Highly Sensitive and Selective SPR Biosensing Using Graphene Oxide

Yury Stebunov, Aleksey Arsenin

Laboratory of Nanooptics and Plasmonics, Moscow Institute of Physics and Technology,
Dolgoprudny 141700, Russian Federation
ystebunov@gmail.com

The last few years the growing branch of the graphene research has focused on the properties and applications of graphene oxide (GO). Graphene oxide exhibits excellent properties such as unique mechanical and thermal behavior, water solubility, a simple method of synthesis, a possibility of chemical or thermal reduction, a simple film deposition process, and conjugation with a variety of biomolecules [1]. All these features make GO a promising candidate for biosensing. Also graphene oxide films have the large surface area, which provides more surface sites for adsorption of biomolecules. So we proposed the biosensor chip based on the thin graphene oxide films for the highly sensitive and specific biosensing using surface plasmon resonance technique.

Surface plasmon resonance biosensing is a powerful instrument for the label-free biosensing, which allows not only to detect the presence of specific molecules in the test solution, but also to study the kinetics of biochemical reactions. Recently several papers were published about the graphene using for SPR biosensing. When graphene was used as a substrate for biomolecules adsorption, the adsorption capacity of proposed scheme was higher than for the thiol-functionalized surface widely used for SPR biosensing [2]. But the described biosensing scheme is non-specific which means that the molecules of different types presenting in the fluid sample can be adsorbed on the graphene surface. Also several papers were published about the influence of graphene on the distribution of the surface plasmon field near the metal film. It was obtained that thin graphene layers deposited on the surface of metal film could improve the sensitivity of SPR biosensing and the increase in the sensitivity is proportional to the number of graphene layers [3-4].

Figure 1 outlines the manufacturing process of the sensor chip intended for biosensing of oligonucleotide sequences. The surface plasmons are excited at the interference between metal films and dielectric media, for our experiments we used the 40 nm thick gold film with 2 nm Ti underlayer deposited on the borosilicate glass. The next step is the deposition of the thin graphene oxide film on the surface of metal. The graphene oxide is deposited from the aqueous solution using the spray-coating technique with the GO flake mean size of about 0.5-1 um. After that the layer of streptavidin molecules was created on the surface of the graphene oxide film. The 100 ug/ml streptavidin solution in 10 mM sodium acetate buffer was injected in the flow cell for 7 min. After streptavidin injection the solution of 200 nM biotinylated oligos in PBS buffer was injected for about 5 min, and due to the biotin-streptavdin interaction the layer of biotinylated oligos was formed. The last stage is an injection of the test solution containing the target oligos, the detection is based on the fact that target oligos interact with the complementary biotinylated oligos. It worth noting that during the processes of the biotinylated oligos and target oligos depositions other molecules do not interact with the surface of the sensor chip which is explained by the uniformity of the streptavidin layer formed on the surface of graphene oxide. Figure 2 illustrates the amount of the biotinylated oligos adsorbed on the surface of the graphene oxide based sensor chip and on the surface of the biochip based on the 150 nm thick layer of the carboxymethylated dextran. In the case of the GO sensor biochip 30% more oligos adsorbed showing the increase in biosensing sensitivity.

In conclusion we proposed the novel sensor chip for SPR biosensing based on the graphene oxide. It shows the increased sensitivity of biosensing compared to the conventional SPR sensor chips based on the self-assembled monolayers of alkanethiolates and the hydrogel layers. Graphene oxide is an excellent choice for using as a linking layer between metal film and layers of biomolecules in SPR sensor chips due to the possibility to create highly selective sensing surface of various types of biomolecules. High bioreactivity of graphene oxide is explained by the mechanism of pi-stacking interaction of GO with almost all types of biomolecules [5]. Also deposition of the biomolecules on the surface of the graphene oxide films is realized without using of any activation process required in the cases of hydrogels and self-assembled monolayers of alkanethiolates. Furthermore GO films deposited on the surface of the metal are stable and could protect the surface of the metal film. It allows us to design biosensing schemes based on the silver films instead of the gold ones, because of silver shows better plasmonic properties [6], but it is too reactive at ambient conditions.

References

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Figures

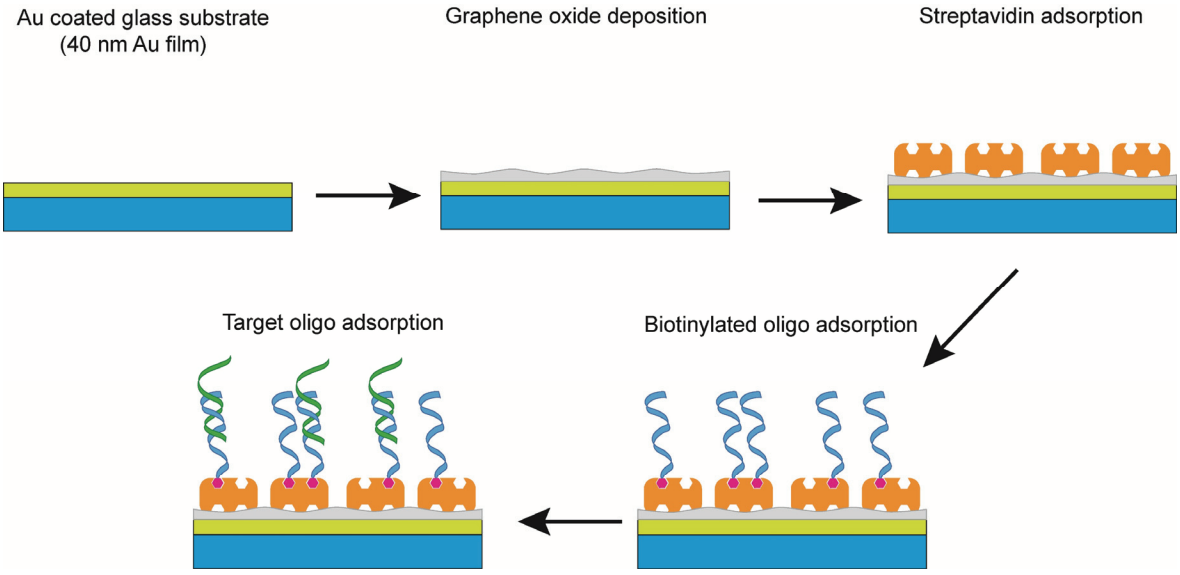

Figure 1. Scheme of the manufacturing process of the SPR sensor chip intended for the sensing of oligonucleotide sequences.

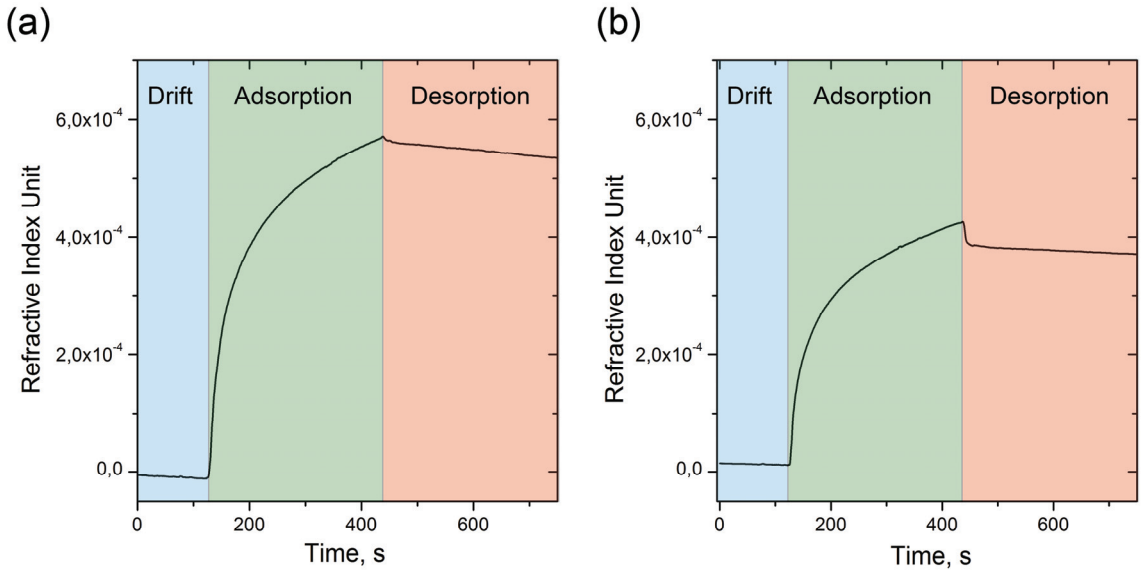

Figure 2. The kinetics curves of the biotinylated oligos adsorption on (a) the graphene oxide based sensor chip and on (b) the sensor chip based on the carboxymethylated dextran.