Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary material for paper

"Nanotechnology Inspired by Nature: Basic Physics and Engineering of Peptide Supramolecular Nanostructures"

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Physical Vapor Deposition Technology of Peptide Nanostructures

Physical vapor deposition (PVD) is one of the basic technologies in microelectronics and its application to biomolecules deposition allows to use in a facile way the unique properties of peptide supramolecular nanomaterials and to integrate them into various wide applications. The PVD technique is based on vaporization process from a solid source in the form of atoms or molecules. The vaporized flux is transported through vacuum, low-pressure gaseous environment or plasma towards the substrate where it condenses. In a thermal vapor evaporation process, the source material is heated to a temperature where there is an appreciable vapor pressure. The process requires vacuum conditions (at least 10^{-4} mbar) to prevent collisions of the vapor flux with gas molecules as it is transported in a line-of-sight trajectory from the source to the substrate. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to dozens of micrometers; however they can also be used to form multilayer coatings, graded composition deposits, very thick deposits and aligned structures.

Peptide nanostructures are related to bioorganic materials. Therefore application of PVD method to peptide nanostructures deposition has definite specific features such as low temperature of biomolecules vaporization and possibility of temperature-induced peptide molecules transformation. It should be emphasized that compared to inorganic materials self assembling of biomolecules could be governed by totally different

mechanisms. All previously published original papers used biomolecules self assembling in liquid environments where the leading forces are hydrophobic/hydrophilic interactions resulting in fabrication of nanotubes, nanospheres , etc.

The developed by us biomlolecules deposition technique[1] consists of two independent systems holder and substrate. Each system include four individually operated heating cells of the substrate holder and the powder holder- (evaporator). The distance between the substrate and the powder holder may be gradually varied in the range 2-5 cm. The temperature of the substrate is controlled in a range of T_S ~25-100 °C, and is optimized for the desired peptide material. The temperature of the powder holder is controlled in a range of T_H~100-300 °C, and is adjusted with sublimation temperature of the evaporated peptide material. The developed setup allows coating at area up to 4X 4 cm^2. The evaporation of the biomaterial occurs at vacuum pressure 10^{-6} mbar. During the deposition of the peptide coating, the precursor monomer powder is placed in the powder holder. The coating is formed on the downward side of the substrate holder (Fig. S1).

Various bioorganic nanostructures of different origin and composition have been self assembled by PVD with the use of dipeptides and amino acids, such as phenylalanine (F), diphenylalanine (FF), tryptophan (W), phenylalanine-tryptophan (FW), tyrosine (Y), dityrosine (YY), dialanine (AA), 9-fluorenylmethylcarbonyl-pentafluorophenylalanine (Fmoc-F5-F), 3,4-dihydroxy-phenylalanine (DOPA),etc.

We present at Fig. S2 examples of deposited FF-dipeptide nanostructures. The average height (1-50 μm, and surface density (10^5-10^8 cm^{-2}) of these PVD peptide nanostructures can be controlled by adjusting the deposition parameters (Fig 2). Variation of them in a wide range (temperatures of the holder and the substrate, temperature rate

and duration of deposition) allowed to fabricate FF-nanostructures of different ordering, shape, nanopacking and scale such as peptide nanoislands, amorphous layers, thin films, nanotubes and nanofibers arrays.

The PVD deposited peptide coatings have been used by us for fabrication of new devices such as microfluidic chips, blue light emitting diodes and energy storage devices. In the latter case we succeeded to modify carbon electrodes of supercapacitors by thin peptide layers of and enlarge their capacitance by 100 times. The devices also showed high rates of charge/discharge process and pronounced stability.

Figure legends

Fig. S1 Proposed assembly mechanism for the formation of vertically aligned PVD FF-PNTs. (a) Schematic of the vapour deposition technique. (b) Illustration of a single peptide nanotube composed mainly of Cyclo–Phe–Phe peptide. (c) Molecular arrangement of six Cyclo–Phe–Phe peptides after energy minimization[1]

Fig. S2 Top-view SEM image of the PVD FF-PNTs after the vapor deposition process. (b) Side view of vertically aligned PVD nanotubular structures demonstrating the elongated micrometer size nanotubular structures with a height of 40 μm. (c) Side view of vertically aligned nanotubular structures with a thickness of 5 μm. The inset shows a high-resolution SEM image of nanotubular structures[1]

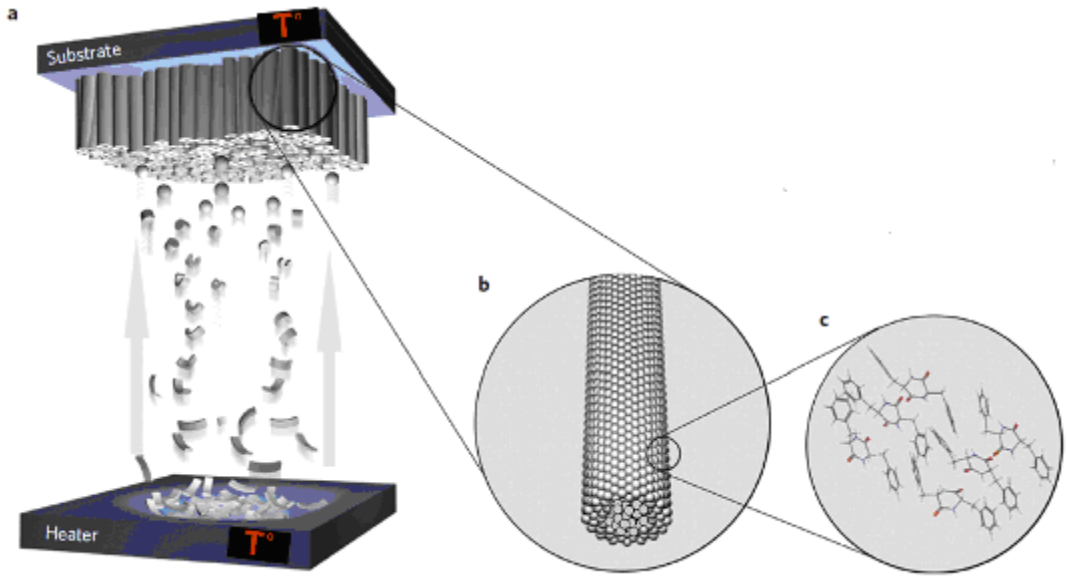

Figure S1

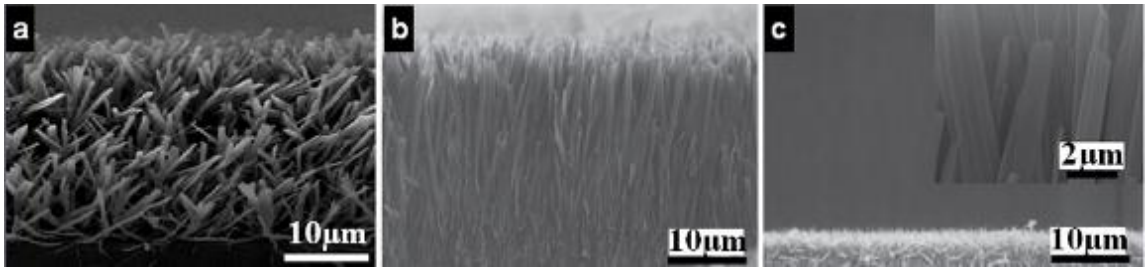

Figure S2

References

[1] L. Adler-Abramovich, D. Aronov, P. Beker, M. Yevnin, L. Buzhansky, G.Rosenman, E. Gazit, *Nature Nanotechnology*, 2009,**4**, 849