Journal of The Electrochemical Society, **165** (13) B638-B643 (2018)
0013-4651/2018/165(13)/B638/6/$37.00 © The Electrochemical Society

Trilacunary Keggin Type Polyoxometalate-Conducting Polymer Composites for Amperometric Glucose Detection

Rukiye Ayranci,[1] Yasemin Torlak,[2] Tugba Soganci,[1] and Metin Ak [1,z]

[1]*Pamukkale University, Faculty of Art and Science, Chemistry Department, Denizli, Turkey*
[2]*Pamukkale University, Cal Vocational High School, Denizli, Turkey*

A new amperometric glucose sensor has been fabricated based on a composite film prepared by electrochemical polymerization of carbazole derivative with having free amino group in presence of the Keggin type polyoxometalate (POM) anion, $(n\mathrm{Bu_4N})_3[\mathrm{PW_9O_{34}}(t\mathrm{BuSiOH})_3]$. During the electropolymerization of 3-Amino-9-ethylcarbazole (AAC) on graphite electrode, simultaneously the POM has entrapped in the produced PAAC polymer film. POM/PAAC composite film was successfully synthesized and characterized with electrochemical techniques and surface morphology analyses. Metal/organic conducting polymeric composite has been composed of positively charged PAAC based conducting polymer and negatively charged POM structures. The amperometric response of the POM/PAAC-GO_x modified electrode versus varying concentrations of glucose was studied at a potential value of −0.7 V (Ag/AgCl). It was determined that the POM/PAAC composite structure with the best sensor response has the lowest oxidation potential among the composite structures prepared at different ratios. Sensitivity of the POM/PAAC based sensor platform for actual glucose detections has been calculated as $66.66\mu A\ mM^{-1}cm^{-2}$ with a linear detection range from 0.1 to 10 mM and detection limit of 0.099 mM. The POM/PACC composite has a unique structure thanks to such advantages the multiple redox reaction, high reactivity and rapid electron transfer of POMs. Especially, as-prepared this composite displayed high electrocatalytic activity for the amperometric detection of glucose with rapid response time, good sensitivity and reproducibility, acceptable recovery and simple preparation.
 [DOI: 10.1149/2.1061813jes]

Manuscript submitted July 16, 2018; revised manuscript received September 14, 2018. Published October 12, 2018.

Polyoxometalates (POMs) offer a well-defined class of inorganic early transition metal oxide clusters which are well known with their catalytic properties. They have electronic application fields such as gas and chemical sensors, electrochromic displays, capacitors, and electrochemical cells. There are advantages such as its reversible progressive redox reactions and they act as electron reservoirs which are important for electronic applications. Thanks to their multifunctional properties, POMs can be used in different application areas such as biotechnology, medicine, nanotechnology, materials science and catalysis.[1–3] This class of early transition metal oxide clusters has different redox characteristics. They act like a redox catalyst in many different areas such as analytical chemistry, catalysis and medicine.[4,5] By incorporating POM clusters into conductive polymer chains with interesting electrical optical properties, metal/organic hybrid composite structures with unique properties can be obtained. POMs can be immobilized into conductive polymers by different methods. The first of these methods is adsorption of POM on the electrodes by dip coating.[6] The second method is the electrodeposition of POM on the electrode surface. The third method involves trapping the POMs into conducting polymers accumulated on the electrode surface by utilizing the interaction with conducting polymers.[7,8] Although studies on sensor applications of POM/conducting polymers composite structure in literature are very limited, the constructing of sensors that utilize superior properties of the POM clusters could provide a numerous advantages in term of sensitivity, selectivity and detection limits.[9–11]

In recent years conductive polymers have been widely used in amperometric sensor applications for determination of some analytes such as glucose, cholesterol,[12] ethanol.[13] For detection of glucose, electroactive monomers containing the free amine functional group such as SNS-NH_2, m(SNS-NH_2),[14] HKCN,[15] (TBT_6-NH_2)[16] have been synthesized and polymerized on the graphite electrode. Thanks to the copolymerization method, the electroactive monomers, which do not have functional groups to bind the enzymes, have found opportunity to use in sensor applications.[17–19] Moreover, carbazole based conducting polymers have advantages to use in sensor applications due to having high electron mobility, photochemical and thermal stability.[20–23] As an example, 3,6-linked carbazole derivatives have been attracted a remarkable interest for electrochemical biosensor. 2,7-linked carbazole derivatives have demonstrated hopeful electrochromic properties in the visible range, while the substitution at N-position of carbazole has primarily employed for more readily soluble in common solvents.[24] Electrochemical methods have been widely used in glucose detection in recent years due to theirs high selectivity and sensitivity.

In the most of the electrochemical sensors, there is a current response that occurs during glucose oxidation on the graphite electrode surface. Additionally, the performance of glucose biosensor depends on the electron transport ability and the catalytic activities of metal oxide nanoparticles or metals. Moreover, POM containing nano-hybrid materials owing to their redox reactions and excellent electrical and optical properties[25] are very important place in the field applications electrochemical catalysts in the detection of nitrate, iodate, bromate, H_2O_2 and glucose.[26,27] POMs can be immobilized to the electrode surface with the aid of methods such as Langmuir-Blodgett (LB) and electrodeposition. POMs have an advantage in the electrochemical glucose sensor because of their electrocatalytic effects.

In this work, a metal/organic hybrid composite film was prepared by electrochemical polymerization of carbazole derivative containing free amine functional group in the presence of Keggin type polyoxometalate for sensor applications. We have used trapping method for incorporate the POMs into conducting polymers as describe in the literature to construct composite electrodes. The metal/organic hybrid composite structure has been formed on graphite electrode by electrostatic interactions between anionic POM clusters and cationic polycarbazole chains (PAAC) formed by electropolymerization. After the GOx enzyme has been immobilized through the free amine groups, the metal/organic hybrid structure exhibits exceptional electrocatalytic activity toward glucose oxidation. POM clusters capable of multiple and reversible redox reactions in PAAC polymer chains exhibited super electrocatalytic activity in the detection of glucose. Thanks to the synergistic effect of the components, the electrochemical sensor produced by this hybrid composite has exhibited very good sensitivity, selectivity and stability in the electrochemical determination of glucose. As a result, POM/PAAC composite can be used as an alternative and efficient electrochemical sensor platform for future sensor applications.

Experimental

Chemicals.—The trilacunary silan-grafted Keggin type POM $(\mathrm{nBu_4N})_3[\mathrm{PW_9O_{34}}(\mathrm{tBuSiOH})_3]$ was synthesized in accordance with the previously reported procedure.[28] Lithium perchlorate ($LiClO_4$) and acetonitrile (ACN) were purchased from Merck. AAC

zE-mail: metinak@pau.edu.tr