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Ni foam supported photocathode platform for DNA detection based on antifouling interface

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ABSTRACT

In this work, the photosensitive needle-like Eu: Co_3O_4 was synthesized on conductive nickel foam (Ni foam) in situ via hydrothermal and subsequent heat treatment, and as the basic material to construct an antifouling photoelectrochemical (PEC) DNA sensor for BRCA1 (breast cancer marker) detection. Ni foam has a great frame structure, which could well control the morphology and size of materials. Then CuS nanoparticles could easily grow on the surface of Eu: Co_3O_4/Ni foam through a sequential ionic layer adsorption reaction to further enhance the PEC response. For BRCA1 sensitivity analyzing, the excellent antifouling property was realized rely on the conjugation of amino-terminal poly(ethylene glycol) (PEG-NH_2). The developed PEC sensor displayed an outstanding stability and great sensitivity under the dissolved oxygen environment, and Ni foam PEC electrode provided potential application for other photosensitive materials-controlled preparation.

1. Introduction

Cancer has always been the number one killer threatening human health, and breast cancer is one of the most common cancers among women. Even with the continuous improvement of diagnostic technology in recent years, and with the continuous development of anticancer drugs, it is still difficult to carry out early breast cancer detection, achieving early-stage detection of breast cancer has an important significance [1]. Cancer-related biomarkers covering RNA, DNA, proteins, lipids, etc., are measurable indicators of specific cancer states. Their monitoring is of great significance for identifying patients with different clinical stages, and formulating adaptive treatment strategies. As we all know, DNA plays a crucial part in storing and transmitting genetic information [2–5], thus BRCA1 as one of the susceptibility genes for breast cancer was detected in this work for breast cancer analysis [6]. Previously, many methods have been achieved for DNA detection, such as fluorescence [7,8], colorimetry [9,10], electrocatalysis [11], imaging mass spectrometry [12], and electrochemical [13,14]. Among these methodologies, photoelectrochemical (PEC) as a branch of electrochemistry was used to detect BRCA1 because of the unique signal transition way, which has low background signal and provides great sensitivity [15,16].

One of the key points for PEC immunoassay is to construct the foundation photoelectrode. There are two kinds of photoelectrode, photoanode and photocathode. Photocathodes consist of p-type semiconductor that have disparate photoelectric properties from the photoanode based on n-type semiconductors. But for real biological samples analysis, photocathode has more accurate detection results than the photoanode [17]. That is because most real biological samples contain various reducing molecules, the absorption of the reducing molecule on the photoanode would inevitably influence the oxidation reaction of immanent holes at the interface between the photoanode and electrolyte, thus inaccurate response is liable to be produced. In addition, the reduction reaction of semiconductors is more resistant to interference than oxidation reaction, which makes the p-type semiconductors more stable than the n-type semiconductors.

As is known to all, cobalt oxide (Co_3O_4) is a representative and eco-friendly p-type metal oxide that has been used as a photocathode in PEC

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field [18,19]. The good conductivity, great stability, and the proper energy band gap (~2.07 eV) could effectively absorb visible light [20,21]. However, the biggest limitation for pure Co_3O_4 in PEC field is the rapid combination of photogenerated electrons and holes [22]. Fortunately, it is reported that the photosensitive performance can be perfected dramatically by enlarging the surface area through morphology controlling, owing to the unique geometric structure, the large surface area may provide a direct transfer path for photogenerated electrons, which is conducive to the effective separation of photogenerated electrons and holes in the photoactive process [23]. Nickel foam (Ni foam) is a less expensive commercial material with high electronic conductivity, three-dimensional, high surface area, and open-pore structure [24,25]. Various morphologies of species, such as nanowires [26,27], nano-needles [28,29], nanosheets [30,31], and core–shell nano-structures [32,33] have been prepared on the surface of Ni foam. Therefore, Co_3O_4 was considered to in situ synthesize on Ni foam to obtain a needle-like structure which owns a larger specific surface area. At the same time, during the synthesized process of Co_3O_4/Ni foam electrode via hydrothermal reaction, Eu element was doped to improve the band gap defects of Co_3O_4. Trivalent lanthanide (Ln^{3+})-doped nanomaterials are currently attracting considerable interest for their application potential in the fields of biosensing owing to their long-lived luminescence, low bio-toxicity high signal-to-noise ratio, and detection sensitivity [34,35]. After Eu^{3+} doping, a defect level was formed in Co_3O_4, which further hindered the recombination of photogenerated electrons and holes, and increased the PEC signal. In the meantime, to further acquire a higher and more stable basic PEC response, the great photosensitizer CuS [36–39] was absorbed on Eu: Co_3O_4/Ni foam electrode via sequential ionic layer adsorption reaction (SILAR), which is an ionic reaction mechanism to grow into an average layer, and cannot destroy the original morphology. This fabricated route with low cost, and without high temperatures or pressures. Nanoneedle-like Eu: Co_3O_4 own great specific surface area offered number of active sites for CuS nanoparticles attachment. Thanks to the matched band energy level between CuS and Eu: Co_3O_4, the photogenerated electrons could be transferred toward the electrolyte solution faster. What's more, the electron acceptors such as dissolved O_2 in the electrolyte solution will accelerate the transfer rate of photogenerated electrons, resulting in a higher cathodic photocurrent [40,41].

Antifouling interface could effectively hinder the nonspecific adsorption during the construction of biosensors [42,43], polyethylene glycol (PEG) with biocompatible, hydrophilic, and nonionic properties has become a prevalent and feasible molecule in the manufacture of antifouling biosensing interfaces [44,45]. In this work, PEG-NH_2 was used to coated on the Ni foam/Eu: Co_3O_4/CuS electrode to fabricate an antifouling interface for sensitivity BRCA1 detection. The proposed DNA sensor was designed by immersing, and adsorbing molecules on the prepared photocathode via layer-by-layer processes, and the smart design of using Ni foam as the photoelectrode simplified the biosensor construction steps, realizing the optimization of the photosensitive material, and improving the sensitivity of target detection.

2. Experimental section

2.1. Preparation of Eu:Co_3O_4/Ni foam electrode

The preparation of Eu: Co_3O_4/Ni foam was synthesized according to a previous reported way with some modifications [46]. Firstly, 0.5821 g of $Co(NO_3)_2{\cdot}6H_2O$, 0.2962 g of NH_4F, and 0.6006 g of urea was co-dissolved to 50 mL of ultrapure water. After mixed equably, 0.0669 g of $Eu(NO_3)_3{\cdot}6H_2O$ was added to the above mixture, and allowed stirring for another 30 min under room temperature. Secondly, Ni foam was ultraphonic treated with HCl (3 M.) solution for 10 min. Then, the cleaned Ni foam was tilt placed in a Teflon-lined autoclave, and the above mixture was poured into it. The autoclave was transferred in an oven and kept at 120 °C for 9 h. After finished reaction, the Ni foam electrode was rinsed by ultrapure water then dried at 60 °C. Finally, the Ni foam was calcined at 250 °C for 3 h with a 1 °C/min heating rate, and the Eu: Co_3O_4/Ni foam was obtained.

2.2. Preparation of CuS/Eu: Co_3O_4/Ni foam electrode

CuS nanoparticles were grown directly on the prepared Eu: Co_3O_4/Ni foam electrode by means of SILAR method, the simple steps were as follows: 0.0604 g of $Cu(NO_3)_3{\cdot}3H_2O$ was dispersed into 50 mL ultrapure water as solution A. 0.0600 g of $Na_2S{\cdot}9H_2O$ was dispersed in another 50 mL ultrapure water as solution B. Then, the as obtained Eu: Co_3O_4/Ni foam electrode was dipped into solution A for 1 min, and washed with ultrapure water subsequently, following the electrode was immersed in solution B for another 1 min, and washed completely with ultrapure water. These two soaking processes were as a cycle, and CuS growth was carried out for 5 cycles. Finally, the CuS/ Eu: Co_3O_4/Ni foam electrode was achieved after drying the electrode in an oven at 60 °C. Other details of reagents and apparatus are shown in *Supplementary Materials* file (SM).

2.3. The assembly of DNA sensor

The proposed PEC sensor relies on Ni foam photocathode is shown in Scheme 1. The as prepared CuS/Eu: Co_3O_4/Ni foam electrode (cut to 2 × 0.8 cm^2) was first soaked in amino-functionalized PEG solution (1 mg/mL) for 30 min, and washed with Tris−HCl buffer solution to get an antifouling interface. Then, the electrode was immersed in the carboxyl-functionalized capture DNA solution (1.0 μM, prepared by 0.1 M PBS, pH 7.4) including EDC (5 mg/mL) and NHS (1 mg/mL) for 40 min. In this process, through the formation of amide bonds, the captured DNA was covalent attached to the PEG-NH_2. The obtained electrode was washed with PBS, and then dipped into various concentrations of target DNA (prepared by 0.1 M. PBS solution, pH 7.4) for 40 min. Eventually, the DNA sensor was cleaned with PBS solution and stored at 4 °C when not in use.

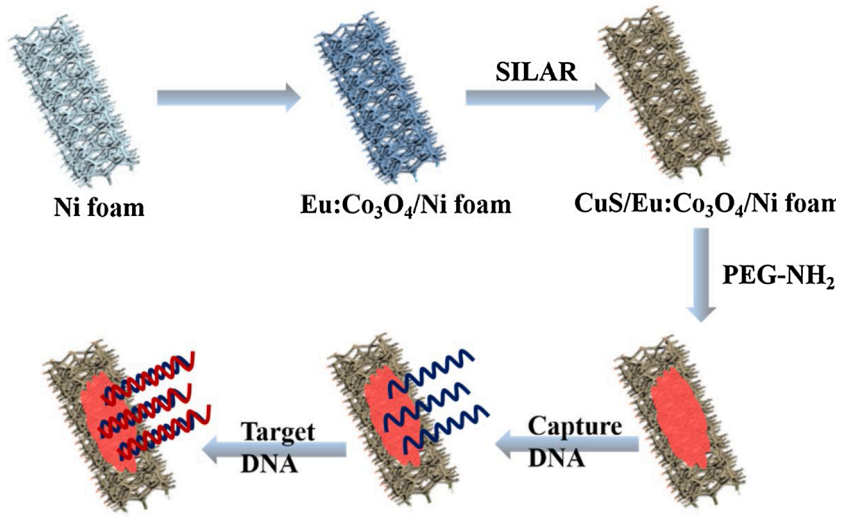
2.4. PEC measurements

The finished DNA sensor as work electrode with saturated calomel electrode (SCE, for reference), and platinum electrode (for auxiliary) was performed on a photoelectrochemical workstation for target analysis. PBS buffer solution (pH 7.4) was used as the measurement electrolyte solution, and performed oxygen bubbling 30 min to provide dissolve oxygen. Using LED light (400−700 nm) as excitation light and switch it on and off every 10 s at 0 V potential (vs. SCE).

3. Experiment results and discussion

3.1. Material characterization

The prepared nanomaterials were performed quantitative and qualitative analysis. First, X-ray diffraction (XRD) pattern was used to characterize Co_3O_4 and Eu: Co_3O_4 (Fig. 1A), the materials were obtained by collecting the precipitate at the bottom of the reactor. It can be seen that the sharp peaks of these two materials fit well with the standard card of Co_3O_4 (PDF #: 43-1003). Meanwhile, after the doped of Eu element, the crystal plane peaks of (220) and (311) became stronger, while the crystal plane peaks of (222) weakened or even disappeared. And the peak position of Eu: Co_3O_4 was shifted slightly, which is a normal phenomenon of doping effect. The results prove that the materials are prepared successfully. The structure and morphology of the prepared Ni foam supported electrodes were characterized by means of scanning electron microscopy (SEM). Fig. 1B shows the frame structure of cleaned Ni foam. After the hydrothermal reaction and heat treatment, Eu: Co_3O_4 was in suit grown on Ni foam electrode, and a needle-like structure (Fig. 1C) was obtained, the diameter was about 40 nm and



Scheme 1. The fabrication process of DNA sensor.

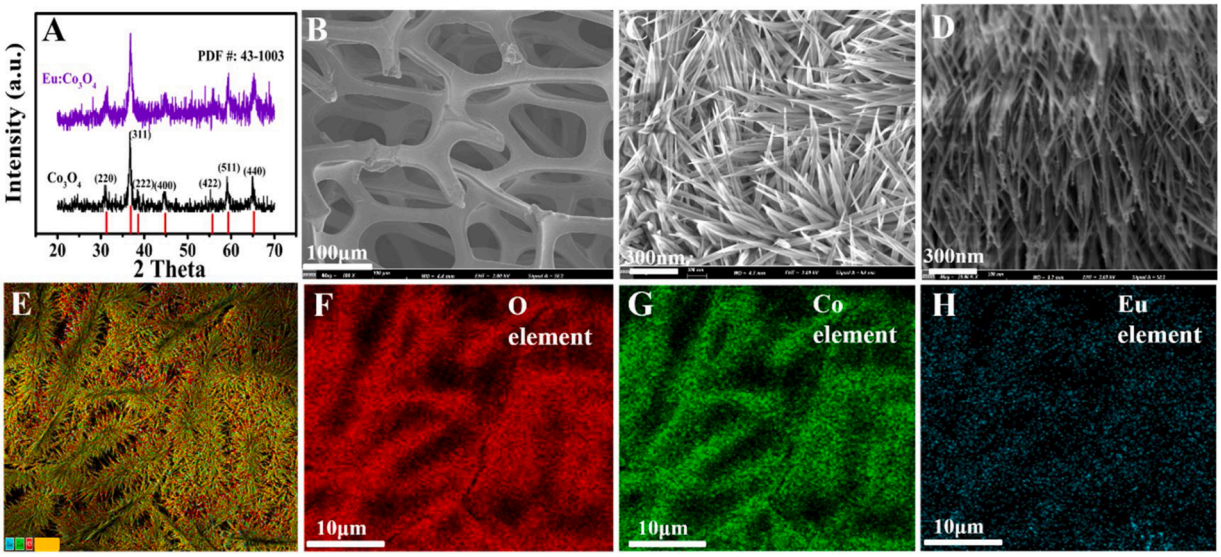


Fig. 1. The XRD image of Co_3O_4 and Eu:Co_3O_4 (A). The SEM image of cleaned Ni foam (B), the Eu:Co_3O_4/Ni foam (C), the CuS/Eu:Co_3O_4/Ni foam (D). The mapping image of the Eu:Co_3O_4 (E), O element (F), Co element (G), and Eu element (H).

the length were about 500 nm, which provides a relatively large surface area for photosensitizer attachment, and the excellent shape may provide a good path for electrons quickly transfer. Fig. 1E displays the mapping image of the prepared Eu: Co_3O_4/Ni foam. It can be seen that the Eu element was successfully doped (Fig. 1H), and no other impurity elements existed (Fig. 1F, G). The energy dispersive X-ray spectroscopy (EDS) image (Fig. S1) also proves it, and the distribution of each element in the Eu: Co_3O_4/Ni foam electrode is shown in Table S1. Meanwhile, CuS nanoparticles as great visible light absorber were fixed on Eu: Co_3O_4/Ni foam electrode by means of SILRA, it can be distinctly viewed from Fig. 1D that small nanoparticles were successfully loaded on the Eu: Co_3O_4/Ni foam electrode in a large amount, and XRD image in Fig. S2 of CuS/Eu: Co_3O_4/Ni foam further proved that these small nanoparticles were CuS nanoparticle The obtained CuS/Eu: Co_3O_4/Ni foam offers a desired basic PEC response for the later target detection.

3.2. Mechanism study of the PEC platform

The electron transfer mechanism is displayed in Fig. 2A. The p-type semiconductor Co_3O_4 as an outstanding photoactive material could effectively absorb visible light, but the narrow band gap limits its application in the PEC field due to the quickly recombination of photogenerated electrons and holes. The doping of Eu^{3+} could restrain the photogenerated charges recombination because of the defect levels generation. The material was directly grown on Ni foam, and obtained a needle-like structure. This wonderful structure may provide a direct transfer path for photogenerated electrons, and also provide a large active surface area for CuS nanoparticles absorption. As an excellent photosensitizer, CuS has the matched energy level with Eu: Co_3O_4, which offered a higher basic PEC response for target detection (the photocurrent of different electrode is shown in Fig. 2B). In the meantime, dissolved oxygen as the hole scavenger was bubbled in the measurement PBS solution, further enhanced the photocurrent (Fig. 2C), and improved the stability as well as the sensitivity of DNA sensor.

3.3. Sensor performance characterization

Before target detection, it is necessary to discuss whether the proposed sensor is constructed resoundingly. In this item, photosensitive materials were grown directly on the Ni foam electrode, and the

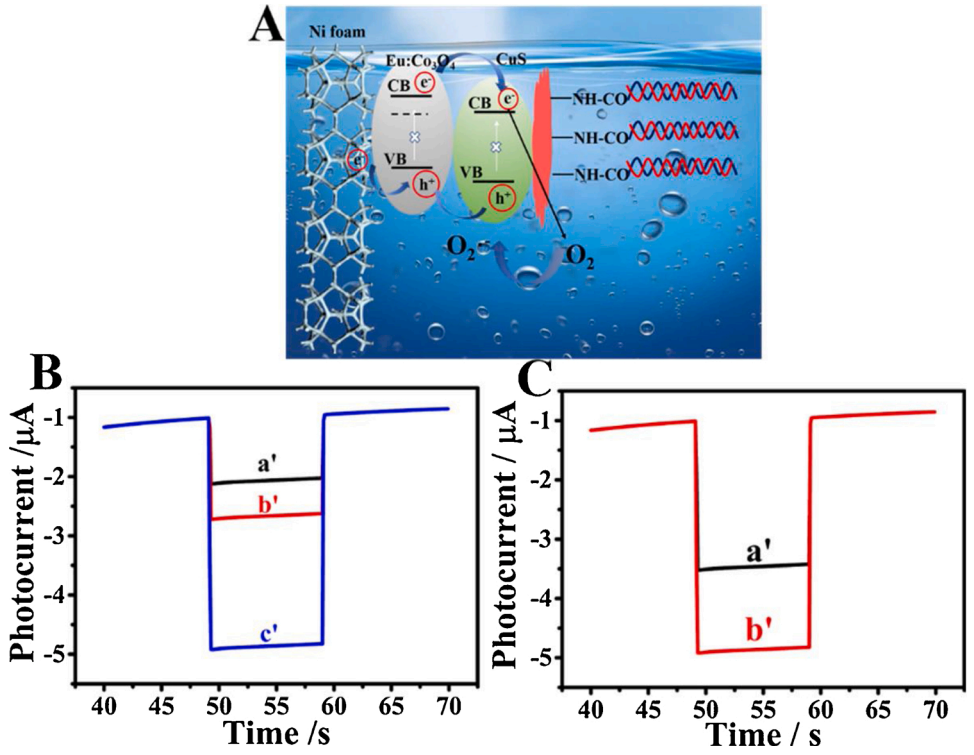


Fig. 2. (A)The electron transfer mechanism of the sensor. (B) The photocurrent of different electrode, (a') Co_3O_4/Ni foam, (b') Eu:Co_3O_4/Ni foam, (c') CuS/Eu:Co_3O_4/Ni foam. (C) The detection photocurrent of CuS/Eu:Co_3O_4/Ni foam electrode without (a') and with (b') O_2.

biomolecules were modified via soaking method. Fig. 3A shows the PEC response after layer-by-layer decoration, cleaned Ni foam has almost no photocurrent (curve a) response, after Eu: Co_3O_4 grown in situ, an obvious photocathode current was obtained (curve b), illustrating the material was successfully grown on Ni foam. After CuS nanoparticles absorption, a higher photocurrent was obtained (curve c), proving that the photosensitizer was also successful loading. Then, the photocathode electrode was dipped into PEG-NH_2 solution for antifouling interface formation, the PEC response was decreased (curve d) because of the inhibition effect on electron transport. After that, carboxyl functional capture DNA was modified thanks to the formation of amido bond, and the photocurrent continued to decrease (curve e). Finally, various concentrations of target DNA were captured onto the Ni foam electrode, the following decreased photocurrent (curve f) testifying the successful construction of the DNA sensor.

Another available way for characterizing the PEC sensor is electrochemical impedance spectroscopy (EIS). Fig. 3B shows that Ni foam with good conductivity exhibited a small impedance (curve a), after the semiconductor Eu: Co_3O_4 grew on, an enhanced resistance value (curve b) was obtained. When the CuS nanoparticles were absorbed, the matched energy level structure with Eu: Co_3O_4 accelerated electron transfer, and the impedance was reduced (curve c). Subsequently, non-conductive biomolecules of PEG-NH_2 (curve d), carboxyl functional capture DNA (curve e), and target DNA (curve f) were modified on photocathode via layer-by-layer processes, the increasing impedance value once again proved that the sensor construction triumphantly.

In order to test whether the antifouling interface was successfully obtained, EIS and photocurrent measurement of Ni foam/Eu: Co_3O_4/CuS/PEG-NH_2 electrode was performed before and after soaked in BSA solution. The testing results are shown in Fig. S3, the almost no change of the results proving the excellent antifouling ability of the sensor.

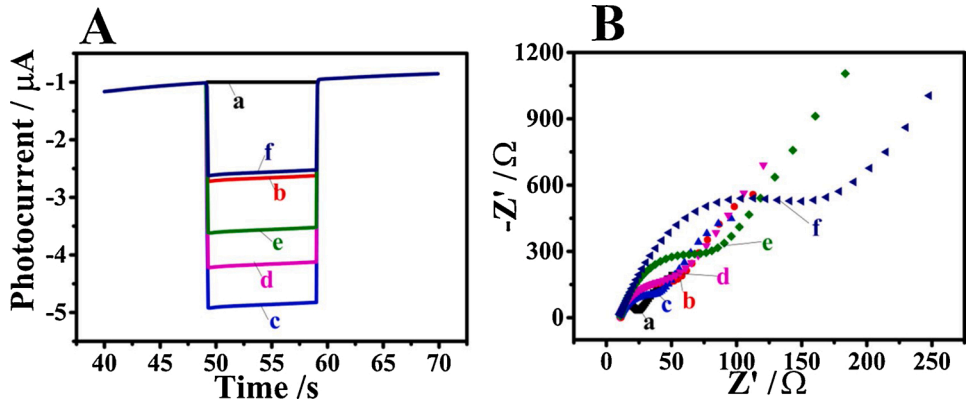


Fig. 3. (A) Photocurrent responses and (B) Nyquist diagrams of (a)Ni foam, (b)Ni foam/Eu:Co_3O_4,(c) Ni foam/Eu:Co_3O_4/CuS, (d) Ni foam/Eu:Co_3O_4/ CuS/PEG-NH_2, (e) Ni foam/Eu:Co_3O_4/CuS/PEG-NH_2/Capture DNA, (f) Ni foam/Eu:Co_3O_4/CuS/PEG-NH_2/Capture DNA/Target DNA. ($c_{\text{target DNA}}$ = 0.001 nM).

3.4. Analytical performance of BRCA1

After characterizing the proposed DNA sensor, the sensor was used to analyze various concentrations of BRCA1. Fig. 4A displays the photocurrent of different concentrations of target, as the concentration increases, the photocurrent gradually decreased, and a great liner relationship was acquired. As shown in Fig. 4B, the photocathode current existed a liner current response in the range of 1×10^{-6}–50 nM, the liner equation is $I = -0.8652 + 0.2699\log c$ (nM) ($R^2 = 0.9958$), and the detection limit is as low as 0.38 fM (S/N = 3). Comparation of the develop DNA sensor with other methodology for target DNA detection was shown in Table S2.

To ensure the accuracy of testing results, stability, reproducibility and specificity of the developed PEC sensor also need to be considered to representation. The satisfactory stability results were acquired via continuous testing of the electrode for 15 cycles (Fig. 4C). And the storage lifetime also tested to characterize the storage stability of the sensor. As can be seen from the Fig. S4, the proposed DNA sensor can still maintain more than 92 % performance after testing the PEC signal after two weeks, which illustrated the good storage stability of the sensor. For analyzing the reproducibility, five uniform electrodes are measured the photocurrent which was decorated under the same conditions. The relative standard deviation (RSD) is 3.8 %, proving that the proposed sensor has great reproducibility. To assess the specificity of the designed DNA sensor, photocurrent was measured in different solutions containing BSA, immune globulin (IgG), one-base mismatch (M_1) sequences and three-base mismatch (M_2) sequences. The results show the great specificity of the developed DNA sensor (Fig. S5 in SM file).

3.5. Real samples analysis

The intention of DNA sensor construction lies in its accuracy for actual samples detection. The possible actual value of the proposed DNA sensor was assessed through adding different concentrations of standard BRCA1 in real human serum samples then detecting the PEC signal. The detecting results are displayed in Table S3 (SM file), and the recovery is 97.7–101 % with the RSD ranging from 3.0 to 4.38 %. The detection results of the DNA sensor in real serum samples are receivable, indicating that the PEC biosensor with antifouling properties supported by Ni foam has the potential application for BRCA1 detection in actual samples.

4. Conclusion

In summary, a novel DNA sensor for BRCA1 detection based on Ni foam supported photocathode antifouling interface is successfully fabricated. The needle-like Eu: Co_3O_4 provided a large active surface area for CuS nanoparticles absorption, after doping Eu^{3+} and the sensitization of CuS, a higher photocurrent is achieved. Using PEG-NH_2 to construct an antifouling interface could effectively hinder the interference of other interfering substances, and improve the selectivity of the sensor. The dissolved oxygen in measurement solution also ensured the stability and sensitivity of the developed DNA sensor for accurately BRCA1 analysis. The developed photosensitive materials-controlled synthesis on Ni foam provides a new way for photoelectrode designed, and the proposed sensor can also provide reference way for other target detection.

CRediT authorship contribution statement

Rui Xu: Conceptualization, Data curation, Writing - original draft. **Yu Du:** Methodology, Data curation. **Xiaoqing Wang:** Data curation. **Huan Wang:** Methodology, Writing - review & editing. **Dawei Fan:** Methodology, Writing - review & editing. **Dan Wu:** Methodology, Data curation. **Xiaojun Sun:** Writing - review & editing. **Qin Wei:** Supervision, Funding acquisition, Formal analysis. **Huangxian Ju:** Formal analysis. **Rongde Wu:** Formal analysis.

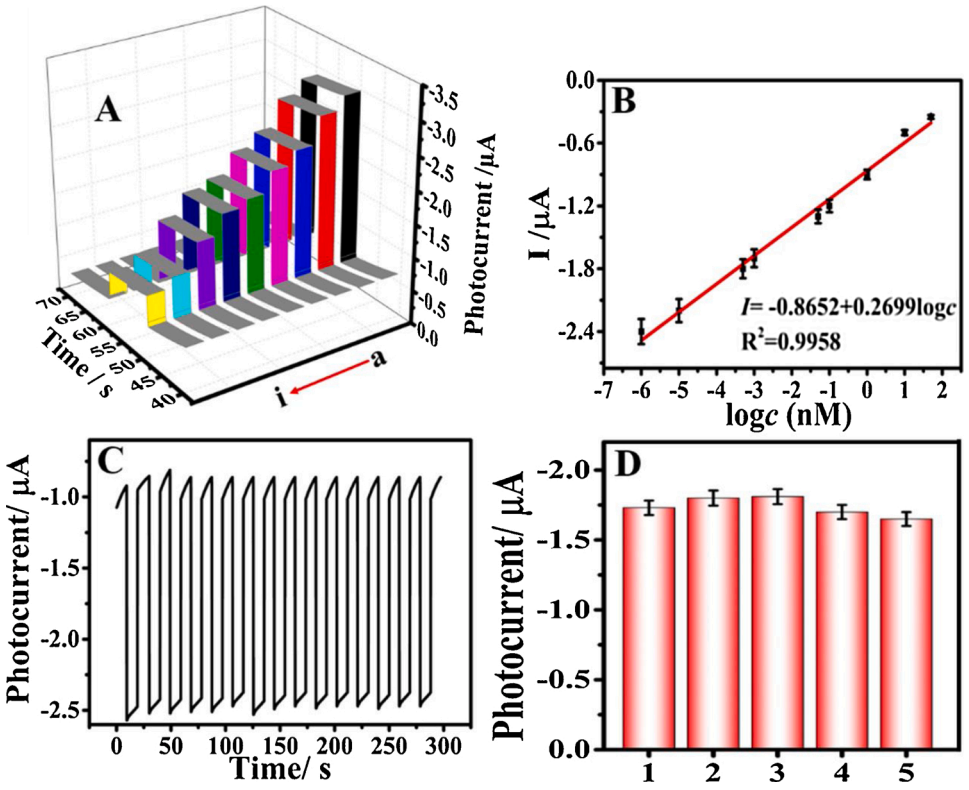


Fig. 4. The analytic performance of the target BRCA1. (A) PEC calibration curve of different concentrations and (B) linear relationship of the sensor: (a-i) 1×10^{-6}, 1×10^{-5}, 5×10^{-4}, 1×10^{-3}, 0.05, 0.1, 1, 10, 50 nM. (C) Stability analysis and (D) reproducibility analysis. ($c_{\text{target DNA}} = 0.001$ nM). Error bars = SD (n = 5).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2021.129593.

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