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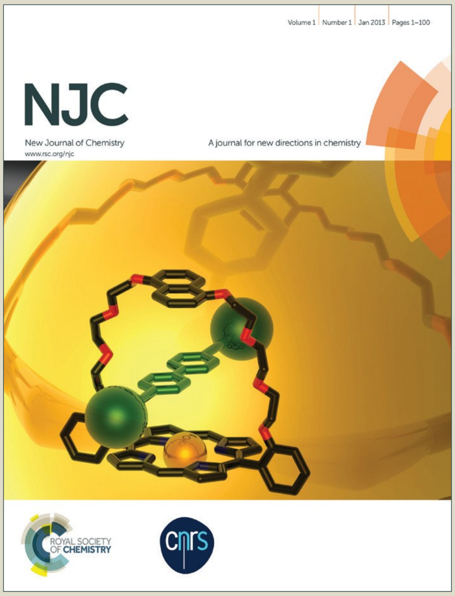

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Amperometric sensor for ascorbic acid using a gold electrode modified with $ZnO@SiO_2$ nanospheres

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Abstract

Here we report a facile synthesis of ZnO coated SiO_2 ($ZnO@SiO_2$) nanospheres as a high-performance sensing materials for ascorbic acid (AA). ZnO nanospheres were first prepared by hydrothermal method and further SiO_2 were coated over ZnO nanospheres by sol-gel process. The sensing prospective of $ZnO@SiO_2$ nanospheres were explored which demonstrated that $ZnO@SiO_2$ nanospheres are responsive for ascorbic acid. By comparing the sensing ability of ZnO nanospheres with $ZnO@SiO_2$ nanospheres, it was deduced that $ZnO@SiO_2$ nanospheres are much more sensitive towards ascorbic acid as compared to ZnO nanospheres. The results recommended that $ZnO@SiO_2$ nanospheres have remarkable sensitivity (0.2232 mA mM^{-1} cm^{-2}) toward ascorbic acid with wide range (0.1 mM ~ 1.5 mM) of detection and lower limit of detection (64.5 μM). The performance of the sensor was additionally optimized by different scan rates. Thus $ZnO@SiO_2$ nanospheres could be prospective material for the production of sensitive and competent ascorbic acid sensor.

Keywords: $ZnO@SiO_2$; Nanospheres; Structural properties; Ascorbic acid; High sensitivity; Lower limit of detection

1. Introduction

Ascorbic acid (AA) has key roles in physiological function of organisms and the deficiency or disturbance of AA level causes the symptoms of several diseases [1-5]. Therefore, detection and quantification of AA is too much important for controlling and monitoring of medicine and food stuff. Significant efforts have been done and too much attention has been paid for the development of trustworthy approaches for the recognition of AA [1-6].

Different techniques (electrophoresis, fluorescence, chemiluminescence, liquid chromatography and electrochemical) have been employed for the recognition, determination and quantification of AA [1,2]. But because of electroactive behavior of AA, electrodes have gained considerable attention due to clinical diagnostic point of view. But the detection of AA at bare conventional electrodes generally foul the electrodes because of the irreversible oxidation process of AA at bare conventional electrodes. The irreversible oxidation process of AA produces 2,3-diketogluconic acid that eagerly adsorbed onto the electrode surface and consequently foul the electrode [1-4]. Therefore, modifications of the bare electrodes with nanomaterials as the redox active site have been used in the design and development of electrochemical sensors. Thus, the design of new nanomaterials is most necessary and has become a challenging research topic.

Several type of nanomaterials have been used for the modification of conventional electrodes but they have limitation either due to their scarcity, cost, sensitivity, detection limit, selectivity, linear responses in narrow concentration ranges, and stability [1-10]. Among them, ZnO is a multifunctional material and has been extensively utilized in numerous fields [11,12]. Zinc oxide is important material but has shown lower sensitivity toward AA sensing [13]. Therefore, the features of zinc oxide require to be reformed for the demand to increase its surface area and reduce the size of ZnO that are responsible for improving numerous assets of ZnO [14,15]. Many attempts have been done to improve the sensing properties of ZnO toward AA and different hybrids and nanocomposite of

ZnO have been utilized but still the sensitivity toward AA sensing is not much improved [16-18] On the other hand, mesoporous materials have been appeared as innovative type of materials and become the center of great attention due to their exclusive electrical, magnetic, optical, and catalytic properties. The interest in mesoporous materials is mainly due their easy preparation method, low cost and has been utilized in different types of electrochemical sensors [19,20].

Therefore, the present exploration is based on synthesis of ZnO coated SiO_2 nanospheres and their sensing potential for AA. The results suggested that ZnO@SiO_2 nanospheres have incredible electro-catalytic property toward AA. The fabricated sensor exhibited high sensitivity, selectivity, wide concentration range and lower limit of detection.

2. Experimental

2.1. Chemicals and reagents

Zinc nitrate, NaOH, AA, ascorbic acid and all other chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA, http://www.sigmaaldrich.com).

2.2. *Synthesis of ZnO nanospheres*

Zinc nitrate was dissolved in distilled water and 0.1 M solution of zinc nitrate was titrated by NH_4OH solution till pH reached above 10.0. This ensuing basic solution was stirrer at 60.0 ^{0}C for overnight and the resulting product was washed with 1:1 mixture of distilled water and ethanol. The product was then dried at room temperature and further calcined at 400.0 ^{0}C for 5 hours [20].

2.3. *Synthesis of ZnO@SiO_2 nanospheres*

$ZnO@SiO_2$ nanospheres were prepared by coating ZnO nanospheres with SiO_2 by well-known sol gel method [19,21] giving rise to $ZnO@SiO_2$ nanospheres. Briefly, the above synthesized ZnO (0.1 g) was added to a conical flask charged with water (10 mL), CTAB (0.3 g) and concentrated ammonia solution (0.5 g, 2.0 mL, 14 wt%) and was well dispersed. After dispersion, 0.2 g of tetraethyl orthosilicate (TEOS) was added dropwise and the reaction was allowed to proceed for 12 h under continuous mechanical stirring. The resulting product was washed with distilled water and ethanol (1:1) and calcinced at 600.0 ^{0}C for 5 hours.

2.4. Apparatus

The morphology of the synthesized product was studied at 15 kV using a JEOL Scanning Electron Microscope (JSM-7600F, Japan). X-ray diffraction patterns (XRD) were taken with a computer controlled RINT 2000, Rigaku diffractometer using the Ni-filtered Cu-K_α radiation (λ = 0.15405 nm). FT-IR spectrum was recorded in the range of 400 to 4000 cm^{-1} on PerkinElmer (spectrum 100) FT-IR spectrometer. Epsiolon cyclic voltammeter (CV) was used for sensing of ascorbic acid.

2.5. Fabrication of sensor for ascorbic acid

First the gold electrode (AuE) was polished and rinsed with alumina powder and distilled water, respectively and dried. Then working electrode was prepared by dispersing 5 mg of $ZnO@SiO_2$ nanospheres on the surface of gold electrode along with nafion (5 mL) and dried at 50 ^{o}C for few hours. Phosphate buffer (0.1 M, pH 7.0) was used through out the experiment as an aqueous media. For the detection of ascorbic acid, three-electrode cell was utilized using working electrode (nanospheres coated electrode), reference electrode (Ag/AgCl (saturated KCl) electrode) and counter electrode (platinum wire).

3. Results and Discussion

3.1. *Preparation and physiochemical characterization of $ZnO@SiO_2$ nanospheres*

The selection and preparation of appropriate materials for the development of efficient AA sensor is crucial from cost, stability, sensitivity, abundance and practical applicability point of view. Therefore, because of low cost, highly abundance, stability and diverse applications, we have selected ZnO which is a multifunctional material and has been extensively utilized in numerous fields [11,12]. However, ZnO has shown lower sensitivity toward AA sensing [13]. Therefore, we made an attempt to make mesoporous ZnO to be reformed for the demand of high sensitivity toward AA. Therefore, ZnO was prepared by simple low temperature and then synthesized $ZnO@SiO_2$ nanospheres by well-known sol gel method [19,21]. $ZnO@SiO_2$ was further characterized by different spectroscopic techniques and fabricated as a sensing element for the detection of AA.

The morphology of synthesized $ZnO@SiO_2$ nanospheres was examined by low and high magnified FESEM images as shown in Fig. 1. FESEM images revealed that the synthesized $ZnO@SiO_2$ has spheres shapes which are nano in size. The average diameter of $ZnO@SiO_2$ nanospheres is around ~30 ± 0.1 nm.

……………………Figure 1……………………

The composition of doped nanospheres was assessed by using EDS which is illustrated in Fig. 2. EDS indicate that only Zn, Si, C and O elements exist in nanospheres. No extra element was found which specify that nanospheres are composed of carbon coated zinc oxide.

……………………Figure 2……………………

Crystal structure of $ZnO@SiO_2$ nanospheres was explored by X-ray powder diffraction (Fig. 3(a)). $ZnO@SiO_2$ nanospheres presented correctly same sequence of typical peaks as that of wurtzite hexagonal ZnO nanoparticle [11,12]. The XRD spectrum define that the prepared nanospheres contains $ZnO@SiO_2$.

……………………Figure 3…………………

FT-IR spectrum of $ZnO@SiO_2$ nanospheres showed peaks at 504, 902, 1400, 1636 and 3420 cm^{-1} (Fig. 3(b)). The sharp peak detected at 504 cm^{-1} is attributed to Zn-O bond [11,12] while the peak at 902 cm^{-1} is due to Si-O bond. The extra peaks located at 1400, 1636 and 3420 cm^{-1} are assigned to CO_2 or CO_3 anion and O-H stretching and bending [14,15].

3.2. Chemical sensing properties

Searching of sensing materials for ascorbic acid recognition is imperative in order to develop a sensor for detection of AA at ultra trace level because AA is an important material exists in fruits, vegetables and other food stuff of daily life [21-24]. For this reason, $ZnO@SiO_2$ nanospheres were utilized as a sensing material in order to fabricate a sensor for recognition of AA using CV and amperometery technique [20]. CV was operated for the determination of redox potential and electrocatalytic behavior of $ZnO@SiO_2$ nanospheres at applied voltage of -1 V to 1 V. The ascorbic acid sensor was fabricated by covering AuE active surface (working electrode) with ZnO@SiO$_2$ nanospheres and the sensing behavior of working AuE toward AA was measured in the presence and absence of AA using cyclic voltammograms (Fig. 4 (a)). Fig. 4 (a) shows that there no reduction peak in the absence of AA while in the presence of AA, working electrode exhibit a prominent catalytic reduction peak at 0.2 V which suggests that working electrode shows electrochemical response toward AA and consequently showing sensing behavior toward AA [20,25-28]. Fig. 4 (a) clearly specifies that the cathodic current increases with addition of AA that recommends that ZnO@SiO$_2$ nanospheres are sensitive toward AA and the working electrode converted chemical information of AA into an analytically important signal.

……………………Figure 4……………………

The concentration effect of AA was examined in the range of 0.1 mM ~ 1.5 mM (Figure 4(b)). It is clearly seen from the graph that cathodic peak is increasing with increase in concentration of AA. The calibration curve (Figure 4(c)) was plotted from the increase in cathodic peak with increase of AA concentration [20]. The cathodic current of the sensor amplified strongly at potential of 0.2 V with rise in concentration of AA. The calibration curve is linear over wide range of concentration. The linear curve indicates that this area is receptive region for AA and the sensor is highly sensitive.

ZnO@SiO$_2$ nanospheres displayed linear dynamic range from 0.1 mM to 1.5 mM (R^2= 0.9936) and detection limit of 64.5 μM, respectively with improved 3 signal-to-noise ratio. The sensitivity is considered as significant performance parameter of any biosensor; therefore, sensitivity of ZnO@SiO$_2$ nanospheres/AuE was investigated from calibration curve of different concentrations of AA *vs.* corresponding peak cathodic currents. The sensitivity of fabricated electrode was estimated to be 0.2232 mA mM^{-1} cm^{-2}.

The influences of potential scan rates on the electrochemical behavior of AA were investigated and the cyclic voltammograms are shown in Fig. 5 (a). With increasing scan rates from 20-500 mVs^{-1}, the reduction peak current increased gradually and linearly, indicating that the reduction of AA at working electrode is due to high electrocatalytic ability of ZnO@SiO_2 nanospheres [20]. The increase in cathodic peak currents (Ipc) indicates the reduction catalytic ability of ZnO@SiO_2 nanospheres toward AA. These outcomes illustrate the promising reduction ability of ZnO@SiO_2 nanospheres towards AA sensing. Fig. 5 (b) demonstrates a plot of Ipc vs. scan rate which is linear. This reduction in Ipc with rising scan rate suggests high electrocatalytic ability of ZnO@SiO_2 nanospheres.

…………………….Figure 5……………………

For amperometric sensing application, the fabricated electrode was further evaluated at fixed potential 0.2 V by measuring peak cathodic current. Figure 6 demonstrated the typical current-time response of sensor in pure N_2-saturated phosphate buffer (pH=7.0) solution on successive addition of 10 μM of AA. When an aliquot of AA solution was pipetted out to the well and slow stirred solution, the cathodic peak current was exponentially rose to a stable limiting current value, indicating fast amperometric response of fabricated electrode towards AA. It is found that the modified electrode has a good electrocatalytic activity for the reduction of AA at the applied potential (Figure 7). The sensor responded rapidly when AA is added, indicating fast diffusion of analyte to the substrate at the modified electrode and high sensitivity. Furthermore, the designed sensor responded linearly to concentration ranging from 0.1 mM to 0.9 mM with the correlation coefficient of 0.9973.

…………………….Figure 6……………………

…………………….Figure 7……………………

4. Conclusions

In summary, ZnO@SiO_2 nanospheres were synthesized and characterized by various spectroscopic techniques. The potential application about electrocatalytic activity was executed and ZnO@SiO_2 nanospheres were found to be an efficient material for the development of ascorbic acid sensor. Conclusively, ZnO@SiO_2 nanospheres are active electrocatalyst for the detection of ascorbic acid and is low cost, can be easily prepared in large quantity and is much more sensitive. This high sensitivity toward ascorbic acid make ZnO@SiO_2 innovative material for the recognition of ascorbic acid.

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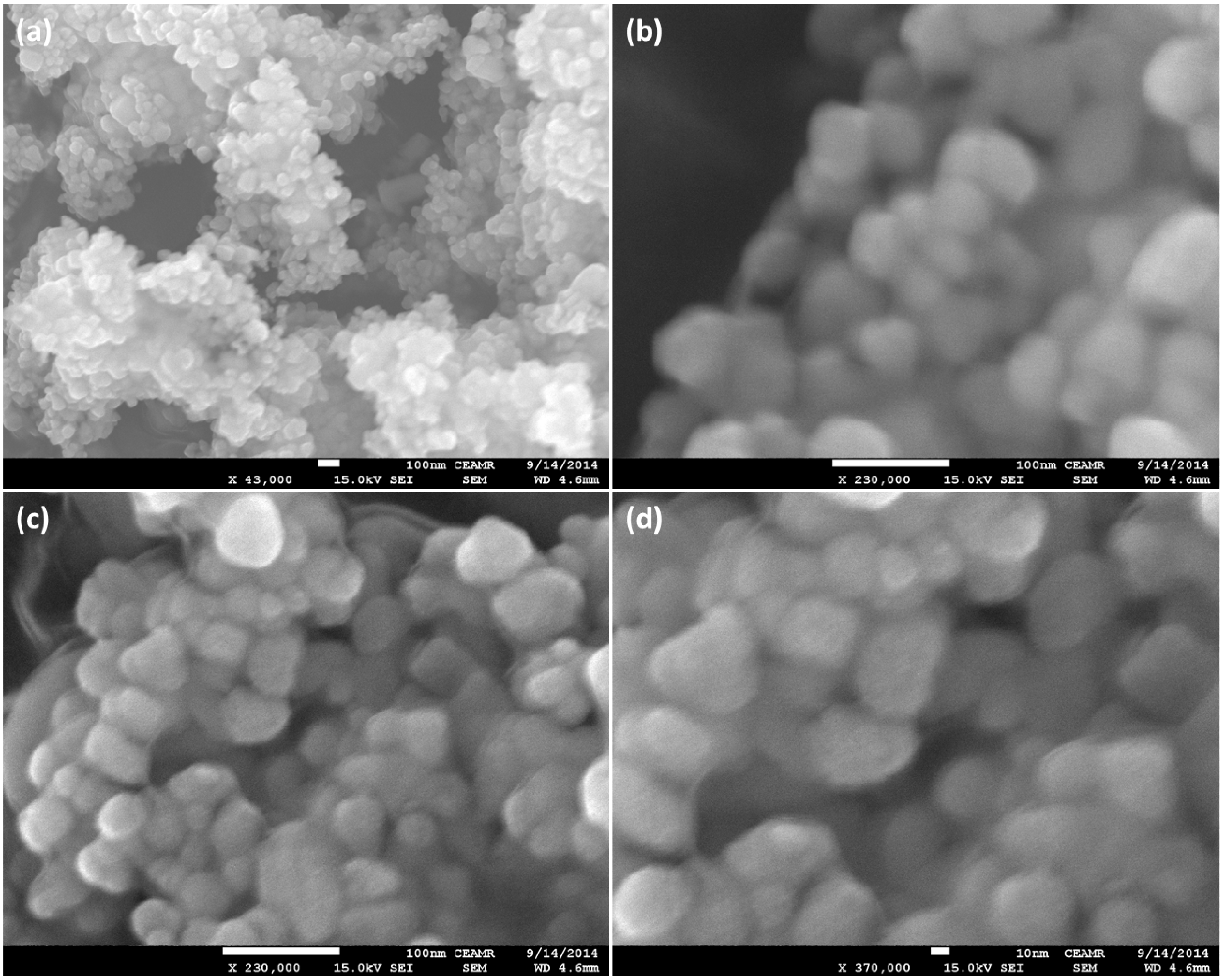
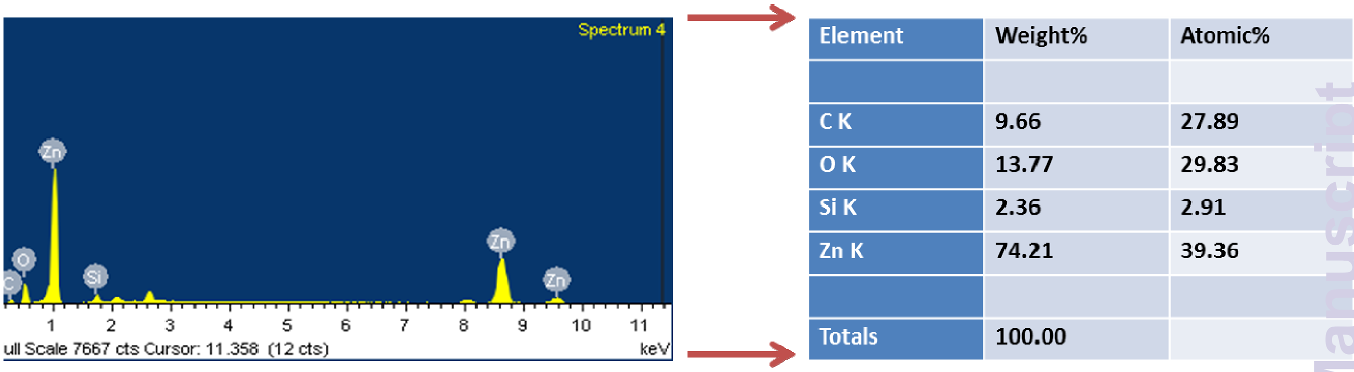


Figure 1. Typical low-magnification and high-resolution ((a) at x 4300, (b) at x 230000, (c) at x 230000 and (d) at x 370000 magnifications) FESEM images of ZnO@SiO$_2$ nanospheres.



Element	Weight%	Atomic%
C K	9.66	27.89
O K	13.77	29.83
Si K	2.36	2.91
Zn K	74.21	39.36
Totals	100.00	

Figure 2. Typical EDS spectrum of $ZnO@SiO_2$ nanospheres.

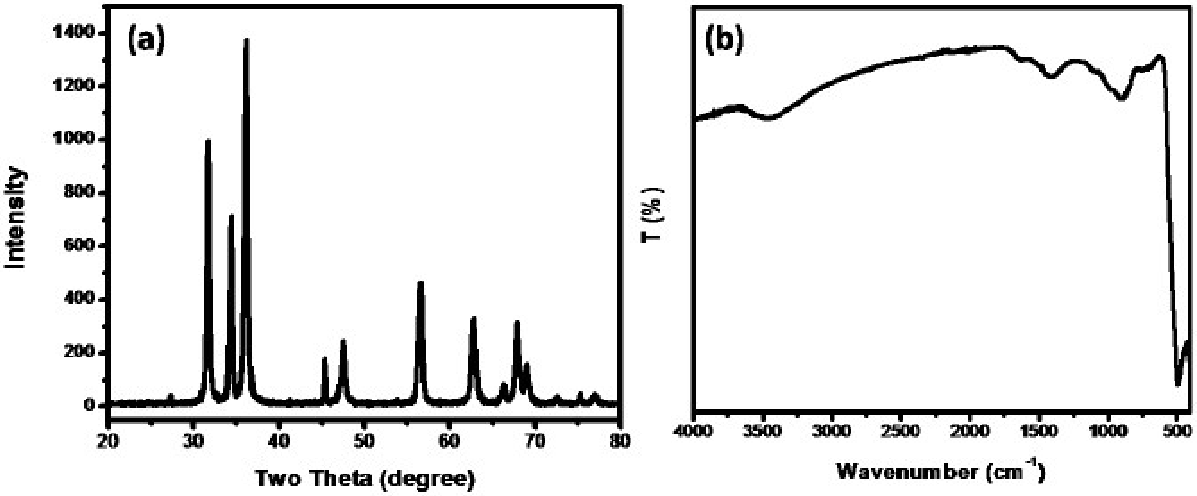


Figure 3. Typical (a) XRD pattern and (b) FTIR spectrum of ZnO@SiO$_2$ nanospheres.

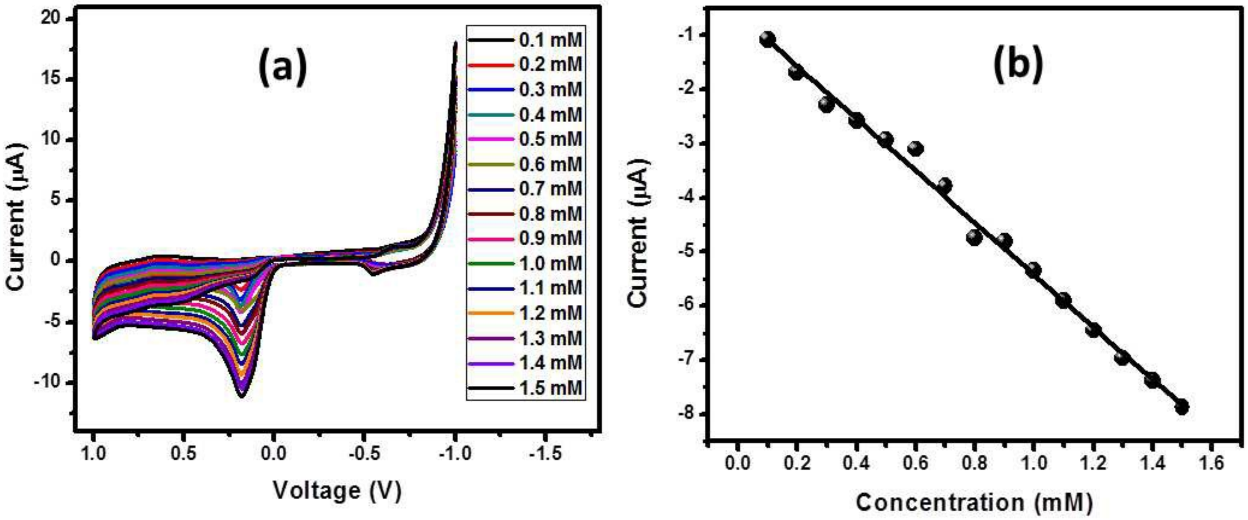


Figure 4. CV of working electrode with different concentrations of AA (a) and calibration curve (b).

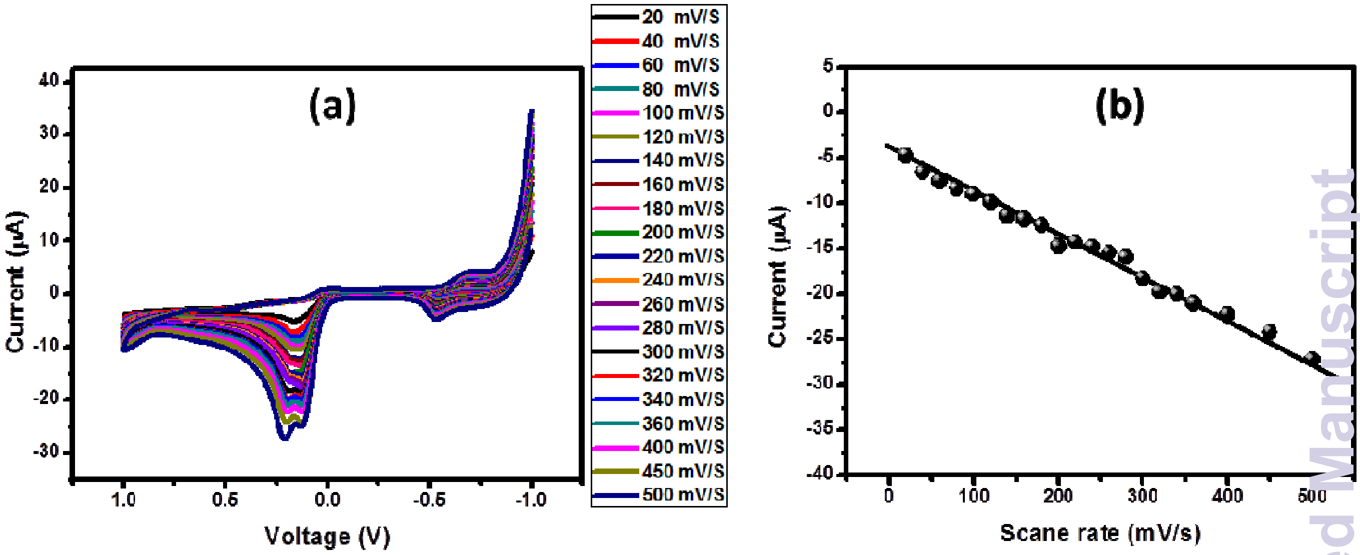


Figure 5. CV of working electrode with different scan rates (a) and current vs scan rate.

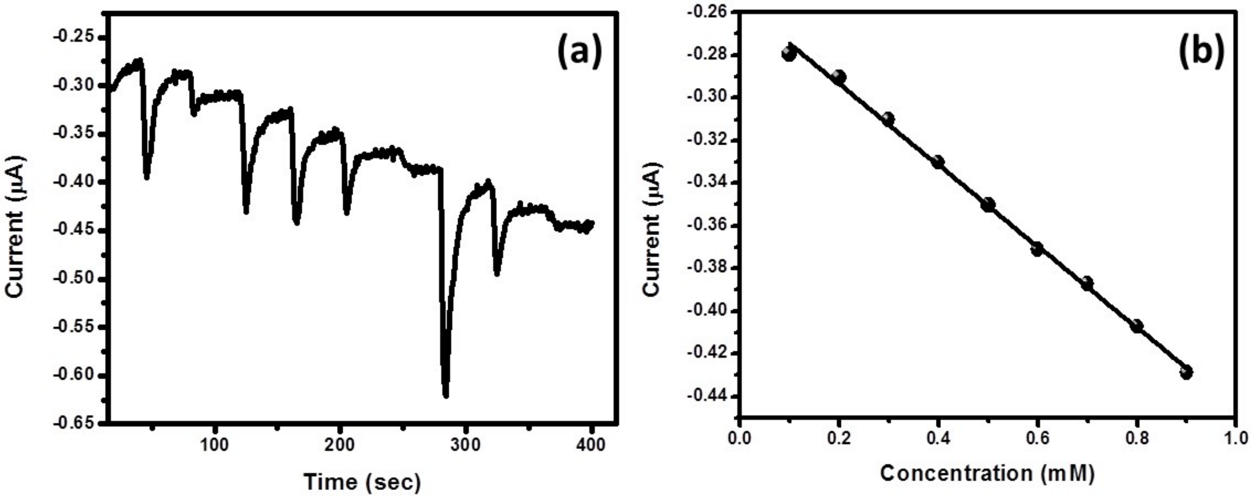


Fig. 6. (a) Amperometric response of working AuE at fixed potential 0.2 V to successive addition of AA into phosphate buffer (pH = 7.0) and (b) Linear calibration response between peak cathodic current and AA concentration.

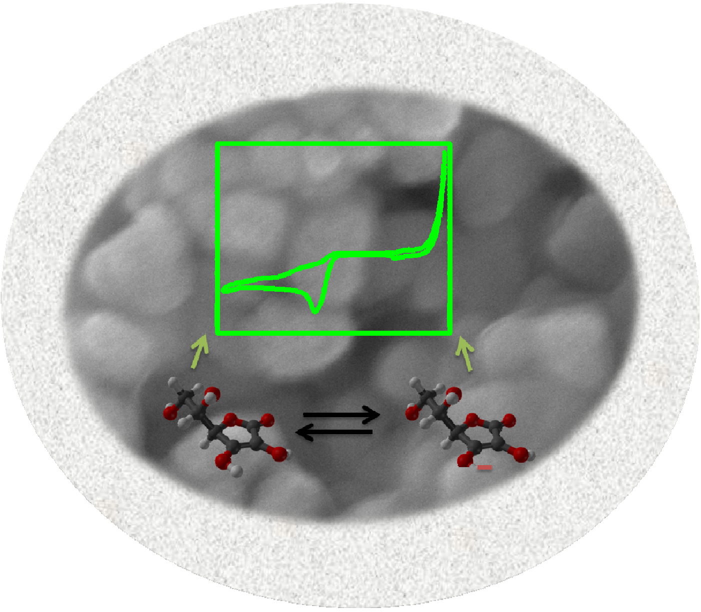


Figure 7. Schematic view of the fabricated AA sensor.

Graphical abstract

A highly sensitive sensor based on ZnO@SiO_2 nanospheres has been developed for the detection of ascorbic acid. The developed sensor is very simple and has been fabricated by using low cost materials.