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Full Length Article

Mesoporous reduced graphene oxide/WSe_2 composite particles for efficient sodium-ion batteries and hydrogen evolution reactions

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ABSTRACT

Mesoporous WSe_2-reduced graphene oxide (WSe_2-rGO) composite particles were prepared by spray pyrolysis and subsequent selenization. The WSe_2-rGO composite particles had both well-dispersed rGO nanosheets and well-faceted WSe_2 nanocrystals with plenty of folded edges. As a comparison sample, hierarchical structured WSe_2 particles were produced by selenization of the bare WO_3 particles obtained by spray pyrolysis. The WSe_2-rGO composite particles showed superior electrochemical properties for sodium-ion batteries (SIBs) and electrocatalytic efficiencies for hydrogen evolution reactions (HERs) compared to those of the bare WSe_2 particles. The discharge capacities of the WSe_2-rGO composite particles and bare WSe_2 particles for the 100th cycle at a current density of 0.5 A g^{-1} for sodium-ion storage were 238 and 36 mA h g^{-1}, respectively; their corresponding capacity retentions measured from the third cycle were 80% and 13%. The WSe_2–rGO composite particles showed much lower onset potential and larger current density (36.5 mA cm^{-2} at η = 300 mV) than those of the bare WSe_2 particles (0.61 mA cm^{-2} at η = 300 mV). The Tafel slopes for the WSe_2–rGO composite and bare WSe_2 particles were approximately 60 and 115 mV dec^{-1}, respectively.

1. Introduction

Layer-structured transitional metal dichalcogenides (TMDs) have recently attracted increasing attention because of their distinctive electronic, catalytic, optical, and electrochemical properties [1–7]. TMDs (MX_2 where M = Mo, W and X = S, Se) have a structure similar to graphite because they are composed of hexagonal metal atoms (M) sandwiched between two chalcogen atom (X) layers. Additionally, there is strong covalent bonding within the M–X–M layers, with only fairly weak van der Waals interactions between neighboring sandwich layers [8–11].

MoS_2, $MoSe_2$, WS_2, and WSe_2 materials with various morphologies have been extensively studied as anode materials for lithium- and sodium-ion batteries, and as electrocatalysts for hydrogen evolution reactions (HERs) [12–19]. Accordingly, tungsten diselenide (WSe_2) could be used in the above applications. The unique WSe_2 structure is expected to allow for the insertion and extraction of relatively large Na^+ ions compared to Li^+ ions present between the layers without any significant volume changes [20,21]. In particular, the nanostructured WSe_2-graphene composite materials could be well applied as electrocatalysts for both HERs and anode materials for sodium-ion batteries (SIBs).

Graphene is expected to improve the electrical conductivities of the nanostructured WSe_2 materials. However, WSe_2 materials have been scarcely studied up till now. Share et al. investigated the sodium-ion storage performance of the bulk WSe_2 material [22]. A reversible capacity above 200 mA h g^{-1} was observed at a 20 mA g^{-1} rate. Zhang et al. synthesized carbon-coated WSe_2 nanomaterials by solid-state reaction. The WSe_2/C nanomaterials showed a reversible sodium storage capacity of 270 mA h g^{-1} after 50 cycles without any notable loss [23]. Wang et al. investigated the electrocatalytic performances of the aligned WSe_2 nanofilms on Si nanowires and a carbon fiber paper [24].

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The WSe_2 nanofilms on the carbon fiber paper acted as a highly efficient electrocatalyst for HERs compared to flat substrates. Liu et al. studied WSe_2 layers anchored on graphene sheets as the electrocatalyst for HERs [25]. The WSe_2/graphene hybrid exhibited excellent electrocatalytic activity in the HER, such as a low onset overpotential of −100 mV, a small Tafel slope of 64 mV per decade, and outstanding stability.

In this study, nanostructured WSe_2-reduced graphene oxide (WSe_2-rGO) composite particles with spherical particles of fine size were prepared for the first time by a simple two-step process. Precursor WO_3-rGO composite particles were prepared by spray pyrolysis and they were subsequently transformed into WSe_2-rGO composite particles by a simple selenization process. The electrochemical properties of SIBs and electrocatalytic efficiencies for the HERs of the WSe_2-rGO composite were compared to those of the bare WSe_2 particles prepared by the same process without applying graphene oxide (GO).

2. Experimental

Mesoporous WSe_2-rGO composite particles were prepared by a two-step process. In brief, the procedure for the particles by spray pyrolysis used a solution containing ammonium metatungstate hydrate [$(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$] and GO nanosheets (Fig. S1) (see supplementary data). The preparation procedure of GO nanosheets are described in our previous reports [26,27]. The reactor temperature and flow rate of N_2 gas during the spray pyrolysis were fixed at 500 °C and 7 L min^{-1}, respectively. To prepare WSe_2-rGO composite particles, the as-prepared WO_3-rGO composite particles were selenized at 500 °C for 12 h under a 10% H_2/Ar reducing atmosphere with selenium metal particles. Bare WSe_2 particles without rGO were also prepared as a comparison sample. Precursor WO_3 particles, prepared by spray pyrolysis, were selenized under identical post treatment conditions as those mentioned above. For simplicity, the WSe_2-rGO composite particles and bare WSe_2 particles without rGO are referred to as "WSe_2-rGO" and "bare WSe_2", respectively. Detailed characterization method, sodium ion battery and electrochemical measurements procedures are described in the Supporting Information.

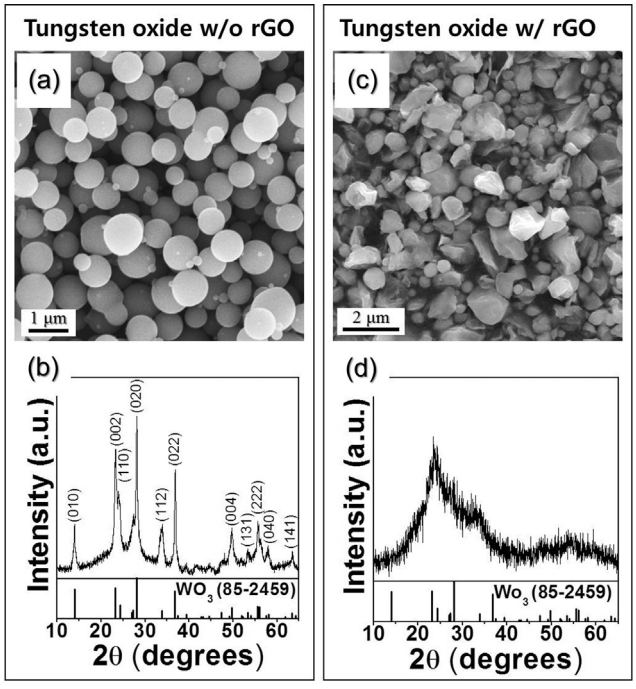

Fig. 1. SEM images and XRD patterns of the (a and b) bare WO_3 particles without rGO and (c and d) WO_3–rGO composite particles prepared directly by spray pyrolysis process at 500 °C under N_2 gas atmosphere.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.07.200.

3. Results and discussion

The morphologies and X-ray diffraction (XRD) patterns of the tungsten oxide particles prepared directly by the spray pyrolysis process from the solution with and without GO are shown in Fig. 1. The particles prepared from the solution without GO were spherical and had a filled structure (Fig. 1a). However, GO uniformly dispersed in the droplet changed the morphology of the tungsten oxide particles into crumpled shapes, as shown in Fig. 1c. The XRD patterns of both particles exhibited diffraction peaks corresponding to the hexagonal phase of WO_3 (JCPDS no. 85–2459), irrespective of GO inclusion (Fig. 1b and d). However, mean sizes of the crystallite domains of the powders prepared from the solution with and without GO were estimated to be 3 and 26 nm, respectively, which are determined from Scherrer's formula. The obvious broadness of the XRD peaks of the sample with GO suggests that the crystallites are at the nanoscale level. During the spray pyrolysis process, GO was reduced to rGO by the thermal treatment at 500 °C under N_2 atmosphere. Therefore, the rGO sheet disturbed the crystal growth of the tungsten oxide formed through the decomposition

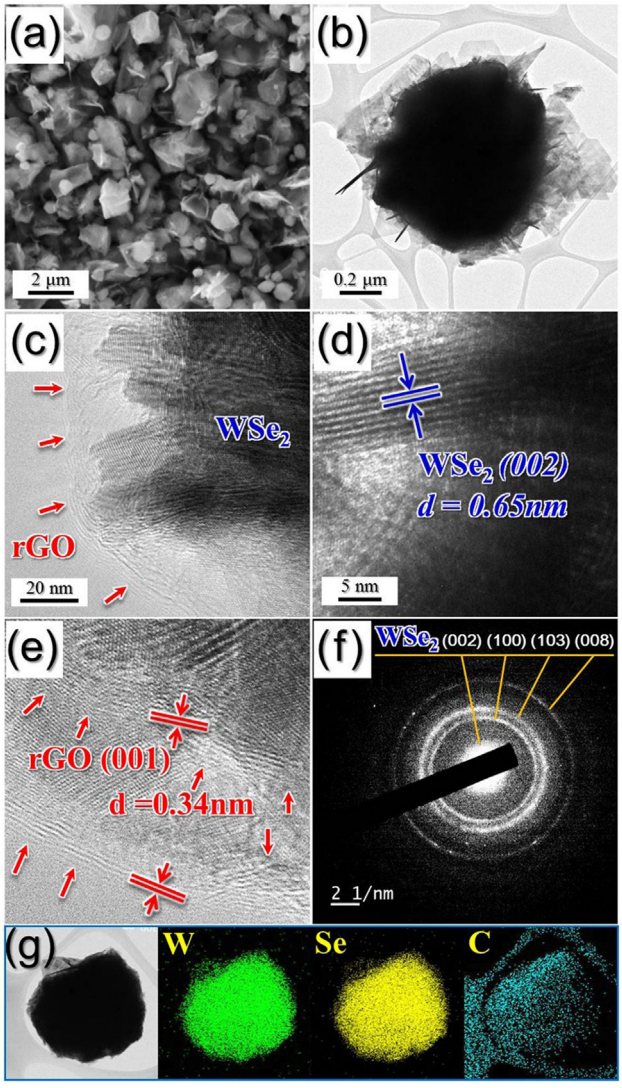

Fig. 2. Morphologies, SAED pattern, and elemental mapping images of the WSe_2–rGO composite microspheres after selenization at 500 °C: (a) SEM image, (b–e) TEM images, (f) SAED pattern, and (g) elemental mapping images.