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Collective use of deep eutectic solvent for one-pot synthesis of ternary Sn/SnO_2@C electrode for supercapacitor

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ABSTRACT

Scalable and simple preparation of metal/metal oxide-carbon composite with high specific surface areas and designated properties are essential for their large scale practical applications. In view of this, we report an ecofriendly deep eutect solvents (DESs) assisted synthesis of Sn/SnO_2@C hybrid composite. Herein, we have investigated the crucial role of DESs which collectively acts as solvent-precursor-reactant system offering an interesting and exciting physicochemical properties and alternative for the conventional solution-based synthesis methods. TEM images reveal that the massive Sn/SnO_2 nanoparticles with average size of 15–20 nm, are uniformly confined in highly layered porous carbon sheets leading to the carbonaceous composite with large surface area of 500 m^2/g after thermal treatment. It is noteworthy that the excellent electrochemical performance of Sn/SnO_2@C hybrid composite for supercapacitor electrode material (109.70 mAh/g at 1.42 mA/cm^2 and almost 100% capacitance retention for 5000 cycles) can be attributed to the higher surface area and synergic properties of Sn and SnO_2. Nevertheless, the carbon matrix with a low degree of graphitization can establishes a good electrical contact and also prevents the detachment of nanoparticles during the course of long-term electrochemical reactions. In addition, selection of less toxic component is possible by virtue of compositional versatility of DESs. Thus the use of DESs can bring froth the twin benefits of solvent-precursor-reactant system and cost effective eco-friendly synthesis route which can be applicable for the synthesis of various metal/metal oxide-carbon composites.

1. Introduction

Since the discovery of energy storage devices such as lithium-ion batteries (LIBs) and supercapacitors (SCs), the tin and tin-based composite materials (SnO_2, Sn/C, and etc.) have become one of the most prominent choices for their use as electrode material [1,2]. Owing to their outstanding features including unique optical and electrical properties, wide band gap [3] (3.6 eV at 300 K), high chemical stability, and competitive cost, they have wide range of applications such as gas sensors, biosensors, and solar cell etc [4–6]. Moreover, the SnO_2 is also considered as a co-material to RuO_2, especially for their use in supercapacitor electrodes due to its low cost, high electric conductivity and chemical stability and no toxicity. However, the low specific capacity of SnO_2 limiting their large scale practical application for supercapacitors. Therefore, to further improve the capacitive properties of SnO_2, different strategies such as carbon coating [7], structural doping [8] and size reduction were extensively employed [1,9,10]. For example Wu et al. [11] prepared the hierarchical SnO_2 nano-sheets by solvothermal method with nano-sheet like structure showing a capacitance of 187.7 and 82.2 F/g at a current density of 1 and 5 A/g, respectively. Liu et al. synthesized SnO_2/carbon nanofiber exhibiting a specific capacitance of 90 F/g at a scan rate 20 mV/s [12]. Li et al. [13] have demonstrated Ni/SnO_2 nano-flowers for supercapacitors that showed the specific capacitance of 437 mF/cm^2 at 2 mV/s. Also the surface area and geometry has a massive impact on the physical and chemical properties of SnO_2, the morphology and a porous structure plays a critical role in the selection of electrode materials. Therefore, it is highly important to construct special morphological moieties which possess higher surface to volume ratio in order to achieve more reactive sites and facile ion transportation. Thus, the development of simple and cost effective synthesis strategy for Sn/SnO_2 based supercapacitor electrodes is challenging and highly desirable. Very recently, the deep eutectic solvents (DESs) have emerged as soft template and reaction media

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for the synthesis of nanomaterials [14,15]. Abbott et al. have demonstrated for the first time the use of DESs as a promising and alternative solvent to ionic liquids [16,17]. Due to the unique characteristic of DESs such as small vapor pressure, biocompatibility, and wide electrochemical potential window it is expected to play a crucial role in the synthesis and properties of Sn/SnO_2@C composite structures.

In this work, we report a rational design of the simple one-step synthesis route for the fabrication of Sn/SnO_2@C composite using the DESs. Since the DESs was prepared by the simple physical mixing of its constituent (choline chloride and tin chloride as carbon and metal source respectively), the synthesis route can be arguably considered to be simple and scalable. It is also extendable due to the compositional versatility of DESs. The morphological and structural properties of the as-synthesized composite material were investigated in detail and correlated to the electrochemical properties. The high surface area (~500 m^2/g) can be achieved by embedding Sn/SnO_2 nanoparticles into the matrix of carbon sheets.

2. Experimental section

2.1. Materials

Choline chloride ($HOC_2H_4N(CH_3)_3Cl$, 99% ChCl, hydrogen bond acceptor and Tin chloride $SnCl_2$, >99%, hydrogen bond donor) were purchased from Sigma-Aldrich Korea and used without any further purification.

2.2. Synthesis of deep eutectic solvents (DESs)

In a typical procedure, both choline chloride and tin chloride with mole ratio (1: 2) were heated at 100 °C with constant stirring in the closed vial until the homogeneous and clear liquid was formed. The synthesized DESs is then transferred to the porcelain boat and pyrolysed in a muffle furnace at an experimental temperature under the flowing nitrogen gas for 2 h with ramping rate 3 °C/min. DESs were pyrolysed at 500, 600, 700 and 800 °C and named as DT500, DT600, DT700 and DT800, respectively in further discussion. The overall synthesis scheme was shown in Scheme 1. For comparison, SnO_2 nanoparticles ($SnO_2$700) were also prepared by the same procedure except the air atmosphere was used for the decomposition of DESs.

2.3. Material characterization

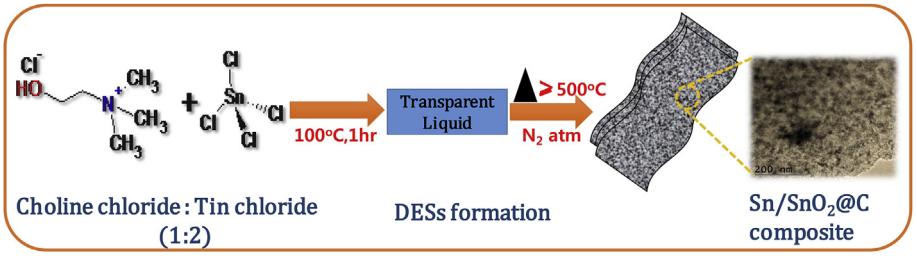
The pyrolysis behavior of DESs was determined by thermogravimetric analysis using TG N100 instrument, from 25 to 800 °C, with a heating rate of 3 °C/min. The phase and morphology of the material were characterized with a powder X-ray diffractometer (XRD, Shimadzu XRD-6000) using a Cu K-alpha irradiation ($\lambda = 1.5406$) source. X-ray photoelectron spectroscopy (XPS) was conducted with two separate systems equipped with monochromatic Al Kα sources (ESCALab250, USA) to analyze the chemical composition of the samples. The specific surface area and pore size distribution were studied by a belsorp mini -II (BEL, Japan) instrument with the method of Brunner-Emmet-Teller (BET) and BJH (Barett-Joyner-Halenda). Prior to the gas adsorption, the sample was degassed at 100 °C for 12 h. The morphology of the composite was examined by the Field emission scanning electron microscopy (FE-SEM, Sigma S-4000) and transmission electron microscopy (TEM, Philips CM 200) equipped with energy dispersive spectroscopy (EDS).

2.4. Electrochemical characterization

All the electrochemical tests were carried out on a ZIVE SP1 electrochemical workstation (Won-A-Tech Co. LTD, South Korea). The supercapacitor tests were performed using a three electrode cell system with an aqueous 2 M KOH solution as the electrolyte, Sn/SnO_2@C as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The working electrode was prepared by pressing the homogeneous slurry of synthesized composite, super P, and polyvinylidene fluoride (PVDF), in a weight ratio of 80:10:10, in N-methyl 2pyrrolidone, onto Ni foam. Then, prepared electrodes were dried at 80 °C for 12 h. Furthermore, cyclic voltammetry (CV) were acquired at different scan rates of 5–100 mV/s with the potential range of 0–0.5 V (vs. Ag/AgCl). Galvanostatic charge-discharge (GCD) measurements were carried out at different current densities, in a potential window of 0–0.5 V (vs. Ag/AgCl). The EIS measurements were performed by applying an AC voltage with 10 mV amplitude in a frequency range of 0.01–100 kHz.

3. Result and discussion

The synthesis of the Sn/SnO_2@C composite herein consisting of the metal/metal oxide within the carbon sheet has its key advantage in the homogenous, liquid state of precursor DESs which itself collectively act as a solvent –precursor –reactant system. The DESs were formed by heating ChCl-$SnCl_2$ (1:2) at 100 °C. The pyrolysis behavior of DESs was examined with the help of thermogravimetric analysis (TGA) under an inert atmosphere. In TGA graph (Fig. 1), weight loss was observed in three stages. The first stage weight loss up to the 250 °C is due to the dissolve moisture and followed by the second stage weight loss up to 470 °C, which was accounted for the decomposition of DESs into the Sn/SnO_2@-carbon composite. The small weight loss from 700 °C was attributed to the carbo-thermal reduction of SnO_2 to the metallic Sn. Accordingly; the DESs were pyrolysed at 500, 600, 700 and 800 °C under an N_2 atmosphere. Furthermore, the Powder X-ray Diffraction (Fig. 2(a)) of as synthesized composite material (DT500, DT600, DT700 and DT800) confirmed the presence of crystalline β-Sn (JCPDS No-01-0163, space group $I4_1/amd$; a = 0.58308, c = 0.31810 nm). In addition, detectable crystallinity of SnO_2 phase



Scheme 1. Schematic representation of the synthesis of Sn/SnO_2@C composite.