CHEMICAL AND BIOLOGICAL SENSORS USING GRAPHENE FIELD-EFFECT TRANSISTORS

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Graphene, planar sheet of sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice, have high potential for sensing applications. Gas molecules and protein adsorptions onto the graphene surface have been electrically detected by graphene field-effect transistors (G-FETs). In this work, we investigated the chemical and biological sensing characteristics using bare and modified G-FETs. As results, solution pH and monovalent ions can be detected by the bare G-FETs with very high sensitivity. And charged proteins can be also electrically detected. By using modified G-FETs, specific biological sensing could be realized.

Single-layer graphene flakes were obtained from kish graphite (Covalent Materials Corp., Tokyo, Japan) by a mechanical micro-cleavage technique using adhesive tape. The G-FET was fabricated on a thermally oxidized 280--nm--thick SiO_2 layer on a p^+-Si substrate. Single-layer graphene flakes were identified by Raman spectroscopy. Gold source and drain electrodes were formed by conventional electron beam lithography, vacuum evaporation, and lift-off procedure. In sensing measurements, a silicone rubber pool was put on the device and an Ag/AgCl reference electrode was used as the top-gate electrode to minimize environmental effects.

The drain current (I_D) versus top-gate voltage (V_{TG}) changed by the solution pH, monovalent ions. Especially, the detection limit (Resolution: signal/noise=3) of the solution pH is as small as 0.025, indicating their high potential for the chemical sensors. The bare G-FETs can also electrically detect the protein adsorption on the graphene channel surface because proteins usually charged in the buffer solution owing to their amino and carboxyl group. However, the bare G-FETs cannot distinguish the each of proteins. In order to realize the specific sensing, receptor-modified G-FETs are needed.

There are two requirements for functionalization process. One is that the height of the receptor molecules on the graphene channel must be smaller than that of the Debye length (Electric double layer). The other is that the functionalization processes must be carried out without introducing defects on the graphene surface. In this study, immunoglobulin E (IgE) and anti-IgE aptamers were used as a target and receptor molecules, respectively. Aptamers are the oligonucleic acid binding to the specific target molecules. The aptamers were functionalized on the graphene surface with 1-pyrenebutanoic acid succinimidyl ester. The pyrenyl group of the linker interacts strongly with the basal plane of graphite via π-stacking. After functionalization process, the drain current increased owing to the negatively charged aptamers. And the slopes of the I_D-V_{TG} curves were almost identical, indicating that no defects were introduced on the graphene surface by the functionalization process. The drain current suddenly decreased after adding the buffer solution with target IgE molecules while almost no current changes were observed after adding the solution with non-target proteins of bovine serum albumin and streptavidin.

The dissociation constant (K_D) between IgE and IgE aptamers was estimated by the IgE concentration dependence of the I_D change. From the fitting curve with Langmuir adsorption isotherm, the K_D was estimated to be about 50 nM. The value of the K_D was comparable with those of other sensing techniques such as quartz crystal microbalance, capillary electrophoresis, fluorescent, and gradient micro free flow electrophoresis, indicating that the modified G-FETs are promising candidates for label-free biological sensors.