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Fabrication of nanosheets Co_3O_4 by oxidation-assisted dealloying method for high capacity supercapacitors

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ABSTRACT

Co_3O_4 nanosheets were straightforwardly fabricated through in-situ dealloying and oxidation process of etching $Al_{65}Co_{35}$ alloy in 1 M NaOH solutions. It exhibited a high specific capacitance of 5747 mF cm^{-2} at a current density of 5 mA cm^{-2} and good rate capability. Meanwhile, the capacitance retention keeps about 108.7% of the initial value after 1000 cycles at a current density of 30 mA cm^{-2}. The simple synthetic process and all these impressive results demonstrated that the Co_3O_4 electrode with flower-like nanoplates is promising for practical applications in supercapacitors.

1. Introduction

High-performance pseudocapacitors are considered to be one of the most promising energy storage devices due to their high specific capacitance [1]. Transition metal oxides and hydroxides, such as MnO_2, Co_3O_4, CoO, NiO and $Ni(OH)_2$ are promising pseudocapacitive materials because of their high theoretical capacitance from surface reversible redox reactions [2–4]. Among these pseudocapacitive materials mentioned above, Co_3O_4 is appropriate candidate for application in electrochemical capacitors because this oxide owns advantage of low cost, great reversibility, and high specific capacitance (3560 F g^{-1}). However, it is still a great challenge to make a balance between excellent pseudocapacitive performance and simplicity of the synthetic pathway.

To solve this problem, a mount of efforts have been carried out to develop three-dimensional (3D) charge conducting nanostructures such as nanostructured carbon [5], nanoporous gold [6] and Ni-foam [7], which all have been used to enhance the conductivity of the pseudocapacitive oxide materials. But the enhancement of the oxide conductivity by additives and binders is often limited by weak oxide/conductor interfaces [8]. Besides, most of these synthetic methods involve more than two steps that make them unsuitable for large-scale synthesis. Thus, it is desirable to develop a simple and facile method to synthesize transition metal oxides with well rational designed architectures. Considering the practical applications, the dealloying approach has been received increasing attention because it is capable of fabricating nanoporous metals by one-step chemical/electrochemical etching. The pore size, porosity and chemical composition of the dealloyed nanoporous metals can be tailored by controlling dealloying condition and precursor composition. Numerous researches have been reported about the dealloyed nanoporous Ni with a large internal surface area, excellent conductivity and naturally formed oxide surface. Because of these characteristics, Ni dealloyed can be directly used as a free-standing electrode for electrochemical supercapacitors [9]. To prepare uniform nanoporous metals by dealloying, it is essential to design suitable precursors, which needs to satisfy two basic requirements: homogeneous single phases and a large electrochemical potential difference between the alloy components.

Our recent works have demonstrated that fabrication of nanosheets Co_3O_4 by one-pot oxidation-assisted dealloying route presents high capacity supercapacitor and excellent cycling stability. In recent years, a wide variety of microstructures and morphologies composed of 1D and 3D nanostructures have been synthesized and tested for capacitance study. However, to the best of our knowledge, there is no report on the electrochemical performance of Co_3O_4 nanostructures by in-situ dealloying in supercapacitor until now. Herein, we report the large-scale etching synthesis of nanosheets Co_3O_4 nanostructures for the first time. These as-prepared nanostructures were composed of many 2D nanoplates with average thickness of 10–30 nm. In summary, our work not only presents a feasible access to synthesize Co_3O_4 nanoslices but also promotes researchers to pay more attention to the simple synthetic method.

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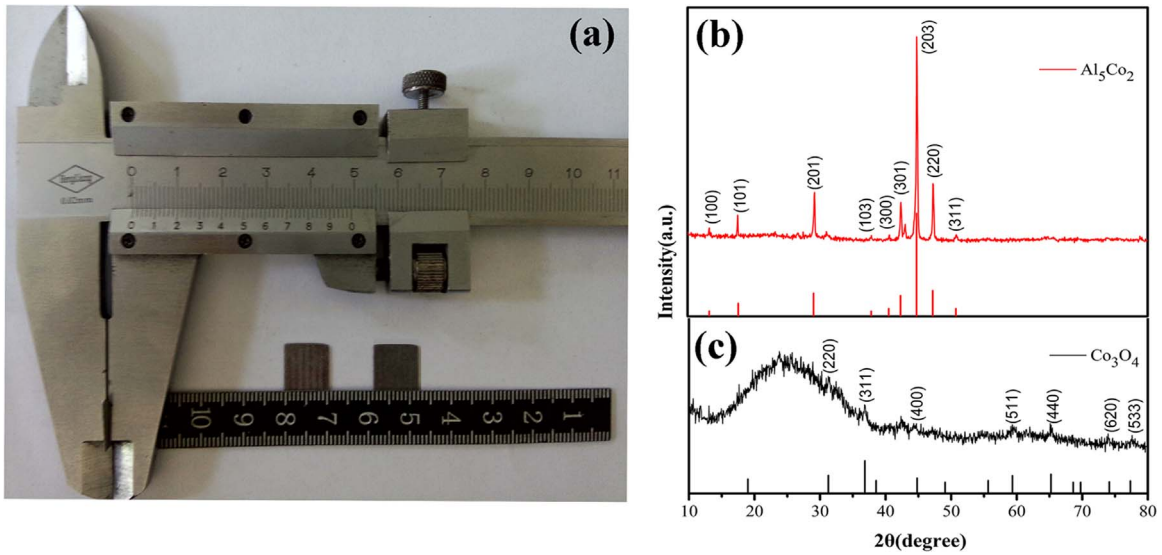

Fig. 1. Photo of the $Al_{65}Co_{35}$ alloy sheets (a), XRD patterns of the $Al_{65}Co_{35}$ precursor before (b) and after dealloying (c).

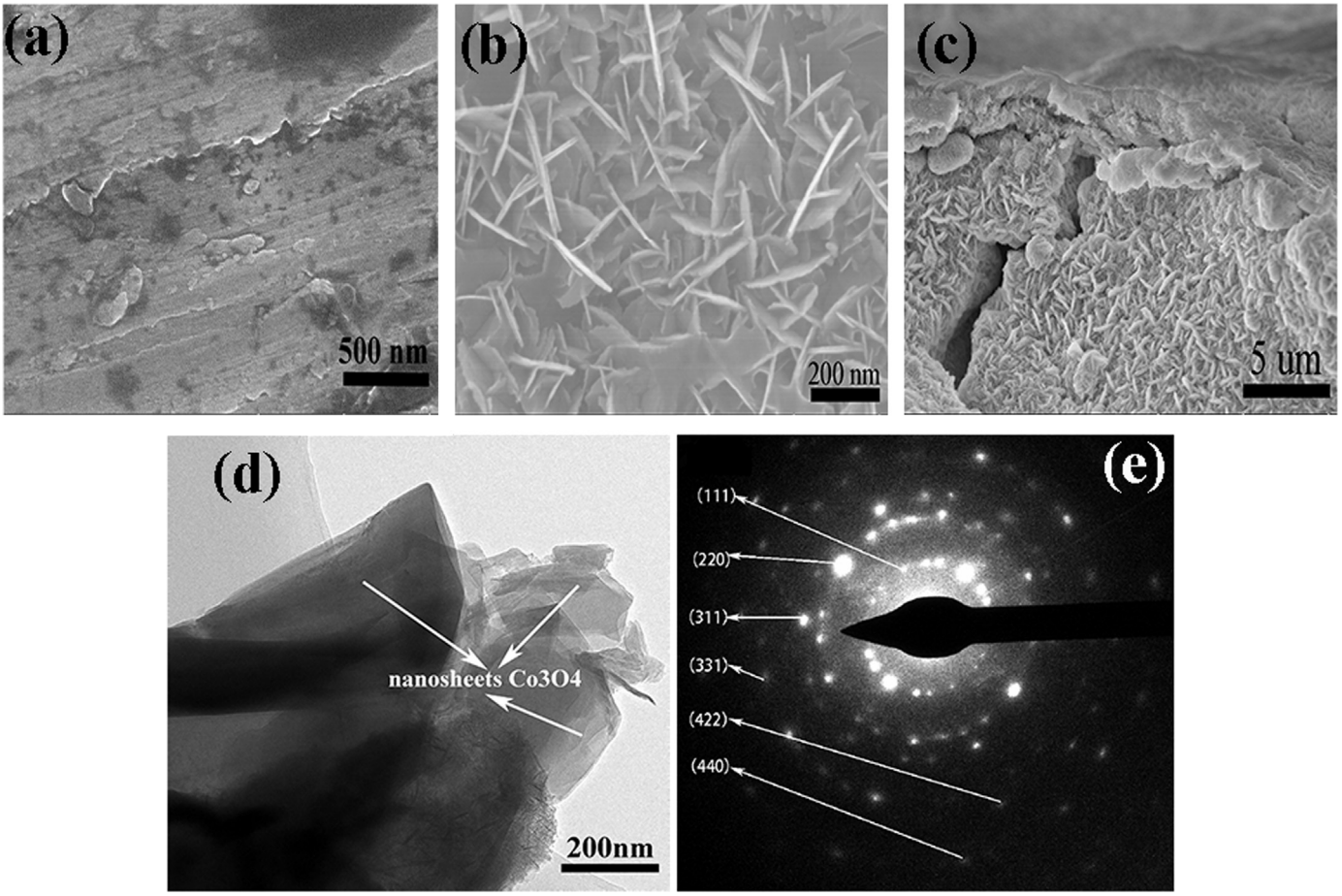

Fig. 2. SEM image of the Al_5Co_2 precursor (a); SEM images of the nanosheets CO_3O_4 obtained by dealloying in 1 M NaOH (b: plane view; c: section view), Bright-field TEM (d), and SAED pattern (e).

2. Experimental procedure

2.1. Sample preparation

Al–Co alloy with nominal composition of 35 at% Co was prepared from pure Al (99.99 wt%) and pure Co (99.999 wt%). Voltaic arc heating was employed to melt the charges in a copper crucible under an argon atmosphere, and then the melt was cooled down into ingots in situ. The electrode samples with sizes of $10 \times 10 \times 0.3$ mm were prepared by wire cutting process (in Fig. 1a). Then, the $Al_{65}Co_{35}$ alloy sheets were immersed in 1 M NaOH solution under a free corrosion condition at 40 °C for 4 h. Finally, the dealloyed flakes were taken out and well rinsed with distilled water and dehydrated alcohol to remove the residual