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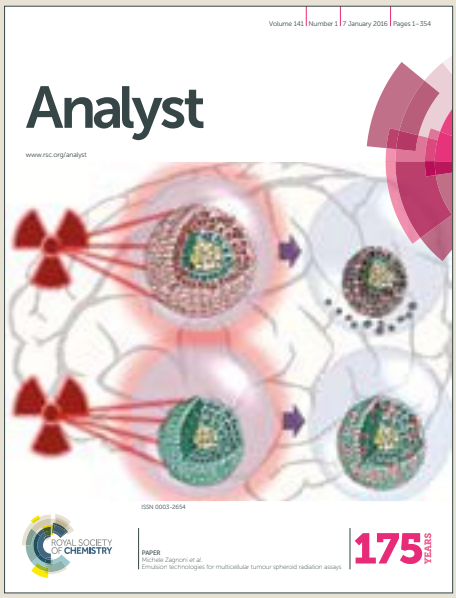

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Ternary nanocomposites of Au/CuS/TiO_2 for ultrasensitive photoelectrochemical non-enzymatic glucose sensor

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A novel and highly sensitive photoelectrochemical biosensor for detection glucose based on ternary nanocomposites of Au/CuS/TiO_2 (Au/CuS/TiO_2) has been fabricated. Highly ordered TiO_2 nanotube (TiO_2 NTs) arrays were prepared by anodization of Ti foils, CuS nanoparticles (NPs) and Au NPs were deposited on TiO_2 NTs by the successive ionic layer adsorption and reaction (SILAR) method. The resultant Au/CuS/TiO_2 exhibited excellent photoelectrochemical behavior as a glucose sensor under white light illumination due to the remarkable photocatalytic capability of TiO_2 and CuS, and surface plasmonic resonance (SPR) effect of Au NPs. The fabricated Au/CuS/TiO_2 non-enzymatic photoelectrochemical sensor showed brilliant catalytic activity, favourable selectivity, good reproducibility and long-term stability for glucose detection under optimized conditions. The linear range was 0.1 ~ 3 μM (R = 0.9942) with the detection limit of 0.03 μM (S/N = 3). Moreover, the proposed sensor detected glucose in human serum samples. Thus, the Au/CuS/TiO_2 appeared to be a promising photocatalyst for non-enzymatic glucose sensor.

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Introduction

Photoelectrochemical (PEC) detection has been a recently developed but dynamically developing detection method, employing light for the sensor excitation source, and electricity energy for the detection signals. Because the excitation source and electrochemical detection signals are separated, PEC has higher sensitivity and lower background signal than conventional electrochemical methods and optical techniques. Besides, photoelectrochemical method only needs low-cost and simple photoelectric devices[1].

The property of photoactive materials plays an important role in the fabrication of PEC sensor. TiO_2 as an n-type wide-band gap semiconductor is promising in heterogeneous photocatalysis for detection of biomolecules because of its nontoxicity, low cost, highly chemical and optical stability and outstanding oxidation capability[2-5]. Compared with the other semiconductor materials, TiO_2 nanostructures are considered for photocatalytic applications due to large porosity and high photo-activity[6, 7]. While, as a photocatalyst, the TiO_2 has not been used widely. The reason is that the band-gap energy of TiO_2 is very large (Eg = 3.2 eV) and the recombination rate of the photo-induced electron hole pair is rapid, limiting the utilization in the visible light spectrum [8, 9]. To improve sensitive and photocurrent, one of the effective strategies is to combine a narrow band gap material[10-12] and develop co-catalyst modified photo catalysts[13-15]. Because CuS has an ideal narrow band gap (2.2 eV), nontoxicity and the abundance of its constituent elements, it is elected as a candidate of narrow band-gap semiconductors[16, 17].

To apply the TiO_2 nanomaterials in the PEC sensor, the deposition of noble-metal co-catalysts onto the composites is usually required to improve PEC reactions efficiency because the surface plasmonic resonance (SPR) could induce electron excitation[18-20]. In addition, nano-structure noble metals could exhibit great catalytic activity for glucose oxidation[21, 22].

As a major energy source for cell metabolism, glucose has an important position in the process of the cell natural growth. Either deficiency or excess of glucose might produce an adverse effect on cell function. As a clinical indicator of diabetes, the fast and sensitive determination of the glucose level in human blood and urine is considered to be important[23-26]. Recently, a large amount of glucose sensors based on glucose oxidase were structured. However, reproducibility, thermal and chemical instability of glucose oxidase remain intrinsic restrictions[27]. Therefore, the non-enzymatic glucose biosensors have received more and more attentions.

Recently, Au-CuS-TiO_2 nanobelts photocatalyst for photocatalytic degradation of antibiotic oxytetracycline was reported[28]. Herein, a novel and simple approach to achieve selective PEC analysis of glucose based on functionalized Au/CuS/TiO_2 hybrid arrays was proposed. The composites were obtained by a simple method: the highly ordered TiO_2 NTs arrays were prepared by anodization of Ti foils, CuS nanoparticles (NPs) and Au NPs on TiO_2 NTs were deposited by the successive ionic layer adsorption and reaction (SILAR) method. In the proposed ternary structure, Au/CuS/TiO_2 formed a plasmonic photocatalyst. Visible light was absorbed by Au NPs inducing a fast transfer of the photo-excited electrons from the Au NPs to the conduction band minimum of CuS and the photo-generated electrons and holes were separated by the metal-semiconductor interface. Thus, the nanocomposites exhibited an enhanced visible-light driven photocatalytic improved for photoelectrochemical glucose oxidation under white light illumination. In this work, Au/CuS/TiO_2 showed a constant value and could be used to achieve a high efficiency in photoelectrochemical detection.

Experimental

Reagents

Ti foil (0.25 mm thickness, 99.7% purity) was purchased from Alfa Aesar. The foil was cut into pieces of 2 × 1.5cm, and were ultrasonic rinsed in 2-propanol. Cupric chloride ($CuCl_2$), chloroauric acid ($HAuCl_4$), sodium citrate ($Na_3C_6H_5O_7$), sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) and glucose were obtained from Sigma-Aldrich. The other analytes were analytical grade. Aqueous solutions used in the experiment were prepared by ultrapure water.

Apparatus

UV-vis spectra were acquired on the T6 new century spectrophotometer (China). Photoelectrochemical measurements were carried out with a photoelectrochemical system, employing 400 W Xe lamp light resource as the irradiation source. CHI900D electrochemical workstation was used to detect photocurrent responses. The conventional three-electrode system was carried out in the experiments including modified Ti foils as working electrode, a Ag/AgCl electrode (KCl-saturated) as reference electrode and a platinum wire as auxiliary electrode.

Real sample analysis

To evaluate the practicability of the proposed sensor, the as-prepared Au/CuS/TiO_2 composite was also employed to determination the glucose concentration in the human serum samples collected from three healthy people. These samples were obtained from our University Health Service with the corresponding informed consent from all the subjects, and proper permissions and approval were obtained.

Fabrication of Au/CuS/TiO_2

The whole synthesis process of Au/CuS/TiO_2 was illustrated in Scheme 1. The preparation of highly ordered TiO_2 NTs arrays was carried out through electrochemical anodizing Ti foil in the two-electrode electrochemical cell with a platinum foil as the counter electrode at room temperature, and the high-voltage potentiostat was used[29]. Before anodization, Ti foil was physically polished firstly, and ultrasonic rinsed in acetone, isopropanol and ethanol, respectively. After that, Ti foil was cleaned with ultrapure water and dried in air. Finally, Ti foil was anodized in ethylene glycol containing 0.25 % NH_4F (wt %) and 0.75 % ultrapure water (wt %) at 30 V for 2 h. After that, the anodized sample was sonicated for 20 s, and annealed at 450 °C for 3 h with a heating rate of 2 °C s^{-1}.

The deposition CuS on TiO_2 NTs was performed by the SILAR method[30]. Firstly, TiO_2 NTs were immersed in 0.1 M $CuCl_2$ for 1 min. Then, they were immersed in 0.1 M Na_2S for 1 min after rinsing with ultrapure water. The process was repeated 4-12 times.

The deposition Au on CuS/TiO_2 was also performed by the SILAR method. The difference from decorating CuS on TiO_2 was that the aqueous solutions were $HAuCl_4$ (1 mM) and $Na_3C_6H_5O_7$ (10 mM), respectively, and the process was repeated 6-14 times.

Results and discussion

Evaluation of Au/CuS/TiO_2

The process of preparing Au/CuS/TiO_2 was characterized by SEM and EDS. Fig. 1A showed a typical SEM image of self-organized highly ordered TiO_2 NTs array film with an average external diameter of about 90±5 nm, a wall thickness of about 15±5 nm and length of ~ 3.6μm. Fig. 1B presented the SEM image of a CuS/TiO_2 and showed that the nanotube surfaces were modified by CuS NPs. When Au NPs were fabricated on the CuS/TiO_2 surface,

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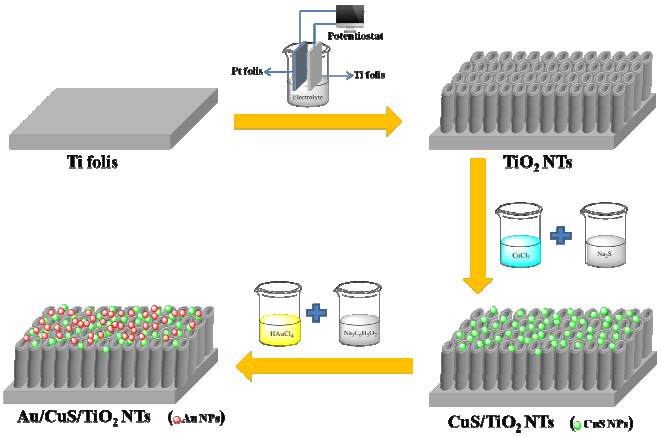
Au/CuS/TiO_2 composite film was obtained as shown in Fig. 1C, and uniformly distributed Au NPs on the CuS/TiO_2 surface were seen obviously. To exactly estimate the structure of the Au/CuS/TiO_2, the EDS was employed (Fig. 1D). The result confirmed the presence of Ti, O, Cu, S and Au, and element content results of Ti, O, Cu, S and Au were 62.44%, 30.48%, 2.53%, 3.44%, 1.14%. The molar ratio of Cu to S in the composite film was close to 1, suggesting that the stoichiometric formation of Cu and S was CuS.



Scheme 1 Scheme 1 Synthesis Process of Au/CuS/TiO_2.

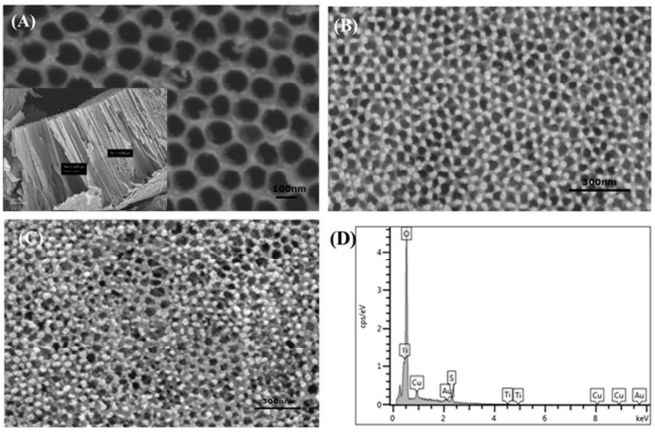


Fig.1 SEM images of TiO_2 NTs (A), CuS/TiO_2 (B), Au/CuS/TiO_2 (C) and EDX spectrum of the synthesized Au/CuS/TiO_2 (D).

The UV-vis of TiO_2 NTs (a), CuS/TiO_2 (b), Au/CuS/TiO_2 (c) were shown in Fig. 2. The absorption band of TiO_2 NTs was at about 390 nm, which was accordance with the intrinsic band gap absorption of anatase TiO_2 (3.2 eV). CuS/TiO_2 showed an increased absorption peak at 425 nm comparing with the TiO_2 NTs, suggesting the successful decoration of CuS on the TiO_2 NTs surface. When Au NPs were fabricated on the CuS/TiO_2 surface, there was obviously a new peak at 520 nm, implying the formation of Au NPs on the CuS/TiO_2 surface.

The detailed chemical composition of the Au/CuS/TiO_2 nanocomposite was further investigated by XPS. As displayed in Fig. 3A, the Au/CuS/TiO_2 was composed of Ti, O, Cu, S and Au. For Cu 2p spectrum (Fig. 3B), the Cu 2p3/2 and Cu 2p1/2 peaks which were typical values for Cu^{2+} in CuS were obtained on 932.7 and 952.8 eV, and symmetrical peaks of the two Cu 2p XPS also suggested the formation of CuS. Two peaks centered at 83.8 and 87.8 eV were displayed in Fig. 3C, originating from Au 4f 7/2 and 4f 5/2 of metallic state. The peak values of Au 4f 7/2 in Au/CuS/TiO_2 nanocomposite (83.8 eV) was lower than bulk metallic gold (84.0 eV) because of the redistribution of electrons at the CuS/TiO_2 contact interface.

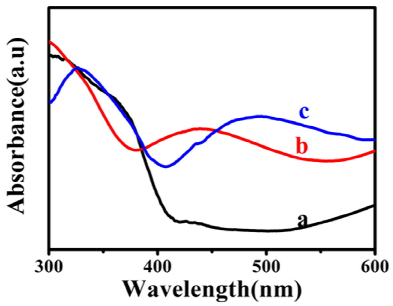


Fig. 2 UV-vis absorption spectra of TiO_2 NTs (a), CuS/TiO_2 (b), Au/CuS/TiO_2 (c).

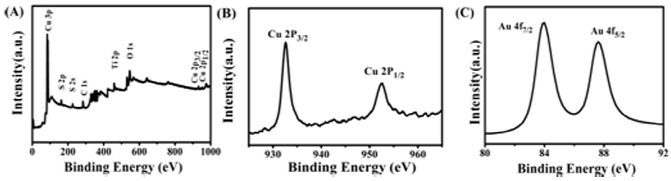


Fig. 3 XPS spectra of Au/CuS/TiO_2 (A), Cu 2P (B), Au 4f (C).

The XRD patterns of the pure TiO_2 NTs (A), CuS/TiO_2 (B), Au/CuS/TiO_2 (C) were shown in Fig. 4. The diffraction planes (101), (103), (004), (204), (116), (205) of TiO_2 NTs illuminated that the partially crystallized TiO_2 NTs/Ti changed into the anatase TiO_2 phase by annealing treatment. Several well-defined characteristic peaks of CuS, such as (006), (104), (108) indicated the successful decoration formation of CuS NPs on the surface of TiO_2 NTs. The diffraction planes (111), (311) of the Au indicated the successful decoration formation of Au NPs on the CuS/TiO_2 surface.

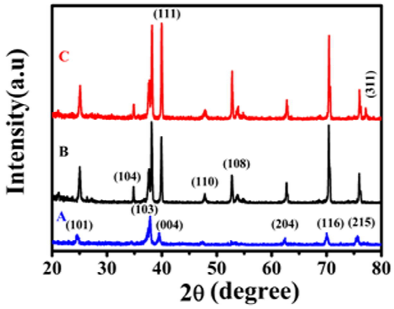


Fig. 4 The XRD patterns of the pure TiO_2 NTs (A), CuS/TiO_2 (B), Au/CuS/TiO_2 (C).

Photoelectrochemical oxidation of glucose

For constructing highly sensitive photoelectrochemical sensor, the high photoelectrical activity is very important. As shown in Fig. 5, the photocurrent of the Au/CuS/TiO_2 (17.79 μA) (Fig. 5c) was much higher than that of the pure TiO_2 NTs (6.57 μA) (Fig. 5a) and CuS/TiO_2 (11.77 μA) (Fig. 5b) in PBS (0.1 M, pH 7.0) containing 10 mM glucose. Au/CuS/TiO_2 exhibited the highest photocatalytic activity because of the unique ternary structure (Scheme 2).When Au NPs were decorated on the CuS surface, the plasmonic photocatalyst Au/CuS/TiO_2 was formed, and a fast and effective photo-excited electrons transfer from the Au NPs to the conduction band minimum of CuS under the visible-light irradiation was occurred resulting from SPR effect. As a result, electron-deficient Au NPs and electron-rich TiO_2 were generated through SPR effect. Thus, the

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photocatalytic oxidation of glucose could take place on the Au NP surface rather than on the CuS or TiO_2 surface [31].

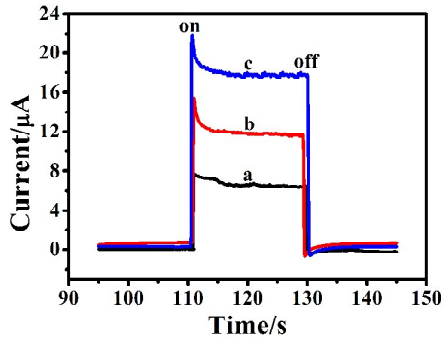
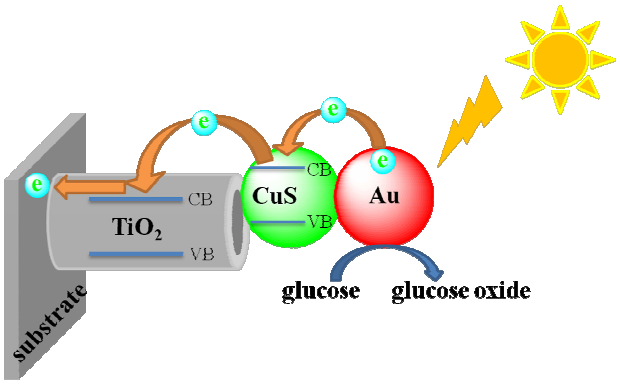


Fig. 5 Photocurrent responses of TiO_2 NTs (a), CuS NPs/TiO_2 (b), Au /CuS /TiO_2 (c) electrode in 0.1 mol/L pH 7.0 PBS containing 10 mM glucose with white light illumination.



Scheme 2 Schematic diagram of the photoelectrochemical process for oxidation of glucose at the Au/CuS/TiO_2 electrode.

Condition optimization

It was very important to investigate the cycle numbers of deposited CuS NPs and Au NPs for producing the photocurrent. As shown in Fig. 6 (A and B) and (C and D), the photocurrent increased as deposit cycles of CuS NPs and Au NPs, and performed an optimum response when cycle numbers of deposited CuS NPs and Au NPs were 8 and 10, respectively, in PBS (0.1 M, pH 7.0) containing 5 mM glucose with white light illumination. Thus, 8 and 10 cycles were used in the deposition of CuS NPs and Au NPs in the experiment, respectively.

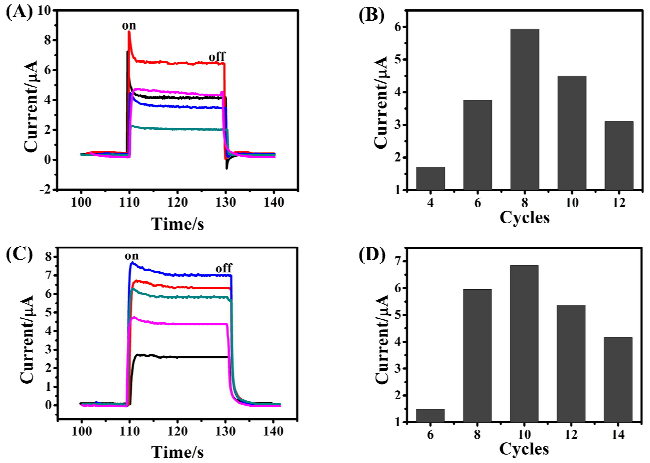


Fig.6 Effect of the cycle numbers of deposited CuS NPs (A and B) and Au NPs (C and D) on photocurrent responses of Au/CuS/TiO_2 electrode in 0.1M pH 7.0 PBS containing 5 mM glucose with white light illumination.

Detection of glucose

The photocurrent-time response of the Au/CuS/TiO_2 to different concentrations of glucose in PBS (0.1 M, pH 7.0) was displayed in Fig.7. The result showed a good linear range from 0.1 to 3 μm (R=0.9942), and the detection limit was 0.03 μM (S/N = 3). Obviously, the proposed photoelectrochemical sensor based on Au/CuS/TiO_2 showed promising application in the simple monitoring of glucose.

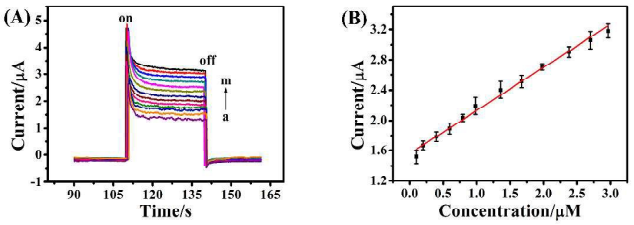


Fig. 7 Photocurrent responses at Au/CuS/TiO_2 electrode in 0.1 M pH 7.0 PBS in the presence of 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.4, 2.7 and 3.0 μM glucose (from bottom to top) with white light illumination (A), linear calibration curve between photocurrent and glucose concentration (B).

In addition, the analytical performance of glucose detection in the photoelectrochemical method with other materials were listed in Table 1. Compared with other materials, the ternary nanocomposites in this work had the lowest detection limit.

Materials	Detection limit (μM)	Linear range (μM)	Reference
Cuprous oxide	0.3	$0.5 \sim 6.0\times10^3$	32
BiOCl-G NHS	2.2×10^2	$5.0\times10^2 \sim 1.0\times10^4$	33
TiO_2(G) NW@ PAPBA-Au HJNH	1.1×10^2	$5.0\times10^2 \sim 2.8\times10^4$	34
Graphene-WO_3-Au-GOD	1.5×10^2	$5.0\times10^2 \sim 7.0\times10^3$	35
Au/CuS/TiO_2	0.03	0.1 ~ 3.0	this work

Table 1 The analytical performance of glucose detection in the photoelectrochemical method with other materials.

Selectivity, reproducibility and stability

To evaluate the selectivity of the Au/CuS/TiO_2 to glucose, Uric acid (UA), Dopamine (DA), and Ascorbic acid (AA) as interferents were used. As shown in Fig. 8 (A, B), the effect of UA, DA, AA for glucose were almost negligible, which indicated the sensor based on Au/CuS/TiO_2 had excellent selectivity toward glucose.

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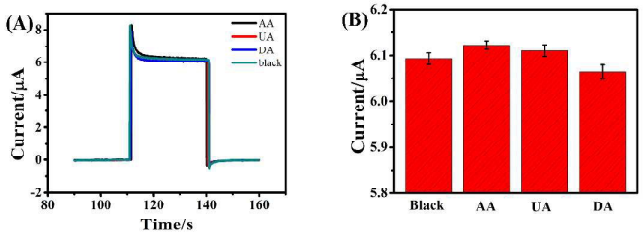

Fig. 8 Effect of interferences on the response currents. Experiments were performed with in 0.1 M PBS (pH 7.0) containing 5 mM glucose in the absence and presence of 20-fold AA, UA, DA with white light illumination.

In addition, the proposed sensor showed nice reproducibility with a relative standard deviation value (RSD) of 5.6% by comparing four parallel prepared Au/CuS/TiO_2. To study the stability of the sensor, the response singal were recorded when the sensor was stored in 4 ℃ for two weeks. It showed that the sensor could retain more than 93.90% of the initial response.

Human serum samples measurement

To evaluate the practicability of this glucose sensor, the as-prepared Au/CuS/TiO_2 composite was also employed to determination the glucose concentration in the human serum samples. For real sample analysis, human plasma samples were diluted 2000 times with PBS solution before being analyzed by the proposed sensor. The results obtained from three different samples were shown in Table 2, the calculated concentrations were all in agreement with the values obtained from the local hospital. It should be noted that the RSD was below 8% even at very low concentration, suggesting the proposed glucose sensor can be utilized for the glucose detection in practical serum samples.

Sample	Concentration measured by hospital (mM)	Concentration measured by the posposed sensor (mM)	Recovery (%)	RSD (%) **(n=5)**
1	5.3	5.46	103.0	6.7
2	4.8	4.70	97.9	7.8
3	4.1	4.02	98.0	6.4

Table 2 Concentration of glucose in human serum samples measured by hospital and the posposed sensor.

Conclusion

In summary, a non-enzymatic PEC glucose sensor using novel ternary nanocomposites of Au/CuS/TiO_2 was fabricated successfully. The fabricated method of Au/CuS/TiO_2 was simple and mild. More specifically, highly ordered TiO_2 NTs arrays was by anodization of Ti foils and CuS NPs and Au NPs on TiO_2 NTs were by SILAR method. The sensor based on Au/CuS/TiO_2 could realize PEC oxidation of glucose under white light illumination with excellent sensing performance, such as high sensitivity, good selectivity to glucose. Furthermore, the proposed sensor detected glucose in human serum samples. Thus, the as-prepared composites was a good PEC material for detection of glucose, and possessed a great potential for the development of alternative non-enzymatic glucose sensor.

Acknowledgments

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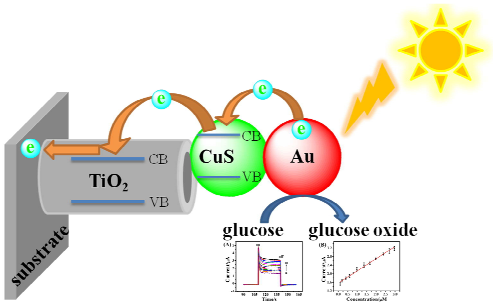

Table of contents. Ternary nanocomposites of Au/CuS/TiO_2 hybrid arrays were prepared for fabricating ultrasensitive photoelectrochemical non-enzymatic glucose sensor.