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Short communication

Sol–gel synthesis of $K_{1.33}Mn_8O_{16}$ nanorods and their applications for aqueous K-ion hybrid supercapacitors

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ABSTRACT

$K_{1.33}Mn_8O_{16}$ nanorods were successfully prepared by a facile sol–gel method with $KHCO_3$, $Mn(Ac)_2$ and citrate acid as raw materials. The cyclic voltammetry results demonstrate that the $K_{1.33}Mn_8O_{16}$ nanorods exhibit a quasi-reversible K^+ intercalation/deintercalation behavior in a 0.5 M K_2SO_4 aqueous solution. It has also been found that the assembled activated carbon (AC)//$K_{1.33}Mn_8O_{16}$ asymmetric hybrid supercapacitor delivers an energy density of 17.74 Wh kg^{-1} at a power density of 210 W kg^{-1}, and an energy density of 8.18 Wh kg^{-1} at a high power density of 2124 W kg^{-1}. Moreover, the AC//$K_{1.33}Mn_8O_{16}$ supercapacitor shows a good cycling property. To the best of our knowledge, the synthesis of $K_{1.33}Mn_8O_{16}$ nanorods *via* the sol–gel route and the use of $K_{1.33}Mn_8O_{16}$ in supercapacitors are reported for the first time.

1. Introduction

Recently, mineral compounds with diversified structures have been attracting considerable attention for their uses as energy storage materials [1–4]. Strikingly, Mn-based alkali metal ion intercalation compounds with a general molecular formula expression of A_xMnO_2 ($A = Li$, Na, K; $0 < x < 1$) have shown promising applications in electrochemical energy storage and conversion [5–8]. In particular, Na_xMnO_2 and K_xMnO_2 have substantially hove into view as novel energy storage and conversion materials due to higher abundance of both Na and K elements than Li element. Moreover, the introductions of large Na^+ and K^+ into the interlayer space of MnO_2 can effectively stabilize the layered structure of MnO_2 over the small Li^+ [9]. Hence, K_xMnO_2 has stirred up interests as active materials for the energy storage devices such as supercapacitors [9,10] and Mg-ion batteries [11,12].

MnO_2 holds diversified tunnel and layered crystal structures, and therefore the insertion of K^+ can constitute a large family of Mn-based K^+ intercalation compounds [13]. As one of Mn-based K^+ intercalation compounds, the artificial $K_{1.33}Mn_8O_{16}$ was first synthesized *via* the molten salt electrolysis by Strobel et al., which exhibits a hollandite-like tunnel structure with the space group of $I4/m$ [14,15]. $K_{1.33}Mn_8O_{16}$ can be also synthesized by the hydrothermal method [16]. However, the synthesis of $K_{1.33}Mn_8O_{16}$ by a sol–gel route has not been documented. As well known, the sol–gel process is of great scientific interest in terms of high purity, stoichiometry, ultrahomogeneity and low sintering temperature.

Among diverse energy storage devices, supercapacitors have attracted legion researchers' attention and effort owing to their high specific powers, fast charge/discharge rates and long cyclelives [17–19]. They are considered as a good complement to batteries, and even in many applications can replace them [20]. Recently, some neutral alkaline metal sulphate aqueous solutions as electrolytes for supercapacitors have received considerable popularity thanks to the wide electrochemical potential window, non-corrosiveness and low cost [21–23]. Consequently, it is quite necessary to investigate the electrochemical performances of active materials in alkaline metal sulphate aqueous solutions.

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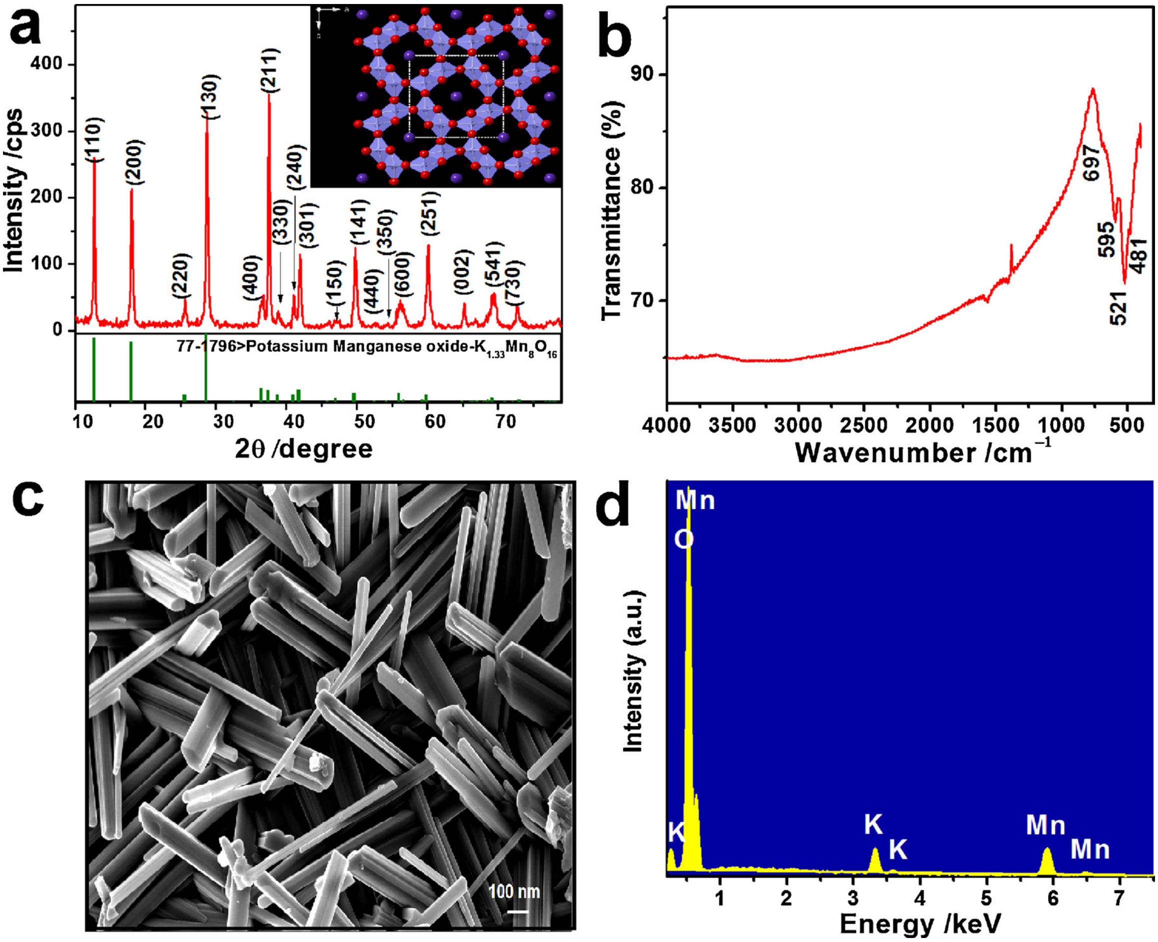

Fig. 1. (a) XRD pattern (inset: crystal structure), (b) FTIR spectrum, (c) SEM image and (d) EDS spectrum of the as-prepared $K_{1.33}Mn_8O_{16}$ nanorods.

In this work, $K_{1.33}Mn_8O_{16}$ nanorods were synthesized *via* a facile sol–gel method with cheap and readily available $KHCO_3$, $Mn(Ac)_2$ and citrate acid as raw materials. Furthermore, the electrochemical behavior of $K_{1.33}Mn_8O_{16}$ nanorods in a K_2SO_4 aqueous solution was examined. The results show that the $K_{1.33}Mn_8O_{16}$ nanorods exhibit a quasi-reversible K^+ intercalation/deintercalation behavior in a 0.5 M K_2SO_4 aqueous solution. The assembled activated carbon (AC)// $K_{1.33}Mn_8O_{16}$ asymmetric hybrid supercapacitor presents excellent electrochemical performance. To the best of our knowledge, the synthesis of $K_{1.33}Mn_8O_{16}$ nanorods *via* the sol–gel method and the use of $K_{1.33}Mn_8O_{16}$ in supercapacitors are reported for the first time.

2. Experimental

2.1. Preparation of $K_{1.33}Mn_8O_{16}$

$K_{1.33}Mn_8O_{16}$ was prepared *via* a sol–gel route. Typically, 0.37 g of $KHCO_3$, 4.60 g of $Mn(Ac)_2{\cdot}H_2O$ and 3.95 g of citrate acid were dissolved in 60 mL of deionized water to give a colorless transparent sol. This sol was dried at 110 °C to yield a white gel, which was then ground and heated to 750 °C at a rate of 10 °C min^{-1} for 6 h in air to produce black $K_{1.33}Mn_8O_{16}$.

2.2. Characterizations

The X-ray diffraction (XRD) pattern of the as-prepared sample was collected on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). The Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet iS10 FTIR spectrometer with a KBr disk. The morphology, size together with energy dispersive X-ray spectroscopy (EDX) were characterized by field emission scanning electron microscopy (FESEM, Zeiss Sigma HD, 10 kV) and transmission electron microscopy (TEM, FEI TF20, 200 kV). The nitrogen adsorption/desorption isotherm of the product was recorded on a Quadrasorb SI-3MP analyzer.

2.3. Electrode fabrications and electrochemical tests

The working electrode was fabricated by pressing a plasticine-like film composed of active material, acetylene black and poly(tetrafluoroethylene) in a weight ratio of 80:10:10 onto a 316 L stainless steel mesh, which could be found elsewhere [24]. The electrode for the single electrode test was rectangular-shaped with 1 cm^2 sectional area (5 mg of total active material mass), and the electrode for the hybrid supercapacitor measurement was rectangular-shaped with 2.25 cm^2 sectional area (15 mg of total active material mass). The AC for the fabrication of AC electrode was purchased from Fujian Xinsen Carbon Co., Ltd. (China) with a Brunauere–Emmette–Teller surface area of 1485 m^2 g^{-1}, and the electrode was rectangular-shaped with 2.25 cm^2 sectional area.

The cyclic voltammetry (CV), chronopotentiometry (CP) and galvanostatic charge–discharge (GCD) techniques were employed to evaluate the electrochemical performance of $K_{1.33}Mn_8O_{16}$ in a 0.5 M K_2SO_4 aqueous electrolyte. The electrochemical measurements for the single electrode were performed in a three-electrode system consisting of a fabricated electrode (working electrode), a Pt foil (4 cm^{-2}, reference electrode) and a saturated calomel electrode (SCE, counter electrode) in a 0.5 M K_2SO_4 aqueous solution on a CHI 760d