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Photoelectrochemical response to glutathione in Au-decorated

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ZnO nanorod array

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Metal nanoparticles assistant photoelectrochemical (PEC) biosensing has been attracted by point-of-care testing due to its fast and low background signal. But the interfacial charge transfer of plasmonic-enhanced biosensing is not fully understood still now. Herein, a plasmonic-enhanced PEC platform has been demonstrated for glutathione (GSH) detection based on a hybrid structure of well-oriented zinc oxide nanorod array (ZnO NRs) with gold nanoparticles (Au NPs) as photoanode. In the PEC system, the self-powered bioanalysis is carried out at 0 V versus Ag/AgCl under simulated sunlight. In detail, the series optical experiments (eg. photoluminescence, PL) and theoretical analysis (eg. finite-difference time-domain, FDTD) illustrate the photoresponse enhancement mechanism of Au NPs-ZnO NRs and reaction process of GSH. The GSH oxidization and related reaction process on pH versus photocurrent response are demonstrated and investigated. The as-prepared surface plasmon resonance (SPR) based PEC sensor could be taken into account for GSH detection in clinical early tumor diagnosis.

Introduction

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Glutathione (GSH) as one of the most abundant antioxidant thiols in the intracellular environment (1-15 mM),^{1,2} plays a vital role in many pathological and physiological processes through interaction with free radicals or enzymes.^{3, 4} It also protects the proteins and other cellular constituents from oxidation by reactive oxygen species (ROS).5 Besides, an insufficient GSH caused various diseases such as HIV, cancer, Alzheimer's disease and diabetes.4, 6 Many technologies have been proposed for GSH detection including mass spectrometry, liquid chromatography tandem mass spectrometry,8 surface-enhanced scattering,9, 10 Raman fluorescence spectroscopy,¹¹⁻¹³ electrochemistry,^{14, 15} and photoelectrochemistry.^{4, 16-18} The search for alternative portable with miniaturized detection instrument and method has always been desired and the characteristics of electrochemical technology make it potential candidate in this aspect. Furthermore, the developing photoelectrochemistry provides an attractive analytical tool with fast and low background signal.

In general, the photoelectrode materials should meet requirements in biocompatibility for their green detection. As one of the biocompatible materials, the n-type semiconductor of ZnO has a high electron mobility and high chemical stability with environmental friendliness and low cost.¹⁹⁻²¹ Moreover, it is a desirable candidate for PEC photoelectrode.^{22, 23} As we know, ZnO has a wide direct band gap (3.2 eV) as well as ultraviolet (UV, 300-400 nm) absoz rption.²⁴⁻²⁷ In order to broaden its light availability, some noble metals have been introduced on ZnO using their SPR effect which effectively

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improves the utilization of visible light in ZnO-based composites.²⁸ Concomitantly, the charge carriers have been easily separated at the semiconductor-metal interface ²⁹⁻³¹ which increases both catalytic and current signals of the substrate. For example, Xu et al.³² formed ZnO (a) Au heterogeneous nanorod arrays on Si substrate to catalyze the water. The ZnO nanotemplates with sensitization of gold nanoparticles have also been developed as photoelectrochemical aptasensor for efficient detection of bisphenol A.³³ In order to reduce a background noise signal that caused at higher working voltage, Zhang et al.¹⁶ synthesized the Au NPs @ ZnO nanorods to realize the self-powered GSH detection. However, an enhanced mechanism of noble metal-ZnO is ambiguous. Hence, it is essential to investigate photo-induced electron transport dynamics. In addition, some factors can influence the photo-induced electron transfer in PEC system. For example, the pH value of electrolyte is not considered in the PEC system generally but it has an obvious influence on photocurrent response of GSH.

In the present work, a biosensing platform has been formed based on Au NPs-ZnO NRs. The proposed photoresponse enhancement has been verified through both experimental analysis and numerical simulation to understand the mechanism clearly. Because of Au NPs' SPR effect, the ultraviolet emission enhancement and visible fluorescence disappearance were observed in Au NPs-ZnO NRs. Moreover, the SPR effect of Au NPs-ZnO NRs hybrid structure with photocurrent enhancement has been verified by monochromatic light illumination and finite-difference timedomain (FDTD) simulations. In the GSH detection, a wide linear range has been obtained with low detection limit. In addition, an influence of pH in GSH biosensing was analyzed deeply. The proposed PEC sensor has great potential for detecting GSH in blood sample or complex sample because it has good anti-interference performance.

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Experimental

A sintered ceramic target of ZnO (ZhongNuo Advanced Material Technology Co., Ltd., Beijing, China, 99.99%) was used as a source material for the preparation of ZnO seed. The SnO₂:F (FTO; 1 cm×2 cm, resistivity of 10 Ω cm⁻²) electrodes were acquired from Luoyang Shangzhuo Technology, Ltd., China. A phosphate buffered saline (PBS, 0.01 mol L⁻¹) was obtained through mixing by 0.2 g of KH₂PO₄, 2.9 g of Na₂HPO₄•12 H₂O, 8.0 g of NaCl and 0.2 g of KCl. The pH values of PBS were adjusted by adding 1 M of HCl or NaOH. Ultrapure water was obtained from Millipore water purification system (\geq 18 M Ω cm⁻¹, Milli-Q, Millipore) which used in the assays. All the reagents are of analytical grade and used in these experiments without any further purification processes.

The ZnO nanorod array was prepared by hydrothermal method according to previous literature.^{34, 35} Initially, an FTO glass substrate was rinsed with acetone, ethanol and deionized water under ultraphonic treatment in sequence to remove contaminants from the surface of substrate. Then, the magnetron sputtering was carried out with radio frequency power of 100 W and sputtering time of 30 min to form a seed layer of ZnO on FTO substrate. The total pressure was kept constantly at 5.0×10^{-5} Pa with O₂ and Ar gas constant flow rates of 5 and 55 sccm, respectively. Moreover, the deposition gas pressure was kept constantly_at 2 Pa. After that, the ZnO NRs were synthesized on FTO glass by hydrothermal method. In a typical process, a seeded FTO substrate was immersed in the aqueous solution of 50 mM of Zn(CH₃COO)₂•2H₂O and (CH₂)₆N₄ with equimolar ratio at 90°C for 6 h. After the gradual cooling process, the ZnO-coated substrate was removed from the solution and rinsed with deionized water and then dried at 60°C for 10 h. Subsequently, the gold particles were deposited on ZnO by using a plasma sputtering method. After that, the Au NPs-ZnO NRs hybrid array was placed in the quartz boat and heated (2 °C min⁻¹) up to the desired temperature of 400°C in air atmosphere. The sample was treated at the target temperature for 30 min and then cool down slowly in order to improve the crystallinity of it.

The morphologies of the as-prepared samples were characterized by using field emission scanning electron microscope (FESEM, Carl Zeiss Ultra Plus) and transmission electron microscope (TEM, FEI JEOL JEM-2100). The energy dispersive X-ray spectroscopy (EDX, EX-250) was used to analyze the elemental distributions of composite which equipped with FESEM. The X-ray diffraction patterns were recorded by using a Rigaku TTRIII X-ray diffractometer to analyze the crystal phase of the samples. The UV-vis absorption spectra were recorded by using a spectrophotometer of Shimadzu UV-2450 (Japan). The photoluminescence spectra were measured by using a micro-PL system which excited by 325 nm femtosecond laser. The PEC behaviors were performed in electrochemical workstation (CS1001 1508123, Wuhan Corrtest Instruments Corp., Ltd., China) by using a standard three-electrode system under Xe lamp which equipped with 350 nm cut-off filter (CEL-HXUV300, Beijing China Education Aulight Co., Ltd., China). In addition, the continuous-wave lasers of 325 nm, 532 nm were employed as excitation sources for the photoresponse enhancement of Au NPs-ZnO NRs. In this system, the as-prepared photo-electrodes were served as working electrodes with counter electrode of Pt wire and reference electrode of Ag/AgCl. In addition, the active area of a working electrode is $\approx 1 \text{ cm}^2$. The light spot (2 cm in diameter) illuminates the whole modified electrode. Scheme 1 illustrates a stepwise fabrication of PEC biosensor. The modified photoanode was immersed in 0.01 mol L^{-1} PBS (pH = 7.0) solution during the detection. The change in photoanode current with different concentrations of GSH was used as a signal response.

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Scheme 1 Schematic illustration of PEC biosensor for GSH based on a hybrid structure of Au NPs-ZnO NRs

Results and Discussion

The dimension and morphology of ZnO NRs and Au NPs-ZnO NRs have been investigated here. A hexagonal prism of ZnO NRs is obtained from in-situ method with average diameter of ~150 nm and length of ~1.2 μ m as shown in Fig. 1(A). Also, the crystalline orientation has been investigated by using XRD spectrum to determine the crystal structure of ZnO NRs. From the spectrum, it can be observed that a strong peak of wurtzite ZnO NRs at 34.66°(JCPDS no. 800074) which corresponding to the plane value of (002) with two weak peaks of FTO substrate at 26.66° and 37.96°.6 To better understand the ZnO/Au interface, the TEM images were investigated and the gold nanoparticles distributed on ZnO uniformly are with a size of ~5 nm (Fig. 1(B)). The EDX spectrum is used to find the compositions of Au NPs-ZnO NRs on FTO as represented in Fig. 1(C). From the spectrum, it can be noticed that there are Zn, O and Au elements in Au NPs-ZnO NRs (the Sn, F comes from FTO substrate). The optical absorption spectra for ZnO NRs, Au NPs and Au NPs-ZnO NRs hybrid structure are illustrated in Fig. 1(D). A strong absorption at below 380 nm of ZnO (the blue line (a)) is observed which related to its band edge position. The Au NPs on the ZnO NRs/FTO and FTO were sputtered for 60 s at the same batch. The corresponding absorption spectrum of Au NPs/FTO has a strong absorption in the visible region. After introduction of Au NPs, the visible absorption is increased at about 520 nm (the red line (c)) which is owing to Au NPs. Furthermore, the utilization of sunlight for PEC sensing is enhanced based on the hybrid structure of ZnO NRs with Au NPs when compared to pristine ZnO.



Fig. 1 (A) SEM images and XRD pattern of ZnO NRs/FTO, (B) TEM images of Au NPs-ZnO NRs, (C) EDX spectrum of Au NPs-ZnO NRs, (D) UV-vis absorption spectra for (a) ZnO NRs, (b) Au NPs, (c) Au NPs-ZnO NRs hybrid structure.

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In order to evaluate the PEC activity of Au NPs-ZnO NRs hybrid structure, the photocurrent response has been measured. Initially, a correlation between photocurrent densities and bias voltage have been analyzed by the linear sweep voltammograms (LSVs) as shown in Fig. 2 (A). The LSV curves are measured at the bias voltage in the ranging between -0.4 V and 0.6 V. The photocurrent densities of both ZnO NRs and Au NPs-ZnO NRs are increased with respect to applied voltage under illumination. At the same time, the Au NPs-ZnO NRs possesses a weak photocurrent density under dark due to their electrochemical properties. Obviously, the Au NPs-ZnO NRs exhibits a higher photocurrent density when compared to ZnO NRs under the same bias voltage. At the bias voltage of -0.1 V, the photocurrent response of both ZnO NRs and Au NPs-ZnO NRs is close to zero current. Subsequently, the photocurrent density-time responses have been measured for ZnO NRs and Au NPs-ZnO NRs at 0 V and represented in Fig. 2 (B). From the figure, it can be identified that the average photocurrent densities of ZnO NRs/FTO (a) and Au NPs-ZnO NRs/FTO (b) are 30.49 μ A cm⁻² and 40.21 μ A cm⁻², respectively. The PEC performance is improved in as-fabricated Au NPs-ZnO NRs/FTO resulting from participation of gold particles. Moreover, the observed photocurrent curves from photocurrent density-time (I-T) are consistent with those obtained by using LSV (Fig. 2 (A)).



Fig. 2 (A) The linear sweep voltammogram curves of Au NPs-ZnO NRs/FTO (blue line) and ZnO NRs/FTO (red line) under simulated sunlight and Au NPs-ZnO NRs/FTO under dark (black line). (B) The photocurrent density-time characteristics at 0 V of (a) ZnO NRs/FTO and (b) Au NPs-ZnO NRs/FTO. (C) The PL spectra for (a) pristine ZnO NRs and (b) Au NPs-ZnO NRs hybrid structure (λ ex= 325 nm).

The Au NPs-ZnO NRs as a photoelectrode has an excellent electron collection efficiency which benefited from high electron mobility of ZnO NRs with better crystallization property and a reductive recombination of electrons and holes. Two main mechanisms have been considered here to explain the PEC behaviors of plasmonic metal/semiconductor photoelectrode: 1) resonant energy coupling and 2) SPR-mediated electron transfer from metal to semiconductor.

Above all, the photoluminescence (PL) spectra have been

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investigated under an excitation of 325 nm last. The ZnO demonstrates a UV emission at 390 nm with defect emission of Au visible region as shown in Fig. 2 (C, a). After the decoration of Au NPs, the UV emission is enhanced whereas the defect emission is decreased at the same time (Fig. 2 (C, b)). These phenomenons are obtained due to strong interfacial interaction between ZnO and Au. In particular, the Au NPs can absorb the visible light photon energies of ZnO which excites the electrons of Au to a higher energy state (hot electron). In addition, the electrons with higher energy favorably transfer to the conduction band of ZnO.³⁶



Fig. 3 (A) The photocurrent density-time characteristics of ZnO NRs/FTO excited by 325 nm only and 325 nm with 532 nm. (B) The photocurrent density-time characteristics of Au NPs-ZnO NRs hybrid structure under an excitation of 325 nm only, 532 nm only and 325 nm with 532 nm. (C) An interfacial field distribution of Au NPs-ZnO NRs in PEC system under 325 with 532 nm laser excitations and the color bar is a normalized electronic field intensity. (D) A schematic illustration for PEC biosensing mechanism of GSH detection at the surface of Au NPs-ZnO NRs hybrid structure-based photoanode

In order to verify the photoelectrochemical enhancement mechanism, the 325 nm and 532 nm continuous-wave (CW) monochromatic light sources have been employed to obtain a photocurrent response in the PEC system. The photocurrent of ZnO NRs has no change between 325 nm only and 325 nm-532 nm co-excitation at 0 V (vs. Ag/AgCl) as shown in **Fig.3** (**A**). It indicates the 532 nm light cannot stimulate the ZnO NRs. However, the photocurrent of Au NPs-ZnO NRs is enhanced than ZnO NRs under 325 nm excitation (**Fig.3** (**A**) and (**B**)). Subsequently, the photocurrent in Au NPs-ZnO NRs is further enhanced under 325 nm with 532 nm (there is almost no photocurrent of Au NPs-ZnO NRs under 532 nm only) (**Fig.3** (**B**)). The results can be assigned that the photoresponse enhancement is ascribed to SPR-mediated electron transfer of Au NPs. 22, 36

To further demonstrate the enhanced behaviors of Au NPs-ZnO as a plasmonic PEC system, a FDTD simulation has been employed. The FDTD simulation has been performed to calculate the electric field distributions of Au NPs-ZnO NRs. The electric field intensity of Au NPs-ZnO NRs is greatly gathered in the visible region based on the mechanism of SPR enhanced electromagnetic field. In electrolyte, the fabricated Au NPs-ZnO NRs play a significant role in light augmenting for photoresponse enhancement as displayed in Fig.3 (C). The performance confirms the enhancement of signal response in PEC sensor based on SPR effect. The electron-transfer mechanism of Au NPs-ZnO NRs as a hybrid structure during glutathione biosensing is schematically illustrated in Fig. 3 (D). The ZnO generated electronhole pairs under an irradiation of UV light. Then, the electrons are excited from valence band (VB) to the conduction band (CB) of ZnO ³⁷ and transported from CB of ZnO to the FTO. On the other hand, at the interface of ZnO and electrolyte, the same amount of holes is left

in the VB which participates in the oxidation of GSH into GSSG.³⁸ After the decoration of gold nanoparticles, the gold nanoparticles absorb the visible lights to generate hot electrons through SPR excitation for improving the PEC performances.^{29, 30} Moreover, the structure of Au/ZnO/FTO photoanode facilitates the photo-induced electrons flow to the photocathode which is beneficial for GSH oxidation.



Fig. 4 The photocurrent density-time characteristics of Au NPs-ZnO NRs/FTO at 0 V with absence of GSH (A), (C) and presence of 1 mM GSH (B), (D) with different pH values.

Furthermore, the pH value is a very important factor for photoelectrode because of its directly effect on photocurrent response values of PEC sensor through electron transfer.³⁹ Under different pH values, the photocurrent density-time curves (versus Ag/AgCl) of Au NPs-ZnO NRs/FTO with absence of GSH have been characterized at 0 V and displayed in **Fig.4 (A) and (C)**. From the figure, it can be observed that the signal response exhibited a continuous increment with pH in the ranging from 5.8 to 8.2. The increment in generation of OH• may enhance the photocurrent response ⁴⁰ which is similar to PEC water splitting ^{41,42}.

Under illumination,

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Au@ZnO + hv -	→ h+ -	+ e⁻	(1-1)
On the photoanode,			

$H_2O + 2 h^+ \longrightarrow$	$1/2 O_2 + 2H^+$	(1-2)
On the Pt electrode,		
	**	(1, 0)

 $2H^+ + 2 e^- \longrightarrow H_2$ (1-3)

When adding the GSH in the electrolyte, the photocurrent response increases until the pH value of 7.0. The response value shows a slight decrement with increasing in concentration of ionized $OH^{-}(Fig.4 (B) and (D))$.

Under illumination,

Au@ZnO +
$$h\nu \longrightarrow h^+ + e^-$$
 (2-1)
On photoanode,

 $2GSH + 2 h^{+} \longrightarrow GSSG + 2H^{+}$ (2-2)
On Pt electrode, $2H^{+} + 2 e^{-} \longrightarrow H_{2}$ (2-3)

For GSH oxidation reaction, a redox potential (ϕ) is varied with respect to the concentration of hydrogen ion (pH) and the following expression is known as Nernstian relation:

$$\varphi = \varphi^0 + \frac{RT}{nF} ln \frac{\left[\frac{c_{ox}}{c^0}\right]^a}{\left[\frac{c_{ox}}{c_0}\right]}$$
(3-1)

Here, R is a gas constant, T is a temperature, F is the Faraday constant, n is a number of electron transfer in half-reaction, c_{ox} and c_{re} are the concentrations of oxidation and reduction products, respectively as well as a and b are the stoichiometric numbers of reaction products under half-reaction. At 25°C with 1 atm, the

Nernstian relation is expressed as (3-2).

The half-reaction of GSH is also acquired and shown in equation (3-3).

$$\varphi = \varphi^{0} + \frac{0.05917 V}{2} lg \frac{\left[\frac{c_{GSSG}}{c_{0}}\right]\left[\frac{r_{H}}{c_{0}}\right]}{\left[\frac{c_{GSH}}{c_{0}}\right]}$$
(3-3)

At the constant concentrations of GSH and GSSG, φ is reduced whereas the pH increases at the same time. Hence, a stronger photocurrent response is acquired with higher pH under an irradiation of the same light source. In addition, the isoelectric point (IEP) of ZnO is 9.5 and IEP of GSH is 5.93.⁴³ At the electrolyte pH of 7.0, the GSH is adsorbed on the surface of ZnO due to electrostatic action.

Based on above described sensing mechanism, GSH has been catalysed by Au NPs-ZnO NRs and oxidized into GSSG by holes from photoexcited ZnO and Au. **Fig. 5 (A)** depicts a photoresponse of Au NPs-ZnO NRs based PEC biosensor with different GSH concentrations at an applied potential of 0 V under illumination. A linear range of 10 to 800 μ M (R² = 0.99197) is obtained in **Fig. 5 (B)** and the estimated limit of detection is 2.7 μ M (S/N=3). Finally, the analytical performances of the proposed electrode are compared with those of other similar nanostructures. According to that, the proposed sensor has a wider linear range when compared to other GSH sensors such as Cu₂O/ZnO heterojunction,⁴⁴ CDs@MS/SAM/Au electrode ⁴⁵ and TiO₂-Au hybrid electrodes.⁴⁶ Moreover, its detection limit is lower than that of CdS/RGO/ZnO nanowire array.⁴⁷

To evaluate a selectivity of PEC sensor in the detection of GSH, the I/I₀ against range of common chemical or biological interfering species such as dopamine (DA), glucose (Glu), cysteine (Cys), ascorbic acid (AA), urea (UA) and ethanol have been compared to GSH as well as various metal ions have been examined under same experimental conditions (the concentration was 100 μ M). The I/I₀ value is lower than that of 1% for all the tested interfering species as shown in Table S1. It can be indicated that these substances cannot interfere with GSH detection which is beneficial for GSH detection in blood samples. This achieved anti-interference ability is attributed to low applied bias potential (0 V) which greatly minimizes the interferences of other reductive molecules.16, 47 In addition, I-T measurement of the prepared PEC biosensor reveals a stable photocurrent response as shown in Fig. S2 (B). Also, the stability and reproducibility of the Au NPs-ZnO NRs/FTO electrodes are investigated as shown in Fig. S3. The Au NPs-ZnO NRs/FTO electrode can keep stable for more than 500 s illumination and the asprepared electrodes have good reproducibility with a relative standard deviation of less than 2.8%. These results can be suggested that the as-prepared Au NPs-ZnO NRs are extraordinary stable and demonstrated a feasibility of this hybrid in practical applications of biosensing.

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Fig. 5 (A) Photocurrent response of Au NPs-ZnO NRs based PEC biosensor with different concentrations of GSH (from left to right) at 0 V under illumination; (B) A linear calibration curve for photocurrent densities vs various concentrations of GSH.

Conclusion

In summary, an efficient of metal nanoparticles assistant PEC biosensor is constructed based on Au NPs-ZnO NRs. The interfacial charge transfer of plasmonic-enhanced biosensing is investigated in detail. The photocurrent enhancement mechanism is caused by resonant energy coupling and SPR-mediated electron transfer from metal to semiconductor, which also confirmed through the introduction of secondary 532 nm monochromatic irradiation with 325 nm. The PEC biosensor for GSH detection realizes good anti-interference performance and self-powered driving. In addition, an effect of pH value on photocurrent response has been comprehended for improving the accuracy in bioanalysis.

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Notes

The authors declare no competing financial interest.

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