Research on Composite and Electrochemical Properties of Carbon Nanotubes Composites

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In this paper, the electrostatic interaction between carbon nanotubes with electronegative surface treated with polyacrylic acid and the hydrotalcite with positively charged laminate is used to and the ZnAl-LDH in-situ growth is installed onto the surface of carbon nanotubes to obtain the hydrotalcite/carbon nanotube composite. The analytical ability of different fluorescein intercalated LDH-PCNT composite modified electrodes for dopamine is studied and the results show that the pH value has a significant impact on the fluorescein intercalated hydrotalcite. The fluorescein in the complex is not only inserted into the hydrotalcite interlayer, but the intercalation composite is well integrated with the carbon nanotubes. Due to the accelerant role of the fluorescein and the carrier-mediated role of carbon nanotubes, the electrocatalytic ability of the composite is improved and the dopamine has a low detection limit on the surface of modified electrodes. The preparation method of the composite is simple and the electrocatalytic performance is good. The analyte has a low detection limit and high sensitivity on modified electrodes, which greatly expands the assembly method and application range of the electrochemical sensor.

1. Introduction

Carbon nanotubes are allotropes of carbon materials, which have unique physical properties. It has surface modification function and can be fused with other materials to form composite. Carbon nanotubes can be compounded with metal compounds, magnetic materials and polymers, and can be processed into special materials. Carbon nanotube composite has good electrical conductivity, stability and photoelectron performance. It is one of the new composites and has extensive application value.

Based on this, the ZnAl-LDH-PCNTs composite and LDH-FI-PCNTs composite are used to study the carbon nanotube composite to analyze the electrochemical behavior and electrocatalytic ability of the material and to evaluate the application effect of the electrochemical performance.

2. Literature review

Carbon nanotubes are allotropes of carbon materials, and their physical properties are unique. It has a surface modification function that can be fused with other materials to form a composite. Carbon nanotubes can be compounded with metal compounds, magnetic materials, and polymers. After processing, it can form special materials. Carbon nanotubes conform to materials with strong electrical conductivity. Stability and photoelectron performance are good. This is one of the new composite materials and has a wide range of applications. In many potential applications of carbon nanotubes (CNTs), their use for reinforcing polymers has attracted considerable attention due to their excellent stiffness, excellent strength and low density of CNTs. This offers many opportunities for new material systems that require high strength and high modulus.

Novel nanostructured composite fibers based on graphene and carbon nanotubes have high tensile strength, electrical conductivity and electrocatalytic activity. It is used to make flexible linear dye-sensitized solar cells and electrochemical supercapacitors. Both of them have high performance. For example, the maximum energy conversion efficiency is 8.50% and the specific capacitance is about 31.50 F g-1. It is further shown that these miniature linear devices are more suitable for flexible and portable electronic devices (Sun, 2014). Sodium-ion batteries (SIBs) are the most promising alternative to lithium-ion batteries, which are suitable for

renewable power plants and smart grids. The cost is low, the natural resources are abundant, and the chemical composition is similar. A simple blend of commercial red phosphorus and carbon nanotubes (CNTs) provides a reversible capacity of 1675 mA h g-1 for sodium ion batteries (SIB). In ten cycles, the capacity retention rate was 76.6%. This will be a promising anode candidate for high capacity and low-cost SIBs (Li et al., 2013). Polyaniline (PANI) nanocones were coated on graphene/CNT composites. Graphene and single-walled carbon nanotube (CNT) composites were studied as electrodes of supercapacitors to obtain graphene/CNT-PANI composite electrodes. The graphene/CNT-PANI electrode and the graphene/CNT electrode are assembled into an asymmetric tantalum capacitor. The highest energy density of 188 Wh kg-1 and the maximum power density of 200 kW kg-1 are achieved. The structure and morphology of graphene/CNT composites and PANI nanocone coatings were characterized by scanning electron microscopy and transmission electron microscopy. The superior performance of assembled supercapacitors is also discussed. The large surface area of the three-dimensional network structure of the graphene-based composite material is effectively utilized. The presence of CNTs in the composite prevents graphene from being re-stacked. Uniform and vertically aligned PANI coatings on graphene provide increased conductivity (Cheng et al., 2013). Zhuo et al. reported a simple method for the synthesis of Co3O4 functionalized carbon nanotubes (Co3O4-f-CNT) composites by thermally decomposing Co3O4 nanoparticles on the surface of functionalized carbon nanotubes (f-CNTs). The composite consisted of 13% carbon nanotubes and 87% by weight of Co3O4 nanoparticles. All Co3O4 particles grow closely along the carbon nanotube axis with a highly uniform dispersion. When it is used as a negative electrode material for a rechargeable lithium ion battery, the composite exhibits high capacity and excellent cycle performance at high current and low current rates. The discharge capacity was 719 mA h g-1 at the second cycle. The discharge capacity was 776 mA h g-1 at the hundredth cycle. Even at a current density of 1 A g-1, the specific capacity remained at about 600 mA h g-1. This excellent electrochemical performance is attributed to the unique nanostructure of the composite. Almost all Co3O4 nanoparticles are immobilized on the surface of the f-CNT. Therefore, the physical aggregation of the nanoparticles is avoided during the charging-discharging process. Furthermore, the good mechanical flexibility of f-CNTs can easily mitigate the large volume expansion/contraction associated with the conversion reaction electrode. Finally, f-CNTs are highly conductive electronic matrices due to their high electrical conductivity, which shortens the electron diffusion path (Zhuo et al., 2013). Ratso et al. studied the electrocatalysis of oxygen reduction on nitrogen-doped layered graphene/multiwalled carbon nanotubes (FLG / MWCNT) composite catalysts. These composites were prepared from different nitrogen precursors, acid treated MWCNTs and graphene oxide (GO), which were synthesized from graphite by a modified Hummers process. Urea and dicyandiamide were used as nitrogen precursors. Doping is achieved by pyrolyzing a mixture of GO and MWCNTs in the presence of these nitrogen-containing compounds at 800 °C. The N-doped composite catalyst samples were characterized by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The latter method shows successful nitrogen doping. The oxygen reduction reaction (ORR) was investigated in 0.1 M KOH on an N-doped FLG / MWCNT electrocatalyst modified glassy carbon electrode using a rotating disk electrode (RDE) method. RDE results indicate that these metal-free nitrogen-doped nanocarbon catalysts have significant electrocatalytic activity on ORR in alkaline media, similar to commercial Pt / C catalysts. The results obtained in this work are particularly important for the development of non-Pt cathode catalysts for alkaline membrane fuel cells (Ratso et al., 2014). Wang et al. prepared a novel magnetic composite adsorbent composed of graphene, multi-walled carbon nanotubes (MWCNTs) and Fe3O4 nanoparticles by solvothermal method. The prepared adsorbent was characterized by X-ray diffraction, scanning electron microscopy, X-ray fluorescence spectrometry and Fourier transform infrared spectroscopy. Fourier transform infrared spectroscopy and particle size distribution of samples before and after adsorption were also performed. The effect of pH and temperature on the adsorption properties of methylene blue on magnetic adsorbents was investigated (Song et al., 2013). The dynamics are well described by pseudo second order and intraparticle diffusion models. Due to its high adsorption properties, magnetic separation and high recyclability, the prepared magnetic composites can be cut off as potential adsorbents for the removal of dye contaminants (Wang et al., 2014). The weakness of the thermal stability of solar cells was investigated. Thermal degradation is reduced by embedding insulating polymer functionalized single-walled carbon nanotubes (SWNTs) in place of organic hole transport materials (Habisreutinger et al., 2014). Zhu et al. produced red P-single carbon nanotube composites by a modified evaporation-condensation method. The red P is evenly distributed between the entangled SWCNT bundles. Due to the non-destructive preparation process, a high conductivity and mechanical strength SWCNT network is retained. The conductivity of the composite is enhanced and the solid electrolyte intermediate phase is stabilized. The cyclic stability of the P/carbon composite was extended from current 100 cycles to 2000 cycles (Zhu et al., 2015). The sandwiched MXene/carbon nanotube (CNT) paper consisting of alternating MXene and CNT layers is independent and flexible. When used as an electrode in a supercapacitor, these laminated

papers have high volumetric capacitance, good rate performance and excellent cycle stability (Zhao et al., 2015).

In summary, precise control of CNT processing factors includes intact CNT structure, uniform dispersion of CNTs in the polymer matrix, effective filler-matrix interface interaction, and orientation/orientation of polymer chains/CNTs. The excellent properties of the composite fiber are applied. Therefore, the manufacturing method plays an important role in determining the microstructure and ultimate mechanical behavior of the composite fiber. Based on this, carbon nanotube composites were mainly studied with ZnAl-LDH-PCNTs composites and LDH-FI-PCNTs composites. The electrochemical behavior and electrocatalytic ability of materials are discussed. The electrochemical performance application effect was studied.

3. Method

3.1 ZnAl-LDH-PCNTs Composite

In order to obtain the crystal chemical characteristics of hydrotalcite, thecrystal unit cell parameters of hydrotalcite are calculated and the results are listed in Table 1. The cell parameter c is three times that of the interlayer spacing of hydrotalcite (sum of thickness of the laminate and the adjacent two layers) and it is easy to calculate the value of c according to the interplanar crystal spacing. The value of c and the disorder of the anions between the layers of hydrotalcite are related to interlayer water molecules. As can be seen from the Table, the cell parameter c value in the composite is slightly higher compared with that in pure LDHs. The reason for this phenomenon is that the laminate is fused with carbon nanotubes in the composite, so relatively the acting force of the anion and laminate between the layers of hydrotalcite is weakened, resulting in a slight increase in the interlayer spacing of the composite. The a value in the pure hydrotalcite and the composite of hydrotalcite and carbon nanotubes is both 0.306 nm, indicating identical laminate structure and composition. (The structural parameters of ZnAl-LDH and ZnAl-LDH-PCNTs-X composite are shown in Table 1 below)

Table 1: structural parameters of ZnAl-LDH and ZnAl-LDH-PCNTs-X complexes

Sample	a	b	c	d	e	f
d003 (nm)	0.860	0.864	0.861	0.862	0.861	0.865
d110 (nm)	0.153	0.153	0.153	0.153	0.153	0.153
Lattice parameterc1 (nm)	2.580	2.592	2.583	2.586	2.583	2.595
Lattice parametera2 (nm)	0.306	0.306	0.306	0.306	0.306	0.306
d0033 (nm)	8.331	9.013	7.236	8.636	8.480	9.100
d0014 (nm)	10.104	14.201	13.985	9.6721	9.575	13.292
d5 (nm)	9.218	11.607	10.611	9.154	9.028	11.196

A certain quantity of carbon nanotubes (20-60 nm in diameter and 5-15 gm in length) are placed in a four-necked flask and then 200 ml of acetone is poured into the four-necked flask. After that, a certain amount of acrylic acid is added. Then, it is sonicated for 30 min at room temperature and 0.5 g of azobisisobutyronitrile initiator is added. It is then refluxed for 8 h in a nitrogen atmosphere. After cooling to room temperature, it is filtered repeatedly, washed until neutral and dried in vacuum at 60 °C for 12 h. At this time, the surface of the carbon nanotube is modified with a polyacrylic acid chain-like compound with a negative carboxylate group. The modified carbon nanotubes are collected and referred to as PCNTs. In order to observe the microstructure and morphological characteristics of the hydrotalcite and carbon nanotube composites, the scanning electron micrograph of carbon nanotubes treated by polyacrylic acid and the composite of carbon nanotubes and hydrotalcite is shown in Figure 1. It can be seen from the scanning electron microscope image that the surface of carbon nanotubes becomes rough after being treated with polyacrylic acid and the pipe diameter is larger than that of the treated carbon nanotubes of 20-40 rim, indicating that the polyacrylic acid is covered on the surface of carbon nanotubes. It can be inferred from the experimental process that when CNTs are dispersed in a mixture of acetone and AA, AA is polymerized to form PAA under the action of initiator AIBN. During the polymerization process, carbon nanotubes participate in the reaction and PAA is distributed on the outer wall of carbon nanotubes.
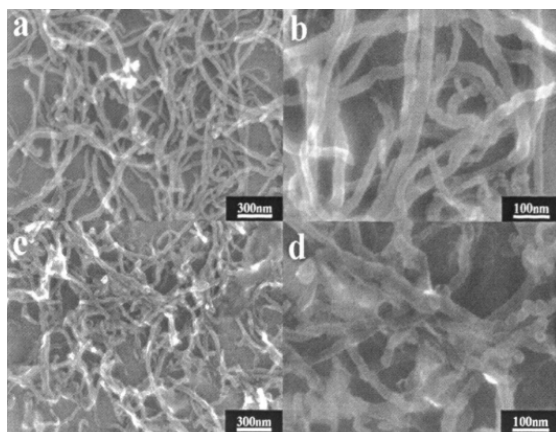
Figure 1: Scanning results of carbon nanotubes and hydrotalcite nanotube complexes

3.2 LDH-FI-PCNTs Composite

LDH-F1 grows well in situ on the surface of PCNTs, covering most of the surface of PCNTs. However, a small amount of free LDH can be observed in Figure a. FI exists around the carbon nanotubes and partial accumulation phenomenon can be observed on some carbon nanotubes. It can be seen in the electron micrograph of larger multiple that the particle size of hydrotalcite is about 10-15 nm and it is evenly distributed on both sides of the carbon nanotubes. The surface of the carbon nanotubes becomes very rough, indicating that the hydrotalcite is well fused with the carbon nanotubes. The fluorescein not only enters the hydrotalcite layer, but the intercalated composite grows onto the surface of PCNTs. (The transmission electron micrograph of LDH-FI-PCNTs is shown in Figure 2)
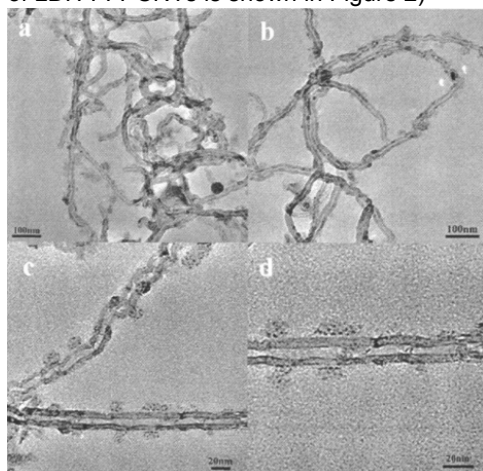

Figure 2: LDH·FI—PCNTs transmission electron microscopy

4. Result Analysis

4.1 Specific Surface and Pore Size Analysis of ZnAl-LDH-PCNTs Composite

It can be seen from the low temperature N2 adsorption and desorption isotherm that the two samples exhibit a similar distribution map, belonging to typical IV isotherm. There is no adsorption platform at the higher P/PO and this adsorption isotherm generally corresponds to the slit-like pore structure formed after the particle reunion. Before and after the hydrotalcite adheres to the carbon nanotubes, the properties of the carbon nanotubes twined to form slit pores are not changed. Similarly, both samples exhibit a D-type hysteresis loop shape and the two adsorbed and desorbed branches have an approximate slope, indicating that the two samples have identical pore structure characteristics. At the same time, the area of the volume of PCNTs and hysteresis loop closure is larger compared with the LDH-PCNTs-0.5 composite, indicating that PCNTs have a relatively large pore volume. This conclusion is also consistent with the value of the total pore volume in the pore structure parameters. The specific surface of the composite is 63.963 m2·g-1 while the specific surface

of PCNTs is 88.067 m2. G-1, which is larger than the composite to a certain degree. The reason for this is that the surface of carbon nanotubes is covered by hydrotalcite. (The specific surface and pore size distribution parameters of PCNTs and LDH-PCNTs-0.5 composite are shown in Table 2)

Table 2: Specific surface areas and pore distribution parameters for PCNTs and LDH-PCNTs-0.5

Samples	Specific aeca m2 . g-1	Total volume mL·g-1	Optimum pore size nm
PCNTs	88.067	0.4266	3.8
LDH-PCNTs-0.5	63.963	0.3292	2.3

4.2 Electrochemical Behavior of Electro-Catalyzed Catechol of Modified Electrodes under Different Scanning Rate

The peak current of catechol increases continuously with the scanning rate. The oxidation potential and reduction potential shift, of which the oxidation potential is shifted positively and the reduction potential is shifted negatively. The reason for this phenomenon is the charge diffusion and the ohmic resistance unable to be compensated timely, thus leading to the instability of the composite modified electrode. This phenomenon is also observed on the cyclic voltammograms of different scanning rate for electroanalytical chemical behavior on many different chemically modified electrodes. First, the catechol is adsorbed to the surface of composite modified electrodes and then an oxidation reaction occurs on the surface of the electrodes. After the hybridization of hydrotalcite and carbon nanotubes, the hydrotalcite grows on the surface of carbon nanotubes. The hydrotalcite has storng adsorption capacity and the carbon nanotubes not only accelerate the electron transfer, but play a good dispersion carrier role. Thus, the synergistic effect of these two enables the modified electrode to reach the optimal electro-catalyzed effect on catechol. (The surface coverage of modified electrodes of different materials is shown in Table 3)

Table 3: surface coverage of different material modified electrodes

Samples	a	b	c	d	e	f	g
*10-9mol·cm-2	0.32	1.23	0.47	1.72	3.59	6.28	5.88

4.3 Electrochemical Behavior of Electro-Catalyzed Dopamine of Modified Electrodes under Different Scanning Rate

There is a very good linear relationship between the oxidation current and the reduction current and the square root of the scanning rate at the scanning rate from 50 mV/s to 200 mV/s. The linear regression equation of the oxidation current to the square root of the scan rate is I(A)=O. 26082+0.72003v(mV/s) and the linear correlation coefficient of the obtained straight line is 0.9966. The linear regression equation of the reduction current to the square root of the scanning rate is I(A)=1.40685.0.8076v(mV/s) and the linear correlation coefficient of the obtained straight line is 0.9997. The results of this experiment indicate that the electrical analysis process of dopamine is a quasi-reversible process of diffusion control in LDH. F1. PCNTs/GCE surface. This also means that when the electrode is immersed into the dopamine solution to be analyzed, the diffusion of dopamine to the electrode surface is a slow rate controlling step. It is necessary to wait for the standing before the test and then start measuring. Therefore, in future LDH-F1 In the - PCNTs/GCE test, it needs to stand for one minute and then to perform subsequent electrochemical performance test. (The relationship between oxidation peak current and reduction peak current and different canning rate is shown in Figure 3)
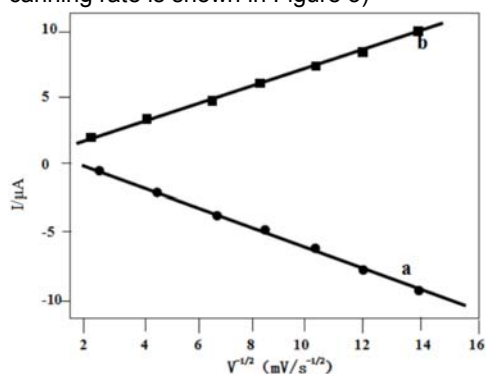

Figure 3: Relationship between peak current and reduction peak current and different sweep rates

5. Conclusion

The hydrotalcite is uniformly adhered to the surface of carbon nanotubes. Different proportion of CNTs and LDH has different analytical properties for the composite modified electrode for catechol. Since the CNTs can accelerate the electron transfer process in the electrochemical process and improve the hydrotalcite peak dispersion, the electrochemical performance of ZnAl-LDH-PCNTs is superior to that of pure LDH and CNTs. The insertion amount of fluorescein is regulated by the surfactant sodium dodecyl sulfate and the prepared intercalation complex is grown in situ on the surface of PAA-treated CNTs. The results show that fluorescein is inserted between the hydrotalcite layers and that the composite grows well on the surface of carbon nanotubes. Due to the promotion effect of the conjugated system of fluorescein and the conductivity of carbon nanotubes for electrochemistry, the fluorescein intercalated LDH-PCNTs have good electrocatalytic properties for dopamine. The research in this paper is limited in length and the research depth on carbon nanotube composite and electrochemical properties is insufficient, which calls for further exploration.

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