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 sensors¹, nonlinear optics², photovoltaic cell³ and field effect transistors⁴. 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 deposition⁵ or electrochemical methods, such as electrocrystallization⁶ and AAO template-based electrophoretic deposition⁷. 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 literature⁸, 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 method⁹. 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 typical 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 nanofibers¹⁰.

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.

Fig. 2. XRD pattern the nickel phthalocyanine fibers

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

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 fibers¹¹.

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 molecule¹¹.

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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