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Binder free 2D aligned efficient MnO_2 micro flowers as stable electrodes for symmetric supercapacitor applications†

Anil A. Kashale,[a,c] Madagonda M. Vadiyar,[b] Sanjay S. Kolekar,[b] Bhaskar R. Sathe,[c] Jia-Yaw Chang, *[d] Hom N. Dhakal [e] and Anil V. Ghule *[a,b]

Herein, δ-MnO_2 micro-flower thin films are grown directly onto a stainless steel mesh via a simple rotational chemical bath deposition technique. Moreover, the influence of the concentration of precursor ratio of $MnSO_4 : KMnO_4$ is investigated and the obtained samples are designated as M1 ($KMnO_4 : MnSO_4 = 3 : 1$), M2 ($KMnO_4 : MnSO_4 = 3 : 2$) and M3 ($KMnO_4 : MnSO_4 = 3 : 3$). The concentration of $MnSO_4$ as a starting material has a significant influence on the reaction kinetics, which subsequently alters the morphology and also the electrochemical performance. Among these three electrodes, the M1 electrode exhibits a high specific capacitance of 376 F g^{-1} at a current density of 5 mA cm^{-2} and a high specific energy of 52 W h kg^{-1}, which is higher than M2 (specific capacitance 312 F g^{-1} and specific energy 43 W h kg^{-1}) and M3 (specific capacitance 283 F g^{-1} and specific energy 39 W h kg^{-1}) electrodes. Due to the interesting performance of the M1 based electrode, the symmetric device is fabricated using two electrodes M1 (3 : 1) and represented as SSM/M1//M1/SSM. The device provides a maximum specific capacitance of 87 F g^{-1} and specific energy density of 32 W h kg^{-1} at a current density of 5 mA cm^{-2}. In addition, the symmetric device of the M1 electrode also exhibits good cycle stability showing 138% capacitance retention up to 2500 cycles. The enhanced electrochemical performance could be attributed to the direct growth of micro-flowers of MnO_2 on a stainless steel mesh, which provides more pathways for easy diffusion of electrolyte ions into the electrode. This study provides new insight and pathways for the development of low-cost and high-performance energy storage devices.

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1. Introduction

Increasing environmental issues and depleting natural energy sources such as coal, gas, and oil have created the need to develop green and sustainable energy sources coupled with energy conversion and energy storage capabilities. In line with this concern, researchers have mostly focused on the development of energy storage devices such as capacitors, accumulators, supercapacitors, and batteries.[1–4] Among these energy storage devices, supercapacitors are considered to be a promising alternative taking into consideration their fast charge–discharge rate, long cycle life, and high power density compared to conventional capacitors and batteries.[5,6] Based on the charge storage mechanism, supercapacitors are classified into electrical double layer capacitors (EDLCs) and redox supercapacitors (pseudocapacitors).[7–10] In EDLCs, the capacitance comes from the charge separation at electrode/electrolyte interfaces[7,8] and in the case of pseudocapacitors, the capacitance arises from faradaic reaction at the electrode/electrolyte surface.[8,9] Recently, researchers have paid more attention towards pseudocapacitor because of the associated higher energy storage capacity compared to carbon-based electrodes (*i.e.* EDLCs).[3] To date, various transition metal oxides *viz.* Co_3O_4,[11] MnO_2,[12] NiO,[13,14] RuO_2,[15] V_2O_5,[16] *etc.* have been explored in pseudocapacitors as an electrode material. Among these candidates, MnO_2 is considered as the most promising electrode material in terms of its low cost, natural abundance, high theoretical capacity (1370 F g^{-1}), high voltage window in aqueous electrolyte and more environment-friendly than other transition metal oxides.[17–22] MnO_2 naturally occurs in five allotropic forms *viz.* α, β, γ, δ and λ. Among these, α, β and γ take a one-dimensional structure, while δ and λ forms two and three-dimensional structures, respectively.[23,24] These structural differences are responsible for the significant differences in their electrochemical properties. A good capacitor requires structures with enough structural gaps, properly sized tunnels or well-separated layers, facilitating

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[a] *Department of Nanotechnology, Dr Babasaheb Ambedkar Marathwada University, Aurangabad 431004, Maharashtra, India*

[b] *Department of Chemistry, Shivaji University, Kolhapur 416004, Maharashtra, India. E-mail: anighule@gmail.com; avg_chem@unishivaji.ac.in*

[c] *Department of Chemistry, Dr Babasaheb Ambedkar Marathwada University, Aurangabad 431004, Maharashtra, India*

[d] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan. E-mail: jychang@mail.ntust.edu.tw*

[e] *School of Engineering, University of Portsmouth, Hampshire PO1 3DJ, UK*

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