A highly sensitive enzyme-less glucose sensor based on pnictogens and silver shell-gold core nanorods composite

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Experimental Procedures

Synthesis of gold@silver nanorods (Au@AgNRs)

Synthesis of the silver coated gold nanorods were performed as reported by Novotný et al,¹ using a two-stage method, a modification of previous work.² In brief, the core gold nanorods (AuNRs) were first synthesized via the well-known seeded-growth method in the presence of silver nitrate and cetyltrimethylammonium bromide (CTAB).³ To clean the as-synthesized AuNRs from the synthesis by-products, the resultant colloid were then subjected to centrifugation and the AuNRs pellets were collected and re-dispersed into cetyltrimethylammonium chloride (CTAC) solution (10×10^{-3} M).

Subsequently, silver shell was grown using silver nitrate on the synthesized AuNRs using elevated pH (sodium hydroxide), ascorbic acid and elevated temperature (60 °C) in the presence of CTAC. After 2 hours of the start of shell overgrowth, the mixture was cooled to ambient temperature and silver coated gold nanorods were purified via centrifugation followed by redispersion into CTAC solution (10×10^{-3} M).

Synthesis of pnictogen nanosheets

Synthesis of shear exfoliated pnictogen nanosheets were performed as reported previously by Gusmão et al..⁴ Briefly, bulk pnictogen materials procured from Alfa Aesar (Germany) were first subjected to sonication in aqueous sodium cholate (SC) surfactant in an ice bath to remove any inorganic impurities and oxides. The resultant mixtures were then centrifuged, and the pellets containing the pnictogen were dried then subjected to shear exfoliation in SC for 2 hours via the use of common kitchen blenders. Upon the 2 hours exfoliation process, the suspensions were centrifuged and the top 75% of the suspensions were recovered to yield As_{SE} (3.9%), Sb_{SE} (8.2%) and Bi_{SE} (8.8%) from the respective pnictogen starting materials.

Synthesis of pnictogen_{se}-Au@AgNRs composites

Desired volume (50, 100 or 150 μ L) of 5 mg/mL of pnictogen samples were added to the gold@silver nanorods (Au@AgNRs) to yield a mixture of 200 μ L solution, incubated over night at 25 °C and gently agitated at 400 rpm using a TS-100 Thermo-Shaker from Biosan. Subsequently, the supernatant containing the free Au@AgNRs was removed and the remaining pnictogen_{se}-Au@AgNRs pellet was resuspended in 100 μ L of ultrapure water.

Characterization of pnictogensE-Au@AgNRs composites

Scanning electron microscopy was performed via the use of Tescan Maia 3. The SEM samples were prepared by drop casting 3 μ L of desired sample suspension onto 200 mesh TEM grid. Energy dispersive X-ray spectroscopy (EDX) spectra were acquired via an energy dispersive spectrometer from Oxford Instruments and analysis was performed via the Aztec software. X-ray photoelectron spectroscopy (XPS) data were acquired via the use of a Phoibos 100 spectrometer (SPECS, Germany) that has been equipped with monochromatic Magnesium X-ray radiation source. The zeta potential measurements of the arsenic nanosheets and the Au@AgNRs were conducted via the use of the Zetasizer Nano ZS (Malvern Instruments, England) under zeta potential mode at 20°C.

Electrochemical Measurements

Cyclic voltammetry and differential pulse voltammetry were performed with an Eco Chemie μ Autolab type III electrochemical analyzer connected to a personal laptop and the NOVA version 1.10 software was utilized to set the experimental parameters. In this study, all measurements were conducted in ambient condition with the use of a classic three-electrode configuration, comprising of a modified glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum counter electrode, in a 10 mL electrochemical glass cell.

Prior to each measurement, GC electrodes' surfaces were carefully renewed via polishing with a range of alumina particle slurry (5 μ m, 1 μ m, 0.3 μ m successively) on a polishing pad. Thereafter, ultrapure water was used to rinse the electrodes and the electrodes were dried via dry polishing on a polishing pad. 3 μ L of pnictogen_{sE}-Au@AgNRs solution was then dropped onto the electrode surface and left to dry under ambient conditions. Cyclic voltammetry measurements were performed under the potential range of -0.2 to 0.5 for glucose detection, with a 50 mV s⁻¹ scan rate in 50 mM NaOH. Differential pulse voltammetry measurements were conducted in 50 mM NaOH at an amplitude pulse of 50 mV and a scan rate of 10 mV s⁻¹.



Figure S1. SEM and SEM-EDX of Sb_{se}-Au@AgNRs with the ratio of 25% Sb_{se} : 75% Au@Ag NRs.



Figure S2. SEM and SEM-EDX of Bi_{SE} -Au@AgNRs composite with the ratio of 25% Bi_{SE} : 75% Au@Ag NRs.



Figure S3. Wide survey XPS spectra of Au@AgNRs.



Figure S4. (a) Wide survey XPS spectrum of As_{se}-Au@AgNRs composite. HR-XPS spectra of (b) silver, Ag and (c) arsenic, As.



Figure S5. Cyclic voltammograms of 50µM glucose in 50 mM sodium hydroxide for As_{se}-Au@AgNRs composite (a), Sb_{se}-Au@AgNRs composite (b), Bi_{se}-Au@AgNRs composite (c) and pure Au@AgNRs (d).

Electrode	Linear Range (µM)	LOD (µM)	Ref.
GC/As _{se} -Au@AgNRs	0.05 nM - 555.55 nM	3.5 pM	This work
GC/Colloidal AgNPs-MoS ₂	0.1 - 1000	0.003	5
GC/NiNPs-MoS ₂	0 - 4000	0.31	6
GC/PTNFs/Graphene Oxide	2 - 10300	2	7
	10.3 mM - 20.3 mM		
GC/Au@PtNPs-MoS ₂	10 - 3000	1.08	8
GC/AuNPs-Graphene	100 - 2000	25	9
	2 mM - 16 mM		

Table 1. Comparison of the analytical performances of the GC/As_{se}-Au@AgNRs glucose sensor with
various electrochemical glucose sensors based upon layered materials decorated with metals.

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