



Preparation of pyrrole-aniline copolymer nanowires and their electrochemical performance

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ABSTRACT

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This experiment mainly studies the reaction of pyrrole and aniline in the proportion of different amounts of substances and the reaction of changing the amount of substances of the initiator, through the analysis of the product and test its electrochemical performances.

In theory, polyaniline has the advantages of higher capacitance, easy preparation, doping and environmental friendliness, so it is considered as one of the most promising electrode materials. Polypyrrole has the characteristics of easy synthesis and excellent electrical conductivity. However, in the structure of polyaniline, the molecular chain rigidity is strong, the conductive stability of polypyrrole is poor, and the processing is difficult because it is neither soluble nor melted. Polymer copolymerization is an important modification method, which can synthesize the advantages of different monomers to obtain better performance of copolymer. In this experiment, pyrrole and aniline are used as raw materials. By changing the proportion of pyrrole and aniline in the experiment and the conditions of the amount of initiator, hydrochloric acid solution is mainly used as the solvent, p-phenylenediamine is mainly used as the initiator, and ammonium persulfate is mainly used as the oxidant. Under the condition of freezing, the reaction is carried out. The reaction has many advantages, such as: green environmental protection, in line with the concept of green chemistry, the efficiency is high. For this reaction, the initiators, oxidants and solvents used in the experiment were screened to obtain the most suitable conditions.

Key words: aniline, pyrrole, copolymerization

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1 INTRODUCTION

With the improvement of the global economic level, the large use of non-renewable resources leads to the rise of global temperature, and the research on renewable energy and clean energy will become more and more important in the future. Therefore, increasing the use of renewable resources such as solar energy, wind power and tidal power, and vigorously developing and using new electric vehicles or hybrid electric vehicles can effectively reduce carbon dioxide emissions. Because wind energy does not exist in large quantities all the time and solar energy cannot be utilized at night, these intermittent energy supply characteristics make clean energy cannot be used in a long-term stable, and the energy conversion rate of these clean energy is generally very low ^[1].

When the emergence of the chemistry, it has been essential to apply experimental research to reach the present. As we all know that methods of research are the most important part of experience. By experiments to get data, obtain real phenomena and obtain more accurate results by repeated experiments.

At present, chemical oxidation polymerization and electrochemical polymerization are the main methods for preparing nano-polymer. Electrochemical polymerization is usually carried out by anodic oxidation, and the morphology of the product is regulated by controlling the current, etc. However, due to the limitation of electrode area, it is only suitable for the preparation of small batches of conductive polymers. The chemical oxidation polymerization method is simple in operation, low in cost and easy in mass production ^[2].

Therefore, the spherical polyaniline/pyrrole nanocomposites were prepared by chemical oxidation polymerization using ammonium persulfate as oxidant, taking advantage of the similar structure of aniline and pyrrole.

As an excellent capacitor material, polyaniline has unique advantages when applied to the electrode material of supercapacitor. However, its main disadvantage is that the volume of polyaniline expands and contracts in the process of repeated charge and discharge, which leads to poor cyclic stability. Composite polyaniline

with good cyclic stability can effectively improve the cyclic stability of the material [3].

Due to the urgent shortage of petroleum energy and environmental pollution, various new energy sources have developed rapidly, such as photovoltaic solar energy, wind power, tidal energy, hydrogen energy, etc. In order to efficiently utilize these new energy sources, it is necessary to develop a novel energy storage device. Among many energy storage devices, supercapacitors have attracted the attention of many scholars at home and abroad because of their advantages such as fast charging and discharging speed, relatively high power density, high cycle life and so on. The research of supercapacitor mainly focuses on electrode materials. At present, the electrode materials studied mainly focus on carbon materials, metal oxides and conductive polymers. The common conductive polymers mainly include polyaniline, polypyrrole and polythiophene. Among these conductive polymers, polyaniline with good specific capacitance, low density, easy synthesis and environmental friendly performance is considered to be a very promising electrode material [4].

Polyaniline and polypyrrole are a kind of important conductive polymer materials, which have good thermal and environmental stability, high conductivity, easy synthesis, and have been widely studied and applied in recent years. Their unique long-range π -electron conjugated backbone structure, on the one hand, enables them to have a series of unique electrical, optical, mechanical and electrochemical properties, which can be used in the development of batteries, electronic and optical devices, electrochromic displays, sensors, corrosion resistant materials and other multifunctional materials and devices. On the other hand, due to the high rigidity of molecular chains and the strong interaction between chain and chain π -electron system, they are brittle, difficult to dissolve and difficult to melt, so that the structure characterization, performance research and manufacturing are difficult. The improvement of its physical and mechanical properties and processing properties has always been the focus of research in this field. Copolymerization is an important modification method, which can effectively integrate the advantages of several chains to obtain new polymers with good comprehensive properties. Therefore, the study of copolymerization modification has become the main content of the study of polyaniline and polypyrrole [5].

At present, the polymerization mechanism of aniline and pyrrole has not been determined. The main differences are as follows: whether the growth process of the polymer chain is the coupling between cationic radicals or the electrophilic substitution of the growth chain to the monomer aromatic ring.

Generally speaking, the oxidation potential of the highest monomer loses an electron (oxidized) cation radicals formed monomer, monomer cation radicals attack can be coupled with each other or another monomer, after losing two protons to form dimers, dimers and loses an electron to form dimers cation radical oxidation state dimer), continue to participate in the reaction, Until the polymer chain grows to the point where its oxidation state is not active enough to participate in the polymerization reaction, or where the polymer chain cannot be oxidized due to side reactions or cross-linking reactions.

From monomer, dimer, trimer to polymer, their oxidation potential is getting lower and lower, and they are more and more easy to be oxidized, and the corresponding cationic radical activity is also getting lower and lower. This is because the cationic radical can delocalize on the aromatic ring. The more the aromatic ring, the more stable it is, and the lower the activity accordingly.

Generally called from monomer to generate dimers caused stage, will grow into a polymer called dimers growth stage, because the trigger phase have more monomer cation radicals participate in the reaction, and the oxidation potential high monomer, and oxidation reaction speed is slow, n polymers ($n > 1$) the oxidation potential of decrease, so the polymerization reaction rate faster ^[6].

In addition, it is considered that the formation of dimer is the coupling between cationic radicals, and the growth stage of the chain is the electrophilic substitution of the oxidized chain on the aromatic ring of the monomer. In short, the polymer chain grows at a rate greater than the initiation rate, thus forming the polymer.

The key of copolymerization modification is to get a mixture of copolymer rather than homopolymer, so the proper monomer and proper polymerization process should be selected. The monomers used for the copolymerization of p-aniline and pyrrole can be divided into three types according to their structure: substituted

aniline and pyrrole, aniline and other conjugated monomers other than pyrrole, and non-conjugated monomers. For the polymerization, the oxidation potential of the monomer is the most important parameter. The lower the oxidation potential, the higher the activity of the monomer. However, the oxidation potential is affected by many factors. For the properties of the copolymer, the respective properties of the two homopolymers must be considered, because the properties of the copolymer are generally between the corresponding properties of the two homopolymers [7].

2 CONDUCTING POLYMER

2.1 Introduction

From the point of view of conductive component composition, conducting polymers can be roughly divided into conductive polymer and structural conductive polymer. Conductive polymer is added in the insulating polymer matrix type conductive material (carbon black, carbon fiber, metal powder, sheet, wire, etc.), made by dispersing compound, composite layer set "the blend of compounds. Structural conductive polymer is to point to need not add material, by its own structure and electrical conductivity of polymer after doping, generally for conjugated polymer, with a large number of conjugated double bonds in molecular chain structure, the electronic freedom of movement within the conjugate system, and thus provides a conductive carrier [8].

Advantages of conductive polymers, it has both electrical and optical properties of metal and inorganic semiconductor with organic polymer flexible mechanical properties and machinability, also has the electrochemical REDOX activity. These characteristics determine its in organic optoelectronic devices and electrochemical devices play an important in the development. Currently conducting polymers have been widely used in conductive materials, color materials, secondary battery anode materials anticorrosive materials, medical materials, antistatic materials, electromagnetic shielding materials, can also be used for the preparation of super capacitor, sensor, actuator, such as solid electrolyte capacitor.

2.1.1 Polyaniline and Polypyrrole

Because of the unique REDOX properties, good thermal stability, excellent electrical conductivity, and synthesis is simple, cheap, polyaniline is one of the earliest studies of conjugated conducting polymers. Compared with other conductive polymers, polypyrrole has advantages of good environmental stability, high conductivity and wide range of variation.

2.1.2 Polypyrrole/polyaniline copolymer

In many conductive polymers, polyaniline and polypyrrole raw materials cheap easy synthesis is simple, good electrical conductivity, good oxidation reducing, etc. Compared with polyaniline conducting polypyrrole as has more excellent electrical properties and electrochemical properties, but poor conductive stability and high cost. Research shows that the aniline and pyrrole slightly copolymerization are important modification methods, can effectively integrated the advantages of several kinds of chain link, can the environment stability of the reinforced material, and to extend its application range. For copolymerization mechanism of aniline and pyrrole is not clear, the main differences lie in: the growth process of polymer chain is the coupling between cation radicals, or growth chain on aromatic electrophilic substitution of monomer, Peters think such as copolymerization reaction is the coupling between cation radicals, based on the mechanism of homopolymerization copolymerization mechanism has three process, and think that the slowest oxidation process to a large extent determines the composition of the polymer [9].

2.2 Pyrrole-aniline copolymer applications

2.2.1 Charge transfer

The photocatalytic semiconductor design of nanotube array structure has always been a research hotspot, because of the nanotube structure is beneficial to the absorption of light and reduce the transport distance of charge carriers. However, these materials tend to be limited by relatively poor charge transfer. Therefore, we studied an easily reusable PPY-PANI/TiO₂ NT photocatalyst in which the polypyrrole-polyaniline copolymer acts as a photosensitizer and electron conductor medium. The prepared PPY-PANI/TiO₂ NT composites have higher visible light absorption, higher charge separation efficiency and A photocurrent of 156 μ A under visible light. All samples were characterized by XRD, FTIR, SEM and photocurrent. The degradation of 4-NP also proved that the TiO₂ modified by polypyrrole-polyaniline copolymer has a good photocatalytic effect [10].

2.2.2 supercapacitor

Conducting polymers with large π -conjugated structure are widely used as multi-functional materials in sensors, secondary batteries, braking and storage devices, corrosion protection and other fields.

Polypyrrole has excellent electrical properties, electrochemical properties, environmental stability and biocompatibility, and is easy to prepare, so it is considered to be the most potential conductive polymer. Compared with other conductive polymers, polypyrrole is more flexible in electrochemical processes, making it particularly suitable for use as electrode materials for ultracapacitors or batteries. However, the strong intramolecular and inter-chain interactions promote the close stacking of polypyrrole molecules during the growth process, which results in two defects in the application of blocky polypyrrole materials in the supercapacitors:

The diffusion of doped ions in the polymer is limited, which will reduce the mass ratio of the material, and the volume of the polypyrrole will expand and contract repeatedly in the process of capacitor cyclic charge and discharge, resulting in the destruction of the physical structure and reducing the cycle life of the capacitor material.

To solve the above problems, it is necessary to prepare submicron or nanostructured polypyrrole. Small size materials can provide relatively short diffusion length and large specific surface area, which is conducive to the diffusion of doped ions, can adapt to repeated volume changes in the process of charge and discharge, and has a higher specific capacitance and cycle life.

At present, there are two main ways to prepare microstructured polypyrrole : microemulsion polymerization, charged monomer copolymerization. In the former way, the amount of surfactant is large and the post-treatment is complex, and the product is not pure, which leads to the deterioration of material properties. Although self-stable and pure pyrrole copolymer nanoparticles can be obtained by the latter approach, suitable co-monomers containing electronegative groups (low reactivity) need to be selected, resulting in a low yield of copolymer and low conductivity ($\times 10^{-4}$ s/cm).

Recently, Snook et al. used the mismatch of chain growth during the polymerization of different monomers to reduce the stacking density between molecular chains, thus changing the polymer morphology, and obtained the micron-level porous ethylenedioxythiophene-pyrrole copolymer, which opened up a new idea for the preparation of micro-structure conductive polymer. Choi has prepared pyrrole-aniline copolymer microrice grains (about 6 μm in diameter) at 0 $^{\circ}\text{C}$, but the properties of the copolymer have not been studied. Zhang studied the electrochemical properties of pyrrole-aniline copolymers, and the results showed that the copolymers had a high specific capacitance, up to 827F/g under specific conditions. However, they did not study the influence of synthesis conditions on copolymerization and the cyclic stability of the copolymers.

It can be seen that pyrrole-aniline copolymer is a kind of super capacitive material with great potential, which is worth studying.

2.3 The significance of the subject research

However, with the development of economy and science and technology, intelligent electronic devices, especially such as smart phones, watches, glasses have completely changed our daily life. Makes the high power density and high energy density increasing demand of energy storage devices. As a new rising super capacitor energy storage device, many other advantages in one, such as charging time is fast, circulation such outstanding advantages as long service life, easy to flexible, lightweight, small, high safety, easy and other functional devices together, so the super capacitor is attention from all walks of life. To sum up, the super capacitor on in-depth study of theoretical significance and practical value. The current study of super capacitor is mainly the development, the electrode material and electrode fluid study, and capacitor assembly these three aspects. The electrode material is the key factor of super capacitor performance.

Had a huge impact on the performance of the electrochemical capacitor electrode material, the development has a high specific capacitance of electrode materials is a hotspot of research on the current super capacitor, the anode material of conductive polyaniline in super capacitor applications exist other materials incom-

parable advantages, however, by the cycle stability of material itself, the limitations of low specific capacitance and single polyaniline as super capacitor Super capacitor electrode material is difficult to meet the various performance indicators. In order to solve the above problems, this paper made aniline and pyrrole participate in the polymerization reaction together, and prepared electrode materials with high capacity and high power density by using the same comprehensive superior performance of the two monomer homopolymers.

3 EXPERIMENTAL SECTION

3.1 Introduction

In this experiment, different proportions of pyrrole and aniline were mixed to form copolymer. Furthermore, purification of p-phenylenediamine and purification of aniline need to be used in the process of experiment. The former purification is weighing 5 g p-phenylenediamine, place it in a small beaker, add an appropriate amount of 50% methanol aqueous solution, shake it, observe the appearance of colorless flash crystal, quickly filter it, wash the solid with 50% methanol aqueous solution, dry the solid in a vacuum drying oven for 6 hours, take it out, seal it, and put it on standby. The latter purification should take 10 mL aniline, put it in 100 mL single-mouth flask, add two zeolites, put the flask in a water bath, install vacuum distillation device, vacuum distillation to collect colorless and transparent liquid. Then place the freshly steamed aniline in a glass jar, seal it, and freeze it in a freezer.

Firstly, putting 0.75 moles of hydrochloric acid solution 60 mL into a three-mouth flask. Next adding aniline and pyrrole, and make the molar ratio of it 1:9, 2:8, 3:7...9:1, then adding the amount of reducing agent to the solution of 1 %~2 % of benzenediamine as initiator, the following is stirring until dissolution, placed in -15 degrees refrigerator pre-freezing.

Secondly, ammonium persulfate was dissolved in 30mL distilled water (the quantity ratio of oxidant to reducing agent was 1:1.5/1:1.2), dissolved by stirring, and placed in a 5 °C refrigerator for pre-cooling.

At last, when the aniline/pyrrole-hydrochloric acid solution is completely solidified, the oxidant is added quickly, the experimental phenomenon is observed and recorded, the heat is kept for 1-3 days, the samples are pumped and filtered, washed with water and alcohol washed, and the samples are collected for testing.

3.1.1 Experimental raw materials

Figure1 Raw material specifications and sources

name	formula	SPE	source
		C	
Hydrochloric	HCl	AR	Shanghai Mylar Chemical Technology Co., Ltd.
Pyrrrole	C ₄ H ₅ N	AR	Tianjin Fuyu Fine Chemical Co., Ltd.
Aniline	C ₆ H ₇ N	AR	Shanghai McLean Biochemistry Co., Ltd.
P-phe-nylenedia-	C ₆ H ₈ N	AR	Shandong West Asia Chemical Co., Ltd.
mine	(NH ₄) ₂ S ₂ O ₈	AR	Shandong West Asia Chemical Co., Ltd.
Ammonium persulfate			

3.1.2 Experimental Instruments

Figure2 Instrument model and source

name	specification	source
Foil electrode	GB/T5977-2010	Shanghai Yueci Electronic Technology Co., Ltd.
Vacuum drying oven	DZE-6020	MTI CORPORATION.
Electric heating constant temperature blast drying oven	PHG1.1-5A	Gongyi Yuhua Instrument Co., Ltd.
Electronic balance	JJ224BC	Changshu shuangjie test instrument factory.
Vacuum pump	SHZ-D(III)	Gongyi Yuhua Instrument Co., Ltd.
Ultrasonic cleaner	KQ-100B	Kunshan Ultrasonic Instrument Co., Ltd.

Electric roller

matching machine MSK-HRP-MR

MTI CORPORATION

3.2 Experimental procedure

3.2.1 Sample preparation

1. Measure 56.25 mL of distilled water in a three-mouth flask, and then measure 3.75 mL (12 mol) of hydrochloric acid in a three-mouth flask. Measured 0.0413 mL of purified pyrrole and 0.4922 mL of aniline, mixed in a beaker, and then added to a three-mouth flask.
2. Weigh 0.013g of p-phenylenediamine (the amount of the initiator is 1% to 4%) in a flask and stir until the solid is dissolved. Then place the flask in a freezer at -22 degrees Celsius for 24 hours.
3. 30ml of distilled water was measured and placed in a beaker, then 1.643g of ammonium persulfate was weighed and dissolved in the beaker, and then placed in a refrigerator of 5 °C for pre -cooling.
4. After an hour, pour the precooled ammonium persulfate solution into a completely frozen flask and observe the phenomenon (Observe every five minutes for the first hour. Observe every half hour for the next two hours), we can find the color of solution that change from purple to gray then black.
5. After five hours, remove the flask and thaw it at room temperature, weighing the filter paper, record. The vacuum filter is assembled and the solution is pumped, put the sample in the drying oven.
6. Take out the sample after 24h, weigh the filter paper again, calculate the weight of the product.
7. After the experiment, the instrument should be sorted out and cleaned for later use.

3.2.2 Electrochemical performance test

1. Take four pieces of stainless steel mesh, respectively weigh their weight, record, They are labeled as 1.2.3.4.

2. Prepare the grinder, weigh 0.002g of PVDF and 0.002g of Acetylene black and 0.016g of polymers, prepare the grinder, pour them into a mortar and grind thoroughly until there is no obvious graininess (about an hour and a half and under a baking lamp).
3. Add the appropriate amount of NMP to the mortar and mortar, mix well and stir (under a baking lamp).
4. Daub the mixed material evenly on the stainless steels' net, and then place it in the drying oven for 24h.
5. After 24h, take out the samples and weigh them separately (Make sure each stainless steels mesh is coated with approximately 3mg sample).
6. Conducting electrochemical tests, separately EIS, CV, CP. Save the data, draw pictures, analyze the data.

3.3 Sample characterization

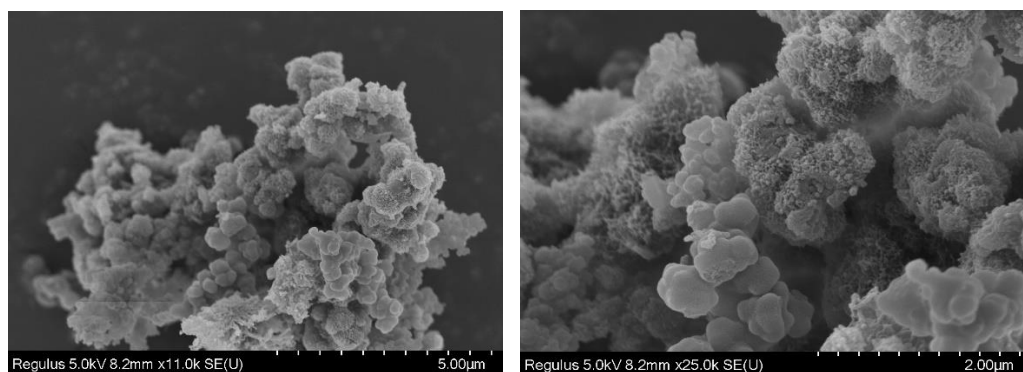


Figure 6(a)

Preparation of polyaniline/pyrrole nanocomposite morphology by scanning electron micro mirror (SEM) analysis of characterization, as shown in figure 6 (a), can be seen from the diagram, the polyaniline/pyrrole nanocomposites is spherical, morphology is poorer, heterogeneity, poor dispersion, so the need for further characterization testing samples of initiator is 2%.

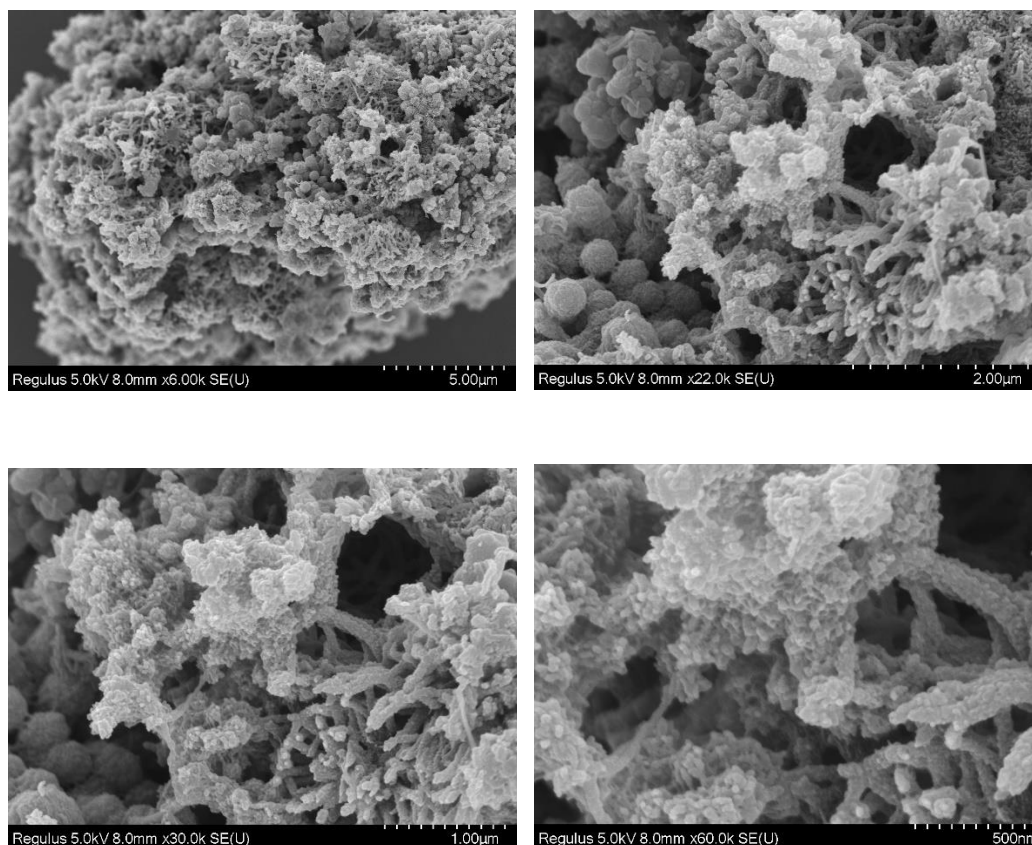


Figure 6(b)

The morphology of the prepared polyaniline/pyrrole nanocomposites was analyzed and characterized by scanning electron microscopy. Figure 5(b) is the SEM diagram of the whole polyaniline/pyrrole nanocomposite. It can be seen from the figure that the obtained polyaniline/pyrrole nanocomposite is spherical with relatively uniform morphology and general dispersion. As can be seen from the magnified photos of the material, the particle size distribution is uniform and the surface is smooth. Significant nanowires have emerged. However, we still did not achieve the desired effect. So, in the next few days, I will continue to refine my experiments and find the conditions to produce the perfect nanowires.

4 RESULTS

The test conditions: the collector is a stainless steel mesh, the reference electrode is a saturated calomel electrode, the electrolyte is 1 mol/L sulfuric acid, the sample: acetylene black: PVDF=8:1:1, the pair electrode is 1*1 platinum sheet.

4.1.1 Py : AN=1 : 9, The initiator is 1%

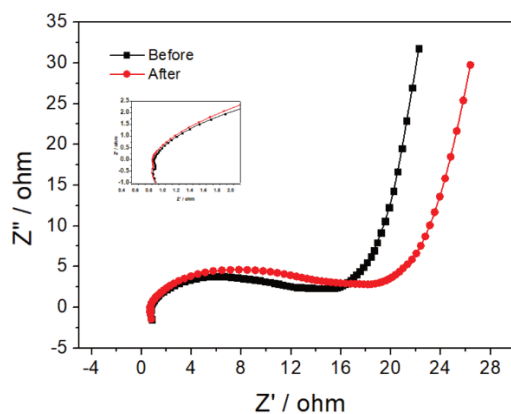


Figure 3 (b) CV of the sample

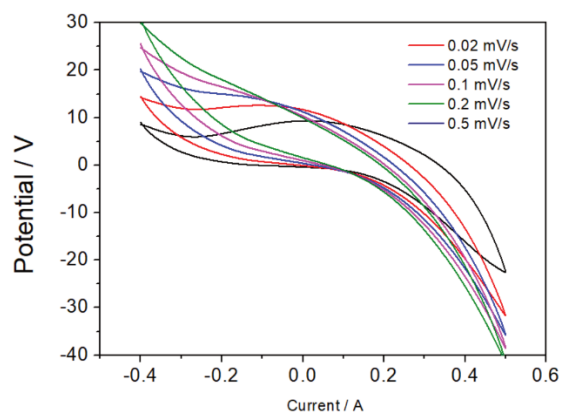


Figure 3 (b) CV of the sample

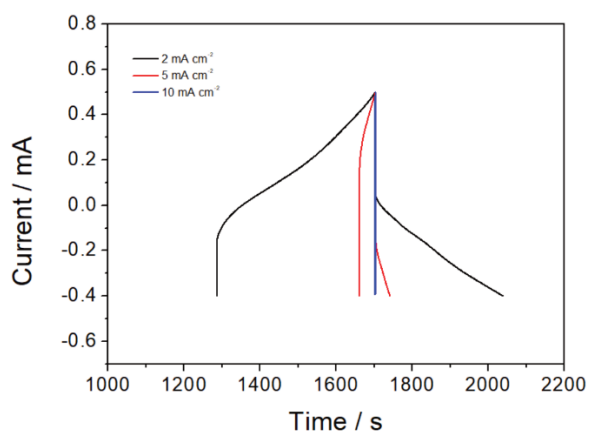


Figure 3 (c) CP of the sample

Figure 3(d) The initiator is 1%'specific capacity

1	M	0.002	0.005	0.01
H ₂ SO ₄				
discharge	time	263.4	77.6	9.1
	(s)			
	specific capacity	26.34	7.76	0.91
	(F/g)			
charge	time	288	79.1	9.1
	(s)			
	specific capacity	28.8	7.91	0.91
	(F/g)			
	Coulomb efficiency	109.3	102.0	100.0
	(%)			

4.1.2 Py : AN=1 : 9, The initiator is 2%

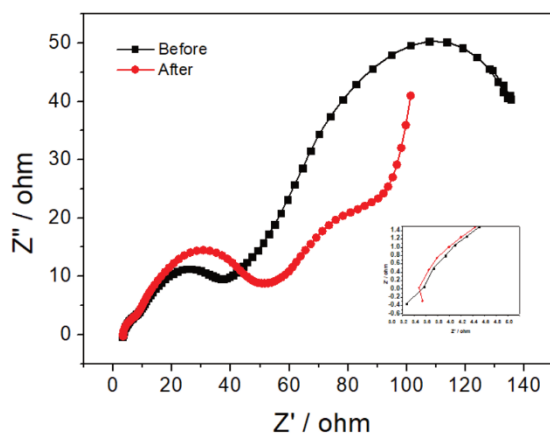


Figure 4 (a) EIS before and after comparison of the sample

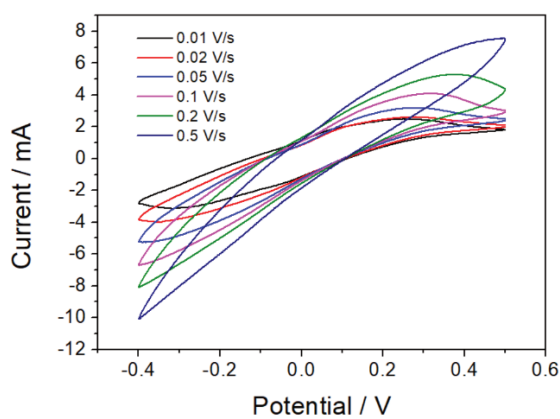


Figure 4 (b) CV of the sample

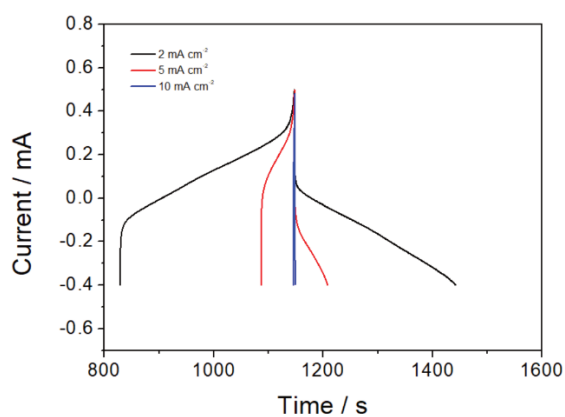


Figure 4 (c) CP of the sample

Figure 4(d) The initiator is 1%' specific capacity

1	M	0.002	0.005	0.01
H ₂ SO ₄				
discharge	time	263.4	61.4	2.5
	(s)			
	specific	26.34	6.14	0.25
	capacity			
	(F/g)			
charge	time	318.7	60	1.3
	(s)			
	specific	31.87	6	0.13
	capacity			
	(F/g)			
	Coulomb	121.0	97.7	52
	efficiency			
	(%)			

4.1.3 Py : AN=1 : 9, The initiator is 4%

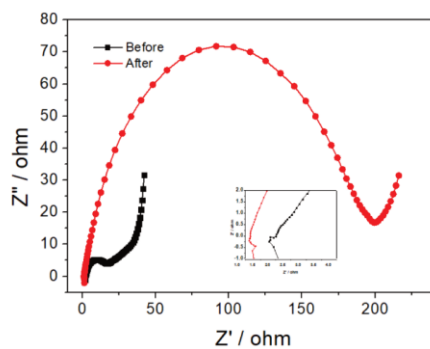


Figure 5 (a) EIS before and after comparison of the sample

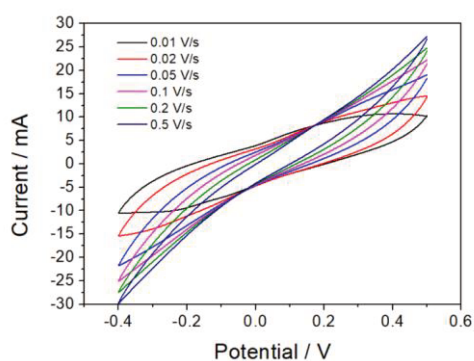


Figure 5 (b) CV of the sample

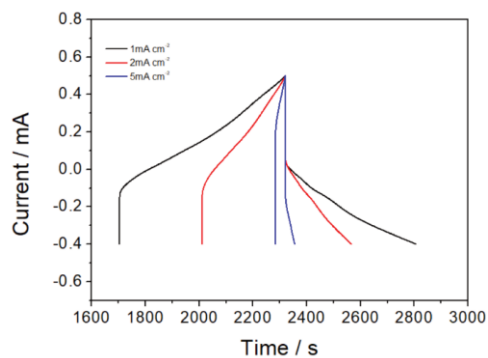


Figure 5 (c) CP of the sample

Figure 5 (d) The initiator is 1%'specific capacity

1	M	0.001	0.002.	0.005
H ₂ SO ₄				
discharge	time	616	209.4	37.4
	(s)			
	specific	61.6	20.94	3.74
	capacity			
	(F/g)			
charge	time	486	246	35.9
	(s)			
	specific	48.6	24.6	3.59
	capacity			
	(F/g)			
	Coulomb	78.9	117.6	96.0
	efficiency			
	(%)			

5 DISCUSSION

In this paper, using aniline and pyrrole as monomers and ammonium persulfate as oxidants, polyaniline/pyrrole nanocomposites were prepared by chemical liquid phase oxidation method. The best electrode materials can be obtained by complementing the advantages and disadvantages of different materials. The materials used in this paper have the advantages of simple preparation and low material cost. In this paper, the copolymerization of two monomers to generate nanowires and the study of electrochemical properties as the theme, by mixing in different proportions, adding different initiators as the conditions to get different materials, trying to find the best preparation method, to obtain the best energy storage electrode materials. Using a variety of instruments on the preparation of electrode materials properties of various characterization. Come to a conclusion as follows: Nanowires of aniline - pyrrole copolymer were synthesized by chemical copolymerization. The best properties of aniline-pyrrole copolymer were obtained when aniline: pyrrole was 9:1 and initiator was 2%. In the electrochemical test, the specific capacitance of aniline-pyrrole electrode is the best under the condition of 2% initiator, which is much higher than that of the electrode under the condition of 4% initiator. In the SEM characterization test figure, aniline-pyrrole nanowires can be clearly seen, and the particle size distribution is uniform.

So far, there have been a lot of kinds of methods to improve the performance of polyaniline and greatly improved the electrochemical properties of aniline. Copolymerization method is adopted in this paper, the preparation of aniline - pyrrole copolymer and to some extent, improved the polyaniline than electric capacity and cycle stability. However, there are still many problems that need to be further solved, such as how to solve the problem of low energy density of electrode materials, how to change the problem of poor cycling stability of electrode materials, and how to further improve the specific capacitance of electrode materials.

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