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Non-Enzymatic Electrochemical Detection of Glucose by Mixed-Valence Cobalt Containing Keggin Polyoxometalate/Multi-Walled Carbon Nanotube Composite

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In this work, a non-enzymatic electrochemical sensor platform was developed for catalyze of glucose using graphite electrode modified with Keggin type $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}].15H_2O$ (Co-POM) and multi-walled carbon nanotube (MWCNT) composite. The Keggin type Co-POM composing of a unique mixed-valence Co(III) and Co(II) structures was confined in a matrix of MWCNT on graphite electrodes to improve the electron transfers. Cyclic voltammetry (CV) and amperometric measurements were performed to investigate the electroanalytical performance of the Co-POM/MWCNT composite for direct electrochemical oxidation of glucose. The proposed this non-enzymatic sensor platform showed a wide linear range from 0.1 mM to 10.0 mM (R = 0.9937) for detection of glucose. Besides it exhibited low detection limit of 1.21 μM and fast response time of 6s and high sensitivity of 256.4 μA mM^{-1} cm^{-2}. The results demonstrated that the proposed Co-POM/MWCNT based sensor platform has a high sensitivity, good stability, excellent selectivity, an enhanced electrocatalytic property and acceptable recovery. Therefore, Co-POM/MWCNT based sensor platform is promising potential application for the development of non-enzymatic sensor and catalyst applications.
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Electrochemical sensors for sensing glucose is widely used since their excellent selectivity and sensitivity properties.[1–10] Especially in biosensors prepared using enzymes, new surfaces are formed by using special modifications and these platforms are used in the specific determination of glucose. Because of the disadvantages of complex production procedures including high cost and short life, analytical application of enzyme-containing biosensors for glucose detection is still limited.[11] Recently, the wide variety of nanomaterials[12–15] such as carbon-based nanocomposites[9,16–18] offers the opportunity to generate electrochemical glucose sensors without enzyme since electronic, chemical and physical properties that allow increasing the sensing affectivity.[19,20] In these materials, various nanocomposite materials prepared with the contribution of MWCNT or graphene based nanomaterials constitute the most remarkable composites used for electrochemical non-enzymatic glucose detection.[21–23] Thanks to its advantageous features like high electrical conductivity, mechanical strength and stable, large surface area and structural flexibility, it is quite remarkable for composite catalysts in sensor applications. While electrocatalytic reactions occur, they act as excellent support to immobilize other particles and accelerate electrochemical kinetics. Effectively accelerates the transfer of electrons between electrode and analytes allows faster and more sensitive current response. To date, non-enzymatic glucose sensor fabrication including metal and metal oxide based graphene nanocomposites has been studied.[24,25] On the other hand, polyoxometalates (POMs) among various electrocatalytic nanoparticles have the ideal characteristic for sensor applications due to their properties such as fast, reversible, multi-electron transfer reactions, unique structural and optical properties.[26–28] A new research area has been created with the excellent performance like high sensitivity, selectivity and low detection limits of glucose sensors obtained by using POM.[25,26] For the last few years, carbon-based materials have been extensively used as appropriate matrices for POM compounds because of their electrical conductivity, powerful affinity and good chemical stability. Carbon-based material such as MWCNT[31–34] are combined with excellent features originating from the fast redox transitions of the POM compound and are used as supporting material for POM in the development of the sensor.

We have studied analytical performance of $(K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}].15H_2O)$/MWCNT composite for detection of glucose. Co-POM compound consisting of specific mixed-valence Co (III) and Co (II) structures is an influential for non-enzymatic sensor with high electrocatalytic activity toward the detection of glucose. As far as we know, many glucose sensor application studies have been published. However no paper has been reported on glucose sensing, using mixed-valence Co(III) and Co(II) $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}].15H_2O$.

When the structural properties of Co-POM are examined, it is clear that, the oxidation process of central Co^{III} and the presence of the environmental Co^{II} are the two main components that allow Co-POM to have considerable stability and catalytic activity. Accordingly, Co-POM as active sensing materials is appropriate to produce carbon-based electrochemical non-enzymatic glucose sensor. Due to synergistic effect of Co-POM and MWCNT, obtained novel sensor platform demonstrated short response time, good performance, high sensitivity and selectivity with linear range.

Experimental

Reagents and apparatus.— *Reagents.*—Acetonitrile (ACN), NaOH, H_2SO_4, HNO_3 and HCl were purchased from Merck. $K_4Fe(CN)_6$, sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$), cobalt (II) acetate tetrahydrate ($Co(OAc)_2{\cdot}4H_2O$), glacial CH_3COOH, Bu_4NBF_4 (tetrabutylammonium tetrafluoroborate), potassium persulfate ($K_2S_2O_8$), KNO_3 and D-(+) glucose were bought from Sigma-Aldrich. Besides, solutions were prepared with doubly distilled water. Stock solutions were freshly prepared as required.

Apparatus.—Electrochemical measurements were performed by using Ivium Compactstat electrochemical working station at 25°C with a conventional three-electrode system. An Ag/AgCl, Pt wire and a graphite rod were used as reference, counter and working electrodes, respectively. The FT-IR spectrum was measured on a Perkin Elmer–2000 Attenuated Total Reflection (ATR) model FT-IR spectrometer. Raman spectra of MWCNT was recorded using Renishaw InVia (the laser energy 1.58 eV (785 nm) spectrometer. UV-visible absorption spectra of Co-POM were recorded using Hitachi-U4100 spectrophotometer. The surface morphology of Co-POM, MWCNT and Co-POM/MWCNT composite was studied using scanning electron microscopy (SEM) by a ZEISS instrument. AFM images were taken in semi-contact mode with NT-MTD Ntegra AFM.

Synthesis of MWCNT.—MWCNT was synthesized by chemical vapor deposition (CVD) technique. The details of synthesis procedure were given in the literature.[35] This procedure was carried out under 600°C in high vacuum (ca. 10^{-6} mbar) using a quartz tube placed horizontally in the furnace. In order to purify MWCNT was treated with the concentrated acid solution (HNO_3-HCl).[35–37] Then, MWCNT were filtrated and washed with water and acetone.

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