Communication

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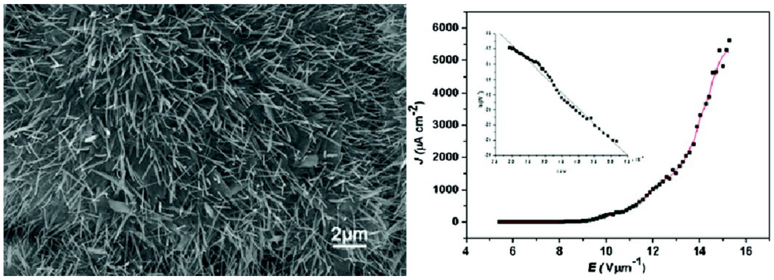

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Fabrication of Polydiacetylene Nanowires by Associated Self-Polymerization and Self-Assembly Processes for Efficient Field Emission Properties

Haiyang Gan,[†] Huibiao Liu,[†] Yongjun Li,[†] Qing Zhao,[‡] Yuliang Li,*[,†] Shu Wang,[†] Tonggang Jiu,[†]
Ning Wang,[†] Xiaorong He,[†] Dapeng Yu,[‡] and Daoben Zhu*[,†]

Key Laboratory of Organic Solids, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China, and Department of Physics, Peking University, Beijing 100871, P. R. China

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In view of extraordinary optical and electronic properties, synthesis of low-dimensional structures of conjugated polymers would be very interesting. For example, polypyrrole nanowires were synthesized by electrodeposition as pH sensors,[1] polyphenylenevinylene nanowires were synthesized by nanolithography as light-emitting materials,[2] sharp conical volcano-like polypyrrole nanostructure was formed for field emission applications,[3] etc. Among many conjugated polymers, polydiacetylenes (PDAs) attain considerable attention due to their quasi-one-dimensional electronic structure, fast and large nonlinearity responses, and very fast photoconduction properties.[4] More interestingly, the properties and performance dependences on morphology of the PDAs have also been studied.[5]

In this aspect, the self-assembly of organic molecules with the assistance of noncovalent forces, such as hydrogen bonding, electrostatic interactions, and π-stacking, provides an efficient method for creating nanoscopic and mesoscopic structures.[6] The self-assembly of a conjugated polymer for forming different morphology is currently attracting considerable attention, and controlled morphology of conjugated polymers is of particular interest for potential applications, such as chemical sensors, electron transfer, solar energy conversion, and molecular devices.[7] We sought to develop a complementary strategy for self-polymerization and self-assembly to produce new aggregate nanostructures of a conjugated polymer, such as nanotubes, nanowires, and nanorods, that would form a novel class of polymer supramolecular systems with unique properties. Recently, we developed a simple method based on the associated effect, that is, self-polymerization and self-assembly of noncovalent intermolecular interaction of $\pi-\pi$ stacking and H-bonding interaction for construction of polymer nanoscale supramolecular materials. Two key conditions are required for the direct formation of polymer aggregate nanostructures by the mentioned associated effect: (I) the monomer is able to self-polymerization by UV light; (II) the self-polymerization polymer could be self-assembled by noncovalent forces. In this communication, we would like to report the associated way for yielding polymer nanowires. More interestingly, compared with inorganic materials and other organic materials, the field emission properties of the PDA nanowires show that they are an excellent potential candidate for field emitters with the turn-on field of 8.2 V/m and the maximum current density exceeding 5 mA/cm^2 at an applied field of 15 V/m.

The diacetylenic derivatives, including 6-carbazol-9-ylhexa-2,4-diyl-1-ol (CYDIOL), were synthesized using Curtis coupling reaction. The CYDIOL is easy to polymerize under UV light, which is clarified by the FT-infrared and Raman spectra.

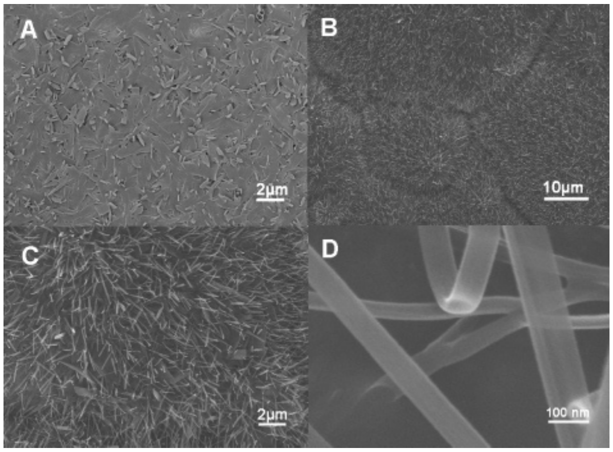

Figure 1. The self-assembled nanostructures on copper foils: (A) without polymerization process (B) and (C) large area of ordered polydiacetylene nanowires (D) with some entangled polydiacetylene nanowires.

A solution of CYDIOL in chloroform was applied onto a piece of copper foil and placed in the dark to let the solvent evaporate. Figure 1A shows the SEM image of the aggregation, which indicated the compound was liable to form one-dimensional nanostructures. While coordinated with a polymerization process, the polymer can form large scale ordered nanowires. Before the solvent was completely evaporated, the foil was irradiated with UV light for 2 h. Figure 1B,C shows the SEM images, with the width of 50−120 nm and the length of several microns. Figure 1D shows several entangled nanowires with the width of 40−100 nm.

Interestingly, ^{1}H NMR spectroscopy studies (in Supporting Information) give the evidences for forming the nanowires by π-stacking and hydrogen-bonding self-assembly. The proton signal at the methylene, beside the diacetylene backbone, underwent an upfield shift with the increasing of the concentration since the electron densities of the protons were increased through the $\pi-\pi$ interaction, leading to their NMR signals being shifted to higher magnetic fields. With the concentration increasing from 2 mM to 0.3 M, the proton signals of methylene connected with the oxygen atom and nitrogen atom shift from 5.14 to 4.98 ppm and 4.28 to 4.15 ppm, respectively. The proton signals at the carbazolyl group shift to higher magnetic fields, too. These results indicate the enhancement of the $\pi-\pi$ interactions with the increase of the concentration. The addition of little amounts of H-bonding solvent CD$_3$OD makes the ^{1}H NMR peaks broaden obviously, indicating the disordering of the self-assembly to the isotropic form.[8a] The role of H-bonding for inducing the π-stacked assembly is further clarified by the fact that the ester derivative could not form nanowires in the same conditions (in Supporting Information). The above evidences indicate that with the evaporation of the solvent,

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[†] Chinese Academy of Sciences.
[‡] Peking University.

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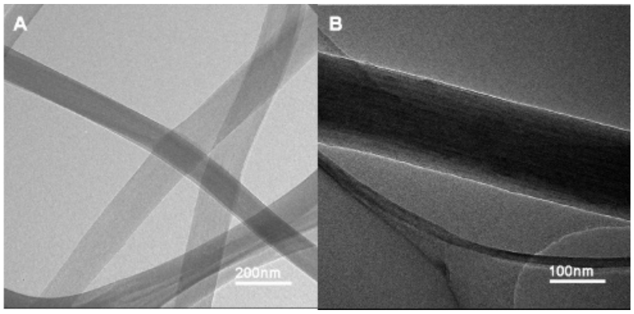

Figure 2. TEM of (A) polyCYDIOL nanowires; (B) a single polyCYDIOL nanowire with striation constructions.

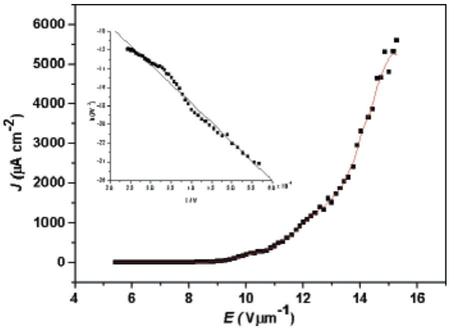

Figure 3. Field emission $J-E$ curves of the polyCYDIOL nanowires. The inset shows the Fowler−Nordheim plot.

the concentration of CYDIOL on the copper foil surface increases, which causes the increase of the noncovalent forces, including interaction of π-stacking and H-bonding. Coordinated with the polymerization process, a balance between self-assembly and polymerization helped the formation of ordered polymer nanowires.

Further characterization of the nanowires was performed by TEM. Figure 2A shows some PDA nanowires with a width from 110 to 150 nm. Figure 2B shows a higher magnification view of a single PDA nanowire with the diameter of about 140 nm, which shows striation construction. This is coincident with our self-assembly mechanism.

In the construction of supramolecular systems, H-bonding and π-stacking often play a prominent role. This has also been proven by others' works. Ajayaghosh has recently reported H-bonding of benzalcohol and the π-stacking of OPV skeleton-induced supramolecular assembly of OPV derivatives.[11] Olesik has reported π-stacking-induced cross-linking of poly(1,8-dihydroxymethyl-1,3,5,7-octatetrayne) to form polymer nanospheres.[9] Suck-Hyun Lee has reported the polydiacetylene supramolecular assembly induced by H-bonds between aromatic dicarboxylic acids and π-stacking of diacetylene moieties.[10] On our side, we suggest that the CYDIOL molecules possess the capability for forming low-dimensional nanostructures by the associated effect of self-polymerization and self-assembly.

The field emission characteristics are presented in Figure 3 by the curve of current density J versus applied field E. The turn-on field of the PDA nanowires was 8.2 V/μm at 10 μA/cm^2 and the maximum current density is larger than 5 mA/cm^2 at an applied field of 15 V/μm. The emission characteristics were analyzed using the Fowler−Nordheim model described as[11]

$$J = E_{\mathrm{loc}}^2 \exp[-6.8 \times 10^7 \phi^{3/2}/E_{\mathrm{loc}}]$$

Here, J is the current density from the emitting tip; E_{loc} is the local electric field, and φ is the work function of the sample. For an isolated hemisphere model, $E_{\mathrm{loc}} = V/(\alpha R_{\mathrm{tip}})$; here, V is the applied voltage, R_{tip} is the tip radius of curvature, and α is a modifying factor. From the above equations, we got

$$\ln\left(\frac{I}{V^2}\right) = \frac{1}{V}(-6.8 \times 10^7 \alpha R_{\mathrm{tip}} \phi^{3/2}) + \text{offset}$$

$\alpha R_{\mathrm{tip}} \phi^{3/2}$ can be estimated from the slope of the $F-N$ plot of $\ln(I/V^2)$ against $(1/V)$, as depicted in the inset in Figure 3. A plot of $\ln(I/V^2)$ versus $1/V$ yields a straight line, indicating that the field emission process from the nanowire film is a quantum tunneling process. Taking $\alpha = 10$ (as used in another report[12]) and $R_{\mathrm{tip}} = 35$ nm, in our case, the evaluated work function of the polyCYDIOL nanowires is around 3.05 eV. This work function is much smaller than that of graphite, which is typically around 4.34 eV, demonstrating that the polydiacetylene nanowires have great potential as a competitive candidate for field emitters.

In summary, we have shown that the associated self-polymerization and self-assembly induces production of polydiacetylene nanowires, which provides a facile and effective method for fabricating stable low-dimensional nanostructures. The resulting nanowires show excellent field emission properties, which exhibit that the turn-on field of the PDA nanowires is 8.2 V/μm at 10 μA/cm^2 and the maximum current density is larger than 5 mA/cm^2 at an applied field of 15 V/μm. This work presents a new concept to fabricate conducting polymer nanowires, and it may have great potential for further applications on fabricating supramolecular materials-based conducting polymer for various fields, such as sensors, optical materials, nanotips in field emission devices, etc.

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Supporting Information Available: The detailed Experimental section, FT-IR and Raman spectra of the PDA, ^{1}H NMR spectroscopy studies of the self-assembly, probable self-assembly scheme and the SEM images of PDA at different self-assembly conditions, and the relevant ester are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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