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Self-assembled peptides for suppression of non-specific binding of biomolecules on graphene

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Abstract

Towards the applications of graphene for biosensing, the surface treatment to prevent its fouling is crucial to maintain its sensitivity and selectivity to target molecules. In this work, self-assembled peptides were used to functionalize the surface of graphene to suppress non-specific adsorption of biomolecules. The peptides were designed to form a monomolecular-thick film on the graphene surface in a manner of self-assembly. Graphene surfaces can be simply coated by peptides with a wet process with peptide solution. This new approach allows us to functionalize the surface of graphene in a cost-effective way for biosensing.

1. Introduction

Graphene is suitable for an active layer for biosensors with high-sensitivity because of their fascinating electrical properties with atomically-flat surface and high specific surface area. Biomolecular immobilization on the active layer of biosensing devices is of vital importance for the functionality, such as sensing with biomolecular probes and protecting from unnecessary unspecific adsorption of biomolecules. However, the immobilization by chemical bonding will introduce atomic defects for graphene, which influences its intrinsic properties to some extent. Self-assembled peptide can be a good candidate. Specific peptides spontaneously form ordered structures through non-covalent intermolecular interactions on the surface of graphene without losing the intrinsic electrical properties of the materials [1][2][3].

Various peptides have been demonstrated to exhibit organizations into ordered monomolecular-thick structures on the surface of 2D materials, such as mica, graphite, and transition metal dichalcogenides. These self-assembled structures of peptides are suitable to be used for simple and massive functionalization of the surface. Furthermore, utilization of these peptides with uniform and ordered structures as a biomolecular scaffold allow us to immobilize the biomolecular probes on the 2D materials with a controlled manner. Some of the above peptides has been utilized as a molecular scaffold for biosensing. In these works, two different kinds of peptides: (1) peptide acts as a molecular scaffold and (2) peptide with a bio-probe in addition to the same sequence of (1) have been mixed. Since these peptides share the sequence with the ability of self-assembly, the peptides with bio-probes can be immobilized on the surface through the co-assembly process. Non-specific adsorption of biomolecule causes a background noise and decrease the sensing ability of a bio-probe. Therefore, the suppression of nonspecific adsorption is an important issue for the realization of high-performance biosensors. To solve these problems, in this research, we designed a new self-assembled peptide and evaluated its performance, aiming at the construction of the surface with the anti-fouling property.

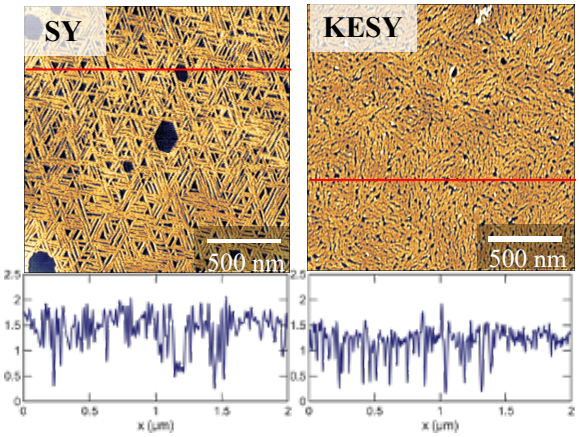

Fig. 1 Atomic force microscope (AFM) images of self-assembled peptides on graphite surface. SY peptide and KESY peptide show linear structures with a monomolecular thickness.

2. Result and Discussions

The designed peptides consisted of three main domains. (1) antifouling domain: hydrophilic and zwitterionic, which is effective in reducing protein adsorption. A repetitive sequence of lysine (K) and glutamic acid (E) is introduced. The hydrophilic groups are known to form a hydration layer and create a physical energy barrier that prevents adsorption. In addition, the zwitterionic ions are alternately negatively and positively charged, thus reducing the electrostatic interaction with foreign substances and It is effective in inhibiting nonspecific adsorption. (2) Peptide-to-peptide interaction domain: inspired by fibroin, a protein of silk thread. The repetitive sequences of glycine (G) and alanine (A) are introduced. Here we expect the formation of a strong and stable peptide monolayer derived from the β-sheet. (3) Scaffolding domain: rich in pi-electrons and expected to be robustly stacked with two-dimensional materials. A repetitive sequence of tyrosine

(Y) and a hydrophilic cysteine (S) was introduced. The peptide designed in this study differs from previous ones in that its interaction site with graphene is biased towards the C-ter-

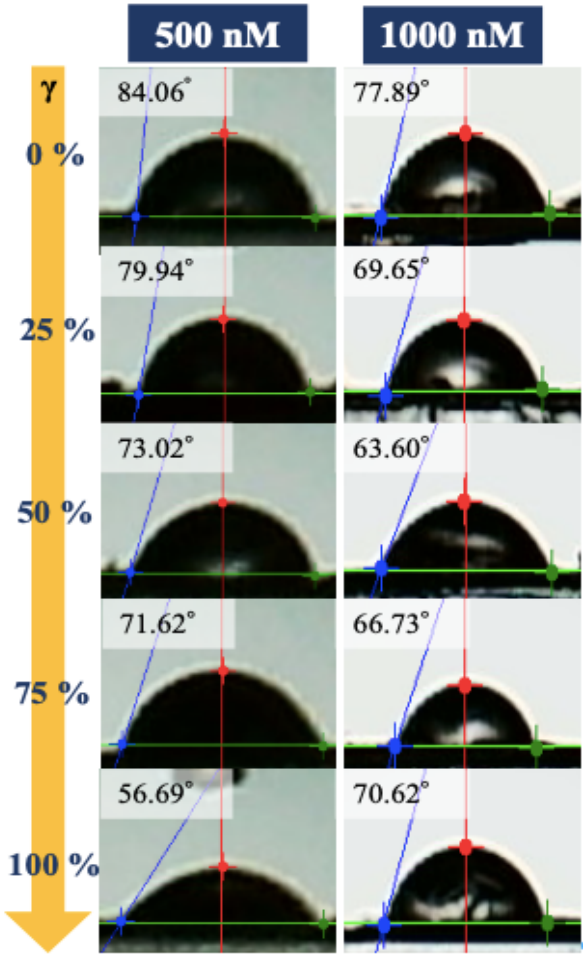

Fig. 2 Contact angle on HOPG: optical images of water droplets on HOPG. The surface of HOPG was functionalized by co-assembly of two peptides, SY and KESY with a mixture ration of γ.

minus. Therefore, we designed it with the aim of creating a structure in which the antifouling domain, which is the N-end side, protrudes uniformly on the surface. The aqueous solution was placed on the surface of graphite to form a self-assembled film of peptides. The surface structure of these samples was assessed using atomic force microscopy (AFM), and the peptides the increase in coverage with increasing concentration and the hexagonal-object self the organized structure was confirmed (Fig. 1). Furthermore, mixing the two peptides of SY and KESY enables us to control the surface hydrophilicity in a contentious manner, which was observed by water contact angle measurements (Fig. 2). The ability of the self-assembled peptides for the anti-fouling of the surface was demonstrated on graphene field effect transistors (GFETs) by using bovine serum albumin (BSA) which is often used a model protein for non-specific adsorption on a surface. The result showed that the conductivity of GFET was not affected by the BSA in the case of the peptide treated GFET.

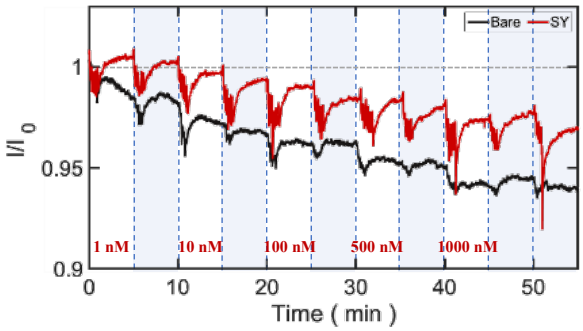

Fig. 3 Conductivity change of graphene field effect transistor (GFET) under 10mM phosphate buffer. While the black curve shows the conductivity change with untreated GFET, the red curve shows the result GFET treated by 100nM peptides. At the each moment, BSA with various concentrations was injected to the test solution to see the impact on the current in the GFET. The peptide-treated GFET shows less change of the conductivity by the BSA.

3. Conclusions

Self-assembled peptides were used to functionalize the surface of graphene to suppress non-specific adsorption of biomolecules. The peptides formed a monomolecular-thick film on the graphene surface in a manner of self-assembly. Graphene surfaces can be simply coated by peptides with a wet process with peptide solution. This new approach allows us to functionalize the surface of graphene in a cost-effective way for biosensing.

Acknowledgements

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