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Facile synthesis of orthorhombic strontium copper oxide microflowers for highly sensitive nonenzymatic detection of glucose in human blood

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ABSTRACT

An efficient cost effective, scalable, template free synthesis of novel strontium copper oxide microflowers via simple co-precipitation fashion. As synthesized $SrCuO_2$ microflowers (SCO MFs) were systematically characterized by X-ray diffraction pattern (XRD), Fourier transformer infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and elemental mapping. The electrochemical behavior of as fabricated SCO MFs film was characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CVs). Fabrication of novel SCO MFs films as a proficient nonenzymatic glucose sensor with high sensitivity (2511.27 μA/mM/cm^2) over applied potential of +0.45 V (*vs.* Ag/AgCl), fast response (<5 s), and broad linear range (0.14–2200 μM) coupled with lower limit of detection (26 nM). The constructed electrode provides good anti-interference ability with acceptable reproducibility and stability. Moreover, the practical applicability of the architectured sensor was evaluated in human blood samples.

1. Introduction

Diabetes, a group of metabolic diseases categorized by a higher level of glucose in the blood, is arised by the defective function of pancreas glands (Type 1) or by the incapability of the body to utilize insulin over the metabolic actions (Type 2) [1]. Hence, monitoring the glucose levels in human blood is an important requirement for clinical diagnostics for proper therapeutic treatment of diabetes [2,3]. The earliest possible sensitive determination of elevated levels of glucose in the blood is significant for proper treatment and reduces the dangers of severe diabetic illness and organ destructions. These factors emphasize the need of precise, reliable, economically feasible tool for precise determination of blood glucose levels. Numerous approaches are known for determination of glucose in fluids such as optical [4], electrical [5], luminescence [6], colorimetric [7], electrochemical methods [8–10]. Among them electrochemical techniques receive great attention due to their unique advantages of cost effective, possibility of device making, fast response, higher sensitivity, good working range and low detection limit. Generally, enzymatic glucose biosensors have been reported based on GOD immobilized at various modified electrodes [10,11]. Although, the enzyme based sensors holds great advantages such as good selectivity and appreciable sensitivity, they still suffer from several disadvantages such as using expensive enzymes, tedious procedure for enzyme immobilization, poor stability (above 40 °C) [2,12]. These drawbacks have encouraged rigorous research efforts aimed to the growth of non-enzymatic electrochemical glucose sensors for the practical application in many fields including chemical and fermentation process [13].

There are numerous non-enzymatic glucose sensors can be found with noble metals and their alloys, transition metals and their oxides [14–18]. Nonetheless, noble metal and their alloys are not suitable for bulk production of sensor matrix, due to the limitations such as high cost and low abundance on earth. In spite, transition metals, their oxides are widespread availability, relatively low cost, ecofriendly nature, as well as intrinsic electronic, optical, electrochemical properties leads to many potential applications of super capacitor [19], Li-ion battery [20], electrochemical sensor [21–23], and catalyst [24]. Meanwhile, alkaline metal (Ca, Ba, and Sr) doped transition metal oxides have great attention in recent times, due to their unique properties such as high surface area, offering large number of catalytic sites, excellent mechanical strength, excellent physical and chemical stability

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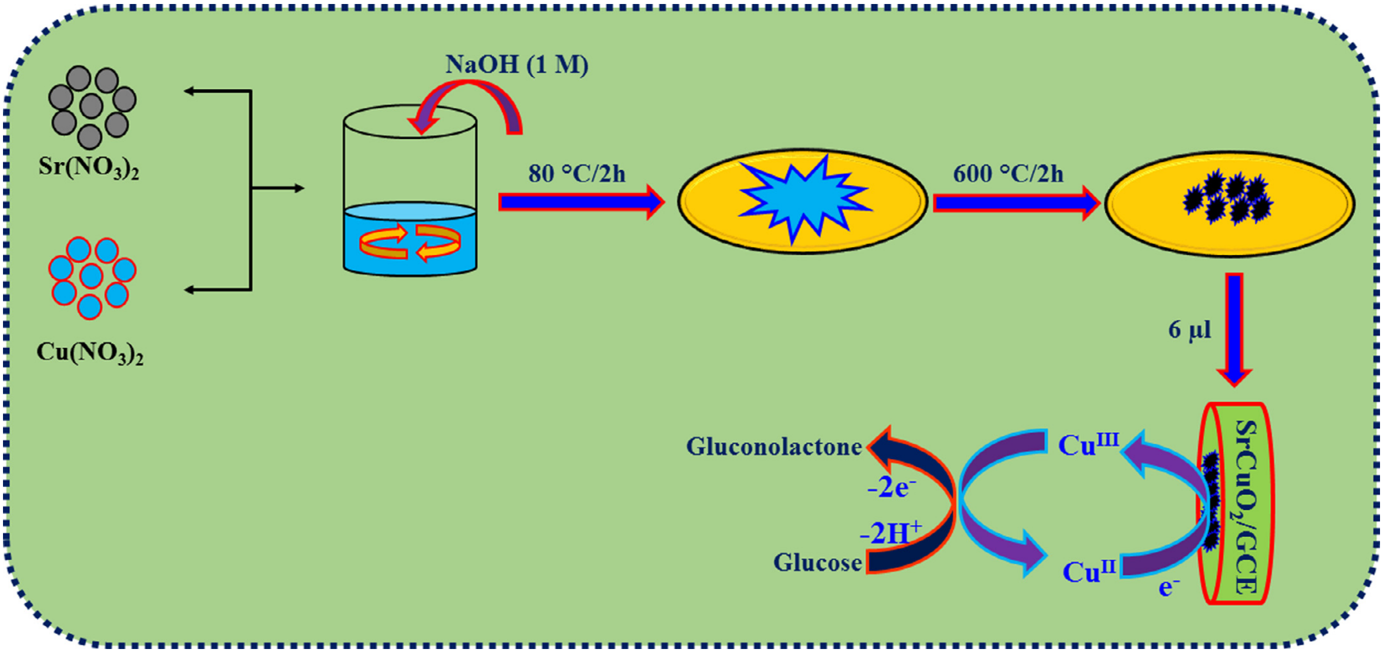

Scheme 1. The synthesis and fabrication of $SrCuO_2$ microflowers based glucose sensor.

[25,26]. These physicochemical parameters of alkaline earth metal doped metal oxides accompany with distinctive catalytic behavior makes them a key material in the fields of photocatalytic degradation [27,28], Aerobic oxidation reactions [29], photocatalytic water splitting [30], oxygen evolution and oxygen reduction [31]. From this, we can conclude alkaline metal doped transition metal oxides have potential catalytic behaviors. CuO is a renowned promising material for electrochemical oxidation of glucose due its high electrochemical activity (fast kinetics), low cost, non-toxic and it's easily incorporated with other materials [32,33]. Though, less studies are reported on strontium doped copper oxide particularly there is no reports on electrochemical sensor application. Many researchers studied its structural and physicochemical properties by means of resistivity and transmittance [34], X-ray diffraction [35]. Moreover, various synthesis methods have been developed such as laser irradiation sputtering [36], pulsed-laser deposition [35, 37], solvothermal fluorination [38], low temperature synthesis [39] and chemical vapor deposition [40]. However, the existing methods for preparation of $SrCuO_2$ are associated with complex procedure, using expensive instrumentations, laborious, and defective materials with less active sites on surfaces, difficult for large scale synthesis, which prevent their practical applicability. Hence, the development of simple synthesis of $SrCuO_2$ nanostructure with unique electrocatalytic activity is a challenging topic. Commonly, co-precipitation method provided well defined nanostructured material with high electrocatalytic activity.

In order to overcome the above mentioned complications, we have attempted to prepare the $SrCuO_2$ by simple, scalable co-precipitation methodology and systematically studied the surface morphology and chemical compositions. There is no report on the co-precipitation method synthesis of $SrCuO_2$ microflowers and its electrocatalytic ability has never been examined until now to the best of our knowledge. Herein, we successfully synthesized the $SrCuO_2$ microflowers (SCO MFs) through a co-precipitation method and examine the electrocatalytic capability of SCO MFs toward the enzymeless electrochemical determination of glucose for the first time. As we expected from the surface analysis the high surface area and active sites of SCO MFs exhibited excellent electrocatalytic activity toward the oxidation of glucose. Moreover, the modified electrode holds excellent sensitivity, good selectivity with a greater limit of detection and broad working range. In addition, the practicality of the as fabricated sensor was studied on human blood, which results showed SCO MFs modified electrode is a suitable platform for non-enzymatic determination of glucose in biofluids. The overall synthesis and electrode fabrication was shown in Scheme 1.

2. Experimental

2.1. Chemical and apparatus

Copper nitrate trihydrate ($Cu(NO_3)_2$ $3H_2O$), strontium nitrate ($Sr(NO_3)_2$), sodium hydroxide (NaOH), and glucose were purchased from sigma Aldrich. All chemicals and reagents were analytical rank used as received without additional purification. All the electrochemical experiments were carried out in CHI 900 work station. The morphological analysis of the $SrCuO_2$ flowers were done by scanning electron microscopy (SEM) on a HITACHI S-3000H electron microscope, transmission electron microscopy (TEM) on a TECNAI G^2 under an accelerating voltage of 200 kV, X-ray diffraction studies XPERT-PRO diffractometer using Cu Kα radiation ($k = 1.54$ Å) and Perkin-Elmer IR spectrometer. Fourier transform infrared (FT-IR) spectra were carried out with KBr window on a JASCO FT/IR-6600 spectrophotometer. Clean pH meter (pH500) with a combined pH glass electrode were employed for pH measurements. The conventional three electrode system was used for the electrochemical studies, with the modified glassy carbon electrode was used as a working electrode (electrode surface area: 0.071 cm^2), saturated Ag/AgCl as a reference electrode and platinum wire used as a counter electrode.

2.2. Synthesis of $SrCuO_2$ microflowers

The $SrCuO_2$ microflowers were synthesized via simple, efficient co-precipitation technique. In a typical synthesis, 0.05 M strontium nitrate was coupled with 0.1 M copper nitrate and stirred to obtain homogenous solution. The pH has been adjusted to pH 8< via addition of 1 M sodium hydroxide, the homogenous mixture was

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