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A facile green synthesis of silver nanoparticles using *Piper betle* biomass and its catalytic activity toward sensitive and selective nitrite detection

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ABSTRACT

A facile, one-pot and environmental benign method exploiting *Piper betle* biomass as a reducing and stabilizing agent was proposed for the preparation of silver (Ag) nanoparticles. The Ag nanoparticles prepared from dried *Piper betle* leaves extract exhibited unique spherical configuration and face-centered-cubic structure with preferred (1 1 1) orientation. The fabricated Ag/GCE sensor exhibited an exceptional electrocatalytic activity toward NO_2^- oxidation with a quick response time, high sensitivity and lower detection limit of 10 s, 1642.27 μAm M^{-1} cm^{-2} and 0.046 μM, respectively. Furthermore, the constructed sensor exhibited long-term stability and excellent anti-interference properties, paving new dimensions for the utilization of bio-mediated nanocatalysts in electrochemical sensors.

Introduction

The quantitative detection and determination of nitrite (NO_2^-) and its compounds are substantial, owing to its extensive utilization as additives, therapeutics, fertilizers and polymer inhibitors and are widely exploited in food science, pharmaceutical, agriculture and rubber industry fields, respectively [1–3]. Although the utmost value of NO_2^- in drinkable water is fixed to be 2.17 μmol L^{-1}, a higher value is reported in the existing drinking water, which induced severe health issues including methemoglobinemia and blue baby syndrome [4–6]. NO_2^- can irreversibly react with hemoglobin and produces methemoglobin, which reduces blood capacity to transport oxygen. In addition to the carcinogenic behavior, N-nitrosamines are also formed by the reaction of NO_2^- with amines. The increased NO_2^- concentration leads to spontaneous abortions, intrauterine growth restriction, defects in the central nervous systems and kidneys, stomach cancer and birth defects [7,8]. Hence, it is inevitable to monitor and control the NO_2^- level in food, pharmaceutical and agriculture fields. Numerous analytical strategies including spectrophotometry [9], molecular absorption spectrometry [10], chromatography [11], fluorescence spectroscopy [12], chemiluminescence [13], flow injection analysis [14], capillary electrophoresis [15] and electrochemical methods [16] have been employed for the quantitative determination of NO_2^-. Among the aforementioned analytical techniques, electrochemical method has received significant attention in the quantitative determination of NO_2^-, owing to its fast response, easier preparation, minimal time consumption, possible miniaturization, reliability, portability, high sensitivity and selectivity [16–18]. However, the sensitivity and detection limit exhibited by the electrochemical sensors are not influential enough for the commercial applications [19]. Therefore it is essential to identify the innovative pathways to increase the electrocatalytic oxidation/reduction at the surface of electrodes, in which the role of metal nanoparticles is more vivacious [20,21], owing to its constructive characteristics such as high surface-to-volume ratio, number of active sites, high electrical conductivity, conduction channels etc., [19,20,22]. Hence, number of nanoparticles including Au [23], Ag [24] and Sn [25] have been exploited for the deduction of NO_2^-. Among the aforesaid nanoparticles, Ag nanoparticles have fascinated the attention, owing to its distinctive physical as well as chemical properties including chemical stability, elevated electrical and thermal conductivity, high catalytic activity,

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surface-enhanced Raman scattering and nonlinear optical properties [26–28]. Hence, assortments of methods including chemical, photochemical, electrochemical and irradiation techniques have been developed for the preparation of Ag nanoparticles. However, the toxic reducing agents such as sodium borohydride, β-cyclodextrin, ascorbic acid, hydrazine hydrate, sodium citrate etc., utilized for the reduction of Ag^+ ions increased the toxicity of prepared Ag nanoparticles, which faded the scale-up processes of Ag nanoparticles. [29–33]. Despite the fact that the reducing agents are vital in tuning the size, morphology and pore properties of Ag nanoparticles, the utilization of hazardous chemicals in aforementioned methods restricted their biocompatible and environmental benign characteristics in the synthesis and application of nanoparticles [34–36]. Hence, the research activities on bio-mediated nanoparticles synthesis has been triggered to its full extent and the salient features of bio-mediated nanosynthesis such as bio compatibility, effectual morphology tuning strategies, less time consumption etc., [37,38] construct this protocol greener and more attractive. From the extensive research efforts, it is clear that various prokaryotes [39] eukaryotes [40] and photosynthetic autotrophs [41] were capable of reducing the metallic ions into their corresponding nanoparticles. Apart from the prokaryotes and eukaryotes, nanoparticles synthesized by using photosynthetic autotrophs are of great significance, owing to the ability of serving as a single reducing and stabilization agent [41], whereas prokaryotic and eukaryotic based nanosynthesis compelled the utilization of external stabilizers or capping agents. Based on the above, various photosynthetic resources such as *Parthenium* [42], *Emblica officinalis* [43], *Aloe vera* [44], *Cinnamomum camphora* [45], tea leaves [46], *Mangosteen* [47], *Ziziphus spina-christi* [48], *Peanut shell* [49], *Cassia tora* [50] *etc.*, have been exploited for the preparation and stabilization of nanoparticles. However, majority of the reports documented the polydispersed nanomaterials and their application toward electrochemical NO_2^- detection has not been reported yet.

Piper betle leaves are creepers belonging to the Piperaceae family and originated in the south and south-east Asia. It is a mild stimulant and is well known for their medicinal values especially in traditional medicines. It possesses several biomolecules such as polyols, alkaloids, steroids, saponins and tannins and is used for the carminative, tonic, aphrodisiac, stomachic and laxative activities [51]. The anti-lipid peroxidation characteristic of these leaves constructs its viable applications in the prevention of atherosclerosis [52]. In addition, it also exhibits antimicrobial and anti-inflammatory, anti-oxidative and radioprotective properties [53]. The major phytochemicals present in *Piper betle* leaves are allylic benzenes, phenolic, amino acids, proteins, alcoholic compounds and several terpenes and terpenoids, which are found to have the reduction tendencies [51]. Hence, this research effort is aimed to synthesize Ag nanoparticles by the utilization of *Piper betle* biomass and is also intended to identify the influence of prepared Ag nanoparticle's catalytic activity toward the electrochemical detection of NO_2^-.

Experimental details

Materials

Piper betle leaves were obtained from local premises. Silver nitrate ($AgNO_3$) (99.99%), sodium nitrite ($NaNO_2$) and phosphate buffer solution (pH = 7.2) were purchased from Sigma Aldrich (India) and used without any further purification. Potassium chloride (KCl), sodium chloride (NaCl), ammonium chloride (NH_4Cl), magnesium sulphate ($MgSO_4$), copper (II) chloride ($CuCl_2$), sodium acetate ($NaCOOCH_3$), sodium carbonate (Na_2CO_3), acetaminophen (AP) and urea (U) were obtained from Merck and used without further purification.

Preparation of *Piper betle* extract

The fresh *Piper betle* leaves were washed with de-ionized water and chopped into fine pieces and dried at room temperature. 10 wt% extract was prepared by boiling the stipulated amount of piper betle leaves with de-ionized water at 80 °C for 10 min. The solution was filtered by using Whatman filter paper and stored at 4 °C overnight for further use.

Preparation of Ag nanoparticles

In a typical preparation of Ag nanoparticles, a suitable volume of 10 wt% fresh/dried *Piper betle* leaves extract was gradually added to 1 mM $AgNO_3$ solution and magnetically stirred for 30 min at 75 °C. For the preparation of dried *Piper betle* powder mediated Ag nanoparticles, a known mass of the dry *Piper betle* powder was added with 1 mM $AgNO_3$ solution and magnetically stirred for 30 min at 75 °C.

Modification of electrode

The glassy carbon electrode (GCE) surface was polished as per the procedure described elsewhere [54]. On the basis of small average particle size, smooth contours and unique morphology, dried *Piper betle* leaves extract mediated Ag nanoparticles have been chosen for the modification of GCE for the effectual electrochemical detection of NO_2^-. 10 μl of the prepared Ag nanoparticles was dropped onto the pre-treated GCE and dried at room temperature and the Ag nanoparticles modified GCE is represented as Ag/GCE.

Characterizations

The surface plasmon resonance of prepared nanoparticles was monitored using an Agilent 8453 diode array UV–vis spectrophotometer in the range of 300–800 nm. Morphological characterizations of the prepared nanoparticles were examined by using a JEOL JEM-2010 transmission electron microscope. The crystalline characteristics of synthesized Ag nanoparticles was ascertained by a Rigaku-X-ray powder diffractometer (XRD) with Cu $K\alpha$ radiation ($l = 1.54178$ Å) and a Bragg angle ranging from 30° to 80°. Fourier Transform Infrared (FT-IR) spectra of the prepared Ag nanoparticles were examined by using a Perkin Elmer FT-IR spectroscopy.

Electrochemical measurements

The electrochemical experiments were accomplished with a CHI-650E electrochemical workstation. The electrochemical oxidation of NO_2^- at GCE and Ag/GCE was studied by cyclic voltammetry (CV) and the CV responses of studied electrodes were recorded in the presence and absence of 1 mM NO_2^- in 0.1 M PBS (pH = 7.2) under the potential range of −0.5 to 1.2 V (*vs.* Ag/AgCl). The amperometric measurements were recorded at an applied potential of 1.0 V (*vs.* Ag/AgCl).

Results and discussion

Absorption studies

The formation of Ag nanoparticles was confirmed by a characteristic color change of the metallic precursor, $AgNO_3$. Thirty minutes after the addition of extract to the $AgNO_3$ solution, a visible color change *i.e.*, from colorless to olive color was observed. The prepared nanoparticles exhibited a SPR band at 420 nm, confirming the formation of Ag nanoparticles (Fig. 1).