# Supporting Information

## 3D Nanoporous Ag@BSA Composite Microspheres As Hydrogen Peroxide Sensor

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### Experimental section

*Reagents and materials*

Silver nitrate ($AgNO_3$), hydrogen peroxide ($H_2O_2$, 30 wt% solution) and Ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent. Co. Bovine serum albumin (BSA) was obtained from MPbio. (Cat No:0218054980, standard grade). All chemicals were used without further purification. Ultrapure water was used throughout the whole experiments. Phosphate buffer saline (PBS, pH =7.4) was prepared by mixing stock solutions of $NaH_2PO_4$ and $Na_2HPO_4$.

*Synthesis and characterization of porous Ag@BSA microspheres*

The porous Ag@BSA microspheres were prepared by reducing $AgNO_3$ with AA in the presence of BSA. Typically, 50 mg of BSA was added into 10 mL water in a 50 mL beaker under vigorous stirring. The solution was heated to 60 ℃ in the water-bateh, and then 10 mL of 10 mM $AgNO_3$ was rapidly injected into the solution and the

mixture became milky white. Subsequently, 50 mg AA was added into the solution and the mixture turned black. The reaction was carried out at 60 ℃ for 30 min. The as-prepared product was collected by centrifugation. The precipitate was redispersed in water and stored at 4 ℃ for characterization and use. Scanning electron microscopy (SEM) measurements were made on a FESEM:ZEISS scanning electron microscope at an accelerating voltage of 5 kv. Energy dispersive spectrometry (EDS) analysis was performed using a Bruker AXS Quantax spectrometer attached to the SEM microscope. Fourier Transform infrared (FTIR) spectrophotometer measurement was recorded with a Bruker EQUINOX 55 FTIR spectrometer in the wavenumber range of 4000–400 $cm^{-1}$.

*Preparation of the $H_2O_2$ sensor*

To prepare the Ag@BSA/Au electrodes, 3 μL each Ag@BSA suspension was dropped onto an Au disk electrode (0.1 $cm^2$) and dried in a vacuum aspirator at room temperature for 24 h. The electrodes were washed with DI water before use.

*Electrochemical measurements*

Electrochemical experiments were carried out at room temperature and performed using a CHI 660D electrochemical workstation (CH instruments Co., Shanghai). A standard three-electrode system was used, including an Au electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire auxiliary electrode. The bare Au electrode was polished with 0.3 and 0.05 μm aluminum oxide slurries respectively and ultrasonically cleaned with ethanol and double distilled water for 10 min to remove contamination. Cyclic voltammetric measurements were performed in $N_2$-saturated 0.5 M PBS buffer (pH=7.4) at a scanning rate of 0.02 V $s^{-1}$.

**Table S1.**

Table S1. Comparison of detection limit for hydrogen peroxide sensor.

| Authors | Materials | Detection limit | References |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Cui et. al. | Ag nanoparticles | 1.7 μM | 1. |
| Zhao et. al. | Ag microspheres | 1.2 μM | 2. |
| Tian et.al. | Ag nanoparticle/Polymer | 4.7 μM | 3. |
| Song et.al. | Ag nanoparticle/Collagen | 0.7 μM | 4. |
| Liu et. al. | 3D nanoporous Ag@BSA | 0.16 μM | In this work |

Table S2. Determination of $H_2O_2$ in various water samples. To evaluate the potential of 3D porous Ag@BSA electrode for $H_2O_2$ detection in real samples as referee suggested, one possible real application in water analysis with various water sources was attempted. Different water samples such as drinking water, tap water and river water containing certain concentration of $H_2O_2$ were detected by 3D porous Ag@BSA using the electrochemical method presented in the manuscript. The detection results showed in Table S1. It indicates that even in real water samples 3D porous Ag@BSA electrode exhibited good selectivity with a reasonable deviation lower than 10%.

**Table S2** Determination of $H_2O_2$ in various water samples

| Samples | Sample No. | Added (mM) | Found (mM) | Recovery (%) | Deviation (%) |
|---|---|---|---|---|---|
| Drinking | 1 | 0.1 | 0.102 | 102.0 | 2.0 |
| water | 2 | 0.15 | 0.156 | 104.0 | 4.0 |
| | 3 | 0.2 | 0.207 | 103.5 | 3.5 |
| Tap water | 1 | 0.1 | 0.108 | 108.0 | 8.0 |
| | 2 | 0.15 | 0.161 | 107.3 | 7.3 |
| | 3 | 0.2 | 0.219 | 109.5 | 9.5 |
| River | 1 | 0.1 | 0.106 | 106.0 | 6.0 |
| water | 2 | 0.15 | 0.157 | 104.6 | 4.6 |
| | 3 | 0.2 | 0.214 | 107.0 | 7.0 |

**Fig. S1.** The contact angle image of 3D nanoporous Ag@BSA microspheres. The average angle is 46.1°, showing that the 3D nanoporous Ag@BSA microspheres are hydrophilic.

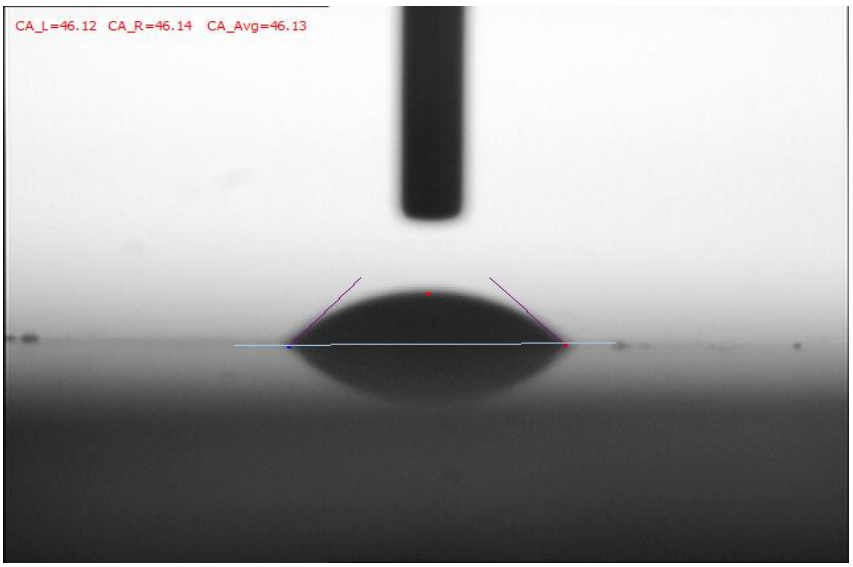



**Fig. S2.** Amperometric responses of 3D nanoporous Ag@BSA microspheres in PBS (pH=7.4) toward 0.1Mm $H_2O_2$, and then 1 mM ethanol, 1 mM methanol, 0.5 mM glucose and 0.2 mM ascorbic acid at -0.6 V vs. SCE(B).

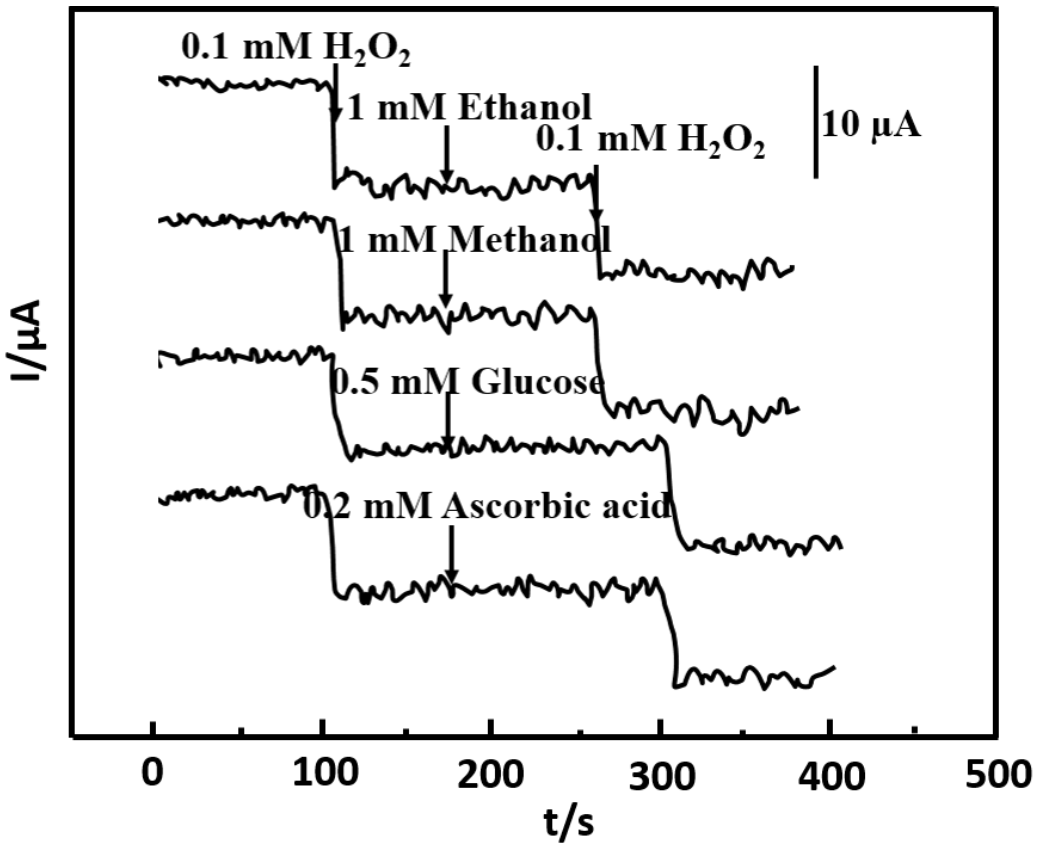
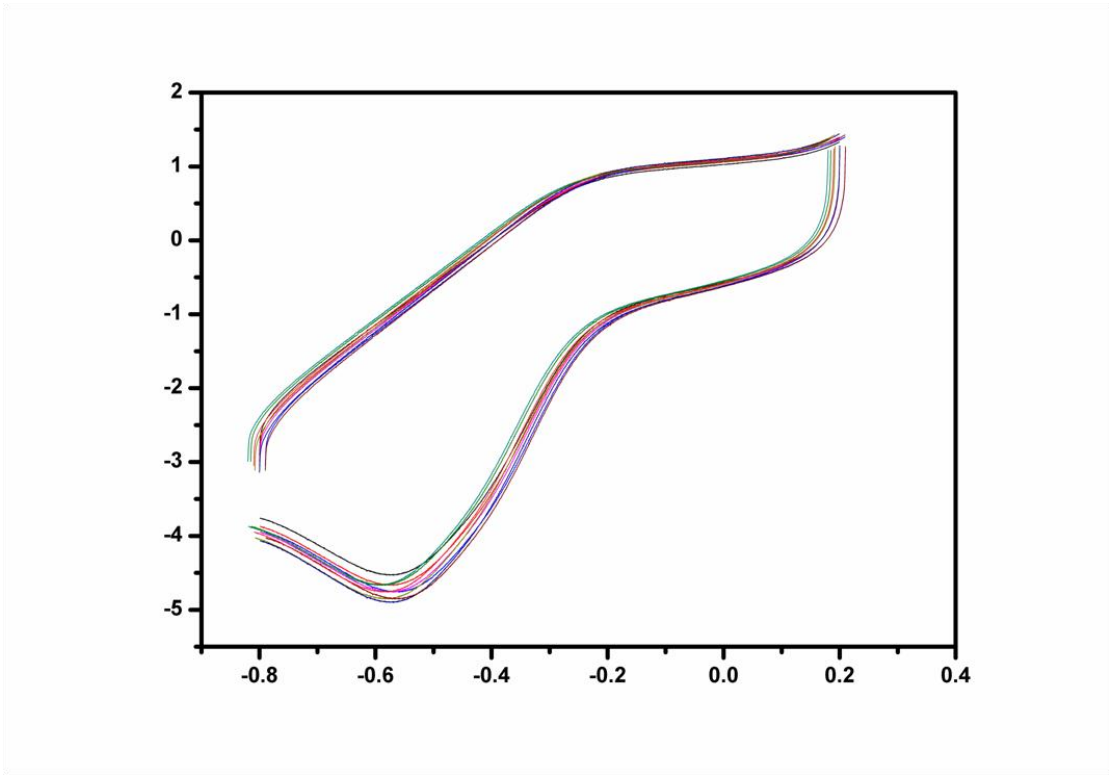



**Fig. S3.** Cyclic voltammetries of 10 equivalent 3D nanoporous Ag@BSA electrodes measured in 0.1 M $H_2O_2$ and 0.5 M PBS (pH=7.4) solution at 50 mV $s^{-1}$.




**References**

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