PVP Assisted Grass-like NiSe@ZnSe Composite for Environmental Energy Applications

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Abstract

Well defined NiSe@ZnSe composite electrode is synthesized along with Polyvinyl pyrrolidone (PVP) and Sodium Lauryl Sulfate (SLS) surfactant whose redox behavior is an interesting approach towards the boosting performance of the supercapacitor. The as-prepared samples were examined through standard characterization techniques. High crystallinity suggests that prepared composite NiSe@ZnSe is well appropriate for the application concerning the supercapacitor electrode material. The Raman spectroscopy identifies the functional group, vibrations, stretching of bonds and presence of defects in the samples. The surface to volume ratio of the loosely packed grass-like structures result in availability of more surface area for the electrolyte which lead to the enhanced reaction rates. As-prepared active synthesized product revealed 442 Fg^{-1} electrochemical capacitance at 1 Ag^{-1} with 99.3% high rate capability at 10 Ag^{-1} after 2000 cycles. Besides, notably capacity retention of the sandwiched asymmetric NiSe@ZnSe//AC device maintains 99.48% after constant charge discharge 2000 cycles displays outstanding electrochemical stability.

1. Introduction

The energy crisis and the rapid depletion of the fossil fuels direct a new way to look for renewable energy storage [1]. To meet the essential need of using more energy, current research focuses on enhanced energy density batteries and high power density supercapacitor (SCs) [2]. Therefore, the electrochemical storage devices have powerful influence on the modern growing society [3]. Especially, the supercapacitor benefitting from the fast dynamic response, efficient capabilities, long term sustainability and environmental friendly emerge inevitable energy storage sources [4]. Nevertheless, low energy density of supercapacitor is inevitable necessities to improve its performance. Hence, increasing of the energy density is an important strategy to lighten the future energy crisis. As a competent portion of the supercapacitor, the electroactive material is enviable for the better performance of the supercapacitor which enables to increase the redox behavior and to generate the pseudo-capacitance [5]. In electrical double layer capacitors (EDLCs), charge storage by the ion adsorption/desorption on the surfaces, in which the charges are separated [6]. They are of stable all through the charge discharge procedure. At same time, the pseudocapacitors are determined by fast reversible redox kinetics on the electrode surface which possesses theoretically high capacitance [7]. Transition metal selenide (TMSe), exhibit a promising prospect owing to their better electronic conductivity [8-10]. Compared with the metal oxides, transition metal selenide exhibits improved electrical conductivity because of anion exchange providing the smaller band gap. However, selenium prevents the self agglomeration and volumetric changes of the transition metal selenide hindering the cycle stability and durability [11-14]. Herein, in the NiSe@ZnSe composite, the Ni being introduced into the composite promotes the electrochemical activity of the metal selenide. Meanwhile, the selenium based compounds boost up charge transfer properties at electrode/electrolyte interface which promotes electrical conductivity and the superior electrochemical properties. Beirong Ye et al. demonstrated NZSe composite with 651 mAhg^{-1} satisfying 97.6% cycle stability. As an asymmetric device delivers the 97.7% capacity retention after continuous 10,000 cycles. Herein, the hydrothermally

synthesized NiSe@ZnSe composite regarded as the valuable material for supercapacitor application is somewhat cheaper, less toxic and environmental friendly. Inspired by the recent outcome for metal selenide, an effort has been taken to incorporate Polyvinyl pyrrolidone (PVP) and Sodium Lauryl Sulfate (SLS) assisted NiSe@ZnSe nanostructures through utilizing a simple hydrothermal method. Furthermore, the effect of different surfactant on the electrochemical studies was explored to specify surfactant role. Additionally, the PVP assisted NiSe@ZnSe composite afford plentiful electroactive sites. The result showed the performance of the electrode materials assisted by using the surfactant (PVP) was better than that of surfactant (SLS). Based on the various analyzing techniques, the as-prepared material shows the good pseudocapacitor properties for supercapacitor application.

2. Experimental Section

The required NiSe@ZnSe composite electrode material products were prepared employing hydrothermal route for energy storage applications. In a typical process, a mixed solution 0.1M nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1M zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were prepared in 50 ml de-ionized water under careful stirring for 30 minutes to form the homogeneous solution. 0.1 M selenium suspended in 20 ml hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was added to prepared solution and the resultant black solution was observed. The autoclave reaction temperature maintained at 180°C was mentioned as NZS-1. The resultant material was thoroughly centrifuged, washed to remove further impurities and dried in the vacuum oven for overnight. Similarly, the nanoball and nanograin-like NiSe@ZnSe was synthesized by same procedure by the addition of surfactant SLS and PVP were mentioned as NZS-2 and NZS-3 respectively. The electrochemical properties of the as prepared electrode material were characterized via biological SP 150 instrument as reported in our earlier studies.

3. Results And Discussion

X-ray diffraction is conducted to confirm crystallinity of NZS composite. The powered XRD spectra of the surfactant assisted samples and the surfactant free NiSe@ZnSe is shown in the **Fig. 1a**. The observed diffraction peak of NiSe phase revealed at 27.2° , 32.4° assigned to (100) and (101) and the crystalline peak at 27.2° , 45.2° , 53.7° , 65.8° , 72.6° attributed to ZnSe phase can be readily indexed to (111), (101), (220), (311), (400), (331) planes of NiSe@ZnSe according to the JCPDS cards (#020892) and (#371463). No peaks from other phases were found, signifying the high purity was obtained. Besides, it is further indicated the surfactant does not change the crystal structure nevertheless observably affects the peak intensities of the as-prepared composite. The high crystallinity suggests that the composite NiSe@ZnSe is well appropriate for the application concerning the supercapacitor electrode material.

Raman studies was executed to study vibrational and structural properties of NiSe@ZnSe. Herein, asymmetric peak observed at 245 cm^{-1} and 535 cm^{-1} ascribed to the longitudinal phonon modes of Raman spectra in ZnSe. Whilst, the peak ascribed to 204 cm^{-1} and 245 cm^{-1} corresponding to the A_g and T_g stretching mode of NiSe. The peak that identifies the selenide formation at 143 cm^{-1} attributed to the

stretching mode of vibration Se-Se pair as shown in **Fig. 1b**. Hence, the observed Raman spectra experiential the existence of phonon group in present work. The SEM image of the sample without surfactant and the samples derived from the SLS and PVP shows schematic spongy cotton, nanoballs and grass-like NiSe@ZnSe composite obtained through the simple hydrothermal route as shown in **Fig. 2a-c**. FE-SEM images of the SLS assisted samples shows the coagulated nanoballs-like morphology. Finally, uniformly arranged nanoparticles are relatively smoothed surfaced and this surface improves the number of reactive sites for the reaction which results in the enhanced electrical conductivity. PVP assisted NiSe@ZnSe composite shows grass-like morphology. The high aspect of surface to volume ratio of the loosely packed grass-like structures result in accessibility of more surface area for the electrolyte and lead to the enhanced reaction rates of electrochemical activity of as-prepared active material.

The comprehensive study about the morphological and the structural features of the as prepared grass-like morphological of NiSe@ZnSe composite (NZS-3) assisted with PVP surfactants were further investigated from TEM analysis. **Fig. 3a-c** exhibits the TEM images of NZS-3 active electrode which was reliable with the SEM observations. The NiSe@ZnSe nanocomposites have number of active site for electrochemical reactions and formed a high surface area which are favorable to the Faraday reaction involving the active electrode and the electrolyte ions. Consequently, grass-like morphology is well appropriate as an electrode material.

To explore the elemental analysis of prepared NiSe@ZnSe composite assisted by the PVP surfactant, XPS analysis was carried out. XPS spectra obviously reveal the NZS-3 composed of Ni, Zn and Se without any further impurities. XPS spectra with deconvoluted curves fitted using the Gaussian methods are presented in the **Fig. 4a**. **Fig. 4b** explored Ni2p. For Ni2p spectrum the peaks at 855.6eV and 873.2eV attributed to the $\text{Ni}^{2+} 2p_{3/2}$ and $\text{Ni}^{2+} 2p_{1/2}$. In the Zn2p spectrum the two dominant peaks at 1021.2 and 1044.3 ascribed to $\text{Zn}^{2+} 2p_{3/2}$ and $\text{Zn}^{2+} 2p_{1/2}$ shown in **Fig. 4c**. The presence of binding energy value at 55.1 eV recognized to the oxidation state of Se3d_{5/2} correspondingly in **Fig. 4d**. This outcome brings out the successful formation of the NiSe@ZnSe composite material via hydrothermal route.

The electrochemical analysis of NZS-3 composite was examined. The cyclic voltammetry (CV) is used to learn the reversibility and capacitive behavior of the active electrode material. Initially, CV was performed for NZS-3 composite electrodes with 0 to 0.6V at 10 to 70 mVs^{-1} . The observed CV results are reliable and signifying the reasonable rate capability of active electrode material. Even at scan rate of 10 mVs^{-1} , the two faradic redox peaks remains symmetrical indicating pseudo capacitive characteristics, that results in fast electron transport and low resistance [15]. Meanwhile, integral CV curves area increased with similar shape also increased [16]. With increase of the sweep rate from 10-30 mVs^{-1} the shape of CV curves are maintained well and peak current increases, presenting promising potential for goods capacitance. To evaluate the electrochemical properties, **Fig. 5a-c** demonstrates CV cures of NZS-1, NZS-2 and NZS-3 composite electrode. The integral area of the active electrode material are given in the following order at the scan 10 mVs^{-1} (NZS-3> NZS-2> NZS-1). The improved NZS-3 electrode presentation is because of the availability of the electroactive sites which results in the better ionic interaction.

To further investigate the electrochemical properties charge discharge analysis was carried out at different current densities. The GCD curves at current densities of 1, 2, 3, 5, 10 Ag⁻¹ are shown in **Fig. 6(a-c)**. NZS-3 explored 442 Fg⁻¹ at the current density of 1 Ag⁻¹. NZS-3 when compared with the other two electrodes, contributes fast electron transfer. The outstanding capacitive performance of NZS-3 is due to the rapid electrons transfer, thus showing the reasonable electrochemical performance.

As-prepared electrode material impedance spectra was performed at the open circuit potential [17]. Nyquist plots **Fig. 5d** shows the typical EIS spectra. The electrode NZS-3 displays the sloping line at the low frequency which reveals more electrolyte ions diffusion to active material. Hence, prepared electrode exhibits improved rate capability. Long cycle life is another significant criterion for supercapacitor. The cycle stability NZS-3 electrode at 10 Ag⁻¹ is shown in **Fig. 6d**. It delivers good cyclic performance of 99.3% after 2000 cycles.

As shown in the **Fig. 7a,b** showing the newly fabricated device illuminates the red (1.5V) light emitting device (LED) and delivers the current of 1.5V suitable for supercapacitor applications [18-21]. The cyclic voltammetry curves of the asymmetric device measured in 0-1.5V at different 10, 20, 30, 40, 50,100 mVs⁻¹ are shown in **Fig. 8a**. The CV curve reported under varying potential window is represented in the **Fig. 8b**. Besides, the specific capacitance of NiSe@ZnSe//AC is 149,118, 82, 25, 8 Fg⁻¹ at the current density of 1, 2, 3, 5, 10 Ag⁻¹ respectively in **Fig. 8c**. The cycle stability was studied by repeated charge discharge cycles at 10 Ag⁻¹. After continuous 2000 cycles the electrode achieved capacity retention of 99.48% is shown in **Fig. 8d**. To further confirm possibility of NiSe@ZnSe//AC for electric devices, the charged asymmetric device is connected in series. **Table 1** explored energy and power density values of the prepared material.

Table 1 Energy and power density

<i>Potential window (V)</i>	<i>Energy density(W h Kg⁻¹)</i>	<i>Power density (W kg⁻¹)</i>
1.5	46	246
	36	487
	25	731

4. Conclusions

To summarize, the NiSe@ZnSe electrode material were synthesized by simple hydrothermal route. The as-prepared NZS-3 electrode results in improved rate capability. Furthermore, the NiSe@ZnSe//AC asymmetric device shows improved energy density of 46 Wh Kg⁻¹ at 246 Wkg⁻¹ and long cycle life of 99.48% of capacity retention. It showed the operating potential of 1.5V with 149 Fg⁻¹ at 1 Ag⁻¹ current

density. The two assembled NiSe@ZnSe//AC asymmetric device explored enhanced behaviour. Practically, the specific capacitance of the SLS assisted NiSe@ZnSe electrode is somewhat little weak, signifying the considerable role played by the PVP assisted grass-like NiSe@ZnSe.

Declarations

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Figures

Figure 1

a) XRD b) Raman for NiSe@ZnSe composite

Figure 2

a) FE-SEM studies of NiSe@ZnSe without surfactant b).SLS assisted NiSe@ZnSe c). PVP assisted NiSe@ZnSe

Figure 3

a-c) HR-TEM images of PVP assisted NZS-3

Figure 4

a) XPS survey spectrum for NZS-3 composite assisted surfactant PVP b) XPS spectra of Ni2p c) Zn2p d) Se3d

Figure 5

a) CV analysis for NZS-1 b) NZS-2 assisted with SLS c) NZS-3 assisted with PVP d. Impedance spectra of NiSe@ZnSe composite

Figure 6

a) Charge discharge analysis for NZS-1 (without surfactant) b) NZS-2 assisted surfactant SLS c) NZS-3 assisted surfactant PVP d) Stability for NZS-3

Figure 7

a,b) LED flash for the fabricated asymmetric device

Figure 8

a) CV for NiSe@ZnSe//AC b) Diverse potential c) GCD d) Stability for NiSe@ZnSe//AC asymmetric device