Journal of Power Sources 390 (2018) 208–214

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Layer-by-layer self-assembled two-dimensional MXene/layered double hydroxide composites as cathode for alkaline hybrid batteries

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HIGHLIGHTS

- $Ti_3C_2T_x$/CoAl-LDH composites were prepared by layer-by-layer self-assembly.
- Two different nanosheets self-assemble and form 2D heterostructure.
- Composite combines high conductivity and high electrochemical activity.
- $Ti_3C_2T_x$/CoAl-LDH shows excellent properties for alkaline hybrid batteries.

ARTICLE INFO

Keywords:
Self-assembly
Heterostructure
Layered double hydroxide
MXene
Energy storage

ABSTRACT

Multifarious layered materials have received extensive concern in the field of energy storage due to their distinctive two-dimensional (2D) structure. However, the natural tendency to be re-superimposed and the inherent disadvantages of a single 2D material significantly limit their performance. In this work, the delaminated $Ti_3C_2T_x$ (d-$Ti_3C_2T_x$)/cobalt-aluminum layered double hydroxide ($Ti_3C_2T_x$/CoAl-LDH) composites are prepared by layer-by-layer self-assembly driven by electrostatic interaction. The alternate $Ti_3C_2T_x$ and CoAl-LDH layers prevent each other from restacking and the obtained $Ti_3C_2T_x$/CoAl-LDH heterostructure combine the advantages of high electron conductivity of $Ti_3C_2T_x$ and high electrochemical activity of CoAl-LDH, thus effectively improving the electrochemical reactivity of electrode materials and accelerating the kinetics of Faraday reaction. As a consequence, as a cathode for alkaline hybrid battery, the $Ti_3C_2T_x$/CoAl-LDH electrode exhibits a high specific capacity of 106 mAh g^{-1} at a current density of 0.5 A g^{-1} and excellent rate capability (78% at 10 A g^{-1}), with an excellent cycling stability of 90% retention after 5000 cycles at 4 A g^{-1}. This work provides an alternative route to design advanced 2D electrode materials, thus exploiting their full potentials for alkaline hybrid batteries.

1. Introduction

Two-dimensional (2D) layered materials have attracted extensive concern in many fields, such as energy storage and conversion, catalysis, optoelectronics and nanoelectronics due to their intriguing physical and chemical properties that are different from their bulk counterparts [1–5]. Inspired by the fascinating properties of 2D layered materials, multifarious inorganic 2D nanosheets have been synthesized and investigated, including graphene [6,7], transition metal dichalcogenides [8,9], transition metal oxides and hydroxides [10,11], metal carbides (MXenes) [12,13] and so on. Layered double hydroxides (LDHs) [14–17], which is represented by a generic formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\cdot mH_2O$ (M represents divalent/trivalent heterogeneous metal cations, and A represents anions), is a kind of typical 2D material. It consists of alternately stacked positively charged host layers and weakly bound charge-balanced intermediate anions. Divalent/trivalent heterogeneous metal cations are sandwiched between two hydroxyl plates compose each host layer. Simultaneously, the interlayer hydration anions locate above/below the trivalent cationic charge centers to equilibrate the positive host charge [18,19]. More importantly, LDHs can be delaminated into single-layer nanosheets with the adjustment of interlayer anion, which is able to improve their properties from the accessible high surface area and unique positively charged feature [14,20,21]. However, the natural restacking tendency of LDHs can result in serious side effects for its practical applications. Additionally, the poor conductivity of LDHs is another main

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https://doi.org/10.1016/j.jpowsour.2018.04.058
Received 11 January 2018; Received in revised form 27 March 2018; Accepted 15 April 2018

disadvantage to limit their practical performance. Therefore, designing well-defined heterostructures with two different 2D nanosheets materials is an effective way to solve these problems and also explores the full potential of these layered materials [22]. For instance, Long et al. assembled a hybrid catalyst exhibited advanced electrocatalytic activity and stability on OER in alkaline solution by alternately stacking the FeNi double hydroxide cation layers with the negatively charged GO layers [23]. Some research efforts of making composite materials have been done in the field of energy storage, recently. For example, Ma et al. successfully prepared genuine superlattice nanocomposites by electrostatic heteroassembly of cationic transition-metal (Co-Al, Co-Ni) LDH nanosheets and anionic GO/rGO nanosheets [10]. The as-prepared superlattice nanocomposites achieved a high capacity up to ca. 650 F g^{-1} as an active electrode material. However, the GO or rGO has a low specific capacitance due to the absence of a redox reaction, which would reduce the energy density of the composite material. Furthermore, the rGO has to be reduced from GO in a further step and it does not show very good electrical conductivity if not completely reduced.

Recently, novel 2D metal carbides and carbonitrides named MXenes by Gogotsi and *co*-works [24,25], which mostly exhibit unique structure, metallic conductivity and hydrophilic surface have attracted wide attention. MXenes ($Ti_3C_2T_x$, Ti_2CT_x, Nb_2CT_x, V_2CT_x, Ti_3CNT_x and Mo_2CT_x, *etc.*) were produced by selective etching of the A element layers from the ternary carbides and nitrides $M_{n+1}AX_n$ with a general formula of $M_{n+1}X_nT_x$, where M is an early transition metal, X is C and/or N, T is a surface terminating functionality typically to be F, O, and OH, and n = 1 to 3. Due to their ultrahigh electrical conductivity up to 150,000 S m^{-1}, MXenes may offer a replacement for carbon-based material in hybrid electrodes [12,26–30]. As the most well researched one, $Ti_3C_2T_x$ has been combined with carbon nanomaterials, metal oxides and conducting polymers to manufacture composite materials in order to improve their electrical conductivity for the enhancing electrochemical properties [31–35]. For instance, Zhao et al. achieved the hybridization of $Ti_3C_2T_x$ with Co_3O_4 or $NiCo_2O_4$. Used as anodes in LIBs, the fabricated composites exhibited excellent reversible capacities [32].

In this work, heterostructures of $Ti_3C_2T_x$/cobalt-aluminum layered double hydroxide composite ($Ti_3C_2T_x$/CoAl-LDH) were skillfully fabricated through the self-assembling method due to the electrostatic interaction between the delaminated $Ti_3C_2T_x$ (d-$Ti_3C_2T_x$) and the delaminated LDH (d-LDH). The negative charged d-$Ti_3C_2T_x$ and the positive charged d-LDH form nanosheet-like 2D morphology with a highly ordered heterogeneous structure and the obtained $Ti_3C_2T_x$/CoAl-LDH heterostructures combine the advantages of high electron conductivity of $Ti_3C_2T_x$ and high electrochemical activity of CoAl-LDH. Benefiting from fast electron/ion transport and integrated structure, the obtained $Ti_3C_2T_x$/CoAl-LDH electrode delivers a high specific capacity of 106 mAh g^{-1} at a current density of 0.5 A g^{-1} with excellent rate capability and outstanding cycling stability.

2. Experimental

2.1. Fabrication of $Ti_3C_2T_x$/CoAl-LDH composite

The 0.8 mg mL^{-1} d-LDH and 0.5 mg mL^{-1} d-$Ti_3C_2T_x$ colloidal solutions were gained as described in Supplementary Materials. Mixing the d-LDH and d-$Ti_3C_2T_x$ colloidal solutions together according to different proportions, positively charged d-LDH layers and negatively charged d-$Ti_3C_2T_x$ layers spontaneously assemble to form $Ti_3C_2T_x$/CoAl-LDH composite through the electrostatic interaction. Typically, different volumes d-LDH colloidal solution and 200 mL of d-$Ti_3C_2T_x$ colloidal solution were mixed together in a conical beaker and stirred under flowing N_2 for 12 h. Subsequently, the product was centrifuged, washed several times with deionized water and absolute ethanol, and then dried in a vacuum oven at 30 °C for 24 h. When the volumes of d-LDH colloidal solution are 125, 250, 375 and 500 mL, the weight percentage of CoAl-LDH in $Ti_3C_2T_x$/CoAl-LDH composites are 50%, 67%, 75% and 80%, respectively. The $Ti_3C_2T_x$/CoAl-LDH composites were correspondingly denoted as L1T1, L2T1, L3T1 and L4T1, respectively.

2.2. Material characterization

The crystallographic structures of the materials were determined through X-ray diffraction (XRD) by a Bruker D8 Advanced X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer PHI 550 spectrometer using an X-ray source of Al Kα, all data collection and processing were done on XPSPEAK software. The morphologies of samples were investigated by scanning electron microscope (SEM, Hitachi S4800), transmission electron microscopy and high-resolution transmission electron microscopy (TEM, HRTEM, JEOL JEM-2010). The d-$Ti_3C_2T_x$ or d-LDH nanosheets for SEM were prepared by dropping the colloidal solution of d-$Ti_3C_2T_x$ or d-LDH on an alumina filter substrate. The ζ-potential was measured using a particle size analyzer (Zetasizer NanoZS, Malvern).

2.3. Electrochemical measurements

All measurements of electrochemical properties were carried out using a three-electrode system in a 6 M KOH electrolyte at room temperature. The working electrodes were fabricated by pressing the as-prepared composites (85 wt%), carbon black (10 wt%) and a polytetrafluoroethylene (PTFE) binder (5 wt%) onto the nickel foam current collectors (1 cm × 1 cm) with a spatula and then dried at 40 °C for 12 h in the vacuum oven. The mass loading of the electrode materials was about 5 mg cm^{-2}. Platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The cyclic voltammetry (CV) was measured by a CHI 660C electrochemical workstation and the galvanostatic charge/discharge (GCD) measurements were performed on a LAND battery program-control test system. In the three-electrode system, the specific capacity (C, mAh g^{-1}) of the electrode can be calculated from the galvanostatic discharge curves according to the following equation:

$$C = Q/M = I(\Delta t/3600)/M = I\Delta t/(3600M) \tag{1}$$

where Q, I, Δt, M are the quantity of charge, constant current (mA), the discharge time (s), the mass of active material in the electrode (g), respectively.

3. Results and discussion

Fig. 1 schematically illustrates the synthetic process of $Ti_3C_2T_x$/CoAl-LDH composite. Firstly, CoAl-LDH was prepared through the assist of urea under refluxing conditions. The as-prepared CO_3^{2-}-LDH is hard to exfoliate in formamide while NO_3^--LDH is easy. So CO_3^{2-}-LDH was transformed to NO_3^--LDH by a two-step ion exchange process with salts of Cl^- and NO_3^-. After vigorous stirring, positively charged d-LDH layers dispersion in formamide was gained. The obtained d-LDH colloidal solution was stored for use in subsequent experimental steps. Meanwhile, MAX (Ti_3AlC_2) was selectively etched out Al layer to obtain the $Ti_3C_2T_x$ plates, which T is −O, −OH and −F functional groups. $Ti_3C_2T_x$ plates were successfully delaminated by centrifugation to produce d-$Ti_3C_2T_x$ sheets after TMA$^+$ ions intercalating between galleries of $Ti_3C_2T_x$. Then, positively charged d-LDH layers (zeta potential: +37 mV) and negatively charged d-$Ti_3C_2T_x$ layers (zeta potential: −35 mV) were layer-by-layer self-assembled to $Ti_3C_2T_x$/CoAl-LDH heterostructure through the electrostatic interaction.

The morphologies of the resulting samples were observed by SEM and TEM. As shown in Fig. 2a, the obviously layered structure illustrates that the Al layers were selectively and effectively etched forming $Ti_3C_2T_x$ plates. After exfoliation, the d-$Ti_3C_2T_x$ nanosheets were