Graphene as Chemical Receptor for Plasmonic Enhanced Sensing of Small Molecules

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One of the envisioned applications of carbon nanomaterials are chemical and biological sensors. We will introduce a novel concept in optical sensing of small molecules by using graphene as receptor, but also to enhance the sensitivity of surface plasmon resonance (SPR) spectroscopy towards the detection of small analyte molecules.
Surface plasmon resonance is a powerful technique to detect changes in refractive index in a sensitive layer of about 300 nm thickness next to a metallic surface. Because of this relatively large sensitive range, it is challenging to detect small molecules, as the change in refractive index upon binding of those molecules to the surface gets too small compared to the signal noise. Here we overcome this limitation by generation of a hybrid sensor surface consisting of a gold layer modified by graphene which confines and enhances the plasmonic field. By miniaturization and fully integration of a fluidic system a sensor was realized allowing the label-free real-time monitoring of oxipurinol, a persistent metabolite of the drug allopurinol, present in tab water. At present stage control measurements for this analyte are labour and time consuming and faster online methods are demanded.
In a first study the SPR sensor was modified by graphene which can be used as recognition element, utilizing its sp^2 hybridized electron system for π stacking, and which additionally enhances the sensitivity due to localized surface plasmon introduction. Graphene was fabricated by different methods, such as chemical (rGO), mechanical (meG) and electrochemical exfoliation (ECG), to be used as receptive layer in the SPR setup for the detection of oxipurinol. A strong dependence in the sensitivity on the fabrication method of the 2D material was found, with the best result for meG. A relation to the number of defects in the resulting graphene material is discussed. The limit of detection for oxipurinol detection is 47 ± 3 $\mu g \cdot L^{-1}$.

Figures

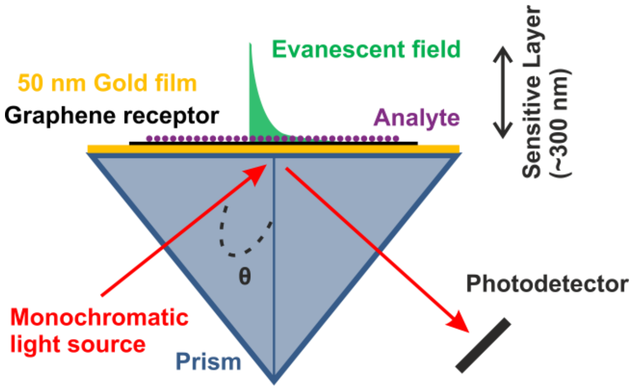

Figure 1: Scheme of a SPR setup, which measures a refractive index, sensitive to changes at the sensor surface. A laser with λ = 650 nm is used for excitation. Graphene is used as receptor layer.

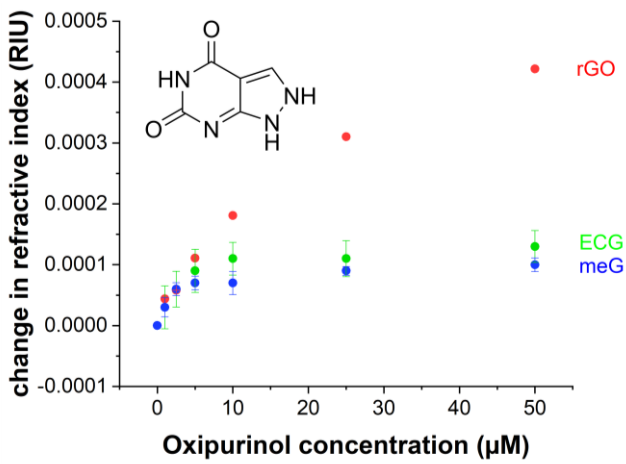

Figure 2: Change in refractive index as a function of the oxipurinol concentration for receptor layers consisting of different graphene materials.