Gold Nanoparticles Sensitized ZnO Nanorods Arrays for Dopamine Electrochemical Sensing

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One-dimensional nanostructure materials offer opportunities for improving performance of electrochemical sensors. In this work, vertically ZnO nanorods (ZNRs) sensitized with gold nanoparticles (GNPs) were designed and fabricated onto indium tin oxide coated polyethylene terephthalate (ITO/PET) film for dopamine sensing. ZNRs that helpful for electric signal collecting by providing electron transfer pathways were electrodeposited on ITO/PET film firstly. Then GNPs that possess excellent electrocatalytic activity toward target were decorated onto ZNRs via potentiodynamic electrodeposition. These gold nanoparticles sensitized ZnO nanorods arrays (GNPs/ZNRs) combine the advantages of GNPs and ZNRs, thus providing chance to develop electrochemical sensors with ultrahigh sensitivity and excellent selectivity. Several important nervous system diseases (such as Parkinson’s disease, schizophrenia, senile dementia, AIDS, et al.) have proved to be associated with dysfunctions of dopamine system. So, the detection of dopamine becomes essential in clinical medical practice and nerve physiology study. When used for dopamine sensing, the fabricated electrochemical sensor shows two linear dynamic ranges (0.01–20 μM and 50–1000 μM) toward dopamine. Moreover, this proposed electrochemical sensor has been successfully applied to the determination of dopamine in human urine with satisfied recoveries (95.3% to 111.3%) and precision (1.1% to 8.4% of RSD).

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As crucial neurotransmitter, dopamine (DA) plays vital roles in central nervous, renal, hormonal and cardiovascular systems. Several important nervous system diseases, including Parkinson’s disease, schizophrenia, senile dementia, AIDS, et al., are proved to be associated with dysfunctions of DA system.1–4 DA is also available in electrochemical reactions.26 The inherent properties of the nontoxic and AlCl3 were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Unless stated otherwise, all chemicals were used as received. All water used was obtained from Milli-Q purification system.

In this work, gold nanoparticles sensitized ZnO nanorods arrays (GNPs/ZNRs) were prepared via a two-step electrodeposition process (Scheme 1). Firstly, vertically ZnO nanorods (ZNRs) were electrodeposited onto ITO/PET film via seed-free method. These sparse vertically ZNRs could be used as high-surface scaffolds for gold nanoparticles (GNPs) deposition and sensitization. GNPs were electrodeposited onto ZNRs to form GNP/ZNRs. GNPs can be used as electrocatalysts for DA oxidation, while ZNRs can provide fast pathway for electron transfer and electrochemical signal collection. So, GNP/ZNRs may promote the electrocatalytic oxidation of DA and enhance the sensitivity and selectivity toward DA. To the best of our knowledge, this work represents the first attempt of fabricating GNP/ZNRs based electrochemical sensor for DA sensing.

Experimental

Chemicals and materials.—Dopamine hydrochloride, ascorbic acid (AA) and uric acid (UA) were purchased from Sigma-Aldrich. HAuCl4·4H2O; Zn(NO3)2·6H2O; Hexamethylenetetramine, KCl and AlCl3 were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Unless stated otherwise, all chemicals were used as received. All water used was obtained from Milli-Q purification system.

Indium tin oxide coated polyethylene terephthalate (ITO/PET) films were obtained from Zhuhai Kaivo Optoelectronic Technology Co., Ltd, with low sheet resistance of 35 /sq.

Synthesis of vertically GNPs/ZNRs arrays.—Before synthesis of GNPs/ZNRs arrays, ITO/PET films were cut into 1 cm × 5 cm, mobility make 1D ZnO nanorods (ZNRs) quite suitable for sensing applications. Furthermore, 1D ZNRs could also be used as matrix for composite 1D nanostructure electrode construction.27 On the other hand, gold nanoparticles (GNPs) have drawn increasing attention of many researchers in the field of electrochemical sensors due to their unique chemical and physical properties (such as large specific surface area, high conductivity and electrocatalytic activity).28–31 Though ZnO-GNPs nanocomposites had been prepared and used for electrode modification,34–37 drop-casting method always lead to stability issue. In this work, gold nanoparticles sensitized ZnO nanorods arrays (GNPs/ZNRs) were prepared via a two-step electrodeposition process (Scheme 1). Vertically ZnO nanorods (ZNRs) were electrodeposited onto ITO/PET film via seed-free method. These sparse vertically ZNRs could be used as high-surface scaffolds for gold nanoparticles (GNPs) deposition and sensitization. GNPs were electrodeposited onto ZNRs to form GNP/ZNRs. GNPs can be used as electrocatalysts for DA oxidation, while ZNRs can provide fast pathway for electron transfer and electrochemical signal collection. So, GNP/ZNRs may promote the electrocatalytic oxidation of DA and enhance the sensitivity and selectivity toward DA. To the best of our knowledge, this work represents the first attempt of fabricating GNP/ZNRs based electrochemical sensor for DA sensing.

Comparison of traditional plate electrode, nanostructured electrodes could provide more sites for electrochemical reactions owing to their tremendous specific surface area. As a result, the sensitivity and selectivity would be greatly promoted by means of the unique physical and chemical properties of the nanostructured materials. Among different nanostructured materials, one dimensional (1D) nanostructure aroused bright hope to build high-performance electrochemical sensors, as the unique 1D configuration could provide not only considerable reaction sites but also the “fast tracks” for electron transfer in electrochemical reactions.26 The inherent properties of the nontoxicity, good biocompatibility, bionic characteristics and high electron

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then cleaned by rinsing with acetone, methanol and deionized water in ultrasonic bath for 30 min. Vertically GNPs/ZNRs arrays were synthesized via a two-step electrodeposition process. ZNRs arrays were firstly synthesized via seed-free electrochemical method with minor changes.27 In typical procedure, ITO/PET film was served as working electrode, while Ag/AgCl electrode and platinum wire electrode were used as reference electrode and counter electrode, respectively. The electrolyte (250 mL aqueous solution) containing 15 mg Zn(NO$_3$)$_2$, 7 mg hexamethylenetetramine, 1.8638 g KCl and trace AlCl$_3$ (the Al$^{3+}$/Zn$^{2+}$ molar ratio of 1:100). The electrodeposition of ZNRs was performed at stationary potential of −1 V for 40 min (65°C). During the whole electrodeposition process, air was continuously bubbled into the electrolyte using a peristaltic pump. After electrodeposition, this ZNRs modified ITO/PET film was rinsed with flowing water and then immersed into another solution containing 0.1 M KCl and 0.005 M HAuCl$_4$. Then, potentiodynamic electrodeposition was performed from −1.0 to 0.2 V for 25 cycles at a scan rate of 100 mV/s, obtaining GNPs/ZNRs modified ITO/PET film. Finally, the GNPs/ZNRs modified ITO/PET film was rinsed with flowing water and blown dry with nitrogen gas.

Apparatus and characterizations.—The morphologies of the as-synthesized ZNRs and GNPs/ZNRs were obtained on a field emission scanning electron microscope (Nano NovaSEM 450, FEI, Eindhoven, Netherlands) with an acceleration voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDS) analysis was performed using accessory (INCA 250) of Nano NovaSEM 450 instrument. The phase and crystallographic structure of as-synthesized ZNRs and GNPs/ZNRs were characterized by X-ray diffraction (XRD, Philips X’ Pert Pro, Eindhoven, Netherlands) using Cu-Ka as radiation ($\lambda = 0.154056$ nm, 40 kV, 40 mA), while Ni as filter and silicon as internal standard. Electrochemical experiments such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed on a CHI660E workstation (ChenHua Instruments Co., Ltd, Shanghai, China) with conventional three electrode system. The ITO/PET films or modified ITO/PET films were used as working electrodes. Platinum wire electrode and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. DPV peak current of dopamine on different modified ITO/PET films was recorded between 0.2 to 0.6 V at a scan rate of 100 mV/s. The EIS was carried out in an aqueous solution containing 0.01 M [Fe(CN)$_6$]$_{3-}$$_{4-}$ and 0.1 M KCl with a frequency range of 1 $\times$ 10$^5$−1 Hz. The bias voltage was set to −0.25 V, while the signal amplitude was set to 5 mV.

Results and Discussion

Preparation and characterization of GNPs/ZNRs.—In this work, vertically ZNRs were grown on ITO/PET films by one step seed-free electrodeposition.27 This process is based on the electroreduction of dissolved oxygen and/or NO$_3^-$ ions to generate OH$^-$ ions, which increase the interfacial pH at the electrode surface, leading to the precipitation of ZnO when Zn$^{2+}$ ions are present in solution.38 As shown in Figure 1a, the ZNRs are vertically oriented to ITO/PET film (ZNRs/ITO/PET). The diameters of ZNRs are distributed in the range of 250–300 nm. The electrodeposition of GNPs on ZNRs/ITO/PET was performed by cyclic voltammetric mode. Like lightning-rods,39 the electric field lines concentrate on the convexity of ZNRs, thus the GNPs were preferentially electrodeposited on ZNRs (Figure 1b). The GNPs on the surface of ITO/PET film showed quasi-spherical shape with sizes in the range of 30–50 nm and relative symmetric distribution. X-ray diffraction (XRD) also used to confirm the GNPs/ZNRs on ITO/PET film (Figure 1c). The broad XRD peak located at about 54° is attributed to PET substrate. The ITO XRD peaks were not observed because the amorphous ITO film was deposited by low-temperature sputtering process.40 After electrodeposition of ZNRs, little sharp peak located at 34° was observed, which could be assigned to (002) planes of wurtzite ZnO (JCPDS, No. 36-1451). The dominant XRD peak confirmed the ZNRs were preferentially grown along the c-axis of ZnO.41 Despite the XRD peaks from ITO/PET film and electrodeposited ZNRs, we observe three well defined Au XRD feature peaks on GNPs/ZNRs/ITO/PET film for (111) at about 38°, (200) at about 44° and (220) at about 65°, which are consistent with the reference pattern for face centered cubic structure of Au (JCPDS, No. 4-0784).42,44 The EDS spectrum of GNPs/ZNRs/ITO/PET film (Figure 1d) shows the presence of Indium, Tin, Oxygen, Zinc, Aluminum and Gold, suggesting the successful modification of GNPs/ZNRs on the ITO/PET film.

XPS analysis was also used to study the composition of GNPs/ZNRs on ITO/PET film (Figure 2). The binding energies were calibrated by C 1s (284.8 eV). The survey XPS spectrum of GNPs/ZNRs on ITO/PET film is shown in Figure 2a, which indicates the presence of Zn, O, Au, In, Sn, C and Al as well. Most of the peaks can be attributed to the elements from materials and reagents used in the synthesis process. High-resolution XPS spectra of the three main elements (Zn 2p, O 1s and Au 4f) are shown in Figures 2b–2d. The peak of Zn 2p (Figure 2b) is split into 1019.7 eV (2p 3/2) and 1042.9 eV (2p 1/2) with a split orbit of 23.2 eV, which is in good accordance with the Zn (II) from ZnO.46,47 The peak located at 530 eV in the O 1 s spectrum (Figure 2c) can be attributed to O$_{3-}$ in Zn-O bonds and/or O$^{2-}$ ions in oxygen-deficient regions within the ZnO matrix.
Due to the semiconductor nature and/or low crystallinity of ZNRs prepared by low-temperature electrodeposition, the direct application of these ZNRs in electrochemical sensor is often limited. So far, a number of typical dopant elements such as F, B, Al, Ga, In and Sn have been used to modify the electrical and optical properties of ZnO. As a cheap, abundant and non-toxic III group element, Al can enhance the n-type electrical conductivity and reduce the resistivity of Al-doped ZnO. In this work, undoped ZNRs were also prepared on ITO/PET film under same conditions but in the absence of AlCl3 as doping precursor. The surface morphology of the undoped and Al-doped ZNRs is shown in Figures 3a and 3b, respectively. The SEM images indicated that undoped and Al-doped ZnO nanorods are all almost vertically on the surface of ITO/PET films with hexagonal facets. However, there are still some slight differences between these undoped and Al-doped ZnO nanorods. Firstly, doping of Al reduced the diameter of Al-doped ZnO nanorods, which is similar with previous report by Chen. Secondly, the surface quality of Al-doped ZnO nanorods is slightly improved, which may imply an improvement of the crystallinity of Al-doped ZnO nanorods. Higher (002) peak intensity of Al-doped ZnO nanorods also confirmed the improvement of the crystallinity of resulted ZnO nanorods (Figure 3c). Chronocoulometric curves recorded during the corresponding electrodepositions are shown in Figure 3d. Higher slope of Al-doped ZnO nanorods indicates that Al-doped ZnO nanorods can provide them ability of faster electron transfer than undoped ZnO nanorods. The electrochemical signal collection ability of undoped and Al-doped ZnO nanorods was studied by EIS method in aqueous solution containing 0.01 M [Fe(CN)6]3−/4− and 0.1 M KCl (Figure 3e). It is obviously that Al-doped ZNRs exhibit smaller semicircle domain present than undoped ZNRs, implying lower electron transfer resistance to redox probe at the interface of Al-doped ZNRs than that of undoped ZNRs. The DPV response of undoped and Al-doped ZNRs in 100 μM dopamine also confirmed that Al-doped ZNRs are beneficial for electronic transmission than that of undoped ZNRs. (Figure 3f).

Optimization of GNPs/ZNRs for electrochemical sensor.—In order to obtain optimal GNPs/ZNRs, thus enhancing sensitivity of GNPs/ZNRs based electrochemical sensor, optimization experiments were performed. In this work, two different factors including the density of ZNRs and GNPs were detailed investigated. The density of ZNRs could be easily controlled by Zn(NO3)2 concentrations used for ZNRs electrodeposition. ZNRs with different density were prepared on ITO/PET film with constant electrochemical parameters (E = −1 V, T = 65 °C, t = 40 min) using different Zn(NO3)2 concentrations (from 0.05 mM to 1 mM). The density of ZNRs increased with the increase of Zn(NO3)2 concentrations. After electrodeposition of GNPs on above ZNRs, they were used to detection 50 μM dopamine by DPV method. As shown in Figure 4a, the DPV peak currents on GNPs/ZNRs increased upon Zn(NO3)2 concentration to reach maxima at 0.2 mM and then decreased upon further increase of Zn(NO3)2 concentration to 1.0 mM. This phenomenon may be explained that too high ZNRs density will reduce the load of GNPs on ZNRs. Therefore, 0.2 mM Zn(NO3)2 was chosen as the optimal value for ZNRs electrodeposition. The density of GNPs could be controlled by changing the CV cycles used for GNPs electrodeposition on ZNRs prepared from 0.2 mM Zn(NO3)2 solution. As shown in Figure 4b, the DPV peak currents on GNPs/ZNRs increased upon CV cycles to reach maxima at 25 cycles and then decreased upon further increase of CV cycles to 35 cycles. High scan cycles lead to extensive electrodeposition of GNPs, which may reduce the specific surface area of the obtained GNPs/ZNRs, reducing the DPV peak current toward dopamine. Therefore, we chose 25 cycles as the optimum CV cycles for further experiments.
Figure 2. XPS spectra of GNPs/ZNRs on ITO/PET film: survey spectra (a); Zn 2p region (b); O 1s region (c); Au 4f region (d).

Figure 3. SEM images of undoped (a) and Al-doped (b) ZNRs on ITO/PET films. XRD patterns of undoped and Al-doped ZNRs on ITO/PET films (c). Chronocoulometric curves of undoped and Al-doped ZNRs recorded during the corresponding electrodepositions (d). EIS recorded in 0.01 M [Fe(CN)₆]³⁻/⁴⁻ using undoped and Al-doped ZNRs (e). DPV response of undoped and Al-doped ZNRs in 100 μM dopamine (f).
The performance of GNPs/ZNRs based electrochemical sensor.—GNPs/ZNRs used as sensing materials for electrochemical sensor may possess two key advantages. Firstly, excellent electrocatalytic activity of GNPs facilitates the conversion from analyte signal (such as dopamine concentration) to electric signal. Secondly, ZNRs are helpful for electric signal collecting by providing electron transfer pathways. Based on these considerations, GNPs/ZNRs were integrated into an electrochemical workstation for dopamine sensing as model. In order to illustrate the potential advantages of such GNPs/ZNRs, bare ITO/PET film, GNPs modified ITO/PET film and ZNRs modified ITO/PET film were also prepared and compared using DPV method. As shown in Figure 5a, bare ITO/PET film and ZNRs modified ITO/PET film do not show obvious response toward dopamine due to low electrocatalytic activity toward dopamine. While, GNPs modified ITO/PET film and GNPs/ZNRs modified ITO/PET film all show well-defined and distinguishable sharp oxidation peak at about 0.2 V. As expected, GNPs/ZNRs modified ITO/PET film displayed much higher current response than that of GNPs modified ITO/PET film, indicating the “fast tracks” for electron transfer provided by ZNRs. EIS can provide useful information on impedance changes of electrode surface to characterize the stepwise construction process.52 Figures 5b and 5c illustrate the Nyquist diagrams of different materials modified ITO/PET films in the presence of 0.01 M [Fe(CN)6]3−/4−. As shown that all curves exist two semicircle domain presents, the smaller semicircle corresponds to the charge-transfer resistance at the platinum wire electrode/electrolyte interface, while the larger semicircle represents charge-transfer resistance at the modified ITO/PET films. Due to the low electrocatalytic activity of ITO toward [Fe(CN)6]3−/4−, the bare ITO/PET film exhibits the largest semicircle domain present. After electrodeposition of ZNRs on ITO/PET film, a decrease in electron transfer resistance was observed, which may be caused by the faster electron transfer of Al doped ZNRs. Meanwhile, GNPs modified ITO/PET film exhibit the lowest semicircle domain present, implying high conductivity and electrocatalytic activity of GNPs. Compared to GNPs modified ITO/PET film, GNPs/ZNRs modified ITO/PET film display an slight increase in electron transfer resistance. This phenomenon may be explained by relatively low conductivity and electrocatalytic activity of ZNRs than that of GNPs.

Determination of dopamine.—GNPs/ZNRs were integrated into an electrochemical workstation and used for dopamine sensing by using DPV method under optimized conditions. The DPV current of dopamine solutions in the range from 0.01 μM to 1000 μM were recorded. The DPV peak current values of GNPs/ZNRs based electrochemical sensor in different dopamine solutions was shown in Figure 6a. As shown, the DPV peak current values of dopamine on GNPs/ZNRs electrochemical sensor increased with the increase of dopamine concentration. Obviously, the DPV peak current values are not linear to dopamine concentration over the whole range from 0.01 μM to 1000 μM. The DPV peak current values versus dopamine concentration show two linear regions and the turning point of the slope occurs at about 50 μM. The linear range at low concentration (from 0.01 μM to 20 μM) shows linear regression equation of y = 0.2947x+1.2641 (R2 = 0.9962, Figure 6b), while the linear range at high concentration (from 50 μM to 1000 μM) shows linear regression equation of y = 0.0081x+16.8880 (R2 = 0.9956, Figure 6c). Non-linearity of the DPV peak current value versus dopamine concentration in whole concentration range maybe mainly due to the distribution of GNPs on ZNRs and ITO/PET film. At low concentration range, dopamine is preferentially oxidized at the surface of GNPs on ZNRs due to the lightning-rods effect.53 In addition, the electrochemical signal collection is benefited from electron transfer channels provided by ZNRs. As a result, the slope of the first calibration curve is relatively high. While at high concentration range, dopamine can be also oxidized at the surface of GNPs on ITO/PET film. Due to the relatively low electrochemical signal collection ability of planar ITO/PET film, the slope of the second calibration curve decreased remarkably. To our
Figure 6. DPV responses of GNPs/ZNRs based electrochemical sensor to dopamine solutions in the range from 0.01 μM to 1000 μM (a). Calibration plots of DPV responses via dopamine concentration at low concentration range (b, 0.01 μM to 20 μM) and high concentration range (c, 50 μM to 1000 μM).

satisfaction, the measuring range for dopamine presented in this work basically covers the relevant physiological range of approximately 0.1–10 μM.

**Selectivity, repeatability and stability of GNPs/ZNRs based electrochemical sensor.**—In order to investigate the selectivity of the proposed GNPs/ZNRs based electrochemical sensor, we used the proposed GNPs/ZNRs based electrochemical sensor to detect of dopamine in the presence of structural analogue (AA or UA). The concentration of dopamine was fixed at 100 μM, while the concentration of AA and UA were ranged from 300 μM to 500 μM. Figure 7 shows the DPV responses of GNPs/ZNRs based electrochemical sensor toward dopamine in the presence of AA and UA. Dopamine shows anodic peak at 0.20 V, while AA and UA show anodic peaks at 0.05 V and 0.40 V, respectively. The separation of the peak potentials between dopamine and AA, dopamine and UA are all larger than 150 mV. The large separation of the peak potential allows selective determination of dopamine in the presence of AA and UA, or simultaneous detection of them in their mixture. As shown, the proposed GNPs/ZNRs based electrochemical sensor did not show large DPV responses toward AA and UA than dopamine, even though the concentration of the structural analogues was 5 times of dopamine. In addition, the DPV responses of GNPs/ZNRs based electrochemical sensor to dopamine did not show significant change (DPV peak values change less than 10%) with the increase of AA and UA from 300 μM to 500 μM. Besides the above structural analogues, a series of foreign species, such as 50-fold of Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺, Al³⁺, Cl⁻, CO₃²⁻, SO₄²⁻ and NO₃⁻ do not interfere with the oxidation signal of dopamine. All these results suggested that the proposed GNPs/ZNRs based electrochemical sensor possess excellent selectivity toward dopamine.

The repeatability and stability of the proposed GNPs/ZNRs based electrochemical sensor was evaluated by using the same sensor electrode for 20 repeated analyses of 100 μM dopamine solution. The DPV responses of GNPs/ZNRs based electrochemical sensor toward dopamine showed a relative standard deviation of 9.97%, indicating very good reproducibility. The stability of the GNPs/ZNRs based electrochemical sensor was investigated by two different ways. When the GNPs/ZNRs based electrochemical sensor was exposed to surrounding atmosphere for 20 days at room temperature, the proposed GNPs/ZNRs based electrochemical sensor still reserved 89.97% of its original response toward 100 μM dopamine solution. The stability of the GNPs/ZNRs based electrochemical sensor was also evaluated within 2 weeks by recording the DPV current responses once each day. The DPV current of dopamine on GNPs/ZNRs based electrochemical sensor also retained 88.62% of its initial current after 2 weeks. These results demonstrated that the prepared GNPs/ZNRs based electrochemical sensor had excellent repeatability and stability.

**Determination of dopamine in real samples.**—In order to investigate the suitability of the proposed GNPs/ZNRs based electrochemical sensor for the determination of dopamine in complex biomatrix, urine samples were analyzed by using standard addition method under optimized conditions. All the urine samples were diluted 10 times with 0.1 M PBS solutions (pH 7.0) and certain amounts of dopamine were added. The concentrations and recoveries were listed in Table I. As shown in Table I, the recoveries ranged from 95.3% to 111.3% and relative standard deviation (RSD) ranged from 1.1% to 8.4%. These

Figure 7. The selectivity of GNPs/ZNRs based electrochemical sensor toward dopamine in the presence of ascorbic acid (left) and uric acid (right).

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results indicated that the proposed GNPs/ZNRs based electrochemical sensor has good accuracy for the determination of dopamine in urine samples.

Conclusions

In this work, we proposed gold nanoparticles sensitized ZnO nanorods arrays as sensing material for electrochemical sensor construction. These GNPs/ZNRs arrays combine the advantages of GNPs and ZNRs, thus providing chance to develop electrochemical sensors with ultrahigh sensitivity and excellent selectivity toward dopamine. The proposed GNPs/ZNRs based electrochemical sensor displayed excellent selectivity, repeatability and stability toward dopamine. The strategy proposed for preparing GNPs/ZNRs based electrochemical sensor may also be used for other biomacromolecules (such as DNA, protein, virus and cells) detection.

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