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Synthesis and characterization of cobalt nitroprusside nano particles: Application to sulfite sensing in food and water samples

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ABSTRACT

A new protocol toward the synthesis of cobalt nitroprusside (CoNP) coordination nanoparticles has been described based on drop-by-drop (DbD) method without using any additives. It was also prepared by sonication as well as bulk mixing methods for comparison purpose. The prepared complex was characterized by Infrared spectroscopy (FTIR), XRD and cyclicvoltammetry (CV) techniques. The CoNP complexes prepared by different synthetic approaches were used as modifier molecules to fabricate carbon paste electrodes (CPE's) toward electrochemical oxidation of sulfite. The experimental results revealed that the cobalt nitroprusside nanoparticles (n-CoNP) prepared by drop-by-drop method showed a considerable enhancement in the electrocatalytic activity when compared to its counterparts prepared by other approaches. Electrochemical behavior of the n-CoNP CPE was studied and used as an electrochemical sensor for the quantification of sulfite at trace level. It showed a linear response over the concentration range 1–5.9 × 10^{-5} M and 2–8 × 10^{-3} M of sulfite. The limit of detection and limit of quantification were found to be 0.4 × 10^{-5} M and 2.29 × 10^{-5} M respectively. The interference of various organic acids and inorganic ions commonly present in different food and water sample matrices were studied. The n-CoNP modified electrode was used for the quantification of sulfite in different food samples and the results were in good agreement with those obtained by the standard iodometric protocol.

1. Introduction

Polycyanide metal complexing reagents, with a general formula $[M(CN)_5L]^{n-}$ where M = Fe, Ru, Os and L a variable ligand (H_2O, CN^-, NH_3, amines, NO, NO_2^-, N-heterocyclic molecules, CO, etc.) has received much attention and systematic investigation of their electronic structure and reactivity are persuaded [1]. Pentacyanonitrosylferrate $[Fe(CN)_5NO]^{2-}$ is also referred as nitroprusside (NP) is one of the important ligands of the above mentioned family because of its ability to complex with various transitional metal ions. Metal nitroprussides (MNP) have received great attention of the scientific community as electrochemical sensors recently due to its versatility and electrocatalytic activity [2–6]. MNP complexes where M = Sn, Ni, Zn, Cd, Co, Pb, etc. were prepared as thin films on the surface of various electrodes using different strategies and successfully used for the quantification of wide range of analytes like ascorbic acid, hydrazine, L-cysteine, hydrogen peroxide, sulfide, sulfite, etc. [2,3,7–12]. In recent years carbon paste electrodes (CPE) have been extensively used over surface modified rigid electrodes for the determination of wide range of analytes due to their easy fabrication, wide potential window, easy surface renewability and low residual currents [13].

Nano scale sized metallic particles are attracting considerable attention for their intriguing properties and potential applications [14]. Recently, materials in the nanometer range have shown superior or advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical/biological sensors. Metal nanoparticles as catalysts have been vigorously investigated because of their specific properties such as large surface area and their superior properties which are different from their bulk counterparts [15]. Inorganic nanoparticles are very useful candidates for electrochemical studies owing to their outstanding activity and catalytic power [16–18]. The large surface-to-volume ratio and the active sites of these nano-sized metal particles in electrocatalysis constitute a part of the driving force in developing the nanosized electrocatalysts. The application of the carbon paste electrodes modified with nanostructures exhibit considerable improvement in the electrochemical behavior of compounds [19,20]. The presence of nanoparticles in electrochemical sensors can decrease the over-potentials of many analytes at common unmodified electrodes. In particular, these analytical devices when modified with metal nanoparticles

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have attracted a remarkable interest to realize electrochemical sensors.

Sulfite is well known for its use in food and beverage industries as a preservative. Sulfite prevents oxidation, inhibit bacterial growth, enzyme activity causing browning and to inhibit the growth of microorganisms during storage [21]. Despite these great advantages, the sulfite content in food and beverages should be strictly limited due to its potential toxicity and harmful effects toward hypersensitive people. Before 1986 sulfites were considered incorrectly harmless for consumers and they received the "Generally Recognized As Safe" (GRAS) status. In the same year US Food and Drug Administration (FDA) revoked the GRAS status and required sulfite declaration on the label of any food item containing 10 ppm levels of sulfite [22]. Sulfite is considered as one among the well known food allergens. Sulfite hypersensitivity is usually, but not exclusively, found within the chronic asthmatic population. Adverse reactions to sulfites in nonasthmatics are extremely rare. Asthmatics who are steroid-dependent or who have a higher degree of airway hyper reactivity may be at greater risk of experiencing a reaction to sulfite-containing foods. Even within this limited population, sulfite sensitivity reactions vary widely, ranging from no reaction to severe. These manifestations may include dermatological, respiratory or gastrointestinal symptoms [23,24]. In order to quantify such trace level sulfite there is a significant progress in its quantification technology. Several methods have been reported for the quantification of sulfite from a variety of sample matrices [21]. These methods are mainly based on techniques like electrochemical [25–33], biosensors [34], chromatography [35], chemiluminescence [36–38] and spectrophotometry [39]. Among these, electrochemical methods find widespread use due to their simplicity, easy modification and easy adoptability. Chemically modified electrodes (CMEs) have become significant ones in recent years due to their tailoring made properties which imparts selectivity as well as analyte specificity.

Pouranghi-Azar and Sabzi [40] have used the glassy carbon electrode electrochemically modified with CoNP complex to oxidize sulfite. A pioneering work on the synthesis of cyano-bridged coordination polymer nano objects like Prussian blue and its analogues have been reported in recent years [41,42]. Different techniques such as reverse micelle, ionic liquid by using stabilizing ligands in solution have been developed to prepare metal nanoparticles [43–45]. Very few reports appeared on the direct synthesis of Prussian blue analogue nanoparticles without any templating and/or additives [46,47].

In most of the earlier mentioned protocols metal nitroprussides are electrochemically coated onto the rigid electrode surface and it has been used as an electrochemical sensor. The surface renewal is quite cumbersome in all these rigid surface modified electrochemical sensors. In order to overcome the surface renewability problem of this type of electrodes, an attempt has been made for the first time to synthesize CoNP nanoparticles in solution phase without any additives. Then the synthesized CoNP nano particles have been used as a modifier in designing an electrochemical sensor for the sulfite quantification. The proposed sensor has been successfully applied for the measurement of sulfite from a variety of food stuff and water samples.

2. Experimental

2.1. Apparatus

All the samples were characterized by X-ray diffraction (Bruker aXS Model D8 Advance powder X-ray diffractometer, Cu Kα source $\lambda = 15.418$ nm, θ–2θ geometry). IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (Diamond crystal ATR mode, resolution 4 cm^{-1}, 400–4000 cm^{-1}). Scanning electron micrographs were obtained using Quanta-200 scanning electron microscope by dispersing sample conducting carbon tape and sputter coating with gold to improve the conductivity.

Cyclic voltammetry experiments were performed using CH Instruments electrochemical work station (Model CHI 619B, CH Instruments, TX, USA) in a standard three electrode cell. A carbon paste electrode as a working electrode, Pt wire as the counter electrode and Ag/AgCl served as the reference electrode.

2.2. Chemicals and reagents

Sodium sulfite Na_2SO_3, cobalt chloride hexahydrate $CoCl_2{\cdot}6H_2O$, sodium nitroprusside dihydrate $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$, potassium chloride KCl were all analytical grade and were used as received. Potassium nitrate KNO_3 (0.5 M) was prepared using 0.05 M acetic acid–0.05 M sodium acetate buffer solution of pH 5. All solutions were prepared using double distilled water.

2.3. Synthesis of cobalt pentacyanonitrosylferrate

CoNP was synthesized by precipitation using three different procedures: Drop by drop, sonication and bulk mixing at a temperature of 5–10 °C.

Drop by drop (*DbD*) *method*: 10 ml aqueous solution of 0.01 M sodium nitroprusside was taken in a dropping funnel and it was added dropwise to 10 ml of 0.02 M aqueous solution of cobalt chloride taken in a beaker which was thermostated at 5–10 °C under vigorous stirring. The solution turns turbid due to the formation of cobalt nitroprusside complex. It is referred as n-CoNP in all further studies.

Sonication method: 10 ml each of aqueous solutions of 0.01 M cobalt nitroprusside and 0.02 M cobalt chloride were mixed at 5–10 °C and sonicated for 30 min. It is designated as s-CoNP.

Bulk mixing method: In this method, 10 ml of aqueous solutions of 0.01 M sodium nitroprusside and 0.02 M cobalt chloride which were maintained at 5–10 °C were mixed immediately in a beaker. The resulting compound has been designated as b-CoNP.

In all the three cases, the pH of the solutions were maintained in acidic condition to avoid the formation of metal hydroxides and the resultant precipitates were left overnight without disturbing. After 24 h the supernatant liquid was decanted and the residue was centrifuged. The prepared CoNP compound was initially washed with plenty of water then finally with alcohol. The residue was collected in a petridish and dried at room temperature. The resulted CoNP particles from all the three procedures were used as a modifier in fabricating carbon paste electrodes.

2.4. Electrode preparation

The modified carbon paste electrode was prepared manually by thoroughly mixing the dispersed graphite powder with n-CoNP at 15:1 mass ratio and subsequently adding 38% (m/m) of mineral oil. The resultant mixture was ground in an agate mortar for 10–15 min. The obtained paste was packed into the capillary tube from the wider end. A copper wire was inserted from the opposite end of the capillary to obtain the electrical contact. Similarly b-CoNP and s-CoNP modified CPE electrodes were prepared. Bare carbon paste electrode was prepared by following the above procedure. All these electrodes were dried for 24 h at room temp and the resistivity was measured using a multimeter, which has been found to be 10–12 Ω.

3. Results and discussion

Cobalt nitroprusside complex has been synthesized from three different approaches. The complex resulted from all the three