Graphene oxide as a novel component in optical biosensors for the detection of biomolecular interactions and enhancement of detection sensitivity

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The development of advanced nanostructured materials offers new opportunities for the design of high-performance optical sensors, including those based on surface plasmon resonance (SPR). Optical biosensing based on SPR is widely used today to investigate biochemical reactions in scientific and pharmaceutical and food research or medical diagnostics. The integration of graphene oxide (GO) with SPR-based biosensors represents a promising strategy for enhancing sensitivity and selectivity in real-time, label-free detection. Owing to its unique structure, large specific surface area, and abundance of functional groups, graphene oxide can amplify the detection signal through π–π interactions and an increase in the local refractive index, while also serving as an efficient interface between the gold sensor surface and biomolecules. This work presents a methodology for modifying gold SPR sensor surfaces with graphene oxide, along with an analysis of the impact of this functionalization on the biosensor's detection performance.

The aim of this study was the controlled and reproducible deposition of mono- and multilayer graphene oxide (GO) films on gold surfaces, along with their comprehensive physicochemical characterization. Various GO suspensions were analyzed, including the determination of particle size, zeta potential, stability, and the presence of functional groups using techniques such as DLS, UV–Vis spectroscopy, and XPS. Model gold-coated QCM-D crystals and dedicated gold SPR sensors were employed for layer deposition. The films were fabricated using the layer-by-layer (LbL) approach, applying both dip-coating and spin-coating techniques. By employing the layer-by-layer (LbL) self-assembly technique (based on electrostatic interactions between layers of charged various nano-objects), we construct hybrid films with precise control over thickness, charge distribution, and chemical functionality, allowing us to directly correlate the structural evolution of the multilayers with their characteristics. Comprehensive spectroscopic, microscopic and morphological analyses were done using: quartz crystal microbalance with dissipation monitoring (QCM-D) measurements, scanning and transmission electron microscopy (SEM/TEM), atomic force microscopy (AFM), ATR-FTIR and SPR cell combined with ellipsometer EP4 Accurion. Through systematic variation of the layer composition and choice of polyelectrolyte such as PDADMAC, PEI, PAH and PLL we demonstrate that the sensory behavior of these hybrid films can be tuned. The obtained mono- and multilayer GO films were expected to exhibit high surface coverage and stability. A correlation between the sensitivity of the gold SPR sensor signal and the number (thickness) of GO layers deposited on its surface was also established. Subsequently, protein solutions (antibodies/antigens) were immobilized on Au and GO surfaces through appropriate reactions or interactions. The immobilization process of antibodies/antigens was monitored and analyzed in real time using the QCM-D technique.

Surface functionalization with graphene oxide can significantly enhance the sensitivity and selectivity of SPR sensors, making it a promising approach for modern detection platforms. These studies will contribute to expanding knowledge on the application of advanced nanomaterials, including graphene oxide, in the biochemistry of sensor systems, as well as in diagnostics, environmental monitoring, and biomedical research.

Keywords:
graphene oxide, polyelectrolytes, sensors, SPR, coatings, layer-by-layer

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