{-1} HF acid solution at 298 K [33]. The preparation conditions were similar to those of $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ alloy.

Characterization

The crystal structure was characterized by X-ray diffraction (XRD, Bruker D8) using the $\text{Cu K}\alpha$ radiation. The morphology, microstructure, and composition were examined using a scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, JEOL JEM-2010F) coupled with energy-dispersive X-ray spectroscopy (EDS). The nitrogen (N_2) adsorption-desorption isotherms and pore size were measured using a BELSORP-max (MP) Brunauer-Emmett-Teller (BET, Micromeritics TriStar II 3020) surface analyser. Differential scanning calorimetry (DSC) experiments were performed with a METTLER TOLEDO STD1600 instrument under a purified argon atmosphere at a heating rate of 0.67 K s^{-1} .

Property measurement

Tensile tests were performed using an Instron mechanical testing machine equipped with an electronic strain gauge at a strain rate of $5.0 \times 10^{-4} \text{ s}^{-1}$. The gauge dimension of

Figure 1 (a) Schematic illustration of the fabrication process of NP Zr-Cu-Al MG ribbons by selective etching $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ alloy ribbon. (b) XRD patterns and (c) DSC curves of $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ alloy ribbons before and after electrochemical etching.

tensile test specimens was $1\text{ cm} \times 17\text{ }\mu\text{m} \times 1.5\text{ mm}$ (length $\times$ thickness $\times$ width). Nanomechanical property was examined by a Nano Indenter (Hysitron TI-Premier) with loading and displacement resolutions of 50 nN and 0.01 nm, respectively. More than ten nanoindentation tests were conducted on each specimen. Moreover, the bending flexibility was evaluated using a simple bend test.

The supercapacitor performance was investigated by galvanostatic charge–discharge (GCD) and cyclic voltammetry (CV) tests. Additionally, the glucose biosensor property was also measured using CV tests. Moreover, the electrical conductivity was detected by electrochemical impedance spectroscopy (EIS) tests. These electrochemical tests were performed on an electrochemical working station (Gamry Interface 1000). The electrochemical tests were performed in a three-electrode system at 298 K using the platinum foil ($1.5\text{ cm} \times 1.5\text{ cm}$) as the counter electrode and Ag/AgCl reference electrode. The 0.2 mol L^{-1} NaOH alkaline solution was used as the electrolyte.

RESULTS AND DISCUSSIONS

Fabrication and microstructure of NP Zr-Cu-Al MG

The NP Zr-Cu-Al MG was prepared by etching the pseudobinary $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ MG ($\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG + $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG) in 0.01 mol L^{-1} HNO_3 acid solution for 500 s [27,32]. The electrochemical etching of $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ MG ribbons was potentiostatically conducted at 0.4 V (vs. (Ag/AgCl)), controlled by an electrochemical workstation (Gamry Interface 1000). This etching potential was determined by considering the thermodynamic and kinetic properties of the two MG components [27]. The $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ MG is relatively inert than $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG because of its lower anodic current density at the applied potential of 0.4 V. Hence, the $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$ MG can be electrochemically dissolved while the relatively stable Zr-Cu-Al MG is retained as the skeletons of nanoporous structure, as schematically depicted in Fig. 1a. The glassy nature was verified by XRD patterns (Fig. 1b). Each XRD pattern of the $\text{Y}_{47}\text{Cu}_{46}\text{Al}_7$, $\text{Zr}_{47}\text{Cu}_{46}\text{Al}_7$ and $\text{Cu}_{46}\text{Zr}_{23.5}\text{Y}_{23.5}\text{Al}_7$ ribbons shows a characteristic broad halo with the absence of crystalline peak, indicating a glassy structure. During the etching process, the active Y-Cu-Al MG was selectively dissolved from the pseudobinary Cu-Zr-Y-Al MG precursors, while the relatively stable Zr-Cu-Al MG was retained [27]. Therefore, the as-corroded Cu-Zr-Y-Al MG still exhibited the characteristic broad XRD pattern after the selective etching (Fig. 1b). The result is further supported by the

DSC curves (Fig. 1c). The DSC trace of pseudobinary Cu-Zr-Y-Al MG precursor is divided into two exothermic crystallisation peaks, which are well consistent with crystallisation peaks of Zr-Cu-Al MG and Y-Cu-Al MG. In the solid state, the Zr-Cu-Al and Y-Cu-Al are immiscible in the Cu-Zr-Y-Al alloy system because of the presence of large miscibility gap between Zr-rich and Y-rich glass components owing to the positive mixing heat ($+35\text{ kJ mol}^{-1}$) between Zr and Y elements [32]. After etching, the crystallisation peak of the Y-rich MG disappeared, while that of the Zr-rich MG remained. It indicates that the active Y-rich MG was removed, while the residual Zr-rich MG built nanoporous skeletons. Nevertheless, the as-corroded Cu-Zr-Y-Al MG revealed a lower heat capacity for the exothermic reaction than the Zr-Cu-Al MG, possibly due to the surface passivation of the as-corroded Cu-Zr-Y-Al MG [27].

The morphology of the as-corroded Cu-Zr-Y-Al MG is shown in Fig. 2. The cross-sectional image in Fig. 2a shows that the three-dimensional (3D), well-interconnected nanoporous structure uniformly spans the thickness of the sample. Meanwhile, the surface image in Fig. 2b also reveals the good ligament/pore morphology with the desirable network connectivity. The microstructural characteristics of the sample were further investigated. The TEM image in Fig. 2c shows the nanoporous structure, which is consistent with the SEM results. The selected area electron diffraction (SAED) pattern (inset of Fig. 2c) and high-resolution TEM image confirm the glassy state of the sample. TEM–EDS measured the composition of the skeletons in the nanoporous structure. The Y element almost disappeared, and Cu content decreased compared with the chemical composition of the Cu-Zr-Y-Al MG precursor (Fig. S1), indicating that the nanopore structure originated from the selective dissolution of the active Y-Cu-Al MG component [27]. Furthermore, the EDS mapping shows that the Cu, Zr, and Al elements are uniformly and spatially distributed within the glassy skeleton, which straightforwardly proves the formation of NP Zr-Cu-Al MG (Fig. 2d). These results also suggest that the porous structure is determined by the original structure of the pseudobinary (Zr-Cu-Al MG + Y-Cu-Al MG) Cu-Zr-Y-Al MG precursor alloy, while the porous structure and porosity can be tailored by tuning the relative ratio of the two MG compositions in the precursors [27]. The NP Zr-Cu-Al MG exhibited a large specific surface area of $58.24\text{ m}^2\text{ g}^{-1}$ and high porosity percentage of 47% (Fig. 2e). The size of nanopores mainly ranged from 10 to 30 nm, and the average pore diameter was 10.66 nm

Figure 2 Structural characterization of the NP Zr-Cu-Al MG alloy. (a, b) Cross-sectional and surface SEM images. (c) TEM image and SAED pattern. (d) High-resolution TEM image and EDS mapping. (e, f) N_2 adsorption/desorption isotherms and pore size distribution.

(Fig. 2f).

Mechanical properties of NP Zr-Cu-Al MG

The mechanical properties of the NP Zr-Cu-Al MG were measured through the nanoindentation and macroscopic tension tests. Fig. 3a shows the nanoindentation force-depth curves under different loads. Fig. 3b shows the dependence curves of nanohardness (H) and Young's modulus (E) on the indentation depth. The H and E of the NP Zr-Cu-Al MG under different indentation depths are approximately 1.27 and 23.7 GPa, respectively. The increment in indentation depth has little influence on the nanomechanical properties, indicating the good mechanical stability under external force loading. The NP

Zr-Cu-Al MG ribbon can be readily shaped into any desired forms without breaking it (insets of Fig. 3b); owing to the excellent bending ductility of MG [34]. Fig. 3c–g show the scanning probe microscopy (SPM) images of the NP Zr-Cu-Al MG subjected to different indentation depths, as shown in Fig. 3a. Stress cracking did not exist even at the indentation depth of 1234 nm, suggesting good mechanical integrity during deformation. Fig. 3h shows a typical tensile stress-strain curve of the NP Zr-Cu-Al MG ribbon. The NP Zr-Cu-Al MG showed the high fracture tensile strength of 240.7 MPa—approximately ten times higher than most of the reported NPMs [21,23,35–37]. The superior strength of NP Zr-Cu-Al MG was derived from the extremely high strength of

Figure 3 Mechanical measurements of the NP Zr-Cu-Al MG alloy. (a) The nanoindentation force-depth curves and (b) the nanomechanical properties as a function of indentation depth. (c–g) SPM images as a function of indentation depth for the indentation traces. (h) Tensile stress-strain curves. (i, j) The fracture morphologies of porous ribbon samples subjected to tension testing.

the Zr-Cu-Al MG, which is significantly higher than that of crystalline Au, Ag, Cu, and Pt metals. The fracture surface of the NP Zr-Cu-Al MG ribbon subjected to the tensile fracture is shown in Fig. 3i and j. They show that the ligaments of NP Zr-Cu-Al MG are uniformly deformed on the fracture surface.

Fabrication and microstructure of NP Cu@Zr-Cu-Al MG composite

The NP Zr-Cu-Al MG was etched in 0.2 mol L^{-1} HF solution at 298 K. Many gas bubbles were formed on the sample surface during the immersion, suggesting that the Zr and Al elements were leached out of the NP Zr-Cu-Al MG. After etching for 1000 s, the formation of gas bubbles was stopped. Moreover, the colour of the NP Zr-Cu-

Al MG changed from argentous to a typical Cu metallic lustre. The XRD patterns of as-dealloyed NP Zr-Cu-Al MG revealed the sharp diffraction peaks of face-centered cubic (fcc) Cu crystalline phase [38] that were superimposed on the broad amorphous halo peak of NP Zr-Cu-Al MG (Fig. 4a). This result indicates that fcc Cu metal was formed on the Zr-Cu-Al MG by selectively dissolving the active Zr and Al elements in HF solution [33,38]. The sample of NP Cu plus Zr-Cu-Al MG is named NP Cu@Zr-Cu-Al MG composite. Moreover, the cross-section of the NP Cu@Zr-Cu-Al MG composite ribbon showed the bicontinuous ligament-channel nanostructure (Fig. 4b). TEM image (Fig. 4c) shows the nanoporous morphology with the ligament size approximately 10 nm. In the SAED pattern (inset of Fig. 4c),

Figure 4 Structural characterization of the NP Cu@Zr-Cu-Al MG hybrid alloy. (a) XRD patterns of NP Zr-Cu-Al MG alloy before and after dealloying. (b) Cross-sectional SEM images. (c) TEM images and SAED pattern. (d) High-resolution TEM images. (e) Schematic illustration showing the formation mechanism of NP Cu@Zr-Cu-Al MG hybrid alloy during dealloying the NP Zr-Cu-Al MG in HF acid solution.

the characteristic amorphous halo pattern of Zr-Cu-Al MG is superimposed with the polycrystal diffraction pattern of fcc Cu crystalline phase. High-resolution TEM image (Fig. 4d) shows the mixed phases of crystal Cu lattice fringes and disordered glassy structure of NP Zr-Cu-Al MG ligaments. The EDS mapping images (Fig. S2a–d) of individual elements in the TEM image (region C of Fig. S2a) display the enriched Cu layer on the ligaments. The ratio of Cu/Zr/Al atoms in NP Cu@Zr-Cu-Al MG was 68:28:4 (Fig. S3); it had higher Cu content than that of NP Zr-Cu-Al MG having Cu/Zr/Al atom ratio of 46:47:7, indicating the formation of Cu layer on the NP Zr-Cu-Al MG ligament. The BET results (Fig. S4) show that the as-prepared NP Cu@Zr-Cu-Al MG consisted of a large specific surface area of $41.6 \text{ m}^2 \text{ g}^{-1}$ and a large porosity percentage of 55%. Additionally, the average pore diameter of the NP Cu@Zr-Cu-Al MG composite was approximately 15.89 nm, which is larger than that of NP Zr-Cu-Al MG. The increment in pore size

after NP Zr-Cu-Al MG etching leads to the decrement in specific surface area.

Fig. 4e schematically illustrates the formation process of the NP Cu@Zr-Cu-Al MG composite. Similar to the dealloying process of monolithic Zr-Cu-Al glassy ribbons [33,39] or bulk Zr-Cu-Al metallic glass rods [38], the dealloying of NP Zr-Cu-Al MG starts from the outer surface of the MG ligaments. The active Zr and Al atoms were selectively dissolved from the ligaments due to the massive difference in the chemical stability between Cu and other two elements in the HF solution [33], leading to many vacancies on the surface of ligaments. Moreover, the residual noble Cu atoms moved along the interface between the ligaments and the HF solution; they then assembled to minimize the total surface and interfacial free energy [21,40]. After that, the Cu-rich layer was formed on the surface of Zr-Cu-Al MG ligaments. The possible formation mechanism of the Cu-coated MG ligaments structure is proposed. First, unlike the solid thin

film or ribbon precursors, the dealloying of NP Zr-Cu-Al MG started from the outer surface of the nano-sized rod-like ligaments, and gradually evolved into the inner ligament matrices. It reduced the surface area between the inner and outer part of the MG ligaments. The specific surface area before and after dealloying the NP Zr-Cu-Al MG was 58.24 and 41.6 m² g⁻¹, respectively (Fig. 2e and Fig. S4). Therefore, a large number of residual noble Cu atoms moved on the surface of these gradually shrinking rod-like MG ligaments, and preferentially assembled together to form an entire Cu coating on the ligament matrices.

The control sample of the NP Cu was prepared by dealloying the melt-spun Zr₄₇Cu₄₆Al₇ MG ribbon in the 0.05 mol L⁻¹ HF acid solution for 5 h at 298 K. The SEM images revealed the hierarchical architecture with homogeneous bicontinuous ligament/pore morphology (Fig. S5a–c). The ligament and pore sizes were approximately 35 and 30 nm, respectively. The XRD and EDS results confirmed the pure fcc Cu phase of the ligament (Fig. S5b and d). The NP Cu had a large specific surface area of 41.04 m² g⁻¹ and porosity of 56% (Fig. S5e).

Mechanical properties of NP Cu@Zr-Cu-Al MG composite

The tensile stress-strain curves are shown in Fig. 5a. Though further dealloying resulted in the reduction of the tensile strength, the NP Cu@Zr-Cu-Al MG still displayed a high tensile strength of 143.9 MPa, which was considerably higher than that of all the reported nanoporous pure metals [21,23,35,36]. The tensile strength of NP Cu in present work is as low as 5.4 MPa. Nevertheless, the NP Cu@Zr-Cu-Al MG composite and NP Zr-Cu-Al MG displayed good bendability without fracture at large bending degree (i.e., ~180°), but the NP Cu was fragile and easily fragmented under bending force, as shown in the insets of Fig. 5a. The crack defects fundamentally determine the macroscopic fragility of NPMs because the cracked NPMs sample is easily crushed since the cracks nucleate from the inherent micro-cracks and quickly propagate along with the concentrated stress [21]. There was no crack defect in the NP Cu@Zr-Cu-Al MG composite (Fig. 4b), while the NP Cu consisted of many large micro-cracks (Fig. S5a). The micro-cracks should have arisen from the hierarchical structure of NP Cu [38]; the outer NP Cu layer could be easily separated and shed from the inner NP Cu layer, and then the crack defect would have formed. Therefore, the excellent flexibility of NP Cu@Zr-Cu-Al MG arises from their non-cracking structure, and the existence of flexible Zr-Cu-Al MG. Fig. 5b and c show the nanoindentation curves and the

corresponding nanomechanical properties of the NP Zr-Cu-Al MG, NP Cu and NP Cu@Zr-Cu-Al MG composite. Fig. 5c shows that the H of NP Cu@Zr-Cu-Al MG is 0.79 GPa, much higher than that of NP Cu ($H = 0.018$ GPa). The corresponding SPM images and 3D plots, as well as the linear sweep and roughness measurements after nanoindentation, are shown in Fig. 5d–g. Both the NP Zr-Cu-Al MG and NP Cu@Zr-Cu-Al MG composite (Fig. 5d, e and g) generated excellent nanoindentation morphology with a smooth profile without the formation of microcracks, indicating good mechanical integrity under external nanoindentation force. On the other hand, the NP Cu (Fig. 5f and g) contains the prominent cracked parts on the rough profile of the sample surface. This result is related to the poor nanoindentation properties for NP Cu (Fig. 5c). Moreover, the nano-hardness value of NP Cu@Zr-Cu-Al MG was approximately three times greater than that of other reported nanoporous pure metals [21,35,36]. The results are summarized in Table 1. The highly strong interior Zr-Cu-Al MG acted as a strengthening phase for absorbing much deformation energy and subsequently delaying the failure of nanoporous ligaments [38].

The superior mechanical performance of NP-Cu@Zr-Cu-Al MG composite can be further explained using the G-A equation [21–23]. Fig. 6 shows the curves of the strength *versus* relative density for the NP Cu@Zr-Cu-Al MG composite, NP Zr-Cu-Al MG, NP Cu, other reported nanoporous pure metals (NP Au [15,20,41–44], NP Ag [17,21,45], NP Cu [46], and NP Ni [35]), and NP MG (NP Mg-Al MG [47] and NP Ni-Pd-P-B MG [48]). The strength and nanohardness of the NPMs were correlated by $\sigma = H/2.65$ ($P < 70\%$) and $\sigma = H$ ($P > 70\%$) [35]. In the present case, the G-A equation is defined as follows:

$$\sigma_{\text{nanoporous}} = 0.3\sigma_{\text{solid}}\phi^{3/2}, \quad (2)$$

$$H_{\text{nanoporous}} = CH_{\text{solid}}\phi^{3/2}, \quad (3)$$

where σ_{solid} and H_{solid} are the strength and hardness of the solid phase (nano-ligaments in NPMs), respectively. C is a constant having an approximate value of 0.47, and ϕ is the relative density of porous materials and can be calculated as $\phi = 1 - P$ [17], where P denotes the porosity obtained from the BET measurements. The G-A lines of the NP Zr-Cu-Al MG were estimated based on the Zr-Cu-Al MG ligaments with the theoretical σ_{solid} of 2000 MPa [29,30] and H_{solid} of 6.75 GPa. Moreover, the G-A lines of the NP Cu were estimated based on the Cu ligaments with the σ_{solid} of 400 MPa [49], and H_{solid} of 1.32 GPa. The H_{solid} of Zr-Cu-Al MG ligaments and Cu

Figure 5 Mechanical measurements of the NP Cu@Zr-Cu-Al MG hybrid alloy. (a) Tensile stress-strain curves. (b) Nanoindentation force-depth curves. (c) Comparison of mechanical properties of the NP Cu@Zr-Cu-Al MG hybrid alloy with NP Zr-Cu-Al MG alloy and NP Cu metal. (d–g) The SPM images, 3D plots, and the linear sweep and roughness measurements of the NP Cu@Zr-Cu-Al MG, NP Zr-Cu-Al MG and NP Cu samples after nanoindentation.

ligaments were extracted by measuring the H_{solid} of pure Zr-Cu-Al glassy alloy and pure Cu, as shown in Fig. S6. The G-A lines for NP Zr-Cu-Al MG and NP Cu are the upper and lower boundaries of the Cu@Zr-Cu-Al MG composite, respectively. The strength of the NP Cu@Zr-Cu-Al MG composite is close to the upper G-A lines, while the NP Cu and other reported nanoporous pure metals are located in the lower G-A line region (Fig. 6). The NP Cu@Zr-Cu-Al MG composite exhibited excellent flexibility, strength, and hardness due to the introduction of the high-strength Zr-Cu-Al MG into the NP Cu.

The failure of NPMs arose due to the initiation and

propagation of micro-cracks, which finally penetrated the entire material. The metal with 3D nanoporous structure cracks more easily than its bulk counterparts owing to its irregular open-cell structures [12,13]. The distributions of the size, shape, and surface curvature of the ligaments in NPMs were irregular. Hence, when the NPMs were subjected to an external loading force, the weakest ligaments would be preferentially ruptured, and then the cracks would form [12,14]. Subsequently, the ligaments failed one-by-one, and consequently, the cracks grew continuously along the direction normal to the applied loading force. Finally, the NPMs were fractured when the

Figure 6 (a, b) Mechanical properties of nanoporous metals. Blue and black lines denote upper and lower boundaries estimated using G-A model (Equations (2) and (3)) for NP Cu@Zr-Cu-Al MG hybrid alloy, respectively.

Table 1 Comparison of the nanoporous metal materials in terms of mechanical properties

Sample	Relative density (%)	Ligament size (d/nm)	Ultimate strength (σ /MPa)	Nanohardness (H /GPa)	Reference
NP Zr-Cu-Al MG	53	25	240.7	1.27	This work
NP Cu@Zr-Cu-Al MG	45	19	143.9	0.79	This work
NP Cu	44	35	5.4	0.018	This work
NP Ag	41	127	68	0.21	[21]
NP Au	35	43	27.5	—	[23]
NP Ni	46	350	30	0.24	[35]
NP Cu	39	43	25	0.24	[36]

cracks propagated through the entire material. If the ligaments are strong enough to sustain loading without breaking down, the initiation and development of micro-cracks are suppressed, and the fracture of NPMs is delayed.

The NP Cu@Zr-Cu-Al MG composite showed much higher intrinsic strength and hardness than NP Cu due to

the Zr-Cu-Al MG reinforced phase in the ligaments (Fig. 5). Because of the uniform amorphous and isotropic structure [29,30], MG alloys have no crystal defects traditionally found in crystalline metals, such as the grain boundaries, stacking faults, and dislocations. As a result, the typical intergranular and transgranular fractures found in crystalline metals would not occur in MG alloys.

Moreover, insufficient toughness of non-uniform crystal structure, which leads to the premature fracture in metallic materials, does not occur in MG alloys [29,30]. The Zr-Cu-Al MG phase for the NP Cu@Zr-Cu-Al MG composite plays a strengthening role for depressing the rupture of individual Cu@Zr-Cu-Al ligament, which could effectively restrain the crack initiation and propagation in the NPMs (Fig. 7a and b), and finally improve the comprehensive mechanical properties.

The NP Cu@Zr-Cu-Al MG and NP Cu were subjected to the high loading force of 0.1 N using the Vickers hardness indentation to verify if NP Cu@Zr-Cu-Al MG could effectively restrain the formation and development of cracks. As shown in Fig. 7c and d, Vickers hardness of the NP Cu@Zr-Cu-Al MG is approximately 148.5, which is much higher than that of the NP Cu. Furthermore, it is easily observed that the single large microcrack ($> 40 \mu\text{m}$) penetrates the entire indentation traces in NP Cu along the edges (Fig. 7c). On the contrary, the multiple small cracks ($< 1 \mu\text{m}$) are well dispersed around the indentation trace region of NP Cu@Zr-Cu-Al MG; these multiple small cracks do not assemble along the indenter edges where the stress is concentrated, indicating its good ability to resist crack initiation and propagation (Fig. 7d). Therefore, the NP Cu@Zr-Cu-Al MG demonstrated the excellent flexibility, strength, and hardness (Figs 5–7). However, the NP Cu displayed the macroscopic fragility and superior low strength and hardness (Figs 5–7).

Electrochemical performance of the NP Cu@Zr-Cu-Al MG composite

The supercapacitor and glucose biosensor properties of the NP Cu@Zr-Cu-Al MG composite were determined by electrochemical tests in 0.2 mol L^{-1} NaOH solution. Fig. 8a shows the CV curves of the NP Cu@Zr-Cu-Al MG composite, NP Zr-Cu-Al MG and NP Cu at a scan rate of 25 mV s^{-1} . All CV curves contain the prominent redox peaks. The capacitance behavior is primarily based on the Faradaic redox reactions, which occurs due to the adsorption of electrolyte ions onto the surface of electro-active materials during the reversible reactions [50]. CV curve of the NP Zr-Cu-Al MG (Fig. 8a) shows one pair of the redox peaks (A_2/C_2); however, CV curves of the NP Cu@Zr-Cu-Al MG composite and NP Cu show two pairs of redox peaks (A_1/C_1 , A_2/C_2), which agree with the results reported in the literature [51,52]. The oxido-reduction processes are described as following [51,52]:

Oxido-reduction peaks (A_1/C_1):

Oxido-reduction peaks (A_2/C_2):

The NP Cu@Zr-Cu-Al MG composite and NP Cu

Figure 7 (a, b) Schematic illustration showing the strengthening mechanism of the NP Cu@Zr-Cu-Al MG composite than the bare NP Cu metal. (c, d) SEM images showing the surface morphologies of bare NP Cu samples and NP Cu@Zr-Cu-Al MG composite samples after high-load Vickers hardness indentations.

Figure 8 Electrochemical capacitive properties. (a) CV curves. (b–d) GCD curves of the three electrodes at different current densities. (e) Volumetric specific capacitances of the three electrodes under various conditions. (f, g) EIS analyses and electrical conductivity. (h) Schematic illustration showing the benefits of the NP Cu@Zr-Cu-Al MG hybrid electrode for high conductive properties.

showed remarkably enhanced capacitive current than the bare NP Zr-Cu-Al MG (Fig. 8a). Fig. 8b–d show the GCD curves of the NP Cu@Zr-Cu-Al MG composite, NP Zr-Cu-Al MG, and NP Cu at various current densities. The volumetric specific capacitance values (C_v , F cm⁻³) of the NP Cu@Zr-Cu-Al MG composite, NP Cu, and NP Zr-Cu-Al MG are calculated from the CV and GCD curves using the following formula [53]:

$$C = \frac{I \Delta t}{V_{sc} \Delta E}, \quad (9)$$

where I is the discharge current (A), and Δt is the discharge time (s), $\Delta E = E_2 - E_1$ is the operation voltage region with $E_1 = 0.5$ V and $E_2 = -1.1$ V, and V_{sc} is the total volume of the as-prepared electrodes (cm³). The NP Cu@Zr-Cu-Al hybrid electrodes and the NP Cu electrodes obtained higher capacitances than the NP Zr-Cu-Al MG electrodes (Fig. 8e). The poor capacitive behavior of

the NP Zr-Cu-Al MG electrode possibly originated from the poor electrical conductivity of MG alloys [31]. Moreover, plenty of the Zr and Al elements in NP Zr-Cu-Al MG damaged its electrochemical behavior owing to their poor chemical activities. On the contrary, the Cu-based crystalline alloys exhibited high conductivity [54]. Therefore, the NP Cu@Zr-Cu-Al MG composite demonstrated better energy storage performance than the bare NP Zr-Cu-Al MG.

The electrical conductivities of the NP Cu@Zr-Cu-Al MG composite, NP Cu, and NP Zr-Cu-Al MG were investigated by EIS tests and a conventional four-probe method [31]. Fig. 8f reveals the Nyquist plots of the three samples. The intercept of the Nyquist plots on the real axis represents the value of an equivalent series resistance (R), which is related to the electrolyte resistance, the intrinsic resistance of electrode material, and the contact

resistance at the interface between the active material and substrate [55]. The NP Cu@Zr-Cu-Al MG composite and NP Cu showed lower R than the NP Zr-Cu-Al MG. Moreover, the electrical resistivity (ρ) of NP Cu was $54.18 \mu\Omega \text{ cm}$, which is 5.9 times lower than that of the NP Zr-Cu-Al MG ($\rho = 376.23 \mu\Omega \text{ cm}$) (Fig. 8g). Therefore, the good conductivity of the NP Cu@Zr-Cu-Al MG composite is attributed to the good conductivity of pure Cu layer on the Zr-Cu-Al MG ligament, as schematically shown in Fig. 8h. The excellent conductivity of materials can enhance the electrode/electrolyte interfacial contact and promote electronic/ion conductivity to accelerate the Faradaic reactions [56,57]. Hence, the NP Cu@Zr-Cu-Al MG composite has a better capacitive performance than the bare NP Zr-Cu-Al MG (Fig. 8e).

The electrocatalytic activities of the flexible NP Cu@Zr-Cu-Al MG composite towards glucose oxidation were examined to evaluate their potential application in glucose electrochemical sensing. Fig. S7a illustrates the CV curves of the NP Cu@Zr-Cu-Al MG composite in 0.2 mol L^{-1} NaOH solution with and without 5 mmol L^{-1} glucose at a scan rate of 25 mV s^{-1} . Moreover, the anodic oxidation current in NaOH solution with glucose is much higher than in NaOH solution without glucose; it indicates that the NP Cu@Zr-Cu-Al MG composite displays glucose sensing performance (Fig. S7a). The increment in current at the first stage ($< 0 \text{ V}$) is possibly due to the electro-adsorption of glucose and generation of adsorbed intermediates (one proton is lost per-glucose molecule in this electrochemical reaction) [58]. In the second stage ($> 0 \text{ V}$), current increment is observed possibly due to the direct oxidation of glucose, resulting in much-transferred charge [58]. Fig. S7b shows the CV curves of the NP Cu@Zr-Cu-Al MG composite with various scan rates in a 0.2 mol L^{-1} NaOH solution containing 5 mmol L^{-1} glucose electrolyte. As shown in Fig. S7c, the two anodic peak currents are found to be linearly associated with the square root of the scan rate; it shows a typical diffusion-controlled electrochemical process, which is useful for quantitative analysis of real detections [59]. Therefore, the NP Cu@Zr-Cu-Al MG composite material is suitable for practical biosensor applications in quantitative analysis of glucose. Moreover, Li *et al.* [52] have reported that for the NP Cu there exists a direct relation between $1/R_{\text{ct}}$ and its glucose concentration; here, R_{ct} is the charge transfer resistance, $1/R_{\text{ct}} = KC_{\text{glucose}}$ with K being a constant parameter. The inverse of charge transfer resistance, $1/R_{\text{ct}}$, is linearly dependent on the glucose concentration in the range of 1 to 10 mmol L^{-1} with a regression coefficient of 0.992. Therefore, the concentrations of glucose can be

quantitatively detected with the NP Cu@Zr-Cu-Al MG by EIS method. Nevertheless, the NP Cu@Zr-Cu-Al MG electrode may not selectively detect the glucose; it is because the nanoporous transition Cu, AuCu, and AuAg metals demonstrated highly sensitive detection towards various biological substances, such as glucose, dopamine and uric acid [52,58,60]. Radhakrishnan *et al.* [61] reported that CuS electrode could selectively detect the glucose from the ascorbic acid (AA), uric acid (UA), dopamine (DA), and fructose (Fru). Therefore, an appropriate sulfuration of NP Cu@Zr-Cu-Al MG to form an amount of CuS should improve the selectivity of the glucose biosensor. In our future work, the research focus will be on the detailed research to achieve the desirable selectivity, good quantitative detectability, and low detection limit of glucose biosensors.

To further investigate the potential of the NP Cu@Zr-Cu-Al MG composite as a flexible free-standing glucose biosensor electrode, the CV tests on the sample subjected to bending under a large angle ($\sim 120^\circ$) were performed (Fig. S7d). Both normal and bending NP Cu@Zr-Cu-Al MG composites display a similar electrochemical performance, indicating the excellent electrochemical stability during bending. The mechanical stability of the flexible NP Cu@Zr-Cu-Al MG composite after CV tests in the glucose was examined by nanoindentation and Vickers hardness. The NP Cu@Zr-Cu-Al MG composite still retains the high nanohardness ($H = 0.74 \text{ GPa}$) and Vickers hardness (118.1 HV0.01), and shows good indentation morphology, indicating superior mechanical stability after the electrochemical testing (Fig. S8). The NP Cu@Zr-Cu-Al MG composite displays good comprehensive properties, such as electrochemical properties, flexibility, and mechanical properties (Figs 5–7 and Table 1). These characteristics are promising for their practical applications in flexible supercapacitors and glucose biosensors, especially as the power source units for bendable electronics and the sensory units for wearable healthcare monitoring devices, such as the roll-up displays, smart watches, portable screens, artificial electronic skins, and implantable medical biosensors.

CONCLUSIONS

The highly strong and flexible NP Cu@Zr-Cu-Al MG composite ribbons were successfully fabricated by dealloying the NP Zr-Cu-Al MG ribbon. The NP Cu@Zr-Cu-Al MG demonstrated a large tensile strength (σ) of 143.9 MPa , nanohardness (H) of 0.79 GPa , and Vickers hardness (HV0.01) of 148.5 ; these values are much higher than those of pure NP Cu ($\sigma = 5.4 \text{ MPa}$, $H = 0.018 \text{ GPa}$,

HV0.01 = 8.4). The Zr-Cu-Al MG phase played a strengthening role in depressing the rupture of individual Cu@Zr-Cu-Al ligament, which effectively restrained the crack initiation and propagation. Finally, it improved the comprehensive mechanical properties. The outstanding comprehensive mechanical properties of the flexible NP Cu@Zr-Cu-Al MG originated from their non-cracking structure and the existence of flexible Zr-Cu-Al MG. Additionally, the flexible NP Cu@Zr-Cu-Al MG composite ribbon can be directly used as a free-standing electrode for supercapacitors and glucose biosensors. The NP Cu@Zr-Cu-Al MG composite showed better electrical conductivity than NP Zr-Cu-Al MG owing to the existence of continuous Cu on the surface of ligaments. The as-prepared flexible NP Cu@Zr-Cu-Al MG materials with the good physicochemical properties are promising candidates for the application in micro-electromechanical systems, such as wearable healthcare and flexible electronic devices.

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Conflict of interest The authors declare that they have no conflict of interest.

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

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双相纳米结构化可实现纳米多孔金属的优异柔性与综合力学性能

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摘要 纳米多孔金属的力学性能对其在柔性电子领域的应用具有重要意义。本文报道了一种高强度、高硬度、柔韧性好的纳米多孔Cu@Zr-Cu-Al金属玻璃(NP Cu@Zr-Cu-Al MG)复合材料, 该材料采用两步脱合金法合成。首先, 从Cu₄₆Zr_{23.5}Y_{23.5}Al₇合金的伪二元MG体系(Zr₄₇Cu₄₆Al₇ MG + Y₄₇Cu₄₆Al₇ MG)中选择性蚀刻活性富Y的MG相, 制备了柔性纳米多孔Zr-Cu-Al金属玻璃(NP Zr-Cu-Al MG)。进一步蚀刻得到NP Cu@Zr-Cu-Al MG, 其中Cu层均匀地覆盖在MG韧带基体上。由于NP Cu@Zr-Cu-Al MG的无裂纹结构和柔性Zr-Cu-Al MG的存在, 使其具有良好的柔性。NP Cu@Zr-Cu-Al MG的抗拉强度高达143.9 MPa, 纳米硬度高达0.79 GPa。Zr-Cu-Al MG强化相抑制了Cu@Zr-Cu-Al韧带的断裂, 有效抑制了裂纹在NP Cu@Zr-Cu-Al MG中的萌生和扩展, 提高了复合材料的综合力学性能。NP Cu@Zr-Cu-Al MG可直接用作超级电容器和葡萄糖生物传感器的电极, 比纯NP Zr-Cu-Al MG电极展现出更好的电导率和超电容容量。