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Nano-architecture: creating complex surface structures using supramolecular self-assembly of tripeptides

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Keywords: self-assembly, supramolecular recognition, artificial silk, unnatural β-peptide

ABSTRACT

Here we report on using small unnatural helical beta peptides to form higher order geometries. These peptides are known to self-assemble by supramolecular recognition, via a unique 3-point H-bonding motif. This self-assembly pattern leads to unprecedented head-to-tail self-assembly, thus continuing the intramolecular helix into a fibrous superstructure. The smallest peptide still capable of self-assembly had a sequence of only three beta amino acids. We demonstrated a hierarchical self-assembly process, which can be designed to form macroscopic silk-like threads as well as complex nanometer scale surface structures. We have achieved radial as well as parallel geometries. Both the synthesis and the derivatization of the fibres is relatively straigthforward, making this platform technology ideally suited for the highly exacting requirements of materials science.

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1. INTRODUCTION

Until recently, nanotechnology has been dominated by top down nanofabrication. While a plethora of bottom-up approaches have been proposed, the ability to create patterns in a spatially consistent manner is still a challenge[1,2]. The most success has been achieved using biomaterials such as peptide amphiphiles[3]. However, the limitations of the amphiphile self-assembly - the low specificity and selectivity of the self-assembly motif, and the dependence on an aqueous environment - still does not allow for the design of hierarchical structures. Supramolecular self-assembly offers the means to overcome the existing limitations and design new functional nanomaterials. The specificity and selectivity offered by supramolecular recognition minimizes defects, while the geometrically optimized physical bonding networks introduce high strength. In recent work[4] we reported the design of a unique supramolecular self-assembly motif for the head-to-tail assembly of small, inherently helical unnatural beta peptides, effectively turning the self-assembled structure into a continuation of the intramolecular helix. These helices have a perfect pitch, with exactly three amino acids per turn, and thus the residues are aligned along the helix. We described how these core fibrils bundled to form microscopic and macroscopic threads. Here we describe the formation of complex geometries based on the same principle.

2. EXPERIMENTAL

MATERIALS. Spectrophotometric grade solvents were purchased from Sigma Aldrich. Peptides were synthesized as described[4] using standard solid state synthetic methods. Beta amino acids were purchased from GL Biochem. Peptide solutions were freshly prepared in methanol, isopropanol, acetone and chloroform solvents by dissolving 1 mg of the lyophylized peptide in 1 ml of each solvent separately. The solutions were vortexed for 3 min, and then incubated for at

least 24 hr before use. Peptide solutions were drop cast onto mica surface, dried under N_2, aged overnight and imaged with AFM.

ATOMIC FORCE MICROSCOPY. Deposits were characterized using atomic force microscopy (AFM) with an Ntegra system (NT-MDT, Russia), in scan-by-sample configuration. NSG30 NT-MDT silicon cantilevers were used with a typical spring constant of 72 N m^{-1} and a nominal tip radius of 10 nm. All samples were imaged under ambient conditions using semi-contact (tapping) mode at 512x512 pixel resolution and 0.5-1 Hz scan rate.

3. RESULTS AND DISCUSSION

The AFM images show fibrous material with a geometry that suggest a well defined one dimensional self-assembly into fibres (figure 1). It is apparent that the smaller fibres twist into consecutively larger structures in a hierarchical manner. Thus the self-assembly follows two motifs. The supramolecular self-assembly provides the fibrous core structure while adhesion between the fibres leads to the formation of branched hierarchical structures.

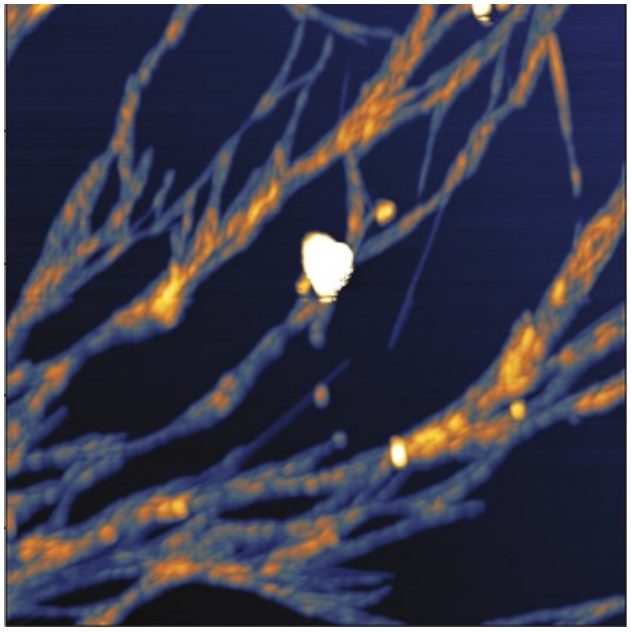

Figure 1 ac-βLβIβA on mica surface, imaged by AFM. The scale is 10 μm. The peptide was dissolved in methanol and mixed with isopropanol for deposition. Typical heights of fibres are 20-30 nm

In the second example, the structures have been radial in appearance (figure 2). In this case the self-assembly process was aborted by quick drying. Imaging revealed the presence of non-assembled material that has coated the surface; the layer is viscous and it causes high probe adhesion to the surface, further confirming its amorphous nature. Since the self-assembly did not proceed, here the initial stages are visible. The fibre nucleation happens simultaneously at several places, and fibre growth proceeds from these sites initially in a distorted radial geometry, forming twisted branches in a hierarchically decreasing geometry from the center outwards.

The major advantage of this process over amphiphilic self-assembly is that the two motifs are distinctly different in their specificity and selectivity, and are responsible for two different geometrical trends. Thus, while it is possible to control the geometry to some extent by the balance of hydrophobic and repulsive interactions in the case of amphiphilic self-

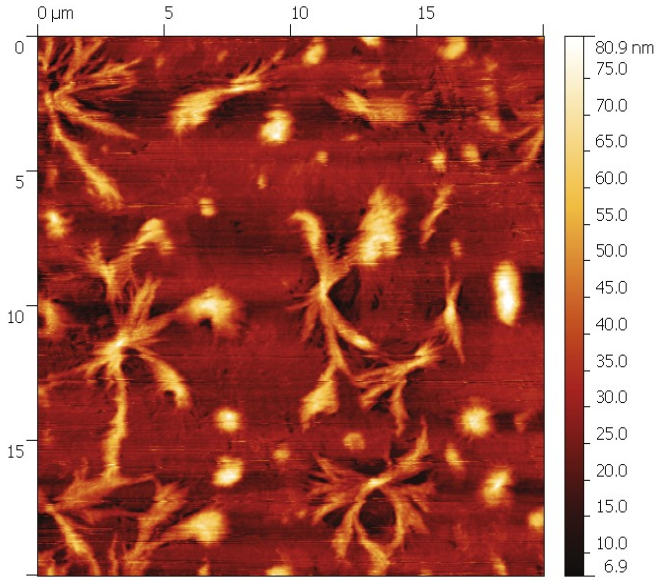

Figure 2 Peptides were deposited from methanol with an addition of isopropanol. Self-assembly was aborted via quick drying. The nucleation sites of fibre formation are visible as radial structures.

assembly[5], the design presented here is superior in that a highly specific and selective supramolecular self-assembly motif provides the core structures.

4. CONCLUSIONS

Fibrous surface structures have been created using supramolecular self-assembly of small unnatural β peptides. These surface structures might be radial or parallel. The structures are based on a 3-point H-bonding motif that implements head-to-tail self-assembly, in essence a continuous helical structure, of small non-amphiphilic peptides. The structure offers itself for easy functionalization with three well-defined functional sites in a trigonal geometry. Thus it is a platform technology for applications that rely on the delivery of complex payload in a spatially controlled geometry.

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Synthesis and electrochemical characterization of novel MOF-reduced graphene oxide composites

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Recently great interest has been drawn towards carbon materials that include graphene and similar 2D materials owing to their unique structural and physical properties [1]. Graphene with its flat 2D structure possess reasonably large surface area and good electrical conductivity. These properties could specifically tune in combination with the other related materials by forming nanocomposites and thereby imparting novel as well as improved properties compared to their parent materials. Another class of materials, Metal-organic frameworks or MOFs are emerging as very interesting porous materials with extremely large internal surface area and tunable chemical properties. These materials are new generation porous crystalline materials suitably formed by the co-ordination of organic - inorganic moieties in a well-defined pattern. The organic linkers connected with metal centres provide them with extremely high surface area and ability to introduce variable functional groups. However, MOFs are generally insulators. It can be hypothesized that a combination of MOF with graphene will generate materials with large surface area and high electrical conductivity, which in turn may lead to the development of efficient supercapacitors. A few studies [2-7] have investigated the MOF–carbon systems with the main focus towards materials for gas separation, gas storage and supercapacitor applications. Jahan *et al.* [6] reported the structure directing role of reduced graphene oxide (RGO) in the synthesis of MOF5. Petit *et al.* [7] synthesized several different novel composites based on a copper based MOF (HKUST-1) and RGO and studied the reactive adsorption of ammonia in order to characterize the mechanisms of the retention process. Guo *et al.* [2] reported that composites synthesized using RGO and a platinum based MOF can be modified further to perform bioanalysis, biocatalysis and environmental monitoring. However, to the authors best knowledge there has not been any study to investigate whether MOF and RGO based composite materials can be used as supercapacitors. Hence, in the present study we have synthesized MOF5 and RGO composites with varying amounts of RGO and have investigated the electrochemical responses of these materials in 1 M sodium sulphate (Na_2SO_4) electrolyte.

In this study, we have synthesized three different MOF5-RGO composites with 3%, 5% and 7% of RGO content using a DMF approach of MOF synthesis [8]. X-ray diffraction (XRD) and Raman spectra were performed to analyse the chemical nature of MOF composites. Although the XRD spectra suggested that the inherent cubical symmetry of MOF5 was absent in case of the composites containing 3% and 5% RGO, it was present in case of the composite containing 7% of RGO. This can be attributed to the fact that the higher content of RGO in the composite containing 7% of RGO maintains the cubical symmetry of MOF5 by wrapping moisture sensitive [9] MOF surface. This was further supported by the scanning electron micrographs (SEM) of the morphology of the composites containing 7% RGO. Raman spectra of all the composites (3%, 5% and 7%) had peaks corresponding to both RGO and MOF5. The BET surface area of the composite containing 7% RGO (1400 m^2/g) was about two orders of magnitude higher than the other two composites (3% and 5%). The electrical conductivity of the composite materials increased with increasing RGO content and the maximum electrical conductivity was observed in case of the composite containing 7% RGO. The electrochemical characterization of all the composites was performed in a three electrode electrochemical cell (composites were used as the working electrode, platinum mesh as the counter electrode and saturated calomel electrode as the reference electrode) in 1 M Na_2SO_4 using a Biologic VSP potentiostat. The cyclic voltametry (performed in the range of 0-0.5 V vs SCE at a scan rate of 20 mV/s) and the galvanostatic charge-discharge (performed at a constant current of 0.5 A/g in the potentials range of 0-1 V vs SCE) showed that the specific capacitance of the composite materials increased with increasing RGO content. The maximum specific capacitance was obtained in case of the composite containing 7% RGO and was about 5 times better than only RGO. The higher specific capacitance obtained in case of the composite containing 7% RGO can be attributed to the fact that this composite material had the combination of the highest surface area and the highest electrical conductivity. The cyclability of the composites was evaluated for 1000 cycles using the galvanostatic charge-

discharge experiments. The specific capacitance retention of the composite containing 7% RGO was significantly high (80%) even after 1000 cycles.

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Tunable reduction and amorphisation of graphene oxide films by focused ion beam irradiation

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ABSTRACT

Graphene has risen to prominence as a scientifically intriguing material with tremendous potential, making its fabrication a key research area. An intriguing and innovative route to its synthesis is the use of focused ion beam irradiation to achieve spatially patterned reduction of graphene oxide. Here we explore the sensitivity of this approach, analysing the key parameter of ion fluence through a systematic study, ranging from 0-0.204 nC/μm^2. We characterize the regimes of preferential reduction and amorphisation, and analyzing changes in the materials bulk conductivity and Raman spectra, as it progresses through these regimes.

1. INTRODUCTION

Graphene has risen to prominence as a versatile and scientifically intriguing material with tremendous potential. Making its fabrication a key research area extensively worked on by the scientific community at large. An intriguing and innovative rout to its synthesis is the spatially patterned reduction of the electrically insulating graphene oxide (GO) to the conductive reduced-graphene oxide (rGO).

This method opens up a top down fabrication approach for all-carbon based electronic devices with the ability to directly write conductive pathways into an electrically insulating material. The use of focused ion beam (FIB) irradiation to achieve this has been demonstrated[1]. Here we explore the sensitivity of this approach, analysing the key parameter of ion fluence.

Presented are the results of a systematic study where the ion fluence was varied from 0-0.204nC/μm^2, with analysis of Raman spectroscopy and atomic force microscopy (AFM) to determine the effect on the surface morphology of the sample. It is expected that increasing the fluence will result in the preferential reduction of the GO being overridden by amorphisation of the sample, leaving two regimes. One regime is where the major effect of ion irradiation is preferential removal of oxygen resulting in rGO, and the other is where there is an increase in damage to the sample, leading to major disruptions of the carbon lattice and hence amorphisation. If the transition between these regimes is gradual it will allow for us to tune the effect of the irradiation, a key in using the FIB for the fabrication of micro to nanoscale patterns, to suit desired application.

2. METHODOLOGY

The GO was synthesized from graphite powder (SP-1 grade 325 mesh, Bay Carbon Inc.) using a modified Hummer method. It was then used to fabricate samples via spin coating on Si to make a continuous GO film that was 80nm in thickness. The samples were then placed into the chamber of an FEI Helios Nanolab 600 FIB-SEM and pumped down to a vacuum level of below 1×10^{-3} Pa. Markers were milled into the surface using a 30 kV beam, 9.3 nA current with a fluence of 2.79 nC/μm2, and the area within the markers was exposed to a controlled fluence of Ga ions ranging from 0 to 0.204 nC/μm^2. Raman spectra were obtained using a Renishaw Confocal micro-Raman Spectrometer equipped with a HeNe (632.8 nm) laser calibrated to the silicon peak. Two point conductivity measurements were conducted using an Agilent B2900Series Precision Source/Measure Unit wired through an EmCal Genelyte Probe Station with 5μm tipped tungsten probes. Measurements were taken by varying the applied voltage between - 4.5 V to +4.5 V. This range was deemed acceptable as studies have shown that 0 – 30 V range is required to stimulate electrically induced reduction of GO[2]. The probes were placed 50 μm apart. The scan rate used in the measurements was 0.8 V/s with a measurement taken every 0.008 V.

3. RESULTS AND DISCUSSION

Initial SEM images displaying the result of increasing fluence clearly show that at higher doses we have greater damage to the sample's surface as seen in figure 1 what is intriguing is the transition between the these two morphologies. From the Raman spectra of the FIB exposed regions seen in figure 2 it is evident that the sample undergoes different levels of reduction and amorphisation[3] as we progressively increase the dosage of ions. At the maximum fluence studied 0.204 nC/μm^2 the sample is completely amorphised as is evident for the broad resonance peak. This is also reflected in the bulk conductivity measurements taken of the samples where the conductivity drops off at higher ion fluences. Initially the conductivity is low (5 x 10^{-4} S/m) as graphene oxide is an insulating material due to the oxygen defects in its basal plane. Upon irradiation by the Ga ions (fluence 0.08 nC/μm^2) the sample is reduced and this partially restores the sp^2 honeycomb structure found in pristine graphene and hence increases its conductivity (3 x 10^{-1} S/m) by 3 orders of magnitude. Finally at higher fluence values the ions do significant damage to the structure and the amorphisation hinders the electron mobility hence reducing the conductivity[4] once again (2.4 x 10^{-6}).

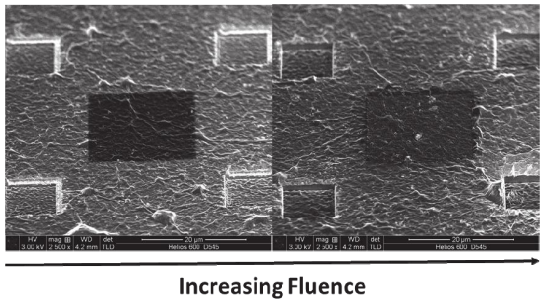

Figure 1. SEM images of the effect of increasing fluence on the GO sample there is an immediate change in contrast initially but it is clear that at higher fluences the surface undergoes significant damage.

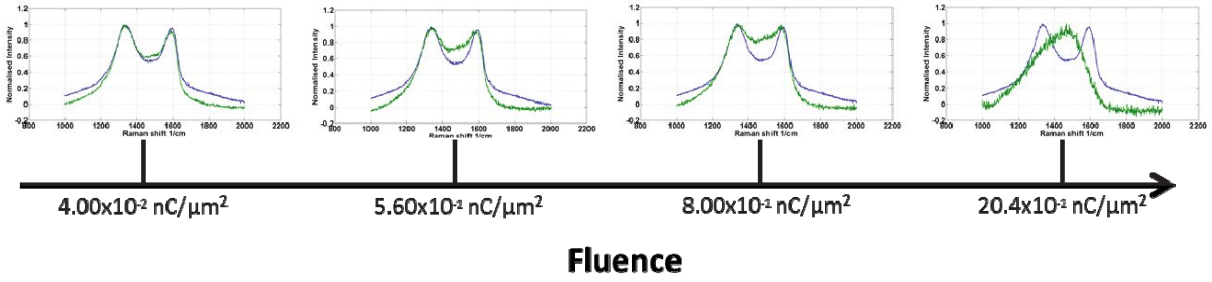

Figure 2. Optical images of the exposed regions with their corresponding Raman spectra, these results show us that the sample initially undergoes reduction and then at higher ion fluences amorphisation.

4. CONCLUSIONS

This work demonstrates that the FIB irradiation of graphene oxide is highly controllable, to the point where damage to the sample can be tuned between reduction and amorphisation. The maximum conductivity was obtained with a fluence of 0.08 nC/μm^2 which lies in a region of reduction and amorphisation. This technique can be used as a tool to directly write all carbon conductive elements into an otherwise insulating film.

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