Control of peptides interactions on two-dimensional nanomaterials

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The Aim of this research
Our research target is the control of the interface between biotechnology and nanotechnology. More specifically, we utilize solid binding peptides or artificially-designed peptides which have specific binding affinities to solid surfaces and an ability to form peptide nanostructures on atomically flat surfaces. These peptides self-assemble into monolayer-thick nanostructures on surfaces of two-dimensional (2D) nano-materials, such as graphene with a thickness of one layer of atoms. New design of peptide sequences and selections of nanomaterials templating peptide self-assembly can create a complex Bio-Nano system, which has two different features arise from the peptides (self-assembly) and nanomaterials (unique electronic properties). In this research, we have focused on a system consists of peptides and graphenes. Graphene is a representative nano-material, which has been intensively investigated by scientists in the past 10 years due to its chemical inertness, mechanical stability, and unique electronic property arises from \( \pi \)-electrons. In the last academic year, we have utilized other 2D nano-materials as well, such as two-dimensional metal chalcogenides (TDMCs) and boron nitride, to study and explore new hybrid system towards establishing a new optoelectronic system. TDMCs are new types of nanosheets recently gaining a wide interest due to their various electric properties, such as semiconducting and insulative. Boron nitride is an insulative nanosheet and a family of graphene with honey-cum structures of nitrogen and boron atoms instead of carbon atoms. The semiconducting nanosheets are good for opto-electrical measurements. In this year, we have focused on the investigation of the electronic interactions between peptides and such semiconducting nanosheets. In addition, we tried to control the peptide self-assembly by external stimuli like electrochemical potential and pH of solution.

Achievements

(1) Understanding of electrical interactions in peptides on single-layer MoS\(_2\)
Here, we investigate the optoelectronic properties of MoS\(_2\) field effect transistors (FETs) fabricated with a resist-free indium micro-soldering technique before and after incubating with peptides (Fig. 2). We utilized two
different peptides, which have positive and negative charges respectively. The both peptides have a binding affinity to MoS$_2$, resulting in a formation of a confluent film on the surface. We carried two experiments: electrical conductivity measurement and photoluminescence (PL) measurement. The PL spectra of the devices were measured over various back-gate voltages to observe the optoelectronic response of the device under an excitation of a 532 nm laser. The results of the pristine MoS$_2$ FET (before coating the peptides on it) show the A (exciton), A- (trion) and B (spin-orbit split) direct gap transitions have a change in their PL intensity and peak energy depending on the applied gate voltage, consistent with those reported in previous studies. After coating peptides on the surface, the trend of the gate response in the FETs shows drastic change. First of all, the both peptides show a significant decrease of the PL intensity. And the trion intensity became dominant over excitons intensity. On the other hand, the negative peptide shows thresh voltage shift in the electrical measurement and the positive peptides shows no shift. It suggests that the optical process in the MoS$_2$ under laser excitation responds sensitively to the adsorbed any peptides. However, the charge carrier density in the MoS$_2$ modulated by peptides can be different depending on the kind of peptides. We have gained the important insight on the MoS$_2$ optoelectronic response to the peptides adsorption in this work.

(2) Electrostatic interactions of peptides with solid surface during the self-assembly

Electrostatic interaction between proteins and surfaces is one of the most essential parameters in the protein adsorption or self-assembly on solid surfaces. Although the adsorption of proteins has been studies with respect to the electrochemical surface potential, the self-assembly of proteins forming nanostructures on surfaces has not been studied in the relation with the surface potential. In this work, we utilize graphite binding peptides which have a specific binding affinity to graphite, and investigate the relationship between the electrochemical potential of the highly ordered pyrolytic graphite (HOPG) and peptide self-assembly on the surface. Under zero electrical bias, graphite binding peptides form nanowire structures with few nanometer thickness and width and micrometer length. Depending on the surface potential, the peptides sensitively change their nanostructure from small islands to longer nanowires. We also test gold binding peptides as a control and observe that they do not show any significant dependence on the surface potential. Our results show a new way to control the peptide self-assembly by mean of applied electrical bias and the importance of the relationship between amino acid sequence of peptides and surface potential in their electrostatic interactions.

(3) Effects of pH and ionic strength on peptide self-assembly

Self-assembled, highly ordered monolayer films of a genetically-selected graphite-binding dodecapeptide and two of its mutants were prepared by room temperature incubation of dilute (0.1~2.8 µg/mL) aqueous solutions on atomically flat, crystallographically pristine graphite substrates. The self-assembled nanostructures were characterized by atomic force microscopy, and observed to change as a function of either salt concentration or pH, over a pH range of 3.5 to 10.5 in sodium phosphate buffer solutions. The modular nature of the peptide, having a 4-amino acid anchoring domain that binds to graphite, and an 8-amino acid amphiphilic tail domain that enables self-assembly, provides a means to control molecular interactions using point mutations. These effects of electrolyte concentration and pH on the peptide nanostructures are attributed to ionic screening of the charged residues in the peptides, and changes in the molecular folding.