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Uniaxial Assembly of Nanostructured Materials by Electrospinning

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Abstract: *Diverse growth and patterning techniques have been used to build up a hierarchy of order (shape, size and position) in the field of self-assembled nanostructures. While the ability to produce nanomaterials with good homogeneity in shape and size improves, it remains challenging to control their lateral alignment and orientation. In this paper, several different anisotropic nanostructured materials are investigated as they were axially assembled by an electrospinning process. During electrospinning, tensile force and shear flow along the axis of the fiber, and confinement due to the fiber formation, induce the preferred uniaxial orientation of encapsulated nanomaterial components. Electrospinning offers a simple but effective means of exerting hierarchical control over nanostructured materials. The oriented nanomaterials produced by this approach can be potentially utilized in various mechanical, electrical, optical, and biological device applications.*

I. INTRODUCTION

The synthesis and assembly of metallic, semiconducting, and biological nanoparticles into ordered arrays have received considerable attention due to the properties associated with the assembled architecture, and their potential in nanoelectronics and nanophotonics [1-3]. The challenge of organizing such nanometer-sized particles on the micron or submicron scales has arisen in the nanoengineering world. Long molecules such as carbon nanotubes, quantum rods, and rod-shaped polypeptides, are functional supramolecular nanostructures, and may be considered as potential building blocks for functional device applications in the nanotechnology field. Developments of new methods to effectively control their position and orientation become highly desirable. Aligning nanocomponents within electrospun nanofibers turns out to be a simple means of realizing the hierarchical control over these nanostructured materials.

Electrospinning is an electrostatically induced assembly process for generating ultra-thin solid fibers from a large wealth of polymer sources [4]. Electrospinning utilizes the external electric field to accelerate and stretch a charged polymer jet. The axial tensile force and shear flow induced by electric field in electrospinning have been well understood [5, 6]. They are expected to direct the orientation of the encapsulated anisotropic

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nanostructured material along the fiber axis. The bending instability leads to the liquid jet being stretched and elongated up to 100,000 times in a short distance and in less than one second [7]. Such extremely large effective draw ratio is also likely to orient the nanofillers mixed in polymer solution unidirectionally along the fiber axis when the nanofiber forms. In this study, we used a scanned-tip electrospinning deposition approach to collect individual and oriented nanofibers on a fast rotating substrate [8]. We believe that in addition to the tensile force, shear flow, and drawing effect induced by electrospinning itself, the rotational stretching force of the substrate also possibly contributes to the uniaxial alignment of the nanocomponents. The proposed idea is

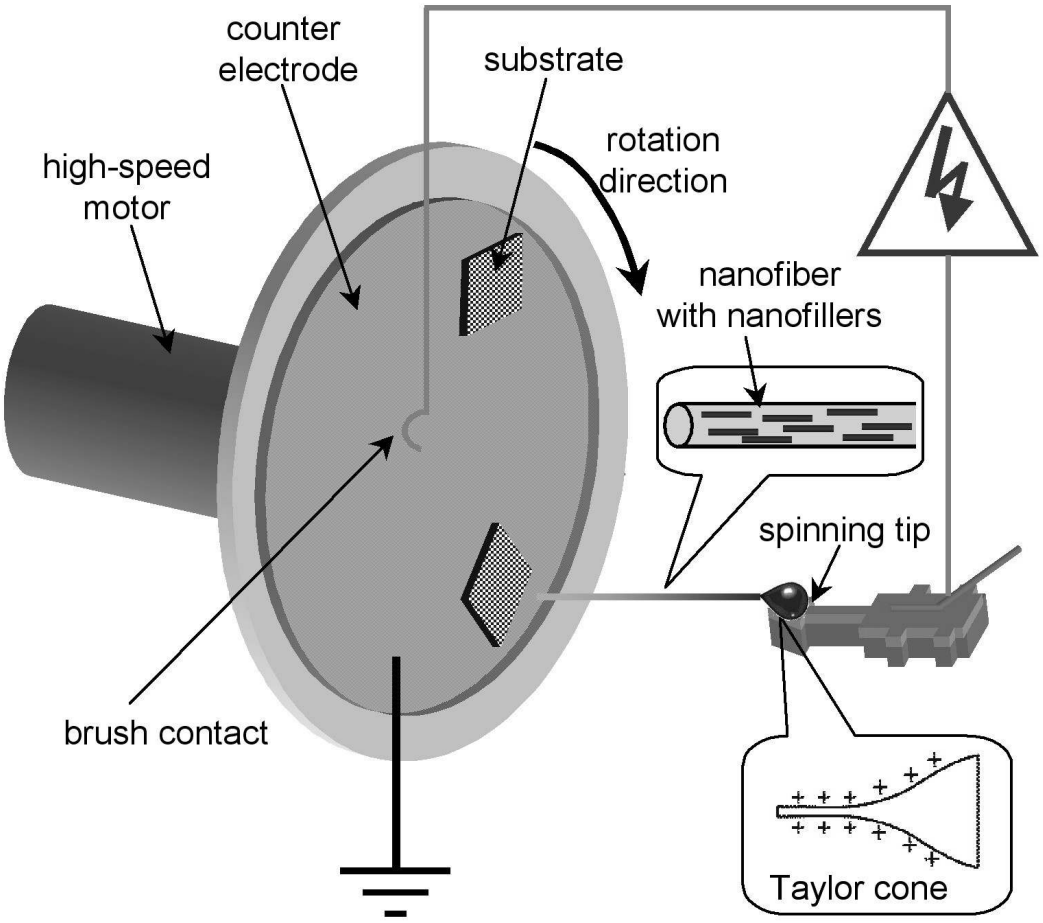

Fig. 1: Schematic of the Scanned-tip Electrospinning Deposition Setup used in this Study to Orient the Anisotropic Nanostructured Materials. The Counter Electrode Rotates at High Speed to Locally Receive Straightened Nanofibers.

depicted in a schematic in figure 1. In our study, assisting polymer was used in some occasions as the supporting matrix, given that high viscosity of the solution is required for electrospinning.

The main purpose of this study was to present a strategy based on electrospinning to create oriented assemblies of anisotropic nanomaterials, and to use such results to offer future directions towards building functional nanodevices utilizing the properties associated with the orientation.

II. EXPERIMENTS AND RESULTS

1. Stretching the Carbon Nanotube

The extraordinary properties of carbon nanotubes offer the potential of their applications in nanoelectronic devices, field electron emitters, and nanocomposite materials [9]. Unlike carbon fibers, the nanotubes tend to form entangled bundles or network as they are produced. The remarkable properties of nanotubes will be of little use unless they can be separated and dispersed evenly, and aligned as individuals or organized as bundles. Many efforts have been taken towards this end, such as melt-bending a nanotube/polymer composite [10], deposition from suspension in strong magnetic fields [11], direct pulling from nanotube arrays [12], flow-induced alignment after dispensing nanotubes in surfactant solution [13], and synthesis of ordered nanotube arrays from nano-patterned precursors [14].

Electrospinning was recently used to embed single-walled carbon nanotube forming composite nanofibers, in which the nanotube alignment within the nanofibers was shown to depend strongly on the quality of the initial dispersions [15]. We aimed to distribute and align multi-wall carbon nanotubes (MWNT) in nanofibers by using the scanned-tip electrospinning in this study. Aqueous MWNT solutions without an assisting polymer did not electrospin and form fibers, because the viscosity of the solution were not high enough to maintain a stable Taylor cone at the end of the spinning tip. The addition of an appropriate amount of poly (ethylene oxide) (PEO) to MWNT solution generated a viscosity and surface tension suitable for electrospinning.

PEO (Mw=900,000), as the hosting polymer, was used as received from Sigma-Aldrich (St. Louis, MO). The PEO was dissolved in water to obtain a stock solution at concentration of w/v 5%. A 30 mg of MWNT (Diameter = 30 nm, Length = 5~20 mm) from NanoLab, Inc (Newton, MA) was slowly added to 10 ml of 1% sodium dodecyl sulfate (SDS) solution in water, followed by a sonication in a bath sonicator (Branson 2510, 40 kHz) for 2 hours to obtain a homogeneous dispersion. The resultant 0.3% of MWNT-in-SDS solution was subsequently mixed with the 5% PEO solution to obtain an MWNT: PEO weight ratio of 1:30. The MWNT/PEO solution was electrospun at 8 kV after a droplet of the solution was dispensed on the spinning tip. A grounded metal counter electrode plate was placed 1.5 cm from the tip of the spinning source and rotated at a high linear speed of 250 cm/s. Continuous MWNT/PEO nanofibers with controlled diameters of 50-200 nm were collected on the silicon substrates attached to the rotating disk.

Atomic force microscopy (AFM) (Digital Instruments 3100) analysis showed a smooth and circular surface on the MWNT/PEO nanofibers (data not shown), suggesting nanotubes were confined in the PEO fiber. In order to reveal the configuration of MWNT inside the polymer fiber, the PEO was completely vaporized by heating the sample on substrate at 120°C for 2 hours in the air, which left an imprint. High-resolution field emission scanning electron microscopy (SEM) (LEO Gemini 1550) was used to examine the MWNT configurations. Individual MWNTs were observed to preferentially orient along the axial direction of the PEO nanofiber according to the imprint direction, as shown by typical SEM images of either single extend tube (figure 2a), or multiple tubes connecting with each other head-to-tail (figure 2b). The results showed excellent agreement with molecular dynamics simulation [16]. Precaution had to be taken on the quality of nanotube dispersion prepared before electrospinning. Low concentrations of nanotube and good sonication assured well-separated tubes to be incorporated as individual elements rather as bundles. Poor dispersion conditions led to twisted nanotube bundles, as seen in figure 2(c). Irregular shaped nanotubes did not appear to mingle well with surfactant and not disperse well in the PEO solution, and therefore in most cases were left out of the polymer nanofiber by electrospinning, as shown in figure 2(d).

Our scanned-tip electrospinning approach successfully extended and aligned MWNT in a PEO nanofiber, and subsequent removal of PEO by heating effectively exposed the MWNT. As demonstrated in our early studies, the scanned-tip electrospinning deposition technique allowed for integration of individual and oriented nanofibers with microfabricated surface structures such as microelectrodes and microtrenches [17, 18]. This technique presents a new opportunity for positioning the extended single MWNT on micropatterned structures for pertinent device studies and characterizations.

2. Lining up the Quantum Rods

As a result of the fully quantized energy levels, and high radiative efficiencies, semiconductor nanocrystals, or quantum dots (QDs), have important technological uses in the fields of photonics and optoelectronics [19]. The realization of QD arrays or networks in well-defined lateral arrangement can be essential for the development of future quantum functional device applications, as new collective traits usually develop. Strategies have been used to climb up the hierarchy of order in the filed of self-assembled semiconductor nanostructures [20]. For example, well-ordered QD arrays have been demonstrated by patterning-related lithography processes [21], and self-organized anisotropic superlattice-mismatched strain engineering [22]. However such patterning approaches are normally based upon or related to molecular beam epitaxy (MBE) or metal-organic vapor phase epitaxy (MOVPE) growth techniques, which are costly in terms of materials and equipment.

Since the pioneering work of Efros (1982) and Brus (1984), the colloidal synthesis route for QDs has been proven to be an extremely flexible approach, with a high degree of control over size, distribution, internal structure, and surface chemistry of the nanocrystals [23]. As for large colloidal QDs, the asymmetry of the wurtzite (hexagonal) lattice structure causes a slight elongation along the c-axis (optic axis) of the nanocrystal,

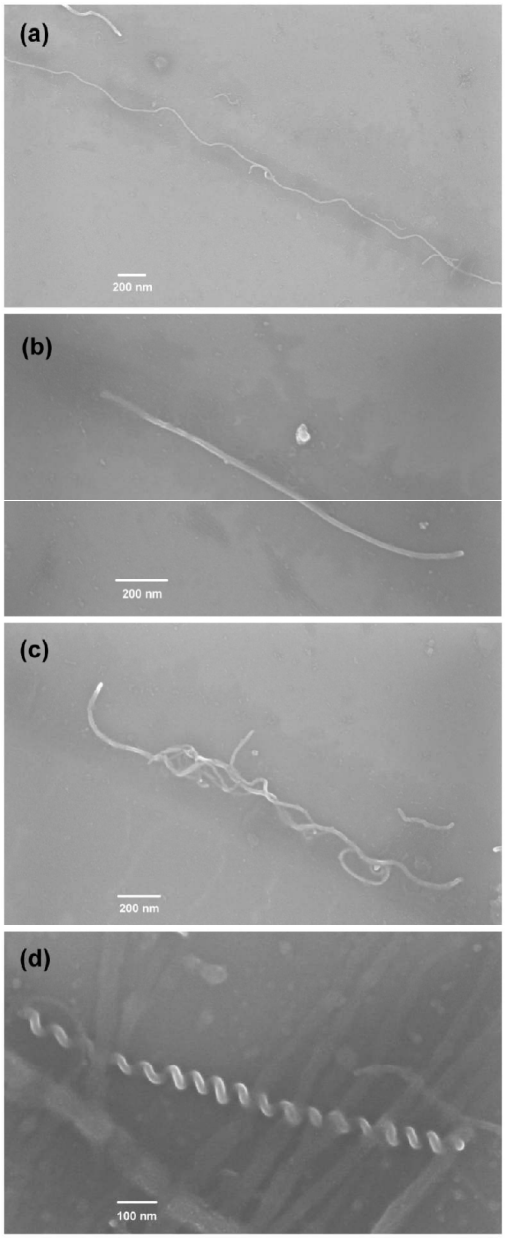

Fig. 2: Orientation of multi-wall carbon nanotube in PEO nanofibers, wherein PEO was vaporized by heating the sample and left as an imprint.

(a)-(b) SEM of MWNT preferentially orienting along the PEO nanofiber axis when good dispersion of the nanotubes was achieved before electrospinning.

(c) SEM of MWNT aggregating as bundles when sonication during dispersion step was not enough.

(d) SEM of irregular nanotube left out of electrospun nanofiber in a curled configuration.

making it prolate deviating from a perfect spherical shape. They present as slightly elongated ellipsoidal (rod-like) shape, named quantum rods. Quantum rods (QRs) have one unique property, which is the linearly polarized emission along the long axis, unlike the spherical dots [24]. Such a linearly polarized luminescent chromophore is highly desirable in a variety of orientation-sensitive applications. Unidirectional alignment of the QRs will make them feasible to use in polarized light-emitting diodes and flat panel displays, as well as the lasing devices.

The external forces exerted by electrospinning were expected to allow for lining up of such anisotropic nanocrystals. Qdot 655 Streptavidin Conjugates (Quantum Dot Corporation, Hayward, CA), with CdSe/ZnS core-shell structure, 15~20 nm in length, rod shape with an aspect ratio of 2:1, were blended with w/v 5% of PEO in a volume ratio of 3:7. The solution mixture was briefly votexed, and electrospun at 8 kV. Continuous nanofibers with consistent diameters of 50-200 nm were collected. An Olympus IX71 inverted microscope (Olympus America, Melville, NY) was used in epifluorescence mode to obtain fluorescence images of the Qdot 655 entrapped in the nanofiber, as seen in figure 3(a). Real-time imaging showed that Qdot 655 inside the fiber was actively blinking, which validated that they existed as individuals, rather than as clusters. AFM and SEM studies indicated the nanofibers had smooth and circular surfaces, suggesting Qdot 655 were embedded inside the fibers but not protruding outwards.

Transmission electron microscopy (TEM) (FEI Philips TECNAI 12 BioTwin) characterization was conducted at an accelerating voltage of 120 kV in imaging mode to investigate the Qdot 655 distribution and orientation in the PEO nanofiber. Electrospun Qdot 655-doped-PEO fibers were deposited on Formvar®-coated copper grids. No staining was needed, since semiconductor nanocrystals are very electron-dense materials compared to polymers. The QRs were clearly observed to line up unidirectionally, with their long axis parallel to the PEO fiber axis, as shown in figure 3(b), 3(c). Crossbar junctions made by QR/PEO nanofibers could be readily obtained by sequential deposition of fibers on the same substrate but turned 90° over. As shown in figure 3(d), 3(e), the QRs were oriented along the fiber axis depending upon which fiber they were incorporated in.

Electrospinning presents an effective means for manipulating quantum structures as putting them into oriented positions. Specifically, it offers the potential for managing the linearly polarized emission generated by the QRs in a collective manner. As the concentration of the QRs increases, we predict to see more compacting alignment of such anisotropic nanocrystals, which may induce the inter-dot interactions. A comprehensive understanding of the electronic structure and relevant dynamical carrier processes of the nanocrystal ensembles are required, which would lead to the realization of quantum functional devices for quantum communication and computing applications in solid state.

3. Alignment of Self-assembling Peptide Microfibril

Fibrous materials in nanometer scale are the fundamental building blocks of living systems. Recent studies indicate that cell attach and organize well around bio-compatible fibers with diameter smaller than the diameter of the cells, and highly oriented nanofibers can

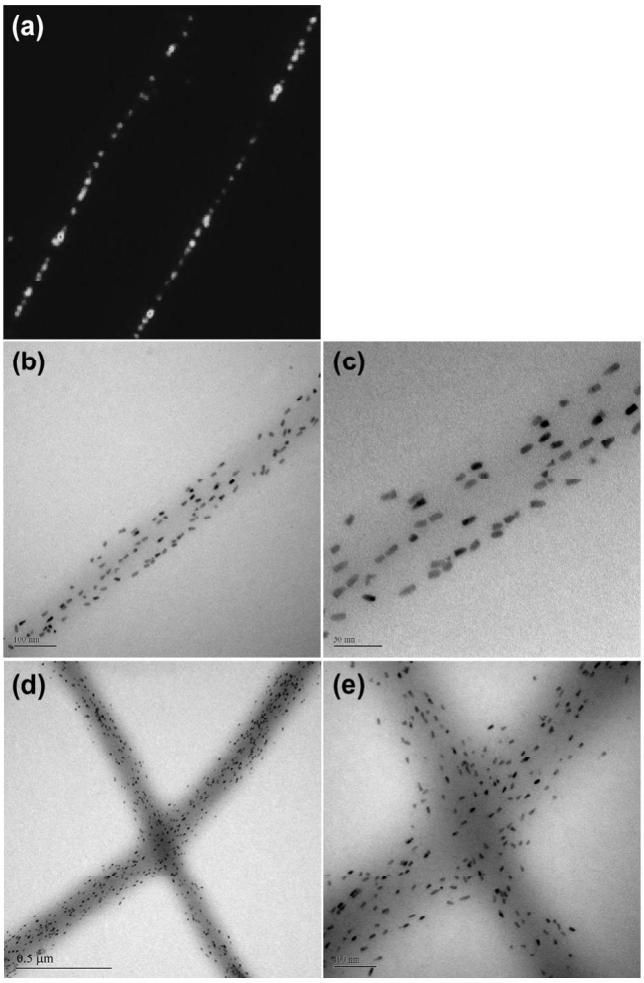

Fig. 3: Orientation of quantum rod Qdot 655 in PEO nanofibers.
(a) One frame of the real-time optical fluorescent imaging of the Qdot 655 in PEO nanofiber (field of view 400 mm ´ 400 mm).
(b)-(c) TEM of Qdot 655 lining up unidirectionally parallel to the PEO nanofiber axis.
(d)-(e) TEM of crossbar junctions made by Qdot 655/PEO nanofibers, with Qdot 655 orienting along the fiber axis in which they were entrapped.

elicit favorable biological responses, such as the significant increase in adhesion, proliferation, as compared to film structure [25, 26]. Cells seeded on such structure tend to maintain phenotypic shape and guided growth according to the fiber orientation. This can be attributed to two reasons pertaining to nanofibers: first, its ability to better mimic the biological microarchitecture; second, the greater available surfaces for cell adhesion as a consequence of the small fiber diameter, which facilitates cell attachment as the first critical step.

Electrospinning has been utilized to generate nanometer diameter fibers from type I collagen [27], silk-like and silk proteins [28, 29], however they were processed into electrospun fibers either with the assistance of PEO, or using the organic solvents, which may interfere with desired biomedical applications. A class of synthetic oligopeptide, originally discovered by Zhang, et al [30, 31], have been widely studied. These molecules can undergo self-assembly into supramolecular nanofibrils in aqueous solution in analogy to physiological amyloid fibrils, an insoluble protein deposits related to Alzheimer's disease and other illnesses. They can be used to inscribe biological signal or information in the self-assembled structures, which are potentially suitable for specific applications in terms of mechanical and cell-interaction properties. The resultant solution of the peptide filaments is highly viscous so that it is readily electrospinable.

Designed with an alternating pattern of hydrophilic and hydrophobic amino acids with the tendency to adopt b-sheet structure, an example of such self-assembly peptide KFE8 (FKFEFKFE) [32] was commercially-synthesized from Invitrogen, Inc (Carlsbad, CA). Aqueous solution of KFE8 was prepared by mixing the lyophilized peptide power with deionized water to a concentration of 1 mg/ml. The solution was clear as prepared with a pH~3.3. When the pH was brought to ~7 adjusted by addition of 0.1N of NaOH, there was a rapid increase in viscosity and the solution was converted to a sol-gel due to net zero charge on the molecule). This suggested the fibril formation upon a rapid self-assembly process. We found that at pH~5.5, the viscosity and surface tension of the peptide fibril sol-gel reached the most desirable values for electrospinning. Electrospun protein fibers with diameter from sub-micron to a few microns could be reproducibly produced.

AFM imaging revealed that the peptide fibrils self-assembled from the short fibrils (figure 4a) to a thicker fibrous motif (figure 4b). To optimize the short peptide fibrils adsorption on substrate when AFM imaging, a droplet of the solution was left on silicon surface for 1 minute and then rinsed with deionized water twice. The silicon surface adsorbed with peptide fibrils was dried in air and imaged immediately. The electrospun fiber was directly deposited onto silicon surface and ready for imaging.

TEM was performed to examine the electrospun peptide fiber (figure 4c-4f). Electrospun peptide fibers were directly deposited on Formvar®-coated copper grids. Negative staining solution of uranyl acetate, a heavy metal salt and therefore electron opaque, was applied to the relatively electron transparent peptide fibrils on the grids waiting for 5 seconds to increase the contrast. This caused the fibrils to appear light against a dark background. Preformed short fibrils were observed to bundle together and extended into longer fibers. The progressive solvent loss during the electrospinning process very likely promoted intermolecular hydrophobic interactions. It however should be noted that staining process led to the dissociation of the fibril bundles to certain extent. The short fibril structures were well oriented along the fiber axis, suggesting its potential as a mechanical scaffold for connective tissues or tissue-engineered ligament.

Interest in self-assembly as a route to aggregates of components larger than molecules has led to many applications in nanoscience field. This work demonstrated a two-step self-assembly process: the molecular self-assembly, and the nanoscopic to mesoscopic

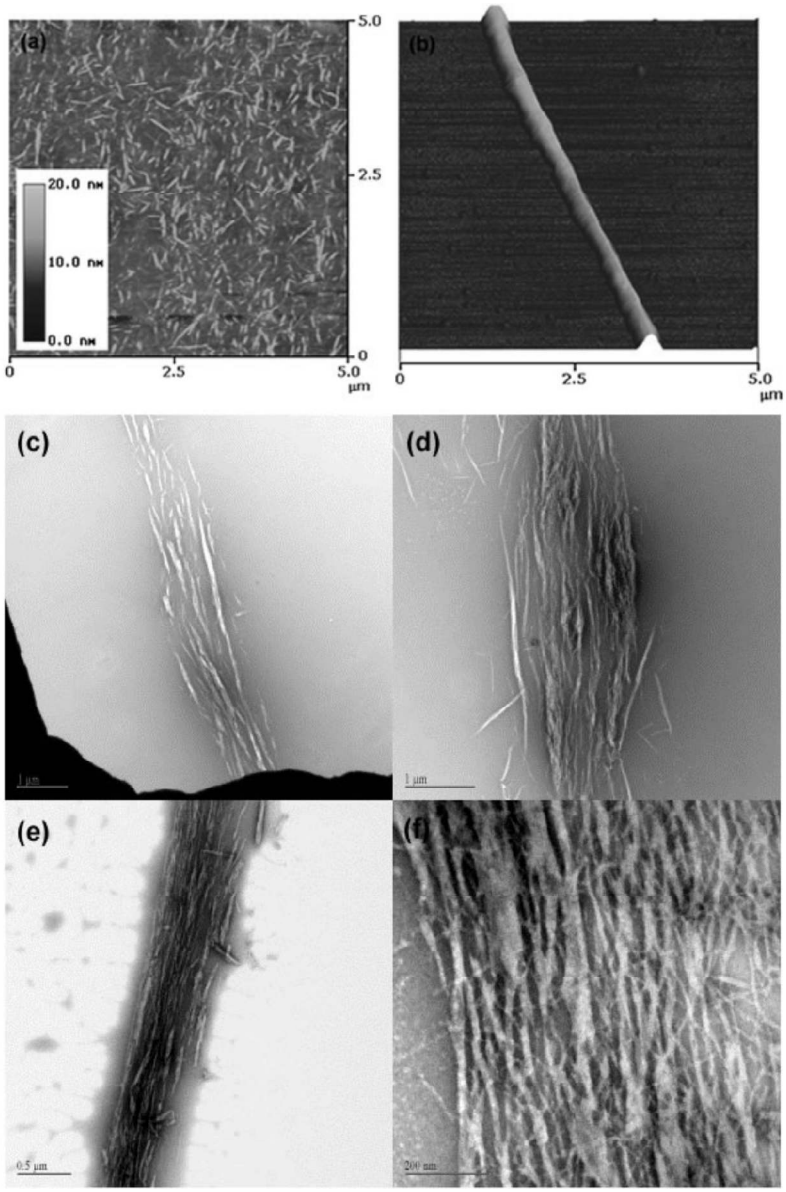

Fig. 4: The self-assembling of KFE8 peptide in aqueous solution became rod shape short fibrils, and were electrospun into oriented thicker fibers.

(a) AFM examination of the self-assembled peptide sol-gel at pH~5.0 deposited on clean silicon surface, which was collected a few minutes after preparation.

(b) AFM examination of the same sample that was electrospun to form a solid nanofiber made of bundles of short peptide fibrils.

(c)-(d) TEM of electrospun fibers formed from self-assembled peptide fibril seen in 4(a), displaying a strong tendency to form parallel fibril arrays with a high degree of order.

self-assembly by an electrospinning process, for objects with dimensions from nanometer to micrometer scale.

III. CONCLUDING REMARKS

Assembling nanometer-scale components into ordered arrays presents great promise and plays a key role in nanoscience and nanotechnology. This study unambiguously demonstrates that electrospinning is an effective approach for orienting nanostructured materials. It offers a new level of control over the characteristics of individual component and over the interactions among them, which will make fundamental investigations tractable and pave a useful way for assembling electrical, optical, and biological components into complex system and devices. The generality of this method can be prospective for design and fabrication of highly ordered and controlled nanomaterials for applications in the wide realm of nanotechnology.

Extensive work both from the standpoint of nanofiber composite science (fabrication, characterization, modeling and simulation) and from industrial base (applications) viewpoint is necessary in the future. The deceivingly simple operational principle of electrospinning for generating oriented nanostructures demands a more profound scientific understanding and engineering development, in order to realize the technology from the kindling of laboratory try-out to the robustness of industrial manufacturing processing.

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