

Supporting Information for

A novel solid-state electrochemiluminescence sensor for the determination of hydrogen peroxide based on an AuNCs@BSA-silica nanoparticle nanocomposite

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1. Materials and reagents

N-(3-dimethylamino-propyl)-N-ethyl carbodiimidehydrochloride (EDC), Tetraethyl orthosilicate (TEOS), (3-aminopropyl)trimethoxysilane and N-hydroxysulfosuccinimide (sulfo-NHS) were purchased from Sigma-Aldrich; bovine serum albumin (BSA) was ordered from Sangon Biotech Co., Ltd.; chloroauric acid (HAuCl₄), hydrogen peroxide (H₂O₂) and NaBH₄ (96%) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received without further purification. Ultra-pure water with a resistivity of 18.2 MΩ·cm obtained from a Millipore purification system (Millipore, Bedford, MA, USA) was used for the experiments.

2. Instruments and Characterization

Fluorescence spectra were recorded with an F-4500 spectrophotometer (Hitachi, Japan); scanning electron microscope (SEM) images were taken using an S-4800 (Hitachi, Japan); transmission electron microscope (TEM) images were collected using a TECNAI F-30 (Philips-FEI, Netherlands); cyclic voltammograms (CV) were recorded with a CHI 660B electrochemical analyzer (ChenHua Instrument, Shanghai, China) using the conventional three-electrode configuration of a modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode; and an Ag/AgCl reference electrode and a Pt foil as reference and auxiliary electrodes, respectively. ECL experiments were carried out on a set-up consisting of a CHI 660B workstation (Shanghai Chenhua Instruments, China) and an IFFM-D FIA Luminescence Analyzer (Ruimai Co., China). The ECL signal was detected and recorded using an IFFM-D flow injection chemiluminescence analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd., China) with a PMT controlled by a personal computer. The PMT was set at 900 V and electrons were multiplied by a factor of 2 in the process of luminescence detection. A homemade electrochemical cell comprising a traditional three-electrode system with a 3 mm GCE as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl as the reference electrode, was used. All potentials in this work refer to the Ag/AgCl reference electrode.

3. Synthesis of AuNCs@BSA

The synthesis of AuNCs@BSA is the same as in previous work.^{S1} In brief, 250 mg BSA was dissolved in 9 mL water and mixed with 1 mL HAuCl₄ solution (the concentration of Au, 0.02 g/mL). After reacting at 37 °C for 0.5 h, 0.5 mL of 1 M NaOH was added to the above solution and stirred for 12 h. The AuNCs@BSA solution was purified via dialysis using a 5000 Da MWCO dialysis bag.

4. Preparation of the AuNCs@BSA-silica NPs modified GCE

The synthesis of the silica core refers to a typical Stöber method with slight modification.^{S2} Solution A was prepared by adding 10 mL ethanol and 0.8 mL ammonia to a proper round-bottom flask. This solution was agitated vigorously for 10~15 min using a magnetic stirrer. Solution B was prepared in a beaker by dissolving 0.75 mL of TEOS in 2.56 mL absolute ethanol. Solution B was loaded into solution A slowly while vigorous stirring was maintained. The reaction was allowed to proceed at room temperature for 23 h.

To modify the silica surface with amino groups, 25 μL APTMOS was added to the above

solution and it was stirred for another 1 h. After the reaction, the prepared sample was centrifuged at 13000 rpm for 10 min to collect the silica cores. The cores were further washed with ethanol and ultra-pure water by centrifugation and decantation several times to remove the unreacted chemicals. The obtained silica particles were dispersed in 2 mL ultra-pure water and stored in a refrigerator before use.

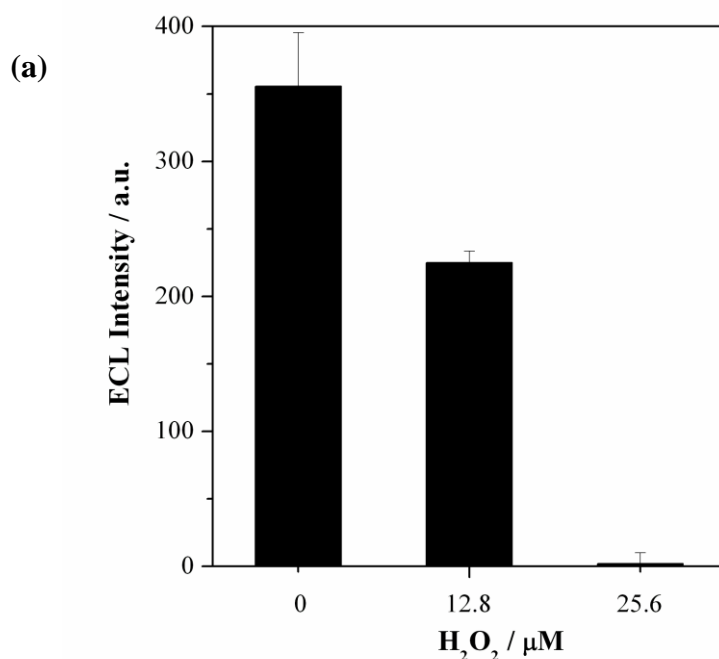
AuNCs@BSA (1 mL, 100 μ M), 2.6 mg EDC and 2.6 mg NHS were added into the obtained silica NPs/water solution (2 mL). The reaction was allowed to proceed at room temperature for 8 h. After the reaction, the solution was centrifuged at 13000 rpm for 8 min to collect the AuNCs@BSA-silica NPs composite. The composite was further washed with ultra-pure water by centrifugation and decantation several times. Finally, the obtained AuNCs@BSA-silica NPs composite was dispersed in 2 mL ultra-pure water and stored in a refrigerator before use.

A 3 mm diameter GCE (CH Instruments, China) was polished with 1.0, 0.3 and 0.05 μ m α -Al₂O₃ powder, together with rinsing and sonication with ultra-pure water successively. After the polishing step, the GCE was rinsed with anhydrous ethanol, and dried in nitrogen flow before each experiment.

After sonication for 10 min, the AuNCs@BSA-silica NPs composite was diluted 10-fold and then mixed with 5% Nafion solution (V/V %=50:50). 5 μ L of the final solution was dropped onto the clean GCE surface and allowed to air dry at room temperature.

5. Study of the solid-state ECL sensor based on AuNCs@BSA modified GCE

Two solid-state ECL sensors were fabricated. 10 μ L AuNCs@BSA with different concentrations (0.01 μ M; 0.1 μ M) was mixed with 10 μ L 5% Nafion solution. Then 5 μ L of the above solution was dropped onto the clean GCE surface and allowed to air dry at room temperature. The performance of solid-state ECL sensors based on the AuNCs@BSA modified GCE was investigated.



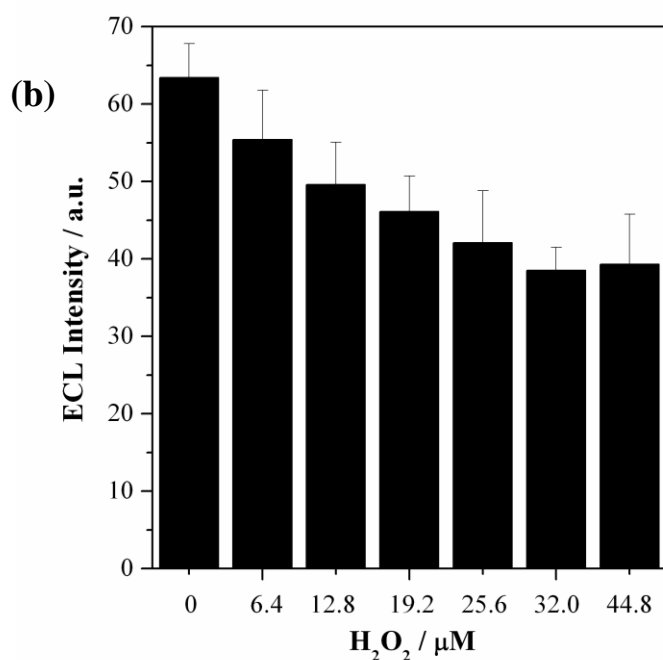


Fig. S1 Relationship of the fabricated solid-state ECL sensor to (a) 0.01 and (b) 0.1 μM AuNCs@BSA, with different concentrations of H_2O_2 .

Without immobilization and distribution on the surface of the silica nanoparticles, the responses of the AuNCs@BSA modified ECL sensors to H_2O_2 were quite diverse. As shown in Fig S1 (a), when the lower concentration of AuNCs@BSA was used, the ECL signal was vulnerable and dramatically decreased with increasing concentration of H_2O_2 . On the other hand, the behavior (Fig S1 (b)) of the solid-state sensor fabricated with a higher dosage of AuNCs@BSA was different. The ECL intensity was small and displayed slow changing with H_2O_2 . These results indicated that the silica nanoparticles not only served as the carrier for the AuNCs@BSA, but also could adjust the response of AuNCs@BSA to H_2O_2 , resulting in a reasonable behavior during determination.

6. References

- [S1] J. Xie, Y. Zheng and J. Y. Ying, *J. Am. Chem. Soc.*, 2009, **131**, 888.
[S2] J. H. Zhang, P. Zhan, Z. L. Wang, W. Y. Zhang and N. B. Ming, *J. Mater. Res.*, 2003, **18**, 649.