Our controlled growth of Ni/ZnO nanorod heterostructures by MOVPE opens up significant opportunities for the fabrication of spintronic device structures on a single nanorod. The simple yet accurate thickness control allows tunable magnetic properties in nanosized magnetic layers on individual nanorods due to a crossover from superparamagnetism to ferromagnetism. These magnetic building blocks may be used as components for nanoscale spin-valve transistors, spin light-emitting diodes, and nonvolatile storage and logic devices. More generally, we believe that the simple “bottom-up” heterostructural approach might readily be expanded to create many other magnetic-semiconductor nanorod heterostructures.

Experimental

For the fabrication of magnetic-metal/ZnO nanorod heterostructures, ZnO nanorods were prepared on Al₂O₃(0001) substrates using a low-pressure MOVPE system [11]. No metal impurity catalyst was deposited on the substrates. For ZnO nanorod growth, diethylzinc, and oxygen were employed as reactants with argon as the carrier gas. For magnetic metal evaporation on the ZnO nanorods, Ni was evaporated on vertically aligned ZnO nanorods at room temperature using an electron-gun evaporation system with a base pressure $7-8 \times 10^{-8}$ torr [12]. During metal evaporation, metal flux was incident on the top surfaces of the ZnO nanorods. The deposition rate was monitored using a thickness monitor and controlled to be 0.2 Å s^{-1} . Metal layer thickness was in the range of 50–400 Å, as determined by TEM [12].

The crystal orientation of nanorod heterostructures was characterized using SR-XRD. The SR-XRD measurements of Ni/ZnO nanorod heterostructures were performed using a four-circle diffractometer of the 3C2 synchrotron X-ray diffraction beam line at the Pohang Accelerator Laboratory [17]. The beam size at the focal point was typically less than 1 mm^2 and a fixed-exit double-crystal monochromator was used. The diffracted beam intensity was measured using a scintillation detector. High X-ray flux yielded a significant signal-to-noise ratio to measure very thin Ni layers on the nanorods. The crystal orientation of Ni layers was confirmed using TEM. Details in the SEM and TEM measurements have been reported elsewhere [11,12].

The topography and magnetic images of Ni/ZnO nanorods were measured using a MFM that was modified from a commercial AFM. The MFM was operated in amplitude detection mode. MFM tips are AFM cantilevers coated with 30 nm of cobalt and have a resonance frequency of 18 kHz. Before measuring the magnetic properties of samples, they were saturated in a fixed direction along their easy axis under the applied magnetic field of 3000 Oe, after which an MFM image was taken to determine its magnetization. The AFM and MFM images were measured simultaneously on the same region.

Further magnetic properties of Ni/ZnO nanorod heterostructures were measured using both SQUID and a high-sensitivity AGM at room temperature in a field of up to 60 kOe. For the data presented here, the diamagnetic background from Al₂O₃ (0001) substrate was subtracted. Both field- and temperature-dependent magnetization curves were measured at the applied magnetic field parallel to the surface of the substrate.

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Organic Semiconductor Nanowires for Field Emission**

By Jiann-Jong Chiu, Chi-Chung Kei, Tsong-P. Perng, and Way-Seen Wang*

Nanotechnology has become an important and popular research subject recently. The quantum size effect of nanostructured materials, such as nanowires and nanoparticles, may induce new optical, electronic, magnetic, and mechanical properties compared with those of conventional materials.^[1] Nanowires or nanoparticles for optoelectronic devices have been investigated for many years,^[2,3] and other special structures such as nanobelts and nanosprings have also been synthesized.^[4,5] However, most of the reported structures are comprised of inorganic materials. Since the strong electroluminescence of organic light emitting diodes (OLEDs) with a low driving voltage was reported by Tang and VanSlyke in 1987,^[6] tris(8-hydroxyquinoline)aluminum (AlQ₃) has become one of the most attractive electron transport and emitting materials for OLED devices. Much attention is therefore turning to nanometer-sized organic materials, due to many unique properties such as flexibility, high photoconductivity, and nonlinear optical effects that may offer novel applications in nano-optoelectronic devices.^[7–9] The field emission properties of nanowires and nanotubes have been observed for many years,^[10] however, no organic nanostructure for field emission has been reported yet. In this work, AlQ₃ nanowires were first synthesized for field emission, and a performance comparable to the well-known carbon nanotubes has been obtained.

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AlQ₃ nanowires and nanobelts were prepared by vapor condensation.^[11] AlQ₃ powder was placed in a graphite boat, and an indium tin oxide (ITO)-coated glass substrate was placed under a liquid nitrogen cold trap. Some AlQ₃ nanobelts were formed on the substrate first, and a thick layer of nanowires was then grown above the nanobelts (Fig. 1a). The morphology of the AlQ₃ nanostructures was examined by a field emission gun scanning electron microscopy (FEGSEM). The nanowires, grown in random directions, are in a dendritic configuration (Fig. 1b). The diameters of the nanowires range from 30 to 50 nm, and the shape is quite uniform in both radial and axial directions (Fig. 1b, inset). After blowing off the nanowires by high-pressure nitrogen gas, some AlQ₃ nanobelts underneath were observed. The nanobelts also grow in random directions, but they do not form a complete layer to cover the substrate.

The nanowires and nanobelts were scraped off from the substrate and examined by transmission electron microscopy (TEM). The TEM image shows that the AlQ₃ nanowires exhibit an excellent flexibility (Fig. 2a). The TEM diffraction pattern shows no diffraction spots or rings, indicating an amorphous structure of the nanowires. The high resolution transmission electron microscopic (HRTEM) image of a typical nanowire shows no lattice image, also indicating an amorphous structure (Fig. 2b). The TEM image of AlQ₃ nanobelts illustrates that some can even be bent over 180° (Fig. 2c). When the electron beam of the TEM was regulated to deviate from the central position, some nanobelts were curled up because of thermal effects.^[12] To study the mechanical properties of the nanobelts, three different current densities of the electron beam in TEM were chosen to irradiate on a specific nanobelt. The nanobelt gradually rolls up along the axial direction (Fig. 2d), indicating its inherent flexibility and excellent thermal stability, even though the AlQ₃ molecules are bonded by relatively weak van der Waals forces. The rolling angle increases with the current density. The large deformation

Fig. 2. TEM images of the AlQ₃ nanostructures. a) TEM image of the AlQ₃ nanowires with a diameter of about 30–50 nm. b) HRTEM image of a typical AlQ₃ nanowire. No lattice image is observed, which refers to an amorphous structure. c) TEM image of the AlQ₃ nanobelts with a width of about 40–60 nm. The bending over 180° is due to excellent flexibility. d) An AlQ₃ nanobelt rolls up along the axial direction after irradiated by the electron beam in TEM. The rolling angle θ increases as the current density increases. Here is only shown the image of a curled nanobelt irradiated by a current density of $3.16 \times 10^{-11} \text{ C cm}^{-2}$.

tion of the nanobelts can be attributed to the flexibility often observed in organic materials. Such characteristics are also perceived in widely explored carbon nanotubes.^[13–15] Moreover, the AlQ₃ nanowires and nanobelts could survive without any change of the surface morphology in the FEGSEM, HRTEM, and TEM when irradiated by electron beam for more than 3 h. This implies an excellent thermal stability of these organic nanostructures.

The growth mechanism of AlQ₃ nanowires cannot be explained by the vapor–liquid–solid (VLS) model.^[16] In this study, it is proposed that the molecules of the evaporated AlQ₃ collide with the Ar atoms and are then rapidly cooled by liquid nitrogen to form nanobelts. The released heat of sublimation induces a narrow temperature inversion region in the vapor–solid interface to construct the trunks of nanowires.

The same mechanism is employed in the trunk surface, thus secondary and tertiary branches are formed subsequently, like the growth of dendrites in pure metals at the liquid–solid interface.^[17]

To examine if the AlQ₃ molecules decompose during evaporation, the chemical bonding was examined by Fourier transform infrared spectrum (FTIR). The AlQ₃ nanowires were deposited directly on a potassium bromide (KBr) pellet, and the spectrum is illustrated in Fig. 3a. For reference, the spectrum of AlQ₃ powder was also measured as

Fig. 1. a) Schematic formation diagram of the AlQ₃ nanostructures. AlQ₃ nanobelts were first grown in less than one layer on the substrate with a width of about 40–60 nm. A thick layer of AlQ₃ nanowires with a diameter of about 30–50 nm was then grown above the layer of nanobelts. b) FEGSEM image of the AlQ₃ nanowires shows a quite uniform diameter distribution. The inset shows the morphology of an individual nanowire.

Fig. 3. FTIR spectra of the AlQ₃ nanowires and original powder. a) AlQ₃ nanowires fabricated at an Ar pressure of 133 Pa and boat temperature of 400 °C. b) AlQ₃ original powder before sublimation.

shown in Fig. 3b. The absorption spectra reveal that there is no fundamental bonding change in the AlQ₃ molecule after sublimation at 400 °C. The relative vibration modes shown in Figure 3 are in agreement with those reported in the literature.^[18]

The photoluminescence (PL) spectrum of the AlQ₃ nanowires deposited on the silicon substrate was obtained by exciting with a He–Cd laser of wavelength 325 nm and power 50 mW. In addition, the spectrum of an AlQ₃ thin film of a thickness 1200 Å grown at 1.33×10^{-3} Pa and a deposition rate of $3\text{--}5 \text{ Å s}^{-1}$ is also measured for reference. The PL spectra of both nanowires and thin film are in the range 450–700 nm, with the maximum intensity at about 540 nm. There is no apparent shift of either peak. A blue shift of the PL spectrum in nanometer-sized inorganic semiconductors is often observed because of the quantum confinement effect. This effect is not expected for organic semiconductors such as AlQ₃ nanostructures because of the relatively weak van der Waals forces among the nearest-neighbor molecules.^[19] No blue shift was observed in this study, which is consistent with the above argument.

Field emission of inorganic materials such as nanowire,^[20] nanorod,^[21] and carbon nanotube^[22] has been observed for many years. As far as we know, the AlQ₃ nanowire reported here is the first organic nanostructure that shows field emission with a relatively low turn-on voltage. The field emission characteristics are presented by the curve of current density J versus applied field E (Fig. 4a). The AlQ₃ nanowires exhibit a turn-on field of $10.0 \text{ V } \mu\text{m}^{-1}$ (Fig. 4b), and the maximum current density is larger than 15 mA cm^{-2} at an applied field of $22 \text{ V } \mu\text{m}^{-1}$. The stability test of the AlQ₃ nanowires was performed at an initial current density of about 8 mA cm^{-2} and an applied field of $20 \text{ V } \mu\text{m}^{-1}$ for more than 3600 s (Fig. 4c). The emission current density degrades significantly in the first 1000 s and then remains steady at about 3 mA cm^{-2} , which is about 40 % of the initial value. Thus, a stable field emission current can be sustained even for such an organic semiconductor.

Fig. 4. a) Field emission J – E curves of the AlQ₃ nanowires. The inset shows the Fowler–Nordheim plot of the AlQ₃ nanowires, which yields a straight line with a slope of about -134 at high applied fields. b) Enlarged portion of the J – E curve to show the turn-on field. The turn-on field is $10.0 \text{ V } \mu\text{m}^{-1}$, according to the definition of $J = 10 \text{ } \mu\text{A cm}^{-2}$. c) Field emission stability of the AlQ₃ nanowires tested at $20 \text{ V } \mu\text{m}^{-1}$ for more than 3600 s.

The Fowler–Nordheim equation of field emission for metals is described as

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(\frac{A\beta^2}{\phi}\right) + \left(\frac{-B\phi^{3/2}}{\beta}\right)\left(\frac{1}{E}\right) \quad (1)$$

where A and B are constants ($A = 1.54 \times 10^{-6} \text{ A eV V}^{-2}$ and $B = 6.83 \times 10^9 \text{ V m}^{-1} \text{ eV}^{-3/2}$), J is current density, E is applied field, ϕ is work function of the emitting material, and β is field enhancement factor related to the emitter geometry.^[23] A plot of $\ln(J/E^2)$ versus $1/E$ yields a straight line with a slope of about -134 at high applied fields (Fig. 4a, inset), demonstrating the field emission phenomenon.^[10]

The electron affinity of AlQ₃ is about 3.0 eV .^[24] The trap energy E_t of the trap states is up to about 0.15 eV below the electron conduction level, and the electron quasi Fermi level lies within the trap states.^[25,26] The work function ϕ of the AlQ₃ nanowires is in the range of $3.0\text{--}3.15 \text{ eV}$, based on the energy gap between the quasi Fermi level and the vacuum level.^[26] According to Equation 1, the field enhancement factor β is estimated to be 275. This value is smaller than that of car-

bon nanotubes, which is in the range of 800–1900.^[22] In general, the field enhancement factor is approximated by the length-to-radius ratio (L/r) of a nanowire.^[21] The average radius of a nanowire estimated from the FEGSEM image is about 20 nm (Fig. 1b). Thus, the length of the AlQ₃ nanowires is calculated to be 5.5 μ m, similar to the thickness of the nanowire layer. This value is reasonable because the AlQ₃ nanowires are grown from the substrate in a dendritic configuration and rolled up to a layer of thickness about several micrometers.

In summary, AlQ₃ nanowires and nanobelts were first synthesized by vapor condensation. Although the AlQ₃ molecules are bonded by relatively weak van der Waals forces, the flexibility and the field emission current density of the nanowires are higher than expected. This provides a new choice of materials for field emission. The potential applications will be of great interest for future study.

Experimental

AlQ₃ nanowires and nanobelts were grown by a vapor condensation system, which consisted of a cylindrical Pyrex vessel (200 mm long, 200 mm diameter, and 7 mm thick) sandwiched by two 304 stainless steel plates [11]. The concave shaped steel plate on the top was filled with liquid nitrogen to act as a cold trap. A graphite boat was employed as a resistive heater, and the temperature was regulated by a power supply and controlled by a K-type thermocouple. AlQ₃ powder (purchased from TCI Ltd., T1527) was put in the graphite boat. A substrate was placed under the liquid nitrogen cold trap. The chamber was evacuated to 1.0×10^{-3} Pa, and argon was then introduced to the chamber. Typical argon pressure and boat temperature were set at 133 Pa and 400 °C, respectively. The temperature of the graphite boat was raised to the working temperature at a rate of 40 °C min⁻¹.

The field emission properties of the AlQ₃ nanowires were measured with a 50 μ m gap between the anode and the cathode under a base pressure of 1.0×10^{-5} Pa. The anode was a spherical platinum probe with an area of about 1.6×10^{-3} cm², and the cathode was the AlQ₃ nanowires deposited on an ITO-coated glass substrate. The field emission instrumentation had a sphere-to-plate geometry rather than plane-to-plane because the platinum probe provided precise motion and manipulation in the high vacuum. Therefore, the field emission properties in any region of the nanowires could be measured. The high voltage was supplied by a power source (Keithley 237) with an accuracy of 10^{-13} A, and the current under increasing applied voltage was recorded.

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Base-Pair Stacking in Oriented Films of DNA–Surfactant Complex**

By Cuiying Yang, Daniel Moses,* and Alan J. Heeger

In addition to its well-known importance to biology, deoxyribonucleic acid (DNA), as a one-dimensional macromolecule, has attracted interest as a material for use in functional mesoscopic electronic devices^[1,2] and in molecular computing.^[3,4] The π -electron overlap between the base pairs within the double helix implies that the stacked base pairs might be a one-dimensional pathway for electronic charge transport.^[5,6] Although the transport properties of DNA have been studied,^[7–10] a wide range of results have been reported with properties spanning the full range from insulating^[11,12] to semiconducting^[13,14] to metallic^[15] and even to superconducting behavior.^[16] Thus, the electronic properties of DNA remain controversial.

The concept of DNA as a “one-dimensional electronic material” requires aligned DNA helices and π -electron overlap between bases along the axis of the double helix. With this as the goal, we have developed oriented films of a DNA–surfactant complex that satisfy both these criteria: aligned double helices separated by 4.1 nm with face-to-face base-pair stacking and bases separated by 0.34 nm.

In the classic DNA structure,^[17,18] the bases within the double helix are oriented perpendicular to the axis of the helix and parallel to each other with a uniform separation distance of 0.34 nm along the axis of the helix. As we report here, this

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