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$W_{18}O_{49}$ nanowires-graphene nanocomposite for asymmetric supercapacitors employing $AlCl_3$ aqueous electrolyte

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ABSTRACT

$W_{18}O_{49}$ nanowires (NWs)-reduced graphene oxide (rGO) nanocomposite is examined as a new active material for supercapacitors electrode, which reveals its high specific capacitance and excellent rate performance in $AlCl_3$ aqueous electrolyte. Electrochemical studies show that the presence of rGO enhances Al^{3+} ions diffusion in the nanocomposite, thus provides more ions for intercalation pseudocapacitance. The fabrication of asymmetric supercapacitor $W_{18}O_{49}$ NWs-rGO//rGO demonstrates high specific capacitance of 365.5 F g^{-1} at 1 A g^{-1} and excellent cycling stability with 96.7% capacitance retention at 12,000 cycles. Interestingly, it delivers high energy density of 28.5 Wh kg^{-1} and power density of 751 W kg^{-1}, which is the highest energy density value for all reported $W_{18}O_{49}$-based supercapacitor device. The work explores $W_{18}O_{49}$ NWs-rGO nanocomposite as a new electrode material for supercapacitors application with superior electrochemical performance, which may open up a new direction for high-performance energy storage in Al^{3+} electrolyte.

1. Introduction

The global modernization requires a substantial amount of energy supply, which can be fulfilled by renewable energy sources. In this context, energy storage system plays a vital role to ensure uninterrupted energy supply, especially for intermittent energy sources such as solar energy [1,2]. Among all energy storage systems, supercapacitors attain remarkable attention. The advancement of nanotechnology successfully engineers various nanomaterials for optimum charge storage in supercapacitors [3,4]. The charge storage in supercapacitors can be divided into electric double-layer capacitors (EDLC) and pseudocapacitors. EDLC involves the ions adsorption/desorption on the electrode surface where high-surface-area materials such as activated carbon (AC), carbon nanotubes (CNTs) or graphene are being popularly deployed [5]. On the other hand, pseudocapacitive materials such as MnO_2 and RuO_x store charge by fast and reversible redox reaction at the electrode surface and they usually show higher energy density than EDLC, however, at the cost of electrode stability [6,7]. Therefore, the quest for stable electrode materials to deliver high energy density is always desired. Recently, a new form of pseudocapacitance mechanism is proposed where the charge storage is achieved *via* intercalation of ions into the crystalline network. It is termed intercalation pseudocapacitance and it sheds light to produce high energy density supercapacitors without compromising structural integrity. Only limited materials such as tungsten oxides and niobium oxides have been reported to exhibit intercalation pseudocapacitance [8–11].

Tungsten oxides (WO_x) are widely studied as electrode materials for supercapacitors application [9,12–16]. Among the WO_x, the monoclinic $W_{18}O_{49}$ nanostructure is regarded as a promising electrode material for the next-generation energy storage device, due to its abundance of oxygen-vacancies for electrical conductivity [17,18]. Most importantly, it possesses a unique crystal structure to render it as a suitable host material for ions intercalation process [19]. Nonetheless, the major issue in utilizing $W_{18}O_{49}$ as intercalation pseudocapacitor is the usage of acidic electrolyte as the source of intercalating H^+ ions, which poses the corrosion problem for long term stability [20]. For these, Al^{3+} ion has been proposed as the substitute for intercalation ions to achieve remarkable electrochemical performance while remaining its long term stability [21–24]. The high charge-per-ion in Al^{3+} renders the supercapacitor to deliver high energy density while maintaining the safety and cost-effectiveness [25,26]. Nonetheless, the high charge density of Al^{3+} ion typically manifests strong electrostatic interaction with the host material lattice, which can cause slow Al^{3+} ion diffusion and decrease its electrochemical performance [27,28]. Therefore, a highly conductive

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