



Self-assembled dipeptide-graphene nanostructures onto an electrode surface for highly sensitive amperometric hydrogen peroxide biosensors

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ABSTRACT

Self-assembled nanowires of diphenylalanine and graphene (FF-G) nanocomposites have been prepared in aqueous solution by a simple one-step method. Hemoglobin (Hb) as a model molecule is further immobilized on the FF-G nanocomposites in order to construct a H₂O₂ amperometric biosensor. According to UV–vis spectroscopy, the immobilized Hb, overall retains its original structure and the bioactivity. Systematic electrochemical tests demonstrate that the Hb/FF-G modified glassy carbon electrode shows high electrocatalytic activity to H₂O₂. The biosensor exhibits a wide linear response in the range from 5.0×10^{-7} to 5.0×10^{-4} mol L⁻¹, with a low detection limit of 1.0×10^{-7} mol L⁻¹. Our results indicate that the nanowires of FF-G nanocomposites obtained in a facile method are promising for application in electrochemical biosensors due to its excellent biocompatibility and good charge-transfer ability.

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1. Introduction

It is well-known that molecular self-assembly is a powerful, bottom-up approach for the fabrication of novel functional nano- or biomaterials [1,2]. In the past twenty years, a peptide-based self-assembly has attracted increasing attentions due to the chemical versatility, biocompatibility, biological recognition, and facile synthesis [3–5]. Among these, self-assembled diphenylalanine (FF)-based nanostructures represent a very simple system and have shown interesting optical, mechanical and electrochemical properties [6,7]. These properties make them a promising material for biosensor applications. Rishpon and coworkers first showed that self-assembled nanotube of FF could act as a novel electrochemical biosensing platform [8]. Subsequently, self-assembled nanowires of FF were also applied in electrochemical sensors for detection of dopamine and immobilization of various biomolecules for biosensing [9,10]. In more recent reports, some functional components (such as polymer, carbon nanotubes or gold nanoparticles) have

been incorporated during self-assembly of FF to fabricate composite materials for high-performance biosensors [10–12]. These findings confirm that self-assembly of FF is an attractive alternative for the fabrication of sensors and biosensors. Despite the progress made, the introduction of more functional components into FF is still highly desirable for new sensors and biosensors with enhanced performance.

Graphene is a two-dimensional carbon material that has very high electrical conductivity, and large surface area. Since its first discovery in 2004 [13,14], it has demonstrated tremendous application potentials in electronic devices [15], energy conversion and storage [16], sensors and biosensors [17]. Recently, reduced graphene oxide (rGO) has been introduced into self-assembled of FF to fabricate electrochemical sensor of dihydronicotinamide adenine dinucleotide (NADH) [18]. The introduction of rGO improves greatly the electronic conductivity of the composite, which is very beneficial to their electrochemical sensing performance. Meanwhile, it is expected that rGO nanosheets embedded in the interface of biological sensors can also increase the effective surface area of the electrode and enhance direct electron transfer between enzymes/proteins and electrodes.

In this work, we present a simple way to fabricate self-assembled nanowires of FF and graphene (FF-G) nanocomposites onto an electrode surface under room temperature. A model molecule, hemoglobin (Hb), was further immobilized on top of such

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nanocomposites for the construction of an electrochemical H_2O_2 biosensor. We demonstrate that such Hb/FF-G modified glassy carbon electrode (GCE) indeed showed high electrocatalytic activity to H_2O_2 . Detailed enhancement mechanism will also be discussed. Our results further reinforce the potential of rGO in the application of biosensor devices.

2. Experimental

2.1. Apparatus and reagents

All the electrochemical measurements were carried out using a CHI 650A electrochemical analyzer (CHI instrumental, Shanghai, China) or a RST5000 electrochemical workstation (Zhengzhou Shiruishi Instrument Co., Ltd., Zhengzhou, China). A conventional three-electrode system was employed with a GCE ($d = 3 \text{ mm}$) or a modified GCE as the working electrode, a platinum (Pt) wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode (KCl saturation). Scanning electron microscopy (SEM) images were obtained with a Quonxe-250 scanning electron microscope (FEI Company, Czech). UV-vis absorbance spectra were recorded on the Model UV-2102 spectrophotometer (UNICO Company, Shanghai, China). Raman measurements were conducted with an inVia Reflex Raman spectrometer (Renishaw Company, China). All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with a standard buffer solution at $25 \pm 0.1^\circ\text{C}$ every day.

FF was acquired from Zhejiang Ontores Biotechnologies Co., Ltd (Zhejiang, China). 1,1,1,3,3,3-Hexa-fluoro-2-propanol (HFIP) was purchased from Aladdin Chemicals Co. Ltd., China. Graphene was got from Nanjing Xfnano Materials Tech Co., Ltd (Nanjing, China). Fig. S1 shows a typical SEM image of graphene. All other reagents were of analytical grade and were used as received. Double distilled water was used for all preparations.

2.2. Preparation of diphenylalanine-graphene dispersion solution

A FF stock solution was freshly prepared by dissolving the lyophilized FF in HFIP at a concentration of 100 mg mL^{-1} . The stock solution was then diluted with a 0.05 mg mL^{-1} graphene dispersion solution to a final concentration of 2 mg mL^{-1} (FF-G dispersion solution).

2.3. Preparation of the modified electrode

Prior to modification, the bare GCE was polished successively with 0.3 and $0.05 \mu\text{m}$ Al_2O_3 powder and rinsed thoroughly with double-distilled water between each polishing step. Subsequently, the GCE was sonicated in ethanol and double-distilled water for 2 min each before drying under N_2 blowing. Modified electrode was fabricated by a simple casting method. Scheme 1 illustrates schematically the fabrication of the modified GCE. Firstly, dispersion solution ($10 \mu\text{L}$) of FF-G was dropped on the surface of GCE and dried at room temperature (named FF-G/GCE). Then the electrochemical biosensor was prepared by dropping $10 \mu\text{L}$ of 10 mg mL^{-1} Hb solution directly onto the surface of FF-G/GCE and dried at 4°C overnight. Finally, $5 \mu\text{L}$ of 0.5 wt% Nafion solution was spread onto the surface of Hb/FF-G/GCE and dried to get the modified electrode (named Nafion/Hb/FF-G/GCE). For a comparison, Nafion/Hb/G/GCE was fabricated by a similar procedure.

3. Results and discussion

3.1. Characteristics of self-assembled nanowires of FF-G

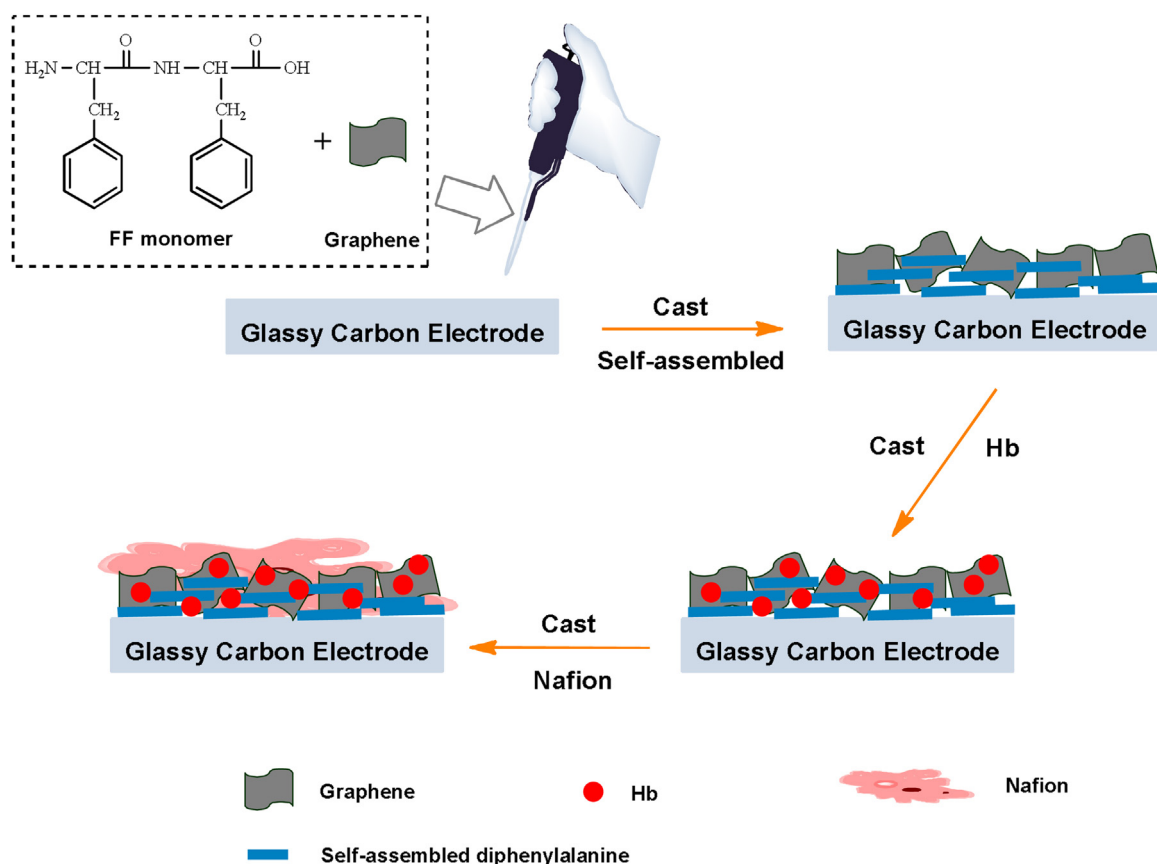
It has been reported previously that FF can be self-assembled into peptide nanowires in an aqueous solution [19]. Fig. 1A shows a typical SEM image of the self-assembled nanowires of FF. When the aqueous solution was replaced with a 0.05 mg mL^{-1} graphene dispersion solution, the high-density and interlacement nanowires of FF-G were clearly observed (Fig. 1B–D). The diameter of the nanowires ranges from several hundreds of nanometers to micrometers but mainly distributed in the range of 100–200 nm (Fig. 1D), which is similar to those reported previously [19]. The characterization of the nanowires of FF-G was further characterized by Raman spectra. Fig. 2 shows the Raman spectra of graphene and self-assembled of FF-G on GCE surfaces. It is clear that the interaction of FF and graphene is confirmed by a blue shift of the G-band from 1580 cm^{-1} to 1571 cm^{-1} in the Raman spectra.

The influence of the graphene concentrations on the self-assembly of FF was also studied. When the concentration of graphene was lowered to 0.01 mg mL^{-1} , the obtained nanowires have a relatively low density and broad range of diameters (Fig. S2). However, with increasing concentration to 0.05 mg mL^{-1} , high-density nanowires with uniform diameters were obtained. Therefore, we chose 0.05 mg mL^{-1} as the optimal concentration of graphene solution. In addition, the influence of the amount of the surface layer on the electrochemical response was studied using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the redox couple (Fig. S3). It is found that the redox current does not significantly change between one-layer and two-layer modified electrodes. The reason might be that thick films have weak adhesion to the electrode interface, and some nanowires of FF-G were dissolved. So one-layer modified films were chosen for the following experiment. We also conducted similar experiment on other substrates including gold, silicon and mica surfaces; similar self-assembled nanowires of FF-G were obtained. Therefore, the self-assembly process of nanowires FF-G is substrate friendly and versatile for various electrochemical applications.

3.2. Characteristics of Nafion/Hb/FF-G film

To demonstrate the advantage of the nanowires of FF-G, Hb as a model molecule was further immobilized on the nanowires of FF-G nanocomposites. Electrochemical impedance spectroscopy (EIS) can provide information on the impedance of the electrodes. EIS experiments were performed in 0.1 mol L^{-1} KCl solution containing $5.0 \times 10^{-3} \text{ mol L}^{-1}$ $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the results were showed in Fig. 3. The diameter of the semicircle usually equals to the electron transfer resistance (R_{et}), which is related to the electron transfer kinetics of the redox probe at the electrode interface. The curves were fitted based on an equivalent circuit model (insert of Fig. 3) using the ZSimpWin software. The fitting results were shown in Table S1. The R_{et} value of GCE (curve a) was obtained to be 120Ω . The R_{et} value for FF-G/GCE (curve b) decreased to 86Ω , indicating that FF-G nanocomposites are more conductive. For comparison, the R_{et} values for Nafion/Hb/G/GCE (curve c) and Nafion/Hb/FF-G/GCE (curve d) increased to 517 and 522Ω , respectively. The relatively large impedance values suggest that the presence of Hb and Nafion on the electrode surface retard the electron transfer rate of $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Correspondingly, SEM images in Fig. 4A–B indicate a considerable change in the morphology. These results indicate that Nafion/Hb/FF-G film was successfully immobilized on the GCE surface just as designed.

We concern if Hb maintains its natural state in the Nafion/Hb/FF-G composite film. To check this, UV-vis spectroscopy was conducted and data is shown in Fig. 5. The Soret band for free Hb is observed at about 406 nm (curve a) which is similar to that reported



Scheme 1. Schematic illustration of the fabrication of the Nafion/Hb/FF-G modified GCE.

in previous study [20]. The position and shape of absorption band for Hb in the Nafion/Hb/FF-G film at 405 nm (curve b) is nearly the same as those for free Hb film. This suggests that the immobilized Hb can retain its original structure and the bioactivity in the Nafion/Hb/FF-G composite film.

3.3. Direct electrochemistry of Hb on Nafion/Hb/FF-G/GCE

Direct electrochemistry of Hb on Nafion/Hb/FF-G/GCE was studied. Fig. 6 shows the cyclic voltammetry (CV) curves of GCE (curve a), FF-G/GCE (curve b) Nafion/Hb/G/GCE (curve c) and Nafion/Hb/FF-G/GCE (curve d) in 0.1 mol L⁻¹ PBS (pH 7.0) at a scan rate of 0.050 V s⁻¹. Clearly no evident redox peaks were seen in the GCE and FF-G/GCE electrodes over the studied potential range. On Nafion/Hb/G/GCE, a pair of asymmetric redox peaks appeared, which is the characteristics of the heme Fe^(III)/Fe^(II) redox peaks of Hb [21]. The result indicates that a slow direct electron transfer between Hb and electrode surface can proceed through graphene as the conductive bridge. After the immobilization of Hb on the surface of self-assembled nanowires of FF-G, the redox peak current level increases about 4 times higher than that of Nafion/Hb/G/GCE, and the peak shape becomes more symmetric. At multi-scan cyclic voltammetry, the redox peaks almost unchanged after continuous potential cycling (Fig. S4). The results could be attributed to the characteristics of nanowires of FF-G. In the high-density and interlacement nanowires of FF-G nanocomposites, graphene interact with FF by the π - π covalent bonding. There may exists a synergy effect in this composite: the self-assembled nanowires of FF exhibits excellent stability and biocompatibility, while graphene provides large surface area with layered structure and can also compensate the poor conductivity of FF.

The influence of scan rate on the electrochemical responses of Nafion/Hb/FF-G/GCE was further investigated by CV (Fig. S5). In the scan rate range from 0.025 to 0.200 V s⁻¹, a pair of symmetric redox peaks appeared and the redox peak currents increased gradually with the increase of scan rate. The linear relationships were established with two linear regression equations as $i_{pc}(\mu A) = 89.89 v (V s^{-1}) - 0.69$ ($R = 0.998$) and $i_{pa}(\mu A) = -85.95 v (V s^{-1}) + 0.57$ ($R = 0.998$) (Fig. S6). The linear response of redox current to scan rate is a clear indication of a typical surface-confined electrochemical behavior. Furthermore, with the increase of scan rate the redox peak potentials also shifted slightly with the gradual increase of peak to peak separation (ΔE_p) value. Redox peak potentials exhibited linearly dependence on natural logarithm of scan rate ($\ln v$) in the range from 0.025 to 0.200 V s⁻¹ (Fig. S7). The heterogeneous electron transfer rate constant (k_s) between Hb and the modified electrode was calculated to be 0.82 s⁻¹ by using the following Laviron equation [22].

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \frac{RT}{nFv} - \alpha(1 - \alpha) \frac{nF\Delta E_p}{2.3RT}$$

where $n = 1$, α is assumed to be 0.5 and all other symbols have the usual meanings. Using the equation reported early: $Q = nFA\Gamma^*$ [23], the surface coverage concentration (Γ^*) of Hb at the modified electrode is calculated as 2.18×10^{-9} mol cm⁻², which is much larger than that of monolayer coverage (2.0×10^{-11} mol cm⁻²) [24]. It is therefore implies that the self-assembled nanowires of FF-G are effective for the immobilized Hb for charge transfer.

The effect of buffer pH on CV responses of Nafion/Hb/FF-G/GCE was further investigated in the pH range from 6.0 to 8.0 (Fig. S8). A good linear regression relationship was obtained between the peak potential (E^0) and pH that can be fitted with the equation $E^0(V) = -0.0494 \text{ pH} - 0.049$ ($R = 0.998$) (Fig. S9). The obtained

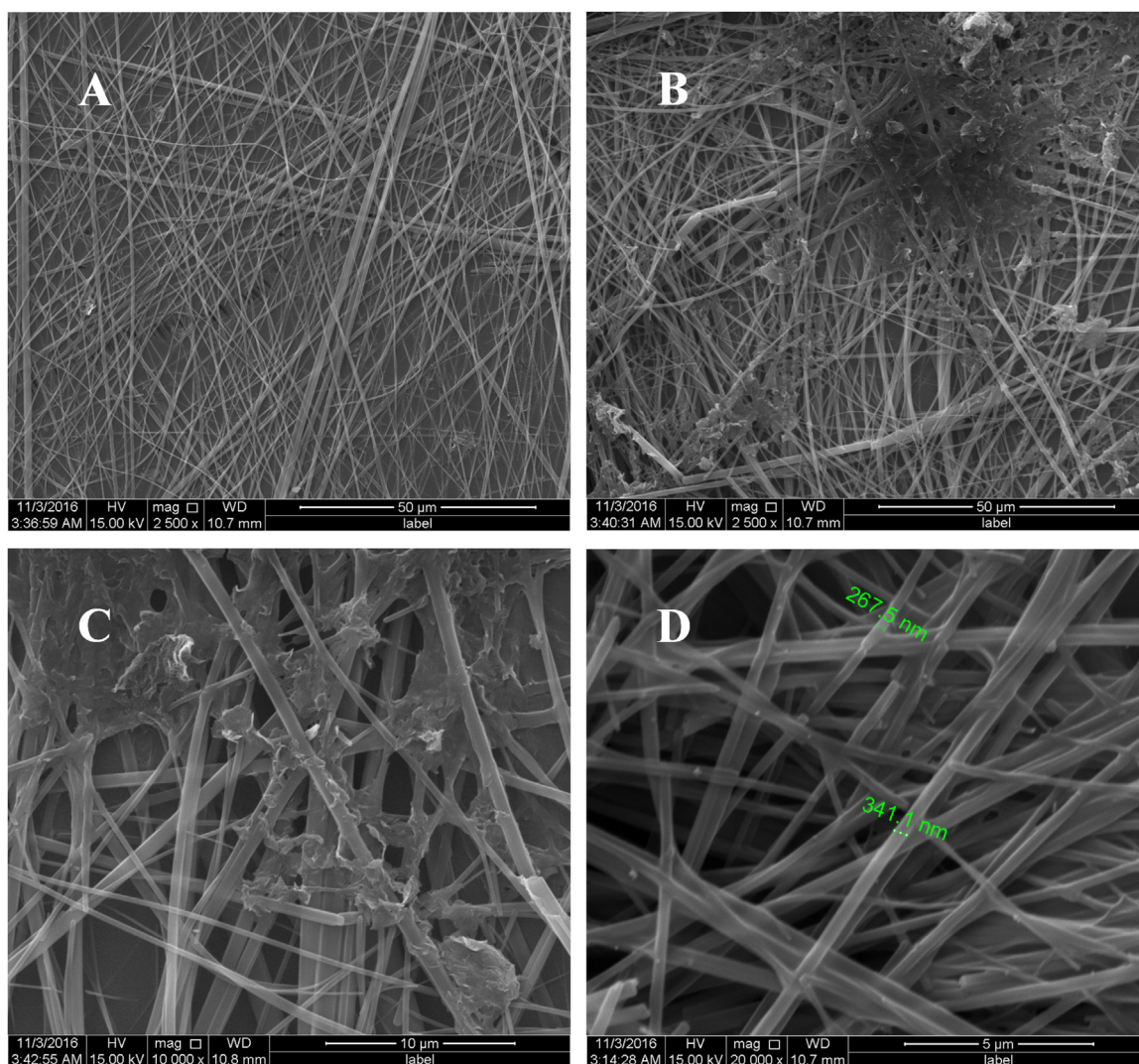


Fig. 1. Typical SEM image of self-assembled of FF (A) and FF-G (B–D), different magnifications of SEM images: (A) 2500 \times ; (B) 2500 \times ; (C) 10000 \times and (D) 20000 \times .

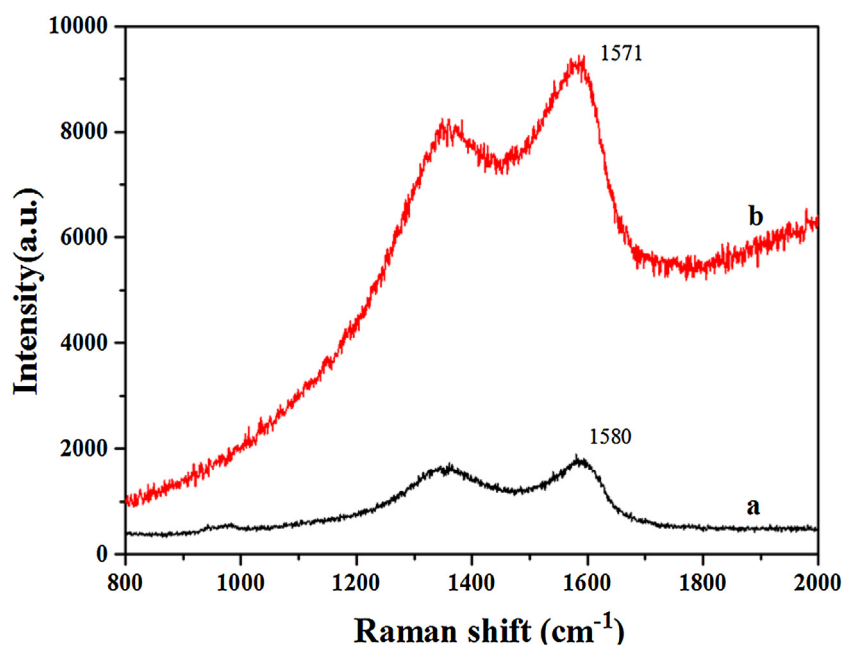


Fig. 2. Raman spectra of graphene and self-assembled of FF-G on GCE surfaces.

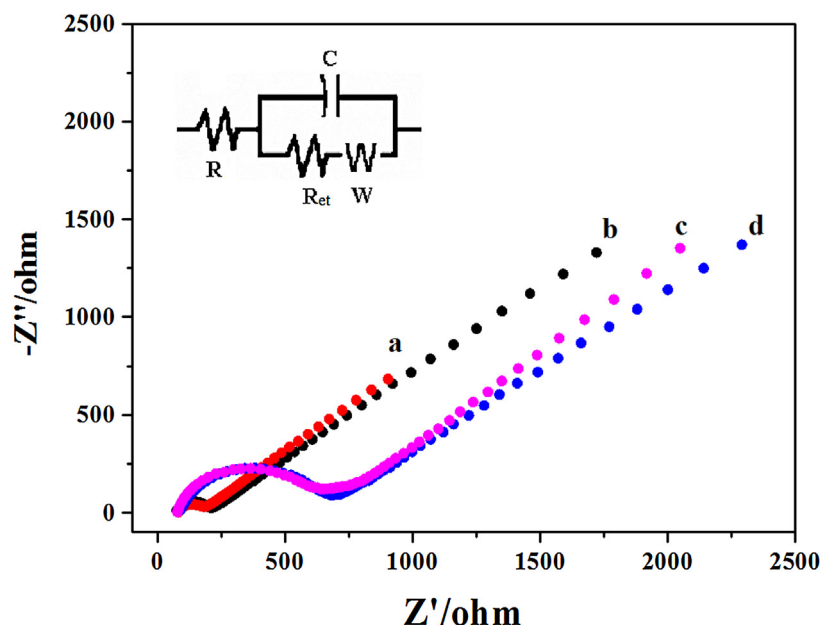


Fig. 3. Electrochemical impedance spectroscopy (EIS) of a bare GCE (curve a), FF-G/GCE (curve b), Nafion/Hb/G/GCE (curve c) and Nafion/Hb/FF-G/GCE (curve d) in $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Fe(CN)}_6^{4-/3-}$ (1:1) solution containing $0.10 \text{ mol L}^{-1} \text{ KCl}$; open circuit potential and amplitude of 5 mV; frequency range: 100000 Hz to 0.01 Hz; the inset is equivalent circuit.

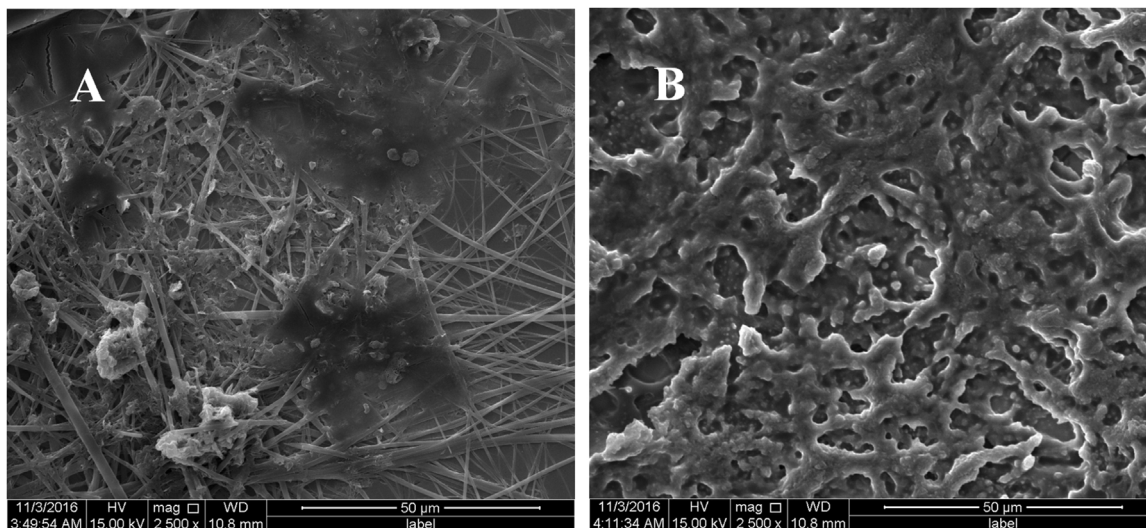


Fig. 4. Typical SEM image of Hb/FF-G (A) and Nafion/Hb/FF-G(B) on GCE surfaces.

slope of -49.4 mV pH^{-1} was close to the theoretical value of -59.0 mV pH^{-1} [25], indicating an equal number of protons (H^+) and electrons (e^-) transferred during the electrode reaction.

3.4. Electrocatalytic properties of Nafion/Hb/FF-G/GCE to the reduction of H_2O_2

To explore the potential application of Nafion/Hb/FF-G/GCE, the electrocatalytic reduction of different amount of H_2O_2 on the electrode has been studied by CV. The CV curves of Nafion/Hb/FF-G/GCE without and with H_2O_2 in nitrogen-saturated $0.1 \text{ mol L}^{-1} \text{ pH } 7.0$ PBS solutions are presented in Fig. 7. With the addition of H_2O_2 , an increase in reduction current of Nafion/Hb/FF-G/GCE is observed, indicating that Hb remains its natural structure after immobilizing in the FF-G film modified GCE and can catalyze the reduction of H_2O_2 .

For a fixed concentration, the response current of H_2O_2 ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) was recorded as a function of applied potential (working potential) in the range of -0.2 to -0.50 V (Fig. 8). The steady-state current reaches maximum at the working potential of -0.40 V . Therefore, -0.40 V was selected as the working potential to obtain a calibration curve for H_2O_2 detection.

Fig. 9 illustrates the steady-state amperometric response of the biosensor to the successive addition of aliquot H_2O_2 into the PBS with an operation potential of -0.40 V . The inset shows a calibration plot based on reduction current responses in the presence of H_2O_2 . Response currents exhibit a good linear relationship with the H_2O_2 concentrations from 5.0×10^{-7} to $5.0 \times 10^{-4} \text{ mol L}^{-1}$. The regression equation was $i_{\text{pa}} (\mu\text{A}) = 2.333 + 0.0334c (\mu\text{mol L}^{-1})$ ($R=0.999$). The detection limit ($S/N=3$) is estimated to be $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ [26]. The comparison of this biosensor with other kinds of Hb modified electrodes was summarized in Table 1 [27–32]. It can be seen that the proposed electrode exhibits

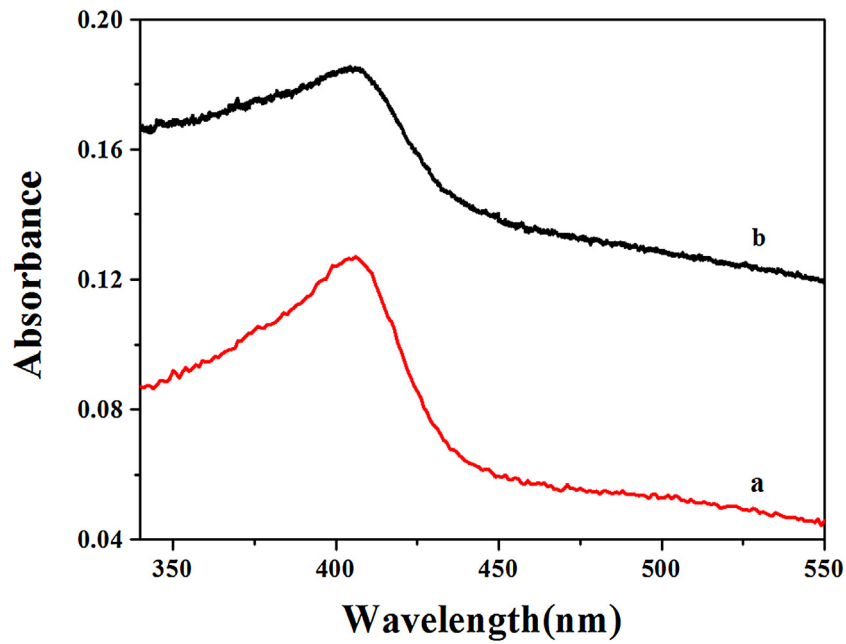


Fig. 5. UV-vis absorption spectra of Hb film (a) and Nafion/Hb/FF-G film (b) on the quartz slide.

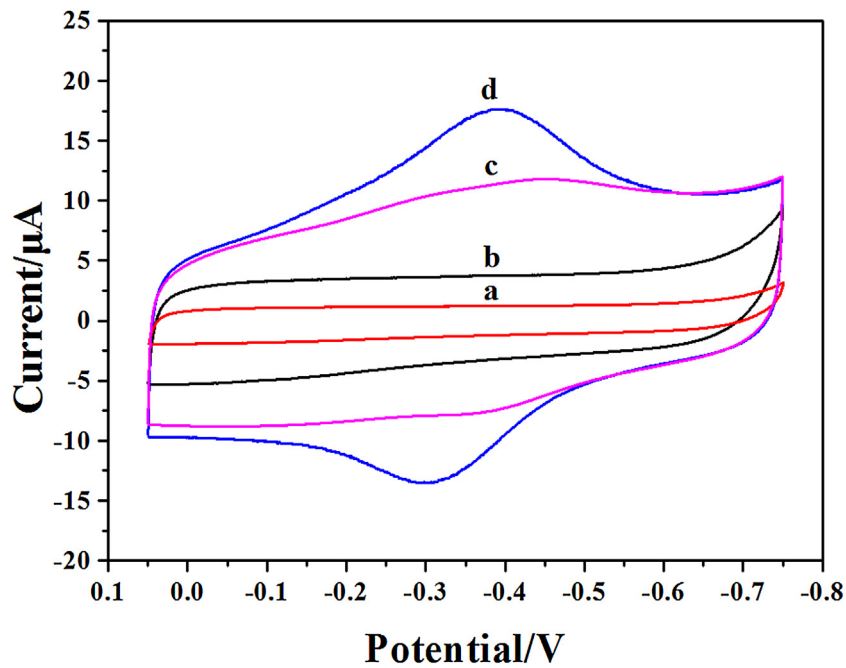


Fig. 6. Cyclic voltammetry curves of GCE (a), FF-G/GCE (b), Nafion/Hb/G/GCE (c) and Nafion/Hb/FF-G/GCE (d) in N_2 -saturated 0.1 mol L^{-1} pH 7.0 PBS; scan rate: 0.050 V s^{-1} .

Table 1

Comparison of the performances of different H_2O_2 biosensors based on graphene composites.

Hb modified electrodes	E_{pa} (V)	E_{pc} (V)	ΔE_p (V)	k_s (s^{-1})	Γ^* (mol cm^{-2})	Linear range ($\mu\text{mol L}^{-1}$)	Detection limit ($\mu\text{mol L}^{-1}$)	Ref.
Hb-G-chitosan/GCE	-0.103	-0.324	0.221	–	3.1×10^{-10}	6.5–230.0	0.51	[27]
Hb- Fe_3O_4 -G/GCE	-0.285	-0.363	0.078	0.91	–	1.5–585.0	0.5	[28]
Hb-G-ZnO nanosphere/Au	0.0	-0.132	0.132	1.0	1.53×10^{-9}	1.8–2300.0	0.6	[29]
Hb/G-Pt/GCE	-0.200	-0.320	0.120	0.14	4.53×10^{-10}	10.0–1000.0	1.0	[30]
Hb/chitosan-[BMIM]PF ₆ -TiO ₂ -G/GCE	-0.148	-0.265	0.117	0.73–3.96	3.21×10^{-10}	1.0–1170.0	0.3	[31]
Nafion/Hb-G-IL/CILE	-0.148	-0.221	0.073	0.92	3.04×10^{-9}	0.08–635.0	0.0137	[32]
Nafion/Hb/FF-G/GCE	-0.297	-0.376	0.079	0.82	2.18×10^{-9}	0.5–500.0	0.1	This work

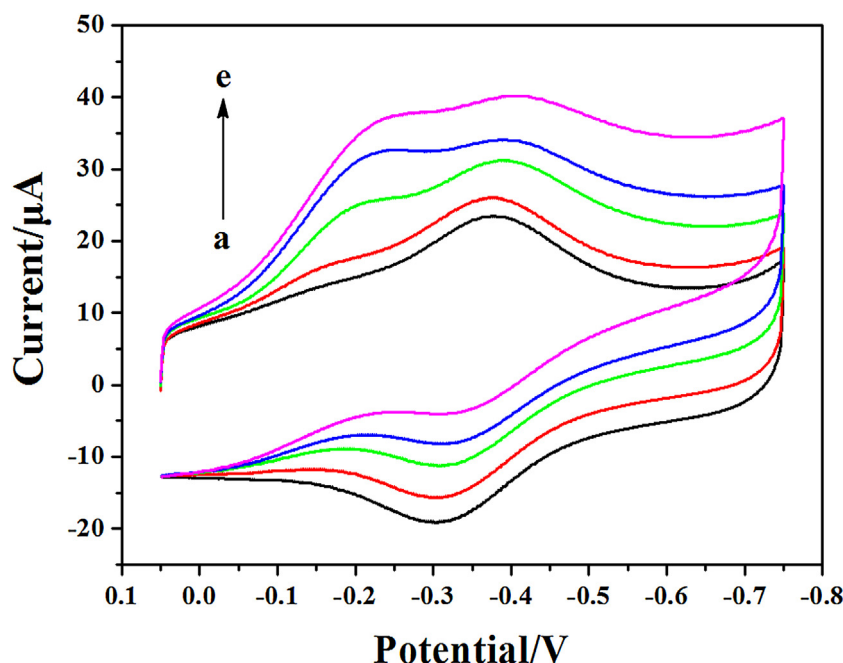


Fig. 7. Cyclic voltammetry curves of Nafion/Hb/FF-G/GCE in N_2 -saturated 0.1 mol L^{-1} pH 7.0 PBS containing H_2O_2 : 0 mol L^{-1} , $1.0 \times 10^{-5} \text{ mol L}^{-1}$, $4.0 \times 10^{-5} \text{ mol L}^{-1}$, $6.0 \times 10^{-5} \text{ mol L}^{-1}$ and $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (a–e). Scan rate: 0.100 V s^{-1} .

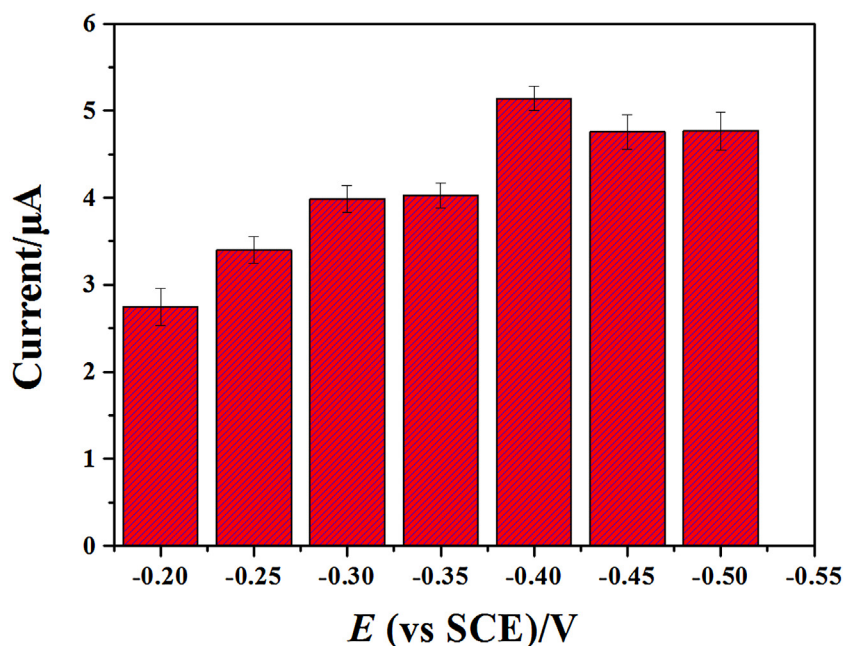


Fig. 8. Effect of the working potential on Nafion/Hb/FF-G/GCE response to $5.0 \times 10^{-5} \text{ mol L}^{-1} H_2O_2$ in N_2 -saturated 0.1 mol L^{-1} pH 7.0 PBS.

better electrochemical performance with a wider linear range and the lower detection limit compared to most of the electrodes, except for Nafion/Hb-G-IL/CILE. But the fabrication process for our proposed electrode is easier than that of Nafion/Hb-G-IL/CILE.

3.5. Repeatability, stability and selectivity of H_2O_2 biosensor

To verify the repeatability of the proposed H_2O_2 biosensor, the concentration of $5.0 \times 10^{-5} \text{ mol L}^{-1} H_2O_2$ was measured consecutively ten times. A relative standard deviation (RSD) of 4.9% was obtained, indicating a good reproducibility for the biosensor in determination of H_2O_2 in its linear range. In addition,

stability is also fundamental requirement biosensors. The stability of our electrode was examined through the response to $5.0 \times 10^{-5} \text{ mol L}^{-1} H_2O_2$. The results revealed that the current response only decreased by 7.5% of its initial value after a storage period of 15 days, indicating that a reasonably good stability.

Selectivity is important in practical use of the biosensors. We evaluated the selectivity with four typical interfering substances (uric acid (UA), ascorbic acid (AA), dopamine (DA), and folic acid (FA)) by using the amperometric current-time method. As showed in Fig. 10, these four tested substances interact rather weakly with the electrode, suggesting that the biosensor had a high selectivity to H_2O_2 .

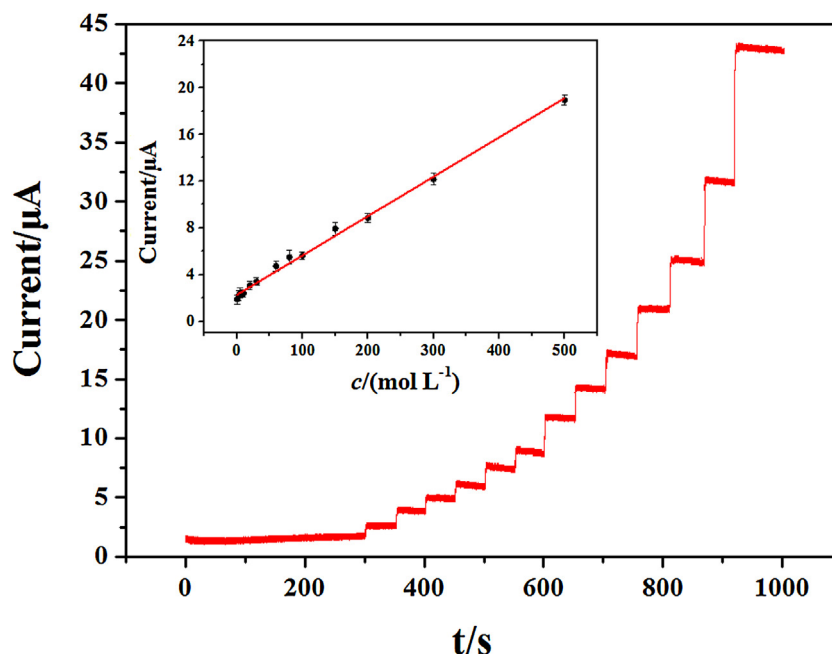


Fig. 9. Amperometric responses of Nafion/Hb/FF-G/GCE in N_2 -saturated 0.1 mol L^{-1} pH 7.0 PBS at -0.40 V on successive additions of H_2O_2 : (a) $5.0 \times 10^{-7} \text{ mol L}^{-1}$, (b) $2.5 \times 10^{-6} \text{ mol L}^{-1}$, (c) $2.0 \times 10^{-6} \text{ mol L}^{-1}$, (d) $5.0 \times 10^{-6} \text{ mol L}^{-1}$, (e) $1.0 \times 10^{-5} \text{ mol L}^{-1}$, (f) $1.0 \times 10^{-5} \text{ mol L}^{-1}$, (g) $3.0 \times 10^{-5} \text{ mol L}^{-1}$, (h) $2.0 \times 10^{-5} \text{ mol L}^{-1}$, (i) $2.0 \times 10^{-5} \text{ mol L}^{-1}$, (j) $5.0 \times 10^{-5} \text{ mol L}^{-1}$, (k) $5.0 \times 10^{-5} \text{ mol L}^{-1}$, (l) $1.0 \times 10^{-4} \text{ mol L}^{-1}$ and (m) $2.0 \times 10^{-4} \text{ mol L}^{-1}$.

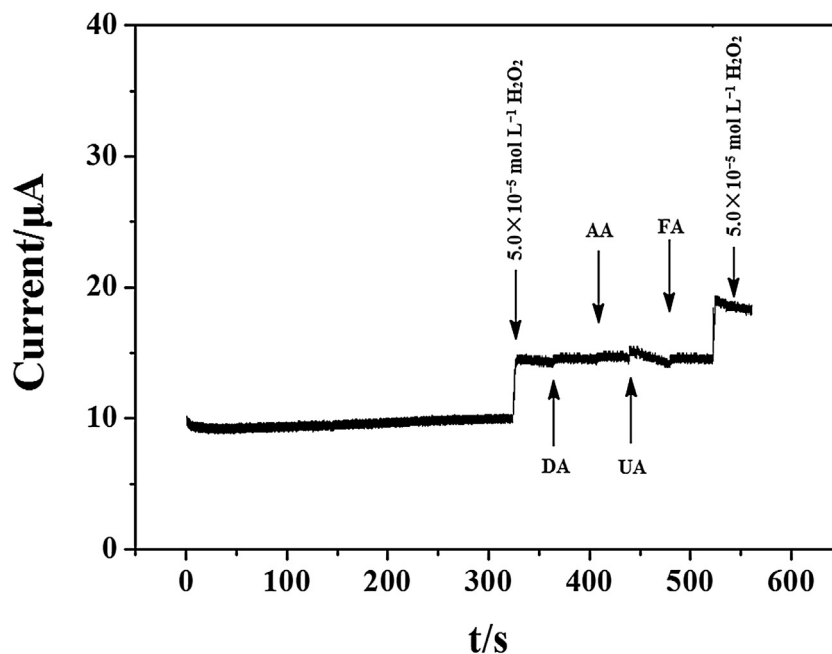


Fig. 10. Amperometric response of Nafion/Hb/FF-G/GCE in N_2 -saturated 0.1 mol L^{-1} pH 7.0 PBS at -0.40 V on successive additions of $5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ DA}$, $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ AA}$, $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ FA}$, $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ UA}$ and $5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$.

3.6. Real sample analysis

Finally, the real analytical applicability of the proposed biosensor was examined by determining the H_2O_2 level in reagent H_2O_2 . The results obtained by the biosensor were compared with those determined by the conventional KMnO_4 titration method. The results were in acceptable agreement. At the same time, we applied also the proposed biosensor in spiked human urine samples for a recovery test. As listed in Table 2, the recovery and RSD values indicate that the proposed biosensor is feasible for the analysis of H_2O_2 in real samples.

4. Conclusions

The self-assembled nanowires of FF-G have been successfully fabricated onto an electrode surface under room temperature by a simple one-step process. Based on the FF-G, an electrochemical H_2O_2 biosensor has been fabricated by further immobilizing hemoglobin (Hb) molecule. Our biosensor exhibited excellent performance, especially with wider linear range and lower detection limit than other control samples of graphene composites. The improved sensing performance could be contributed to the excellent biocompatibility of FF and the good charge transport in the

Table 2
Recovery results of the proposed biosensor to H₂O₂ in spiked human urine samples (n = 3).

Sample	H ₂ O ₂ concentration (μmol L ⁻¹)		Recovery (%)	RSD (%)
	Added	Found		
1	10.0	9.74	97.4	2.4
2	20.0	19.28	96.4	3.7
3	30.0	28.97	96.6	5.7

composite rendered by the graphene layer. Our results demonstrate that the self-assembled nanowires of FF-G are an attractive electrochemical biosensing platform.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2017.01.048>.

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