

Supporting Information

Development of electrochemical enzyme-free glucose sensor based on self-assembled Pt-Pd bimetallic nanosuperlattices

Victor Vinoth^{a, b}, Nalenthiran Pugazhenthiran^a, Ramalinga Viswanathan Mangalaraja^{c, d}, Asad Syed^e, Najat Marraiki^e, Héctor Valdés,^{a,*} Sambandam Anandan^{b,*}

^a*Clean Technologies laboratory, Facultad de Ingeniería, Universidad Católica de la Santísima Concepción, Concepción, Chile*

^b*Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Tiruchirappalli-620 015, India*

^c*Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, University of Concepcion, Concepcion, Chile*

^d*Technological Development Unit (UDT), University of Concepcion, Coronel Industrial Park, Coronel, Chile*

^e*Department of Botany & Microbiology, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*

E-mail: sanand@nitt.edu, hvaldes@ucsc.cl, Tel.: +91-431-2503639, +56-41-2345044, Fax: +91-431-2500133.

S Number	Details	Page Number
1	Experimental Procedure	3-4
2	Figure S1	5
3	Tables (S1-S3)	6-7

Experimental Procedures

Chemicals

Palladium (II) acetate (99.98% Pd(OAc)₂), chloroplatinic acid (99.9%, aqueous solution of H₂PtCl₆ · 6H₂O), polyvinylpyrrolidone, ethylene glycol, silver nitrate (AgNO₃), D-glucose, galactose, sucrose, fructose, lactose, L-ascorbic acid, potassium ferricyanide (K₄[Fe(CN)₆]), and Nafion (5 wt%) were received from Sigma Aldrich. Mono, and disodium phosphates (99%), hydrochloric acid (HCl), nitric acid (HNO₃), and sulfuric acid (H₂SO₄) were purchased from Merck. Further, all remaining chemicals were of analytical grade and were used as obtained. Aqueous solutions were prepared with Milli-Q-water. Before use, all glasswares were properly washed with aqua regia (1: 3 HCl / HNO₃ (v/v)) and then washed with Milli-Q-water. All experiments were performed in accordance with the Guidelines "Department of Chemistry", and approved by the ethics committee at "National Institute of Technology". Informed consents were obtained from human participants of this study.

Preparation of Pt-Pd bimetallic nanosuperlattices (Pt–Pd BMNSLs)

Pt–Pd bimetallic nanosuperlattices were synthesized by an eco-friendly approach using the polyol assisted sonochemical method. The ultrasonic irradiation was executed by a standing wave sonication system (Kaijo 30110 (QR – 003) type lot. no. SM1460009, Oscillator 30301 type; power, 50 W; frequency, 38 kHz). About 5 mL of a PVP solution (37.5 mM) and 0.6 mL of 50 mM AgNO₃ were mixed with 5 mL of a solution of 6.25 mM Pd(OAc)₂ diluted in ethylene glycol, producing a yellow solution. This yellow solution was sonicated for 20 minutes. During the reaction the color was changed from yellow to dark brown, indicating that the Pd seeds were formed at this stage. Then, 5 mL of an aqueous solution of H₂PtCl₆ (6.25 mM) was added to the ultrasonication reaction system. Thereafter, the reaction mixture was kept under ultrasonication during 2 h in an inert atmosphere using argon gas. Here, H₂PtCl₆ · 6H₂O and Pd(OAc)₂ were completely reduced with ethylene glycol (EG). After 2 h of reaction time, the solution became dark brown, indicating the formation of Pt–Pd BMNSLs. This colloidal solution was washed with ethanol and acetone. Pt–Pd BMNSLs were dispersed by adding ethanol combined with following centrifugation treatments at 8000 rpm for 15 minutes.^{S1} As a way of comparison, the Pt-NPs without Pd-NPs and Pd-NPs without Pt-NPs were synthesized using the same experimental procedure as described above.

Characterization of synthesized nanomaterials

The morphology of synthesized materials was demonstrated by a high-resolution transmission electron microscope together with an energy-dispersive X-ray (EDX) detector and selected area electron diffraction (SAED) patterns (JEOL JEM 2010 model at an accelerating voltage of 200 kV). The optical spectra were obtained by an Analytik Jena (Specord 600S) diode array UV-vis spectrophotometer. The X-ray diffraction (XRD) experiments were conducted at $2\theta = 10-80^\circ$ on a Rigaku X-ray diffractometer, Cu-K α radiation ($\lambda = 0.1542$ nm), Japan. X-ray photoelectron spectroscopy (XPS) measurements were accomplished by Physical Electronics PHI 5600 XPS instrument with a monochromatic Al-K α (1486.6 eV) as an excitation source.

Electrochemical assessment

Prior to use, the GC working electrode was polished using alumina suspensions with different particle sizes (1, 0.3, and 0.05 μm) until obtaining a mirror-like surface. A volume of 10 μL of the synthesized sample (Pt–Pd BMNSLs or PtNPs, PdNPs) was dropped onto the GC electrode surface. The modified GC electrode (Pt–Pd BMNSLs/GC or PtNPs/GC, PdNPs/GC) was dried at room temperature. Before starting any electrochemical experiments, the electrolytic solution was aerated with argon for 15 min.

All cyclic voltammetric (CV), differential pulse voltammetric (DPV), and amperometric (i-t) studies were accomplished using in a CHI 650C electrochemical workstation (Austin, TX, USA). A three-electrodes system was employed, comprising of a glassy carbon electrode (GC) ($\theta = 3$ mm diameter) or a modified electrode (Pt–Pd BMNSLs/GC or PtNPs/GC, PdNPs/GC) as a working electrode, platinum wire, and an Ag/AgCl (sat. KCl) electrode as the auxiliary and the reference electrode, respectively. All the potentials were referred to as the reference electrode. The measurements were accomplished in a phosphate buffer saline (PBS, pH 7.4) solution with 0.1 M KCl at room temperature.

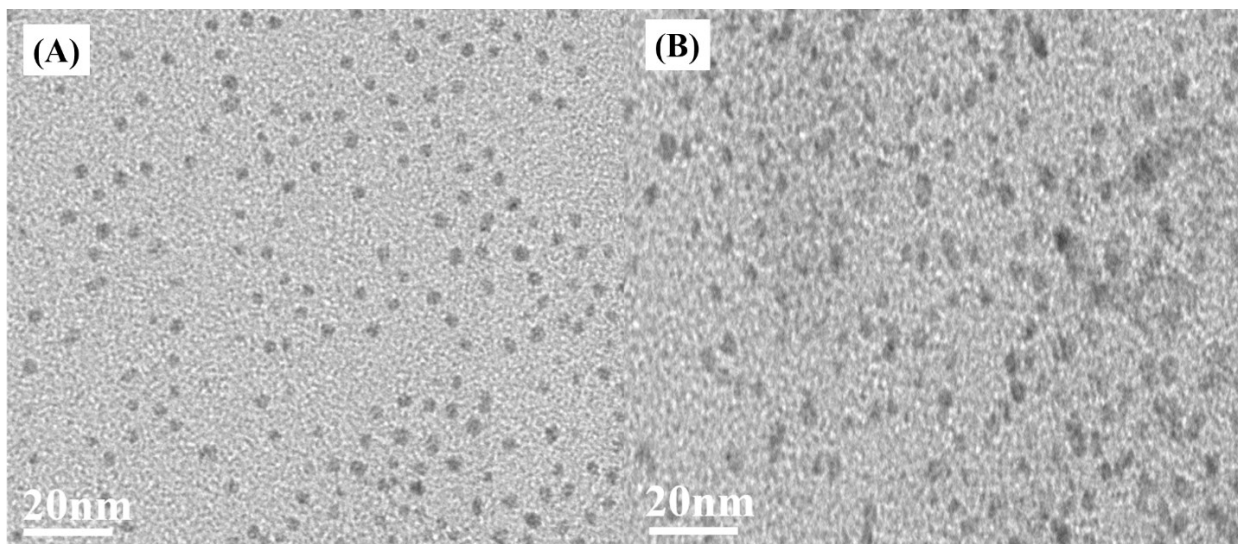


Figure S1. TEM image of Platinum (A) and Palladium (B) nanoparticles distribution

Table S1. Comparison of detection limit using Pt-Pd BMNSLs/GC electrode to various modified electrodes using the amperometric method previously reported in the literature.

Electrodes	Dynamic range (μM)	Limit of detection (μM)	References
Pt-replaced porous Cu-modified SPCEs	1000-11000	385	(S2)
GOx-PtNPs-PAA-aSPCE	20-2300	7.6	(S3)
Pt/rGO/P3ABA modified SPCE	250-6000	44.3	(S4)
GOD-CS/GP-PANI/Pt disc electrode	10-1048	1.7	(S5)
Pt/Au/BDD	10 - 7500	7.7	(S6)
Pt – NiO/rGO/GCE	8-14500	2.67	(S7)
PtNCs/graphene (PVP)/GCE	1000–25000	30	(S8)
Pt/Ni@rGO	20–5000	6.3	(S9)
PtPd BMNSLs	1-500	1	This work

Table S2. Comparison of glucose sensing obtained using Pt-Pd BMNSLs/GC electrode with a commercial meter in human blood serum samples.

Sample	Commercial meter	Pt-Pd BMNSLs/GC electrode		
	Concentration (mM)	Concentration (mM)	RSD (%) (N=3)	Recovery (%)
1	5.83	5.76	2.28	98.79
2	5.51	5.43	3.11	98.64
3	6.15	6.03	2.97	97.73
4	5.64	5.57	2.91	98.75

Table S3. Comparison of glucose sensing obtained using Pt-Pd BMNSLs/GC electrode with a commercial meter in urine samples.

Urine samples	Prepared concentration (mM)	Pt-Pd BMNSLs/GC electrode		Commercial meter
		Detected concentration (mM)	Recovery (%)	Detected concentration (mM)
1	1	1.01	101	1.01
2	2	1.95	97	1.98
3	4	3.94	98.5	3.98
4	5	4.97	99.4	4.99

References

- (S1) N. V. Long, T. D. Hien, T. Asaka, M. Ohtaki, and M. Nogami, *Int. J. hydrog. Energy*, 2011, **36**, 8478-8491.
- (S2) Y. Hu, X. Niu, H. Zhao, J. Tang and Minbo Lan, *Electrochim. Acta*, 2015, **165**, 383-389.
- (S3) F. J.-Fiérrez, M. I. G.-Sánchez, R. J.-Pérez, J. Iniesta and E. Valero, *Sensors*, 2020, **20**, 4489.
- (S4) S. Phetsang, J. Jakmunee, P. Mungkornasawakul, R. Laocharoensuk, and K. Ounnunkad, *Bioelectrochemistry*, 2019, **127**, 125–135.
- (S5) X. Feng, H. Cheng, Y. Pan, and H. Zheng, *Biosens. Bioelectron.*, 2015, **70**, 411–417.
- (S6) S. Nantaphol, T. Watanabe, N. Nomura, W. Siangproh, O. Chailapakul, and Yasuaki Einaga, *Biosens. Bioelectron.*, 2017, **98**, 76-82.
- (S7) L. Wang, X. Lu, C. Wen, Y. Xie, L. Miao, S. Chen, H. Li, P. Li and Y. Song, *J. Mater. Chem. A*, 2015, **3**, 608 – 616.
- (S8) G. Chang, H. Shu, Q. Huang, M. Oyama, K. Ji, X. Liu, and Y. He, *Electrochim. Acta*, 2015, **157**, 149–157.
- (S9) R. Ayranci, B. Demirkan, B. Sen, A. Şavk, M. Aka, F. Şenb, *Mater. Sci. Eng. C*, 2019, **99**, 951-956.