

Organic Thin-Film Transistors based on Alkoxy naphthalene End-capped Divinylbenzene

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Abstract

The new organic semiconductor, which is composed of a divinylbenzene core unit and alkoxy naphthalene on both sides, 1,4-bis-2-(6-hexyloxy)naphthalen-2-yl-vinylbenzene, was synthesized via Wittig reaction. The obtained oligomer was characterized via FT-IR, mass and elemental analysis, UV-visible spectroscopy, cyclovoltammetry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The vacuum-evaporated film was characterized via X-ray diffraction and atomic-force microscopy (AFM). It formed a highly ordered polycrystalline vacuum-evaporated film and exhibited a good field-effect performance, with a hole mobility of $0.015 \text{ cm}^2/\text{V}\cdot\text{s}$, an on/off ratio of 1.18×10^5 , and a subthreshold slope of 0.69 V when it was deposited at $T_s=90^\circ\text{C}$ on HMDS-treated SiO_2 .

Keywords: Semiconductor, alkoxy naphthalene end group, organic thin-film transistor

1. Introduction

Organic thin-film transistors (OTFTs) are of great interest because of their potential application in plastic electronics [1-6]. Among the materials that have been investigated over the past 20 years for the active semiconductor layer in OTFTs, it has been noted that the solution-processed polymer films [7-12] and the vacuum-deposited films are low-molecular-weight species [13-17]. Their intrinsic charge carrier mobility depends on the degree of molecular ordering and on the extent of the π π stacking. Oligomers are of particular interest because they generally

possess good molecular ordering properties when processed using vacuum-sublimation techniques. Moreover, they have the capability to be soluble in organic solvents with the introduction of proper chemical substituents. A large number of oligomers have demonstrated interesting performances in OTFTs, such as fluorene, acenes, and carbazole derivatives [18-21]. The synthesis of new π -conjugated units that could be incorporated in oligomeric structures is desirable for the significant optimization of the OTFT performance and for a better understanding of the structure-property relationship [22-24].

For low-cost manufacturing, the processing should be carried out under ambient conditions, which requires the materials to be stable in the face of ambient environmental effects [25]. Recently, several groups reported significant enhancements of the stability of OTFTs under ambient conditions with semiconducting small molecules [26-27] and oligomers [28-31].

These authors recently reported that alkoxy naphthalene end-capped oligomers showed high mobility because the introduced alkoxy groups tuned the electronic properties of small fused acenes with the ability to donate electrons, and increased the stacking properties via self-assembly [23].

In the present paper, alkoxy naphthalene end-capped divinylbenzene was synthesized and characterized to create high-performance semiconducting materials that can be

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synthesized and mass-produced easily from commercially available starting materials.

2. Experiment

2.1 Materials

2-naphthaldehyde, triphenylphosphine, α,α' -dibromo-p-xylene, N,N'-dimethylformamide (DMF), and toluene were purchased from Aldrich.

2.2 Synthesis

2.2.1 Synthesis of 2-bromo-6-hexyloxy-naphthalene

6-Bromo-2-naphthol (10g, 44.8mmol), 1-bromohexane (7.77g, 47.1mmol), KOH (3.27g, 58.3mmol), and NaI (0.67g, 4.5mmol) were dissolved in ethanol (100mL). The mixture was heated to 80°C for 24 h under a nitrogen atmosphere. After the reaction, the ethanol was removed via rotary evaporation. The reaction was then poured into water and was extracted with ethyl acetate. After the extract was dried over $MgSO_4$, the organic solvent was removed via rotary evaporation. The resulting crude product was purified via chromatography with hexane. The product was recrystallized from methanol. Yield: 7.46g (40%) 1H -NMR (300 MHz, $CDCl_3$, ppm) δ =7.92 (d, 1H), 7.65~7.66 (d, 1H), 7.57~7.61 (d, 1H), 7.48~7.51 (dd, 1H), 7.16~7.18 (dd, 1H), 7.11 (d, 1H), 4.05~4.07 (t, 2H), 1.82~1.85 (m, 2H), 1.48~1.53 (m, 2H), 1.29~1.38 (m, 4H), and 0.87~0.92 (t, 3H).

2.2.2 Synthesis of 6-hexyloxy-2-naphthaldehyde

n-BuLi (7.8 ml, 19.5 mmol) was added dropwise to a cooled (-78°C) mixture of 2-bromo-6-hexyloxy-naphthalene (5g, 16.3mmol) in an anhydrous THF (75ml) solution, under a nitrogen atmosphere. After stirring for 1 h, the mixture was cooled to -40°C, and 1-formylpiperidine (2.2g, 19.5mmol) was added to it. The mixture was stirred for 3 h at room temperature and was then poured into a 20% NH_4Cl solution and extracted with diethyl ether. The organic layer was dried over $MgSO_4$. The solvent was removed via rotary evaporation. The product was recrystallized from hexane. Yield: 2.9g (68.4%) 1H -NMR (300 MHz, $CDCl_3$, ppm) δ =10.11 (s, 1H), 8.27 (d, 1H), 7.95~7.89 (t, 2H), 7.82~7.79 (d, 1H), 7.27~7.23 (dd, 2H), 7.19~7.18 (d, 1H), 4.15~4.10 (t, 2H), 1.91~1.84 (m, 2H), 1.53~1.50 (m, 2H), 1.29 (m, 16H), 0.92~0.88 (t, 3H); FT-IR(KBr) (cm^{-1}): 2917 (aromatic C-H), 2846 (aldehyde C-H), 1695 (C=O),

1625 (aromatic C=C), 1476 (CH_2), and 1384 (CH_3).

2.2.3 Synthesis of phenylenebis(methylene)bis(triphenylphosphonium) bromide

1,4-Bisbromomethylbenzene (10g, 75.8mmol) and triphenylphosphine were added to DMF (30mL). The mixture was heated to 160°C for 24 h, with oil bath. After cooling to room temperature, DMF (50mL) was added to the mixture. The solid product was filtered and washed with DMF: ether (1:10). Yield: 15.53g (52%) 1H -NMR (300 MHz, $CDCl_3$, ppm) δ =7.80~7.77 (t, 6H), 7.72~7.23 (m, 24H), 6.92 (s, 4H), and 1.67 (s, 4H).

2.2.4 Synthesis of 1,4-bis-2-(6-hexyloxy)naphthalen-2-ylvinylbenzene (BHNVB)

6-hexyloxy-2-naphthaldehyde (2g, 7.8 mmol), phosphonium salt (2.05g, 2.6mmol), and NaH (0.62g, 26mmol) were dissolved in toluene (50mL). The mixture was stirred for 4 h at 120°C. After cooling the mixture to room temperature, 2-naphthaldehyde (2.5g, 16mmol) was added and was heated to 120°C again for 12 h. The mixture was poured into 2N-HCl (200mL) for 1 h. The precipitate was filtered and washed successively with methylenechloride, H_2O , and ethanol. Yield: 0.8g (52.8%) EI-MS: m/z =582 (M^+); FT-IR (KBr) (cm^{-1}): 3051~3022 (aromatic, vinyl C-H), 1617 (vinyl C=C), 1595~1510 (aromatic C=C), 1417 (CH_2), 1361 (CH_3), 955 (out-of-plane bending=C-H). Anal. calcd. for $C_{42}H_{46}O_2$: C, 86.55%; H, 7.96%; O, 5.49. Found: C, 85.45%; H, 9.63%; and O, 4.92.

2.3 Measurements

The FT-IR spectra, GC mass spectrometry, and 1H -NMR spectra were recorded on a Bruker IFS66 spectrometer, a JEOL GC Mate2, and a Bruker Avance-300 MHz NMR spectrometer, respectively. UV-visible absorption and photoluminescence (PL) spectra were obtained using a Perkin Elmer LAMBDA-900 UV-visible spectrometer and a Perkin Elmer LS50B luminescence spectrophotometer, respectively. The cyclic voltammograms were recorded on an Epsilon E3 at room temperature, in a 0.1M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile, under nitrogen gas protection, at a scan rate of 50 mV/s. A Pt wire was used as a counterelectrode, and an Ag/AgNO₃ electrode was used as a reference electrode.

Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on a TA Instruments 2050 thermogravimetric analyzer. The sample was heated at a

10 °C/min heating rate from 30 to 700 °C. Differential scanning calorimetry (DSC) was conducted under a nitrogen atmosphere on a TA Instruments 2100 differential scanning calorimeter. The sample was heated at 10 °C/min from 30 to 400 °C.

The film microstructure and morphology of a vapor-deposited thin film of BNDV grown on SiO₂/Si was investigated via X-ray diffraction (XRD) and atomic-force microscopy (AFM). The X-ray diffraction spectra and AFM morphology of a BNDV-based thin-film vacuum deposited at 90 °C were investigated.

For the fabrication of the OTFTs, a highly doped p-Si wafer with a 300-nm thermally grown oxide layer was used as a substrate. The wafer served as a gate electrode, and the oxide layer acted as a gate insulator. Prior to the surface treatment of the silicon oxide layer, the wafer was cleaned with DI water, acetone, and IPA (isopropyl alcohol). As an organic interlayer material between the organic active material and the dielectric layer, 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Aldrich) was applied to the SiO₂, using a dipping method, to improve the field-effect mobility of the OTFTs by enhancing the quality of the organic active material/dielectric interface. After HMDS treatment, an organic semiconductor was deposited onto the substrates at a thickness of 60nm, under a pressure of 3×10^{-6} Torr and at a rate 6 Å/s. The devices were completed by evaporating gold through a shadow mask to define the source and grain contacts. The channel length and width were fixed at 50 and 100 nm, respectively.

3. Results and Discussion

BHNVB was synthesized as shown in Fig. 1. It was easily synthesized through alkylation, formylation, and Wittig reaction, and was purified via soxhlet extraction, using toluene. Further purification was carried out through sublimation under a vacuum. The obtained BHNVB was verified via IR, mass spectrometry, and elemental analysis. The thermal properties of the synthesized BHNVB were evaluated via TGA and DSC under a nitrogen atmosphere. In the TGA, the obtained oligomer showed high thermal stability, but 5% weight loss was observed at 410 °C. In the DSC, BHNVB displayed liquid crystalline behavior. In the heating trace, three endothermic peaks at 201, 283, and 296 °C were observed. On the other hand, in the cooling trace, only two exothermic peaks at 286 and 291 °C were observed

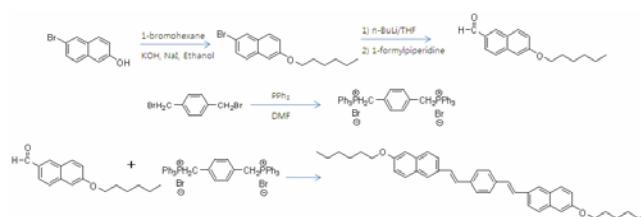


Fig. 1. Synthetic route for the compound BHNVB

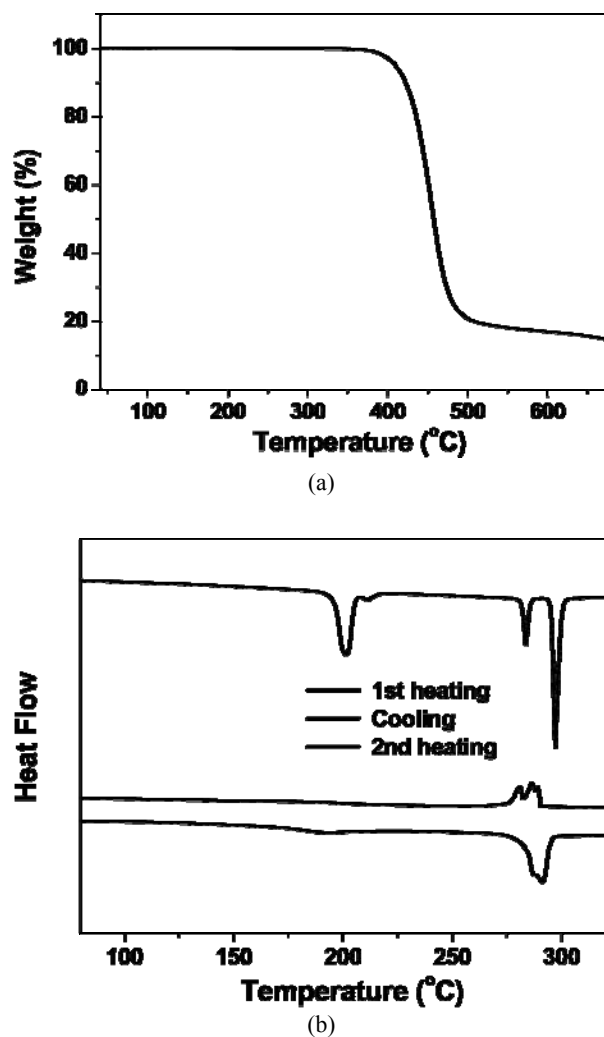


Fig. 2. (a) TGA and (b) DSC of the compound

(Fig. 2). It is suggested that the transition at 201 and 283 °C may have been side chain melting and liquid crystal transition, respectively, during the heating trace. The thermal responses of BHNVB reveal that it is crystalline. This suggests that well-ordered thin films can be formed through the thermal evaporation processes.

The optical properties of BHNVB were investigated using UV-vis and photoluminescence (PL) spectroscopies

(Fig. 3). The new BHNVB exhibited absorption maxima at 370 nm in a dilute chlorobenzene solution, and at 350, 375, and 420 nm in film, respectively. The main absorption peak of the thin film was blue-shifted by 20 nm, and other well-defined bands appeared at 375 and 420 nm compared with the solution. The phenomenon may be explained by H-aggregates or J-aggregates, which are usually related to the excitonic coupling between the adjacent molecules in a closely packed structure [23]. In the PL spectra, the thin film of BHNVB showed a red shift relative to the solution spectrum. This result may have also originated from the aggregation or excimer formation due to $\pi \rightarrow \pi^*$ stacking, or from the intermolecular interaction caused by the planar structure. The optical bandgap can be estimated from the absorption edge of the thin-film spectrum: It was larger than 2.88 eV, which shows that BHNVB is not easily oxidized and has better stability in air. In the cyclic voltammetry measurement of BHNVB in a 0.1M solution of tetrabutylammonium perchlorate (BuNClO₄) in acetonitrile, under nitrogen gas protection, at a scan rate of 50 mV/s (Fig. 4), a Pt wire was used as a counterelectrode, and an Ag/AgNO₃ electrode was used as a reference electrode. A 1.35 eV oxidation peak was observed, corresponding to an estimated highest-occupied molecular orbital (HOMO) level of -5.79 eV, which is very low compared with the reported p-type semiconductors, indicating BHNVB's higher oxidative stability.

OTFT was fabricated using BHNVB thin film as the active layer, and its electrical property was characterized. The mobility (μ_{FET}) and threshold voltage (V_{TH}) of the OTFTs were

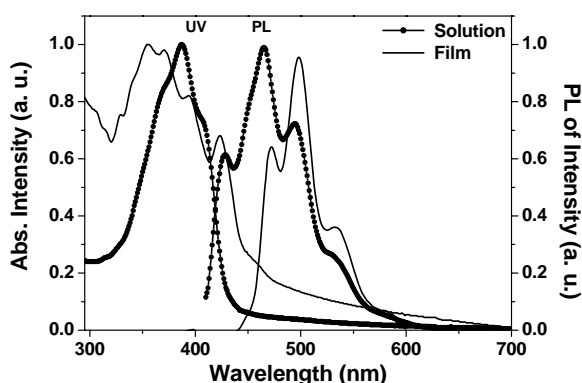


Fig. 3. Optical absorption (UV) and emission (PL) spectra of the compound in chlorobenzene (solution) and in the solid state (film).

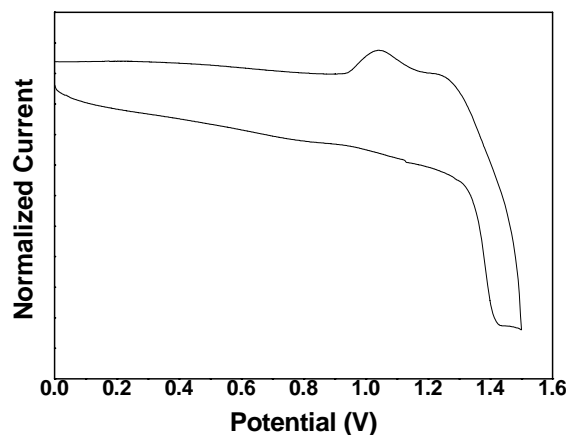


Fig. 4. Cyclic voltammogram of the compound.

obtained from eq. (1), for the saturation regimes.

$$I_D^{sat} = (W/2L)\mu_{FET}C_i(V_G - V_{TH})^2, \quad (1)$$

where L is the channel length, W the channel width, and C_i the capacitance per unit area of the gate dielectric layer ($C_i = 10$ nF/cm² for 300-nm-thick SiO₂). The output characteristics showed very good saturation behavior and clear saturation currents that are quadratic to the gate bias.

The BHNVB thin-film transistor was found to exhibit typical p-channel FET characteristics. Fig. 5a shows the drain current (I_D) vs. drain-source voltage (V_{DS}) characteristics of the fabricated device at a substrate temperature (T_{sub}) of 90°C. Clearly, a significant change in the drain current can be observed for the devices when a gate voltage (V_G) is applied. Fig. 5b shows a plot of the $I_D^{1/2}$ vs. V_G and I_D vs. V_G characteristics of the devices. The mobility in the saturation regime was determined using eq. (27). From the equation, a mobility of 0.015 cm²/V·s, an on/off ratio of 1.18×10^5 , and a subthreshold slope of 0.69 V for the compound with a treated gate dielectric were obtained.

To understand the performance of OTFT using BHNVB as a semiconductor, the film microstructure and morphology of a vapor-deposited ($T_{sub} = 90^\circ\text{C}$) thin film of BHNVB grown on SiO₂/Si were investigated via XRD and AFM. In Fig. 6, the sharp and strong reflections up to the second order indicate a high degree of lamellar ordering and crystallinity. The d-spacing obtained from the first reflection peak ($2\theta = 2.3$) was 38.72 Å. As the molecular length of BHNVB obtained from the theoretical calculations via AM1 geometry optimization was 37.8 Å, the molecule of BHNVB is considered perpendicular to the sub-

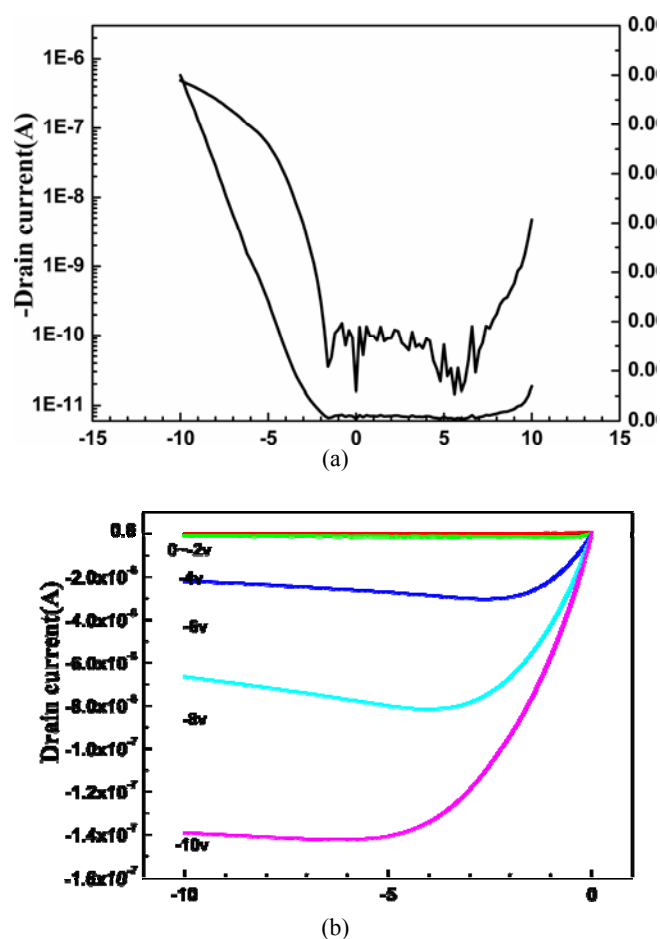


Fig. 5. (a) Plot of the drain current (I_D) vs. drain-source voltage (V_{DS}) characteristics of the compound TFT at different gate voltages (V_G). (b) Plot of the I_D vs. V_G and $I_D^{1/2}$ vs. V_G characteristics of a TFT prepared using a compound as the semiconductor material at a V_{DS} of -10 V.

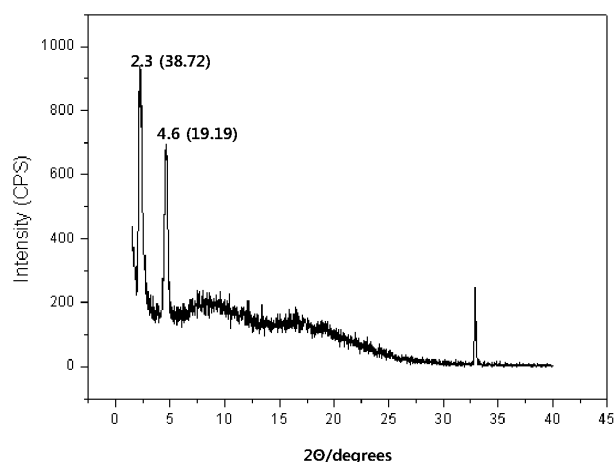


Fig. 6. XRD pattern of the compound.

strate, which is an ideal molecular arrangement for charge transport. The AFM image of BHNVB showed that the surface morphology was smooth and that the substrate was

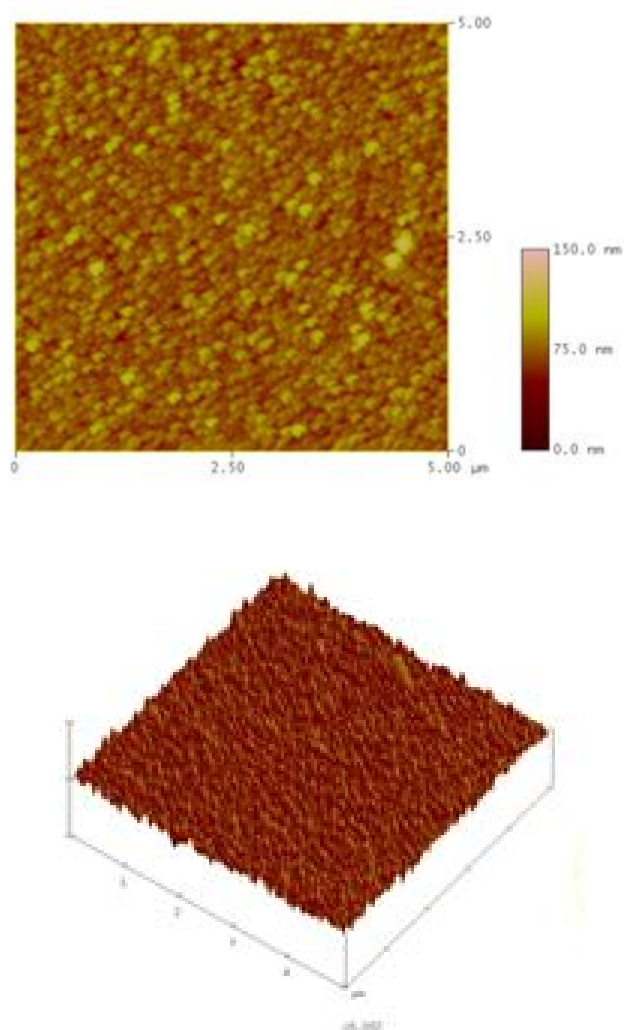


Fig. 7. Topographic AFM images of the compound film grown.

fully covered with the material (Fig. 7). The grain size, however, was slightly small, although the mobility was $0.015 \text{ cm}^2/\text{V}\cdot\text{s}$. Based on the results that were obtained, it is suggested that the mobility can be improved by optimizing the device.

4. Conclusion

OTFT was fabricated based on a new synthesized organic semiconductor. The oligomer was found to have good oxidation stability due to its high oxidation potential and good thermal stability. The oligomer also exhibited good field-effect performance, with its mobility as high as $0.015 \text{ cm}^2/\text{V}\cdot\text{s}$. The XRD pattern reveals that the film, grown via vacuum deposition, is highly crystalline, although the AFM

revealed that its grain size was slightly small.

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