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Research Paper

Synergistic Effect of Core-Shell Heterogeneous V_2O_5@MV_6O_{15} (M = Na, K) Nanoparticles for Enhanced Lithium Storage Performance

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ABSTRACT

Synergistic effects of heterostructures can improve electrochemical properties of electrode materials. Herein, core-shell heterogeneous structures of V_2O_5@MV_6O_{15} (M = Na, K) nanoparticles were designed and successfully synthesized through a facile "semi-solid" method. V_2O_5@NaV_6O_{15} nanoparticles showed a high discharge capacity of 140 mAh g^{-1} at 200 mA g^{-1} which retained 94.9% after 200 cycles, higher than those of V_2O_5 nanoparticles (116.1 mAh g^{-1} and 58%). Moreover, through an advanced *in-situ* XRD technology, the synergistic effect of buffering and smoothing Li^+ diffusion from MV_6O_{15} outer layer was revealed. This facile strategy could be widely applied to improve the electrochemical performances of other electrode materials.

1. Introduction

Energy storage systems based on lithium-ion batteries (LIBs) are one of the most suitable and promising candidates for portable electronic devices [1]. However, the energy/power density, rate performance and energy efficiency of the current commercial LIBs still need to be improved to meet the growing demand of energy storage systems in the applications of electric vehicles (EVs), hybrid electric vehicles (HEVs) and etc [2–4]. For example, most of the promising cathode materials suffer from poor structural stability, low electronic/ionic conductivity and inert electrochemical kinetics, such as sulfur, NMC materials, transition metal fluorides and vanadium pentoxide (V_2O_5) [5–9], which result in low rate performance and energy efficiency, as well as limited cycling life in LIBs. Therefore, development of high-performance electrodes without above drawbacks through facile strategies such as complex structural design, nanotechnology and composite materials is hotspot and frontier in the energy storage field [6–11].

Recently, constructing heterostructures which was widely studied in energy storage systems has been demonstrated as an effective strategy to enhance the electrochemical properties for cathode materials in both LIBs and sodium-ion batteries (SIBs) [12–15]. Lee et al. constructed a layered P2/O3 intergrowth cathode for SIBs, which was interlocked from the layer shifting. The beneficial synergistic effect from the intergrowth structure promoting the smooth diffusion of Na^+ under a high rate testing was revealed by an *in-situ* synchrotron X-ray diffraction (XRD) study [13]. Wu et al. reported a $Li(Ni_xMn_yCo_z)O_2$@$LiFePO_4$ core-shell nanostructure with an atomic interdiffusion at the interface and an array of interconnected aligned Li^+ tunnels, which showed a high reversible capacity when used as a cathode in LIBs [14]. V_2O_5, a typical layered transition metal oxide, has attracted much attention for decades on account of its relatively high theoretical capacity, abundant resources and low cost, but it also suffers from the aforementioned problems of poor cycling stability in LIBs [8–11]. By contrast, MV_6O_{15} (M = Na, K) vanadates with "pillar-like" ions between the V-O interlayers and higher electronic conductivity show a more stable crystal structure and satisfactory cycling performance, and provide a faster Li^+ diffusion path, but deliver low capacity (Fig. S1) in LIBs [18–20,29]. Therefore, to combine the merits from heterostructures and MV_6O_{15}, well designing of core-shell

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heterogeneous V_2O_5@MV_6O_{15} nanoparticles (NPs) as cathode materials is expected to be able to enhance the electrochemical performances via a biphase synergistic effect.

Herein, utilizing a simple "semi-solid" method based on highly concentrated solution, we designed and constructed core-shell heterogeneous structures of V_2O_5@NaV_6O_{15} and V_2O_5@KV_6O_{15} NPs. When tested as cathodes in LIBs, both the core-shell heterogeneous structured NPs exhibit higher specific capacity, longer lifespan, as well as better rate capability compared to bare V_2O_5 NPs. Moreover, *in-situ* XRD tests were conducted and a synergistic effect (i.e. buffering and smoothing Li^+ diffusion) of the MV_6O_{15} outer layer was revealed, which accounts for the excellent lithium storage performance.

2. Experimental

2.1. Material

Vanadium pentoxide (V_2O_5, AR, Xiya reagent Corporation, China), oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$, AR, Sinopharm Group Chemical Reagent Co., Ltd., China), potassium citrate tribasic monohydrate ($K_3C_6H_5O_7{\cdot}H_2O$, AR, Sinopharm Group Chemical Reagent Co., Ltd., China), trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, GR, Sinopharm Group Chemical Reagent Co., Ltd., China) and sodium alginate ($(C_6H_7NaO_6)_n$, CP, Sinopharm Group Chemical Reagent Co., Ltd., China) were purchased and used without any purification.

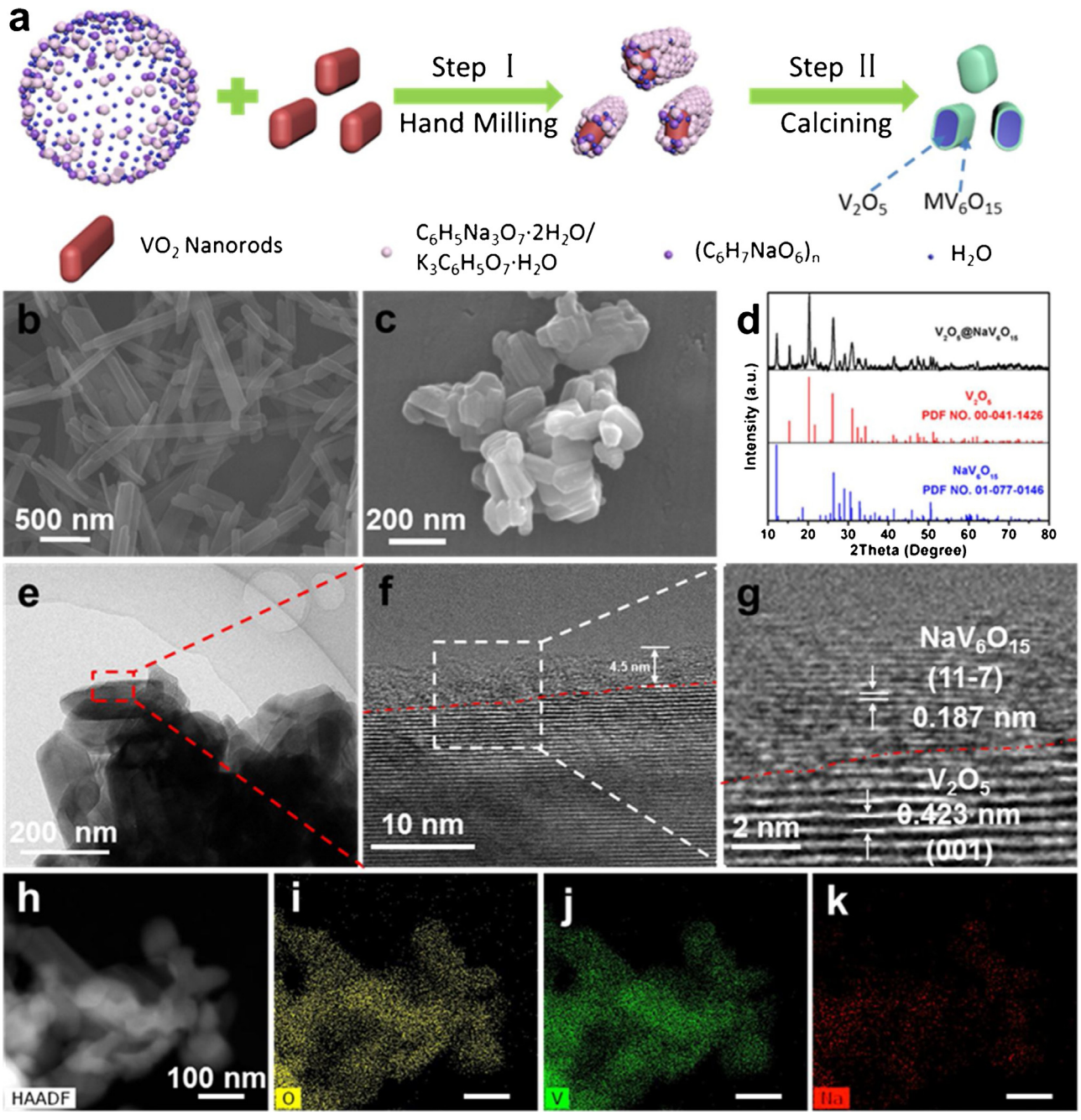

Fig. 1. (a) Schematic diagrams of the formation process of core-shell heterogeneous V_2O_5@MV_6O_{15} NPs. SEM images of as-prepared (b) VO_2 nanorods, (c) V_2O_5@NaV_6O_{15} NPs. (d) XRD pattern of V_2O_5@NaV_6O_{15} NPs. (e) TEM and (f, g) HRTEM images of V_2O_5@NaV_6O_{15} NPs. (h-k) HAADF images with mapping of as-prepared V_2O_5@NaV_6O_{15} NPs.