

Electronic Supplementary Information

Synthesis of Ag nanoparticle-decorated 2,4,6-tris (2-pyridyl)-1,3,5-triazine nanobelts and their application for H₂O₂ and glucose detection

Xiaoyun Qin,^a Wenbo Lu,^a Yonglan Luo,^a Guohui Chang,^a Abdullah M. Asiri,^{bc}

Abdulrahman O. Al-Youbi^{bc} and Xuping Sun^{*abc}

^a State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

^b Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

^c Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

*To whom correspondence should be addressed. Tel/Fax: +86-431-85262065. E-mail: sunxp@ciac.jl.cn

Experimental Section

H_2O_2 (30 wt %), glucose, Na_2HPO_4 , NaH_2PO_4 and 2,4,6-tris (2-pyridyl)-1,3,5-triazine were purchased from Aladin Ltd. (Shanghai, China). AgNO_3 , $\text{NH}_3\cdot\text{H}_2\text{O}$, NaOH , HCl , ethanol, ascorbic acid (AA), dopamine (DA), acetaminophen (AP) and uric acid (UA) were purchased from BeiJing Chemical Works. Glucose oxidase (GOD) was purchased from Aldrich Chemical Company. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system. Phosphate buffer saline (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4 and a fresh solution of H_2O_2 was prepared daily. Human blood serum was obtained from Institute of Virology and AIDS Research, First Affiliated Hospital, Jilin University, Changchun, Jilin, People's Republic of China.

TPTNBs were prepared as follows: for a typical experiment, at room temperature, 0.0053 g of 2,4,6-tris (2-pyridyl)-1,3,5-triazine was immediately added into 20 mL of H_2O containing 50 wt % of ethanol under stirring. 1 mL of 1 M HCl aqueous solution was added into the mixture to form a clear solution. Subsequently, 1.2 mL of 1 M $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to the mixture solution and simultaneously the TPTNBs were formed by reprecipitation from solution. The precipitates were washed with water by centrifugation three times. Finally, the TPTNBs were re-dispersed in water for further use. To prepare AgNP-TPTNBs, 2 μL of 0.1 M AgNO_3 aqueous solution was added into 20 μL of the above TPTNBs with the aid of 600 μL of 0.08 M NaOH aqueous

solution to give brown precipitate which was washed with distilled water several times and then dispersed in water for characterization and future use.

As a control experiment, citrate-protected AgNPs were synthesized by the modified method of Wang et al.¹ Briefly, an aqueous solution of 0.5 mM AgNO₃ (5 mL) was added into the equivalent volume of aqueous solution containing 2 mM of NaBH₄ and 0.13 mM of trisodium citrate under the cooling in ice-bath, forming a yellowish colloidal solution of AgNPs. The colloidal solution was heated to 70 °C to decompose excess NaBH₄, and then cooled to room temperature.

Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating applied potential of 20 kV. The sample for SEM characterization was prepared by placing a drop of the dispersion on a bare indium tin oxide coated glass substrate (ITO) and air-dried at room temperature. FT-IR spectrum was measured by casting the solution on a CaF₂ plate with BRUKER Vertex 70 FTIR. Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a GCE (geometric area=0.07 cm²) as the working electrode, a Ag/AgCl (3 M KCl) electrode as the reference electrode, and platinum foil as the counter electrode. All potentials given in this work were referred

to the Ag/AgCl electrode.

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GCE was polished with 1.0 and 0.3 μm alumina powder, respectively, and rinsed with doubly distilled water, followed by sonication in ethanol solution and doubly distilled water successively. Then, the electrode was allowed to dry in a stream of nitrogen. For the cyclic voltammetry experiment, 3 μL of AgNP-TPTNBs were dropped on the surface of pretreated GCE and left to dry at room temperature. Then, 4 μL of 38 mg mL^{-1} GOD aqueous solution was dropped on the resulting AgNP-TPTNB/GCE to dry at 4 $^{\circ}\text{C}$ for 3 hours. For current time experiment, 2 μL of 1 wt % chitosan solution was additionally cast on the surface of the above materials modified GCE and dried at 4 $^{\circ}\text{C}$ for 2 hours before electrochemical experiments.

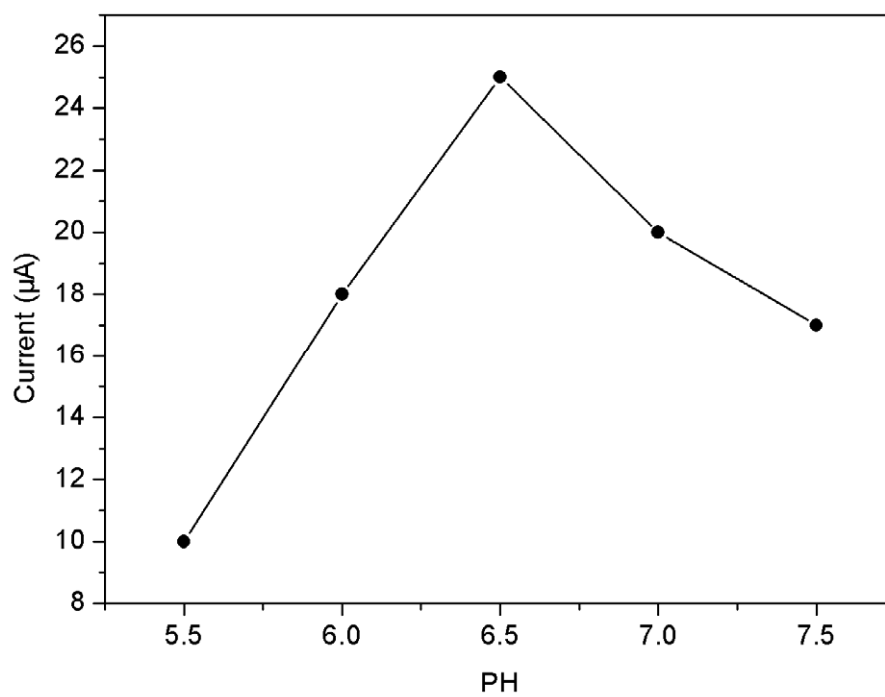


Fig. S1 The amperometric responses of AgNP-TPTNB/GCE in 0.2 M PBS with different pH values from 5.5 to 7.5 in the presence of 1.0 mM H₂O₂.

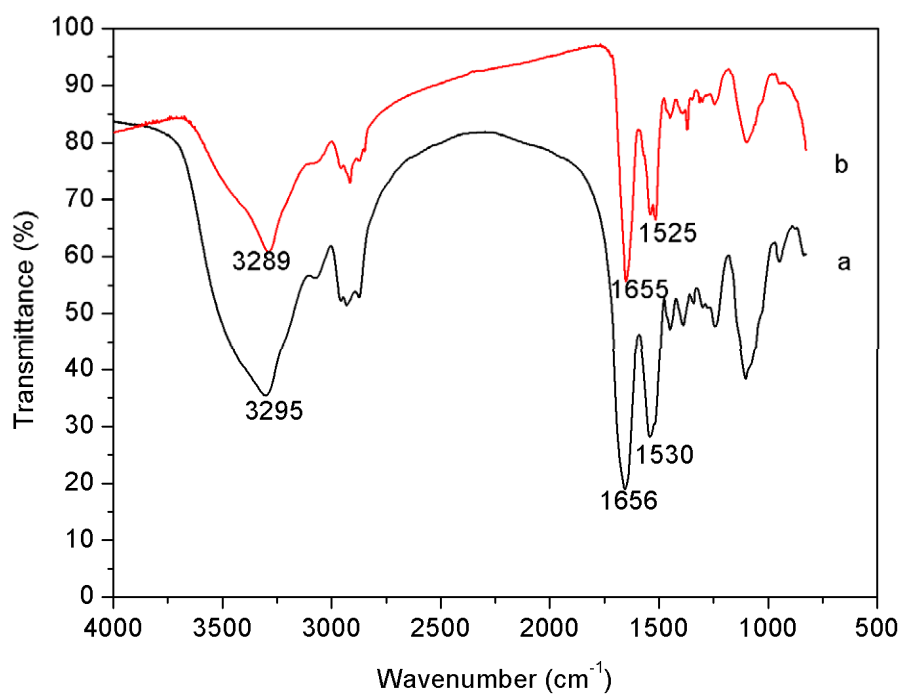


Fig. S2 FT-IR spectrum of native GOD (a) and AgNP-TPTNBs film covered with GOD (b).

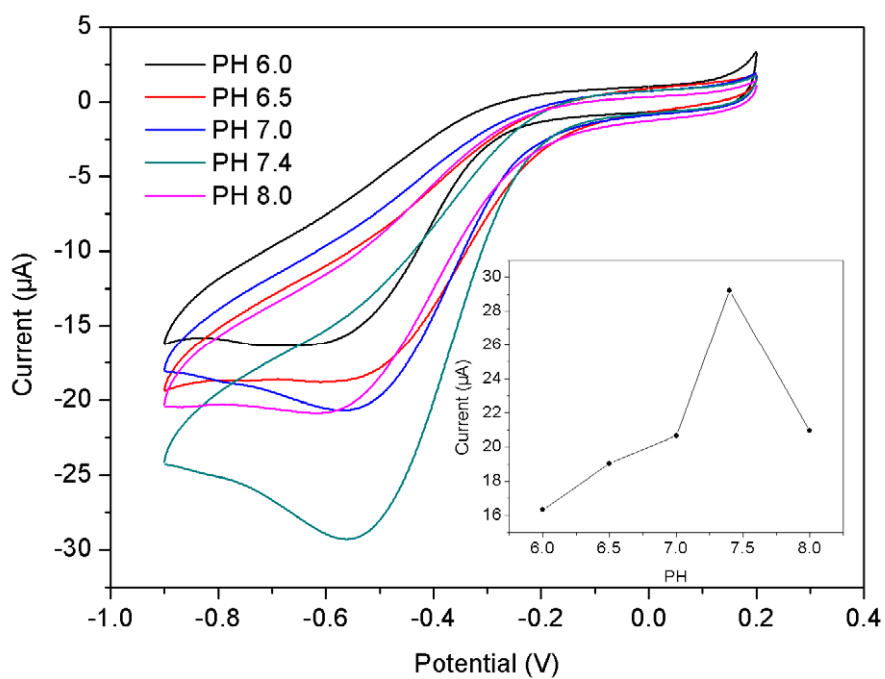


Fig. S3 CVs of GOD/AgNP-TPTNB/GCE in 0.2 M PBS solution at various pH values: 6.0, 6.5, 7.0, 7.4, 8.0 saturated with O₂ at a scan rate of 50 mVs⁻¹. Inset: effect of solution pH value on the amperometric response of GOD/AgNP-TPTNB/GCE toward 4 mM glucose.

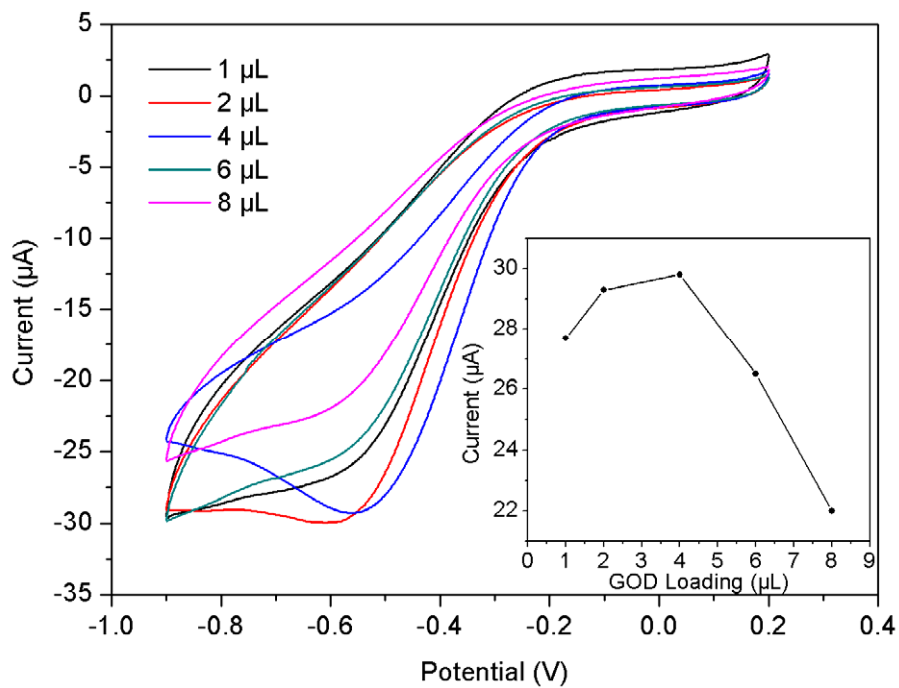


Fig. S4 The effect of GOD loading on the amperometric response of GOD/AgNP-TPTNB/GCE toward 4 mM glucose.

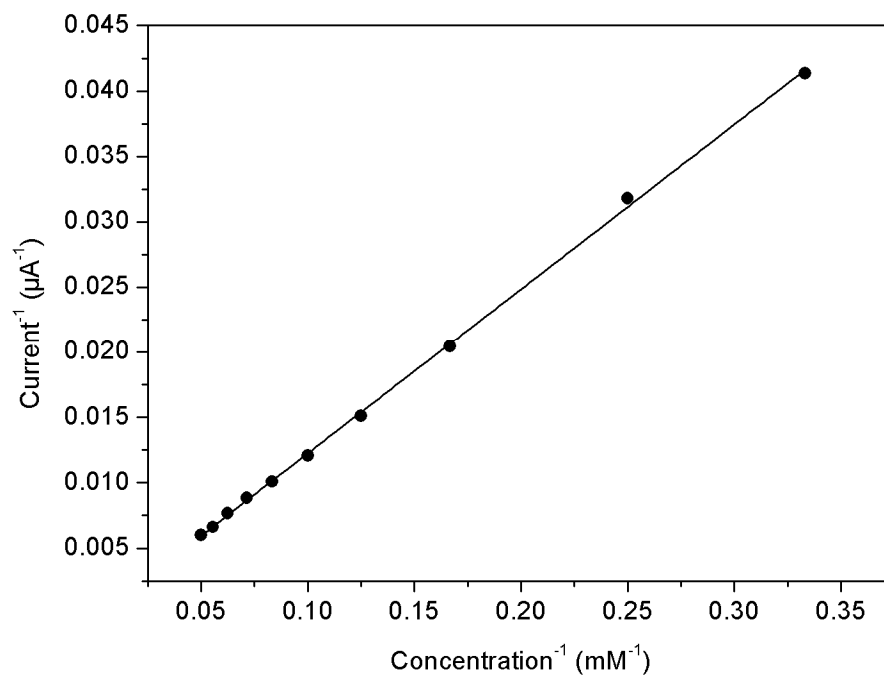


Fig. S5 The Lineweaver–Burk plot of GOD/AgNP-TPTNB/GCE.

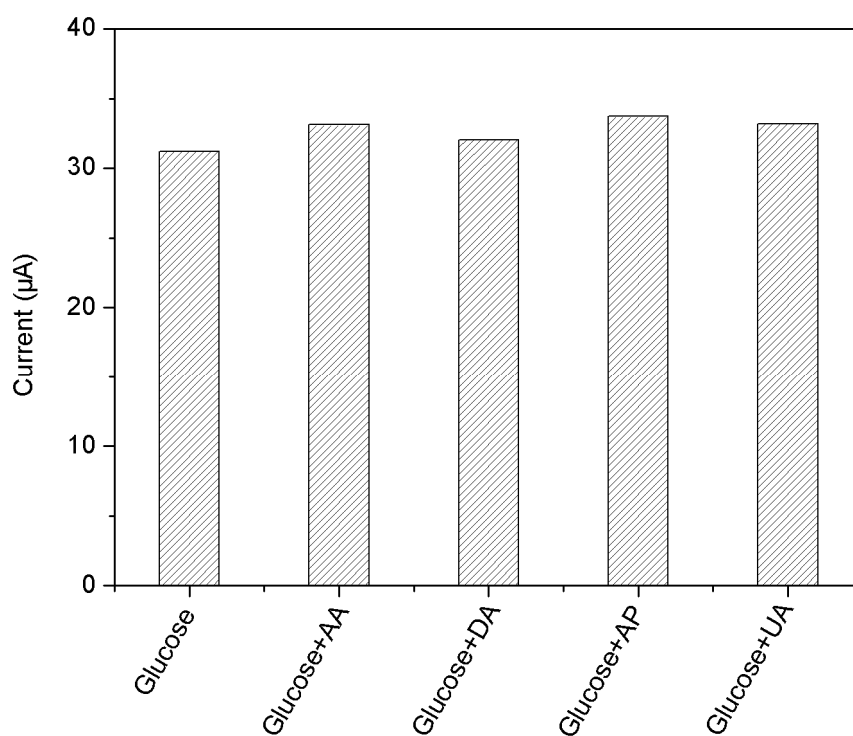


Fig. S6 Comparison of the responses of GOD/AgNP-TPTNB/GCE to the addition of 5 mM glucose, 5 mM glucose with 0.5 mM ascorbic acid (AA), 5 mM glucose with 0.5 mM uric acid (DA), 5 mM glucose with 0.5 mM uric acid (AP), and 5 mM glucose with 0.5 mM dopamine (UA) in O₂ saturated 0.2 M PBS (pH 7.4).

Table S1 A comparison of this work with literature work regarding the performance of the glucose assay using several enzyme electrodes.

Electrode	Linearity range (mM)	Detection limit (μM)	K_M (mM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Refs.
GOD/AgNP/F-SiO ₂ /GO/GCE	2-12	310	-	-	2
CS/GOD/Au nanoplate/GCE	2-20	200	-	-	3
GOD/Au _{nano} /Pt _{nano} /CNT/AuE	0.5-17.5	400	10.73	-	4
G/AuNPs/GOD/CS/GCE	2-10	180	-	0.55	5
GOD/Ppy/PtE	0-10	-	37.6	0.007	6
PB/MWNTs/GOD/CS/ICPTES/GCE	0.025-1.3	7.5	3.67	15.2 cm ⁻²	7
GOD/G/CS/GCE	0.08-12	20	4.4	37.93 cm ⁻²	8
GOD/Pt/C/GCE	0.3-45	< 300	-	125 cm ⁻²	9
GOD/AgNP-TPTNB/GCE	3-20	190	25.1	109.6 cm ⁻²	This work

GOD, glucose oxidase; AgNP, Ag nanoparticle; F-SiO₂, functional SiO₂; GO, graphene oxide; GCE, glass carbon electrode; CS, chitosan; CNT, carbon nanotube; AuE, gold electrode; G, graphene; AuNPs, Au nanoparticles; Ppy, polypyrrole; PtE, platinum working electrode; PB, prussian blue; MWNTs, multi-walled carbon nanotubes; ICPTES, 3-isocyanatopropyltriethoxysilane.

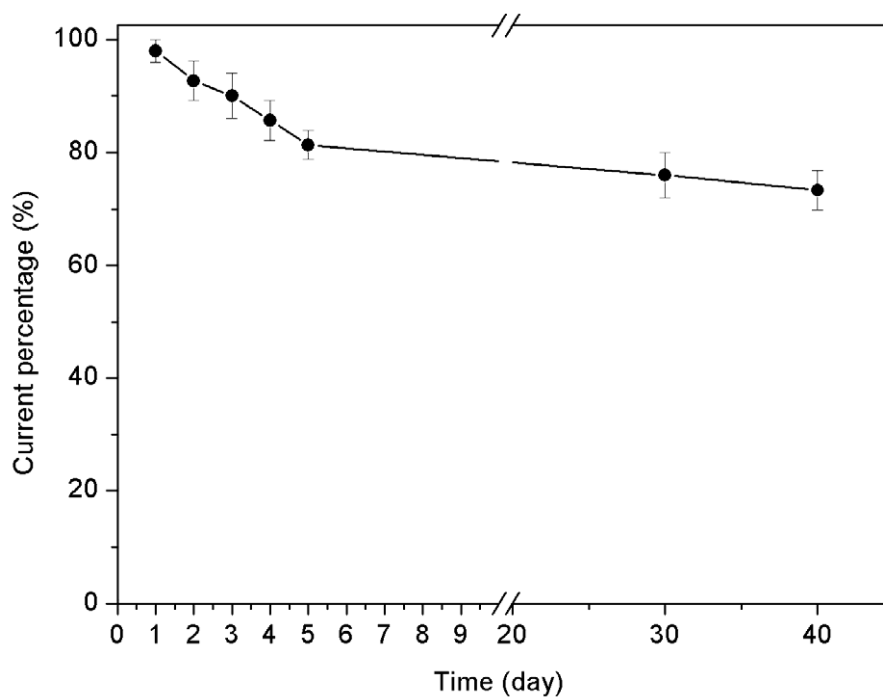


Fig. S7 The variation in the response current of 3 mM glucose in PBS solution (pH 7.4) at the GOD/AgNP-TPTNB/GCE at a scan rate of 50 mVs^{-1} for 60 days.

References

1. W. Wang, S. Efrima and O. Regev, *Langmuir*, 1998, **14**, 602.
2. W. Lu, Y. Luo, G. Chang and X. Sun, *Biosens. Bioelectron.*, 2011, **26**, 4791.
3. Y. Zhang, G. Chang, S. Liu, W. Lu, J. Tian and X. Sun, *Biosens. Bioelectron.*, 2011, **28**, 344.
4. X. Chou, D. Duan, G. Shen and R. Yu, *Talanta*, 2007, **71**, 2040.
5. C. Shan, H. Yang, D. Han, Q. Zhang, A. Ivaska and L. Niu, *Biosens. Bioelectron.*, 2010, **25**, 1070.
6. Y. M. Unag and T. C. Chou, *Biosens. Bioelectron.*, 2003, **19**, 141.
7. G. Fu, X. Yue and Z. Dai, *Biosens. Bioelectron.*, 2011, **26**, 3973.
8. X. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu and Y. Lin, *Biosens. Bioelectron.*, 2009, **25**, 901.
9. M. Ammam and E. B. Easton, *Sens. Actuators, B*, 2011, **155**, 340.