Facile Synthesis of Porous Tubular Palladium Nanostructure and its Application for a Nonenzymatic Glucose Sensor

Hongyan Bai,[a] Min Han,[a] Yuezhi Du,[b] Jianchun Bao*[a] and Zhihui Dai*[a]

[a] Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing, 210097, P R China
Email: baojianchun@njnu.edu.cn and daizhihuii@njnu.edu.cn
[b] Department of Biomedical Engineering, Tsinghua University, Beijing, 100084, P.R. China

Experimental

Reagents. β-D-(+)-glucose, ascorbic acid (AA), uric acid (UA) and p-acetamidophenol (AP) were purchased from Sigma and used as received. Porous anodic alumina (PAA) membranes with the pore sizes of 20 and 100 nm were from Whatman Corporation. The quoted pore diameters of the PAA membranes were 20 and 100 nm, but actually, according to the SEM image of the PAA membrane, there was a pore diameter distribution mainly in the range of 40-60 nm and 150-220 nm, respectively.[1] $PdCl_2$ was purchased from Shanghai Chemical Reagent Co. Polyvinyl alcohol (PVA, average degree of polymerization, 1800±100) was purchased from Shanghai Laize Factory of Fine Chemicals. Phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared by mixing stock standard solutions of K_2HPO_4 and KH_2PO_4 and adjusting the pH with H_3PO_4 or NaOH. All other chemicals were of

analytical grade and were used without further purification. All solutions were made up with doubly distilled water.
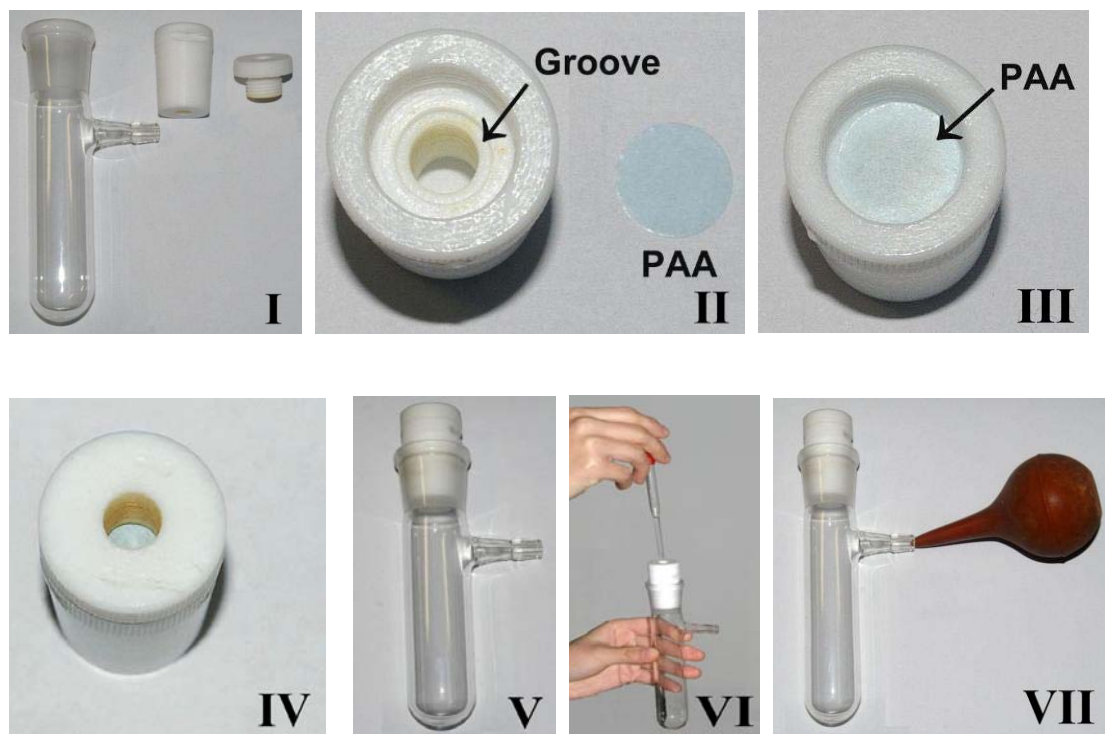

Fig. S1. A schematic diagram of the CdS modifying pore wall of PAA. (I) overview of the branch tube, groove and lid (from the left to the right). (II) groove and PAA template (the real color of PAA is white). (III) two overlapped PAA templates were placed in the groove. (IV) put the lid to the groove. (V) put the groove to the branch tube. (VI) reactant was injected to the pores of PAA templates. (VII) a suction process with rubber suction bulb.

Preparation of porous tubular palladium nanostructure. Fig. S1 shows a schematic diagram of the CdS modifying pore wall of PAA. Two overlapped PAA templates were placed in the groove of teflon. The upper PAA template was with pore size of 100 nm and the bottom was with pore size of 20 nm. 0.1 M of $CdCl_2$ was firstly introduced to the pores of PAA templates by a slight suction method, and then injecting 0.1 M of Na_2S solution. CdS was deposited on the pore wall of the PAA template by the reaction of Cd^{2+} and S^{2-}. After that, the upper template was taken out, washed with doubly distilled water and allowed to dry under ambient conditions. The PAA template displayed yellow which indicated CdS intercalating the pores of PAA. Then, a thin Au layer was evaporated on one side of the PAA membrane as a working

electrode. The electrolyte consisted of 1.5 g L^{-1} of H_2PdCl_4 ($PdCl_2$ dissolved in the diluted HCl solution) and 25 g L^{-1} of H_3BO_3 with pH of 6.5 to 7.0 adjusted by 2.0 M of NaOH. Electrodeposition was carried out in a three-electrode electrochemical cell with the bare side of the PAA membrane facing upward and the deposition solution confined to the bare side of the PAA membrane, a platinum wire as the counter electrode and a saturated calomel electrode as a reference electrode. The electrodeposition proceeded in a constant-current mode with a typical deposition current density of 0.4 mA cm^{-2} for 10 h. After the deposition, the PAA template was dissolved by 2.0 M of NaOH solution. 2.0 M of HCl solution was used to further dissolve CdS. For comparison, the electrochemical deposition of palladium without CdS pre-deposition was also employed.

Preparation of spherical palladium particles. The spherical palladium particles were prepared according to our previous work.[2] In brief, 20 mg of $PdCl_2$ was dissolved in 1.0 mL of concentrated HCl to make solution A. Then solution A, 33.3 mg $Na_4P_2O_7$ and 74 mg NH_4F were added to 4.0 mL of 0.33 g mL^{-1} polyglycol (M_w 20000) aqueous solution, followed by the addition of 25% ammonia. The pH value of the solution was then adjusted to 8.0 to obtain solution B. 1.0 mL of 80% hydrazine hydrate was added to 2 mL of 0.33 g mL^{-1} polyglycol aqueous solution to make solution C. Next, solution B was added to solution C under sonication at 60 ^{o}C. After the obtained mixture was further sonicated for about 2 min, and then separated by centrifugation. The deposit was washed with deionized water and ethanol several times. After vacuum drying, the black dendritic Pd was obtained. The NH_4F and $Na_4P_2O_7$ used here act as a ligand and a stabilizer of the solution, respectively.

Electrode modification. Schematic diagram and a digital photo of screen printed electrode (SPE) were shown in Fig. S2. It was fabricated as follows. Firstly the silver ink was screen-printed on a nylon sheet as conductive bands. Then the graphite ink was imprinted to cover the area that served as the working and auxiliary electrode. After that the silver chloride ink was applied onto the area of reference electrode. Finally, the conductive bands were insulated by overlaying an insulating dielectric material except for the area of electric connectors and the three electrodes. The

distance between the working electrode and refer1ence electrode was about 1 mm. 0.3 mg porous tubular palladium nanostructure was dispersed into 0.1 mL water to obtain a suspension of 3 mg mL^{-1} porous tubular palladium nanostructure. 0.8 μL of suspension and 1 μL of 3% PVA solution of ethanol/water (v:v 1:1) were successively dispersed on SPE surface, and allowed to dry under ambient condition for 3 h. After the modified electrode was rinsed with doubly distilled water twice or thrice, the porous tubular palladium nanostructure modified SPE was obtained. Fig. S3 shows a FESEM image of the electrode surface containing Pd nanomaterials. It can be seen that tubular palladium nanostructure has been loaded on the surface of granular graphite (SPE working electrode). The real area of the modified electrode was 0.94 cm^2. The spherical palladium particles modified SPE was prepared in the same way by using spherical palladium particles instead of porous tubular palladium nanostructure.
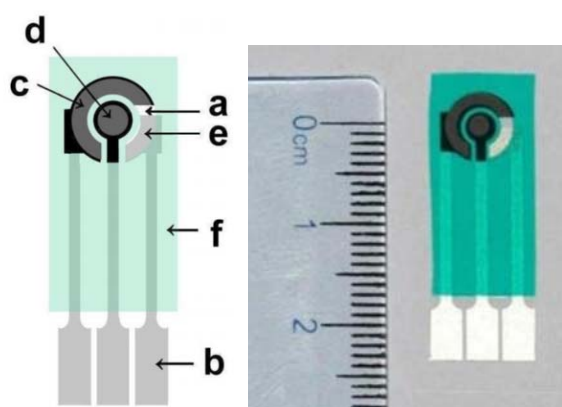

Fig. S2. Schematic diagram (left) and a digital photo (right) of three-electrode SPE system (a) Nylon sheet, (b) silver ink, (c) graphite auxiliary electrode, (d) graphite working electrode, (e) Ag/AgCl reference electrode, (f) insulating dielectric.
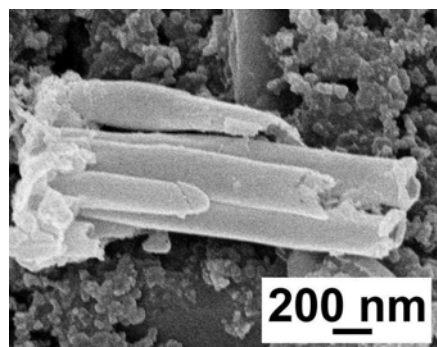

Fig. S3. FESEM image of the electrode surface containing Pd nanomaterials.

Apparatus and measurements. Phase characterization was performed by means of XRD using a D/Max-RA diffractometer with Cu Kα radiation, The morphology and particle sizes of the samples were characterized by JEM-200CX TEM working at 200 kV and LEO1530 VP FESEM at an acceleration of 15 kV. A small amount of the yellow sample was dispersed in ethanol, and then a drop of this solution was deposited on a carbon-coated copper grid for TEM observation. EDS was performed on the FESEM with a PV9100 scanning electron microanalyzer. Nitrogen adsorption-desorption isotherms were obtained using an ASAP 2000 instrument (Micromeritics. Norcross, GA). Cyclic voltammetric and amperometric measurements were performed on CHI 660B electrochemical workstation (CH Instruments, USA). All electrochemical experiments were carried out in a cell containing 5.0 mL of 0.1 M PBS at room temperature (25±2 ^{o}C) and using the modified electrode as the working electrode. The amperometric experiments were carried out by applying a potential of 0.60 V on a stirred cell. The sensor responses were measured as the difference between total and residual currents.

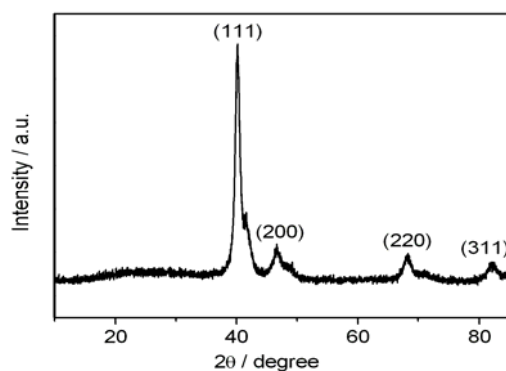## XRD pattern of the palladium nanostructure

Fig. S4. XRD pattern of the palladium nanostructure prepared by the electrodeposition using PAA membrane pre-deposited with CdS as a template.
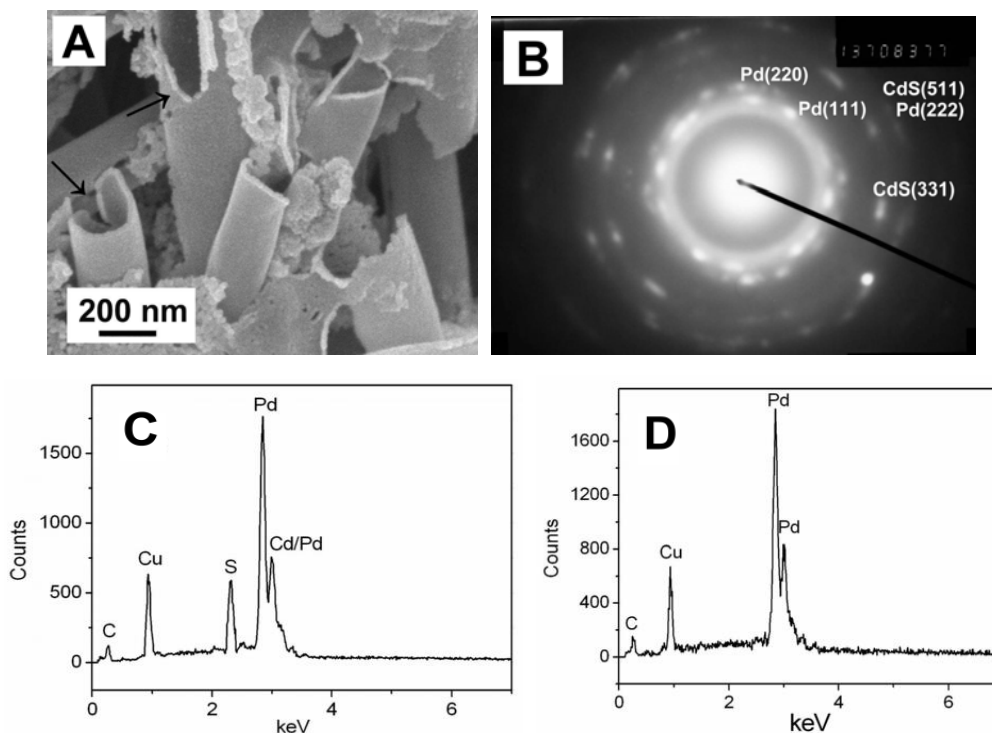
Fig. S5. FESEM (A) images of tubular palladium nanostructure prepared by using PAA as a template *via* pre-deposition of CdS after removal of PAA membrane. SAED (B) of the sample from Fig. 1A in the main text. EDS patterns of tubular palladium nanostructure after removal of PAA membrane (C) and removal of PAA membrane and CdS (D), respectively.

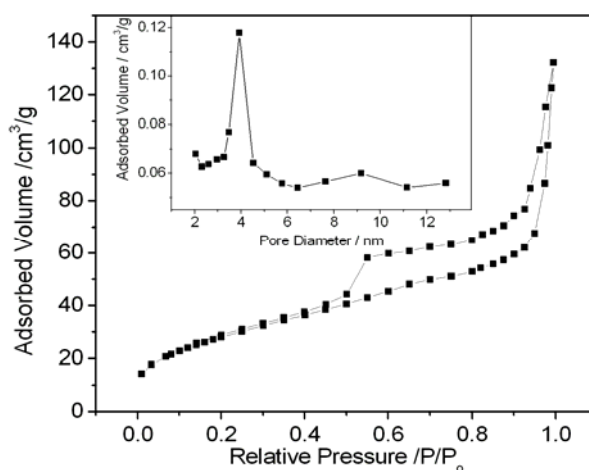## Nitrogen adsorption-desorption isotherms of porous tubular palladium

Fig. S6. Nitrogen adsorption-desorption isotherms of porous tubular palladium. Inset: pore size distribution of porous tubular palladium.
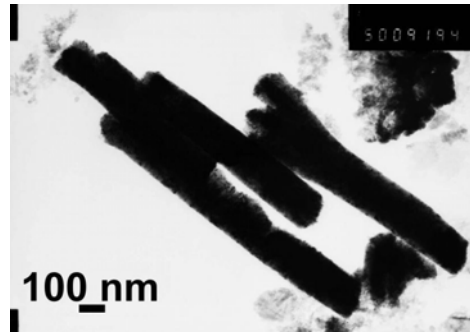
TEM image of the solid palladium nanorods

Fig. S7. TEM image of the solid palladium nanorods obtained by the electrochemical deposition using an unmodified PAA membrane.

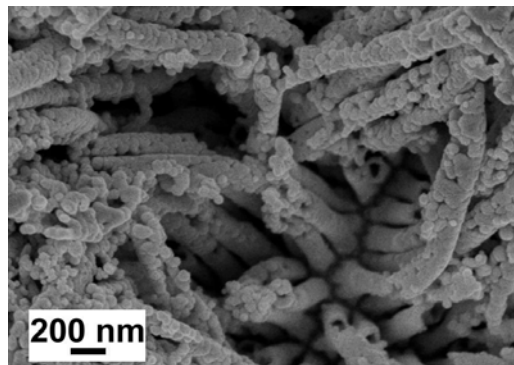## FESEM image of tubular gold nanostructure

Fig. S8. FESEM image of tubular gold nanostructure after removal of the PAA membrane and CdS.

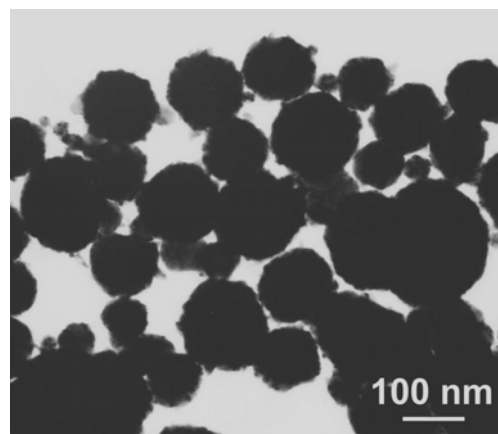## TEM image of the spherical palladium particles

Fig. S9. TEM image of the spherical palladium particles.

Effects of kind of colloid, pH of PBS, the applied potential and the amount of palladium nanostructure on amperometric responses

To know the performance of the sensor, various factors influencing the response of the sensor were investigated, including the kind of colloid, pH of PBS, the applied potential and the amount of palladium nanostructure covered on the surface of the working electrode. To investigate the effect of colloid on the response of the sensor, PVA, the performances from Nafion and chitosan were evaluated. It was found that the performance of PVA was better than those from Nafion and chitosan. PVA is a kind of polymer which can prevent the adsorbed nanomaterials from leaking out of the sensor. It is also of porous structure which glucose can penetrate the PVA membrane and have electron exchange with Pd nanomaterials. 0.8 µL of Pd nanomaterials suspension and 1 µL of 3% PVA solution of ethanol/water (v:v 1:1) was the optimum ratio to reach the maximum response. When the amount of PVA was less, the response of the sensor was small because some adsorbed Pd nanomaterials leaked out of the sensor. While the amount of PVA was large, the response of the sensor also became small. The possible reason might be that the membrane of the modified electrode was thick, inhibiting the diffusion of glucose. The influence of pH on the responses of the sensor was illustrated in Fig. S10A. The response of the oxidation of glucose increased with the increase of pH value. When the pH was 8.1, the response current reached maximal value. The effect of the applied potential on the response of the oxidation of glucose was illustrated in Fig. S10B. When the applied potential increased from 0.4 to 0.6 V, the current increased and did not change when the potential was more positive than 0.6 V. The influence of the amount of the palladium nanostructure covered on the surface of electrode was illustrated in Fig. S10C. It showed that the response of the oxidation of glucose was the highest when the amount of palladium nanostructure was 0.8 µL (the concentration of 3 mg mL^{-1}). When the electrode was prepared with 0.7 µL or less than 0.7 µL of palladium nanostructure, the current of the electrode was small because the amount was less and the sensor could not reach the maximal response. While the electrode was prepared with 0.9 µL or more than 0.9 µL of palladium nanostructure, the current of the electrode became small. The possible reason might be that the membrane of the modified electrode was thick, inhibiting the diffusion of glucose to the electrode surface. Therefore, 0.1 M pH 8.1 PBS at 0.6 V and 0.8 µL palladium nanostructure covered on the surface of the working electrode were chosen as the detection solution of glucose.
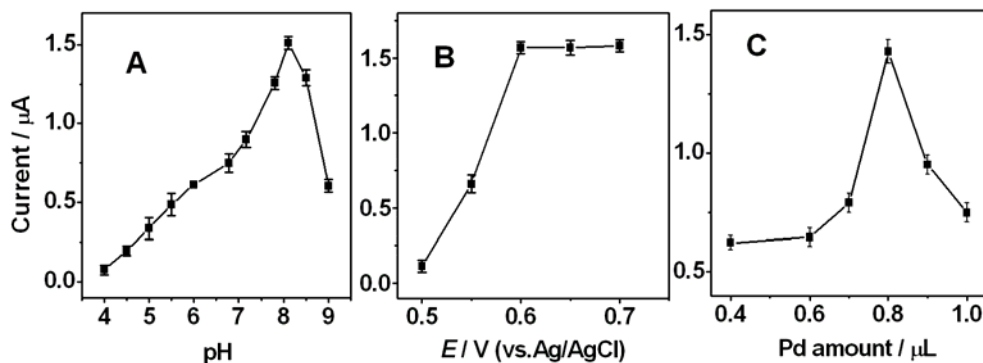
Fig. S10. Effects of the pH (A), applied potential (B) and palladium nanostructure volume (the concentration of 3 mg mL^{-1}) (C) in PBS in the presence of 0.6 mM glucose of porous tubular palladium modified SPE and keeping other conditions constant.

The interferences

Table S1. The interferences to glucose oxidation

Substrate	Response current (μA)
glucose (1 mmol L^{-1})	1.991
ascorbic acid (0.1 mmol L^{-1})	0.069
uric acid (0.1 mmol L^{-1})	~ 0
p-acetamidophenol (0.1 mmol L^{-1})	~ 0

Notes and references

1 J. C. Bao, D. P. Xu, Q. F. Zhou, Z. Xu, Y. Y. Feng and Y. M. Zhou, *Chem. Mater.* 2002, **14**, 4709.
2 P. Zhou, Z. H. Dai, M. Fang, X. H. Huang and J. C. Bao, *J. Phys. Chem. C* 2007, **111**, 12609.