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Microwave-assisted synthesis of simonkolleite nanoplatelets on nickel foam–graphene with enhanced surface area for high-performance supercapacitors

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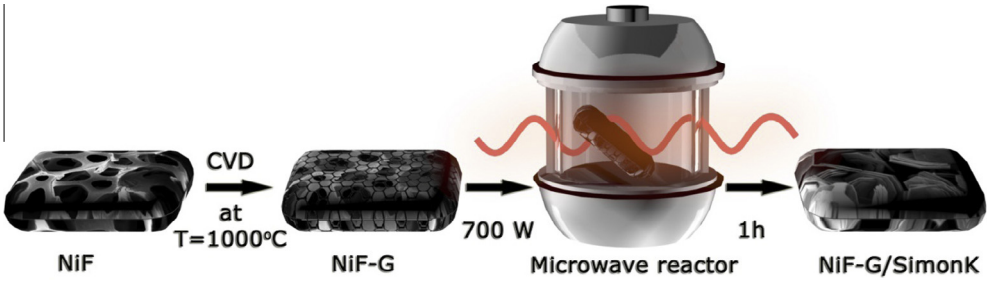
GRAPHICAL ABSTRACT

Nickel foam–graphene (NiF–G) was synthesized by chemical vapor deposition (CVD) followed by a simple microwave-assisted hydrothermal technique to grow simonkolleite nanoplatelets on the NiF–G to form NiF–G/SimonK electrode for supercapacitor application.



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ABSTRACT

Simonkolleite ($Zn_5(OH)_8Cl_2{\cdot}H_2O$) nanoplatelets has been deposited on nickel foam–supported graphene by using an efficient microwave-assisted hydrothermal method. The three-dimensional (3D) porous microstructure of the as-fabricated nickel foam–graphene/simonkolleite (NiF–G/SimonK) composite is beneficial to electrolyte penetration and ions exchange, whereas graphene provide improved electronic conductivity. Structural and morphological characterizations confirmed the presence of highly crystalline hexagonal-shaped nanoplatelets of simonkolleite. Field emission scanning electron microscope (FE-SEM) of the NiF–G/SimonK composite revealed that the SimonK nanoplatelets were evenly distributed on the surface of NiF–G and interlaced with each other, resulting in a higher specific surface area of 35.69 $m^2\,g^{-1}$ compared to SimonK deposited directly on NiF 17.2 $m^2\,g^{-1}$. Electrochemical measurements demonstrated that the NiF–G/SimonK composite exhibit a high specific capacitance of 836 $F\,g^{-1}$ at a current density of 1 $A\,g^{-1}$, and excellent rate capability and cycling stability with capacitance retention of 92% after 5000 charge/discharge cycles.

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1. Introduction

Recently, great research efforts have been made to improve the energy density, power density and service life of energy storage devices [1]. Supercapacitors, sometimes referred to as electrochemical capacitors or ultracapacitors, bridge the gap between low power/high energy rechargeable batteries and high power/low energy electrolytic capacitors due to their high rate capability, fast charging/discharging rate, long operating lifetimes, high levels of electrical power and low maintenance cost [2]. In general, supercapacitors can be divided into two categories of electrochemical double-layer capacitors (EDLCs) and pseudocapacitor based on their energy storage mechanism [3,4]. Furthermore, carbon and transition metal oxides (e.g. CNT [5], carbon aerogel [6], graphene nanosheets [7], Co_3O_4 nanowire [8,9], mesoporous NiO [10], RuO_2-$\cdot xH_2O$/carbon [11], graphene/SnO_2 [12], graphene–MnO_2 [13], $V_2O_5{\cdot}0.6\ H_2O$ nanoribbons [14] and so forth) are the most used materials for supercapacitors fabrication due to their large surface area. Lately, graphene has been proven to be an effective material for supercapacitor electrodes fabrication due to its high electrical conductivity, high mechanical stability and large surface area [15,16]. Graphene can be a perfect conductive support, or additive for electrode materials with pseudocapacitance properties [17]. Metalic nanoparticles [18], nanostructured oxides [19–21] and conducting polymers [22] were coupled with highly conducting graphene nanosheets and reduced graphene oxide to improve performance of Li-ion batteries and supercapacitors.

Simonkolleites ($Zn_5(OH)_8Cl_2{\cdot}H_2O$) nanoplatelets, which possess a high degree of anisotropy with nanoscale thickness and microlength in other dimensions, have attracted tremendous attention due to their unique morphology associated with prominent physical and chemical properties and potential applications, such as in H_2 gas sensing and energy storage applications [23–25]. Simonkolleite forms hexagonal micro to nanoplatelet crystals with a cleavage parallel to the (001) direction [26]. It is a soft compound with a Mohs hardness of ~1.5 and a specific gravity of 3.2 [23]. The crystal structure of the synthesis analogue of simonkolleite was reported by Nowacki and Silverman [27] and Allmann [28]. Simonkolleite is electrochemically active due to the existence of oxygen vacancies on its surface, similar to ZnO nanostructures. Moreover, the *n*-type donors nature of these vacancies has a significant contribution to the material's conductivity [23]. Due to the intrinsically lower electronic conductivity and dense morphology of simonkolleites, great efforts have been made to improve capacitive performance of this material with graphene composites [24,25]. It is worthwhile to mention that, graphene grown directly on the current collectors by chemical vapor deposition (CVD) method [29] offers the advantages of binder-free and low contact resistance, which are important to fabricate the electrodes with higher specific capacitance and improved power capability.

Low temperature hydrothermal growth of simonkolleites on 3D NiF–G for electrochemical supercapacitors was reported in our previous work [24]. The weakness of conventional hydrothermal aqueous solutions based techniques, typically carried out at low temperature ~90 °C, is the long time scale required for the synthesis. This may lead to defects being introduced in the simonkolleite nanomaterial and resulting in compromised quality and performance to achieve the desired level of energy storage [30]. Despite being very versatile, hydrothermal aqueous-based reaction systems for simonkolleites synthesis exhibit a fairly complex relationship between reaction mechanism and reaction parameters controlling structural morphology. Thus, hydrothermal aqueous-based synthesis recipe for simonkolleites micro- and nanostructures demands a high degree of reaction parameter control to accurately produce the desired structural morphology and hence high electrochemical performance.

As an alternative to hydrothermal aqueous-based synthesis, microwave-assisted synthesis can significantly decrease the time required for synthesizing simonkolleites micro- and nanostructures [31]. Microwave irradiation heats a substance by two mechanisms, which are dipole polarization and ionic conduction whereas another called interfacial polarization is a combination of the two [32]. It shortened reaction time by interacting with the reaction mixtures on a molecular level leading to an accelerated rate of reaction and hence the growth of the nanomaterial. And usually a high degree of morphological control during the synthesis of nanostructured materials is achieved by using microwave-assisted approaches; this technique can also provide an almost instantaneous and dynamic control over reaction temperature [32].

In this work, we present a simple microwave-assisted hydrothermal technique to grow simonkolleite nanoplatelets on a 3D nickel foam–graphene (NiF–G/SimonK) for supercapacitor application. The NiF–G/SimonK composite has a high spicific electrochemical active surface area and three-dimensionally interconnected networks. The SimonK deposited by the microwave technique exhibited a nanoplatelets structure uniformly anchored on 3D porous nickel foam–graphene. The unique structure of the fabricated NiF–G/SimonK electrode improved ion and electron exchange in electrochemical processes and also served as a 3D platform for combination and integration of SimonK on the NiF-G. The NiF–G/SimonK composite acting as supercapacitor electrode material displays high specific capacitance, remarkable rate performance and prominent cycle stability.

2. Experiments and methods

2.1. Growth of graphene on nickel foam (NiF–G)

Nickel foams (NiF) (Sigma–Aldrich, 450 $g^1\ m^{-2}$ in bulk density, 95% porositry and 1.6 mm in thickness) were used as the templates for the CVD growth of graphene and also employed as the current collector of supercapacitor electrode. The precursor gases were CH_4:H_2:Ar. The NiF was annealed at 800 °C in the presence of Ar and H_2 for 20 min in order to reduce the native oxide layer on the surface of NiF. This process was immediately followed by CH_4 gas introduction at 1000 °C (Fig. 1). The flow rates of the gases (CH_4:H_2:Ar) were 10 sccm: 10 sccm: 300 sccm, respectively. After 15 min of growth, the sample was rapidly cooled down to the room temperature at a cooling rate of 100 °C/min under H_2/Ar flow.

2.2. Growth of simonkolleite on NiF–G

An efficient microwave-assisted hydrothermal technique was used to deposit SimonK nanoplatelets on the NiF–G (Fig. 1). A 25 ml Pyrex® round-bottom tube was filled with an equimolar (10^{-1} M) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), hexamethylenetetramine (HMT) and sodium chloride (NaCl). Subsequently, the NiF–G samples were immersed in the solution and subjected to microwave irradiation of 700 W under a pressure of up to 100 bar for 1 h in a single-mode microwave reactor which is pre-pressurized with N_2 gas to prevent boiling of the solution. The microwave reactor consists of a circular cavity, containing a waveguide, which delivers single-mode microwaves for uniform sample heating without any hot or cold spots in the reaction vessel that are typical for a domestic microwave ovens. The single-mode microwave cavity is designed to provide a higher energy density per unit volume of the sample allowing for an efficient preparative chemistry. Thereafter, the microwave reactor was allowed to cool down to ambient temperature. The final NiF–G/SimonK composite was obtained after washing and drying. The