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Electronic Supplementary Information

Facile and Controllable Synthesis of Triplex Au@Ag-Pt@Infinite Coordination Polymers Core-shell Nanoparticles for Highly Efficient Immobilization of Enzymes and Enhanced Electrochemical Biosensing Activity

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1. Fabrication of ICPs-GOx/Pt, Au-ICPs-GOx/Pt, and Au@Ag@ICPs-GOx/Pt, Au-pre-synthesized Pt NPs-ICPs-GOx/Pt and Au@Ag-pre-synthesized Pt NPs-ICPs-GOx/Pt electrodes

For the synthesis of ICPs-GOx and Au-ICPs-GOx, typically, 80 μL of 0.038 M H_2PtCl_6 aqueous solution was introduced into 2 mL of water or 30 nm Au colloid solution and then vigorously stirred for 30 min. Subsequently, 1 mL of freshly prepared 0.5 mg mL^{-1} DMcT aqueous solution with 9.0 mg GOx dissolved was added dropwise to the dispersion under continuous stirring.

For the synthesis of Au@Ag@ICPs-GOx, typically, 1 mL of freshly prepared 0.5 mg mL^{-1} DMcT aqueous solution with 9.0 mg GOx dissolved was firstly introduced into 2 mL of Au@Ag colloid solution. Then, 80 μL of 0.038 M H_2PtCl_6 aqueous solution was added to the dispersion under continuous stirring.

For the synthesis of Au-pre-synthesized Pt NPs-ICPs-GOx and Au@Ag-pre-synthesized Pt NPs-ICPs-GOx, small Pt NPs with diameters about 4.0 ± 0.8 nm were firstly synthesized according to a previous research.[1] Then, 200 μL of small Pt NPs solution was introduced into 2 mL of 30 nm Au or Au@Ag colloid solution and vigorously stirred for 30 min. Subsequently, 80 μL of 0.038 M H_2PtCl_6 aqueous solution and 1 mL of freshly prepared 0.5 mg mL^{-1} DMcT aqueous solution with 9.0 mg GOx dissolved were added into the dispersion at the same time under continuous stirring.

After stirring for about 3 h at room temperature, all of the products as mentioned above were collected by centrifugation, and resuspension with deionized water for three times. Then, 1 mL of them as synthesized was finally concentrated and redispersed in 150 μL water. At last, 5 μL of them were carefully cast onto the Pt electrode and dried at room temperature to fabricate the corresponding enzyme electrodes.

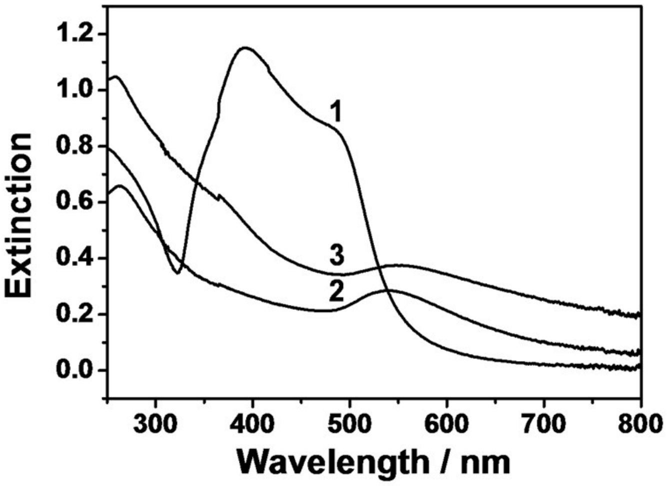

Fig. S1 Extinction spectra of Au@Ag NPs (1), Au@Ag-Pt nanostructures (2), and Au@Ag-Pt@ICPs NPs (3).

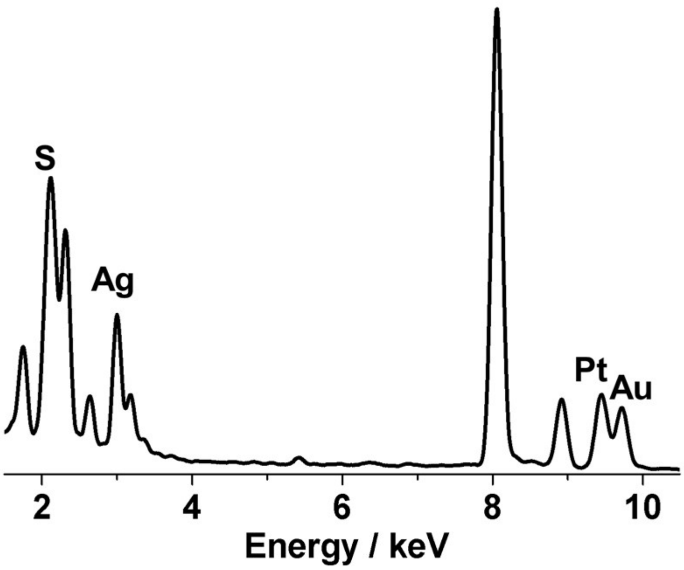

Fig. S2 EDX data of the Au@Ag-Pt@ICPs NPs.

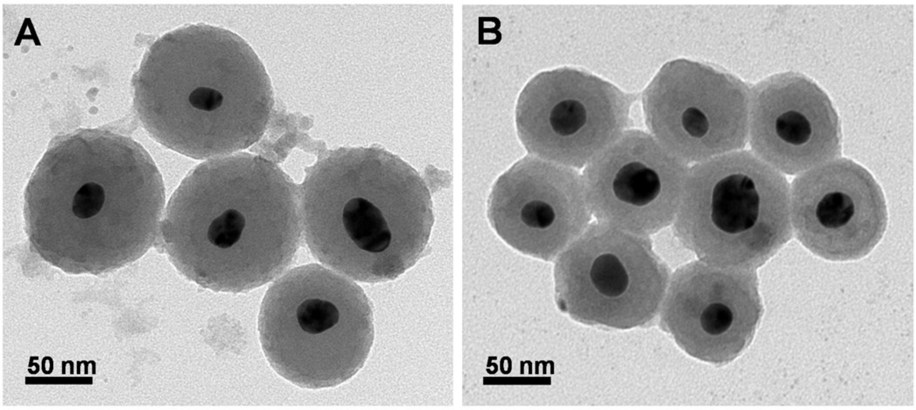

Fig. S3 TEM images of Au@ICPs (A) and Au@Ag@ICPs (B).

Table S1. Elemental concentration of the Au@Ag-Pt@ICPs sample by XPS analysis.

C1s	**S2p**	**N1s**	**Pt4f**	**Ag3d**	**Cl2p**
25.71	11.84	9.57	1.54	2.48	0.56

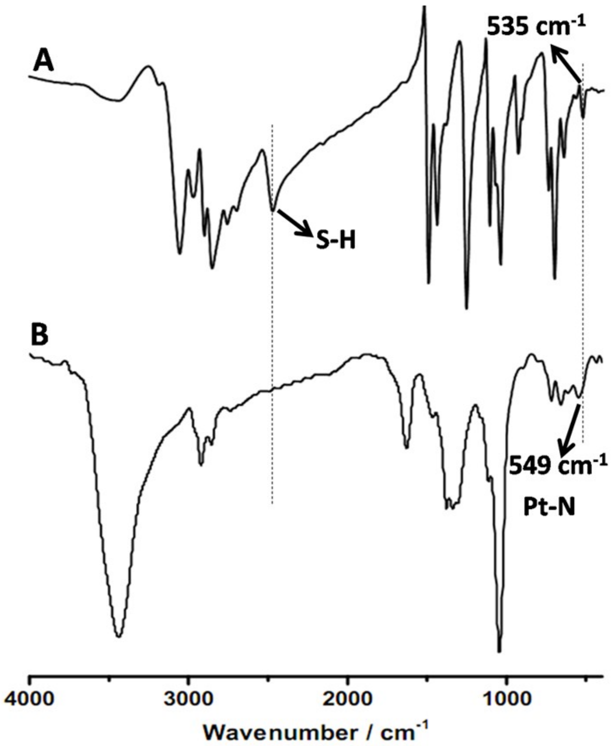

Fig. S4 FT-IR spectra of (A) DMcT in solid state and (B) Au@Ag-Pt@ICPs NPs.

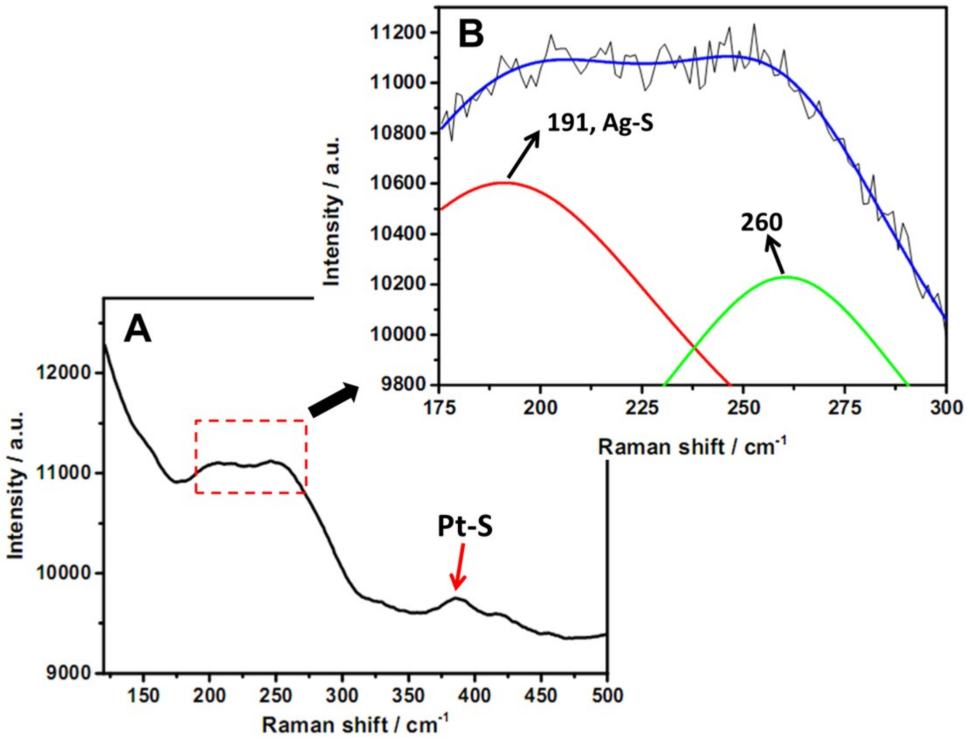

Fig. S5 (A) Raman spectra of Au@Ag-Pt@ICPs NPs; (B) Fitting Raman spectra of the part of Red dashed box in A by Origin software.

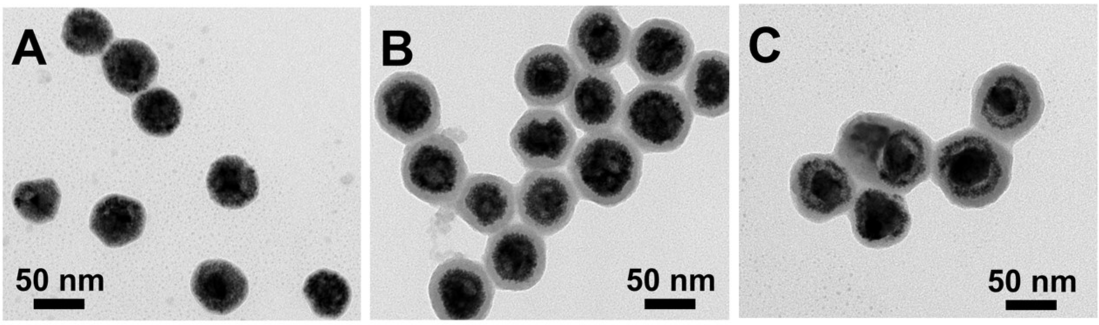

Fig. S6 TEM images of the influence of the volume of H_2PtCl_6 on the Au@Ag-Pt@ICPs NPs: (A) 20, (B) 60, and (C) 100 μL.

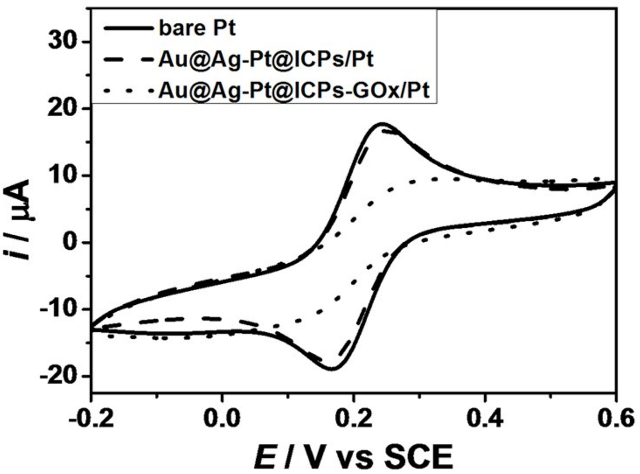

Fig. S7 Cyclic voltammograms of different modified electrodes: bare Pt (solid line), Au@Ag-Pt@ICPs/Pt (broken line) and Au@Ag-Pt@ICPs-GOx/Pt (dotted line); supporting electrolyte 0.1 M KCl containing 1mM of $Fe(CN)_6^{3-/4-}$; scan rate = 50 mV/s.

Table S2. The optimization of the experimental variables.

Experimental variable	Testing range	Optimized value
c_{GOx} [mg mL^{-1}]	1.0—5.0	3.0
c_{DMcT} [mg mL^{-1}]	0.25—2.0	0.5
$V_{H_2PtCl_6}$ [μL]	20—100	80
V_{AgNO_3} [μL]	50—600	100
Detection potential [V]	0.4—0.9	0.7
pH of detection solution	4.0—9.0	7.0
Cast-coating volume of material [μL]	2.5—12.5	5.0

Table S3. The performance of GOx-based electrodes.

	S (μA cm^{-2} mM^{-1})	LDR (× 10^{-3} M)	LOD (× 10^{-6} M)	r^2
1	15.8	0.005—2.225	2.7	0.9988
2	5.1	0.005—2.325	5.0	0.9991
3	26.4	0.005—3.325	1.1	0.9986
4	82.1	0.0005—3.325	0.06	0.9995

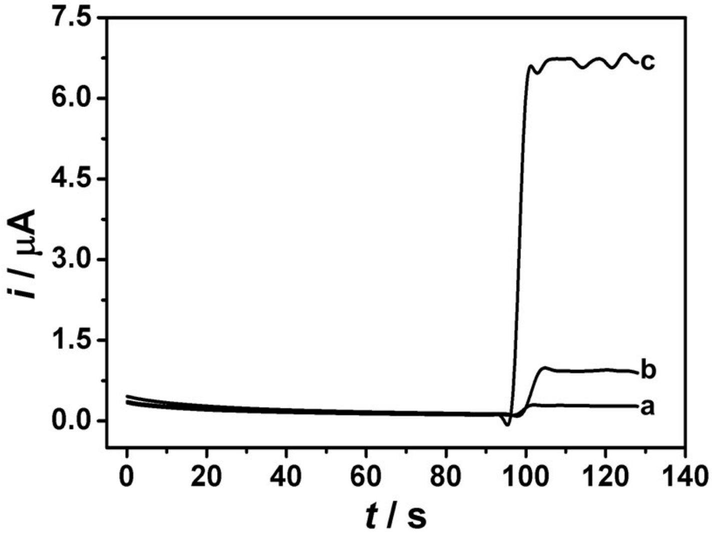

Fig. S8 Current responses of Au-pre-synthesized Pt NPs-ICPs-GOx/Pt (a), Au@Ag-pre-synthesized Pt NPs-ICPs-GOx/Pt (b) and Au@Ag-Pt@ICPs-GOx/Pt (c) to 1.0 mM glucose in pH 7.0 PBS at 0.7 V vs SCE.

Table S4. Comparison of stability of glucose biosensors fabricated based on ICPs or metal NPs.

Modified electrode	**Retention of initial current response (%)**	**Storage time (days)**	**Ref**
MEBCs**3**/Au	85	30	**2**
MCPGHs/GOD/GCE	95.7	7	**3**
HRP/Ag@C/ITO	92	30	**4**
Pt (or Pd)/xGnP/GCE	70	30	**5**
Nafion/GOx/Pd-HCNFs/GCE	84	30	**6**
Pd/graphene/carbon/GCE	84.5	7	**7**
Cu/MoS_2	96.4	14	**8**
ICPs-GOx/Pt	90	49	This work
Au@Ag-Pt@ICPs-GOx/Pt	90	98	This work

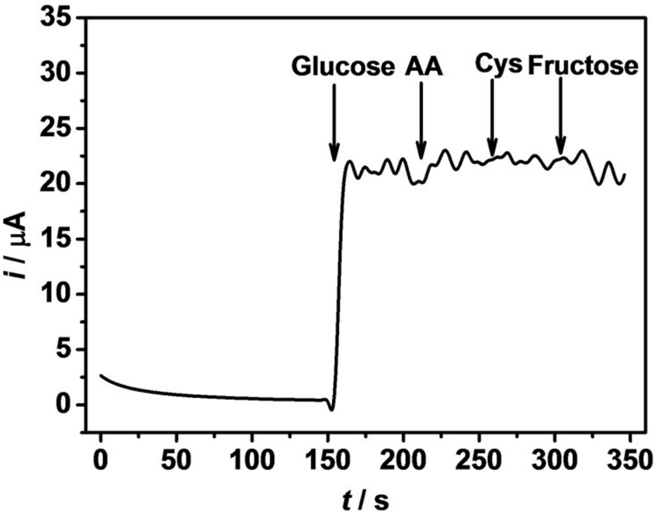

Fig. S9 Amperometric responses of the Au@Ag-Pt@ICPs-GOx/Pt electrode upon subsequent additions of 3.0 mM glucose, 0.1 mM ascorbic acid (AA), 0.05 mM L-cysteine (Cys) and 0.1 mM fructose in 0.1 M PBS at 0.7 V vs. SCE.

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