Three-dimensional architecture of tin dioxide doped polypyrrole/reduced graphene oxide as potential electrode for flexible supercapacitors

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Abstract

In this work, a facile one-pot chronoamperometry method was adopted to prepare the three-dimensional (3D) SnO_2 incorporated polypyrrole/reduced graphene oxide to achieve high stability and elevated electrochemical properties. A detailed study has been performed to correlate the structure, surface morphology, redox reaction at the electrode and its impact on the suitability of the material. The morphology analysis showed the presence of SnO_2 nanoparticles on graphene sheets forming irregular flower-like coarse clusters consisting of spinule-like structures on the surfaces that are embedded in polypyrrole matrix. The electrochemical performance reveals that SnO_2-PG exhibits a high specific capacitance of 330 F g^{-1} at a current density of 1 A g^{-1} in 1 M KCl electrolyte and an excellent cycling stability of 82 % even after 2000 cycles, a significant value for polymer nanocomposite. The existence of a high degree of porosity, considerably improved active surface area and the conductivity of SnO_2-PG facilitated the better ionic penetration which demonstrates a new architecture for high performance supercapacitor.

1. Introduction

Because of the many technologically important properties such as, e.g., rapid charge/discharge cycles, study of supercapacitors have attracted increased research attention. Despite short-term energy storage, they are used in various applications in, e.g., transportations, regenerative breaking, short-term energy storage devices, burst-mode power delivery, etc. Recent breakthroughs in supercapacitors involve novel electrode materials which are conducting, porous with improved electrochemical performances. They are also reported to possess greater energy densities than common conventional dielectric capacitors [1]. The mechanism of energy storage is related to not only charging of electrochemical double layer at the electrode-electrolyte interface, but also to pseudocapacitance involving reversible faradaic charge transfer reactions [2]. Conducting polymers offer advantages of low materials and deposition cost. They can be synthesized from a monomer, an oxidizing agent and a dopant [3]. To improve performance of the conducting polymers and to extend their function, additional materials are incorporated. Composites of polypyrrole (PPy) and graphene were successfully prepared by electrochemical reduction of pyrrole and graphene oxide [4]. Incorporation of metal oxide is an attractive alternative to provide high specific capacitance and low resistance making it easier to construct high energy, high power supercapacitors [5]. SnO_2 has become the important functional material due to its large band gap and excellent optical and electrical properties [6] and has been extensively explored recently as a high energy density alternative anode material to traditional graphite. The key issues hindering the commercialization of tin oxide are poor conductivity retention and large volume expansion. The use of highly conductive matrix is employed to improve the cycling stability of metal oxides by suppressing their volume changes and by increasing their electrical conductivity.

We demonstrate a novel one-step, facile approach of electrochemical deposition of a novel 3D ternary material. SnO_2 doped graphene/polypyrrole (SnO_2-PG) composite has been

deposited on a flexible current collector for the elevated electrochemical performance. SnO_2 doping is found to enhance the capacitance, concomitantly to improve the capacitance retention, and cycling compared to those of PPy and PG. The fabricated electrodes are binder free, conductive additive free and are highly flexible.

2. Experimental

Preparation of SnO_2-PG

Graphene oxide (GO) was synthesized from graphite flakes by a modified Hummers method and purified by dialysis, the details of which were described in the literature [7]. The synthesis of 3D ternary architecture of SnO_2-PG was carried out by electrodeposition method where the electrochemical polymerization of pyrrole monomer and electrochemical reduction of GO are supported (supplementary data, Experimental section).

3. Results and discussion

Figure 1a shows the X-ray powder diffraction (XRD) patterns for SnO_2-PG, which is consistent with JCPDS card no. 41-1445. The peaks at 26.6°, 33.6° and 51.6° correspond to (110), (101) and (211) respectively. The highly broadened diffraction peaks indicate formation of small size SnO_2 nanocrystals [8]. The diffraction peaks of reduced GO (rGO) are observed at 26.2° and 44.5° in PG corresponding to (002) and (100) (JCPDS card 15-1621) and the reduction of GO is confirmed by the absence of sharp peak at 26°. The peak at $2\Theta = 26°$ indicates the typical characteristic peak of PPy [4].

Figure 1b shows comparison of the Raman spectra for PPy, PG and SnO_2-PG. The broad peaks at 1599 and 1586 cm^{-1} are assigned to G band and characteristic peaks at 1358 and 1326 cm^{-1} correspond to the D band of graphene in PG and SnO_2-PG respectively [9]. The

calculated I_D/I_G ratios are 0.84 and 0.83 for PG and SnO_2-PG respectively indicating better reduction of GO in SnO_2-PG. The bands at 1577 cm^{-1}, 1404 cm^{-1}, 1053 cm^{-1} and 978 cm^{-1} represent that of PPy and are suppressed in PG and still diminished in SnO_2-PG which validated the incorporation of rGO and SnO_2 in the polymer matrix.

The morphologies of SnO_2-PG, PG and PPy are investigated by FESEM [Fig. 2]. The SnO_2 nanoparticles grew on graphene sheets and form irregular flower-like coarse clusters, and with many spinule-like structures on their surfaces manifested into lots of voids. The PG shows an aggregated morphology and provides fairly less area for the insertion and extraction of ions. By comparison with the FESEM images of samples, it is observed that the tiny SnO_2 nanoflowers with spinules [10] distributed on the curly graphene nanosheets act as spacers to prevent the re-stacking of individual grapheme nanosheets where as PPy exhibits a rough surface of bulbous morphology. The EDS spectrum (Fig. S1) reveals the presence of Sn, O and C in the prepared ternary nanostructure.

Electrochemical performance of the SnO_2-PG electrode is evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) using standard three-electrode system with 1 M KCl as the electrolyte, and is compared with those of PPy and PG. Figure 3a displays the results for CV, which shows enhanced current output from SnO_2-PG. The larger area of the closed CV loop indicates the enhanced electrochemical performance of SnO_2-PG electrode. It may be due to the engineering of the active material from its individual counterparts. The result implies that SnO_2 nanoparticles play a critical role in promoting the electrochemical performance. The as-obtained electrode material obeys two mechanisms of energy storage such as the electric double-layer capacitor (EDLC) and pseudocapacitance. The results for PPy deviats from the typical rectangular form and suggests the pseudocapacitive nature. The SnO_2 nanoparticles act as spacers to prevent the restacking of individual graphene

sheets whereas rGO serves as the framework for anchoring the SnO_2 nanoflowers and these structures are embedded in PPy matrix.

Figure 3b shows the galvanostatic charge/discharge processes for PPy, PG and SnO_2-PG at a current density of 1 A g^{-1}. All the curves are linear and exhibit a typical triangular shape, which denotes good electrochemical capacitive characteristics and that the charge is stored at the electrode-electrolyte interface. Specific capacitance (C) of the electrode can be calculated from the charge–discharge measurements using the Eq. [11]

$$C = (I.t) / (\Delta V.m) \tag{1}$$

where C is the specific capacitance of the electrode material, I is the constant discharge current, t is the discharge time, m is the mass loading of the active material and ΔV is the potential window during discharge. The specific capacitance of SnO_2-PG is found to be   330 F g^{-1} whereas PG and PPy electrodes exhibit 129 and 76 F g^{-1} at 1Ag^{-1} respectively.

The cycling stability at a constant current density of 1 A g^{-1} as a function of the cycle number is shown in Fig. 3c. High capacity retention of 82% of its initial capacitance is demonstrated by SnO_2-PG even after 2000 cycles. PPy and PG retain only 54 and 70 % of their initial capacitance under the same conditions. This enhanced electrochemical activity is attributed to the voids created by formation of SnO_2 nanoflowers in PG. SnO_2 nanoparticles in turn increase the stability to the rGO sheets which acts as a frame work for holding PPy and SnO_2 preventing the swelling and shrinking during the charge/discharge process and responsible for better cycling stability of SnO_2-PG. The inner layer of the well-dispersed graphene enhances the mechanical strength of the SnO_2-PG electrode avoiding the damage of the electrode material. For the preparation of electrodes, highly flexible stainless steel mesh is used as the current collector. This results in a flexible, freestanding electrode (Fig. 3c (inset)) which is conductive additive and binder free one.

The energy density and power density were calculated using the formula [11]

$$E = \frac{1}{2}C\Delta V^2, \tag{2}$$

$$P = \frac{E}{t}, \tag{3}$$

where "E" is the energy density, 'C' is capacitance of the material, 'ΔV' is the potential window (Volt), 'P' is the power density and 't' is the discharge time. Ragone plots of PPy, PG and SnO_2-PG are shown in Fig. 3d. Compared to PPy and PG, the ternary composite SnO_2-PG exhibits high energy and power density. SnO_2-PG provides a maximum power density of 5 kW kg^{-1} and maximum energy density of 201Wh kg^{-1}.

4. Conclusions

In summary, a novel flexible 3D ternary architecture of SnO_2 doped PG electrode has been designed and fabricated by a facile electrochemical deposition method by which the combined effect of the three materials is tapped successfully. PPy provides a conductive matrix for efficient electron transport whereas, the anchoring of SnO_2 on graphene effectively reduces the degree of restacking of graphene sheets and enhances the surface area utilization efficiency. The binder-free, conductive additive free, flexible electrode exhibits remarkable supercapacitive performance with a high specific capacitance of 330 F g^{-1} at a current density of 1 A g^{-1} and pronounced cycling life of 2000 cycles in 1 M KCl aqueous electrolyte solution. This approach is highly relevant to achieve commercial supercapacitors supporting portable energy storage devices.

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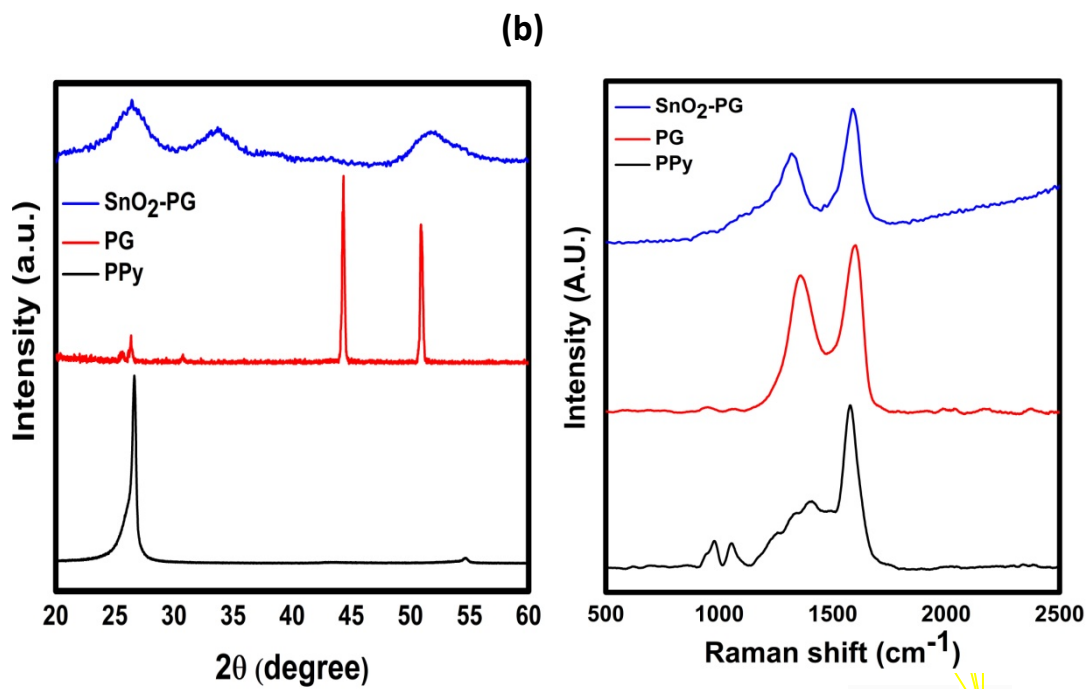
(b)

(b)

Fig. 1.
(a)

XRD patterns of SnO_2-PG, PG and PPy
(b) Raman spectra of SnO_2-PG, PG and PPy
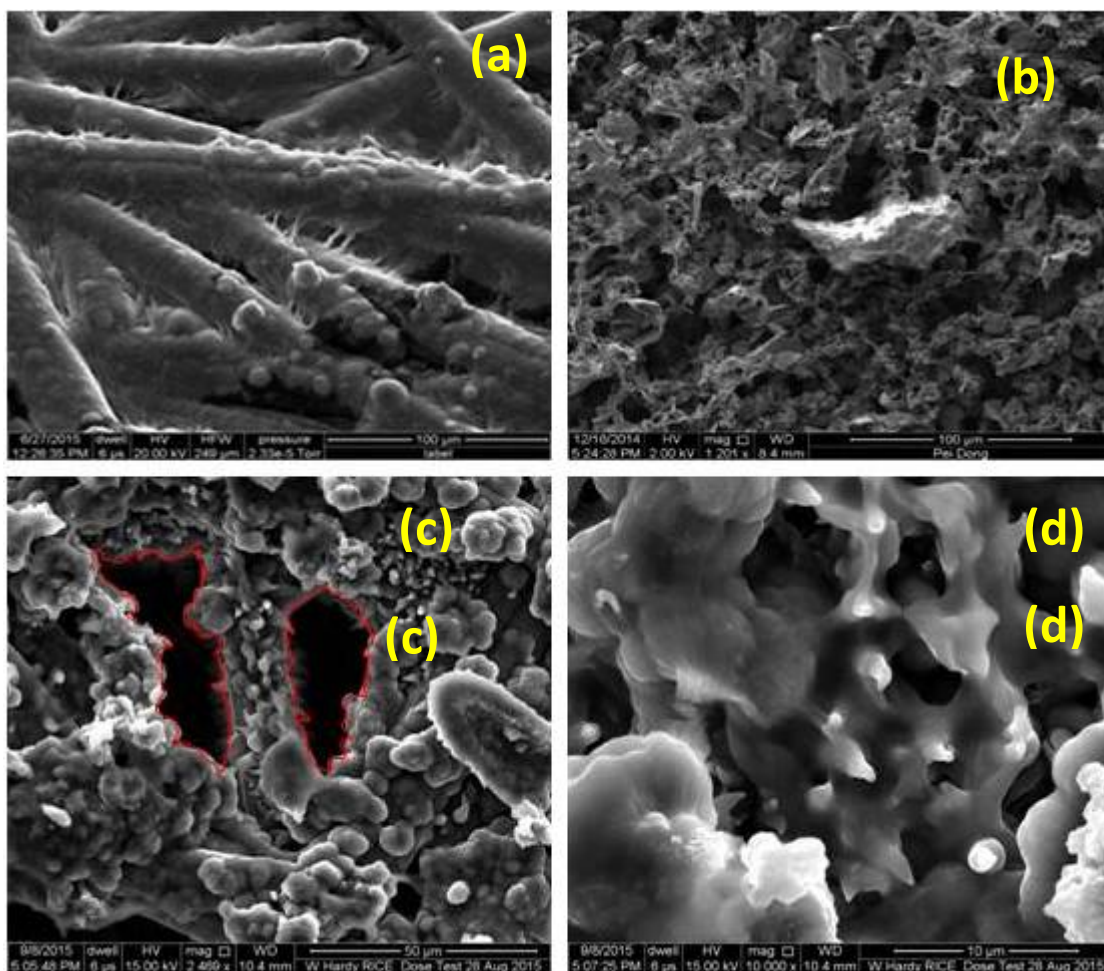
Spinules

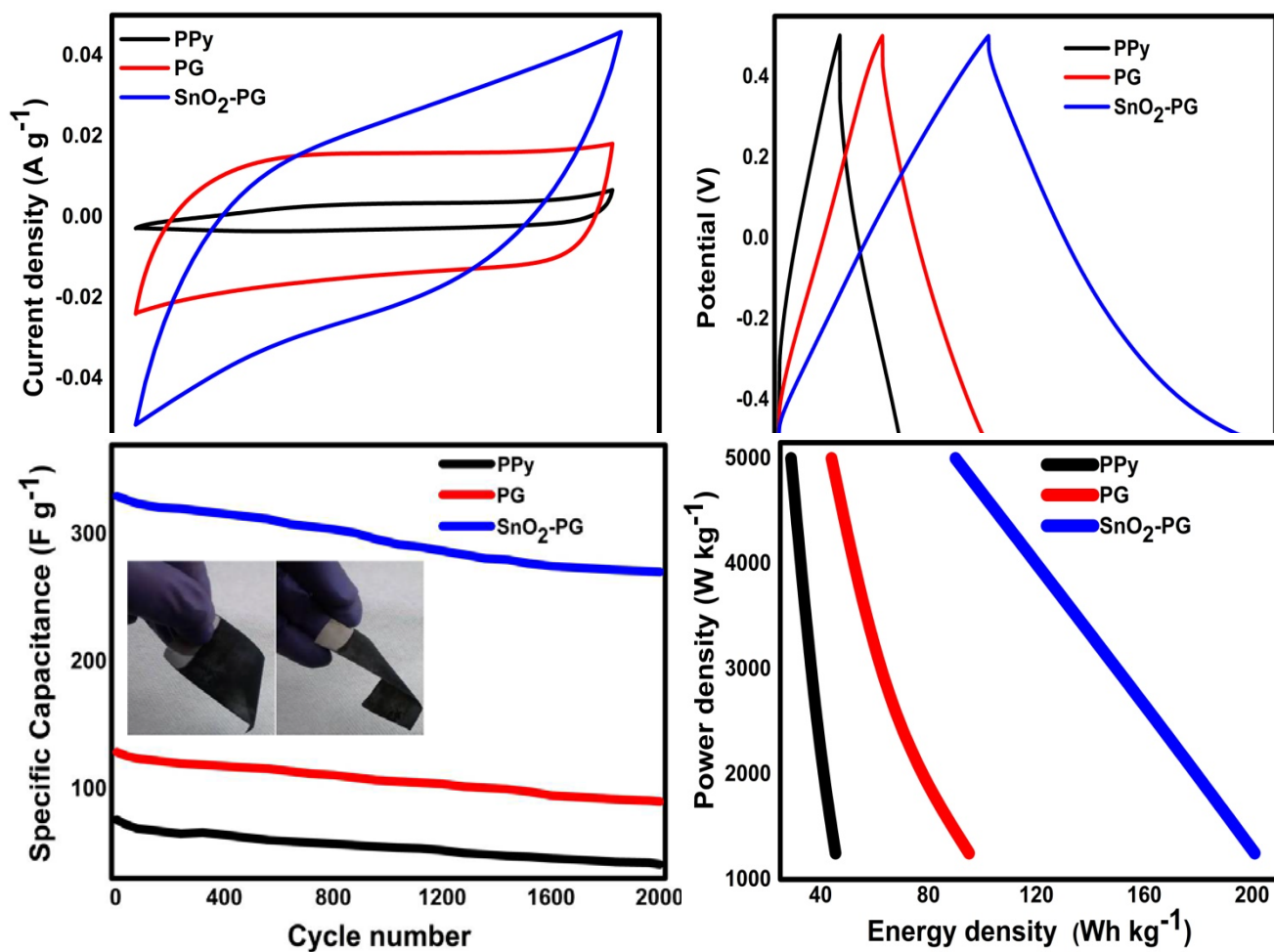**Fig. 2.** FESEM micrographs of (a) PPy (b) PG and (c,d) SnO_2-PG.

Fig. 3. (a) Cyclic voltammograms at a scan rate of 10 mV s^{-1} (b) Galvanostatic charge/discharge curves (c) Cycling stability at a current density of 1 A g^{-1}, (inset) images of flexible electrode (d) Ragone plots of PPy, PG and SnO$_2$-PG electrodes.