Silver nanoparticle impregnated mesoporous silica as a non-enzymatic amperometric sensor for an aqueous solution of hydrogen peroxide

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A B S T R A C T

Silver nanoparticles (AgNPs) were impregnated in amine functionalized mesoporous silica (NH$_2$-SBA-15) particles, by *in situ* chemical reduction, for making a hydrogen peroxide (H$_2$O$_2$) sensor. AgNPs formed were isolated and well dispersed in hydrophilic NH$_2$-SBA-15 at a loading of 17.2 wt.%, with mean particle diameter 4.5 nm and standard deviation 0.4 nm. AgNP impregnated NH$_2$-SBA-15 was used as a modifier of glassy carbon electrode (GCE) for an enzyme-less amperometric sensor. It showed good electrocatalytic activity towards H$_2$O$_2$. Optimum composition of the modifier on the GCE surface (12.2 μg Ag in AgNP-NH$_2$-SBA-15/cm^2 surface area of GCE) resulted in a high sensitivity of 171.3 μA cm^{-2} mM^{-1} and a wide linearity range (5.3–124.5 mM H$_2$O$_2$), due to the high loading of electrically conductive AgNPs in NH$_2$-SBA-15 host. The sensor was selective to only H$_2$O$_2$, even in presence of high concentrations of both reducible and oxidizable interfering agents, like, sodium nitrate, sodium nitrite, urea, glucose or ascorbic acid. The response time was also less than 3 s. Therefore, it achieved the desirable sensor-characteristics, like linearity, sensitivity, selectivity and speed of response. Our results are better than other reported H$_2$O$_2$ sensors with impregnated AgNPs (in terms of linear range and sensitivity), compared to even those with good conducting hosts (like carbon nanotube, graphene oxide). Therefore, performance of any sensor can be improved by ensuring uniform dispersion of isolated NPs at a high loading, when impregnated in a hydrophilic host.

1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is widely used in many applications, for example, dental disinfectant formulations [1], aseptic packaging [2], disinfection of fruits and vegetable [3], etc. Due to widespread use, one may get exposed to it, during its improper usage or storage. Being a strong oxidizing agent, it can cause eyes and skin irritation, respiratory problems, gastrointestinal inflammation, etc. [4], depending upon mode and level of exposure. Therefore, sensitive and accurate detection of H$_2$O$_2$ is required.

Detection of H$_2$O$_2$ by electrochemical method is better compared to other methods such as titrometry, spectrometry, chemiluminiscence and fluorescence, due to its fast response, high sensitivity and accuracy [5,6]. These desirable features can be achieved by either enzyme-based [7] or enzyme-less [8,9] approaches. The former includes immobilization of enzyme (such as, horse radish peroxidase) in a host. However, activity of immobilized enzyme itself gets altered on immobilization, and furthermore depends on its favorable conformation, which is affected by change in pH, temperature, presence of toxic chemicals, etc. In contrast, enzyme-less sensors, which are specific to an analyte, do not have such limitations and hence are popular.

A good electrochemical sensor, consisting of an electrode and an electrode modifier, needs: (i) high selectivity, which depends on a good electrocatalytic activity towards the analyte and (ii) high sensitivity, which is facilitated by a high electrical conductivity and a large contact area between the analyte and the modifier, for the electrochemical reaction. The desired large contact area can be achieved by increasing the hydrophilicity (by achieving a very small contact angle with water) of the modifier [10]. Noble metal nanoparticles, such as platinum [11], gold [12], silver [13] and palladium [14] are used as electrode modifiers because of their high selectivity towards H$_2$O$_2$. Among them, to address the issue of sensitivity, the highest electrical conductivity of silver nanoparticles (AgNPs) [15] makes it the preferred choice. However, to have a large contact area, aggregation of AgNPs (part of the modifier) needs to be prevented in the aqueous synthesis media itself, before making of electrodes. The most common approach of preventing aggregation is to uniformly disperse nanoparticles in a solid host, often having excellent electrical conductivity too [16,17]. Known examples of electrochemical sensors (designed for H$_2$O$_2$ sensing

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with AgNP dispersion) use electrically conductive hosts, such as ordered mesoporous carbon [11], graphene nanosheets [18,13], multiwalled carbon nanotubes (MWCNTs) [5] and conducting polymers [9]. However, these are hydrophobic in nature with a low contact area for electrochemical reaction, thus providing a possibility for further increasing sensitivity by increasing surface hydrophilicity.

In literature, hydrophilic hosts such as amine functionalized mesoporous silica (NH_2-SBA-15) were also used for preventing aggregation of AgNPs, but could achieve only a small AgNP loading (4.1–4.9 wt.%) [19,20]. This led to a low sensitivity of the H_2O_2 sensor. Therefore, the challenge is to achieve a higher sensitivity, possibly by a uniform dispersion of high AgNP loading in NH_2-SBA-15 host.

Therefore, in the present work, a superior performance of enzyme-less amperometric H_2O_2 sensor was attempted by a high AgNP loading in NH_2-SBA-15 host. The results were compared from literature with different hosts, which were either electrically conductive but hydrophobic, or electrically non-conductive but hydrophilic in nature, in order to assess the role of a non-conductive, but hydrophilic host, like NH_2-SBA-15.

2. Experimental

2.1. Materials

Chemicals for SBA-15 synthesis: Tetraethyl orthosilicate (TEOS, Fluka), Pluronic123 (P123, Sigma Aldrich), decane ($C_{10}H_{22}$, Sigma Aldrich), hydrochloric acid (HCl, Merck, 35%), and ammonium fluoride (NH_4F, Hi-Media). 3-Aminopropyltriethoxysilane (APTES, Sigma Aldrich) was used for amine functionalization. Chemicals for silver nanoparticle synthesis: Silver nitrate (S.D. Fine chemicals) and sodium borohydride (Merck). Chemicals for pH 7 buffer solution: Sodium dihydrogen phosphate (Merck) and disodium hydrogen phosphate (Merck). Analyte of interest was hydrogen peroxide (Merck, 30 wt.%). Interfering species were sodium nitrate (Qualigens), sodium nitrite (Qualigens), L-ascorbic acid (S.D. Fine chemicals), glucose (Hi-Media), urea (Qualigens). Nafion (Sigma Aldrich, 5 wt.% in lower aliphatic alcohol and water) was diluted to 0.5 wt.% with water before use. Deionized water was used in all experiments. All chemicals were used as received without further purification.

2.2. Synthesis of mesoporous silica (SBA-15)

SBA-15 synthesis was based on the work of Tian et al. [21]. 1.5 g Pluronic 123 was dissolved in 55 ml of 1.3 M HCl solution (P123 concentration of 4.7 mM) at 30 °C. Then 27 mg NH_4F was added followed by 11.762 ml decane, with continued stirring at the same temperature for 5 h. Finally, TEOS (3.464 ml) was added drop wise for 2 min. The mixture was stirred at 30 °C for 20 h and then kept in a closed vessel under static conditions, for further reaction at 100 °C for 48 h. The molar ratio of reactants used was as follows:

$$P123 : HCl : NH_4F : C_{10}H_{22} : H_2O : TEOS = 1 : 261 : 1.8 : 135$$
$$: 11278 : 60.$$

The solid product was filtered, washed, dried at ambient condition and calcined at 540 °C for 6 h.

2.3. Synthesis of amine functionalized mesoporous silica (NH_2-SBA-15)

Amine functionalization of SBA-15 was carried out by post-synthesis grafting [22], using APTES as the amine source. Briefly, 1.2 g of SBA-15 was added to a round bottom flask, containing 50 ml of dry toluene. Then 4 ml of APTES was added in nitrogen atmosphere, and reaction under stirring was carried out at 110 °C in reflux condition for 12 h. The resulting powder was filtered, washed with ethanol and water, and dried in air to get NH_2-SBA-15. Presence of amine functional groups was confirmed by FTIR (Fig. S1) and CHN analyses. The latter showed carbon, hydrogen and nitrogen to be 9.8, 0.2 and 3.9 wt.%, respectively, giving an amine functional group density of 2.7 mmol/g. Synthesis of AgNPs in NH_2-SBA-15 is shown schematically in Fig. 1, where the latter is impregnated with silver ions and finally chemically reduced. The details are discussed below.

2.4. Synthesis of silver nanoparticle impregnated mesoporous silica (AgNP-NH_2-SBA-15)

Before impregnating silver nanoparticles, NH_2-SBA-15 powder sample was dried at 100 °C for 12 h. Then 86 mg of the powder was dispersed in an eppendorf tube, containing 2 ml water and sonicated for 5 min. The suspension was then transferred into a reactor, to which 1 ml of silver nitrate solution in water (181 mg of silver nitrate in 1 ml water) was added in dark, under magnetic stirring. The stirring was continued for 24 h at room temperature of 27 °C. This step was carried out, in order to allow the adsorption of silver ions in NH_2-SBA-15. The contents were centrifuged at 13,000 rpm (approximately 16060 g) for 5 min. The bottom product had a pale brown color, which was washed three times with water and dispersed in 2 ml water, with sonication for a min.

In a separate beaker, sodium borohydride ($NaBH_4$) solution in water (9.37 ml) was prepared by dissolving $NaBH_4$ (86 mg) under magnetic stirring at room temperature. To this solution, the suspension (silver ion adsorbed NH_2-SBA-15 in water) was then added drop-wise under magnetic stirring. The reaction was carried out for 60 min. Finally, the brown suspension was centrifuged, washed with water and dried at 100 °C for 4 h. This product was named AgNP-NH_2-SBA-15. The absorbance of the suspension was recorded as a function of time at 0 (before adding the contents to $NaBH_4$ solution), 10, 30 and 45 min, in order to observe the change in silver nanoparticle diameter as a function of time. Synthesis protocol of AgNPs has been compared with the literature to highlight improvement and discussed in Section S4 of SI.

2.5. Electrode preparation

5 mg of AgNP-NH_2-SBA-15 (17.2 wt.% Ag, Section 3.1) was dispersed in 1 ml water and sonicated for 5 min to obtain the suspension. Afterwards, 5 electrodes with different compositions were made to optimize electrode performance. Electrodes were made by drop-casting different volumes of this suspension (10, 5, 3, 1 and 0.1 μl) on a cleaned surface of glassy carbon electrode (GCE, 3 mm diameter) and dried at 4 °C. This was followed by coating with a Nafion layer, via a drop-cast of 5 μl of 0.5 wt.% Nafion and drying at 4 °C. These electrode compositions were referred to as C1, C2, C3, C4 and C5, which had loading of 122.8, 61.4, 36.8, 12.2 and 1.2 μg Ag in AgNP-NH_2-SBA-15/cm^2 surface area of GCE, respectively. Two more electrodes were made for control experiments – (i) C4 without AgNP and (ii) only GCE (without AgNP and NH_2-SBA-15). For sensing experiments, a known concentration of hydrogen peroxide (H_2O_2) was added to 20 ml of 0.2 M phosphate pH 7 buffer (deoxygenated by nitrogen bubbling for 30 min), under stirring (110–120 rpm), for H_2O_2 detection. The applied potential was −0.4 V vs. standard calomel electrode (SCE). A blank run of the electrode in pH 7 buffer was carried out without H_2O_2 aliquots, to record the background current. This current was then subtracted for data analysis from the runs where H_2O_2 aliquots were added, in order to generate a H_2O_2 calibration plot.