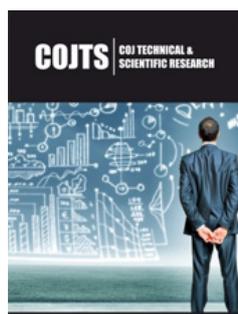


Significance of Functional Group in Indole Molecule: Toward Sensitivity of Biosensor

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Abstract

In this opinion, I focus my attentions on the effect of the functional group in indole molecules onto their potential response with disuccinimidyl suberate (DSS) modified indium tin oxide (ITO) electrode. It was aimed to discuss the variation of potential response of self-assembled monolayer modified ITO electrode for various molecules containing indole ring. A great response with different sensitivity was demonstrated to achieve a linear relationship with the different analyte concentration. However, the magnitude of the potential shift was found to depend on the molecular structure. From a fundamental viewpoint, it seems that interest is based not only on high sensitivity but also on the effect of the functional group substituted onto the indole ring.

Keywords: Modified electrode; Potential response; Sensitivity; Biomolecules; Functional group

Introduction

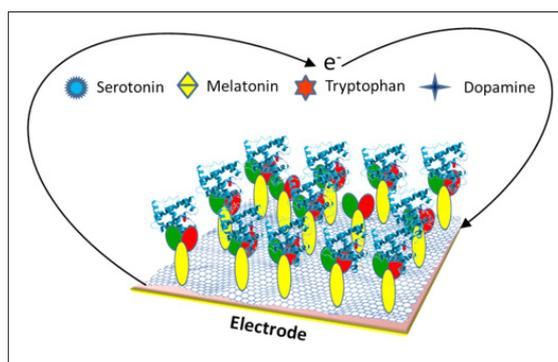


Figure 1: SAM modified electrode for biomolecule detection.

Detection of biomolecules is of great interest in the view of biological and medical science from last few decades. Different types of modified electrodes have been used as amperometric/potentiometric sensors for this purpose of detection (Figure 1). Recently, we found that the successive modification of an ITO electrode with aminopropyltriethoxysilane (APTES) and disuccinimidyl suberate (DSS) is useful for the potentiometric sensing of molecules containing an indole ring [1-3]. A commercial development of biosensors for industrial applications requires their optimization in terms of the stability and sensitivity [4]. The sensitivity of the biosensor is very important for practical applications. The sensitivity depends not only upon the adsorption on the surface but also upon the bioactivity, immobilization, and interaction conditions etc. We focus our attention on the structure of the indole molecule as one of the factors affecting the magnitude of potential shift. Several researchers have reported the effect of the functional group on the electrochemical behaviour of indole molecules [5-7]. We showed that the enhancement of the potential shift depended on the substituted group that was introduced into the indole ring. Molecules containing the 5-hydroxy group on their indole ring have an enhanced potential shift [1]. It is well established that the transport properties of a molecule to electrode depend on the intrinsic properties of the molecule, such as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the molecular conformation, and the molecular bond characteristics (e.g., saturated versus unsaturated). In addition, the

chemical groups anchoring the molecule to the electrode, the work function of the electrode, and the contact geometry of the molecule-electrode interface [8,9]. From our experiment it was clear that the enhanced potential shift with 5-hydroxy group, such as serotonin (5HT), 5-hydroxyindoleacetic acid (5-HIAA), and 5-hydroxy

tryptophan (5-HTP) is stronger than that of with 5-methoxy group, such as melatonin (MT). Large potential shift might be obtained for 5-hydroxy indoles during measurement concerning their redox reaction that enhanced the sensitivity during potentiometric measurement.

Significance of functional group

Table 1: Analytical parameters for 5-HT, 5-HTP, 5-HIAA, and MT measurement. The sensitivity was calculated from the slope (correlation coefficient was 0.995 in all cases).

Analyte	Sensitivity mV decade ⁻¹	Linear Range mol/L	Detectable Concentration mol/L
5-HT	198	1nM to 100µM	0.1nM
5-HTP	124	1nM to 100µM	1nM
5-HIAA	132	1nM to 100µM	1nM
MT	78	1nM to 100µM	1nM

Previously we have reported that DSS treated ITO can detect several biomolecules. (Table 1) shows the sensitivity and detection limit of 5HT, 5-HIAA, MT, and 5-HTP with DSS modified ITO electrode. A high sensitivity of 198mV decade⁻¹ with a minimum detectable concentration of 0.1nM was observed for 5-HT, whereas for 5-HTP, 5-HIAA, and MT, the sensitivity was 124, 132, and 78mV decade⁻¹, respectively. Even though 5-HT, 5-HTP, and 5-HIAA are redox active molecules bearing the 5-hydroxy group in their indole ring, the highest sensitivity and lowest detection limit was observed for 5-HT.

A possible explanation can be given by focusing attention on

the side chain on C3 position of indole ring. 5-HT has an uncharged side chain, whereas 5-HTP and 5-HIAA have a negatively charged carboxylic group in the side chain (Figure 2). The redox-active moiety in the compounds and the radicals is the indole ring whose electronic structure may affect by the electron-donating or electron withdrawing group substituted in the C3 position. The influence of the charge of the side chain of 5-hydroxyindole derivatives on the kinetics of their reactions with charged substrates might affect the magnitude of the potential shift in electrochemical measurement [10]. As a result, we observed higher potential shift for 5-HT, comparing with 5-HTP and 5-HIAA.

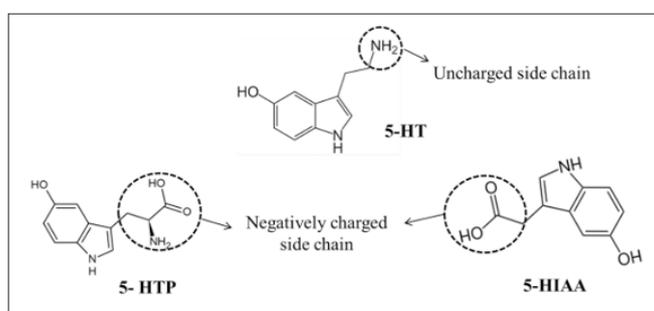


Figure 2: Structure of 5-HT, 5-HIAA, and 5-HTP.

For the efficient charge transfer, the relative position of donor LUMO and acceptor LUMO is crucial [11]. For the efficient charge transfers from donor to acceptor component, effective charge transport are important parameters for different potential response mechanism elucidation (Figure 3). To estimate the relative position of HOMO/LUMO levels, valuable information can be given by electrochemical data [8,11]. During potentiometric measurement the knowledge of these levels is required to find the donor-acceptor behavior. The values of energy levels of LUMO and HOMO and energy band gap estimated from the electrochemical data can be an explanation of the effect of function group on the potential shift. 5-hydroxy indoles have a high electron density at the HOMO level [11]. When the LUMO level shifts towards downwards as the

acceptor group in the backbone increases, then the electron affinity increases as the number of acceptor group increases [8], thereby we might observed enhance potential shift for 5-hydroxy indoles. But the highest response was observed for 5-HT with additional uncharged side chain onto the indole ring. This indicates that the decrease in LUMO is more as compared to that of the HOMO. In the case of melatonin, the formerly HOMO-1 in indole introduced by methoxy substituent as an additional node in the molecular, and which becomes the HOMO in 5-methoxyindole. By this way the energy ordering between indole, 5-methoxyindole and melatonin are changes for the HOMO and HOMO-1 [9]. Hence, the energy mismatch of LUMO levels will be more than the mismatch of HOMO levels at the interface [9,12].

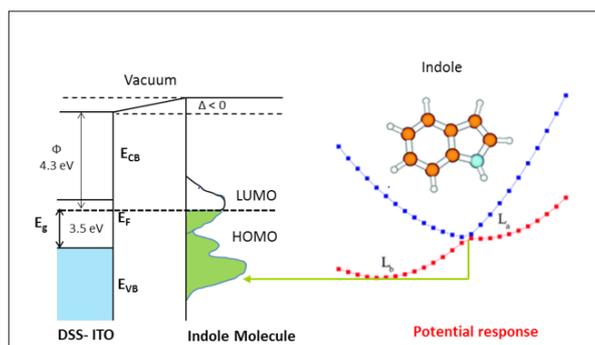


Figure 3: Equilibration of chemical potential leads to a charge transfer.

Concluding remarks and recommendation

The contribution of redox processes and functional group attached to the indole ring to the potential response of the electrode seems important from the above discussion. 5-hydroxyindole with uncharged side chain shows higher response than those has a negatively charged group in the side chain. It is evident that the enhanced potential shift is closely related to the functional group substituted onto the indole ring. Details mechanism considering the electronic structure of indoles can be a future target investigation. A details density functional theory (DFT) calculation might be effective to understand density of energy states of different analyte and their response behavior.

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