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RESEARCH ARTICLE

Facile solvothermal synthesis and photoconductivity of one-dimensional organic Cd(II)-Schiff-base nanoribbons

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Abstract One-dimensional (1D) organic nanoribbons built on N-*p*-nitrophenylsalicylaldimine cadmium complex were synthesized via a facile solvothermal route. Scanning electron microscope images revealed that the as-synthesized products were ribbon like with widths of 500 nm, thicknesses of about 50 nm, and lengthes up to several hundred micrometers. Fourier transform infrared spectrum was employed to characterize the structure. The conductivity of a bundle of nanoribbons was also measured, which showed that Schiff base cadmium nanoribbons had good photoconductive property. This work might enrich organic photoconductive materials and be applicable in nano photoswitch devices in the future.

Keywords Schiff base cadmium complex, organic nanoribbons, photoconductivity

1 Introduction

During the past decade, one-dimensional (1D) nanostructured materials, such as nanorods, nanowires, nanotubes, nanobelts and nanoribbons, have attracted much attention in the emerging fields of nanoscience and nanotechnology because of their unique physical and chemical properties, and their promising applications in electronic and optoelectronic nanodevices [1–4].

Up to now, most reported 1D nanostructures are based on inorganic materials. In recent years, 1D organic nanomaterials have attracted more and more interest [5–8], because they exhibit many advantages over the inorganic counterparts, such as diversity for property optimization, tailorability, multifunctionality, high flexibility, low cost of materials fabrication, ease for large area processing, compatibility with flexible and lightweight plastic substrates. Thus the synthesis and functionalization of 1D organic nanomaterials has become one of the most highly energized research areas.

The assembly of organic molecules to nanostructures with defined morphologies usually needs driving forces from the molecules themselves including hydrogen bond, π-π stacking, Van der Waals contact, etc. Sometimes the self-assembly process also requires induction from the surroundings like the interactions between the organic molecules and the solvents or auxiliaries [9]. There have been a few successful preparation methods available for 1D organic nanomaterials, such as self-assembly in solution [10,11], chemical vapor deposition [12], re-precipitation (or/and solvent exchange) [13] and template-induced self-assembly [14,15]. However, simple, rapid, template-free, inexpensive, environmentally friendly, and effective synthesis of 1D organic nanostructures on a large scale still remains a challenge for researchers.

To date, most organic molecules utilized as building blocks for functional 1D organic nanostructure were focused on large rigid conjugate molecules, donor-acceptor molecules, charge transfer molecules and metal organic complexes. Since the efficient low-voltage-driven organic light-emitting diodes based on tris(8-hydroxyquinoline) aluminium were first reported in 1987 [16], organometallic complexes have attracted a lot of attentions in organic photoluminescent material regions for their particular merits of both high melting point and good stability [17].

Schiff base metal complexes are promising materials for photoelectronic applications, and the easiness of synthesis allows structural designability for optimization of material properties [18–22]. In this report, N-*p*-nitrophenylsalicylaldimine (Schiff base) Cd(II) nanoribbons were synthesized via a facile solvothermal route without the use of template, catalysts or the contamination of surfacts. The obtained 1D nanoribbons' photoconductive property was measured. The results showed good photoconductive property and good response to light on/off, which might

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find potential application in the fabrication of nano-photosensor or nano-photoswitchs in the future.

2 Experiment

2.1 Materials

Salicylaldehyde was distilled under reduced pressure and *p*-nitrophenylamine was recrystallized from ethanol before used. Cadmium chloride ($CdCl_2$), methanol and ethanol were commercially available and used without further treatment.

2.2 Preparation of nanoribbons of N-*p*-nitrophenylsalicylaldimine cadmium

The Schiff base ligand N-*p*-nitrophenylsalicylaldimine was synthesized according to the correlative literature [23]. The obtained crude product was recrystallized from ethanol before used. In a typical synthesis of Schiff base cadmium complexes nanoribbons, 0.25 mmol $CdCl_2$ and 0.5 mmol N-*p*-nitrophenylsalicylaldimine were dissolved into 40 mL methanol under stirring, which was then transferred into a stainless 50 mL Teflon-lined autoclave, heated at 160°C for 8 h and cooled to room temperature. Then isovolumetric ultrapure water was added dropwise into the resulting solution. After 6 h, the resulting yellowish flocculent suspension was separated centrifugally, washed with ultrapure water for several times, and then dried under vacuum at 60°C for 10 h.

2.3 Characterization

The powder X-ray diffraction (XRD) pattern was recorded on X'Pert-Pro Materials Research Diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm); a scanning rate of $0.0167° \cdot s^{-1}$ was applied to record the pattern in the 2θ range of 10°–35°. The size and morphology of samples were studied by field emission scanning electron microscopy (FESEM, FEI Co., model Quanta-200). Fourier transform infrared (FTIR) spectrum was obtained with KBr pellets for solids on a ProStar LC240 spectrometer. The photoconductivity measurements were tracked with a CHI 620B electrochemical workstation. The low magnification image was captured by an Olympus optical microscope.

3 Results and discussion

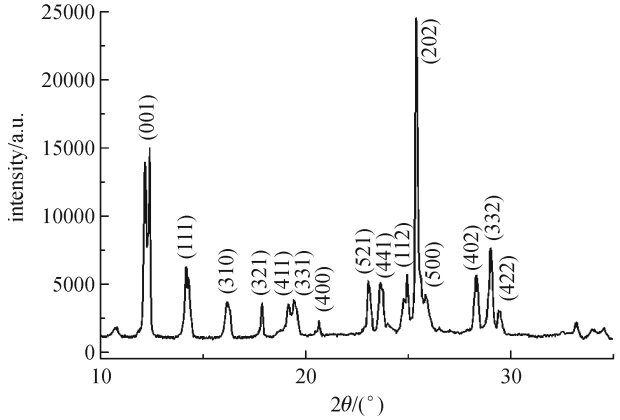


Fig. 1 XRD pattern of products

Figure 1 shows the XRD pattern of the obtained Schiff base cadmium nanoribbons. The peaks at 2θ = 12.24°, 14.18°, 16.16°, 17.88°, 19.18°, 19.50°, 20.69°, 22.96°, 23.72°, 24.89°, 25.34°, 25.87°, 28.35°, 29.04°, and 29.48° show the as-prepared samples are crystalline in nature. This pattern was indexed as tetragonal phase with crystal constants $a = 20.8041 \pm 1.028$ nm, and $c = 7.8036 \pm 0.428$ nm, using the Hesse-Lipson method [24,25].

The FTIR spectrum is recorded to reveal the composition of products as shown in Fig. 2. The intense infrared stretch at 1632 cm^{-1} is assigned typically to the imine C = N bond. The aromatic vibrations peaks are found at (C = C, 1602, 1471 cm^{-1}; C–H, 754 cm^{-1}). The ν(C–O) phenolic band in the complexes was shifted to lower frequency in the 1185 cm^{-1} range indicating the coordination of the phenolic oxygen atom with the metal ion. The peaks at 536 and 420 cm^{-1} were respectively attributed to Cd–O and Cd–N stretching vibrations. The symmetry stretching vibration peak of $-NO_2$ is at 1300 cm^{-1}. These vibrational modes are in good agreement with the previous reports [26,27], which further supports that the as-prepared products are N-*p*-nitrophenylsalicylaldiminato cadmium complexes.

The scanning electron microscopy (SEM) images in Fig. 3 reveal the morphology and size of the as-prepared

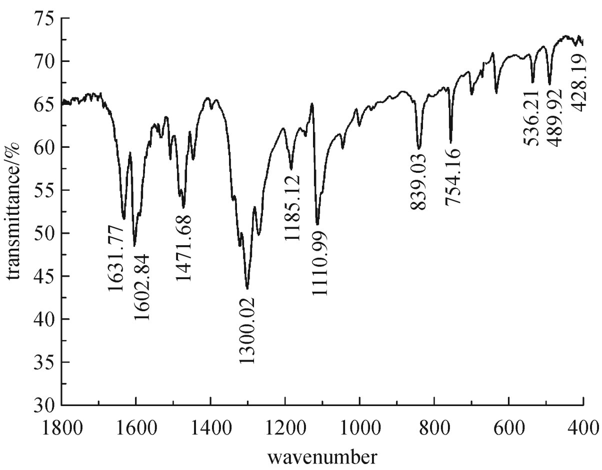
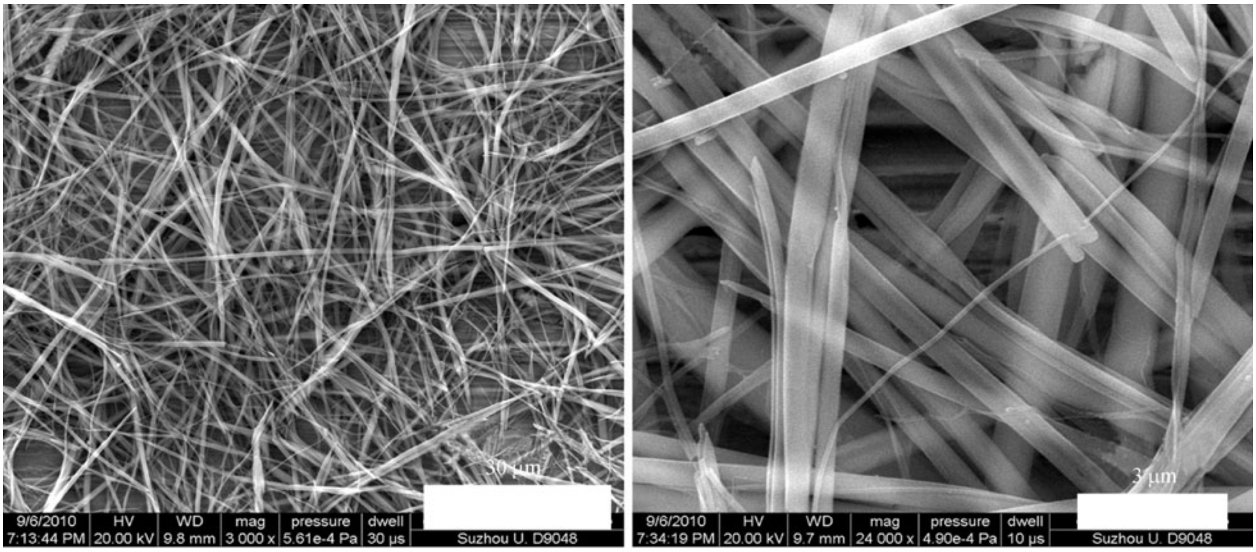


Fig. 2 FTIR spectrum of products



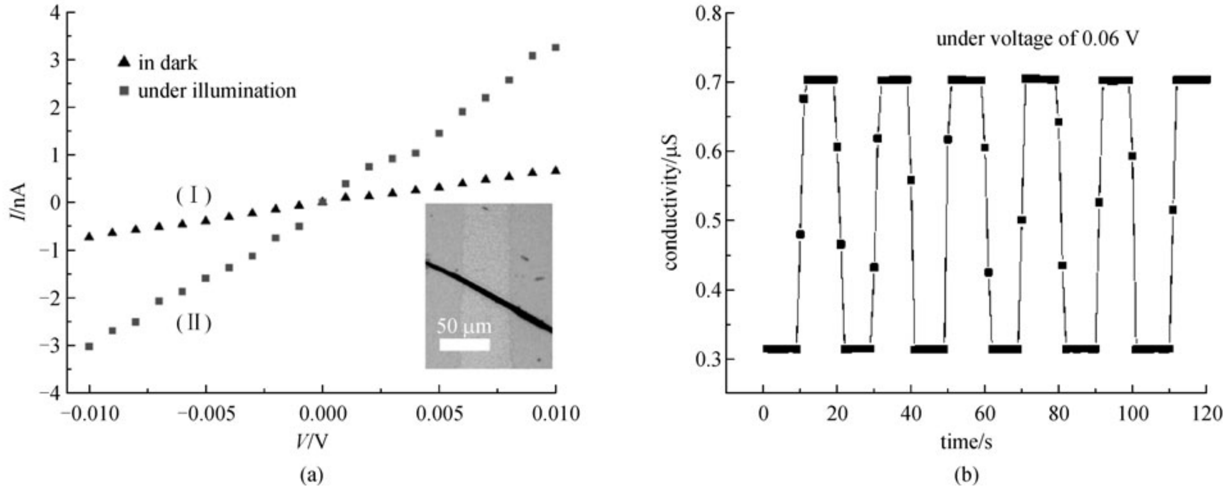
(a) (b)

Fig. 3 SEM images of products. (a) Low magnification; (b) high magnification

products. Figure 3(a) displays a panoramic SEM image which shows that the sample consists of highly flexible nanoribbons with lengths of several hundred micrometers. The high magnification SEM image shown in Fig. 3(b) further reveals the ribbons with an average width of 500 nm and a thickness of 50 nm.

The nanoribbons were cast across the prefabricated electrodes to form a typical bottom-contact device. The patterned indium tin oxide (ITO) coated glass with the electrode gap of 50 µm was employed as the substrate. To increase injection of the device, Au gap electrodes were fabricated on the substrate by thermal evaporation with a micrometer-sized Au wire as the mask, by slightly moving the Au-wire mask, Au-Au gap electrodes were deposited. Then the conductivity was measured in a dark box or under illumination with an incandescence lamp (12 V, 10 W). In order to decrease thermal effect, the power of the incandescence lamp was only 10 W and the distance of the device-to-light source was 10 cm. Figure 4(a) shows the $I-V$ curves measured in the dark or under illumination. The approximately linear shape of the curves reveals a good ohmic contact of the bundle of nanoribbons with the Au electrodes. It is clearly observed that the conductivity of the Schiff base cadmium nanoribbons increases evidently under illumination with an incandescence lamp.

Figure 4(b) shows the photoconductive characteristics of



(a) (b)

Fig. 4 Photoresponse of a bundle of nanoribbons. (a) $I-V$ curves of the products measured (I) in a dark box or (II) under illumination by using incandescence lamp (12 V, 10 W), and image of products between two Au electrodes from optical microscope (inset); (b) photoconductive characteristics of device under light switched on/off. (A voltage of 0.06 V was applied across the Au-Au electrodes, and the current was recorded during the light alternatively on and off at 10 s intervals) the device during light switched on/off. A voltage of 0.06 V was applied across the Au-Au electrodes and the current was recorded during the light alternatively on and off at 10 s intervals. Obviously, the current through the Schiff base cadmium nanoribbons promptly jumps up and down according to the illumination on and off, which shows a photosensitivity. This can be explained as follows: Under illumination, the energy from the light excites the electrons in the semiconductor nanoribbons jumping from the valence band into the conduction band, leaving holes in valence band, increasing the charge carrier concentration via direct electron-hole pair creation and thus enhancing the current of the nanoribbons.

4 Conclusions

In summary, the Schiff base cadmium nanoribbons were successfully synthesized in large scale via a facile solvothermal approach. The nanoribbons exhibited fast and reversible photoswitching response under on/off light exposure conditions. This conclusion was interesting and might find potential application in light-controlled devices in the future.

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