

Study on Synthesis and Self-assemble Nano-materials of Tetra-substituted Phenoxy Nickel Phthalocyanine

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Abstract. Tetra phenoxy substituted nickel phthalocyanine nanofibers were prepared in large scale by self-assembling via a simple solvent diffusion method. The size of them was 100-200 nm in diameter and several micron in length. The formation mechanism of nickel phthalocyanine fibers was discussed and studied by UV-visible spectra.

Introduction

Phthalocyanines and their derivatives are widely applicable organic semiconductors[1,2]. Recently, a great scientific interest has been focused on the synthesis of one-dimensional nanostructures of phthalocyanines, because of the larger surface areas which can cause the enhanced electronic and optical properties[3,4]. In this paper, we synthesized a tetra phenoxy substituted nickel phthalocyanine. And the phthalocyanine nanofibers were obtained by a simple solvent diffusion method.

Experimental

Synthesis of Nickel Phthalocyanine

The Pc precursor, 4-(4-tert-butyl-phenoxy)-phthalonitrile, was provided by the Northeast Normal University. The other chemicals were purchased from commercial suppliers and used without purification. 2,9(10),16(17),23(24)-tetra(4-tert-butylphenoxy) nickel phthalocyanine (NiPc) was synthesized by phthalonitrile derivative and NiCl₂ according to the literature, as shown in Fig.1[5]. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer. UV-Vis spectra were measured on a Cary 500 UV-VIS-NIR spectrophotometer. MS spectra were obtained on a QUSTAR-TOF mass spectrometer.

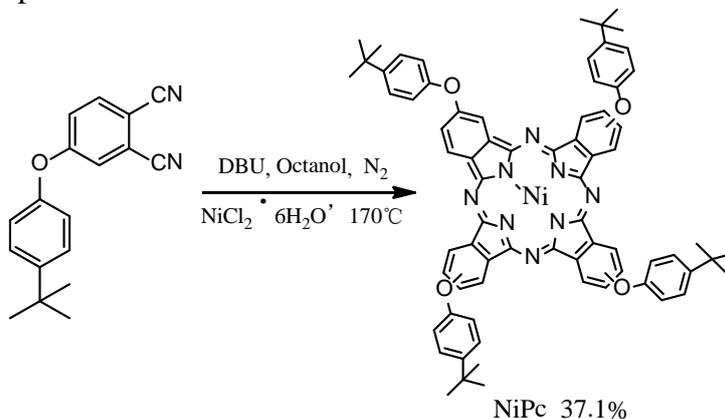


Fig.1 Synthesis and chemical structure of NiPc

2,9(10),16(17),23(24)-tetra(4-tert-butylphenoxy) Nickel Phthalocyanine (NiPc)

Yield: 215 mg (37.1%). UV-Vis (CHCl_3): λ_{max} nm=298, 331, 609, 674; MS (MALDI-TOF, CHCl_3): $m/z=1162.9[\text{M}]$; IR (KBr): $1238\text{ cm}^{-1}(\text{C-O-C})$.

Synthesis of NiPc Nanofibers

The NiPc molecules could self-assemble nanofibers via a simple solvent diffusion method. When methanol was added dropwise into NiPc solution (chloroform, 2.5 mg/mL), then the NiPc molecules self-assembled into nanofibers. Finally the fibers were washed carefully by ethanol to remove chloroform.

Results and Discussion

Morphologies

Fig.2 shows the FESEM micrograph (NiPc-a) and HRTEM micrograph (NiPc-b) of the fibers. Most of the fibers are arranged in nanostructures. The fibers are 100-200 nm in width and 2-10 μm in length. The length-diameter ratio is 50-100. The fibers are fascicular, multilayer deposition is obtained, and the surface is not smooth.

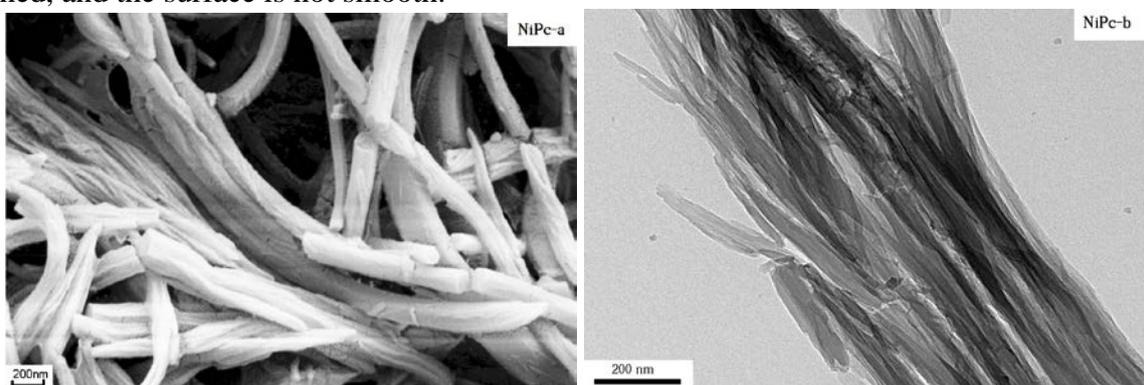


Fig.2 The FESEM micrograph (NiPc-a) and the HRTEM micrograph (NiPc-b)

UV-Vis Spectra

Fig.3 shows the UV-Vis absorption spectra of the NiPc solution (5×10^{-5} mol/L in chloroform) and the fibers. The spectra exhibits the characteristic Q band (550-750 nm) and B band (250-450 nm) absorption of the phthalocyanine. In the region, the two bands are different in shape and shift. Both the two bands of the NiPc fibers are blue shifted. The B band absorption is related to the front orbital of the central metal in the metal-Pc. This means that the surrounding conditions of the central Ni ions are changed in the nanofibers which exclude the formation of Ni-O coordination bond between the neighboring nickel phthalocyanine molecules. The Q band absorption is related to front orbital of the metal-Pc rings, thus this indicates a tight packing between the nickel phthalocyanine molecules by strong p-p interaction in the fibers[7].

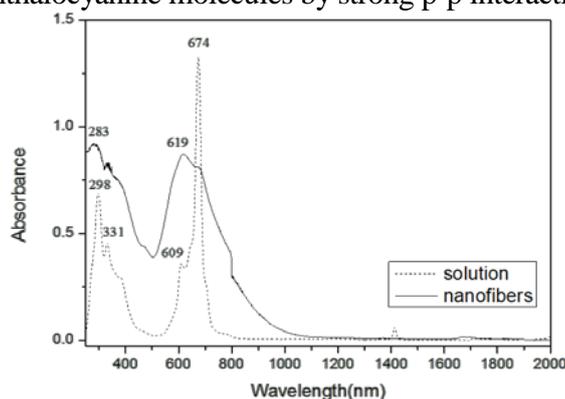


Fig.3 UV-Vis absorption spectra of the NiPc solution and the fibers

Formation Mechanism

The formation of nickel phthalocyanine fibers is embodied in the UV-visible spectra, which could be understood by three interactions of the molecules. First of all, it's the p-p interaction of the nickel phthalocyanine molecules that drives to self-assemble and causes the UV-visible spectra of nickel phthalocyanine nanofibers blue shift compared with the solution. The second interaction is the p-p interaction between the benzene rings around nickel phthalocyanine rings. The third interaction is a coordination of the central Ni ion and the oxygen atom in the aryloxy group of another molecule[7].

Conclusion

In summary, the nickel phthalocyanine nanofibers have been successfully achieved by self-assembling via a simple and reproducible solvent diffusion method. The fibers are arranged in nanostructures with 100-200 nm in width and 2-10 μm in length. The length-diameter ratio is 50-100. Based on the UV-Vis spectra studies, the main interactions to form the nanofibers are considered to be the p-p interaction of nickel phthalocyanine molecules, the Ni-O coordination and the p-p interaction between the benzene rings of the peripheral substitutes, respectively. The NiPc nanofibers have potential application on organic function devices.

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