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Ruthenium sulfide nanoparticles as a new pseudocapacitive material for supercapacitor

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ABSTRACT

Transition metal chalcogenides received much attention as high performance electrode materials for energy storage devices during this decade. In this article, we demonstrated the sonochemical preparation of cubic RuS_2 nanoparticles with average size in the range of 20 nm and investigated their supercapacitive properties in detail using cyclic voltammetry, charge-discharge analysis and electrochemical impedance spectroscopy, respectively. The RuS_2 electrode delivered a specific capacitance of 85 $F g^{-1}$ at a constant discharge current density of 0.5 mA cm^{-1} using a three electrode configuration. The RuS_2 symmetric supercapacitor device delivered a specific capacitance of 17 $F g^{-1}$ and excellent cyclic stability of about 96.15% capacitance retention over 5000 cycles. The electrochemical impedance spectroscopy (Nyquist and Bode) analysis together with the frequency dependent capacitance (real and imaginary) studies confirmed the ideal capacitive nature of the RuS_2 supercapacitor. The experimental findings ensure the potential application of RuS_2 nanoparticles as a novel electrode material for electrochemical energy storage devices.

1. Introduction

Electrochemical capacitors or supercapacitors become an ultimate choice of energy storage devices due to their high power density (compared to batteries), high energy density (compared to conventional capacitors) and long cycle life [1]. These intriguing properties make them as a suitable candidate for potential applications in hybrid electric vehicles, power electronics, and military equipments as well as powering implantable devices [2]. Based on the mechanism of charge storage, supercapacitors can be classified as (i) electric double layer capacitors (EDLCs) which stores charge in an electric field at the electrode/electrolyte interface, and (ii) pseudocapacitors which stores the energy via rapid reversible faradaic reactions at the electrode surface [3]. Numerous electrode materials for EDLCs (activated carbon, carbon nanotubes, graphene, and graphdiyne) and pseudocapacitors (transition metal oxides (TMOs), binary metal oxides, conducting polymers) have been studied extensively in this decade [4–6]. However, the increasing global energy requirements motivate the researchers to explore the possibility of novel materials with exceptional properties for supercapacitor applications. Recently, graphene analogue layered transition metal chalcogenides (TMCs) such as MoS_2, VS_2, $MoSe_2$, TiS_2, and M'Xenes (layered transition metal carbides and nitrides) are demonstrated as high performance supercapacitive materials [7–10]. Other TMCs such as nickel sulfide (NiS, Ni_3S_2, NiS_2), cobalt sulfide (CoS, CoS_2, Co_3S_4), copper sulfide (CuS, Cu_2S) and binary metal sulfides are explored as high rate pseudocapacitive materials [11,12]. The distinct physicochemical and electronic properties of TMCs such as high conductivity compared to TMOs, and rich redox chemistry makes them an alternate candidate over conventional TMOs for electrochemical energy storage applications [13]. There is always a demand in the development of novel materials for supercapacitor applications due to the increasing perception in the energy storage sectors.

In this regards, ruthenium based materials are well known for exceptional electrochemical properties due to their rich redox chemistry and multiple valence states [14]. A variety of ruthenium based materials such as ruthenium complexes, metallic Ru, hydrous RuO_2, amorphous RuO_2, and crystalline RuO_2 are examined for various electrochemical applications such as electrochemical sensors, electrocatalysis, supercapacitors, and batteries [15–19]. Previous studies reported that hydrous RuO_2 (105.1 $F g^{-1}$) possesses a higher specific capacitance than

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anhydrous RuO_2 (48.9 F g^{-1}) [20]. In this regards, ruthenium sulfide (RuS_2) is one of the promising TMCs with fundamental and technological applications in photoelectrochemical energy conversion, photocatalytic water splitting, and also used as a cathodic catalyst in direct methanol fuel cells, respectively [21,22]. It is a narrow band gap semiconductor (1.85 eV) with an excellent stability towards hydrogen and oxygen evolution from aqueous solutions making it an ideal candidate for photoelectrolysis of water under visible light [23,24]. Although studies on the energy storage properties of TMCs are rapidly increasing and ongoing, the effectiveness of ruthenium disulfide (RuS_2) as an electrode for electrochemical energy storage devices and the underlying charge storage mechanism is not examined upto-date. On the other hand, RuS_2 is proven to be a superior catalyst compared to MoS_2 (about one order higher) and other TMCs in the hydro-desulfurization of thiophene, and hydrogenation of biphenyl, respectively [21,25]. These intriguing electrochemical and catalytic properties of RuS_2 motivated us to explore the electrochemical properties of this material for energy storage applications. In this study, we used a rapid sonochemical route for the preparation of RuS_2 nanoparticles and explored their use as an electrode material for supercapacitor.

2. Experimental section

2.1. Preparation of ruthenium sulfide (RuS_2) nanoparticles

The RuS_2 nanoparticles were prepared via a sonochemical method using ruthenium chloride and thiourea as the starting precursors in the molar ratio 1:2 [26]. Briefly, two aqueous solutions containing 0.05 M of ruthenium chloride (in 75 mL) and 0.1 M of thiourea (in 75 mL) were prepared separately and mixed together (a total capacity of 150 mL) followed by purging argon nearly for 30 min. Then, the resulting solution was subjected to ultrasound irradiation for 2 h using a direct immersion titanium horn (SONIC VCX-750 system). The sonochemical reaction was conducted without any cooling and a temperature of about $60 \pm 5\,^{\circ}C$ was reached at the end of the reaction. After completion of the reaction, the final product (amorphous) was separated via centrifugation process (using water and ethanol) and allowed to dry at 80 °C for 6 h. Finally, the amorphous product was heated at a temperature of 650 °C for 2 h under argon atmosphere to obtain the crystalline RuS_2 nanoparticles.

2.2. Instrumentation

The phase purity and crystallite size of the RuS_2 nanoparticles were determined by Rigaku X-ray diffractometer (XRD) operated at 40 KeV and 40 mA with Cu K α radiation. The surface morphology of the RuS_2 nanoparticles was examined using high-resolution transmission electron microscope ((HR-TEM), JEOL JEM 2011, JEOL Ltd.). The Raman spectrum of the RuS_2 nanoparticles was obtained using LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France). The Raman system was operated at 25 mW laser power using an excitation wavelength of 514 nm with an Ar^+ ion laser. The data was collected using a 10-s data point acquisition time. The chemical composition and state of elements present in the outermost part of the RuS_2 nanoparticles was obtained by X-ray photoelectron spectroscopy (XPS) techniques using ESCA-2000, VG Microtech Ltd. Here, a monochromatic X-ray beam source at 1486.6 eV (aluminum anode) and 14 kV was used to scan the sample surface. A high-flux X-ray source with an aluminum anode was used for X-ray generation, and a quartz crystal

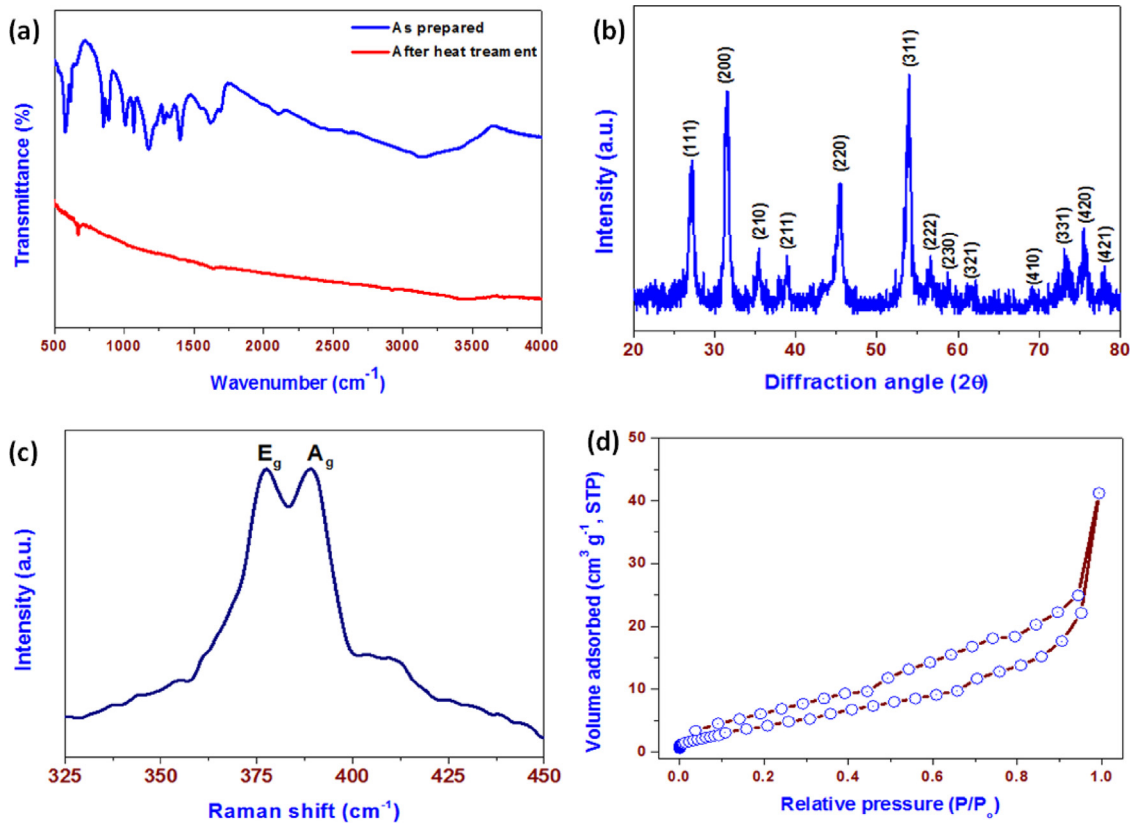

Fig. 1. (a) Fourier transformed infra red spectroscopy of sonochemically prepared RuS_2 before and after thermal treatment, (b) X-ray diffraction pattern, (c) laser Raman spectrum and (d) Nitrogen adsorption–desorption isotherm of RuS_2 nanoparticles.