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Facile Preparation of Polyaniline Nanosheets Via Chemical Oxidative Polymerization in Saturated NaCl Aqueous Solution for Supercapacitors

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The well-defined polyaniline nanosheets are prepared via the facile chemical oxidative polymerization of aniline in the saturated NaCl solution for the first time. The specific capacitance of 778.6 F g^{-1}, much higher than those supercapacitors based on PANI prepared via the chemical oxidative polymerization without any conductive substrate reported, is calculated from the charge-discharge curve at a specific current density of 10 mA cm^{-2} in the potential range -0.2~0.8 V, when they are used as the electrode materials for supercapacitors with 1.0M $NaNO_3$ as electrolyte and about 80% of its original capacitance is preserved after 500 cycles. The high specific capacitance and good cycling stability make them promising electrode materials for the high performance supercapacitors.

Keywords: polyaniline; nanosheets; chemical oxidative polymerization; saturated saline solution; supercapacitor

1. INTRODUCTION

Nanostructured conducting polymers have attracted increasing interests due to their highly conjugated molecular structure, metal-like conductivity, and potential applications [1]. Especially, conducting polymers have been regarded as promising pseudocapacitive materials because the kinetics of the charge-discharge processes of polymers with suitable morphology is fast, and they can generally be produced at lower cost than noble metal oxides and comparable to that of activated carbons [2,3].

Among the conducting polymers, polyaniline (PANI) has been studied extensively because it is inexpensive, easy to synthesize, and has good environmental stability, redox reversibility, and electrical conductivity [4]. Nanostructured PANI materials with various morphologies [5], such as nanoparticles [6], nanocapsules [7], nanotubes [8], nanofibers and nanowires [9], nanobelts [10], and nanoflowers [11] have been successfully prepared. However, there is only one report on the preparation of PANI nanosheets from discotic nematic lyotropic liquid crystal (LLC) solutions [12] except for the intermediate product in the formation of rose-like PANI microstructures under a higher relative humidity [13].

Recently, PANI nanofibers had been prepared as chemiresistors to reversibly detect chemically aggressive vapors like NO_2, via the chemical oxidative polymerization in the saturated NaCl aqueous solution with H_2O_2 as oxidant [14]. In this work, aniline is polymerized in the saturated NaCl aqueous solution with ammonium persulfate (APS) as oxidant and hydrochloric acid as dopant. It is amazing to find that the morphologies of the PANI nanomaterials formed have changed from nanowires and nanorods to nanosheets with the increasing of the aniline monomer feeding amount. The PANI nanosheets exhibit the highest electrical conductivity and a high specific capacitance and excellent cyclability as electrode materials for supercapacitors.

2. EXPERIMENTAL

2.1. Chemicals

Aniline (analytical grade reagent, Xi'an Reagent Co., Xi'an, China) was freshly distilled under reduced pressure before use. Ammonium persulfate (APS), NaCl, and hydrochloric acid were analytical reagent grade from Tianjin Chemical Co., China, and were used without further purification. Distilled water was used throughout.

2.2. Synthesis

Certain amount (1.0, 2.0, 3.0 and 4.0 g) of aniline was added into 100 mL 1.0 M HCl and saturated NaCl mixture solution. The mixed solution was precooled in an ice-water bath under electromagnetic stirring. Then 50 mL 1.0 M HCl and saturated NaCl mixture solution containing APS (molecular ratio to aniline: 4:3) was added drop by drop to the above solution, and stirring was continued for 10 h under ice-cold condition. The resulting polyaniline materials were purified by being poured into a large excess of distilled water, filtered, and washed with distilled water and ethanol until the filtrate become colorless. The black powder samples were dried under vacuum (0.1 mm of Hg) for 24 h prior to further analysis. The products were denoted as S1, S2, S3, and S4 with the aniline feeding amount of 1.0, 2.0, 3.0 and 4.0 g, respectively. The highest aniline feeding amount in the work was 4.0 g. As for the 5.0 g aniline, the corresponding amount of oxidant APS can not be dissolved completely in the 1.0 M HCl and saturated NaCl mixture solution.

2.3. Characterizations and electrochemical properties

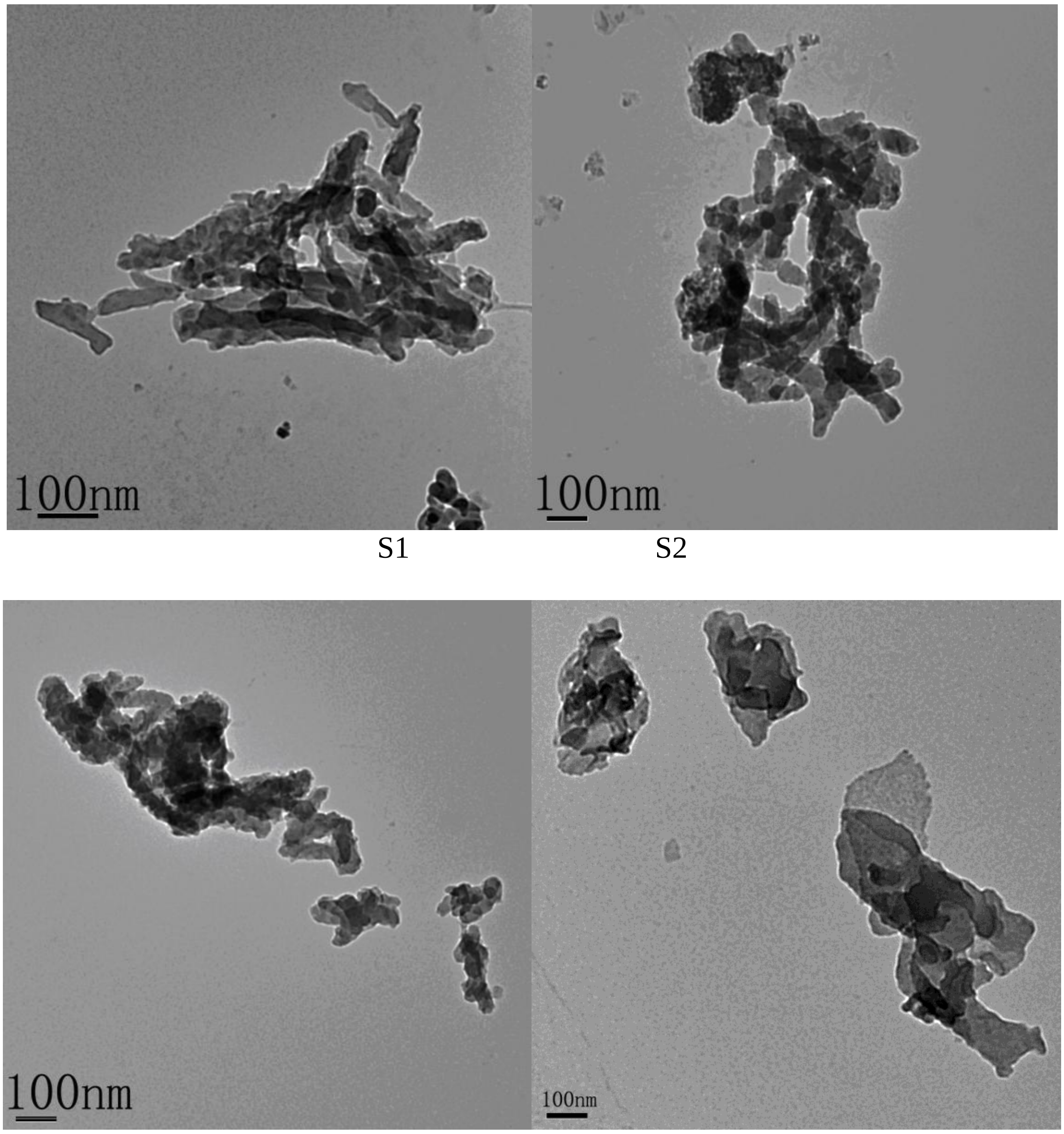
The electrical conductivities of the polyaniline samples were measured using SDY-4 Four-Point Probe Meter (Guangzhou Semiconductor Material Academe) at ambient temperature. The pellets were obtained by subjecting the powder sample to a pressure of 30 MPa. Each value given is an average of at least three times measurements.

The morphologies of the polyaniline samples were characterized with a JEM-1230 EX/S transmission electron microscope (TEM; JEOL, Tokyo, Japan), after being dispersed in water in an ultrasonic bath for 30 minutes and then deposited on a copper grid covered with a perforated carbon film.

The electrochemical measurements were carried out on CHI660B electrochemical working station in 1.0 M $NaNO_3$ aqueous solution as electrolyte at ambient temperature. The working electrodes were prepared as following: 80 wt.% of active materials (2.80 mg) was mixed with 15 wt.% of carbon black in an agate mortar until a homogeneous black powder was obtained. Then 5 wt.% polyvinylidenefluoride (PVDF) was added with a few drops of dimethyl formamide (DMF). The resulting paste was uniformly laid on a piece of Ni foam about 0.25 cm^2 which was served as a current collector and then dried at 50 ºC for 4 h before use. The Ni foam coated with the PANI samples was pressed for 1 min under 1.0 MPa. A typical three-electrode experimental cell equipped with a working electrode, a platinum foil counter electrode and then a saturated calomel reference electrode (SCE), was used to measure the electrochemical properties of the working electrodes.

3. RESULTS AND DISCUSSION

It is well-known that the conducting polymers with various nanostructures could be prepared via the facile template-free approach, in which the dopant molecules and/or their aniline salts self-assembled into a microstructured intermediate as supramolecular template [15,16]. In the present of hydrochloric acid, aniline can form anilinium salt which could form the micelles in the chemical oxidative polymerization as the soft templates [17,18], so the PANI nanowires and nanotubes should be produced. In the present work, the products obtained changed from nanowires and nanorods, to nanorods, then to nanorods and the compressed nanoparticles, to the nanosheets with uniform thickness finally (Fig. 1), as increasing of the feeding amount of aniline monomer from 1.0 g to 4.0 g. Compared with the PANI nanowires and nanotubes prepared with the template-free approach in water reported previously, here we also obtained the PANI nanosheets in the saturated NaCl aqueous solution. It is resulted from the high ionic strength and the common-ion effects in the saturated NaCl aqueous solution. The dissolution *of aniline and its salt here was decreased* remarkably so the excess anilinium salt formed the lamellar micelles in the saturated NaCl aqueous solution so as to produce the PANI nanosheets [19]. However, with the comparative amount in water solution, it might only form the tubular micelles and lead to the PANI nanowires and/or nanotubes.



S1 S2

S3 S4

Figure 1. TEM image of the PANI products.

The well-defined PANI nanosheets exhibited the highest room-temperature electrical conductivity (4.88 S cm^{-1}) among the polyaniline samples prepared via the chemical oxidative polymerization in the saturated NaCl aqueous solution with different aniline feeding amount, which might be due to their unique structures.

Based on the unique nanosheet structure and high conductivity, the PANI nanosheets were expected to have potential application as high-performance supercapacitor electrode materials. To evaluate the applicability as the electrode materials for supercapacitors, the mass specific capacitance, the cycling performance, and the electrochemical impedance spectroscopy (EIS) of the PANI nanosheets have been investigated in 1.0 M $NaNO_3$ aqueous solution.

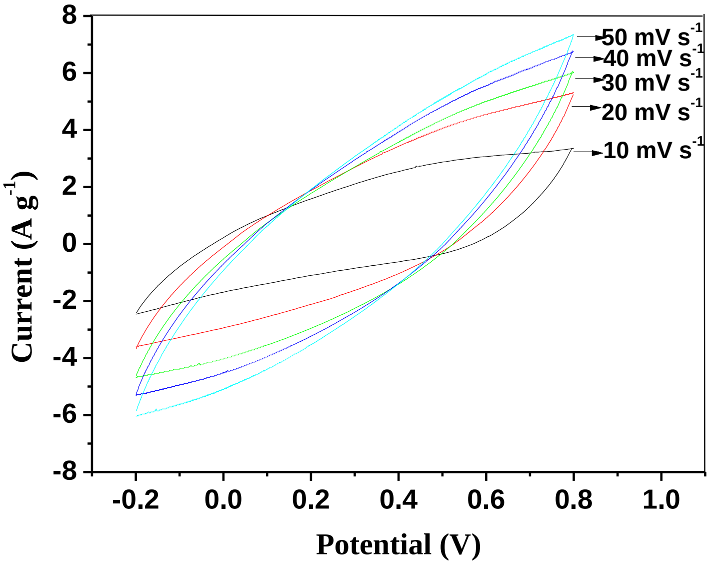


Figure 2. Cyclic voltammograms of PANI nanosheets at various scan rates in 1.0 M $NaNO_3$ solution.

The cyclic voltammograms of the PANI nanosheets electrode, recorded at different potential sweep rates from 10 to 50 mV s^{-1}, are presented in Fig. 2. The CV data demonstrate the stability of electrodes within the applied potential range -0.2 to 0.8 V. The typical rectangle-like shape of all the CV curves revealed the perfect electrochemical capacitive behavior of the PANI nanosheets electrode. With the scan rate increasing, the effective interaction between the ions and the electrode greatly reduced, the deviation from rectangularity of the CV became obvious. Fig. 3 shows the charge-discharge curves of the PANI nanosheets electrode.

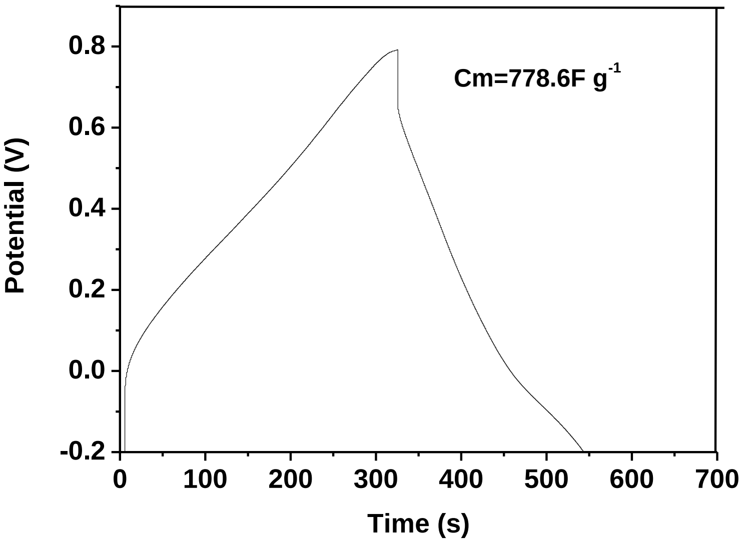


Figure 3. Galvanostatic charge-discharge curve of the PANI nanosheets electrode at a current density of 10 mA cm^{-2} in 1.0 M $NaNO_3$ solution.

The specific capacitance of the PANI nanosheets was found to be high as 778.6 F g^{-1}, at a current density of 10 mA cm^{-2}. The value is much higher than those supercapacitors based on PANI prepared via the chemical oxidative polymerization without any conductive substrate reported in the range of 160-500 F/g [20,21], it might be also due to it well-defined nanosheet morphology.

The cyclic characterization was evaluated using the galvanostatic charge-discharge over 500 cycles. One can find a total loss of about 15% of the initial discharge capacitance was found after 200 cycles, but a fairly stable capacity was maintained thereafter, from the experimental data presented in Fig. 4. The loss of about 6% of the initial discharge capacitance was found after the other 300 cycles. That is to say that about 80% of the initial discharge capacitance was remained after 500 cycles. Therefore, the PANI nanosheets electrode shows higher stability and remains its electrochemical capacitance property over 500 cycles.

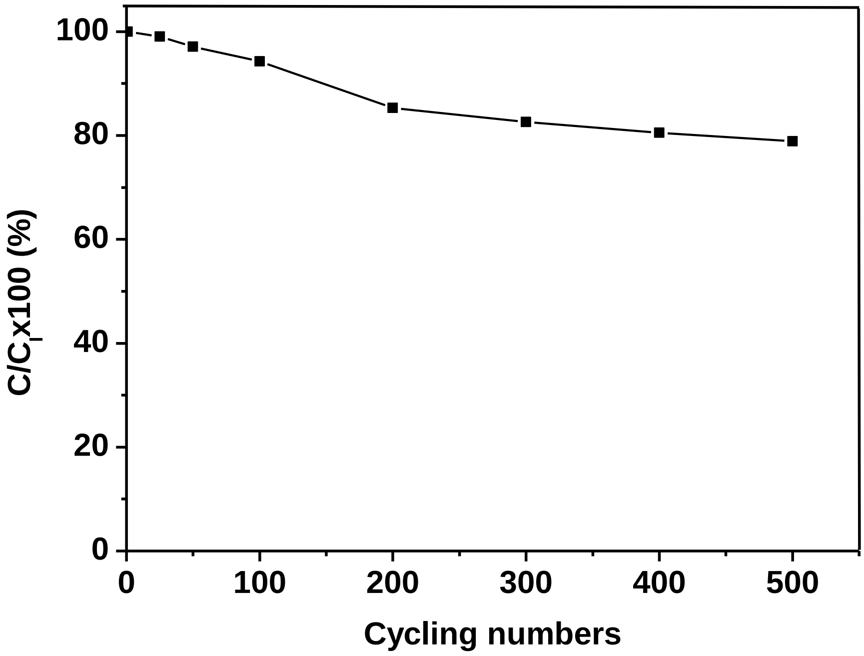


Figure 4. Specific capacity during galvanostatic cycles at a current density of 10 mA cm^{-2} in 1.0 M $NaNO_3$ solution.

To get more information about the ability of the PANI nanosheets electrode for supercapacitors, EIS experiment was carried out in 1.0 M $NaNO_3$ solution at 0.4 V (vs. SCE). There are two features for both the curves: firstly, in the high frequency intercept of the semicircle with the real axis, an electrolyte solution resistance *Rs* can be observed as about 5 Ω in 1.0 M $NaNO_3$ electrolyte. At high frequencies, the semicircle was resulted by the charge-transfer resistance (Rct), at the same time the Rct of the PANI nanosheets is estimated to about 27 Ω (Fig. 5). Secondly, in the medium-to-low-frequency region, the unequal semicircular can be discovered from both the curves. In the low frequency range, the impedance plots indicated a limiting diffusion process in electrolyte [22].

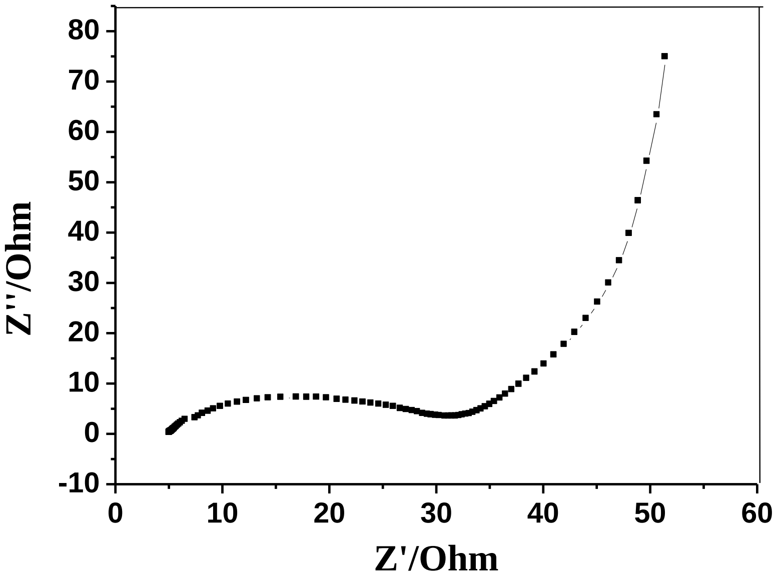


Figure 5. Impedance Nyquist plots of the PANI nanosheets (S4) in the frequency range of 0.004-10^5 Hz.

4. CONCLUSIONS

In summary, the well-defined PANI nanosheets were successfully synthesized via the facile chemical oxidative polymerization in the saturated NaCl aqueous solution. Due to the well-defined morphology, the PANI nanosheets exhibited the highest electrical conductivity of 4.88 S cm^{-1}. Its specific capacitance was found to be 778.6 F g^{-1} at a current density of 10 mA cm^{-2}. The PANI nanosheets electrode also showed high stability and retained its electrochemical capacitance property over a large number of cycles. The high specific capacitance and good cycling stability of the PANI nanosheets electrode coupled to the low cost and environmentally benign nature may make them attractive for supercapacitor applications.

ACKNOWLEDGMENTS
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References

1. H. D. Tran, D. Li and R. B. Kaner, *Adv. Mater.*, 21 (2009) 1487
2. G. A. Snook, P. Kao and A. S. Best, *J. Power Sources*, 196 (2011) 1
3. J. L. Liu, M. Q. Zhou, L. Z. Fan, P. Li and X. H. Qu, *Electrochim. Acta*, 55 (2010) 5819
4. S. Bhadra, D. Khastgir, N. K. Singha and J. H. Lee, *Prog. Polym. Sci.*, 34 (2009) 783
5. M. X. Wan, *Adv. Mater.*, 20 (2008) 2926

6. J. Pecher and S. Mecking, *Chem. Rev.*, 110 (2010) 6260
7. P. Liu and L. Zhang, *Crit. Rev. Solid State & Materi. Sci.*, 34 (2009) 75
8. Y. Z. Long, M. M. Li, C. Z. Gu, M. X. Wan, J. L. Duvail, Z. W. Liu and Z. Y. Fan, *Prog. Polym. Sci.*, 36 (2011) 1415
9. H. M. Zhang, Q. Zhao, S. P. Zhou, N. J. Li, X. H. Wang and F. S. Wang, *J. Power Source*, 196 (2011) 10484
10. G. R. Li, Z. P. Feng, J. H. Zhong, Z. L. Wang and Y. X. Tong, *Macromolecules*, 43 (2010) 2178
11. Z. J. Wang, L. S. Jiao, T. Y. You, L. Niu, S. J. Dong and A. Ivaska, *Electrochem. Commun.*, 7(2005) 875
12. L. Shi, X. D. Wu, L. D. Lu, X. J. Yang and X. Wang, *Synth. Met.*, 160 (2010) 989
13. Y. Zhu, H. Y. He, M. X. Wan and L. Jiang, *Macromol. Rapid Commun.*, 29 (2008) 1705
14. S. P. Surwade, S. R. Agnihotra, V. Dua, N. Manohar, S. Jain, S. Ammu and S. K. Manohar, *J. Am. Chem. Soc.*, 131 (2009) 12528
15. H. J. Qiu and M. X. Wan, *Macromolecules*, 34 (2001) 675
16. M. X. Wan and J. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 38 (2000) 2359
17. H. J. Ding, Y. Z. Long, J. Y. Shen and M. X. Wan, *J. Phys. Chem. B*, 114 (2010) 115
18. Z. X. Wei, Z. Zhang and M. X. Wan, *Langmuir*, 18 (2002) 917
19. P. Kluson, H. Luskova, O. Solcova, L. Matejova and T. Cajthaml, *Mater. Lett.*, 61 (2007) 2931
20. D. S. Dhawale, A. Vinu and C. D. Lokhande, *Electrochim. Acta*, 56 (2011) 9482
21. H. Guan, L. Z. Fan, H. C. Zhang, and X. H. Qu, *Electrochim. Acta*, 56 (2010) 964
22. A. Kepas and M. Grzeszczuk, *Electrochim. Acta*, 51 (2006) 4167