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# Preparation and research of organic luminescent materials in confined space of carbon nanotubes

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The molecules in the graphene confined space show unique "nano-confined characteristics", which is used to study the photoelectric properties of the luminescent polymer polyfluorene. The first preparation is reported of the epoxy/carbon nanotube multipleural membrane, with the concentration difference and pressure difference to increase the spontaneous diffusion of the carbon nanotube to the filling efficiency of the carbon nanotube cavity, to avoid the absorption of luminescent material in the outer wall of the carbon nanotube. In this paper, the special luminescence properties of polyfluorene in the carbon nanotube cavity were systematically studied, and it was found that the proposed preparation scheme could not only improve the filling efficiency, but also effectively overcome the defect of poor filling selectivity due to capillary action. After the filling into the carbon nanotube, the spectrum of polyfluorene all showed blue shift, and the degree of blue shift was related to the limited size of the carbon nanotube.
**Keywords**: carbon nanotubes, confined space, luminescent materials.

Молекулы в замкнутом пространстве графена демонстрируют уникальные "наноограниченные характеристики", которые используются для изучения фотоэлектрических свойств люминесцентного полимера полифлуорена. Сообщается об изготовлении мембраны из эпоксидной смолы/углеродной нанотрубки с разностью концентраций и перепадом давления. Изучены люминесцентные свойства полифлуорена в полости углеродных нанотрубок. Обнаружено, что предложенная схема приготовления может не только улучшить эффективность заполнения, но и эффективно преодолеть дефект плохой селективности наполнения за счет капиллярного действия. После заполнения углеродной нанотрубки весь спектр полифлуорена сдвигается в коротковолнрвую область, степень сдвига связана с ограниченным размером углеродной нанотрубки.

**Підготовка та дослідження органічних люмінесцентних матеріалів в обмеженому просторі вуглецевих нанотрубок**. *X.Chen, Z.Xiong*

Молекули у замкнутому просторі графену демонструють унікальні "нанообмежані характеристики", які використовуються для вивчення фотоелектричних властивостей люмінесцентного полімера поліфлуорену. Повідомляється про виготовлення мембрани з епоксидної смоли/вуглецевої нанотрубки з різницею концентрацій і перепадом тиску. Вивчено спеціальні люмінесцентні властивості поліфлуорену у порожнині вуглецевих нанотрубок. Виявлено, що запропонована схема виготувлення може не тільки поліпшити ефективність заповнення, а й ефективно подолати дефект поганої селективності наповнення за рахунок капілярної дії. Після заповнення вуглецевої нанотрубки весь спектр поліфлуорену показав синій зсув, ступінь якого пов'язаний з обмеженим розміром вуглецевої нанотрубки.

## 1. Introduction

The carbon nanotubes are one-dimensional nanotube structures that are formed by the $sp^2$ hybridization of carbon atoms [1]. Carbon nanotubes have good electrical, mechanical and other physical properties. Through the modification of carbon nanotubes, the stability of carbon nanotubes can be improved, and the materials can be modified by composite with other materials to expand the application range of carbon nanotube composites [2]. Compared with the planar graphene flake structure, the constrained tubular nano-cavity structure of carbon nanotubes can make the molecular arrangement inside the filling highly oriented, and the rigid structure of carbon nanotubes can also improve the stability of the filling [3].

In the 1980s, the organic luminescent film technology began to develop, and the research on organic luminescent materials began to receive attention [4]. In recent years, researchers have begun to focus on the process of filling the carbon tubes with materials, and there are various forms of rigid inorganic materials and flexible organic materials that have been filled to carbon nanotubes through physics or chemistry. Thus, in [5] molecules of indoles were filled into carbon nanotubes with control of their release under the action of infrared light, so as to realize the possibility of carbon nanotubes as controllable release drug carriers, which is of great significance for the application of carbon nanotubes in the medical field. The authors of [6] mixed several carbon nanotubes with different chirality with polyfluorene in their experimental study. By observing the change of the emission spectrum of the mixture, it was inferred that polyfluorene and carbon nanotubes were wrapped externally to form spiral wrapping and parallel arrangement, and the arrangement was determined by the chirality and radius size of carbon nanotubes [6]. By wrapping polyfluorene and carbon nanotubes with different branched chains, studies were carried out on the interaction mode between branched chains and the outer wall of carbon nanotubes and the influence on the arrangement mode of the outer wall of carbon nanotubes [7].

The polyfluorene polymer is an efficient new organic luminescent polymer, the ring structure of the height and the rigid backbone structure, which gives it a good chemical stability, thermal stability, and easy treatment to be [8]. The hydrogen atoms in the cluster of the polyfluorene nine are more reactive and reactive to replace the reaction, and by modifying it to get more and more variety of polyfluorene derivatives, it helps to improve the solubility of the molecules, and enhances the hypermolecular structure.The confined space of carbon nanotubes can not only change the stacking state of the filling molecules, but also change the interaction between the carbon nanotubes and the filling material, so that the physical and chemical properties of the material change greatly compared with its intrinsic state [9].

## 2. Experimental

Synthesis of carbon nanotube arrays: the article uses a horizontal pipe furnace growing carbon nanotube array. First, the substrate of the catalyst, which is the substrate of the catalyst, is cut to 1 $cm^2$ with a silicon slice, and in order to put it in the tube furnace, it will be fixed and connected to the exhaust pipe. Large flow of argon was injected for 5 min, then 300 sccm of argon and 300 sccm $H_2$ were injected to regulate the flow rate of hydrogen into the water. In order to remove more of the non-qualitative carbon during growth, water is required in the tube furnace. If the water velocity is too high, the carbon nanotube array growth and the non-qualitative carbon content will be affected, causing the carbon nanotube array to crack and limit the array height; If the water velocity is too small, excessive non-qualitative carbon will occur in the carbon nanotube array, resulting in reduced carbon nanotube permeability. Therefore, the water velocity should be controlled in a certain range. When the temperature reaches 775°C in argon gas containing moisture, the growth for 10–15 min after stopping the heating and closing the ethylene gas; after waiting for tubular furnace temperature drops to 600°C, close the air supply; when the temperature is down to room temperature, close Ar gas, open the tube furnace, remove the grown good carbon nanotube arrays.

The preparation steps of carbon nanotube-epoxy resin porous film are as follows:

1. Growing multi-wall carbon nanotube arrays.
2. Prepare epoxy resin precursors embedded array.
3. Heat and solidify slices.
4. Multi-wall carbon nanotubes porous composite membrane plasma membrane treatment.

5. KCl diffusion is used to inspect the pores of multi-walled tubules.

To dissolve the 0.02 g polyfluorene into a 250 ml methanol/aqueous solution, which is a mixture of methanol/water = 1/1, and then mixed with a steady polymer solution. The teflon diffusion pool and the silica gel plate were assembled into a pair diffusion device, and the carbon nanotubes/epoxy resin porous composite film was fixed between the holes of the two silica gel plates. The prepared polymer solution was placed on the left side of the diffusion pool, and an equal amount of methanol solution was put on the right side. The solution level should be higher than the pore of the diffusion pool. The device is sealed with plastic wrap to reduce the evaporation of methanol. Finally, the diffusion device was stored away from light for 5 to 6 days at room temperature. After the diffusion is completed, the composite film is taken out from the silica gel plate, and the film surface is washed with methanol solution to remove all residual polyfluorene polymers on the surface. After drying at room temperature, store away from light for testing.

The carbon nanotube/polyfluorene porous composite film to be tested is placed into a 20 ml screw bottle, and 5 ml of concentrated hydrochloric acid is added to avoid light storage. When the composite membrane is completely dissolved and no obvious undissolved clustered tube bundle samples can be observed, the dissolved samples are absorbed with a syringe and placed in a filter with a PTFE filter film. After the filter is placed on the filter film, the residual hydrochloric acid is washed repeatedly with deionized water. The filter film was placed in a screw bottle containing methanol and dispersed ultrasonically to obtain a polyfluorene polymer filled carbon nanotube sample.

## 3. Results and discussion

### 3.1. Characterization of polyfluorene compounds filled inside carbon tubes

Fig. 1 shows the TEM picture of polyfluorene macromolecule filled in multi-wall carbon nanotubes. In Fig. 1d the nano linear structure with high contrast in the center of carbon tube is polyfluorene molecule filled in the inside of carbon tube. As shown by arrows in Fig. 1b and Fig. 1c, when polyfluorene luminescent polymer is filled into the carbon nanotube, due to the interaction between the polyfluorene chain segment and the tube wall, the polyfluorene molecule that is filled into the carbon nanotube tube

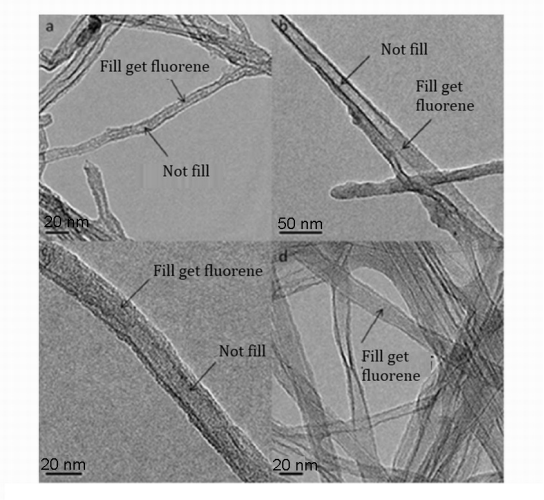


Fig. 1. TEM images of carbon nanotubes filled with polyfluorene.

will be stranded, resulting in a hollow structure in the carbon nanotube tube. As indicated by arrows in Fig. 1a, b and c, polyfluorene molecules cannot completely occupy the cavity in the carbon tube, so it shows an intersectional distribution. According to the results of transmission electron microscope, it can be preliminarily determined that polyfluorene macromolecule has been filled into the carbon nanotube, and the more detailed composition can be further determined by elemental analysis.

In Fig. 1,the original EDX chart for PFS @cnt is used to determine the elements of the polymer that are filled in the carbon tube. In Fig. 2, the black line is the spectrum of the unfilled PFS single-walled carbon nanotube composite membrane sample, and the EDX spectrum does not detect the element S. The red line is the EDX spectrum of PFS samples filled in single-walled carbon nanotubes. The presence of S element can be clearly observed, which confirms that the PFS has been filled into the carbon nanotubes. This method can also be used to verify that pfn-br has been filled into the carbon nanotubes.

In order to compare with polyfluorene molecules filled inside the carbon nanotubes, samples containing mixed polyfluorene were prepared in the experiment. According to the TEM in Fig. 3, after the carbon nanotube is mixed with polyfluorene solution by ultrasound, the carbon nanotube is tightly wrapped with a layer of material, indicating that polyfluorene forms a uniform polymer coating on the outer wall of the carbon tube, with a covering thickness of about 3–5 nm, while the hollow morphology with low

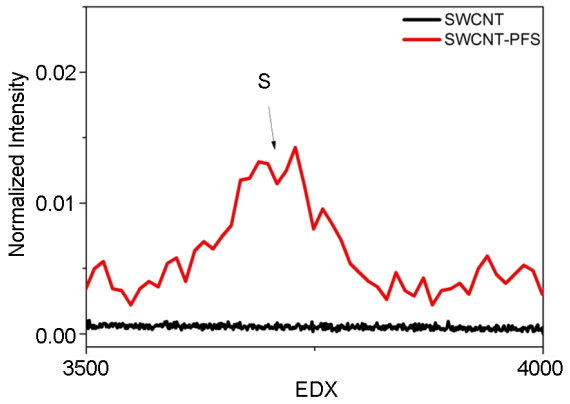


Fig. 2. EDX analysis spectra of PFS filled carbon nanotubes and blank carbon nanotubes.

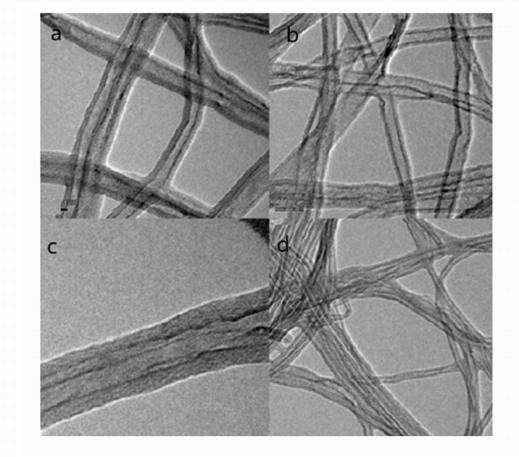


Fig. 3. (a) and (b) are PFN-Br wrapped on the outside of carbon nanotubes, (c) and (d) are PFS wrapped on the outside of carbon nanotubes.

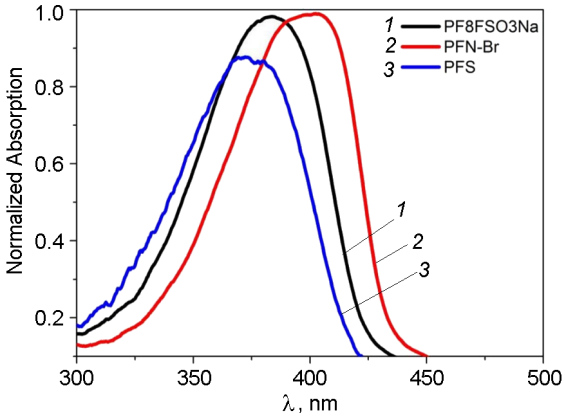


Fig. 4. UV absorption spectra of PF8 (*1*), pfn-br (*2*) and PFS (*3*) in methanol solution.

electronic contrast is still shown in the carbon nanotube cavity due to the lack of filling. The experimental results are essentially different from the morphology of polyfluorene filled in carbon nanotubes, which further proves that the scheme adopted in this paper successfully fills polyfluorene molecules into the cavity of carbon nanotubes.

In the process of polymerized fluorohydra/methanol solution and carbon nanotubes, the carbon nanotube is evenly distributed in the polyfluorene solution, which means that the carbon tube that was modified by the ionized polyfluorene package has good water, and the dispersion stability of the water solution increases significantly. In the methanol solution, the carbon nanotubes will reassemble and precipitate. It is concluded that the force between polyfluorene and carbon tube is different in different solvents. The strong force in aqueous solution is beneficial to improve the stability of polyfluorene/carbon nanotube composite.

### *3.2. Electrochemical properties of polyfluorene compounds filled inside carbon tubes*

Fig. 4 shows the ultraviolet absorption spectra of three different kinds of polyfluorene molecular methanol solutions. As shown in the figure, the maximum absorption peaks of PFS, PF8FSO3Na and pfn-br polyfluorene molecules in methanol solutions were respectively 363 nm, 385 nm and 400 nm. The carbon nanotube/epoxy membrane can cause the absorptive intensity of the absorbent spectrum, and during the spectroscopic testing, due to the effect of the epoxy film, there will be a small amount of light scattering that affects its ultraviolet absorption. Therefore, in the experiment, concentrated hydrochloric acid was used to dissolve the carbon nanotube-epoxy resin composite film, and the epoxy resin outside the carbon nanotube array was removed, leaving only the carbon nanotubes filled with polychrysanthemum material. After the composite membrane was dissolved in hydrochloric acid, the carbon nanotube dispersion solution was filtered onto the membrane with a hydrophilic polytetrafluoroethylene filtration membrane with a pore size of 1 nm, then rinsed with deionized water and cleaned with methanol. Finally, the filtration membrane was placed in a screw-mouth bottle containing methanol, and the carbon nanotube was ultrasonic washed down to measure the ultraviolet absorption spectrum of the dispersed liquid sample.

Fig. 5 shows the UV absorption spectra of PFS solutions with mass fractions of

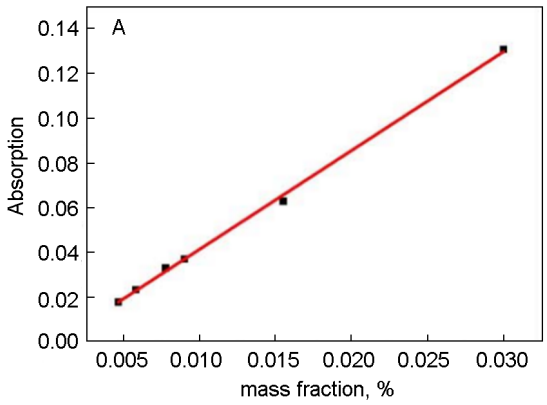


Fig. 5. Relation between UV absorbance and concentration of PFS solutions with different concentrations at 363 nm.

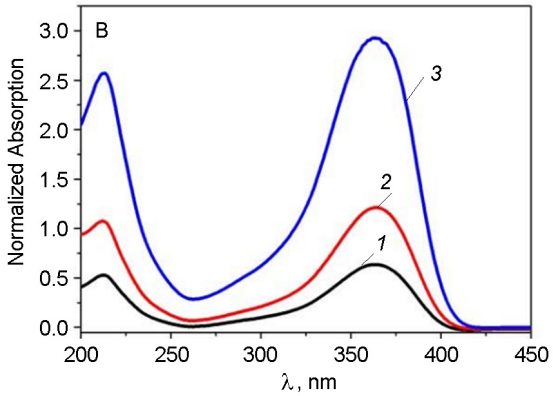


Fig. 5b. UV spectrogram of UV absorbance of PFS solutions with different concentrations at 363 nm.

0.0155 %, 0.009 %, 0.00775 %, 0.0058 % and 0.00465 %, respectively. Fig. 5b shows the UV visible absorption spectra of PFS polyfluorene macromolecule methanol solutions with different concentrations. It can be seen from the spectrogram that the UV absorption peak position of polyfluorene molecular solution does not change with the change of polyfluorene molecular concentration, but the absorption intensity shows a linear increase trend with the increase of concentration within a certain range. It is shown that that structure of the aggregation state of the polyfluorene molecule do not change with the concentration in a concentration range.

## 4. Conclusion

In this paper, chemical vapor deposition (CVD) method was used to grow vertically oriented multi-wall carbon nanotube arrays. Epoxy resin embedding and curing combined with microchip technology were used to prepare epoxy resin/carbon nanotube nanoporous composite films. Polyfluorene polymers were filled into the carbon nanotubes by diffusion technology. A series of tests including UV spectrum, fluorescence spectrum, SEM and TEM were carried out on the filled compound to compare the differences of the polyfluorene molecules filled inside the carbon nanotube and the polyfluorene molecules wrapped outside the carbon nanotube in the structural interaction, absorption and emission spectra and other properties. Finally, the organic luminescent small molecules were filled into the carbon tube, and polyfluorene was filled into the nanogap of the shrink carbon nanotube array, and the polyfluorene samples were compared with the polyfluorene samples filled into the carbon nanotube, so as to explore the interaction mode between the luminescent molecules and the nanotube under the restricted environment of nano. In this paper, the diffusion of polyfluorene solution is realized by using the concentration difference. The operation is simple, and the comparison of polyfluorene macromolecule in the capillary-assisted filling experiment of disordered large scale carbon nanotubes shows that epoxy resin/carbon nanotube array composite film filling polyfluorene can not only improve the filling efficiency, but also effectively overcome the defect of poor filling selectivity due to capillarity. By comparing the absorption and emission optical spectra of the luminescent molecules filled into the carbon nanotubes through spectral detection technology, it is found that the spectrum of polyfluorene after the ultraviolet absorption spectra and the filling into the carbon nanotubes all show blue shift, and the degree of blue shift is related to the limited size of the carbon nanotubes.

## References

1. Z.Shan, J.Li, Q.Li, *Electrochimica Acta*, **212**, 621 (2016).
2. A.R.Hopkins, A.C.Labatete-Goeppinger, H.Kim, *Carbon*, **107**, 77 (2016).
3. Y.Zhang, L.Xue, M.Zhang, *Ceramics International*, S0272884217315924 (2017).
4. J.A.Samareh, E.J.Siochi, *Nanotechnology*, **28**, 372001 (2017).
5. H.Shinohara, *Jap. J. Appl. Phys.s*, **57**, 020101 (2017).
6. G.Bepete, L.Khan, Z.Chiguvare, *Phys. Status Solidi*, **214**, (2017).
7. L.Winkless, *Mater. Today*, **19**, 423 (2016).
8. F.Hennrich, W.Li, R.Fischer, *Acs Nano*, **23**,1888 (2016).
9. D.Fong, G.M.Andrews, A.Adronov, *Polymer Chemistry*, **9**, 2873 (2018).