

Mechanochemical synthesis of poly(2,5-dimethoxy aniline) nanobelts and its electrochemical performance in hybrid supercapacitors

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Abstract A solvent-free mechanochemical route for the preparation of poly(2,5-dimethoxyaniline) hydrochloride nanostructures is developed and reported in the article. High conductivity, good crystallinity, and nanostructured morphology are observed for the prepared polymer. This polymeric powder is utilized as a cathode material in hybrid supercapacitor and its electrochemical performance is evaluated and discussed in this short report. The maximum specific capacitance of the poly(2,5-dimethoxyaniline) hydrochloride/activated carbon hybrid supercapacitor is found to be 125 F g^{-1} at 1 mA cm^{-2} current density. The cell delivers a specific energy as high as 50 Wh kg^{-1} at a specific power of 97 W kg^{-1} and also exhibits an excellent cycle performance with more than 99% coulombic efficiency and the maintenance of 85% of its initial capacitance after 1,000 cycles.

Keywords Polymers · Energy storage · Electrical properties · Field emission scanning electron microscopy · X-ray diffraction technique

Introduction

The growing demand to prepare high quality nanostructured conducting polymers through simpler and efficient route for

applications in various emerging technological areas [1–5] activates the researchers across the globe to develop alternate but attractive and efficient synthetic routes. In this process, several synthetic methodologies have been developed for preparing conducting polymers, in particular polyaniline (PANI) [6]. The methodologies adopted for synthesizing nanostructured PANI often do not suit for the preparation of its derivatives [7]. Hence, many different approaches are needed to synthesize high quality polymers from aniline derivatives that are easily processable than PANI. In this perspective, a simple, sustainable, and novel solid-state route has been successfully developed for preparing highly conductive and crystalline poly(2,5-dimethoxyaniline), and the findings are reported in this article. Poly(2,5-dimethoxy aniline) is an important processable polyaniline derivative that has been used for a variety of applications [8]. Electronically conducting polymers (ECPs) are promising materials for the realization of high-performance supercapacitors, as they possess high specific capacitances and conductivities in the charged states; furthermore, their charge–discharge processes are generally fast. Application of the ECPs in energy storage devices is well known [9], and recent studies [10–13] in this area gave impetus to fundamental and applied research on ECPs-based new materials. In the present report, we also present the electrochemical performance of mechanochemically prepared poly(2,5-dimethoxy aniline) hydrochloride (herein termed as PDMA-HCl) when employed as a cathode in asymmetric hybrid supercapacitor.

Materials and methods

In a typical procedure, 1.53 g of solid 2,5-dimethoxy aniline (Sigma-Aldrich, 98%) taken in a glass mortar was

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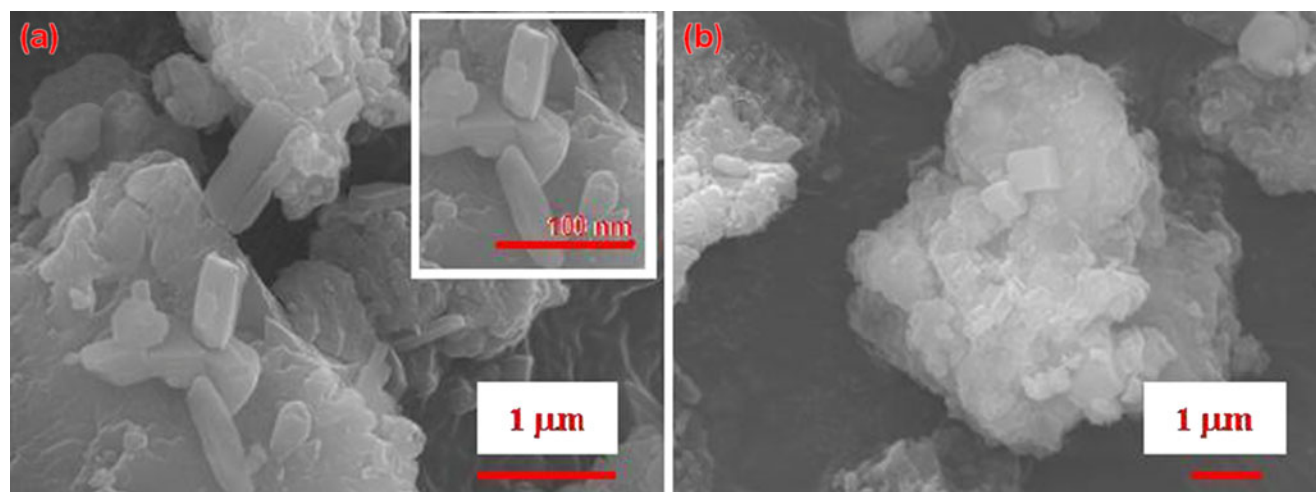


Fig. 1 FE-SEM micrographs of **a** PDMA-NBs and **b** PDMA-UD

thoroughly hand-ground with 0.5 ml of HCl (Merck, AR Grade) for 30 min. To this finely ground mixture, 2.7 g of solid FeCl_3 (Sigma-Aldrich, 99%) was added spontaneously and the same was continuously hand-ground for 20 min until the color of the reactant mixture completely turned dark green. The resultant polymer was washed with copious amount of double-distilled water, acetone, and ethanol until the washings turned colorless. PDMA-HCl was then dried in a vacuum oven at 40 °C overnight. The purified dry PDMA-HCl powder was used for characterization. Undoped counterpart of PDMA (herein termed as PDMA-UD) was also prepared as detailed above in the absence of doping agent for comparative purposes. The morphology of the PDMA samples was examined by field emission scanning electron microscopy (JSM 35 CF JEOL FE-SEM operating at 15 kV using normal incidence). The crystallinity of the prepared PDMA-HCl and PDMA-UD was studied by X-ray diffractometry (XRD, X'PERT PRO PANalytical, Netherlands) with $\text{CuK}\alpha$ as a radiation source. The conductivity measurements were made

using KEITHLEY and made four probe conductivity meter for the polymer samples pressed into pellets. The electrochemical performance of the hybrid supercapacitor was studied in the form of an assembled CR 2032 coin-type cell. The positive electrode was prepared by mixing 80 wt.% PDMA-HCl/PDMA-UD, 15 wt.% Ketzen black (KB) as the conductive additive, and 5 wt.% teflonized acetylene black (TAB) as the binder. This was then pressed on a 200-mm² stainless steel mesh that acted as the current collector. The negative electrode was prepared by the same method and it consisted of 85 wt.% activated carbon, 10% KB, and 5 wt.% TAB. The mass ratio of the cathode to anode was approximately 1:2. The PDMA-HCl/activated carbon (AC) and PDMA-UD/AC cell was assembled within an argon-filled glove box and was composed of a PDMA-HCl/PDMA-UD, respectively, as cathodes, a porous polypropylene separator (Celgard 3401), and an AC anode in 1.0 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 v/v) electrolyte. Cyclic voltammograms of the PDMA-HCl/AC and PDMA-UD/AC cells were obtained with an

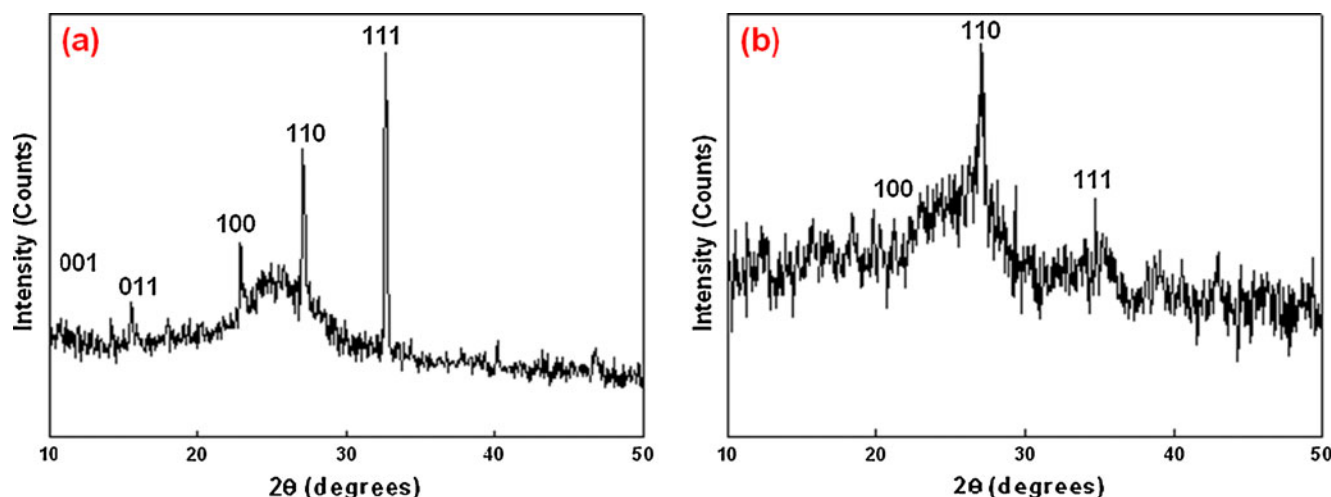


Fig. 2 XRD patterns of **a** PDMA-NBs and **b** PDMA-UD

electrochemical analyzer (SP-150 Bio-Logic, France). Galvanostatic charge/discharge experiments were carried out between a cell voltage of 0–3 V and at a current density of 1 mA cm^{-2} using a cycle tester (WBCS 3000, WonATech, South Korea).

Results and discussion

The surface morphology of PDMA-HCl prepared through solid-state route indicates the formation of shorter nanobelts with size ranging from 90 to 100 nm (Fig. 1a). In some areas of the FE-SEM image, one could notice stacked rod-like structures which may be due to the aggregation of polymeric particles. Since the mechanochemical reaction pathway induces the reactants only on their surface, it is quite difficult to control the morphology of PDMA-HCl as such. FE-SEM image of PDMA-UD (Fig. 1b) shows the formation of larger polymeric particle. This may be due to more agglomeration as a result of the absence of a doping agent in the solid reaction mixture. We suppose that the presence of the doping agent induces the formation of a nanostructure. Our supposition is evidenced by the well-established fact that the structure of the products depends on the rate of nucleation and the growth of the products in the solid-state reaction [14].

X-ray diffraction pattern of resultant PDMA nanobelts (PDMA-NBs) (Fig. 2a) shows three sharp and less intense peaks at $2\theta=11.5^\circ$ (001), 17° (011), and 24° (100). There are two other sharp and intense peaks at $2\theta=27^\circ$ (110) and 33° (111). The former peaks may be due to the presence of dopant anions in the polymer chains. The peak noticed around 27° represents the characteristic distance between the ring planes of benzene rings in adjacent chains or the close contact interchain distance while the one at 33° may be attributed to the periodicity perpendicular to the polymer chain. Figure 2b displays the XRD profile of PDMA-UD. Most of the peaks observed for PDMA-HCl could not be located in the diffractogram of PDMA-UD. This is due to the absence of dopant anions in the polymer backbone. In addition, the only one intense peak is observed at $2\theta=27^\circ$. These observations indicate the difference in crystallinity of PDMA-UD and PDMA-HCl. This inference is found to be consistent with the information obtained from the surface morphological studies. These results are further supported by the conductivity values obtained for the PDMA pellets. A very high conductivity value of 2.24 S cm^{-1} for PDMA-NBs does prove the efficiency of solid-state route adopted for its preparation. Meanwhile, the conductivity of undoped counterpart of PDMA is 0.5 S cm^{-1} . It is also worthwhile to mention the fact that the newly adopted synthetic strategy produces PDMA-NBs in good yield and the same are easily processable in common solvents. Taking into account the

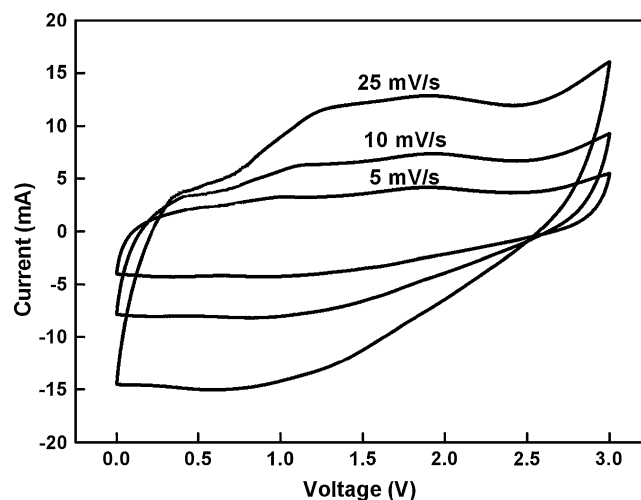


Fig. 3 Cyclic voltammograms of PDMA-NBs/AC cell at different scan rates

attractive physicochemical properties of PDMA-NBs, its performance as a cathode material in a hybrid supercapacitor is tested and the preliminary findings are discussed below.

Cyclic voltammograms (CVs) for the PDMA-NBs/AC cell recorded at different scan rates are presented in Fig. 3. The CV curves obtained at different scan rates showed the redox behavior of the composite electrode. The capacitive current increased nearly linearly with an increase in scan rate. This implies that the above cell exhibits a better capacitive performance in the potential window of 0–3 V. The CV curves also show that the potential difference between the peaks increases with scan rate and thereby indicates the presence of electric polarization phenomenon. Galvanostatic charge/discharge curves for the PDMA-NBs/AC at a constant current density of 1 mA cm^{-2} between 0 and 3 V are presented in Fig. 4. The results show that the hybrid system is a combination of double-layer capacitor and battery characteristics. It can be seen from the charge/

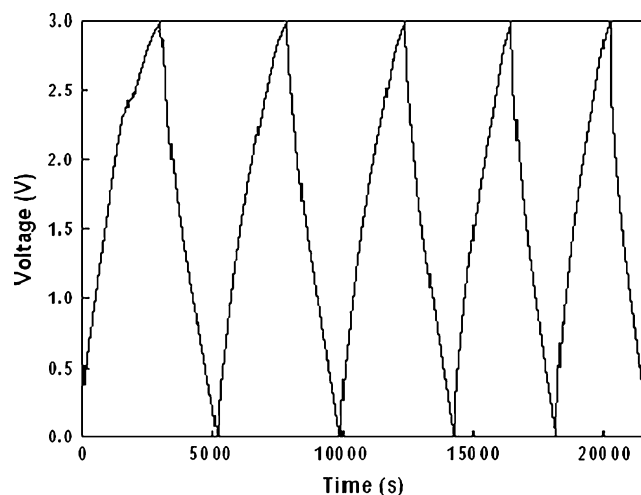


Fig. 4 Charge/discharge curves of PDMA-NBs/AC cell

discharge curves that the potential linearly varies with time during charge and discharge with a constant slope for the charge/discharge curves. The curves have a symmetrical trilateral shape and thereby reveal that PDMA-NBs/AC cell has excellent cycle performance and high electrochemical reversibility. A maximum specific capacitance (C_s) of 125 F g^{-1} obtained at a 1 mA cm^{-2} for PDMA-NBs/AC cell shows that this hybrid supercapacitor has an excellent cycle life with a specific capacitance that is maintained at more than 85% of its initial value after 1,000 cycles. Several factors like nanostructured morphology, high conductivity due to doping, and strong polymer backbone are believed to contribute to the better performance of PDMA-NBs/AC cell. The coulombic efficiency values also show a very stable efficiency of greater than 99%, even after 1,000 cycles for PDMA-NBs/AC-based supercapacitor. The specific energy and power densities obtained for PDMA-NBs/AC-based supercapacitor are 50 Wh kg^{-1} and 97 W kg^{-1} , respectively, explicitly proving that mechanochemically prepared PDMA-NBs serves as an efficient electrode material for asymmetric hybrid supercapacitor applications.

Conclusion

The mechanochemical synthetic route adopted for preparing PDMA has successfully yielded highly conductive polymeric nanobelts with good crystallinity. The presence of HCl in the solid-phase mixture favors nanostructured morphology for PDMA. The electrochemical performance of PDMA-NBs when employed as an active material in

cathode for supercapacitor application shows promising results. Further investigations on the mechanochemical route for improving the surface and electrical properties of PDMA-NBs is currently under progress in our laboratory.

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References

1. Janata J, Josowicz M (2003) *Nat Mater* 2:19
2. Huang J, Virji S, Weiller BH, Kaner RB (2003) *J Am Chem Soc* 125:314
3. Virji S, Huang J, Kaner RB, Weiller BH (2004) *Nano Letters* 4:491
4. Sukeerthi S, Contractor AQ (1999) *Anal Chem* 71:2231
5. Liang L, Liu J, Windisch CF, Exarhos GJ, Lin Y (2002) *Angew Chem Int Ed* 41:3665
6. Sapurina I, Stejskal J (2008) *Polym Int* 57:1295
7. Jain S, Surwade SP, Agnihotra SR, Dua V, Eliason PA, Morosec GJ, Manohar SK (2010) *Green Chem* 12:585
8. Ye XR, Jia DZ, Yu JQ, Xin XQ, Xue Z (1999) *Adv Mater* 11:941
9. Conway BE (ed) (1999) In *electrochemical supercapacitors scientific fundamental and technology applications*. Kluwer, New York
10. Mark H, George Z, Milon SPS, Derek JF, Windle AH (2002) *Chem Mater* 14:1610
11. He BL, Zhou YK, Zhou WJ, Dong B, Li HL (2004) *Mater Sci Eng* 374:322
12. Mastragostino M, Arbizzani C, Soavi F (2001) *J Power Sourc* 97:812
13. Sun LJ, Liu XX (2008) *Eur Polymer J* 44:219
14. Zhou C-F, Du X-S, Liu Z, Ringer SP, Mai Y-W (2009) *Synth Met* 159:1302