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ZIF-67/PEDOT Hybrid Conductive Composite as a Superior Electrode for All-Solid-State Symmetrical Supercapacitor

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Abstract

Conducting polymers are gaining attention to enhance the electrical conductivity of non-conducting metal organic frameworks while maintaining their high porosity. In this work, a facile combination of ZIF-67 and PEDOT are explored as a composite electrode for all solid-state symmetrical supercapacitors. The ZIF-67/PEDOT composite supercapacitor possesses a high specific capacitance and energy density as compared to pristine ZIF-67 electrode.

1. Introduction

The continuous demand for clean and alternate energy is the need of an hour. Therefore, alternate energy storage devices like batteries and supercapacitors are attracting recent research attention. In view of this supercapacitors are the energy storage devices possessing high specific capacitance, high cyclic stability, high energy and power density [1]. To further extend the demand of supercapacitors, a novel composite of ZIF-67 and PEDOT are synthesized which is beneficial to enhance the conductivity of pristine ZIF-67 while maintaining the porosity and surface area characteristics of ZIF-67. Furthermore, the ZIF-67/PEDOT composite electrode shows a high specific capacitance of 107 F/g at a current density of 1 A/g which is much higher than pristine ZIF-67 electrode (35 F/g).

Also, an all-solid-state symmetrical supercapacitor is assembled using two equally weighted ZIF-67/PEDOT composite electrodes. The assembled device shows a high energy density of ~11 Wh/kg along with a power density of ~200 W/kg. These studies confirm the superiority of ZIF-67/PEDOT composite as compared to pristine ZIF-67 when used as an electrode for supercapacitor applications.

2. Experimental Section

Synthesis of ZIF-67/PEDOT composite

450 mg of cobalt nitrate hexahydrate is dissolved in 3 mL of deionized water and 1 mL of Polyethylene dioxythiophene (PEDOT) were dispersed separately in 20 mL of deionized water. The PEDOT sample was sonicated for 30 minutes to get a clear dispersion, followed by the addition of 5.5 g of 2-methylimidazole ligand. The metal ion solution was then added to the mixture of PEDOT and ligand and the resulting reaction is left to stir for 6 hours at room temperature. After the completion of the reaction, the ZIF-67/PEDOT composite is obtained by centrifugation at 10,000 rpm for 20 minutes. The obtained product was washed with deionized water (twice) and methanol (once) before drying it under vacuum conditions i.e., 80 ºC, 12 hours.

3. Results and Discussion

The structural and morphological characterization of ZIF-67/PEDOT composite is performed using XRD and FESEM measurements. Fig. 1a depicts the XRD patterns of ZIF-67/PEDOT composite in which the observed peak positions are in good agreement with previous reports. The XRD pattern of ZIF-67/PEDOT composite shows peaks at 7.3° (011), 10.3° (002), 12.6° (112), 14.6° (022), 16.3° (013), 17.9° (222), 22° (114), 24.42° (233) etc. depicts the peak of ZIF-67 crystals. On the other hand, the peak at 26.5° corresponds to the characteristic peak of PEDOT [2]. These peaks confirm the successful formation of ZIF-67/PEDOT composite. Fig.1b shows the morphology of ZIF-67/PEDOT composite using Scanning Electron Microscopy (SEM) characterization. The morphology reveals the formation of ZIF-67 crystals along with PEDOT layers with overall size in the range of few 100 nanometers. The porous characteristic of as synthesized composite is determined using BJH pore size distribution. The BJH study reveals that the ZIF-67/PEDOT composite consists of proper distribution of micropores and mesopores. The average pore size determined for ZIF-67/PEDOT composite is 1.26 nm. This hierarchal distribution of micro- and mesopores are beneficial for better transport of electrolyte ions when employed as an electrode for supercapacitors.

These material characterizations confirm the formation of ZIF-67/PEDOT composite efficiently.

The electrochemical performance of as synthesized ZIF-67/PEDOT composite electrode is determined using cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) analysis. Firstly, the composite electrode is tested in three electrode system for CV analysis at various scan rates varying from 5 to 100 mV/s. The composite electrode shows a specific capacitance of 34 F/g at a scan rate of 5 mV/s. The electrochemical analysis in three electrode system is performed using 1 M H_2SO_4 as an aqueous electrolyte within a potential scan of 0 to 0.5 V. Fig. 1c shows GCD curves for composite electrode at current densities varying from 0.5 to 10 A/g. From GCD curves, the composite electrode shows a high specific capacitance of 107 F/g at a current density of 1 A/g within a potential window of 0 to 0.5 V. The specific capacitance value so obtained is much higher than pristine ZIF-67 electrode at same conditions i.e., 35 F/g. The Fig.1c also reveals that with increase in current density, the specific capacitance decreases continuously. This is because at higher current densities the electrolyte ions do not get enough time to access all the pores of active electrode.

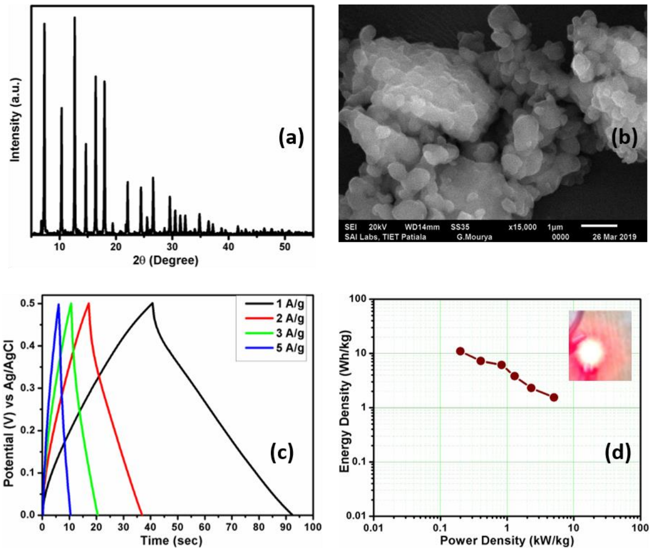

Fig. 1 Characterization of ZIF-67/PEDOT composite (a) XRD spectra and (b) SEM image, (c) GCD analysis at various current densities and (d) Ragone plot for ZIF-67/PEDOT//ZIF-67/PEDOT Symmetrical Supercapacitor.

The study of composite electrode in three electrode system confirms the superiority of the composite in terms of high specific capacitance values. However, the practicality of the electrode is shown by assembling the overall supercapacitor. For this approach an all-solid-state symmetrical supercapacitor is assembled using two composite electrodes and PVA-1 M H_2SO_4 polymer gel electrolyte. The device works commendable with an operating potential window of 0 to 1.6 V. The device is tested in two electrode configurations using both CV and GCD techniques. Fig. 1d shows Ragone plot which determines the energy density wrt to corresponding power density of the as assembled symmetrical supercapacitor device. The device shows a very high energy and power densities i.e., 11 Wh/kg and 200 W/kg respectively which is much higher than their pristine ZIF-67 counterparts. This is ascribed with the synergistic effects associated between ZIF-67 and PEDOT. The comparison of present work with other MOFs based supercapacitors is given in Table I below.

Table I Performance Comparison of ZIF-67/PEDOT Based Symmetrical Supercapacitor with Other MOFs Based Supercapacitors

Symmetrical Supercapacitor	Electrolyte	Energy Density (Wh/kg)	Reference
Cu-CAT NWA	PVA-KCl	2.6	[3]
Mn-MOF/CNT	1M Na_2SO_4	6.9	[4]
MOF-5 NPC	PVA-Na_2SO_4	8.26	[5]
Co-MOF derived Co_3O_4/C	PVA-KOH	8.54	[6]
MOF-199 derived NPC/CNT	6M KOH	9.1	[7]
ZIF-67/PEDOT	PVA-1M H_2SO_4	11	This Work

4. Conclusions

In this paper, ZIF-67/PEDOT composite is synthesized using simple one-pot stirring approach. The novel composite is utilized as an electrode for solid state supercapacitors. The as fabricated composite electrodes are tested using 1 M H_2SO_4 electrolyte within a potential window of 0 to 0.5 V. Further, the practical utility of the composite is determined by determining their energy and power density. The device delivers a high energy density of 11 Wh/kg and power density of 200 W/kg. These values confirm that the novel ZIF-67/PEDOT composite based device is beneficial for next generation alternative energy storage devices.

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