Electronic Supplementary Material

N-(aminobutyl)-N-(ethylisoluminol) functionalized gold nanoparticles on cobalt disulfide nanowires hybrids for non-enzymatic chemiluminescence detection of $H_2O_2$

Qiuju Zhu,$^{a,b}$ Jianshe Huang,$^b$ Mengxia Yan,$^{a,b}$ Jing Ye$^{a,b}$, Dewen Wang,$^{a,b}$ Qingqing Lu$^{b,c}$ and Xiurong Yang*$^{a,b}$

$^a$ Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

$^b$ State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China

$^c$ University of Chinese Academy of Sciences, Beijing 100049, China

* Corresponding author. Tel.: +86 431 85262056; fax: +86 431 85689278. E-mail address: xryang@ciac.ac.cn
Experimental section

**Materials:** N-(aminobutyl)-N-(ethylisoluminol) was obtained from TCI (Japan). A stock solution of ABEI (4 mM) was prepared by dissolving ABEI in NaOH solution (0.1 M) and was kept at 4 °C. Sodium sulfide nonahydrate (Na₂S·9H₂O) was purchased from Xilong Chemical Co., Ltd. Zinc(II) chloride (anhydrous, 99.9%, Aldrich), copper(I) chloride (Cu₂Cl₂·6H₂O, 97%, Loba Chemie), iron(III) acetylacetone (97%, Aldrich), oleylamine (OLA, technical grade, 70%, Aldrich), sulfur (100 mesh, Aldrich), 1-octadecene (ODE, technical grade, 90%, Aldrich), oleic acid (OA, technical grade, 90%, Aldrich). Copper nitrate, absolute ethanol, Chloroaauric acidtetrahydrate (HAuCl₄·4H₂O), Cobalt(II) sulfate heptahydrate (CoSO₄·7H₂O), glycerol, urea and so on were purchased from Beijing Chemical Corp. All other reagents were of analytical grade. The water used throughout all experiments was purified through a Millipore system.

**Prepare Co(CO₃)₀.₅(OH)·0.₁₁H₂O nanowires:**
Co(CO₃)₀.₅(OH)·0.₁₁H₂O nanowires (NWs) were prepared by hydrothermal synthesis. 0.56 g CoSO₄·7H₂O and 0.1 g urea were dissolved in ca.40mL of a glycerol 20% (v/v) aqueous solution in a 50 mL PEEK-lined stainless-steel autoclave. The autoclave was heated at 170 °C for 24 h in a ventilated forced-air convection oven. The precipitate was collected by centrifugation and washed with water and ethanol several times and further dried at 60 °C.

**Prepare CoS₂ NWs:**
0.24g Na₂S·9H₂O was dissolved in 40 mL of deionized water, and then the production of Co(CO₃)₀.₅(OH)·0.₁₁H₂O NWs were added into above solution. The ultimate mixture was transferred to a 50 ml Teflon-lined stainless autoclave and maintained at 150 °C for 6 h in an electric oven. After the autoclave cooled down slowly at room temperature, the precipitate was collected by centrifugation and washed with water and ethanol several times and further dried at 60 °C.

**Prepare ABEI/AuNPs/CoS₂ NWs:**
AuNPs decorated CoS₂ nanocomposite was synthesized by a facile one-step microwave assisted method. A 555 μL of 4 mmol/L ABEI stock solution was mixed well with 5 mL of CoS₂ NWs (0.05 mg/mL) suspension and then 100 μL of 6 mM HAuCl₄ stock solutions were added rapidly into a 20 mL quartz tube under vigorous stirring. After 5 min, the vial was sealed and heated in a domestic microwave oven (Galanz P70F23P-G5) equipped with a 700 W magnetron operating at 2450Hz for 2 min. The resulting solution was centrifuged twice at a speed of 10000 rpm for 15 min to remove residual ABEI and HAuCl₄. Finally, ABEI/AuNPs/CoS₂ NWs were re-dispersed and diluted 1000 times.

**Prepare ABEI/CoS₂ NWs:**
A 555 μL of 4 mmol/L ABEI stock solution was mixed well with 5 mL of CoS₂ NWs (0.05 mg/mL) suspension and then 100 μL H₂O₂ were added rapidly into a 20 mL quartz tube under vigorous stirring. After 5 min, the vial was sealed and heated in a domestic microwave oven (Galanz P70F23P-G5) equipped with a 700 W magnetron operating at 2450Hz for 2 min. The resulting solution was centrifuged twice at a speed of 10000 rpm for 15 min to remove residual ABEI. Finally, ABEI/CoS₂ NWs were re-dispersed and diluted 1000 times.
**Prepare ABEI/AuNPs**:
A 7 mL portion of 6 mM HAuCl$_4$ stock solution was mixed with 45 mL ultrapure water. 5 mL of 4 mmol/L ABEI stock solutions were added rapidly under vigorous stirring, the mixture was stirred for 2 hours at room temperature. Then another 6 mL portion of HAuCl$_4$ stock solution was added and the reaction was kept on for another 2 hours, during which a color change from yellow to black to purple was observed before a wine-red color was reached, then stored at 4 °C. The resulting solution was centrifuged twice at speed 10000 rpm for 15 min to remove residual ABEI and HAuCl$_4$. Finally, ABEI/AuNPs were dispersed.

**Prepare CuS$_3$ and ABEI/AuNPs/CuS**:
In a typical synthesis, 0.25 mmol Cu(NO$_3$)$_2$·3H$_2$O and 0.5 mmol sulfur powder were added into a 20 ml Teflon-lined stainless steel autoclave. Then 16 ml absolute ethanol was added with vigorous stirring. The autoclave was maintained at 180 °C for 12 h and then cooled naturally to room temperature. Finally, the black precipitates were centrifuged and washed with water and ethanol three times and dried under vacuum at room temperature. For comparison, ABEI/AuNPs/CuS was synthesized and diluted under identical conditions except the replacement of CoS$_2$ NWs with CuS.

**Prepare CuZnFeS$_4$ and ABEI/AuNPs/CuZnFeS**:
Syntheses have been carried out according to literature. In a typical synthesis, 0.1 mmol copper(I) chloride, 0.1 mmol zinc (II) chloride, 0.1 mmol iron (III) acetylacetonate, 0.5 mL of oleylamine (OLA), 0.5 mL of oleic acid (OA) and 6 mL of 1-octadecene (ODE) were taken in a three necked round-bottom flask and degassed with nitrogen at 120 °C for 30 minutes to remove the moisture and oxygen. The reaction system was then slowly heated to 200 °C and 0.6 mmol sulfur dissolved in 3 mL ODE was quickly injected into the reaction system. Upon injection of sulfur, the reaction solution immediately turned into magenta black color indicating the rapid formation of the CZIS NCs. The reaction was stopped after 2 minutes by removing the heating mantle and slowly cooled down to room temperature. The as-prepared NCs were purified by several cycles of precipitation–dispersion using chloroform and ethanol. The synthesized CZIS NCs were dried and stored in powder form for further characterization. For comparison, ABEI/AuNPs/CuZnFeS was synthesized and diluted under identical conditions except the replacement of CoS$_2$ NWs with CuZnFeS.

**Microwave safety instructions**
1. Apart from professional maintenance personnel, do not disassemble microwave oven to prevent electric shock.
2. A metal bar cannot be used to probe the interlock switch at the front of the furnace chamber.
3. It is impossible to exert too much reverse force on the furnace door, which may lead to deformation of the furnace door and microwave leakage.
4. Keep the environment clean inside the furnace cavity.
5. When the microwave oven is installed and used, it must be grounded and ventilated environment.
6. When using the microwave, please close the oven door and stand farther away.
7. Seal well with heat-resistant glassware and take out carefully after heating to avoid burns.

**Characterizations**: Scanning electron microscopy (SEM) measurements were performed on a
XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) and high-resolution TEM images of ABEI/AuNPs/CoS$_2$ NWs were made on a JEM-2000 FX (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. The transmission electron microscopy (TEM) images of Co(CO)$_3$$_0.5$(OH)$·0.11$H$_2$O nanowires and CoS$_2$ NWs were obtained by H-600 (Hitachi, Tokyo, Japan) with an accelerating applied potential of 100 kV. Energy-dispersive X-ray spectroscopy (EDS) analysis and elemental mapping of the material was performed along with TEM. ABEI/AuNPs/CoS$_2$ NWs were decorated on Si substrates. XPS measurements were measured on an ESCALABMK II X-ray photoelectron spectrometer using Al K$_\alpha$ as the exciting source. X-ray powder diffraction (XRD) patterns of the various samples were recorded using a D8-Advance system (Bruker, Germany) with Cu K$_\alpha$ radiation ($\lambda=0.154$nm). UV-vis absorption characterization was performed on a Cary 50 Scan UV–vis spectrometer (Varian, USA) with a fused-silica cuvette.

**CL measurements:** CL measurements were carried out on a BMG LABTECH microplate reader (Lumi STAR, Germany). The assay is carried out using the following parameters: Gain 3600, well mode, No.of intervals=50, Measurement interval time=0.1s, Interval time=0.2s, Total Measurement time/well=10s, Time to normalize the results=0s, Measurement start time=0s, Injection time=2s. Reaction conditions: 100 $\mu$L of 10 mM H$_2$O$_2$ in 0.01 M NaOH was injected into 100 $\mu$L aqueous solution.
Fig. S1 XRD pattern of CoS$_2$ NWs.

Fig. S2 (A) SEM and (B) TEM image of Co(CO$_3$)$_{0.5}$(OH)$\cdot$0.11H$_2$O. (C) SEM and (D) TEM image of CoS$_2$ NWs.
Fig. S3 The size distribution histogram of Au nanoparticles measured on 80 particles from the TEM image of ABEI/AuNPs/CoS$_2$ NWs.

Fig. S4 (A) EDX elemental mapping of N, C and O for ABEI/AuNPs/CoS$_2$ NWs. (B) EDX spectrum of ABEI/AuNPs/CoS$_2$NWs.
Fig. S5 UV-Visible absorption spectra of (a) CoS$_2$ NWs, (b) ABEI/CoS$_2$ NWs, (c) ABEI/AuNPs/CoS$_2$ NWs, and (d) ABEI.

Fig. S6 The deconvolution of high-resolution Co 2p and S 2p XPS spectra in CoS$_2$ NWs (A, B), and ABEI/AuNPs/CoS$_2$ NWs (C, D).
Fig. S7 (A) CL kinetic curves of ABEI/AuNPs/CoS$_2$ NWs synthesized using different volume (0-1000 μL) of 6mM HAuCl$_4$. (B) The plot of CL intensity as a function of HAuCl$_4$ volume. (C) Effect of pH of H$_2$O$_2$ solution on CL response of ABEI/AuNPs/CoS$_2$ NWs. Reaction conditions: 100 μL of a 10mM H$_2$O$_2$ in B-R buffer (pH 9-11.58) and NaOH solution (pH 12.0-13.0) was injected into 100 μL ABEI/AuNPs/CoS$_2$ NWs water dispersion in a microwell.

With the increasing amount of HAuCl$_4$, the CL intensity firstly increases, and then it decreases due to the occupied active sites of CoS$_2$ NWs (Fig. S7A&B, ESI †). Finally, 100 μL of 6 mM HAuCl$_4$ was chosen as optimized conditions. Then, the pH effect of H$_2$O$_2$ was further researched. Fig. S7C (ESI †) shows the effect of 1mM H$_2$O$_2$ with different pH values on CL signal. The CL intensity increases sharply with increasing pH, due to more intermediate radicals produced at high pH. Then CL signal decreases because strong alkaline environment has an impact on the coagulation of materials. Therefore, pH 12 was select as optimized conditions for the CL reaction.

Fig. S8 TEM image of (a) CuS, (b) ABEI/AuNPs/CuS.
Fig. S9 TEM image of (a) CuZnFeS, (b) ABEI/AuNPs/CuZnFeS.

Fig. S10 XRD pattern of CuS.

Fig. S11 XRD pattern of CuZnFeS.
Fig. S12 CL kinetic curves of (a) ABEI/AuNPs/CuZnFeS, (b) ABEI/AuNPs/CuS, (c) ABEI/AuNPs/CoS$_2$ NWs. Inset: Magnification curves of a and b.

Fig. S13 (A) CL kinetic curves of ABEI/AuNPs/CoS$_2$ NWs under oxygen-saturated, air-saturated and nitrogen-saturated. CL kinetic curves of ABEI/AuNPs/CoS$_2$ NWs in the absence and different concentrations of (B) SOD and (C) Thiourea.

Figure S14 Relative CL intensity response of the proposed method for interferents (10 μM).

Reaction conditions: 100μL 10 μM H$_2$O$_2$ (pH 12.0) was injected into 100 μL ABEI/AuNPs/CoS$_2$ NWs solution, including various interferents. Relative CL intensity=(I$_{\text{Blank}}$-I$_{\text{CL}}$)/I$_{\text{Blank}}$ *100%
Table S1. Comparison of Existing non-enzymatic method detection of $\text{H}_2\text{O}_2$.

<table>
<thead>
<tr>
<th>methods</th>
<th>materials</th>
<th>linear range (μM)</th>
<th>detection limit(μM)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemically modified electrodes</td>
<td>silver–polyaniline nanotube</td>
<td>100–90000</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>chemically modified electrodes</td>
<td>PAA/AuSPE</td>
<td>50–500</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>chemically modified electrodes</td>
<td>Nafion/E3GO/Co3O4/GC</td>
<td>1–100</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>colorimetry</td>
<td>Gold nanoparticles</td>
<td></td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>FIA- chemiluminescence</td>
<td>luminol–Cu2+</td>
<td>1-200</td>
<td>0.5</td>
<td>7</td>
</tr>
<tr>
<td>chemiluminescence</td>
<td>CTAB–CNSs</td>
<td>5–1000</td>
<td>2.6</td>
<td>8</td>
</tr>
<tr>
<td>chemiluminescence</td>
<td>MIL-101(Cr)</td>
<td>3–100</td>
<td>0.5</td>
<td>9</td>
</tr>
<tr>
<td>chemiluminescence</td>
<td>ABEI/AuNPs/CoS2 NWs</td>
<td>1-100</td>
<td>0.3</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table S2. Determination of $\text{H}_2\text{O}_2$ concentration in tap water.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>added (μM)</th>
<th>found (μM)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10.4 ± 1.26</td>
<td>104.0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>9.6 ± 0.58</td>
<td>96.0</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>9.7 ± 2.13</td>
<td>97.0</td>
</tr>
</tbody>
</table>

Mean ± SD of three measurements.

Table S3. Determination of $\text{H}_2\text{O}_2$ concentration in human serum samples.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>added (μM)</th>
<th>found (μM)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>9.02± 0.0057</td>
<td>90.2</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>9.62 ± 0.0072</td>
<td>96.2</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>9.87 ± 0.0058</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Mean ± SD of three measurements. The samples were progressively diluted 100000 times with 0.01 M PBS before the assay.

References

