Facile Functionalization of Graphene to Tune Response of Printed Electrochemical Sensors to Neurotransmitters

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Abstract

Neurotransmitters are small molecules involved in neuronal signaling and can also serve as stress biomarkers.[1] Their abnormal levels have been also proposed to be indicative of several neurological diseases such as Alzheimer's disease, Parkinson's disease, Huntington disease, among others. Hence, measuring their levels is highly important for early diagnosis, therapy, and disease prognosis. In this work, we investigate facile functionalization methods to tune and enhance sensitivity of printed graphene sensors to neurotransmitters. Sensors based on direct laser scribing and screen-printed graphene ink are studied. These printing methods offer ease of prototyping and scalable fabrication at low cost.

The effect of functionalization of laser induced graphene (LIG) by electrodeposition and solution-based deposition of TMDs (molybdenum disulfide[2] and tungsten disulfide) and metal nanoparticles is studied. For different processing methods, electrochemical characteristics (such as electrochemically active surface area: ECSA and heterogenous electron transfer rate: k^0) are extracted and correlated to surface chemistry and defect density obtained respectively using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. These functionalization methods are observed to directly impact the sensitivity and limit of detection (LOD) of the graphene sensors for the studied neurotransmitters. For example, as compared to bare LIG, it is observed that electrodeposition of MoS_2 on LIG improves ECSA by 3 times and k^0 by 1.5 times.[3] Electrodeposition of MoS_2 also significantly reduces LOD of serotonin

sensitivity and limit of detection (LOD) of the graphene sensors for the studied neurotransmitters. For example, as compared to bare LIG, it is observed that electrodeposition of MoS_2 on LIG improves ECSA by 3 times and k^0 by 1.5 times.[3] Electrodeposition of MoS_2 also significantly reduces LOD of serotonin and dopamine in saliva, enabling detection of their physiologically relevant concentrations (in pM-nM range). In addition, chemical treatment of LIG sensors is carried out in the form of acetic acid treatment. Acetic acid treatment has been shown previously to improve C-C bonds improving the conductivity of LIG sensors.[4] In our work, in particular, acetic acid treatment leads to larger improvement of LOD of norepinephrine compared to MoS_2 electrodeposition.

In addition, we investigate the effect of plasma treatment to tune the sensor response by modifying the defect density and chemistry. For example, we find that oxygen plasma treatment of screen-printed graphene ink greatly improves LOD of norepinephrine up to three orders of magnitude, which may be attributed to the increased defects and oxygen functional groups on the surface as evident by XPS measurements. Defects are known to play a key role in enhancing the sensitivity of 2D materials to surface interactions, and have been explored in tuning/enhancing the sensor sensitivity.[5] Building on our previous work,[3] we apply a custom machine learning-based data processing method to further improve that sensitivity and LOD, and also to automatically benchmark different molecule-material pairs.

Future work includes expanding the plasma chemistry and conditions, studying the effect of precursor mixture in laser-induced solution-based functionalization, and understanding the interplay between molecule-material system. Work is also underway to improve the machine learning model by using nonlinear learning models such as neural networks to improve the sensor sensitivity, selectivity, and robustness.

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