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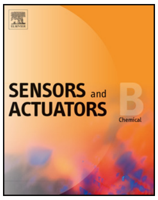

Highly sensitive and selective electrochemical sensor for detection of vitamin B12 using an Au/PPy/FMNPs@TD-modified electrode

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ABSTRACT

A new electrochemical sensor for sensitive and selective detection of vitamin B12 (VB12) was constructed by the electropolymerization of pyrrole (Py) in the presence of ferromagnetic nanoparticle-incorporated triazine dendrimer (FMNPs@TD) on a gold electrode (Au). The gold/polypyrrole/ferromagnetic nanoparticles/triazine dendrimer (Au/PPy/FMNPs@TD) electrode showed electrocatalytic activity for the reduction of VB12 in Britton-Robinson buffers. The performance and interaction of the Au/PPy/FMNPs@TD with VB12 were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), differential pulse voltammetric (DPV), UV–vis spectroelectrochemistry, and density functional theory calculations. The resulting sensor exhibited excellent performance for determination of VB12 with a wide linear range (2.50 nM–0.5 μM), highly reproducible response (RSD of 2.3%), low percentage of interferences, and long-term stability. The limit of detection (LOD) and limit of quantitation (LOQ) values for the determination of VB12 were 0.91 and 3.00 nM, respectively. The electron transfer rate constants (k_s), charge transfer coefficient (α), surface concentrations of electroactive species (Γ), and disproportionation equilibrium constant (K_D) for Au/PPy/FMNPs@TD-modified electrodes were calculated. Finally, the constructed sensor was applied to the determination of VB12 in food samples.

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1. Introduction

Vitamin B12 (VB12), also called cyanocobalamin or cobalamin, is an essential nutrient for maintenance of the myelin sheath surrounding nerve cells in humans and is useful for a healthy immune system [1]. This is also essential for multiple metabolic functions including enzyme production and synthesis of DNA during cell division, particularly bone marrow tissue responsible for red blood cell formation and the cardiovascular system [2]. VB12 has benefits to energy level, memory, mood, heart, skin, hair, and digestion. The major sources of VB12 include meat, eggs, liver, fish, clams, and milk [3]. In human physiology, VB12 is an important species requiring monitoring as deficiency causes diseases such as pernicious anemia. The daily requirement of VB12 is one to two μg, and it is essential to determine the amount. However, it seems that VB12 depends on human body weight and has a much lower typical level than other vitamins [4]. Due to the impairment of VB12 absorption during aging, people over the age of 60 are at risk of deficiency. The chemical, spectroscopic, and spectrophotometric methods for determination of VB12 including high-performance liquid chromatography, capillary electrophoresis, chemiluminescence assay, fluorimetric assay, time-of-flight mass spectrometry radioisotopic assay, microbiological assay, and other techniques have been studied and reported in detail [5,6]. The above-mentioned methods have their own advantages. However, they have certain drawbacks of being laborious, less safe, nonspecific, less sensitive, requiring sophisticated instruments, and expensive.

Among many techniques, the electrochemical method has drawn tremendous attention due to its easy operation, high sensitivity, and low cost. The electrochemical study and electroanalytical determination of VB12, based on modified or unmodified electrodes or biosensing electrodes, have been employed by various researchers [7–18]. Different electrodes, such as a carbon paste electrode modified with trans-1, 2-dibromocyclohexane, single-walled carbon nanotube-chitosan-modified disposable pencil graphite electrode, gold electrode, mercury electrode, plated bismuth-film electrode, and graphite screen-printed electrode, have been used for the quantification or determination of VB12 [7–18]. In previous studies, the various detection limits for VB12 were obtained over a wide range of pH and concentrations.

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However, most modified and unmodified electrodes used in acidic media. There were no reports focused on the determination of VB12 with higher sensitivity and interference study for several components. According to the above reports and cyclic voltammetry results, two reduction peaks for VB12 were observed [7–18]. The first peak with a more negative potential (≈−1.0 V) was attributed to the reduction of Co (II) to Co (I), whereas the second peak (≈0.0 V) was due to the reduction of Co (III) to Co (II). Normally, the first reduction peak has been used for monitoring of VB12 [7–18]. The determination of VB12 by its reduction peak current at a more negative potential and anodic stripping voltammetry can be accompanied by interference of reducible compounds, such as Fe^{2+}, Cu^{2+} or other cations, that can be reduced at negative potential values. There are several advantages of using the second reduction peak compared to the first. Increasing the possibility of complexation of Co (III) and Co (II) in the VB12 by ligands (Cob-L) and the increased concentration of VB12 in the electrode surfaces enhance the selectivity and reduce the reduction of other materials around the second reduction peak position.

The main aim of this study was to develop a highly sensitive and selective electrochemical sensor for detection of VB12. The ferromagnetic nanoparticle-incorporated triazine dendrimer (FMNPs@TD) and pyrrole monomer were fabricated on a gold electrode to produce a novel modified gold electrode (Au/PPy/FMNPs@TD). Dendrimers are a unique class of monodispersed, tree-like structures, with a large number of peripheral functional end groups. Triazine dendrimers with chemical functional groups (i.e., NH_2 group) on the periphery have wide application in organocatalysis and biomedical fields. These nanostructured macromolecules have versatility in drug delivery and high functionality with properties that resemble bioactive molecules and sensors [19,20]. In previous studies, VB12 has been studied using modified and unmodified electrodes [7–18] under acidic conditions. The advantage of using Au/PPy/FMNPs@TD-modified electrodes compared to mercury and bismuth-film electrodes includes easier usage, nontoxicity, and the use of a highly alkaline electrolyte solution. Here and unlike most previous work, the determination of VB12 has been carried out in pH = 7. Moreover, higher sensitivity, lower detection limit without any preconcentration step, and interference studies for more than 12 components were studied and considered. In comparison with other reports and for clarifying the interaction between modifier and analytes, the electrochemical, spectroelectrochemical and computational studies has been done and discussed in detail. The electrochemical behavior of VB12, relative to other works, in wide pH and scan rate range, were investigated. The important parameters such as α, k_s, Γ, K_D, and E^0 were calculated. This study led to the development of a novel Au/PPy/FMNPs@TD-modified electrode for determination of VB12 with improved capabilities such as simple electrode preparation, a wide linear range, higher selectivity, and greater stability. Also, for the first time, the second reduction peak current of VB12 at the surface of Au/PPy/FMNPs@TD was used for its monitoring. The electrochemical performance for the determination of VB12 was studied by cyclic voltammetry and UV–vis spectroelectrochemistry methods. The interaction of FMNPs@TD with VB12 was investigated by DFT calculations, e.g., natural bond orbital (NBO) and energy decomposition analysis (EDA).

2. Experimental section

2.1. Reagents

Pyrrole (Py) was obtained from Merck and was distilled under reduced pressure. The FMNPs@TD was synthesized according to a previous method [21,22]. All other chemicals were of reagent grade and obtained from Merck or Fluka Company. A stock solution of 1.0 mM was prepared by dissolving an appropriate amount of VB12 in distilled water. This solution was stored in the dark at 4 °C. Other diluted solutions were prepared by diluting the stock solution. All used solutions were prepared using doubly distilled deionized water. Britton-Robinson buffer with pH = 7.0 was used as the supporting electrolyte.

2.2. Apparatus

Voltammetric experiments were performed with an Autolab (Eco Chemie B. V.) PGSTAT302N potentiostat/galvanostat. A conventional three-electrode system was used with a modified working electrode (Au or Au/PPy/FMNPs@TD) and an SCE and a Pt wire as the reference and counter electrode, respectively. Solutions were deoxygenated with high purity nitrogen for 5 min prior to each experiment. The measurement was performed at room temperature under a nitrogen atmosphere. A Metrohm-691 pH-meter (Switzerland) was used for pH adjustments. The sample morphology was studied using TEM (Philips XL) and scanning electron microscopy (Philips SEM model XL30) accompanied with a sputter coater BAL-TEC, model SCD050. Scanning electron microscopy with a secondary electron (SE) detector was used to observe the surface of the detector precisely.

2.3. Electrode modification

To prepare a modified electrode, the Au bare (2 mm diameter) electrode was polished with emery paper, followed by alumina (1.0 and 0.05 μm) and then thoroughly washed with double-distilled water. After polishing, in order to remove any adsorbed substance from the surface, the electrode was ultra-sonicated in ethanol and doubly distilled water for 5 min. Afterward, the electrode was dried under nitrogen flow and used for subsequent experiments. For electrosynthesis of PPy, concentrations of the nanocomposites materials in acetonitrile with 2% water, monomer, modifier, and supporting electrolyte were [Py] = 0.1 M, [FMNPs@TD] = 0.1 M, and [$LiClO_4$] = 0.1 M, respectively. After vigorous mixing and nitrogen purging (10 min), electropolymerization was affected by scanning the electrode potential from −0.50 to 0.90 V accompanied by stirring the samples at a scan rate of 50 mVs^{-1}. For spectroelectrochemical measurement, a 250 μL micro volume cell (Fig. S1) was used. The PPy/FMNPs@TD samples were deposited on an indium tin oxide (ITO)-coated quartz sheet (working electrode (ITO/PPy/FMNPs@TD), Praezisions Glas & Optik, Germany, R = 20 ± 5 ohm/cm^2) and used for in situ UV–vis (Perkin Elmer, 55 OSD, spectrophotometer) spectroscopy. Seven cycles between −0.50 and 0.90 V were used to deposit polymer-nanocomposite (PPy/FMNPs@TD) on the ITO glass electrode. The electropolymerization of nanocomposites under magnetic stirring leads to the formation of thicker and homogenous polymer nanocomposite films on gold and the ITO electrodes containing a significant quantity by weight. Stirring (120 cycles per minute) will keep the nano materials in suspension and causes the nanoparticles to be continuously in contact with the electrode surface, where the composite films are being deposited. As cycling continues, steady-state is achieved after several scans. The electrode was rinsed with distilled water and dried under nitrogen flow.

2.4. Computational details

The geometries of all compounds investigated were optimized with density functional theory (DFT) calculations using hybrid functional M06 and def2-SVP basis sets in a suite of GAUSSIAN 09 programs [23]. Natural bond orbital (NBO) analyses [24] were also performed. To investigate the L → Co bonding nature, energy

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