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One step facile synthesis of silver nanoparticles for the simultaneous electrochemical determination of dopamine and ascorbic acid

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ABSTRACT

A silver nanoparticles modified carbon paste electrode (MCPE) was developed for the detection of dopamine using voltammetric techniques. The silver nanoparticles (AgNPs) were synthesized through a biological method by using leaf extract act as a reducing agent. The prepared AgNPs were characterized by X-ray diffraction (XRD) and UV–visible absorption spectroscopy (UV–vis). AgNPs are ideally suited for implementation in electrochemical applications due to their high electrical conductivity, high heterogeneous electron transfer rate, and low production cost. The electrochemical response of dopamine at a MCPE prepared with AgNPs is compared with the response of surfactant assisted synthesized AgNPs (S-AgNPs). The effect of pH suggests that an equal number of protons and electrons are involved in the electrochemical oxidation of dopamine. Differential pulse voltammetric technique (DPV) was used for the simultaneous determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA). The peak potential separations for DA-AA and DA-UA were about 181 mV and 168 mV respectively, and the detection limit was 0.085 μM for DA. This work presents a simple approach to the determination of DA in the presence of AA and UA.

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1. Introduction

Metallic nanoparticles have attracted much attention in recent years due to their unique properties [1,2]. Among the noble metals, silver nanoparticles (AgNPs) are widely utilized in material science, physics, and chemistry because of their particular optical, magnetic, electronic, and catalytic properties [3]. AgNPs have been used for the determination of cyanide [4], thiocyanate [5] and ammonia [6]. The synthesis of AgNPs in aqueous solutions is difficult due to the affinity of AgNPs to aggregate irreversibly. The controllable synthesis of AgNPs is the first challenge that must be met before they can be used in applications. Colloidal AgNPs can be prepared by physical, biological and chemical methods. The chemical approach is employed the most in which silver salts are treated with a chemical reducing agent such as hydrazine or sodium borohydride [7]. Such reducing agents are considered environmentally unfriendly. The preparation of AgNPs via a facile process should be evaluated using three considerations: the choice of the solvent medium, the toxicity of the reducing agent, and the use of environmental friendly materials for the stabilization of the AgNPs. Water is generally used as the environmental friendly solvent [8].

Plant extracts contain metabolites [9]. The metabolites can serve as reducing agents for metal ions. They also act as capping agents, which

help to minimize the agglomeration of AgNPs. Thus, it is possible to use plant extracts to control the morphology and to protect/stabilize the AgNPs. The use of medicinal plants gained importance soon after the first reports by Gardea-Torresdey et al. [10] on the formation of AgNPs. In the study presented here, a bio-method is described for preparing stabilized AgNPs with and without surfactants. The prepared NPs are then applied to the sensing of electro active species, which are discussed next.

Dopamine (DA), ascorbic acid (AA), and Uric acid (UA) are compounds of biomedical interest. They play significant roles in the functioning of the human metabolism, and the central nervous and renal systems [11]. For instance, AA is an essential vitamin for humans, and has been investigated for the prevention and treatment of the common cold, mental illness, infertility and cancer [12]. Dopamine is an important neurotransmitter in the brain's neural circuits [13] and its depletion leads to Parkinson's disease [14]. Abnormal dopaminergic transmission has also been implicated in Huntington's disease and neuroendocrine disorders [15]. Uric acid (UA) is a nitrogenous compound found in urine and it is a product of purine metabolism in the human body. High levels lead to many clinical disorders [16]. High levels of UA in the blood (hyper uricemia or Lesch-Nyhan syndrome) are linked with body disorders like gout, kidney and cardiac problems [17]. In order to increase the sensitivity and selectivity of these compounds by sensors, many various chemical and biological materials are required [18,19]. Modified electrodes enable the increase in the selectivity of these compounds to a level not achieved using bare electrodes [20,21]. For

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example, the modification of electrodes can significantly increase their analytical applicability [22–31].

Our research group previously published methods for the determination of DA, AA and UA using various modified carbon paste electrodes (CPEs). The modifications included surfaces containing carbon nanoparticles, hydrogen double salt, CuO, and reduced graphene oxide nanoparticles for the detection of DA [32–35]. Other work used pretreated/carbon paste electrodes for the detection of DA [36], SDS/R-GO/MCPE employed for the detection of DA [37], a polyglycine modified CPE used for simultaneous detection of DA and AA [38], and a poly (naphthol green B)-film modified CPE utilized for simultaneous detection of DA and UA [39].

In the present work, the improvement of the sensitivity and selectivity of a dopamine sensor is achieved by using AgNPs as modifiers of a CPE. The modifiers are synthesized by a biological method. This work illustrates that such a sensor can be used for the selective determination of DA even in the presence of high concentrations of interfering materials such as AA and UA. A comparison with literature values shows that the electrodes modified with AgNPs exhibit the lowest detection limit for DA.

2. Experimental

2.1. Reagents

Banyan leaf (*Ficus tinctoria*) was collected from Shankaraghatta, Shimoga a town in Karnataka, India. AgNO₃, DA, AA, UA, and the surfactant sodium dodecyl sulphate (SDS) were obtained from Himedia Chemicals. Sodium hydroxide, perchloric acid, sodium dihydrogen orthophosphate dihydrate, and di-sodium hydrogen phosphate anhydrous were obtained from Merck. Graphite powder was acquired from Lobo Chemical. All chemicals were analytical grade. Stock solution of 25 × 10⁻⁴ M DA, 25 × 10⁻³ M AA, and 25 × 10⁻⁴ M UA were prepared by dissolving the solute in 0.1 M perchloric acid solution, double distilled water, and 0.1 M NaOH respectively. All reagent solutions were prepared in double distilled water.

2.2. Apparatus

Electrochemical measurements were carried out with a CHI model 660c Electrochemical Workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare carbon paste electrode or the carbon paste electrode modified with the AgNPs was used as working electrodes. The counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE). All potentials reported are with respect to the SCE. A Microwave oven (ONIDA-MO 175JP1W, 2.45 GHz) was used for extracting phytochemicals from the Banyan leaf in water and subsequently in the synthesis of AgNPs.

X-ray diffraction (XRD) patterns of AgNPs samples were obtained using a PHILIPS PW3710 diffractometer (Cu, K α radiation) with a step scan at 0.2° in a 2 θ range from 30°–80°. Optical absorption spectra were recorded by using a UV–visible spectrophotometer (UV-1650PC/SHIMADZU). Samples were loaded in a quartz cell and measurements were taken in the wavelength range 200–800 nm.

2.3. Synthesis of AgNPs

Ten grammes of chopped Banyan leaf (*F. tinctoria*) were added to 200 ml distilled water. The mixture was kept under microwave irradiation for about 120 s to extract the phytochemicals from the leaf. The solution was filtered through a 0.2 μ m membrane filter under hot conditions to remove fibrous impurities. Two aqueous solutions were made for the synthesis. One solution contained only leaf broth and the other contained leaf broth and SDS. The concentration of surfactants used was 3 mM. The stock-solution 10 ml, was added to 50 ml of

1 mM AgNO₃ solution. The reaction mixtures were subjected to microwave radiation for different time intervals (0 to 100 s). A change in colour from light yellow to dark brown indicated the formation of AgNPs.

Trace amounts of AgNO₃ were removed by adding NaCl to the solution. The cessation of a white precipitate forming signalled that most of the AgNO₃ was consumed. The final washing of the AgNPs with plenty of water ensured removal of any unreacted AgNO₃. The product was dried in a vacuum oven at 70–80 °C for about 12 h. The final product was in the powder form. The synthesis of AgNPs is compared with reported methods tabulated in Table 1. The data reveal that, for the present method, reduction of Ag⁺ → Ag⁰ takes less time.

2.4. Preparation of the CPE and the AgNPs/MCPE

The bare carbon paste electrode was prepared by mixing graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. The carbon paste electrode modified with AgNPs (AgNPs/MCPE) was prepared by immobilizing the AgNPs solution on the CPE surface using a micropipette. The electrode was then incubated for various times at room temperature. The electrode was later thoroughly rinsed with water to remove unabsorbed modifier. It was dried in air at room temperature. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

3. Results and discussion

3.1. Characterization of AgNPs

The prominent peaks in the XRD pattern of AgNPs are shown in Fig. 1. The peaks are at 2 θ = 38.1°, 43.3°, 64.4° and 77.6° corresponding to (111), (200) (220) and (311) respectively, which can be indexed to the face centred cubic structure of Ag metal (JCPDS 03-0931). The average crystallite size *d* of the AgNPs was calculated to be about 17 nm using Scherer formula, which is given by $d = K\lambda/b\cos\theta$, where *K* is the shape factor which is 0.9, λ is the incident X-ray wavelength (Cu K α = 1.542 Å), *b* is the full width at half maximum in radians of the prominent line (111), and θ is the position of that line in the pattern. The data indicates the green synthesis of AgNPs was achieved here using Banyan leaf (*F. tinctoria*) extract under microwave radiation.

UV–vis spectrophotometry was used to evaluate the optical properties of the AgNPs. Fig. 2 shows the UV–vis absorption spectrum of the aqueous AgNPs suspension. The absorption band observed at 424 nm is the absorption band that results from the formation of spherical shaped AgNPs [40]. The time in Fig. 2 is the time that the samples were subjected to microwave radiation. The longer the time the more silver is reduced. The samples that have low reduction exhibit low-intensity absorption bands, i.e. the intensity of the AgNPs absorption spectra increases with increasing AgNPs reduction. This observation allows the prediction of AgNPs yields from the UV–vis spectrum.

Variation in the particle size of AgNPs can produce a spectral blue-shift, by which Henglein [41] exploited to estimate the particle size. Anionic surfactants such as SDS give a spectral shift towards shorter wavelength (blue-shift) as can be seen in Fig. 3 where absorption bands are observed at 416 nm. The shift is larger at lower surfactant concentrations. At sufficiently large concentrations the surfactants saturate the system and local changes in concentration does not produce a shift.

3.2. Mechanism of reduction of silver

A probable reduction mechanism involving Banyan leaf (*F. tinctoria*) broth and silver nitrate that produces AgNPs involves the reaction of the components of the leaf. Phytochemical investigations have demonstrated that tannins, polyphenols, triterphenoids, flavonoids and saponins

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