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Conformal construction of polyaniline shell on cobalt oxide nanoflake core for enhanced Li ion storage

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ABSTRACT

It is of great importance to controllably synthesize non-axial metal oxide/conducting polymers arrays for construction of high-performance electrochemical devices. In this work, we develop a facile electro-polymerization method to conformally coat interwoven polyaniline (PANI) shell on the preformed porous Co_3O_4 nanoflakes forming non-axial Co_3O_4/PANI core/shell arrays. Uniform conductive PANI network and high porosity are realized in the non-axial core/shell arrays. As active materials for Li ion storage, the Co_3O_4/PANI core/shell arrays show superior high-rate performance including lower polarization, higher reactivity and better cycling life, as compared to the unmodified Co_3O_4 nanoflake arrays. The capacity deterioration of the Co_3O_4/PANI arrays is restricted to a very lower level with a capacity of 871 mAh g^{-1} at 0.25 A g^{-1} after 100 cycles, better than the Co_3O_4 counterpart (669 mAh g^{-1} at 0.25 A g^{-1}). This non-axial combination opens up a new door for developing advanced composite arrays for energy storage.

1. Introduction

Rational construction of active organic-inorganic composites is highly important for the advancement of electrochemical energy storage because of their potential reinforcement effects for capacity and rate capability [1–4]. Integrated metal oxide/conducting polymers (CPs) arrays are becoming one of the most popular electrode forms due to binder-free and additive-free characteristics. Particularly, sophisticated integration of conducting polymers (such as polyaniline (PANI)) and metal oxides (e.g., Co_3O_4) into a tailored core/shell array structure is highly attractive due to that they can modify each other to obtain enhanced transfer path of electrons and better volume buffer layer arising from CPs [5–7]. The current challenge is to directionally fabricate metal oxide/CPs composites that keep or enhance the best properties of both components while eliminating or reducing their particular limitations [1,8–11]. Hence, facile and directional synthetic strategies are highly desirable.

To date, there are two common ways to assemble CPs on metal oxides. The first way is chemical polymerization [12], which is usually adopted to prepare powder composites. But it is difficult to control the precise morphology because of the complex reaction conditions. The second one is electro-polymerization [13,14], which possesses unique flexibility in the control of morphology of the final products via accurate choice of electrolyte and electrodeposition conditions. Electro-polymerization is considered to be an ideal method for preparation of metal oxide/CPs composite arrays. Over recent years, metal oxide/CPs core/shell arrays have been widely studied and enhanced electrochemical performance has been demonstrated in different electro-polymerized systems including CoO/polypyrrole (PPY) [15], TiO_2/polyaniline (PANI) [16], NiO/PANI [17], NiO/PEDOT [18], cobalt oxide/PEDOT [16], because the composite interface/chemical distributions are homogeneous and electron/ion transfer are greatly improved [1]. However, the above metal oxide/CPs core/shell arrays are focused on coaxial arrays, not non-coaxial. It is known that electron transfer and structural stability would be reinforced on lengthwise at coaxial core/shell arrays with the help of CPs [19], but still weak on transverse. Therefore, it would be very interesting to fabricate non-coaxial metal oxide/CPs core/shell arrays with new electrical/electrochemical properties on both lengthwise and transverse for electrochemical energy storage.

Free-standing cobalt oxide (Co_3O_4) nanoarrays have been widely studied as active materials for electrochromics [20], electro-catalysis [21], supercapacitors [22,23], and lithium ion batteries [24]. Previously, we reported coaxial Co_3O_4/CPs core/shell arrays with coaxial nanowire structure [16]. In this work, we report

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a facile method for conformal deposition of PANI shell on Co_3O_4 nanoflake core forming non-axial Co_3O_4/PANI core/shell arrays. Non-axial interwoven PANI conductive shell is realized by the electro-polymerization. Compared to the unmodified Co_3O_4 nanoflake arrays, the designed non-axial Co_3O_4/PANI core/shell arrays show improved high-rate capacity and long-term cycles due to the unique non-coaxial structure with accelerated electron/ion transfer and better structural stability. The developed synthetic strategy can be used to prepare other non-axial metal oxide/CPs composite arrays for application in energy storage and catalysis.

2. Experimental

2.1. Preparation of non-axial Co_3O_4/PANI core/shell arrays

Firstly, the porous Co_3O_4 nanoflake arrays were prepared by a facile hydrothermal synthesis method as follows. The reaction solution was composed of 7.5 mmol of $Co(NO_3)_2$ and 37.5 mmol urea in 75 ml of distilled water, and then transferred into Teflon-lined stainless autoclave liners. Nickel foam substrates were immersed into the reaction solution. After growth for 12 h at 95 °C, the samples were rinsed and then annealed at 450 °C in argon for 3 h to obtain self-supported porous Co_3O_4 nanoflake arrays. Then, the non-axial Co_3O_4/PANI core/shell arrays were fabricated by the following electro-polymerization method. The Co_3O_4 nanoflake arrays were acted the backbone for the growth of PANI shell. Electrolyte for electro-polymerization of PANI was obtained by dissolving 1 ml aniline into 150 ml of 0.05 M H_2SO_4 solution. The electro-polymerization of PANI was carried out in a three-compartment system, the above Co_3O_4 nanoflake arrays electrode as the working electrode, Ag/AgCl as the reference electrode and a Pt foil as the counter-electrode. The PANI film was deposited by applying constant anodic current density of 3 mA cm^{-2} for 1800s to form the final non-axial Co_3O_4/PANI core/shell arrays.

2.2. Characterizations

The samples were characterized by X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation), field emission scanning electron microscopy (FESEM, FEI SIRION), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F)

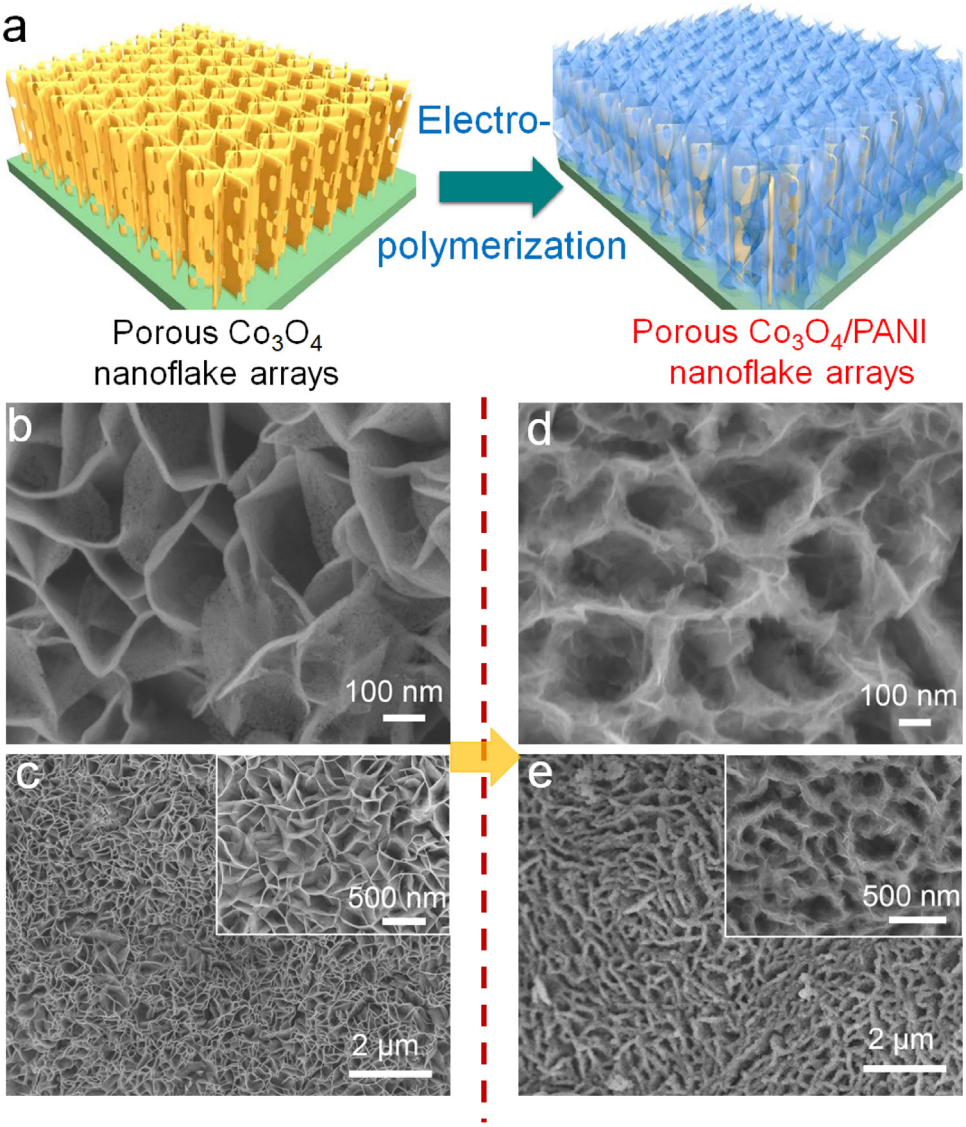

Fig. 1. (a) Schematics of growth of non-axial Co_3O_4/PANI core/shell arrays. SEM images of (b, c) porous Co_3O_4 nanoflake arrays and (d, e) non-axial Co_3O_4/PANI core/shell arrays.