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Freestanding Cu nanowire arrays on Ti/Cr/Si substrate as tough nonenzymatic glucose sensors

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Abstract

Exploring a tough, reusable and reproducible nonenzymatic sensor for glucose detection is required. Cu nanowire array electrodes on Ti/Cr/Si substrate are prepared from anodic aluminum oxide template films covered Ti/Cr/Si substrate by an electrodeposition method. The scanning electron microscope results indicate that Cu nanowires with a diameter of 50 nm and a length of hundreds nm freestanding on the Ti/Cr/Si substrate are obtained. Electrochemical measurements indicate the freestanding nanowire array electrodes showing sensitivity of $1067\mu A\ mM^{-1}\ cm^{-2}$ and detection limit of $1.87\mu M$ when using the arrays as glucose sensors. The most attractive characteristics of the electrodes are the outstanding reusability and reproducibility, realizing a 1.77% relative standard deviation (RSD) of one electrode in five time tests and a 3.33% RSD of five electrodes for one sample. The application of the electrodes on determining the glucose concentration in human serum samples indicates the array electrode is a promising candidate as a practical sensor.

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1. Introduction

Glucose concentration acts as a crucial indicator of diseases such as diabetes and endocrine metabolic disorders.[1] For diabetic patients, regular measurements of blood glucose levels are required to determine whether the treatments are working effectively.[2] Glucose oxidase (GOD) based sensors owing to its high sensitivity and selectivity to glucose, has been widely applied to construct various amperometric biosensors for glucose detection. However, GOD has intrinsic limitations such as lack of stability, the need of an enzyme immobilization process, the high cost of enzymes, the requirement of low temperature storage and the narrow operation temperature window etc. Recently, efforts to develop a practical nonenzymatic glucose sensor have been centred on achieving a breakthrough in electrocatalysis.[3] In this context, there are various nanomaterials modified non-enzymatic biosensors have been reported, such as nano/meso porous Pt,[4-6] porous Au,[7,8] Pd NPs,[9, 10] Ni NPs, [11, 12] Cu NPs,[13-16] Cu nanowires,[17-19] bimetallic Cu–Ag superstructures,[20] Cu_xO nanostructured material[21-27,30,33] et al.. The primary limitation associated with noble metals is high cost, which renders it less competitive in commercial application. Furthermore, noble metal electrocatalysts are vulnerable to chloride ion as well as other adsorbed reaction intermediates, which exist abundantly in human blood.[2, 17] Compared to noble metals, Cu based materials not only show an excellent electrocatalytic activity for glucose

oxidation, but also have the advantages of low cost and anti-poisoning of chloride ion.[17, 18] Meanwhile, people find that the highly active surface area of the electrode material plays a key role in the electrooxidation of glucose.[3] However, the electrochemical performances of the sensors are affected by whether the active materials can be peeling off from the electrodes easily, which decides whether the electrodes can be used as glucose sensors practically. However, in most of nonenzymatic glucose sensor studies, the general preparation strategy of electrodes is casting the as-prepared materials onto the surface of glassy carbon electrodes or gold electrodes, and entrapping them with Nafion to obtain modified electrodes. In this case, active surface area of the electrode material decreases with the material aggregation and electrode materials can peel off from the electrodes after several cyclic voltammetry (CV) scanning. Moreover, reproducibility of the electrodes prepared with this strategy is hard to ensure due to the uncontrollable manual operation. Therefore, exploring reproducible, tough and highly active electrodes to detect glucose accurately is necessary for the practical application of nonenzymatic glucose sensors. Preparing self-supported electrodes on conductive substrates for nonenzymatic glucose detection is an attractive strategy, in which, active materials grow on conductive matrix directly, behaving low interface resistance and good adhesion with substrates. Therefore, this strategy can provide an accessible means without the pretreatment and modification of the electrode,[25-33] guarantee the fastness of the active materials on the conductive substrates, and insure the reproducibility of the electrodes due to the accessible preparation processes without modifying the

glassy carbon electrodes or golden electrodes.

In present study, we prepare freestanding Cu nanowire arrays on Ti/Cr/Si substrate (Cu NWAs/Ti/Cr/Si) for nonenzymatic glucose detection. The Cu NWAs can provide abundant active sites and endow facilitated mass transport when used as the glucose detection sensors, due to the vertically freestanding architecture. The freestanding nanowire array structure helps the electrodes realizing detection limit of 1.87 μM and sensitivity of 1067 μA mM^{-1} cm^{-2}. Otherwise, the electrodes obtained by the bottom-up process are so tough that preventing active material peeling off, leading the electrodes good reusability, stability and reproducibility. Meanwhile, the processes of manufacturing NWAs/Ti/Cr/Si are post-CMOS (Complementary Metal Oxide Semiconductor) compatible, due to the carbon- and binder-free strategy of electrode preparation using a bottom-up electrodeposition assistant method. This advantage can help the electrodes integrating into biochip used for efficient batching detection.

2. Experimental

All chemical reagents were of analytical grade and were obtained commercially. Highly pure Al film (99.999%, ~1.0 μm), a Ti (~5 nm) and a Cr (~5 nm) layer were deposited on the p-type Si substrate by thermally evaporated deposition to form Al/Ti/Cr/Si wafers (1.0 cm × 1.0 cm). An anodic oxidation was performed in 0.3 M oxalic acid solution at 40 V and room temperature until the anodizing current decreased to be constant, indicating the barrier layer was removed and the Al film was oxidized completely. The scheme of preparing AAO templates on Ti/Cr/Si substrate is shown in Fig. 1a. A three-electrode electrochemical cell comprising a stainless foil (1

cm×2 cm) as counter electrode, a saturation mercury electrode (SCE) as reference electrode, and the anodized wafer as working electrode was assembled for electrochemical deposition experiments. The electrolyte solution for deposition was 0.1 M $CuSO_4$ aqueous solution. The electrodeposition was carried out using a constant current deposition in a reduction current of 2 mA with 500 s. The as-prepared sample was immerged in 0.01 M NaOH for 1 hour to remove the AAO films. Then the samples were rinsed sufficiently with deionized water, and dried at room temperature in a vacuum oven.

A CHI 660 electrochemical workstation was used for electrochemical experiments. A three-electrode cell was assembled with the Cu NWAs/Ti/Cr/Si as working electrode, a platinum foil as counter electrode and an Ag/AgCl as the reference electrode. All potentials were referenced to the Ag/AgCl (sat'd KCl) electrode. NaOH aqueous solution (0.1 M) was used as the electrolyte. Hydrodynamic chronoamperometric measurements were performed in magnetic stirring. Scanning electron microscope (SEM) images were obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were obtained on a PANalytical X´pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å).

3. Results and discussion

3.1 The structure of Cu NWAs on Si substrate

SEM images of AAOs' surface are shown in Fig. 1b and c. Compared with the AAO templates obtained on the traditional Al foils, the nanoholes are not very regular because of the ultrathin Al films used in our work. It is known that the longer anodic

time, the more regular nanoholes can be obtained.[34, 35] However, these holes standing on Ti current collector vertically are competent for growing freestanding nanowire arrays. Cu metal was deposited in the holes by constant current deposition method. After the subsequent dissolution of AAO templates, the Cu NWAs were obtained, as shown in Fig.1d and e. The apparently freestanding architecture of Cu NWAs can be detected from the SEM results. The diameter of the nanowires is identical with the pores of AAO templates, about 50 nm, and the length of the nanowires is about several hundred nanometers. The freestanding architecture can be seen in Fig 1e obviously, which generates adequate interspace in the nanowire arrays. The distinct structure guarantees all the active sites on the nanowires working successfully in the electrochemical sensing, promoting the utilization rate of the active materials. On the other hand, abundant interspace among the nanowires endows the electrodes facilitated mass transport in the electrochemical processes.

Fig. 1

Fig. 2

XRD pattern of Cu NWAs/Ti/Cr/Si has been presented in Fig. 2. The peaks of Ti (JCPDS: 65-5970) and Cu (JCPDS: 04-0836) can be observed clearly. As shown in inset pattern starting off the scan from 2theta = 40°, the peaks located at 43.3°, 50.4° and 74.1° can be assigned to the diffraction from the (111), (200), (220) planes of the face-centered cubic lattice of Cu(0). The strong diffraction patterns located at 38.4° and 82.3° can be assigned to the diffraction from the (110) and (220) planes of the face-centered cubic lattice of Ti(0), which comes from Ti conductive layer

pre-deposited on Ti/Cr/Si substrate.

3.2. The Cu nanowire array electrodes as glucose sensors

In order to investigate the applicability of Cu NWAs/Ti/Cr/Si in nonenzymatic glucose sensing, CV and continuous amperometry techniques were employed. Fig. 3a shows the changes of CVs with increasing concentrations of glucose in 0.1 M NaOH. The addition of glucose from 0 mM to 3.0 mM causes the obvious increase of the peak currents starting from 0.45 V to 0.70 V in CV, which corresponds to the irreversible glucose oxidation reaction. Oxidation peak of the curves marked with 1 at −0.35 V represents the transition of Cu(0)/Cu(I) while peak 2 at −0.07 V represents the conversion of Cu(0)/Cu(I) and Cu(0)/Cu(II).[18,36,37] Although the exact mechanism for the oxidation of glucose in alkaline media at Cu electrodes or Cu modified electrodes is still not known with certainty, it is commonly believed that the oxidation of glucose occurs in the process of forming Cu(III) from Cu(II) at 0.55 V where Cu(III) species have been proposed to act as an electron transfer mediator.[38,39] Peak 4 and 5 at −0.56 V and −0.83 V in the cathodic scan can be attributed to the transitions of Cu(II)/Cu(I) and Cu(I)/Cu(0), respectively.[17,37] There are no peaks related to the transition of Cu(III)/Cu(II), suggesting that Cu(III) is consumed in the electro-oxidation of glucose.

Fig. 3

For confirming the detection potential, the amperometric detections of glucose on Cu NWAs/Ti/Cr/Si were carried out by successive injection of glucose (50 μM) into 0.1 M NaOH solution at the potentials of 0.55, 0.56, 0.58, 0.60 and 0.62 V (Fig.

3b). Obviously, sensitivity at 0.60 V is the highest in the five applied potentials. Fig. 3c shows the amperometric response of Cu NWAs on examined at 0.60 V with successive additions of glucose (once every 50 s) spiked into 0.1 M NaOH solution. The response curve turns downward with increasing concentration because an increasing amount of intermediate species is adsorbed onto the electrode surface, prolonging the reaction time. The calibration curve for the glucose sensor is shown in the inset of Fig. 3c, which provides the regression equation, y(mA) = 1.0675x(mM) + 0.9505 with correlation coefficient of R^2 = 0.9896. The electrode has a linear concentration range of $2 \times 10^{-6} \sim 2.156 \times 10^{-3}$ M, sensitivity of 1067 μA mM^{-1} cm^{-2}, and a detection limit of 1.87 μM (1.87×10^{-6} M) (signal/noise = 3). The response current increases as the glucose concentration increases, and the current gradually reaches a saturated value at high concentrations, which suggest that the active sites of Cu NWAs/Ti/Cr/Si are saturated at those glucose levels. The high sensitivity may be due to the promoted electron transfer by freestanding array structure, while the low detection limit can be attributed to the integral one-dimensional nanowire structure of metallic copper which not only possesses the advantages of large surface area, but also inherits the prominent conductivity of metallic copper.

We also investigated the interferences from Dopi Amine (DA), Uric Acid (UA), ascorbic acid (AA) toward the detection of glucose, which commonly exist together with glucose in real samples (human blood). The normal physiological level of glucose is about 3–8 mM, which is much higher than the concentrations of interfering species like DA, UA and AA. In this work, we evaluated the interfering effect of

0.002 mM DA, 0.01 mM UA, and 0.005 mM AA compared to 0.1 mM glucose at the

potential of 0.60 V. As shown in Fig.3d, there is no obvious current response observed

with the addition of DA, UA and AA. On the contrary, an obvious current response

with the addition of 0.1 mM glucose appeared. So, the current response of the three

common biomolecules DA, UA and AA caused negligible interference in the response

of glucose on the Cu NWAs on Cr/Ti/Si substrate.

Fig. 4

The most attractive features of Cu NWAs/Ti/Cr/Si are the good reusability,

stability and reproducibility, as shown in Fig. 4. The reusability of an electrode was

investigated by inspecting the amperometric responses on the addition of 0.2 mM

glucose solution for the respective five times, as shown in Fig. 4a. The results

demonstrate the five response currents are very close, that their relative standard

deviation (RSD) is 1.77%. The long-term stability of the sensor electrode is also an

important parameter for evaluating the performance of the sensor. The proposed

sensor based on the Cu nanowire array electrodes was stored in air at room

temperature, and its current response to 0.2 mM glucose was checked every three

days within a 21-day period through amperometric response at 0.60V. The result

indicates that the sensitivity loss of 15% over a period of three weeks stored (Fig. 4b),

suggesting the highly operational stability of Cu NWAs/Ti/Cr/Si. Another significant

feature of the electrodes in practical application is the repeatability. We studied the

amperometric responses of five electrodes prepared with the same method on the

addition of 0.2 mM glucose solution, as shown in Fig. 4c. The five electrodes realize

outstanding consistency, since the RSD of their response currents is 3.33%. The good reusability, stability and reproducibility of Cu NWAs/Ti/Cr/Si lead them becoming a promising candidate as the practical non-enzymatic glucose sensors.

The comparison of Cu NWAs/Ti/Cr/Si with different non-enzymatic glucose sensors based on Cu nanowires modified glass carbon electrode is summarized in Table 1. As can be seen that Cu NWAs/Ti/Cr/Si in our work exhibit comparative analytical performances. Furthermore, the most attractive features of our electrodes are self-supporting, tough and robust, which are significant for the practical sensors.

Table 1

Table 2

Table 3

The feasibility of the Cu nanowire array electrodes as practical glucose sensors was performed by determining the glucose concentration in human serum samples provided by Hospital of Harbin Institute of Technology. The determined results of the blood serum sample shown in Table 2 are in accordance with those tested by the hospital. The recovery was measured by adding 8 mM glucose in dependently to the solution containing the serum samples. The recovery (Table 3) of the Cu NWAs is 99.13% and the RSD of three parallel test results is 4.24%, indicating that the as-prepared Cu NWAs/Ti/Cr/Si can be utilized for practical sample testing with favorable accuracy and precision.

4. Conclusion

Cu nanowire array electrodes are prepared by electrodepositing metallic Cu into

the nanopore arrays of the AAO template coated Ti/Cr/Si substrates. Cu nanowires with a diameter of 50 nm and a length of hundreds nanometers freestanding on Ti/Cr/Si substrate are obtained after dissolving the AAO template, and the nanowire arrays on Ti/Cr/Si substrate are used as glucose sensors. Thanks for the high use ratio of active sites and facilitated mass transport from the freestanding architectures of the electrodes, sensitivity of 1067 μA mM^{-1} cm^{-2} and a detection limit of 1.87 μM were realized as the nanowire arrays in glucose sensing. The most attractive characteristics of the Si wafer supported Cu nanowire array electrodes are the outstanding reusability and reproducibility, behaving 1.77% RSD of one electrode in five time tests and a 3.33% RSD of five electrodes for one sample. The feasibility of the electrodes as practical glucose sensors is also performed by determining the glucose concentration in the human serum samples, indicating the Ti/Cr/Si substrate supported electrodes can be utilized for practical sample testing with favorable accuracy and precision.

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Fig. 1. (a) Scheme of the preparetion process of Cu NWAs/Ti/Cr/Si. SEM images of AAO templates on Si wafers (b, c), and as-prepared Cu NWAs/Ti/Cr/Si (d, e).

Fig. 2. XRD pattern of the Cu NWAs/Ti/Cr/Si. Inset is the pattern starting off the scan from 2theta = 40°.

Fig. 3. (a) CVs of Cu NWAs/Ti/Cr/Si electrodes in 0.1 M NaOH solution in the presence of glucose in different concentrations with a 30 mV s^{-1} scan rate; (b) amperometric responses of the Cu NWAs/Ti/Cr/Si electrodes on the addition of glucose solution at different potentials in the solution of 0.1 M NaOH at an applied potential of 0.6 V; (c) amperometric responses of the Cu NWAs/Ti/Cr/Si electrodes on the addition of glucose solution of different concentrations. Inset of top left: amplification of part with low glucose concentrations. Inset of bottom right: calibration curve for current density vs. concentration of glucose; (d) Amperometric responses of Cu NWAs/Ti/Cr/Si electrodes in 0.1 mM glucose at different stages with the addition of 0.002 mM DA, 0.01 mM UA, 0.005 mM AA, in the solution of 0.1 M NaOH. Inset: Comparison of sensitivities of the tested analytes, at an applied potential of 0.6 V.

Fig. 4. The reusability, stability and reproducibility of Cu NWAs/Ti/Cr/Si electrodes: (a) amperometric responses of an electrode on the addition of 0.2 mM glucose solution for respective five times, the relative standard deviation (RSD) is 1.77%; (b) the curve of response current varying with the storing time of the Cu NWAs/Ti/Cr/Si electrodes in air at room temperature; (c) amperometric responses of five electrodes prepared with the same method on the addition of 0.2 mM glucose solution, the RSD is 3.33%.
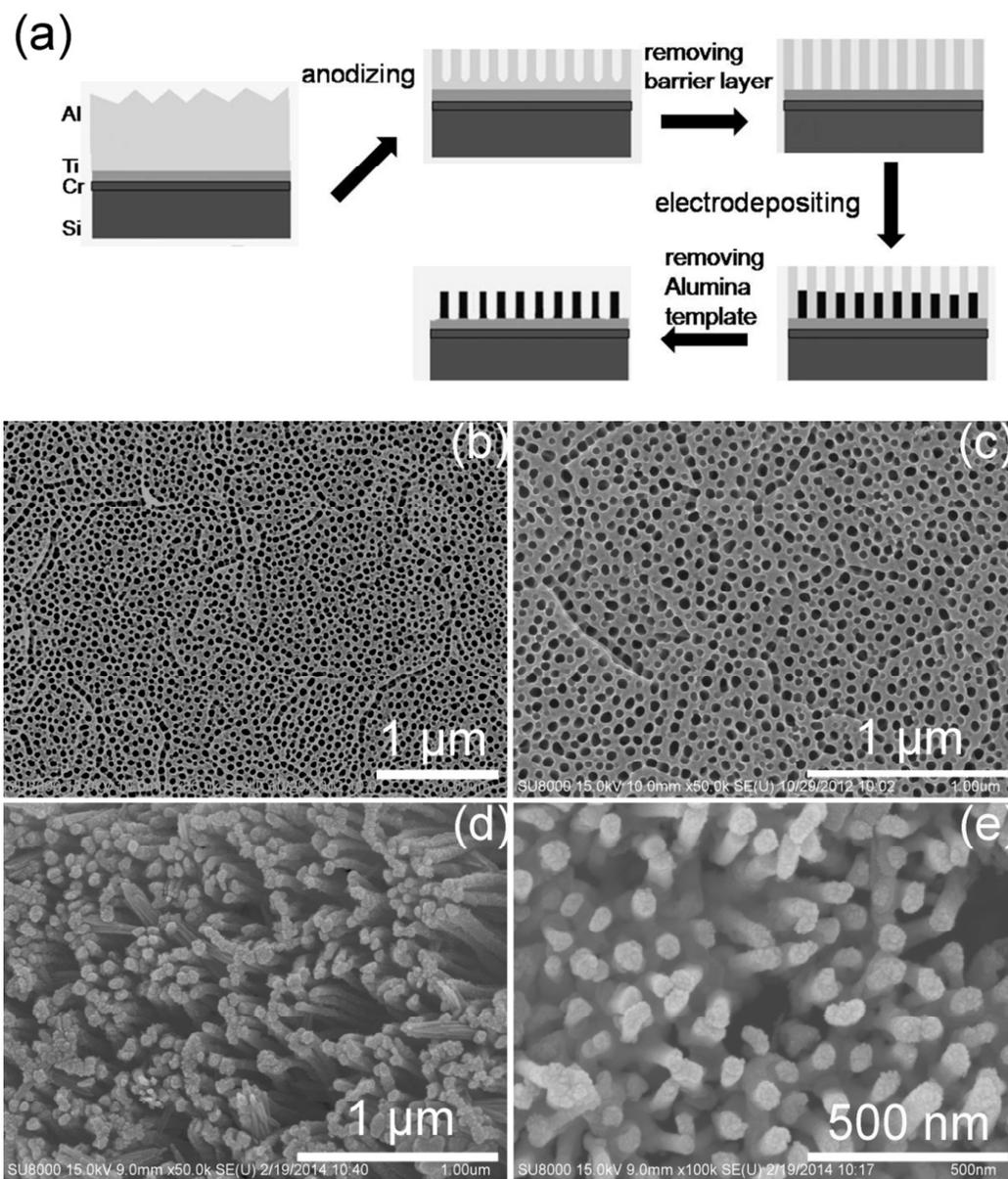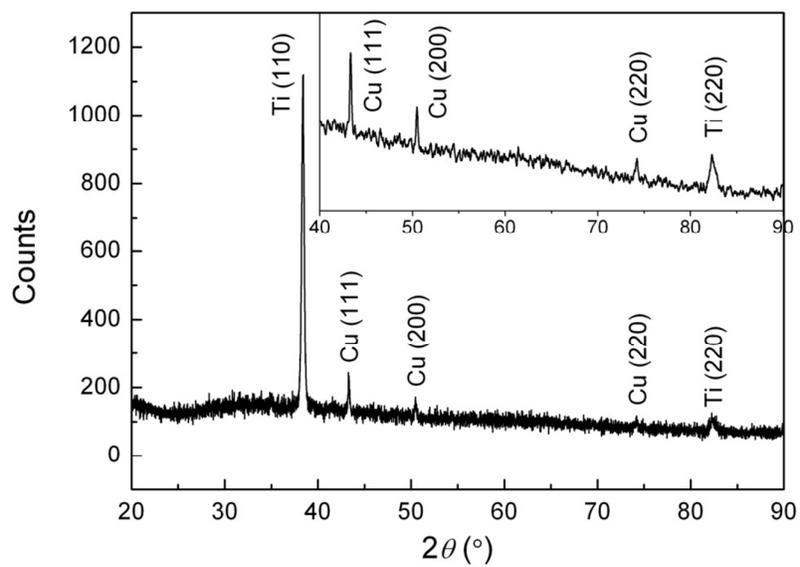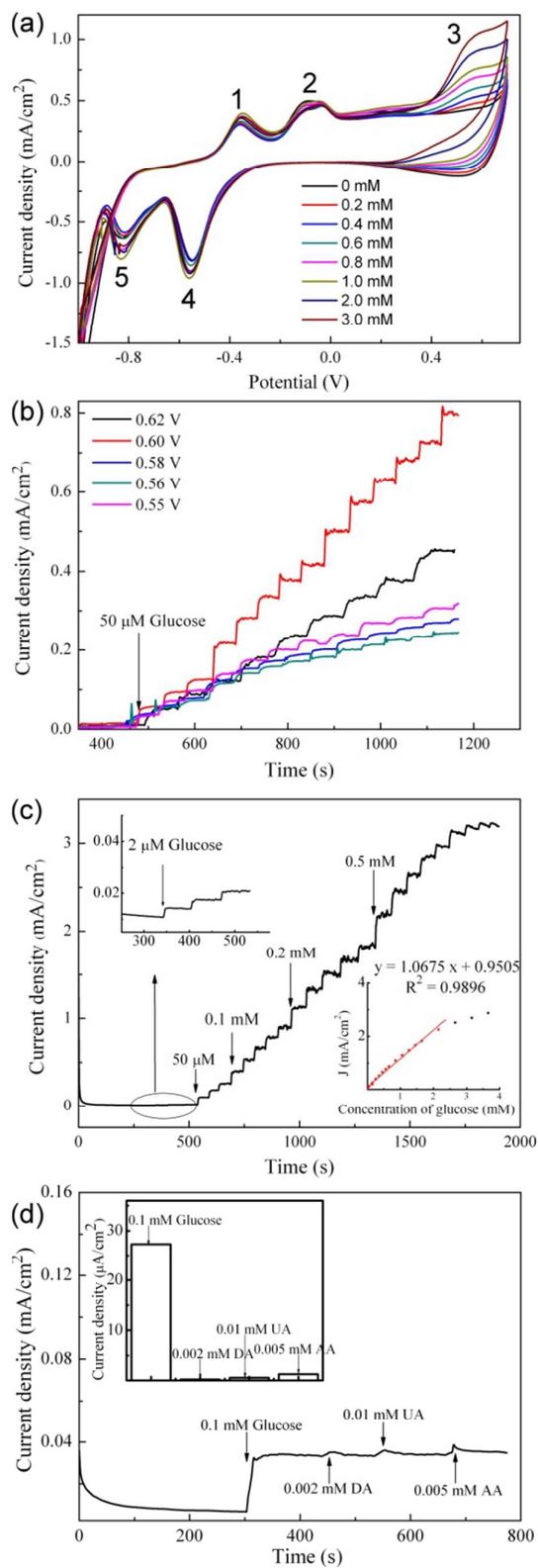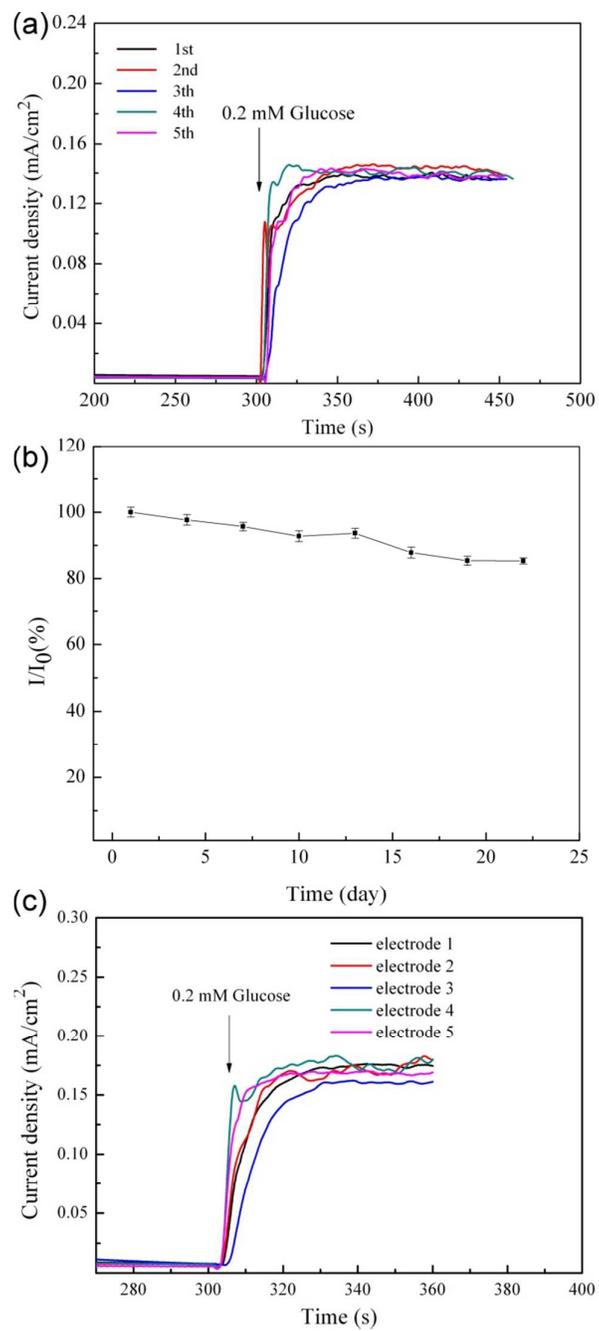
Fig. 1

Fig. 2

Fig. 3

(a)

(b)

(c)

Fig. 4

Table 1. Comparison of the performance of CuNWAs Ti/Cr/Si glucose sensor with

that of non-enzymatic glucose sensors base on Cu nanowires

Electrode composition	Potential(V) vs.Ag/AgCl	Liner range (M)	detection limit(M)	Sensitivity ($\mu AmM^{-1}cm^{-2}$)	Self-supported or not	Ref.
Cu nanowires	0.60	up to 3.0×10^{-3}	3.5×10^{-8}	420.3	Not	17
Copper nanowires/CNTs	0.55	up to 3.0×10^{-3}	2.6×10^{-7}	1995	Not	18
CuO@Cu nanowire array	0.65	$1.0\times10^{-6}\sim1.0\times10^{-2}$	6.9×10^{-7}	1250.8	Not	19
CuNWAs Ti/Cr/Si	0.60	$2\times10^{-6}\sim2.156\times10^{-3}$	1.87×10^{-6}	1067	Yes	This work

Table 2. Results for determinations of glucose in blood serum sample.

Hospital (mmol·L^{-1})	Our biosensor (mmol·L^{-1})	RSD (%)
	6.487	
6.933	7.091	4.45
	6.818	

Table 3. The recovery test of the Cu nanowire arrays on Si wafers.

Glucose concentration in the serum (mmol·L^{-1})	Added amount (mmol·L^{-1})	Our biosensor (mmol·L^{-1})	Recovery (%)	RSD (%)
7.91±0.04	8.0	15.84±0.04	99.13	4.24