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Synthesis of silver nanoparticles-decorated $FePO_4$ nanosphere at a gas-liquid interface for the electrochemical detection of Hydrogen peroxide

DEJIANG RAO, JIAN ZHANG and JIANBIN ZHENG*
Institute of Analytical Science, Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry,
Northwest University, Xi'an, Shaanxi 710069, China
e-mail: zhengjb@nwu.edu.cn

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Abstract. Silver nanoparticles were prepared by chemical reduction of acetaldehyde gas in the absence of protective gas, and Ag/$FePO_4$ nanocomposites were synthesised by modified silver mirror reaction at a gas-liquid interface. A hydrogen peroxide (H_2O_2) electrochemical sensor was constructed through immobilizing Ag/$FePO_4$ nanocomposites on gold (Au) electrode. The morphology and composition of the nanocomposites were characterized by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). The electrochemical investigations of the sensor indicated that it exhibited excellent analytical performance with a wide linear range from 3.0×10^{-5} to 1.1×10^{-2} mol·L^{-1} and a low detection limit of 4.7 μmol·L^{-1} at a signal-to-noise ratio of 3. Meanwhile, it also showed acceptable reproducibility and anti-interference ability. This study may provide a new method for the synthesis of highly dispersed metal nanoparticles which might be used in other related fields.

Keywords. Electrochemical sensor; gas-liquid interface; $FePO_4$; hydrogen peroxide; silver.

1. Introduction

Hydrogen peroxide (H_2O_2) plays vital roles in industry, biomedicine, pharmaceutical chemistry and many other fields.[1–3] Therefore, it is of great importance to develop an efficient method for selective and sensitive determination of H_2O_2. Many methods have been reported for detecting H_2O_2, such as titrimetry,[4] fluorometry,[5] chromatography,[6] spectrophotometry,[7] chemiluminescence[8] and electrochemistry.[9] Among these methods, the electrochemical detection methods have attracted more and more attention because of low cost, simplicity and high efficiency.[10–12] The electrochemical detection of H_2O_2 could be classified into two main categories: enzymatic detection and non-enzymatic detection. However, enzyme-based sensors suffer from the expensive enzyme material, poor stability and complex fabrication procedure for sensor.[13,14] Thus, many people are committed to the study of non-enzymatic sensors. Moreover, with the emergence and development of nanotechnology, nanoparticles (NPs) play an important role in the non-enzymatic electrochemical sensors due to their good catalytic performance and biocompatibility.[15,16] Especially, metal nanoparticles with good catalytic properties and conductivity can be modified on the electrode. Among these nanoparticles, NPs of Pd,[17] Cu,[18] Au[19] and Ag[20] have been used to construct electrochemical sensors for detecting H_2O_2..

Comparing with other metal nanoparticles, excellent catalytic properties of Ag NPs are getting greater attention of the researchers. Ag NPs have attracted much interest in the sensor applications due to their low cost, high surface-to-volume ratio and excellent conductibility.[21,22] In addition, in our group, the dispersed AgNPs were synthesized by using methyl aldehyde as reducing agent at a gas-liquid interface, which could slow down the rate of reduction reaction, and thus the aggregation of AgNPs was avoided.[23]

In recent years, phosphate nanomaterials have been reported, such as $LiFePO_4$,[24] $AlPO_4$,[25] and $FePO_4$.[26] Among them, $FePO_4$ is a particularly promising material because of good electrochemical activity and has aroused wide attention.[27,28] Besides, $FePO_4$ nanosphere has many advantages, including environment-friendliness, low-cost, large surface area, good electron transfer capability and good thermal stability.[29–31] It has been reported that the amorphous $FePO_4$ nanosphere can be a catalyst supporter for loading Au NPs, and the obtained Au/$FePO_4$ catalyst can catalyze oxidation of

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*For correspondence

CO.[32] Therefore, $FePO_4$ nanosphere could also be used as a catalyst support with a great potential. The high surface-to-volume ratio and negative surface charge of $FePO_4$ nanosphere could provide a large surface to load more Ag NPs, and thereby improve the catalytic performance toward the reduction of H_2O_2. To the best of our knowledge, Ag NPs decorated $FePO_4$ nanosphere has never been reported so far. Besides, the synthetic method of $FePO_4$ nanosphere is much simpler than other catalyst supports such as graphene.[33]

In this study, Ag/$FePO_4$ nanocomposites were prepared at a gas-liquid interface. Based on this, we developed a new type of non-enzymatic sensor for electrochemical detection of H_2O_2. This paper may provide a good catalyst support and a simple method for the development of H_2O_2 electrochemical sensors.

2. Experimental

2.1 *Materials*

Hydrogen peroxide (30%, v/v aqueous solution), acetaldehyde (C_2H_4O, 40%) and ammonium ferrous sulfate ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$) were purchased from Tianjin Tianli Chemistry Reagent Co., Ltd (Tianjin, China); Chitosan (CS, MW 5–6×10^5, >90% deacetylation) was purchased from Shanghai Yuanju Biotechnology Co, Ltd (Shanghai, China); 0.1 M phosphate buffered saline (PBS, pH 7.2) as the supporting electrolyte in electrochemical experiments. In addition, other reagents and chemicals were analytical reagent grade. Doubly distilled water was used in all the experiments.

2.2 *Apparatus and Electrochemical Measurements*

The transmission electron microscopic (TEM) measurements were executed with Tecnai G^2 F20 S-TWIN (FEI, USA). The energy-dispersive Xray spectroscopy (EDS) was performed during the scanning electron microscopic JSM-6700F (JEOL, Japan) measurements.

Electrochemical measurements were executed with a classical three-electrode electroanalysis system of CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China). The bare Au electrodes (diameter: 2.0 mm), $FePO_4$ modified Au electrode and Ag/$FePO_4$ modified Au electrode were used as working electrodes in respective experiments. The saturated calomel electrode (SCE) and platinum wire electrode were used as the reference electrode and counter electrode, respectively. The whole experiment was conducted at room temperature (25 ± 2°C).

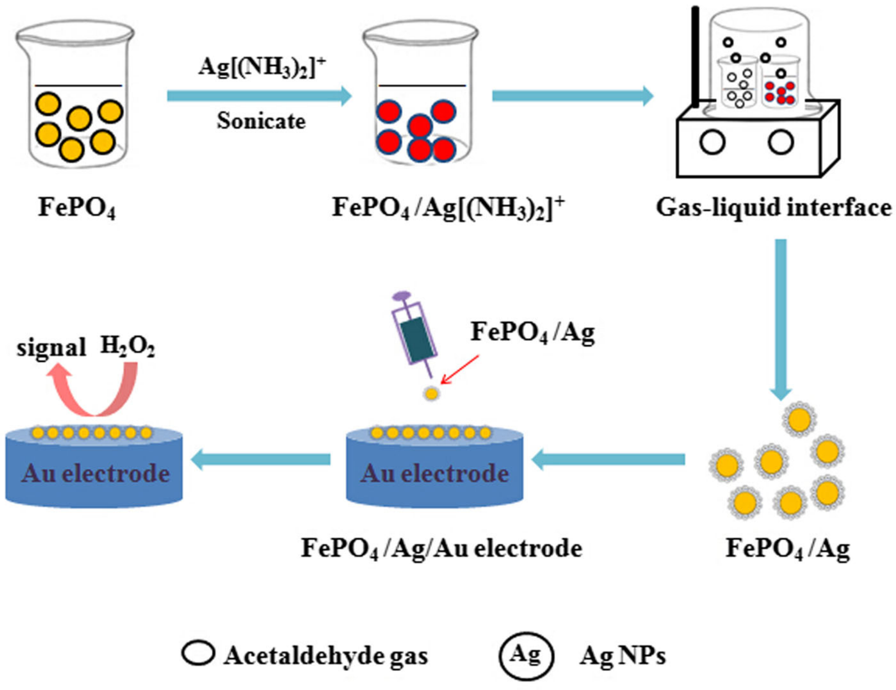
2.3 *Fabrication of the Sensor*

2.3a *Synthesis of $FePO_4$ nanospheres*: $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (0.4 g), urea (1.0 g) H_3PO_4 (14 μL) and sodium dodecylsulfate (SDS, 0.1 g) were dissolved in 20 mL doubly distilled water. The mixture was stirred vigorously for about ten minutes, and then decanted into a 25 mL-Teflon-lined autoclave, heated and kept at 80°C for 12 h. The autoclave was naturally cooled to room temperature after completion of the reaction. The final sediment was collected by centrifugation at 7000 rpm for 8 min, washed twice with doubly distilled water and then dried at 6°C for 12 h.

2.3b *Synthesis of Ag/$FePO_4$*: 10 mL of $AgNO_3$ (10 mM) was added to a 25 mL beaker containing 10 mL of doubly distilled water. Then, 200 μL of NaOH (1 mol L^{-1}) solution was added to this beaker under stirring condition until a fine brown precipitate of Ag_2O was formed. The brown precipitate of Ag_2O gradually disappeared until clarification when 25% $NH_3{\cdot}H_2O$ (300 μL) was added drop by drop under stable stirring condition. $Ag[(NH_3)_2]^+$ solution (4.88 mM) was prepared and left for future use.

$FePO_4$ powder (15 mg) was completely dispersed to 45 mL of ethanol-water (1:1, v/v) solution by ultrasound for 30 min, and then ultrasonically mixed with 5 mL of abothe ve as-prepared $Ag[(NH_3)_2]^+$ solution. After a while, the mixture and another beaker which with 10 mL of CH_3CHO solution were placed in a sealed beaker. This modified silver mirror reaction was performed for 1 h under stable stirring at room temperature. The composite products was collected by centrifugation at 7000 rpm for 8 min, washed thrice with doubly distilled water, and then dried at 5°C for 10 h.

2.3c *Modification of electrode*: The Au electrode was prepared by a simple method. Before use, the Au electrode was polished with 1.0 and 0.3 μm alumina powder to obtain a mirror-like surface. Then washed with doubly distilled water, completely cleaned in ethanol solution and doubly distilled water in proper order under ultrasonic condition. The Au electrode was dried in a stream of nitrogen. 1 mg of Ag/$FePO_4$ nanocomposite was dispersed in 1 mL of chitosan (wt%, 0.5%) solution under ultrasonic condition for 30 min. The obtained suspension (5 μL) was dropped to the surface of Au electrode and dried in air at room temperature. The modified electrode can be labeled as Ag/$FePO_4$/Au electrode. The process of the synthesis of the material and the modification of the electrode are shown in scheme 1.



Scheme 1. Schematic illustration for the synthesis of $Ag/FePO_4$ nanocomposite and modification of the Au electrode.

3. Results and Discussion

3.1 *Characterization of $Ag/FePO_4$ Nanocomposites*

The transmission electron microscopic (TEM) measurements are an efficient tool to characterize the morphology of nanocomposites. The morphology of $FePO_4$ (A, B) and $Ag/FePO_4$ (C, D) nanocomposites are shown in figure 1. From figure 1A and B we can know that the $FePO_4$ composite was more likely a spherical nanomaterial with an average diameter of 650 ± 50 nm. Compared with figure 1D, it is clearly seen that $FePO_4$ nanospheres were successfully decorated with well-dispersed Ag nanoparticles according to the synthesis method. The average diameter of Ag NPs is ranging from 8 to 10 nm. Moreover, a large amount of Ag NPs with small spherical particles were observed uniformly on the surface of the $FePO_4$ nanosphere. Furthermore, the EDS analysis had also been used to characterize the elements in $Ag/FePO_4$ nanocomposites. The EDS spectrum is shown in figure S1 in Supplementary Information.

3.2 *Electrochemical behavior of $Ag/FePO_4$*

Electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate the interfacial properties of chemically modified electrodes. Generally, the semicircle diameter of the nyquist plot represents the electron transfer resistance (Rct).[34] The suitable equivalent circuit obtained by CHI 660 software is shown in figure 2. Here, R_s is the ohmic resistance of the electrolyte solution; *Cdl* indicates an ideal capacitor; Q is used to represent a constant phase element which is an accumulation of all capacitive effects in the measurement; R_{et} is the interfacial electron-transfer resistance and W is a Warburg impedance which models the diffusion of ions from the bulk electrolyte to the electrode. As shown in figure 2, the diameter of semicircle of the $Ag/FePO_4/Au$ electrode (curve a) is smaller than those of the bare Au electrode (curve b) and $FePO_4/Au$ electrode (curve c). Moreover, the semicircle diameter has increased from 50 Ω to 300 Ω when the $FePO_4$ is fixed to the surface of Au electrode. However, the R_{et} decreased extremely after addition of the Ag NPs to the surface of $FePO_4$ composite. It should be noted that the curve for the $Ag/FePO_4/Au$ electrode looks approximately like a straight line in that frequency range, indicating that the R_{et} of the $Ag/FePO_4$ is pretty small. Therefore, the $Ag/FePO_4$ could efficiently enhance the electron transfer efficiency.

Figure 3 shows the electrochemical responses of the bare Au electrode, $FePO_4$ modified Au electrode and $Ag/FePO_4$ modified Au electrode as working electrode, respectively. The red arrow indicates the direction of sweep (as in other CVs). From the figure 3, we can know that the bare Au electrode (curve b), $FePO_4$ modified Au electrode (curve c) and $Ag/FePO_4$ modified Au electrode (curve a) show almost no electrochemical response in the absence of H_2O_2. However, the electrochemical responses have been changed

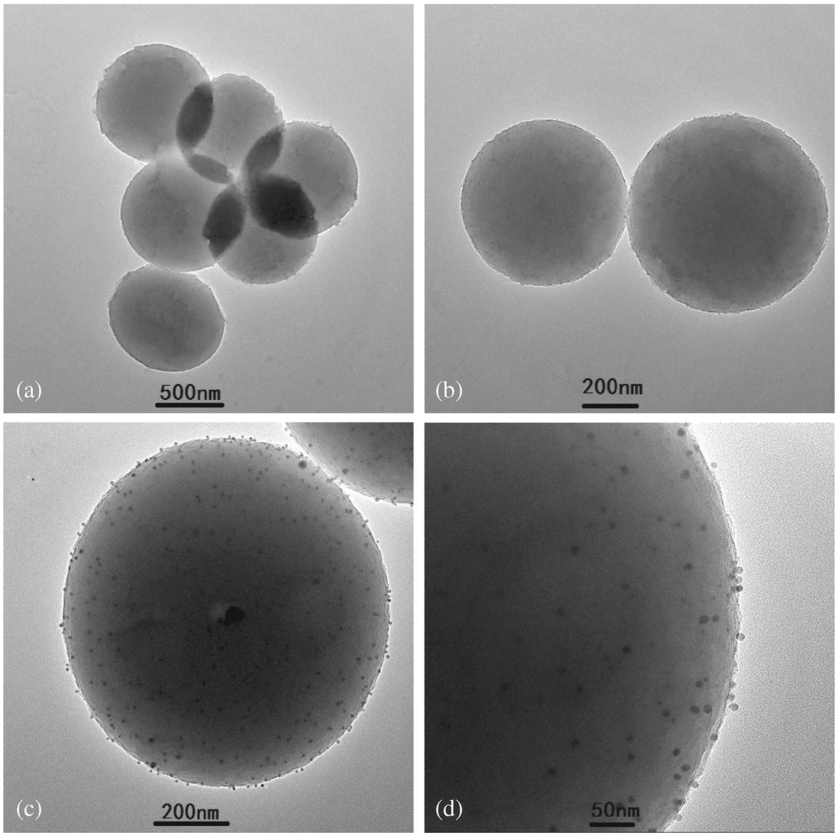


Figure 1. TEM images of $FePO_4$ (A, B), and $Ag/FePO_4$ (C, D).

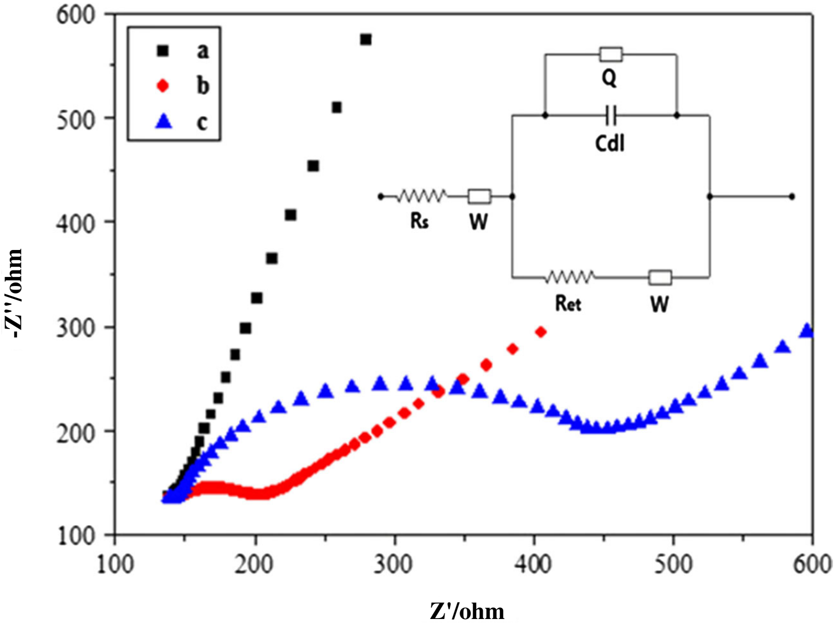
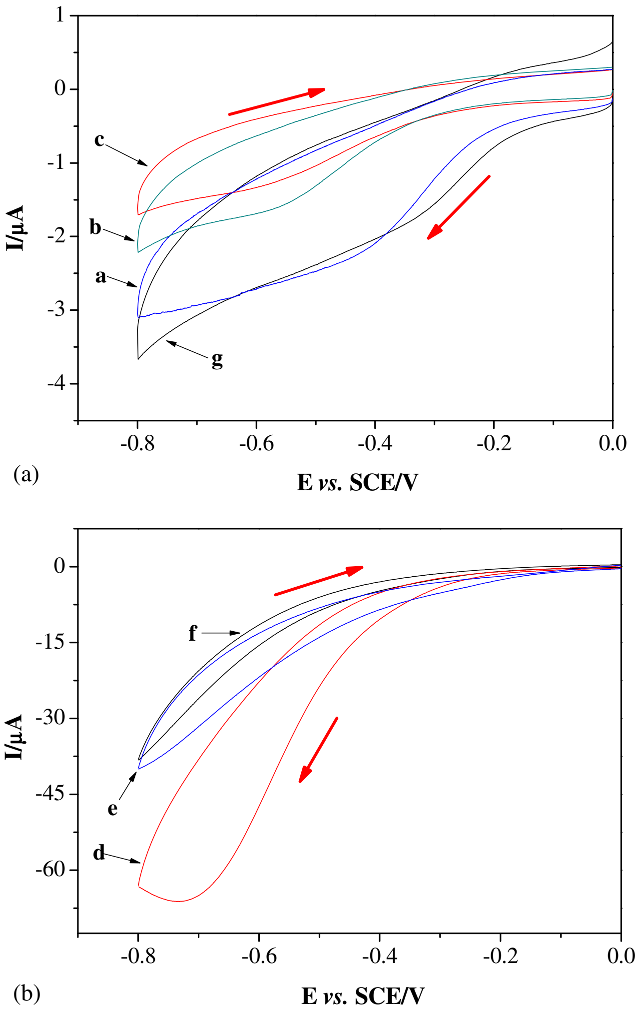


Figure 2. Nyquist plots of (a) $Ag/FePO_4/Au$ electrode, (b) bare Au electrode and (c) $FePO_4/Au$ electrode in KCl solution (0.10 M) containing 5.0 mM $[Fe(CN)_6]^{4-/3-}$ at open-circuit potential conditions. Frequency range: 0.01 Hz to 10 kHz; AC amplitude: 5.0 mV. Inset: Equivalent electrical circuit obtained by CHI 660 software.



(a)

(b)

Figure 3. CV curves (b, e) of bare Au electrode, (c, f) FePO$_4$ modified Au electrode and (a, d) Ag/FePO$_4$ modified Au electrode in N$_2$-saturated 0.1 M PBS (pH 7.2) in the absence (b, c and a) and presence (e, f and d) of 5 mM H_2O_2 at a scan rate of 0.1 V/s. (curve g) Ag/FePO$_4$/Au electrode in O$_2$-saturated 0.1 mol·L^{-1} PBS (pH 7.2) in the absence of H_2O_2.

significantly when 5 mM H_2O_2 was added (figure 3B). Comparing with Ag/FePO$_4$ modified Au electrode (curve d), the bare Au electrode (curve e) and FePO$_4$ modified Au electrode (curve f) exhibited low electrochemical responses. The CV curves of Ag/FePO$_4$/Au electrode (curve g) in O$_2$-saturated 0.1 M PBS (pH 7.2) in the absence of H_2O_2 are shown in figure 3A. The reduction current of oxygen was small enough to be negligible. It shows that oxygen had a negligible effect in the electrochemical experiments. The Ag/FePO$_4$ modified Au electrode showed an apparent catalytic current peak of approximately −65 μA at nearly −072 V. Thus, the Ag/FePO$_4$ nanocomposites show good catalytic performance towards the electroreduction of H_2O_2.

The mechanism of H_2O_2 electro-reduction can be expressed as follows:[35]

$$H_2O_2 + e^- \rightleftharpoons OH_{(ads)} + OH^- \tag{1}$$

$$OH_{(ads)} + e^- \rightleftharpoons OH^- \tag{2}$$

$$2OH^- + 2H^+ \rightleftharpoons 2H_2O \tag{3}$$

When the surface of the electrode is modified by the Ag NPs, the cathodic reaction is the reduction of H_2O_2 as the first electron transfer reaction and the anodic reaction is the dissolution of Ag NPs. Actually, the Ag NPs disproportionate the balance of the reaction and speed up the reaction rate in the buffer solution, and the reaction becomes more irreversible:[35]

$$H_2O_2 \xrightarrow{\text{Ag}} 1/2\ O_2 + H_2O \tag{4}$$

$$O_2 + 2e^- + 2H^+ \xrightarrow{\text{Au electrode}} H_2O_2 \tag{5}$$

However, the presence of oxygen in the above action could become the detection lsignal on electrode. The electroreduction of O_2 on electrode occurs by the mechanism shown below.[36]

$$O_2 + e^- \rightleftharpoons [O^{\cdot}{}_2{}^-]_{\ (ads)} \tag{6}$$

$$[O^{\cdot}{}_2{}^-]_{\ (ads)} + H_2O \rightleftharpoons HO_2{}^{\cdot}{}_{(ads)} + OH^- \tag{7}$$

Then,

$$\begin{aligned} &HO_2^{\cdot}{}_{(ads)} + [O_2^{\cdot}] \rightleftharpoons HO_2^-{}_{(aq)} + O_2 \\ &\text{or } HO_2^{\cdot}{}_{(ads)} + e^- \rightleftharpoons HO_2{}^-{}_{(aq)} \end{aligned} \tag{8}$$

Because of the excellent catalytic properties of Ag NPs for H_2O_2, the response signal of H_2O_2 was detected after Ag NPs were fixed on the surface of FePO$_4$.

The amount of as-prepared $[Ag(NH_3)_2]^+$ solution is critical to electrochemical experiments because Ag NPs could enhance the electron transfer efficiency for the determination of H_2O_2.[23] The different amounts of as-prepared $[Ag(NH_3)_2]^+$ solution can be used to synthesize Ag/FePO$_4$ nanocomposites decorated with different amounts of Ag NPs. Therefore, the Ag/FePO$_4$ nanocomposites with different amounts of Ag NPs were prepared to construct the modified electrode to detect H_2O_2 by CVs. The experimental results are shown in figure 4. As seen in figure 4, the peak current increased at the beginning and then decreased with the raise of $[Ag(NH_3)_2]^+$ solution and the maximum peak current was observed with 6 mL as-prepared $[Ag(NH_3)_2]^+$ solution. However, more Ag NPs were easily aggregated and the catalytic properties were then reduced. Therefore, we chose 5.0 mL of as-prepared $[Ag(NH_3)_2]^+$ solution as appropriate.

The reduction peak current increased with the increasing concentration of H_2O_2 from 0.5 to 5.0 mM

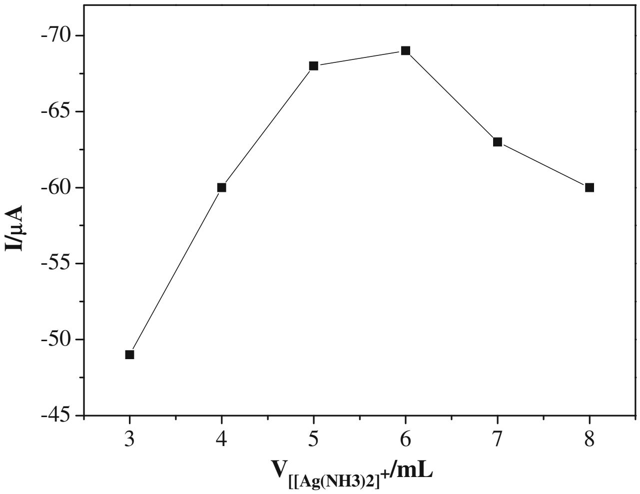


Figure 4. The current response (peak current) values obtained by Ag/$FePO_4$/Au electrode in N_2-saturated 0.1 M PBS (pH 7.2) containing 5 mM H_2O_2 at a scan rate of 0.1 V s^{-1} with different amounts of 4.88 mM as-prepared $[Ag(NH_3)_2]^+$ (3, 4, 5, 6, 7 and 8 mL).

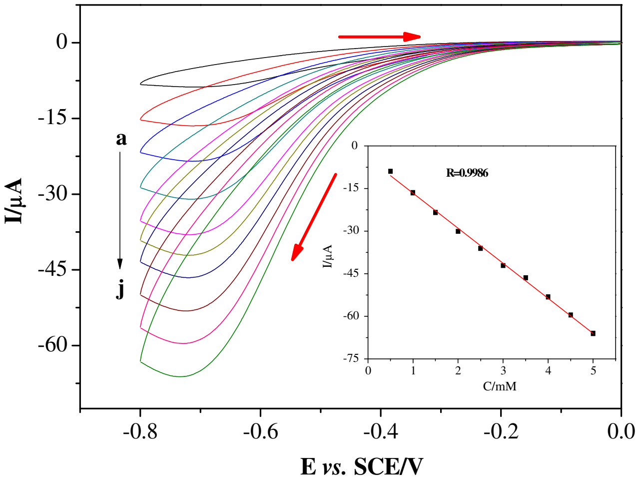


Figure 5. CV curves of Ag/$FePO_4$ modified Au electrode in the presence of different H_2O_2 concentrations (from a to j: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5.0 mM) in N_2-saturated 0.1 M PBS (pH 7.2) at a scan rate of 0.1 V s^{-1} Inset: Linear fitting of the reduction peak current with H_2O_2 concentration.

on the Ag/$FePO_4$ modified Au electrode as shown in figure 5. Figure 5 inset shows that there is a good linear relationship (R = 0.9986) between reduction peak current and concentration of H_2O_2. These results strongly demonstrate that the Ag/$FePO_4$ nanocomposites had remarkable electrocatalytic performance towards H_2O_2.

The reduction current at different scan rates with 4.0 mM H_2O_2 is shown in figure 6. The reduction peak current changed linearly with the square root of the scan rate when the scan rate gradually increased from 0.02 to 0.14 V s^{-1}. Therefore, the electrochemical

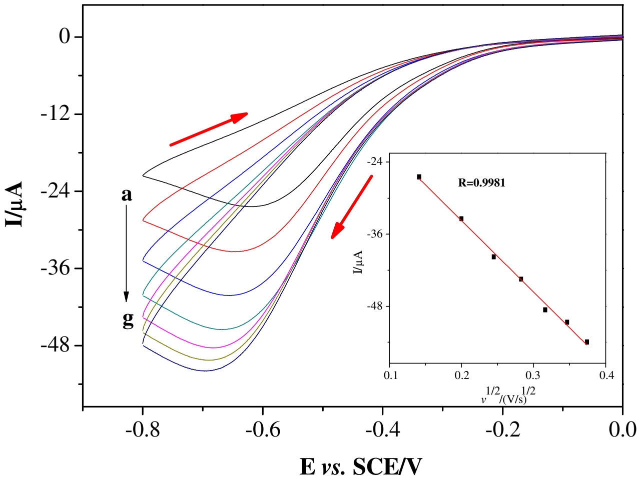


Figure 6. CV curves of the Ag/$FePO_4$ modified Au electrode in N_2-saturated 0.1 M PBS (pH 7.2) containing 4.0 mM H_2O_2 at different scan rates (from a to g: 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 V s^{-1}). Inset: Linear fitting of reduction peak current versus $\upsilon^{1/2}$.

process of H_2O_2 reduction on the Ag/$FePO_4$ modified Au electrode is diffusion-controlled.

Figure 7A shows the amperometric current−time curve of the Ag/$FePO_4$ modified Au electrode in N_2-saturated 0.1 M PBS (pH 7.2) under stirring condition. The calibration curve for the Ag/$FePO_4$ modified Au electrode is shown in figure 7B. It can be observed that the Ag/$FePO_4$ modified Au electrode exhibits quick response within 4 s. The linear regression equation is I_p (μA) = −2.6 C (mM) - 1.24 with a correlation coefficient of 0.9995. Moreover, the Ag/$FePO_4$ modified Au electrode has linear amperometric response to concentration of H_2O_2 in the range of $3 \times 10^{-5} - 1.1 \times 10^{-2}$ M is shown in figure 7B. The sensitivity and detection limit were calculated to be 82.8 μA cm^2 mM^{-1}, 4.7 μM (Signal-to-noise ratio: 3), respectively. The comparison of the performance of our sensor with other non-enzymatic H_2O_2 sensors are listed in table 1. It is noticeable that our sensor had higher sensitivity than other reported sensors. In addition, our sensor has an acceptable linear range and detection limit. The good performance may be because excellent electrocatalytic properties of AgNPs for electro-reduction of H_2O_2

3.3 *Interference Study*

The amperometric response of the Ag/$FePO_4$ modified Au electrode upon the injection of H_2O_2 (0.5 mM) and other electroactive species (0.5 mM) in N_2-saturated 0.1 M PBS (pH 7.2) with stirring condition at −0.45 V are shown in figure 8A The addition of 0.5 mM H_2O_2 exhibits an obvious amperometric response, while the amperometric current was not changed obviously when glucose, ethanol, ascorbic acid (AA) and uric acid (UA) were added. The amperometric response of the Ag/$FePO_4$ modified Au electrode in O_2-saturated (curve a) and N_2-saturated (curve b) 0.1 M PBS are shown in figure 8B. From the figure 8B, we can clearly see the stability of the current responses and a good signal-to-noise ratio in N_2-saturated 0.1 M PBS at −0.45 V (curve b). The background noise increased because of the electro-reduction of O_2 when it was detected in O_2-saturated 0.1 M PBS (curve a). But the response current

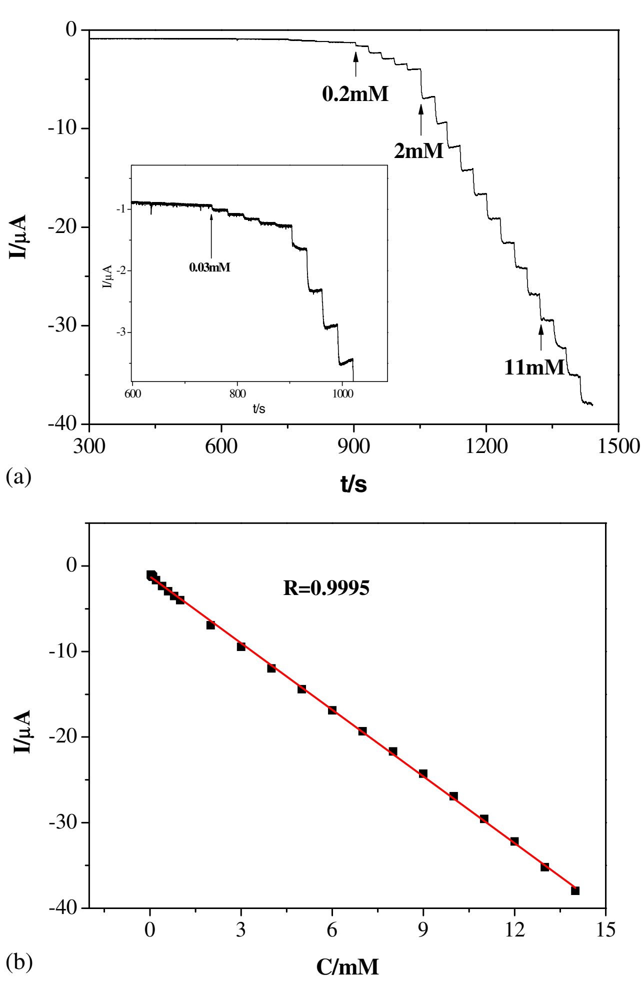


Figure 7. (A) Amperometric response of the Ag/$FePO_4$ modified Au electrode upon successive injection of H_2O_2 in N_2-saturated 0.1 M PBS (pH 7.2) under stirring condition Applied potential: −0.45 V. Inset: Amplification of the plot for low concentrations. (B) Calibration curve of current versus its concentration.

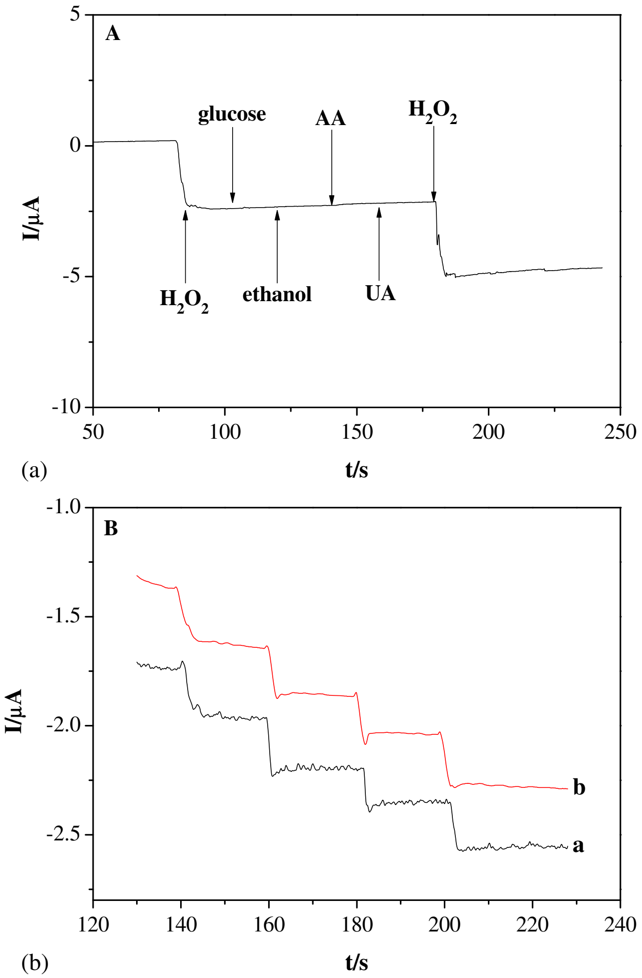


Figure 8. (A) Amperometric response of the Ag/$FePO_4$ modified Au electrode to successive addition of H_2O_2, glucose, ethanol, ascorbic acid (AA), and uric acid (UA) (0.5 mM, respectively) in N_2-saturated 0.1 M PBS (pH 7.2) under stirring condition. (B) Successive addition of H_2O_2 (0.15 mM) in (a) O_2-saturated and (b) N_2-saturated 0.1 M PBS (pH 7.2). Applied potential: −0.45 V.

Table 1. Comparison of analytical performance of our H_2O_2 sensor with other non-enzymatic H_2O_2 sensors.

Sensors	Applied potential (V)	Linear range (mM)	Sensitivity (µA mM^{-1} cm^{-2})	Detection limit (µM)	References
Ag-PQ11/GCE	−0.30	0.1–180	_	33.9	37
Ag/MWCNT/Au electrode	−0.20	0.05–17	20	0.50	38
MnO_2/carbon fiber microelectrode	+0.58	0.012–0.26	10.6	5.4	39
Ag-CP/GCE	−0.30	0.7–70	_	0.9	40
Ag@TiO_2/GCE	−0.73	0.83–43.3	25.23	0.83	41
Ag/$FePO_4$/Au electrode	−0.45	0.03–11	82.8	4.7	This study

Table 2. H_2O_2 detection in detergent samples by the standard addition method.

Sample	H_2O_2 added (mM)	H_2O_2 found (mM) (n = 3)※	Recovery (%)
detergent sample	—	0.142 (±0.03)	—
Sample 1	0.1	0.240 (±0.05)	98.0
Sample 2	0.25	0.389 (±0.03)	98.8
Sample 3	1.5	1.651 (±0.02)	100.6

※Average of three determinations (± relative standard deviation).

almost remained unchanged. So the Ag/$FePO_4$ modified Au electrode exhibited excellent performance of anti-interference to O_2. Hence we conclude that the H_2O_2 sensor has a favorable ability of anti-interference to other electroactive species and O_2.

3.4 *Repeatability and stability study*

The repeatability and stability of Ag/$FePO_4$ modified Au electrode is extremely important for the entire experiment. The amperometric current responses of five the Ag/$FePO_4$ modified Au electrodes at −0.45 V are compared. The relative standard deviation (RSD) was about 3%, so the modified electrode has good repeatability. The Ag/$FePO_4$ modified electrode remained at 90% of its initial current response after four weeks. To sum up, the Ag/$FePO_4$ modified electrode has acceptable reproducibility and stability.

3.5 *Real sample analysis*

The real sample analysis of our H_2O_2 sensor was tested for detecting a detergent by the standard addition method. Briefly, the detergent sample (1.0 mL) was added to 9.0 mL of 0.1 M PBS (pH 7.2) and recorded the amperometric responses of H_2O_2 reduction in N_2-saturated 0.1 PBS. The experimental results are listed in table 2. It is noticed that our H_2O_2 sensor could be used for the detection of H_2O_2 in the real samples.

4. Conclusions

In summary, the Ag/$FePO_4$ nanocomposites were synthesized by a modified silver mirror reaction at gas-liquid interface. Then the non-enzymatic H_2O_2 sensor was fabricated using this nanocomposites modifying the surface of the gold electrode. The non-enzymatic H_2O_2 electrochemical sensor presents excellent catalytic performance for the detection of H_2O_2 with a wide linear range and anti-interference ability. This study may be propitious to develop new methods for H_2O_2 electrochemical sensors.

Supplementary Information (SI)

The EDS spectrum of Ag/$FePO_4$ nanocomposites (figure S1) is given in the supporting information available at www.ias.ac.in/chemsci.

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