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Hierarchical nanoporous metal/metal-oxide composite by dealloying metallic glass for high-performance energy storage

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ABSTRACT

A free-standing nanoporous YNiCo metal/metal-oxide composite with hierarchical porosity is fabricated by chemically dealloying $Al_{85}Y_6Ni_6Co_3$ metallic glass in alkaline solutions. The mixed core–shell-like metal/metal-oxide structure formed during dealloying due to the active properties of these metals. Time-dependent etching experiments suggest that the formation of large and small pores occur simultaneously, which may be related to the different dissolution rate of Al at different sites. The nanoporous composite with a highly conductive metal core exhibits a high areal capacitance. Moreover, this strategy can be extended to fabricate other nanoporous composites considering that the composition of metallic glass can be easily tuned.

1. Introduction

Nanoporous metals have attracted growing research interests in both potential applications and theoretical studies owing to their unique physicochemical properties such as interconnected interior voids, large surface areas and high catalytic activities [1–4]. A general route toward nanoporous metal involves the deposition of a shell of designed metal on removable templates. The use of the templates in principle allows one to manipulate the morphology and pore size by controlling the templates. However, the templating method is relatively complex, which requires multi-step treatment. Recently, dealloying (i.e., selective removal of one active component from an alloy) has been demonstrated to be a good strategy to fabricate nanoporous metals with three dimensional (3D) ligament-pore structure due to the simplicity and high efficiency [2,3,5–8]. To prepare uniform nanoporous metals by dealloying, it is essential to design suitable precursors, which satisfy two basic requirements: homogeneous single phases and a large electrochemical potential difference between the alloy components [9]. Since dealloying is essentially an etching process under relatively harsh conditions, the dealloying strategy is usually limited to produce nanoporous noble metals such as Pt, Pd, Au, Ag and their alloys due to their high chemical stability [1,2,10]. Driven by low-cost practical applications such as electrochemical energy storage, developing economic nanoporous transition metals, such as nickel, has been the topics of recent studies [11–15]. For example, uniform nanoporous Ni and NiCu alloy have been prepared recently as supercapacitor electrodes by dealloying single-phase NiMn and NiCuMn alloy [11,12]. Besides Mn-based precursors, Al-based precursor should also be a good choice for the fabrication of nanoporous active metals because the dealloying Al-based precursors can be carried out in alkaline solutions where many other active metals can be preserved. One successful example is Raney nickel which is prepared by dealloying NiAl alloy in alkaline solutions [16]. However, the Al-based alloys often contain many intermetallic phases [17], which is not favorable for the fabrication of uniform and monolithic nanoporous metals for energy-storage electrodes.

The limited single-phase crystalline Al alloys inhibit the development of dealloyed nanoporous metals. Compared with crystallized precursors (i.e., alloys), metallic glasses with multi-component (i.e., containing 2–6 elements) show monolithic and isotropic phase with a homogeneous composition and structure down to nanoscale [18,19]. Due to the metastable far-from-equilibrium nature, the composition of metallic glasses can be tuned continuously in a wide composition range. Thousands of metallic glasses have been fabricated in different alloy systems [20]. These combined properties of metallic glasses provide a promising route to obtain nanoporous metals with uniform microstructure by dealloying. The use of metallic glasses as precursors to fabricate

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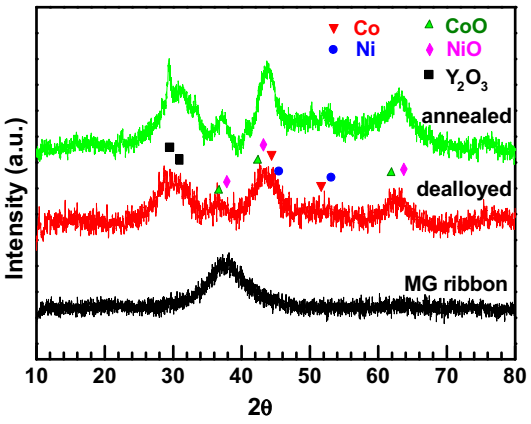

Fig. 1. XRD patterns of AlYNiCo MG ribbon (black), as-dealloyed np-YNiCo in 2 M NaOH (red) and annealed np-YNiCo at 400 °C for 1 h (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

nanoporous noble metals, such as Pd, Au and Cu, has been demonstrated in previous work [21–25]. However, the fabrication of technically important but chemically active metals, such as Ni and Co by dealloying metallic glasses for electrochemical energy storage, is still a challenging target. In this work, we fabricated nanoporous $Y_{40}Ni_{40}Co_{20}$ (np-YNiCo) by dealloying an $Al_{85}Y_6Ni_6Co_3$ metallic glass (MG). As a binder-free supercapacitor electrode, the as-prepared np-YNiCo with a conductive ligament network and naturally formed metal oxide films exhibits a high and stable capacitance.

2. Experimental

Pure metals with high purity (>99.9 wt.%) were designed with the nominal composition of $Al_{85}Y_6Ni_6Co_3$ (at.%) and melted in BN crucible using an induction-melting furnace. The master alloy was remelted in a quartz tube and subsequently injected onto a rotating Cu wheel to obtain metallic glass ribbon with a thickness of about 20 μm. The dealloying of the metallic glass precursor was carried out in NaOH aqueous solutions with different concentrations at room temperature. After dealloying, the samples were rinsed with deionized water.

The crystal structure of the precursor alloys and dealloyed samples were characterized by X-ray diffraction using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The microstructures of the dealloyed samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010F) and

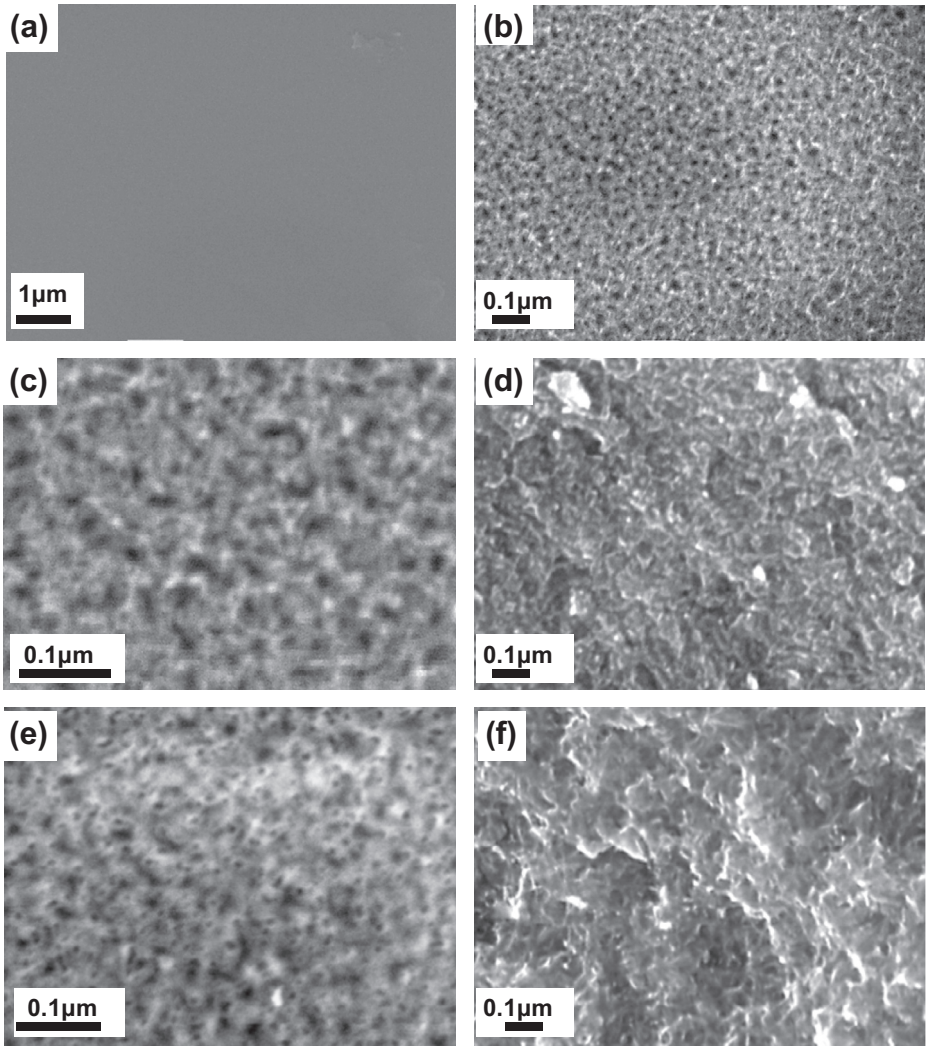

Fig. 2. SEM image of the AlYNiCo precursor (a); SEM images of the np-YNiCo obtained by dealloying in 2 M NaOH solution ((b) low magnification plane-view image; (c) high magnification plane-view image; (d) section-view image); SEM images of the np-YNiCo obtained in 1 M NaOH aqueous solution ((e) plane-view image; (f) section-view image).