

Facile synthesis of Au–SnO₂ hybrid nanospheres with enhanced photoelectrochemical biosensing performance

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Au–SnO₂ hybrid nanospheres (HNSs) were synthesized by a facile, one-step method, which was achieved via a redox reaction between the reductive stannous (II) ions and oxidative auric (III) ions and dissolved O₂, and then *in situ* formation of Au nanoparticles (NPs) and SnO₂ NPs. The results indicated that the Au NPs are able to trap electrons, improve the electron–hole pairs' life, and enhance the visible light absorption intensity that are all beneficial for enhancement of the visible light photoelectrochemical performance. Cysteine was chosen as a model molecule in photoelectrochemical biosensing experiments. The biosensor displayed excellent analytical performance for detection of cysteine with an extremely broad linear range (from 0.4 μ M to 12 mM), and a low detection limit (0.1 μ M). Therefore, the Au–SnO₂ HNSs will be promising candidates for photocatalysts, photoelectrochemical biosensors, and other photoelectric devices.

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Introduction

To incorporate new functionalities and improve the physical and chemical properties, various nanoscale oxide-based materials are combined with noble metal nanoparticles (NPs) to form hybrid noble metal-oxide nanostructures, which combine different properties into a single structure. The synergistic properties exceed the functionality of the individual components and bring about new functionalities for a wide range of promising applications, including labelling/sensing,^{1,2} solar energy conversion,³ catalysis,⁴ lithium ion electrode materials,⁵ field emission emitters,⁶ electronic devices,⁷ *etc.* To date, a number of M-oxide nanostructures have been designed and prepared, such as M–SiO₂,⁸ M–SnO₂,⁹ M–TiO₂,¹⁰ M–CeO₂,¹¹ and M–ZnO,¹² (M = Ag, Au, Pd, and Pt).

As one of the most extensively studied hybrid nanostructures, the Au–SnO₂ system has attracted great attention because of its highly enhanced optical, electronic and catalytic performance. First of all, SnO₂ is one of the post-transition metal oxides and n-type wide-band gap ($E_g = 3.6$ eV) semiconductors^{13–15} with high thermal and chemical stability,¹⁶ low toxicity, low cost, and high electron mobility.¹⁷ Specifically, the

electron mobility of SnO₂ is ~ 250 cm² V^{−1} s^{−1},¹⁸ which is remarkably larger than <1 cm² V^{−1} s^{−1} of conventional TiO₂ photoanode materials.¹⁹ Besides, SnO₂ has low electrical resistance and high optical transparency in the visible range, which make it a promising anode material for optoelectronic devices.²⁰ Furthermore, the doped Au NPs could significantly enhance the photoelectric properties of SnO₂, which was likely attributed to the following reasons: (1) when Au NPs are doped into SnO₂, a Schottky barrier could be formed in the interfacial region of Au and SnO₂.^{21,22} The presence of the Schottky barrier is favourable for the separation of electrons and holes and prevents the recombination of electron–hole pairs. The internal electric field existing in hetero-junctions between SnO₂ and Au NPs could induce faster carrier migration, thus enhancing the photoelectrochemical performance. (2) The doped Au NPs could increase the visible light absorption due to the strong surface plasmon resonance (SPR) of Au NPs.²³ (3) The presence of Au NPs could improve the conductivity of the electrode due to the good carrier transport property of Au NPs. By far, several methods have been reported to synthesize Au–SnO₂ nanocomposites such as the microwave hydrothermal method,²⁴ deposition–precipitation,²⁵ and intermetallic-based dry oxidation method.²⁶ However, the synthesis procedures mentioned above either needed harsh reaction conditions or complex operations, and the irregular morphology and agglomerate of the samples limited their applications. Therefore, it is urgent to develop a simple method for the fabrication of Au–SnO₂ hybrids with well-designed and controlled nanostructures.

In the present work, uniform Au–SnO₂ hybrid nanospheres (HNSs) were synthesized *via* a facile, one-step method. The

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synthesis of Au–SnO₂ HNSs was achieved *via* a redox reaction between the reductive stannous (II) ions and oxidative auric (III) ions and dissolved O₂, and then *in situ* formation of Au NPs and SnO₂ NPs. The results indicated that the as-prepared Au–SnO₂ HNSs were composed of tens of SnO₂ NPs (~3 nm) and Au NPs (5–7 nm). The surrounded SnO₂ NPs acted as physical barriers to protect the Au NPs from aggregation. The Au NPs were embedded into the SnO₂ HNSs, with a nanostructure similar to the plum-pudding model proposed by Thomson.²⁷ The photoelectrochemical biosensing performance of the Au–SnO₂ HNSs was explored through monitoring their photocurrent response to cysteine. The result indicated that the photoelectrochemical biosensor showed a considerable wide linear range to cysteine, from 0.4 μM to 12 mM. The detection limit of this biosensor was about 0.1 μM at a signal-to-noise ratio of 3. Thus it could be seen that the Au–SnO₂ HNSs presented promising applications in the fields of photoelectrochemical biosensors and photoelectric devices.

Experimental section

Chemicals

SnCl₂·2H₂O, NaOH, NaH₂PO₄, Na₂HPO₄, Cd(NO₃)₂·6H₂O, Na₂S·9H₂O and polyvinylpyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co. Ltd., HAuCl₄·4H₂O was purchased from Shanghai Chemical Reagent Co. Ltd. Ethanol was purchased from Aladdin Reagent Co. Ltd. All reagents were of analytical purity and were used without further purification. All aqueous solutions were prepared with ultrapure water (18 MΩ cm⁻¹), which was obtained from a Milli-Q water purification system.

Synthesis of Au–SnO₂ HNSs

PVP (0.3 g) and SnCl₂·2H₂O (0.5 mmol) were dissolved into 40 mL absolute ethanol under stirring at room temperature under the N₂ protection. Then 0.5 mL aqueous solution of HAuCl₄ (24.3 mM) was added into the above solution. After 2 min, 3.5 mL NaOH aqueous solution (1.0 M) was slowly added to the above mixture solution, followed by addition of 16.5 mL of H₂O. The solution was maintained at 60 °C with stirring for 3 h. The final purple-red precipitate was collected by centrifugation, and washed with ethanol and water several times, then dried at 60 °C for 12 h.

Synthesis of SnO₂ NSs

Pristine SnO₂ NSs were prepared using the same method without adding HAuCl₄ solution.

Fabrication of Au–SnO₂/CdS modified ITO electrodes (ITO/Au–SnO₂/CdS)

Indium tin oxide (ITO) slices (sheet resistance 20 Ω per square) were sonicated in isopropanol, ethanol, and water for 15 min, respectively. Then, 20 μL of the Au–SnO₂ HNS dispersion solution (5.0 mg mL⁻¹) was drop-cast onto a piece of ITO slice with an area of 0.25 cm². After drying in air, the film was calcined at 400 °C for 30 min to remove any organic compound and

improve the contact between the HNSs and the substrate. Pristine SnO₂ films were also made using the same method. The Au–SnO₂ HNS coated ITO is referred as an ITO/Au–SnO₂ electrode. The CdS NPs were deposited on the Au–SnO₂ HNS surface through a successive ionic layer adsorption and reaction technique.²⁸ In brief, the ITO/Au–SnO₂ electrode was immersed alternately in Cd²⁺ and S²⁻ solution in an aqueous solution of 0.08 M [Cd(NH₃)₄]²⁺ and 0.1 M Na₂S at room temperature for 30 s, respectively. The ITO/Au–SnO₂/CdS electrode with 6 layers was fabricated, and then rinsed thoroughly with water and air dried.

Characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Hitachi HT7700). High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL-2100 high resolution transmission electron microscope with an accelerating voltage of 200 kV. Energy dispersive X-ray (EDX) analysis was performed with an Oxford INCA detector installed on the HRTEM. The ultraviolet-visible (UV-vis) absorption spectrum was measured using a Shimadzu UV-3600 UV/vis spectrophotometer. X-ray diffractometry (XRD) analysis was carried out using a Rigaku XRD with a Cu Kα (λ = 0.15418 nm) source with a Ni filter. Electrochemical impedance spectroscopy (EIS) was carried out on an Autolab potentiostat/galvanostat (PGSTAT30, Utrecht, The Netherlands) in 0.1 M KCl containing a redox probe of 10.0 mM K₃[Fe(CN)₆]-K₄[Fe(CN)₆] (1 : 1) mixture at an open-circuit potential of 216 mV with an applied voltage of 5 mV over a frequency range of 0.1 Hz to 100 kHz. Dynamic light scattering (DLS) measurements were performed using a Brookhaven instrument (90 Plus/BI-MAS) equipped with a 15 mW solid state laser with an output at a scattering angle of 90°.

Photoelectrochemical measurements and L-cysteine sensing

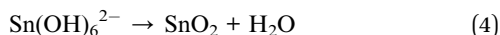
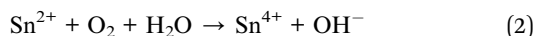
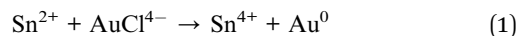
Photoelectrochemical measurements were performed with a homemade photoelectrochemical system. A 500 W Xe lamp equipped with a monochromator was used as the irradiation source. Photocurrent was measured on a CHI 660D electrochemical workstation. ITO/Au–SnO₂/CdS, ITO/SnO₂/CdS, ITO/Au–SnO₂, and ITO/SnO₂ electrodes were employed as the working electrode. A Pt wire electrode and a Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. Phosphate buffer solution (PBS, pH 7.4, 0.1 M) containing 10 mM cysteine was used as the electrolyte for photocurrent measurements. The solution was deaerated with nitrogen for 15 min before experiments, and then a N₂ atmosphere was kept in the entire experimental process.

Results and discussion

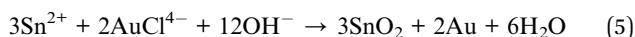
Reaction mechanism of Au–SnO₂ HNSs

According to the standard electrode potential value, Sn²⁺ (Sn⁴⁺ + 2e⁻ → Sn²⁺, E⁰ = +0.154 V), which is much lower than that of AuCl₄⁻ (AuCl₄⁻ + 3e⁻ → Au⁰, E⁰ = +1.50 V). As a result, the auric

(iii) ions were reduced by stannous (ii) ions and the stannous (ii) ions were oxidized by auric (iii) ions and dissolved O_2 .^{29,30} After adding NaOH solution, the stannic (IV) ions were then *in situ* hydrolyzed to $Sn(OH)_6^{2-}$, and easily dehydrated to SnO_2 , and the formed Au NPs were surrounded by the SnO_2 NPs. The possible reaction equation of Au- SnO_2 HNSs can be considered as follows:



From (1), (2), and (3), we can obtained the equation:



Characterization of Au- SnO_2 HNSs

The morphology of the as-prepared Au- SnO_2 HNSs was investigated by SEM and TEM. From the images (Fig. 1A & C) of the panoramic morphology, the as-obtained sample showed a uniform sphere structure with the average diameter of 150 nm. The particle size distribution also confirmed that the major diameter was 160 nm (inset in Fig. 1A). The Au NPs were highly dispersed in the SnO_2 HNSs. This was believed to favour the photogenerated electron transfer between the gold and SnO_2 .³¹ Moreover, the enlarged SEM and TEM images shown in Fig. 1B & D revealed that the Au NPs with the diameter of 5–8 nm decorated in the SnO_2 NSs, which was quite similar to the structure of the plum-pudding model proposed by Thomson.²⁷ The HRTEM image indicated that the SnO_2 nanospheres were polycrystalline. The clear preferential lattice orientation in Fig. 1E confirmed that the Au- SnO_2 HNSs were composed of several small nanograins. The clearly marked interplanar spacing d_1 was 0.336 nm, which corresponded to the (110) lattice planes of cassiterite SnO_2 . The interplanar distance d_2 of 0.23 nm could be attributed to the (111) plane of Au. Furthermore, detailed analysis of the HRTEM results confirmed that the Au- SnO_2 hybrid HNSs were assembled by tens of SnO_2 primary NPs with a dimension of ~ 3 nm and Au nanoparticles with a dimension of ~ 5 nm. In the HNSs, SnO_2 played the key role of physically separating the Au NPs from each other. The steric hindrance effect of the SnO_2 NPs benefit to keeping the original shape, size, surface state, and activity of Au NPs. In addition, the doped Au NPs greatly enhanced the photoelectrochemical response ability of SnO_2 , because the Au NPs acted as a reservoir of photoelectrons, improving the interfacial charge-transfer and retarding the recombination of photoexcited electron-holes.³² The energy dispersive spectrum in Fig. 1F confirmed the presence of Au element and the content percent was about 2.0%. The elemental ratio of Sn to O was 1 : 2, which also confirmed the composite of Au- SnO_2 .

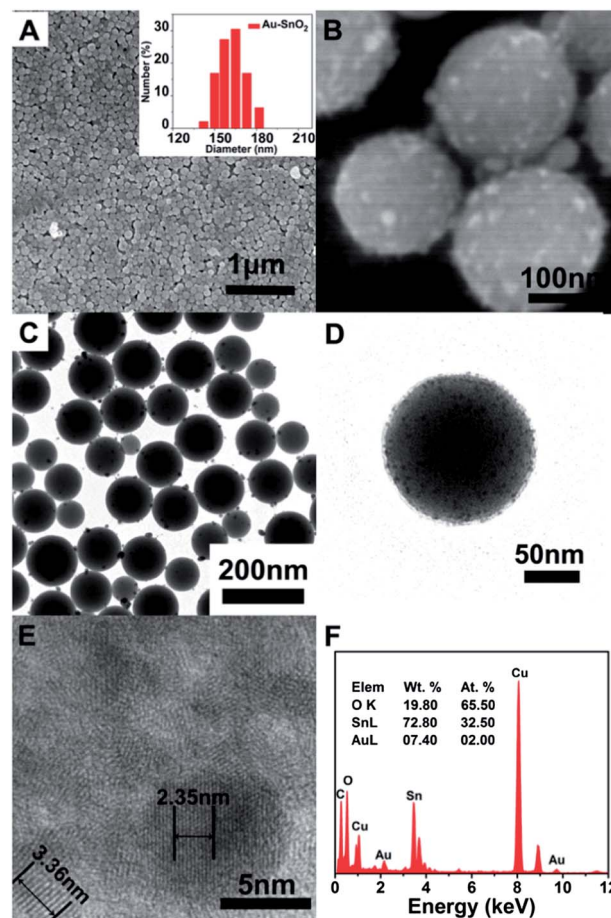


Fig. 1 (A and B) SEM images of as-prepared Au- SnO_2 HNSs and DLS of particle diameters (inset of image A). (C and D) TEM images of Au- SnO_2 HNSs. (E) HRTEM images of Au- SnO_2 HNSs. (F) The EDS spectra of Au- SnO_2 HNSs.

The crystal structure of the Au- SnO_2 HNSs was further characterized by X-ray diffractometry (XRD). As shown in pattern a (Fig. 2), all the peaks could be assigned to the tetragonal rutile structure of SnO_2 with the lattice parameters of $a = 0.4736$ and $c = 0.3186$, which agrees with the standard data (JCPDS # 41-1445). In pattern b, for Au- SnO_2 HNSs, except for the four strong SnO_2 peaks (110), (101), (211) and (112), the

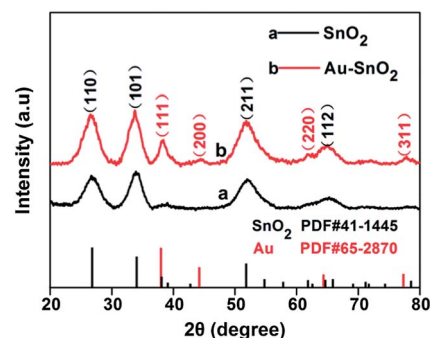


Fig. 2 XRD patterns of Au- SnO_2 HNSs and SnO_2 NSs.

presence of Au (111), (200) and (311) peaks could be well assigned to face-centered cubic Au (JCPDS # 65-2870).

Fig. 3 shows the UV-vis absorption spectra of SnO_2 , Au- SnO_2 , SnO_2/CdS and Au- SnO_2/CdS . Compared with the absorption spectra of SnO_2 and SnO_2/CdS films (curves a & c, Fig. 3), Au- SnO_2 and Au- SnO_2/CdS films (curves b & d, Fig. 3) offered the obvious absorption peaks around 540 nm, which matched very well with the characteristic SPR spectra of Au NPs. Meanwhile, as a sensitizer, the decorated CdS NPs significantly enhanced the whole absorption in visible light. It was concluded that both Au NPs and CdS NPs enhanced the visible absorption intensity of SnO_2 films.

The introduction of Au NPs could improve the conductivity of the electrode due to the good carrier transport property of Au NPs. To gain further insight into the electron-transport properties of the Au- SnO_2 HNSs, electrochemical impedance spectroscopy (EIS) of different electrodes was performed using $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ as a redox probe (Fig. 4). The diameter of the semicircle was equal to the electron-transfer resistance (R_{et}). It can be seen that after the SnO_2 and CdS were coated onto ITO, R_{et} increased (curves b & d, Fig. 4), indicating that the formed compact SnO_2 or CdS NPs hindered the access of the redox probe ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) to the electrode surface. However, in the case of ITO/Au- SnO_2 and ITO/Au- SnO_2/CdS

(curves c & e, Fig. 4), the embedding of Au NPs promoted the transfer of the redox probe to the electrode, and thus led to a decrease of the R_{et} value, which was smaller than that of the electrode without Au NPs (curves b and d, Fig. 4).

Photoelectrochemical measurements

The photoelectrochemical performance of the Au- SnO_2 HNSs was studied using CdS QDs as the photosensitizer. The structure of the Au- SnO_2 HNS photoanode is shown in Fig. 5A, the Au NPs were embedded in the SnO_2 NS, which could not only arouse the SPR effect, but also enhance the conductivity of SnO_2 NS. In addition, the introduction of narrow band gap CdS QDs as the photosensitizer was favourable for the generation and separation of electron-hole pairs under visible-light.³³ As shown in Fig. 5B, upon irradiation with visible light (>420 nm), the ITO/ SnO_2 electrode showed a photocurrent of 27 nA at an applied potential of 0 V (curve a), whereas the ITO/Au- SnO_2 electrode showed a photocurrent of 84 nA (curve b), indicating the obvious enhancement of the photo-current conversion efficiency of SnO_2 by the addition of Au NPs. After being sensitized with CdS NPs, the photocurrents of the ITO/ SnO_2 electrode and the ITO/Au- SnO_2 electrode were both significantly enhanced, they reached to 13.6 μA and 44.3 μA , respectively (curves c and d). It should be noted that the photocurrent for an electrode containing Au NPs was about three times higher than that for the electrode without Au NPs. In this case, the incorporation of the Au NPs mainly acted as a sink for photo-induced electrons and decreased the recombination of photo-generated electrons to enhance the photocurrent of the composite film. The enhanced photocurrent of Au- SnO_2 HNSs makes them to be a promising candidate for the fabrication of the photoelectrochemical biosensor.

Photoelectrochemical sensing of cysteine

Cysteine, as an essential sulphur-containing amino acid, plays a critical role in many biological processes. Diseases like slow growth, leucocyte loss, and liver, edema, muscle, and skin lesions were observed to be accompanied by a deficiency of cysteine.^{34–36} According to the literature, the photoelectrochemical method was a rapid and sensitive technique for testing cysteine.^{37–39} Therefore, the as-prepared Au- SnO_2 HNSs were used to fabricate a cysteine biosensor by the photoelectrochemical method. The mechanism for the measurement of cysteine is displayed in Fig. 6A. Cysteine, as an electron donor, scavenged the hole of the excited CdS under visible-light irradiation. The photoexcitation electrons of CdS could transfer from its valence band (VB, -6.38 eV) to its conduction band (CB, -3.98 eV), then injected to the CB of SnO_2 (-4.50 eV). Au NPs served as an electron relay to induce the electron transfer from SnO_2 to the ITO electrode, thus resulting in an efficient charge transport and an enhanced photocurrent signal. In this process, cysteine served as the electron donor (hole scavenger) and the sacrificial reagent could transfer electrons to the holes located on the excited state of CdS, avoiding electron-hole recombination effectively, leading to a sharp increase of the photocurrent. Au NPs acted as not only electron traps for facilitating charge

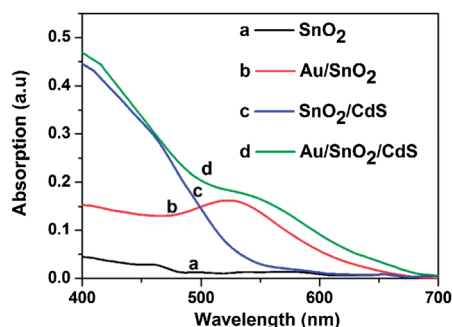


Fig. 3 UV-vis absorption spectra of the different nanostructure modified-ITO electrodes: (a) SnO_2 NSs, (b) Au- SnO_2 HNSs, (c) SnO_2/CdS and (d) Au- SnO_2/CdS .

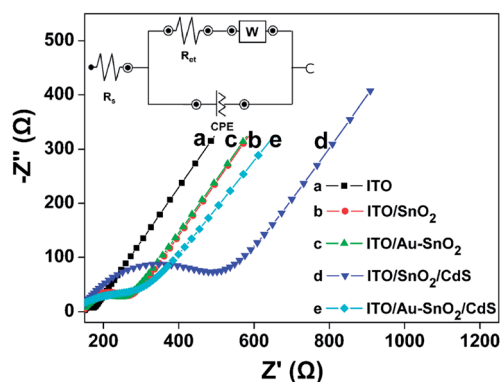


Fig. 4 Electrochemical impedance Nyquist plot and equivalent circuit (inset) of modified ITO electrodes: (a) ITO, (b) ITO/ SnO_2 , (c) ITO/Au- SnO_2 , (d) ITO/ SnO_2/CdS and (e) ITO/Au- SnO_2/CdS .

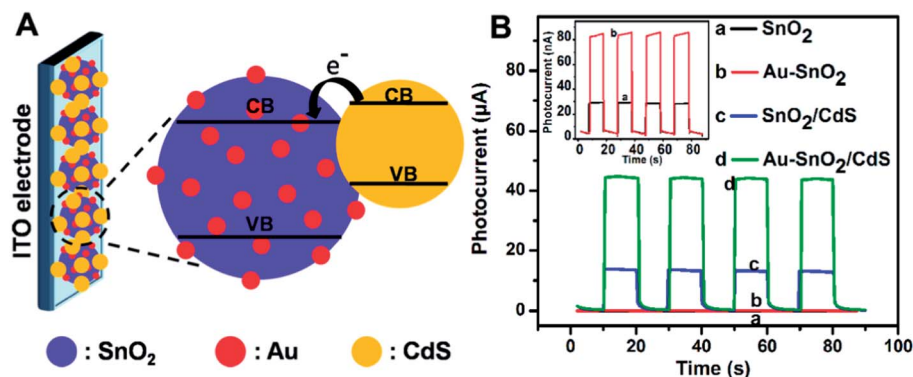


Fig. 5 (A) Schematic illustration of an ITO/Au-SnO₂/CdS film. (B) Photocurrent responses of (a) SnO₂, (b) Au-SnO₂, (c) SnO₂/CdS and (d) Au-SnO₂/CdS modified ITO electrodes in 0.1 M PBS (pH 7.4) containing 10 mM cysteine. The applied potential was 0 V, the light wavelength was >420 nm.

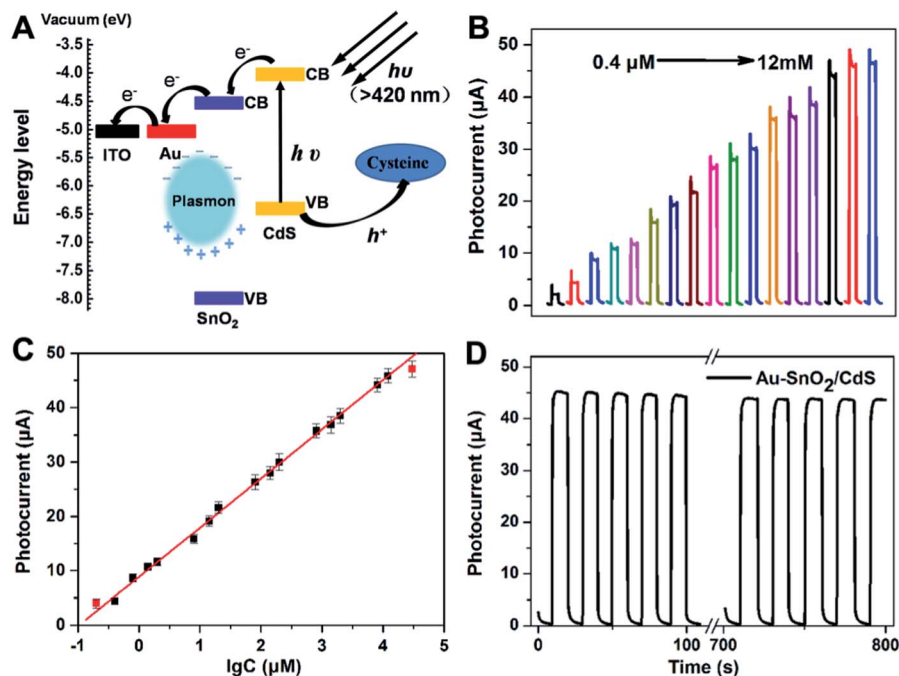


Fig. 6 (A) The schematic illustration of the electron-transfer process at the Au-SnO₂/CdS/ITO electrode under visible light. (B) Photocurrent responses of ITO/Au-SnO₂/CdS in 0.1 M PBS (pH 7.4) in the presence of the cysteine ranging from 0.4 μM to 12 mM (from left to right) at 0 V under illumination with the visible light (>420 nm). (C) Linear calibration curve according to (B). (D) Time-based photocurrent response of the ITO/Au-SnO₂/CdS electrode in 0.1 M pH 7.4 PBS containing 10 mM cysteine with irradiation on/off repeated every 10 s.

separation, but also the light trapping or scattering agents.^{40–42} Due to the superior electrical conductivity of Au, it serves as an excellent electron-transport matrix to capture electrons and transport electrons from excited CdS to ITO rapidly, avoiding electron-hole recombination effectively, resulting in a much more sensitive response to visible light. To verify the performance of the photoelectrochemical sensor in the determination of cysteine, its photocurrent response with increasing concentration of cysteine was measured (Fig. 6B). The photocurrent response showed a linear relationship with the logarithm of cysteine concentration under visible light illumination (>420 nm). The linear response range was from 0.4 μM to 12 mM (Fig. 6C), which was wider than the previous reports, as shown in Table 1. The detection limit was estimated to be 0.1 μM at a

signal-to-noise ratio of 3. Since the normal level of cysteine in human plasma was in the range of 240–360 μM,^{43,44} the present biosensor showed enough sensitivity for the detection of cysteine in real samples.

Table 1 Comparison of the cysteine detection by different methods

Method	Linear range	Detection limit	Reference
UV absorption spectra	5–250 μM	0.04 μM	43
Electrochemical	18–1000 μM	50 nM	44
Fluorescence spectra	2.5–110 nM	5.1 nM	45
Photoelectrochemical	0.2–2.8 μM	0.1 μM	37
Photoelectrochemical	0.6–157 μM	0.2 μM	38
Photoelectrochemical	0.1–100 μM	25 nM	39
Photoelectrochemical	0.4–12 000 μM	0.1 μM	This work

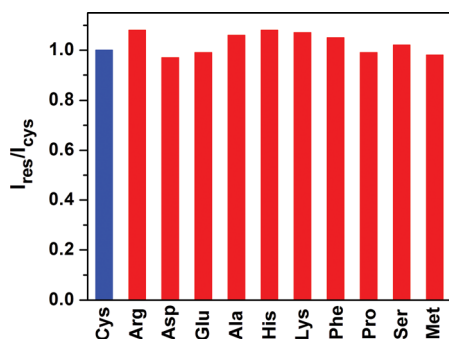


Fig. 7 Photocurrent response of Au-SnO₂/CdS/ITO electrodes upon addition of 10 mM of arginine (Arg), asparagines (Asp), glutamine (Glu), alanine (Ala), histidine (His), lysine (Lys), phenylalanine (Phe), proline (Pro), serine (Ser) and methionine (Met) to 0.1 M PBS (pH 7.4) containing 1 mM cysteine, respectively. The applied potential was 0 V, the light wavelength was >420 nm.

In addition, the stability of the photoelectrochemical biosensor was examined in the presence of 10 mM cysteine. From Fig. 6D, we could find that after 800 s, the photocurrent intensity still remained 97.7% of the initial value, suggesting a good stability of the Au-SnO₂/CdS-modified film. The repeatability of the photoelectrochemical biosensor was tested at the cysteine concentrations of 100 μ M. The relative standard deviation for five measurements was 4.7%, thus giving a good repeatability. Moreover, the response could reach the steady signal within 5 s, which made the strategy more convenient with a shorter detection time.

In order to evaluate the selectivity of the photoelectrochemical sensor, we measured its photoresponse toward cysteine and other ten different types of amino acids. Arginine, asparagine, glutamine, alanine, histidine, lysine, phenylalanine, proline, serine and methionine at ten fold concentration of cysteine had no obvious influence on the photoelectrochemical response of cysteine (Fig. 7). Therefore, the as-prepared photoelectrochemical biosensor would have good discrimination ability for monitoring of cysteine in amino acid samples.

Conclusion

In summary, Au-SnO₂ HNSs were successfully prepared through a facile, clean and one-step method. These uniform Au-SnO₂ HNSs were completely built up by spontaneous self-assembly of Au and SnO₂ NPs. The Au-SnO₂ HNSs combined with CdS NPs could be used to fabricate the photoelectrochemical cysteine biosensor. A broad linear range from 0.4 μ M to 12 mM appeared with a detection limit of 0.1 μ M. This proposed biosensor shows good performance and high applied potential in the field of biological detection for its advantages such as rapid response, wide detection range, low cost, and good reproducibility. This simple approach can be a useful method for making nanostructures of other metal-SnO₂ HNSs with different components, which can be used in the fields of catalysis, photoelectrochemical devices and biosensors.

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