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Synthesis and Self-Assemble Nanofibers of Tetra Phenoxy Substituted Nickel Phthalocyanine†

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Tetra phenoxy substituted nickel phthalocyanine nanofibers were synthesized in large scale by self-assemble. The FESEM and HRTEM micrographs indicated that the sizes of the fibers are 20-60 nm in width and 0.2-5 μm in length. The formation mechanism of nickel phthalocyanine fibers was discussed and studied by XRD and UV-visible spectra. The nickel phthalocyanine nanofibers have potential application on organic function devices.

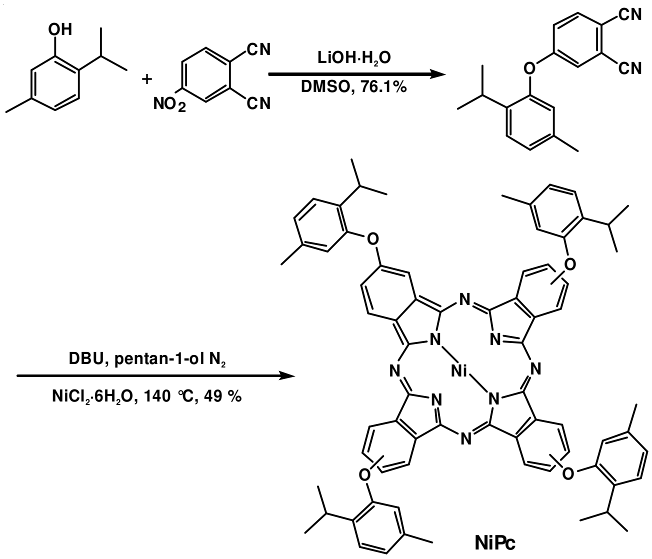
Keywords: Nickel phthalocyanine, Nanofibers, Synthesis, Self-assemble.

INTRODUCTION

Phthalocyanines (Pcs) and their derivatives are excellent organic semiconductors. They have potential applications in chemical sensors[1], nonlinear optics[2], photovoltaic cell[3] and field effect transistors[4]. Recently, one-dimensional nanostructures of phthalocyanines attract great interest, because of the larger surface areas which can cause the enhanced optical and electronic properties. Normally, the one-dimensional nanostructures of phthalocyanines are prepared under ultrahigh vacuum atmosphere, such as organic vapor-phase deposition[5] or electrochemical methods, such as electrocrystallization[6] and AAO template-based electrophoretic deposition[7]. But, the equipments are expensive or the yields are low, which greatly minimize the applications of phthalocyanines. Therefore, simple method with high yields is a new focus on the fabrication of 1D nanostructure phthalocyanines. In this paper, a simple and reproducible solvent diffusion method was applied for the fabrication of nickel phthalocyanine (NiPc) nanofibers in large scale.

EXPERIMENTAL

Synthesis of nickel phthalocyanine: 2,9(10),16(17),23(24)-Tetra(2-isopropyl-5-methylphenoxy) nickel phthalocyanine (NiPc) was provided by the Northeast Normal University. The nickel phthalocyanine was synthesized by phthalonitrile derivative and $NiCl_2$ according to the literature[8], as shown in **Scheme-I**.



Scheme-I: Synthesis and chemical structures of nickel phthalocyanine

Synthesis of nano-fibers of nickel phthalocyanine: The nickel phthalocyanine molecules could self-assemble to nanofibers *via* a simple solvent diffusion method[9]. First, methanol was added dropwise into chloroform solution of nickel phthalocyanine (2.7 mg/mL). Then the nickel phthalocyanine molecules self-aggregated into fibers. The fibers were washed carefully by ethanol to remove chloroform. The morphology of the nickel phthalocyanine fibers were observed by the FESEM (LEO1550) and HRTEM (FEI-Technai20). The molecular packing of the

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aggregated nickel phthalocyanine was demonstrated by the XRD (Bruker D-8) and the UV-VIS (Cary-500).

RESULTS AND DISCUSSION

Morphologies: Fig. 1 shows the typibal FESEM micrograph (nickel phthalocyanine-a) and HRTEM micrograph (nickel phthalocyanine-b) of the nickel phthalocyanine fibers. Most of the fibers are arranged in nanostructures. The fibers are 20-60 nm in width and 0.2-5 μm in length. The fibers are smooth and uniform.

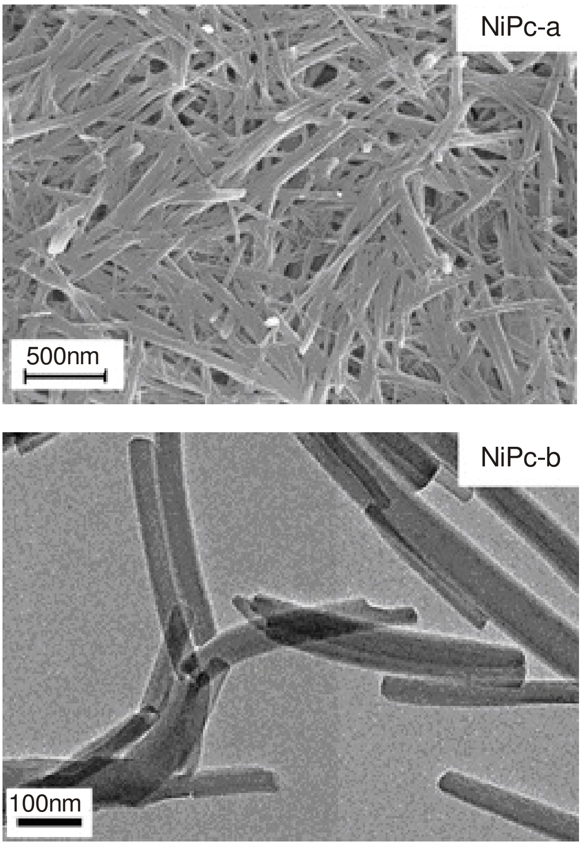

Fig. 1. FESEM micrograph (nickel phthalocyanine-a) and the HRTEM micrograph (nickel phthalocyanine-b)

XRD: Fig. 2 demonstrates the XRD of nickel phthalocyanine nanofibers as deposited on a quartz substrate at room temperature. In the XRD spectrum, two clear diffraction peaks are found at 4.75 and 25.79°, whose plane separations are approximately 18.6 and 3.5 Å, respectively. The two peaks of the fibers show that the nickel phthalocyanine molecules have been arranged in highly long-range ordered lamellar structures and the two separations are the interlayer spacing of the nanofibers[10].

UV-visible spectra: Fig. 3 shows the UV-visible absorption spectra of the nickel phthalocyanine solution (5×10^{-5} mol/L in chloroform) and the fibers. Their UV-visible absorption spectra exhibit the characteristic B band (250-450 nm) and Q band (550-750 nm) absorption of the phthalocyanine. In the region, the two bands are different in shape and shift. When the nickel phthalocyanine molecules self-aggregated, the B band and Q band 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 π-π interaction in the fibers[11].

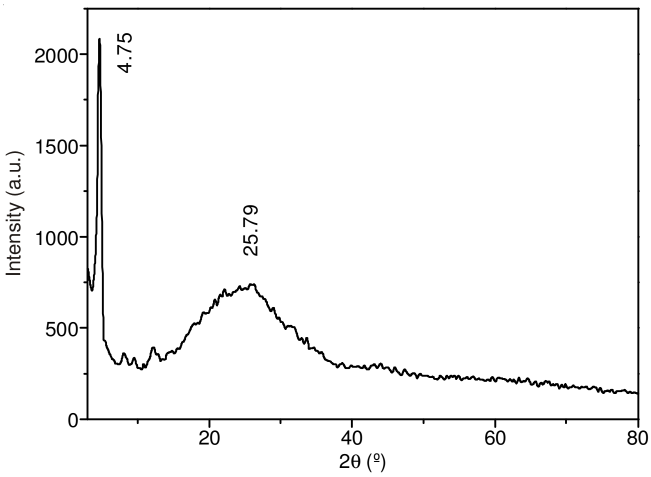

Fig. 2. XRD pattern the nickel phthalocyanine fibers

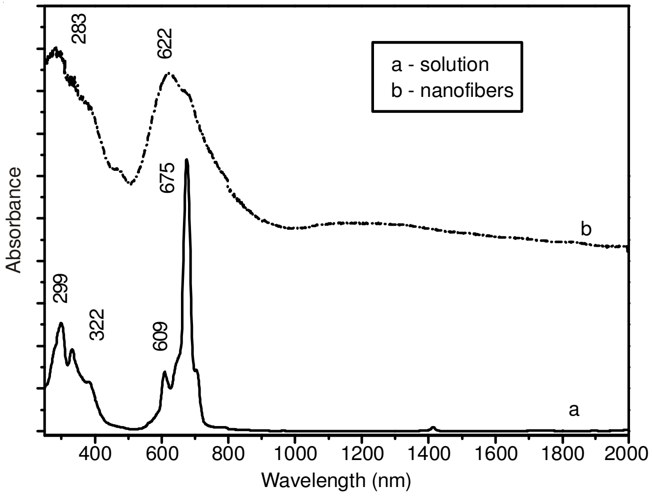

Fig. 3. UV-VIS absorption spectura of the nickel phthalocyanine solurion (a) and the fibers (b)

Formation mechanism: The formation of nickel phthalocyanine fibers is embodied in the XRD and UV-visible spectra, which could be understood by three interactions of the molecules. First of all, it's the π-π 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 π-π 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[11].

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 20-60 nm in width and 0.2-5 μm in length. Based on the XRD and UV-visible studies, the main interactions to form the nanofibers are considered to be the π-π interaction of nickel phthalocyanine molecules, the Ni-O coordination and the π-π interaction between the benzene rings of the peripheral substitutes, respectively. The nickel phthalocyanine nanofibers have potential application on organic function devices.

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