Hemin/Au nanorods/self-doped TiO$_2$ nanowires as a novel photoelectrochemical bioanalysis platform$^\dagger$

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As a recently developed detection technique, photoelectrochemical (PEC) measurement has received extensive attention. However, owing to the lack of a comprehensive approach to engineer the photo-generated carriers, the performance is still limited. As an example, a significant use of PEC measurement might be in understanding the roles of glutathione in physiological and pathological processes. Here, we developed a new approach for engineering the photo-generated carriers with the aid of the synergic effect of self-doping, surface plasmon resonance, electrical field amplification effect, etc. Thus, a highly sensitive multicomponent PEC platform has been developed, in which Au nanorods are decorated on the surface of self-doped TiO$_2$ nanowires, followed by surface receptor functionalization with hemin for capturing glutathione. The synergic effect effectively increases generation, separation and transfer kinetics of the photo-generated carriers, which can be further increased by using a mixture of Au nanorods with different aspect ratios to tune the absorption wavelength to the entire UV-visible region. As a result, this system exhibits a broad linear range from 10 nM to 17.5 $\mu$M and low detection limit down to 8.6 nM for detecting glutathione, about 1–2 orders of magnitude lower than most existing PEC sensors.

Introduction

As a recently developed detection technique, photoelectrochemical (PEC) measurement has received extensive attention, since the PEC method efficiently decreases background noise and increases sensitivity by introducing large amounts of photo-generated carriers in the electrochemical detecting process, compared with other technologies.\textsuperscript{1,2} Previously, some photoactive inorganic semiconductors, such as ZnO,\textsuperscript{3} WO$_3$,\textsuperscript{4,5} and TiO$_2$,\textsuperscript{6,7} have been widely used to construct the optoelectronic platform for PEC devices. Among them, TiO$_2$ has been extensively investigated for various PEC applications owing to its low cost, strong optical absorption and high chemical stability.\textsuperscript{8} However, the performance of the PEC detectors is still limited, as a result of predominant absorption in the UV region,\textsuperscript{9} as well as sluggish separation of photo-generated electrons and holes.\textsuperscript{10,11} Thus, several approaches have been developed to improve the sensitivity of TiO$_2$-based PEC sensors via engineering photo-generated carriers. Self-doping is an effective surface defect engineering approach to improve the absorbance in the visible region, to reduce the number of recombination centers for photo-generated carriers and to enhance the carrier generation through electronic transition from the valence band to the inter-bands and/or from these inter-bands to the conduction band.\textsuperscript{12,13} As another approach, the integration of Au nanoparticles (NPs)/nanorods (NRs) into TiO$_2$ nanostructures can generate strong surface plasmon resonance for enhancing the electrochemical field effect amplification and light absorbance, as well as the carrier generation.\textsuperscript{14–16} Moreover, the formation of one-dimensional nanostructures, such as nanowires (NWs) and nanotubes (NTs), is also a normally used approach, which enables efficient photo-generated carrier separation and provides fast charge transport both through the nanometer-scale diameters and across the micrometer-scale axial lengths.\textsuperscript{17} Till now, PEC sensors have been used to detect H$_2$O$_2$,\textsuperscript{18} H$_2$S,\textsuperscript{19} adenosine,\textsuperscript{20} prostate-specific antigen,\textsuperscript{21} fetoprotein,\textsuperscript{22} and others.\textsuperscript{23,24}

Glutathione (GSH), as the most abundant antioxidant thiol in the intracellular environment, plays a key role in many pathological and physiological processes through interaction with free radicals or enzymes.\textsuperscript{25} Change in the level of GSH is usually related with diseases,\textsuperscript{26} such as cancer, leukocyte loss, neurodegenerative disease, liver damage, etc. Therefore, the monitoring of GSH level is of utmost importance. Several technologies have been proposed for the determination of GSH, including mass spectrometry,\textsuperscript{27} surface-enhanced Raman scattering,\textsuperscript{28} fluorescence spectroscopies,\textsuperscript{29} luminescence analysis,\textsuperscript{30} electrochemistry,\textsuperscript{31} photoelectrochemistry,\textsuperscript{32} and so on. However, as a result of the absence of a platform to comprehensively engineer photo-generated carriers, the per-
formance of PEC is still confined via the above-mentioned approaches, which hampers practical applications of this technology in detection of low concentration targets.

Herein, via a comprehensive photogenerated carrier engineering approach, a highly sensitive multicomponent PEC platform has been developed for the label-free and selective detection of GSH. In this platform, the self-doped (SD) TiO$_2$ NWs are modified with a mixture of Au NRs (m-Au NRs) with two different aspect ratios as the core sensing unit and hemin for recognition. The self-doped TiO$_2$ NWs (SD-TiO$_2$ NWs) deposited with Au NRs largely enhance generation, separation and transfer kinetics of photo-generated carriers owing to the synergic effect of self-doping, surface plasmon resonance, electrical field amplification effect, etc., which can be further enhanced by using a mixture of Au NRs with different aspect ratios to tune the absorption wavelength to the entire UV-visible region. Moreover, hemin increases the light absorption, realizes highly selective recognition of the GSH targets, and modulates the photo-generated carrier transfer between electrode and test solution. Via the above technologies, comprehensive engineering of the photo-generated carriers is realized in the PEC detection of GSH. As a result, the photocurrent is almost two times larger than that of the pristine TiO$_2$ NWs, and the PEC sensor consisting of hemin/m-Au NRs/SD-TiO$_2$ NWs exhibits a broad linear range from 10 nM to 17.5 μM and low detection limit down to 8.6 nM for detecting GSH, which is about 1–2 orders of magnitude lower than that of most existing PEC sensors, and is comparable to or better than other GSH detection technologies.

Experimental section

Materials and chemicals

The fluorine-doped tin oxide (FTO)-coated glass substrates (14 Ω per square) were supplied by Wuhan Ge-Ao Ltd, P. R. China. Tetrabutyl titanate (TBOT), chloroauric acid (HAuCl$_4$), hexadecyl trimethyl ammonium bromide (CTAB), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), dopamine (DA), glutathione (GSH), N-hydroxysuccinimide (NHS), 3,4-dihydroxyphenylacetic acid (DOPAC), glutathione disulfide (GSSG), cysteamine and hemin were purchased from Sigma-Aldrich. Ascorbic acid (AA), uric acid (UA), NaBH$_4$ and AgNO$_3$ were supplied by Aladdin. Glucose, sucrose and hydrochloric acid (37 wt%) were all obtained from Sinopharm Chemical Reagent Co., Ltd. Other reagents were of analytical grade. All the aqueous solutions were prepared using double distilled water (DDW) with a resistivity of 18.2 MΩ cm.

Apparatus and instrument

PEC measurement was performed with a CHI 660E electrochemical workstation (Chenhua, Shanghai). PEC characterization was carried out using a three-electrode cell under simulated sunlight from a Xe lamp coupled with an AM 1.5G filter (Solar-500, NBET), with an Ag/AgCl electrode (saturated with KCl) and a Pt foil electrode as the reference electrode and counter electrode, respectively. The supporting electrolyte was phosphate buffer solution (PBS, 0.1 M, pH 7.4) and the pH value was adjusted with a pH meter. The size of the active sample area was in the range 0.045–0.050 cm$^2$. All measurements were carried out at ambient temperature. The UV-visible absorption spectrum was measured with a Lambda 750 UV-visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on a PHI5300 instrument. X-ray diffraction (XRD) was carried out by an X'pert PRO diffractometer. Transmission electron microscopy (TEM) observations were carried out on a Tecnai G2 20 TWIN microscope. Field emission scanning electron microscopy (FESEM) images were obtained using an Ultra 55 scanning electron microscope.

Preparation of TiO$_2$ NWs

The arrays of TiO$_2$ NWs were grown on FTO-coated glass substrates by a hydrothermal method reported elsewhere. Prior to the synthesis, the FTO-coated glass plate was first thoroughly cleaned by sonication in soapy water, ethanol, and 1.0 M KOH solution, respectively. The FTO substrates were rinsed with DDW and then dried with a pure nitrogen stream. Afterward, the FTO-coated glass substrates were immersed in a mixed solution of 13.0 mL of hydrochloric acid (37 wt%), 15.0 mL of H$_2$O$_2$ and 0.25 mL of TBOT within a sealed Teflon reactor, and were heated at 150 °C for 12 h. After that, the prepared TiO$_2$ NWs samples were cleaned with DDW, dried in air, and were further annealed in air at 450 °C for 2 h to improve the crystallinity of the TiO$_2$ nanowires.

Fabrication of SD-TiO$_2$ NWs

The electrochemical self-doping process was carried out in a three-electrode system, with the TiO$_2$ NWs, an Ag/AgCl reference electrode and a Pt wire as working electrode, reference electrode, and counter electrode, respectively. The electrochemical reduction was conducted by setting a negative potential of −1.5 V vs. Ag/AgCl on the TiO$_2$ NWs in an electrolyte of 1.0 M Na$_2$SO$_4$ for 20 min. The electrode was denoted SD-TiO$_2$ NWs.

Fabrication of m-Au NRs/SD-TiO$_2$ NWs

Au NRs solution was fabricated using a previously reported seed-mediated growth method by a two-step process. For the synthesis of Au seeds, 9.75 mL of 0.1 M CTAB was totally added to 0.25 mL of 0.01 M HauCl$_4$ solution, and the solution mixture was kept stirring for 10 min. After that, 0.60 mL of ice-cold 0.01 M NaBH$_4$ solution was quickly added to the solution of CTAB and HauCl$_4$ forming Au seeds. The brown–yellow seed solution was stirred for 10 min and then aged for 1 h at 27 °C before use. For Au NRs synthesis, 5.0 mL of 0.01 M HAuCl$_4$ was first mixed with 95 mL of 0.1 M CTAB solution, and then 0.09 mL of 0.01 M AgNO$_3$ was added into the solution mixture to form the growth solution. The addition of AgNO$_3$ could control the aspect ratio (AR) of Au NRs. Next, 0.55 mL of 0.1 M ascorbic acid was added to the growth solution, and 0.12 mL of gold seed solution was added under vigorous stirring. When the solution became pink in color after 15 min, the stirring was slowed, and the solution was allowed to age at 27 °C for
increases the number of defects. After carefully depositing wires exhibit a rough surface, as a result of self-doping, which perpendicularly to the substrate. As seen in Fig. 1d, the nano-Fig. 1c further confirms that all nanowires are grown almost 1.0
on the surface of the m-Au NRs/SD-TiO2 NWs by amide for-
m-Au NRs (AR = 1.1) solution was obtained by adding 1.40 mL of 0.01 M AgNO3 to the growth solution by the above-mentioned procedure. To deposit m-Au NRs onto SD-TiO2 NWs, the SD-TiO2 NWs were soaked in the diluted mixed Au NRs solution (1:1 by volume) for 3 h, during which the m-Au NRs were adsorbed onto the SD-TiO2 NWs surface. The electrode was thoroughly washed by DDW and air dried. The obtained electrode was denoted as m-Au NRs/SD-TiO2 NWs.

Fabrication of hemin/m-Au NRs/SD-TiO2 NWs

The m-Au NRs/SD-TiO2 NWs were reacted with 1.0 M cysteamine for 5 h to allow conjugation to the Au NRs by the free –SH group, and then washed with DDW and air dried. The electrode was denoted as Cys/m-Au NRs/SD-TiO2 NWs. After that, the electrode was soaked in 2.0 mg mL−1 hemin solution for 12 h, adding EDC and NHS as the catalysts. After being washed twice with DDW, the electrode was dried at 70 °C and denoted as hemin/m-Au NRs/SD-TiO2 NWs.

Results and discussion

Characterization of the developed sensor

The design and fabrication procedures of the PEC sensor of hemin/m-Au NRs/SD-TiO2 NWs is schematically shown in Fig. 1a. Briefly, the TiO2 NW arrays on FTO-coated glass were first fabricated through the hydrothermal method to yield uniform TiO2 NWs, and further annealed to improve the crystallinity. Then, electrochemical reduction was conducted by applying a negative potential to induce self-doped defects in the TiO2 NWs. After electrochemical reduction, m-Au NRs with different aspect ratio were decorated on the TiO2 NWs surface to form m-Au NRs/SD-TiO2 NWs. Finally, hemin was covalently attached on the surface of m-Au NRs/SD-TiO2 NWs through amide linkage between –COOH groups and –NH2 groups. Thus, a PEC sensor for GSH was established and GSH could be recognized by hemin and further oxidized by photo-generated holes.

A FESEM image of TiO2 NWs arrays prepared on the FTO-coated glass substrate is shown in Fig. 1b. The whole FTO substrate is covered by a white and homogeneous film, which consists of dense and vertically aligned nanowire arrays. As-prepared TiO2 NWs are highly uniform with a smooth surface and a rectangular cross section. The average diameters of nanowires are around 100–200 nm with lengths in the range 1.0–2.0 μm. The side-view image of the nanowire arrays in Fig. 1c further confirms that all nanowires are grown almost perpendicularly to the substrate. As seen in Fig. 1d, the nanowires exhibit a rough surface, as a result of self-doping, which increases the number of defects. After carefully depositing m-Au NRs (Fig. S1, ESI†), the FESEM image shows that the surface of the nanowires is uniformly covered with a layer of Au NRs (Fig. 1e); thus hemin molecules can be immobilized on the surface of the m-Au NRs/SD-TiO2 NWs by amide for-

To determine the crystal structure of TiO2 NWs, the crystalline orientation was investigated by X-ray diffraction (XRD) spectra before and after electrochemical reduction. Besides the peaks from the FTO substrate, two typical diffraction peaks centered at 35.8° and 62.5° are observed in Fig. 2a from the pristine TiO2 NWs and SD-TiO2 NWs arrays, corresponding to the (101) (002) facets, respectively. The sharp (002) peak is dominant over the (101) diffraction peak, which is in good accord with the growth axis of the TiO2 NWs. The peak intensity decreases after electrochemical reduction, which could be attributed to the increase of defect density in TiO2 NWs structure. The diffraction peaks from the SD-TiO2 NWs and TiO2 NWs samples are consistent with the characteristic peaks of tetragonal rutile TiO2 (JCPDS no. 21-1276). The results further confirm that the SD-TiO2 NWs are rutile TiO2, the same as the pristine TiO2 NWs.

The XPS technique was employed to track the modification processes of the electrodes. In the XPS spectrum of Ti 2p3/2 (Fig. 2b), the Ti3+ peak is shifted a little to a lower binding energy after self-doping owing to electron transfer to the Ti3+ centers.38 After loading of Au NRs, a small positive shift of the Ti 2p1/2 peak exists, which should be attributed to the electron transfer between Au and the oxygen vacancies of TiO2 NWs. Au 4f7/2 and Au 4f5/2 peaks located at about 83.6 eV and 87.2 eV
covered with a layer of TiO2 NWs (Fig. 2c). Meanwhile, a single peak located at 164.1 eV for S 2p (curve iv in Fig. 2d) appears after immobilizing cysteamine molecules on the Au NRs by means of Au–S bonding through the thiol group, and the TiO2 NWs surface is coated with a layer of −NH2 groups. After that, the m-Au NRs/SD-TiO2 NWs electrode is immersed in a solution of hemin and Fe 2p1/2 of (i) TiO2 NWs, (ii) SD-TiO2 NWs, (iii) m-Au NRs/SD-TiO2 NWs, (iv) Cys/m-Au NRs/SD-TiO2 NWs and (v) hemin/m-Au NRs/SD-TiO2 NWs. The dark current of hemin/m-Au NRs/SD-TiO2 NWs (pink curve) was plotted for comparison.

**Photoelectrochemical properties of hemin/m-Au NRs/SD-TiO2 NWs**

To assess its potential as a PEC sensor, a set of linear sweep voltammograms of the different electrodes were recorded, as shown in Fig. 2f. Upon illumination, the bare TiO2 NWs, SD-TiO2 NWs and m-Au NRs/SD-TiO2 NWs present pronounced photoresponse, and the SD-TiO2 NWs electrode show a weak enhancement of the photocurrent compared with bare TiO2 NWs at 0.2 V vs. Ag/AgCl, since the self-doping process creates surface defects to accelerate the generation and transfer of photo-generated carriers. In comparison, m-Au NRs/SD-TiO2 NWs exhibits much larger photocurrent density, mainly caused by the electrical field amplification effect and hot electron excitation by surface plasmon resonance, in the entire UV-visible region from 300 to 800 nm (Fig. S2, ESI†). The photoactivity of m-Au NRs/SD-TiO2 NWs is greatly enhanced in the entire UV-visible region by decorating with different aspect ratio of Au NRs nanostructures, implying the crucial role of Au NRs in photocurrent generation under white-light illumination through the surface plasmon resonance enhancement effect. After hemin is immobilized on the m-Au NRs/SD-TiO2 NWs sample, hemin/m-Au NRs/SD-TiO2 NWs achieves the highest point photocurrent density with an ∼100% increase compared with the bare TiO2 NWs at 0.2 V vs. Ag/AgCl. Therefore, owing to the synergic effect of electrochemical self-doping and surface plasmon resonance as well as the enhanced light absorption of hemin (Fig. S3, ESI†), the hemin/m-Au NRs/SD-TiO2 NWs electrodes show higher performance in detection of GSH than existing PEC electrodes.

**Analytical performance for GSH assay**

For the determination of GSH, the sensitivity and selectivity of the GSH sensor strongly depended on the applied potentials (Fig. S4, ESI†). On one hand, the sensitivity of the present sensor for GSH increased with the positive shift of the applied potentials, namely, the more positive the applied potential, the higher the sensitivity. On the other hand, as the potential shifted positively, the interference from AA became higher. At more positive potential, e.g. 0.3 V vs. Ag/AgCl, 0.1 μM AA produced 15.3% of the current obtained with 0.1 μM GSH; however, at 0.2 V vs. Ag/AgCl, 0.1 μM UA and 0.1 μM AA produced 2.7% and 3.6%, respectively, of the currents obtained with 0.1 μM GSH. Therefore, considering both the selectivity and sensitivity of the present sensor, 0.2 V vs. Ag/AgCl was selected as the optimized working potential. Fig. 3a displays a typical amperometric response of the hemin/m-Au NRs/SD-TiO2 NWs electrode toward successive additions of 0.1 μM GSH in 0.1 M PBS (pH 7.4) at the applied potential of 0.2 V vs. Ag/AgCl. The photocurrent quickly increased and rapidly reached a well-defined steady-state with obvious response to the successive additions of GSH. Under the same conditions, the hemin/m-Au NRs/SD-TiO2 NWs sensor showed an observable amperometric response after the addition of 10 nM GSH (Fig. S5, ESI†). The response time of the PEC sensor for GSH was observed to be less than 10 s. For comparison, the pristine...
Table 1. Analytical performance of the present hemin/m-Au NRs/SD-TiO2 NWs sensor for GSH, compared with sensors previously reported in the literature.

<table>
<thead>
<tr>
<th>Method</th>
<th>Nanocomposite</th>
<th>Linear range (µM)</th>
<th>Detection limit (nM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorimetry</td>
<td>AuNC-polymer</td>
<td>0–6</td>
<td>29</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>CBT-Cys(SEt)</td>
<td>0–87</td>
<td>1000</td>
<td>41</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>PEI-capped AgNCs</td>
<td>0.5–6</td>
<td>380</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Lysozyme VI-Au8</td>
<td>0.06–10</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>HPLC</td>
<td>OMC electrode</td>
<td>3–130</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Cu(OH)2-CILE</td>
<td>1–50</td>
<td>30</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>NiONPs/GCE</td>
<td>12.5–2300</td>
<td>200</td>
<td>47</td>
</tr>
<tr>
<td>Photoelectrochemistry</td>
<td>Porous TiO2–Pt</td>
<td>0.5–40</td>
<td>100</td>
<td>48</td>
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<td>rGO/ZnO NRs array</td>
<td>10–200</td>
<td>2170</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>GR–CdS</td>
<td>10–1500</td>
<td>3000</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>FeTPPS–TiO2 NPs</td>
<td>50–2400</td>
<td>30 000</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Hemin/m-Au NRs/SD-TiO2 NWs</td>
<td>0.01–17.6</td>
<td>8.6</td>
<td>This work</td>
</tr>
</tbody>
</table>

TiO2 NW electrodes did not show signals in response to the additions of GSH (Fig. S6, ESI†). The calibration plot of steady-state currents against concentrations of GSH is shown in Fig. 3b. The dynamic detection linear range is from 10 nM to 17.5 µM and the detection limit is 8.6 nM (S/N = 3.0). Compared with the results reported previously, as shown in Table 1,33,34,39 the performance of the sensor is comparable to or better than that of most of the other GSH detection methods.

High sensitivity of the hemin/m-Au NRs/SD-TiO2 NWs multicomponent PEC platform should be attributed to the optimized generation, separation and transfer process of photo-generated carriers with the aid of the synergic effect of many factors. The PEC sensing process of the hemin/m-Au NRs/SD-TiO2 NWs for the detection of GSH is demonstrated in Fig. 4. When the hemin/m-Au NRs/SD-TiO2 NWs is exposed to white-light illumination, electrons transfer from the excited state of hemin into the Au NRs nanostructure, which is thermodynamically favorable. The photoexcitations of the Au NPs will result in the collective oscillations of hot electrons and hence plasmonic charge separation at the Au NPs surface.14–16 When in intimate contact with TiO2 NWs, the plasmonic electrons separated from the Au NPs are quickly injected into the conduction band of the SD-TiO2 NWs, leaving the oxidized Au NPs to be restored by electrons from hemin. In this process, m-Au NRs with two different components realizes surface plasmonic resonance across the entire UV-visible region, which greatly enhances the generation, separation and transfer process of photo-generated carriers. Moreover, owing to the self-doping effect12,13 and the one-dimensional morphology17 of TiO2 NWs, the generation, separation and transfer process of photo-generated carriers are further accelerated. For the reduced TiO2 NWs, a new state is formed within the band gap, located at ≈0.7 eV below the ~0.29 eV of the conduction band of TiO2 NPs corresponding to ~0.1 V. The oxidation potential of the excited state of hemin is ~0.82 V, which is lower than the potential of the new energy level of the reduced TiO2 NWs. Therefore, electrons can easily transfer from the excited state of hemin to the new energy level of TiO2 NWs to generate electron–hole pairs under irradiation. When hemin/m-Au NRs/SD-TiO2 NWs is exposed to GSH in solution, GSH plays the role of an electron donor and sacrificial reagent. It loses electrons and transfers electrons to the holes of the excited state of hemin under irradiation. These photoexcitation electrons subsequently transfer into the FTO electrode, which leads to an increase in the photocurrent. Meanwhile, GSH is further oxidized to glutathione disulfide (GSSG) by formation of thiol radicals (GS−).39

Moreover, extremely high catalytic activity of the PEC materials usually leads to poor recognition of functional biomolecules; thus the selectivity of PEC sensors is usually perturbed by the complex environment in real biological systems.
If some specific recognition units are integrated into the PEC sensors to modulate the photo-generated carrier transfer between electrode and test solution, a selective and sensitive strategy for the determination of analyte can be proposed. As a biomimetic enzyme, hemin not only exhibits high absorption coefficient, ultrafast electron injection and good chemical stability, but also possesses the ability to accurately and rapidly recognize the targets.\textsuperscript{49} TiO\textsubscript{2}-based PEC sensors functionalized with hemin can efficiently increase the amount of light absorbed and improve the selectivity of the sensors for GSH with rapid response and good reproducibility.\textsuperscript{32,41} The selectivity of the hemin/m-Au NRs/SD-TiO\textsubscript{2} NWs sensor was demonstrated by measuring the response to adding different interfering substances, such as metal ions, as well as common chemical/biological samples. These show much smaller or negligible signals compared with GSH (Fig. 3c and d). To measure its stability, the hemin/m-Au NRs/SD-TiO\textsubscript{2} sensor was investigated by monitoring the photocurrent response every other day. The results show that more than 90.3\% of the initial photocurrent response was still maintained after 16 days storage (Fig. S7, ESI†). The superior sensing performance and long-term lifetime stability of the hemin/m-Au NRs/SD-TiO\textsubscript{2} NWs sensor should be attributed to the stable structure and excellent biocompatibility of TiO\textsubscript{2} NWs and Au NRs, as well as the strong chemical interaction between hemin and Au NRs and between Au NRs and SD-TiO\textsubscript{2} NWs.

Conclusions

In summary, we have demonstrated a new type of PEC detection platform, in which m-Au NRs with different aspect ratios are decorated on the self-doped TiO\textsubscript{2} NWs surface, followed by surface receptor functionalization for capturing GSH. The synergic effect of the self-doped centers and surface plasmonic resonance from the m-Au NRs increases generation, separation and transfer kinetics of the photo-generated carriers, which can be further increased by using a mixture of Au NRs with different aspect ratios to tune the absorption wavelength across the entire UV-visible region. Hemin enhances the photo-absorption and selectively recognizes the GSH targets. As a result, the hemin/m-Au NRs/SD-TiO\textsubscript{2} NWs electrode offers enhanced photocurrent almost two times higher than that of pristine TiO\textsubscript{2} NWs. This work provides a new approach to comprehensively engineer the generation, separation and transfer process of photo-generated carriers in a PEC sensing platform, which combines advantages from self-doping, hot electron generation due to surface plasmon resonance and the specificity of the receptor. Moreover, this new PEC platform would also be valuable for developing other high performance photo-energy-driven electrochemical devices.

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Notes and references