Electronic Supplementary Material

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

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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 ($Na_2S\cdot 9H_2O$) was purchased from Xilong Chemical Co., Ltd. Zinc(II) chloride (anhydrous, 99.9%, Aldrich), copper(I) chloride ($Cu_2Cl_2\cdot 6H_2O$, 97%, Loba Chemie), iron(III) acetylacetonate (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, Chloroauric acidtetrahydrate ($HAuCl_4\cdot 4H_2O$), Cobalt(II) sulfate heptahydrate ($CoSO_4\cdot 7H_2O$), 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 $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ nanowires:

$Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ nanowires (NWs) were prepared by hydrothermal synthesis. 0.56 g $CoSO_4\cdot 7H_2O$ 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 CoS_2 NWs[1]:

0.24g $Na_2S\cdot 9H_2O$ was dissolved in 40 mL of deionized water, and then the production of $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ 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/CoS_2 NWs:

AuNPs decorated CoS_2 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 CoS_2 NWs (0.05 mg/mL) suspension and then 100 μL of 6 mM $HAuCl_4$ 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 $HAuCl_4$. Finally, ABEI/AuNPs/CoS_2 NWs were re-dispersed and diluted 1000 times.

Prepare ABEI/CoS_2 NWs:

A 555 μL of 4 mmol/L ABEI stock solution was mixed well with 5 mL of CoS_2 NWs (0.05 mg/mL) suspension and then 100 μL H_2O_2 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/CoS_2 NWs were re-dispersed and diluted 1000 times.

Prepare ABEI/AuNPs[2]:

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 ºC. 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 $Cu (NO_3)_2$ $3H_2O$ 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 $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ 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 Kα 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 Kα radiation (λ=0.154nm). 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 μL of 10 mM H_2O_2 in 0.01 M NaOH was injected into 100 μL aqueous solution.

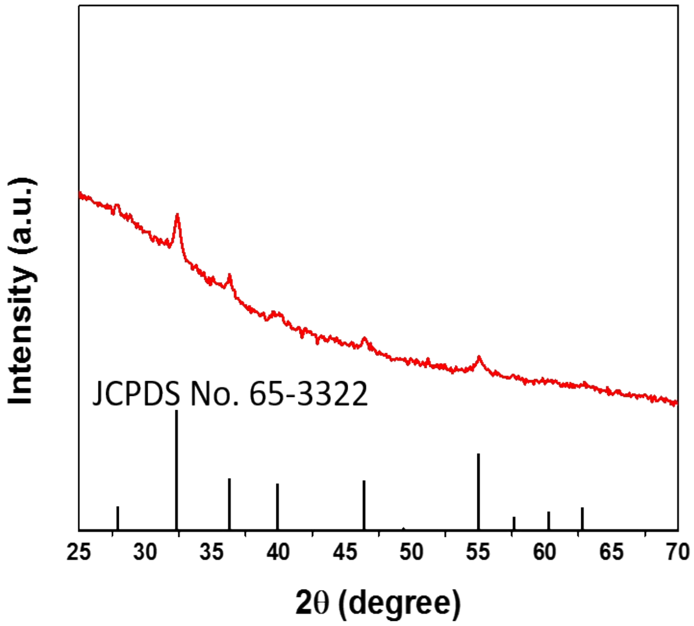


Fig. S1 XRD pattern of CoS_2 NWs.

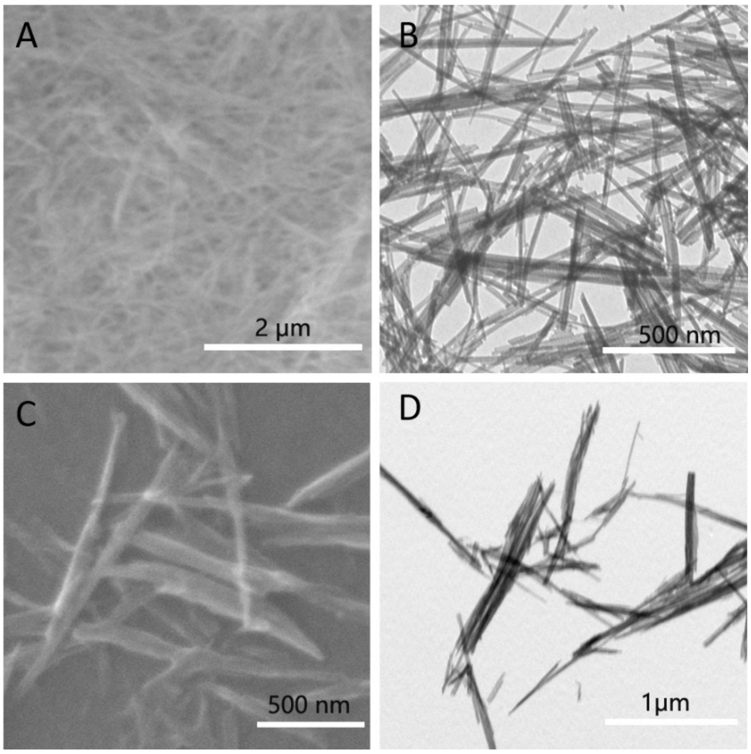


Fig. S2 (A) SEM and (B) TEM image of $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$. (C) SEM and (D) TEM image of CoS_2 NWs.

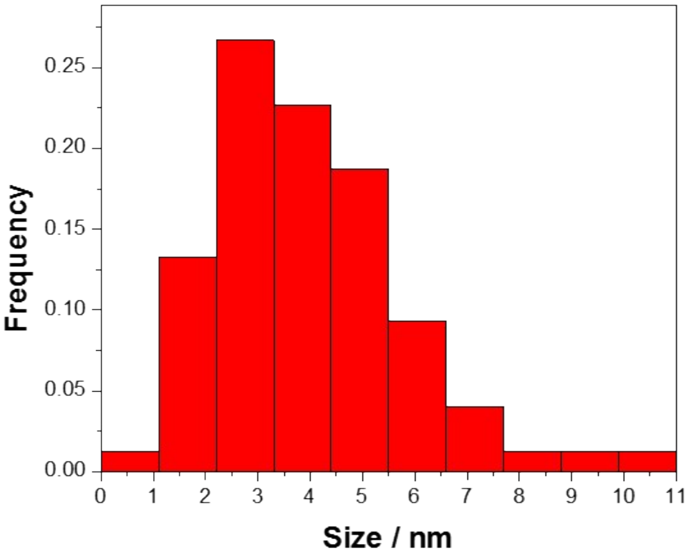
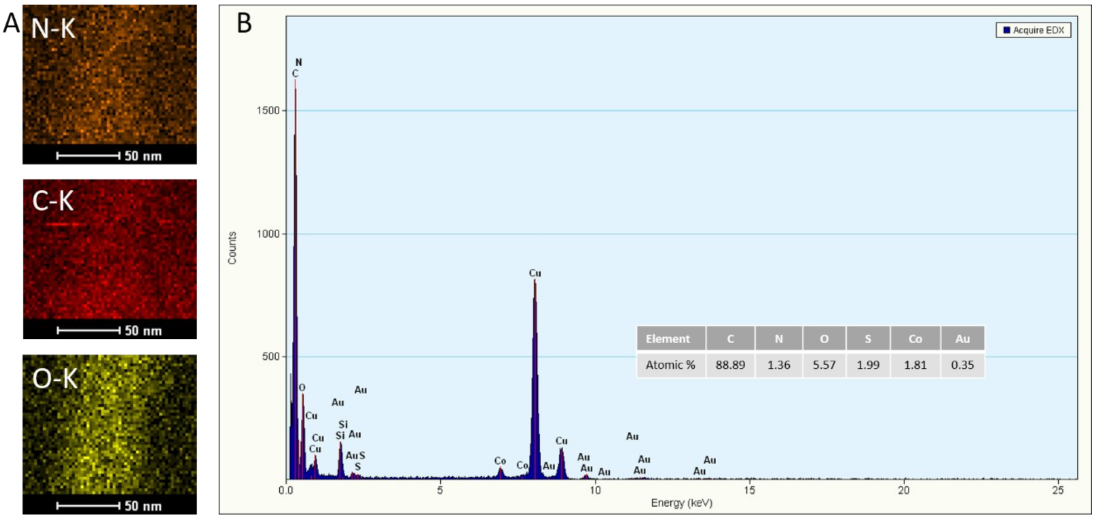


Fig. S3 The size distribution histogram of Au nanoparticles measured on 80 particles from the TEM image of ABEI/AuNPs/CoS_2 NWs.



Element	C	N	O	S	Co	Au
Atomic %	88.89	1.36	5.57	1.99	1.81	0.35

Fig. S4 (A) EDX elemental mapping of N, C and O for ABEI/AuNPs/CoS_2 NWs. (B) EDX spectrum of ABEI/AuNPs/CoS_2NWs.

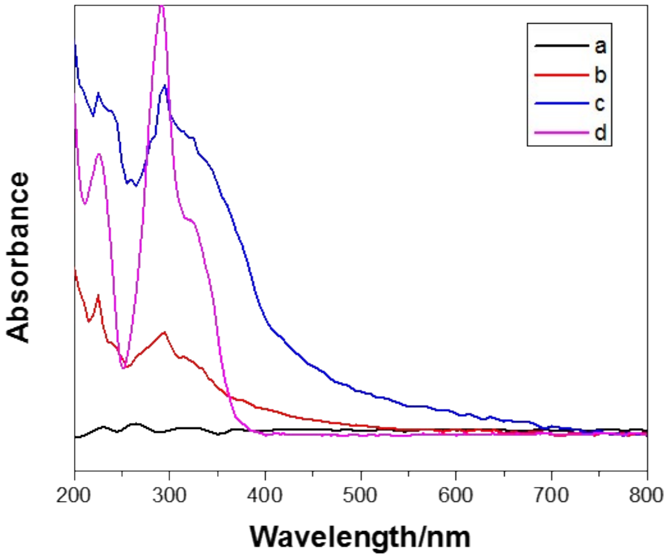


Fig. S5 UV-Visible absorption spectra of (a) CoS_2 NWs, (b) ABEI/CoS_2 NWs, (c) ABEI/AuNPs/CoS_2 NWs, and (d) ABEI.

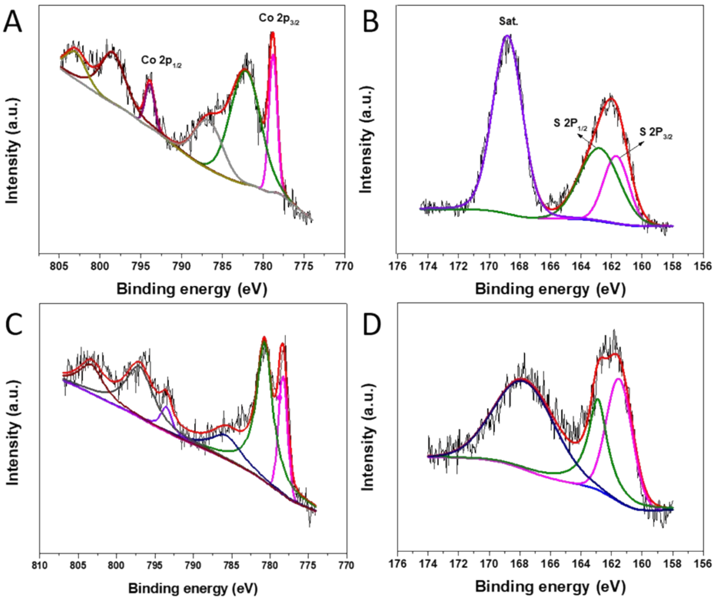


Fig. S6 The deconvolution of high-resolution Co 2p and S 2p XPS spectra in CoS_2 NWs (A, B), and ABEI/AuNPs/CoS_2 NWs (C, D).

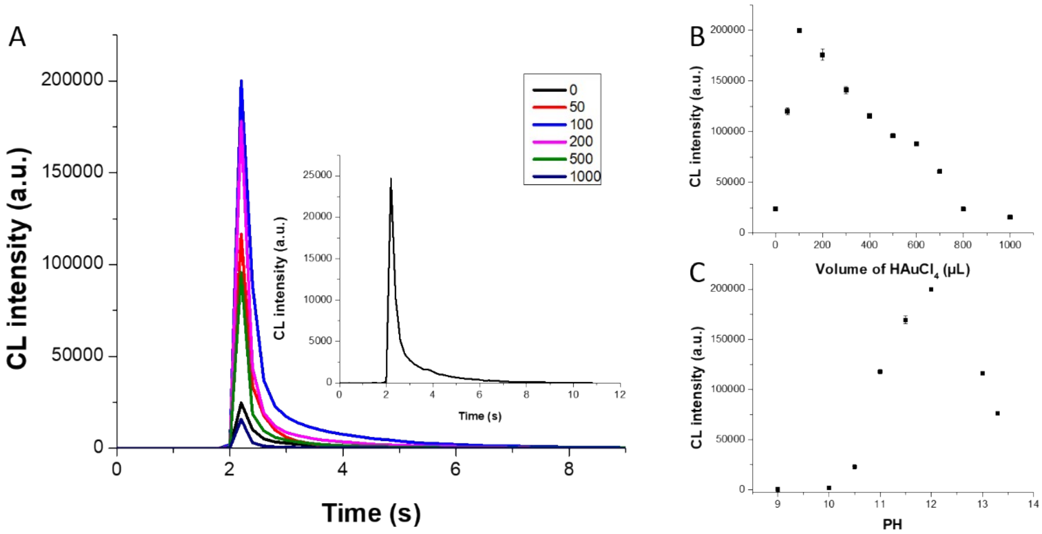


Fig. S7 (A) CL kinetic curves of ABEI/AuNPs/CoS_2 NWs synthesized using different volume (0-1000 μL) of 6mM $HAuCl_4$. (B) The plot of CL intensity as a function of $HAuCl_4$ volume. (C) Effect of pH of H_2O_2 solution on CL response of ABEI/AuNPs/CoS_2 NWs. Reaction conditions: 100 μL of a 10mM H_2O_2 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_2O_2 was further researched. Fig. S7C (ESI †) shows the effect of 1mM H_2O_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.

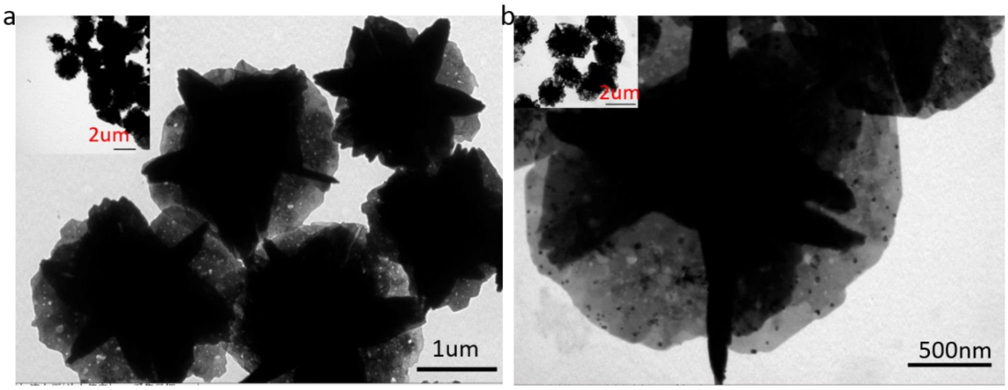


Fig. S8 TEM image of (a) CuS, (b) ABEI/AuNPs/CuS.

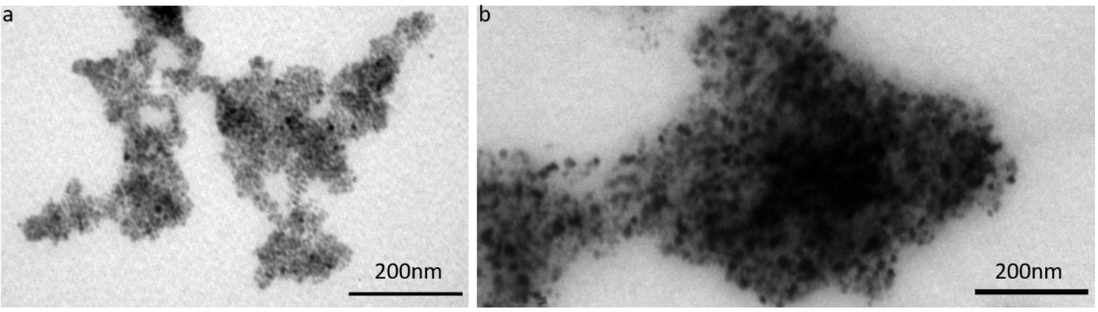


Fig. S9 TEM image of (a) CuZnFeS, (b) ABEI/AuNPs/CuZnFeS.

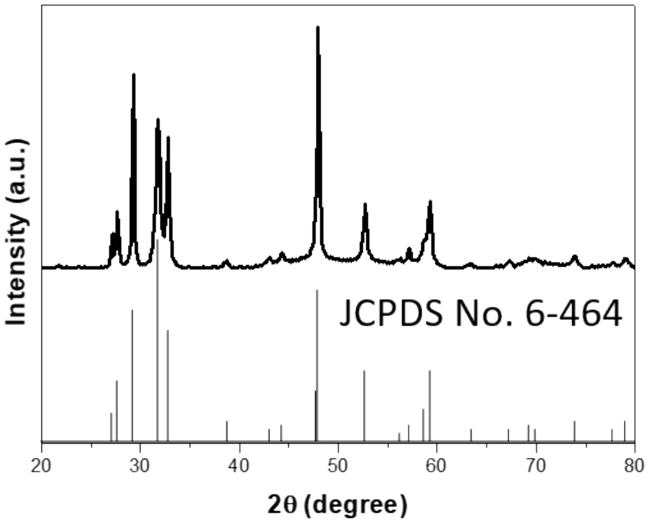


Fig. S10 XRD pattern of CuS.

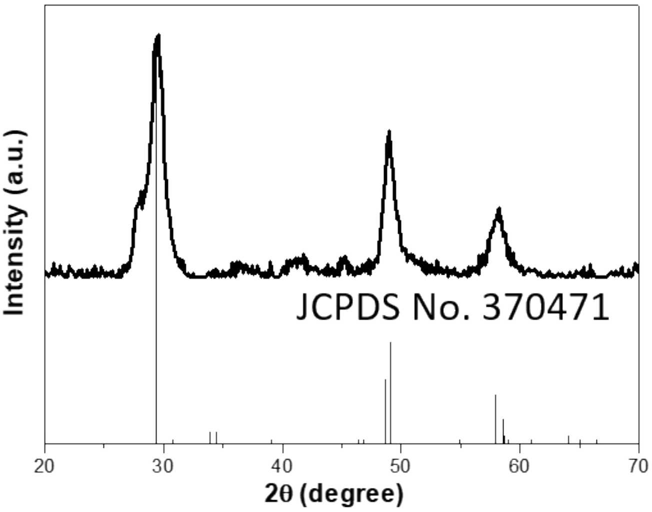


Fig. S11 XRD pattern of CuZnFeS.

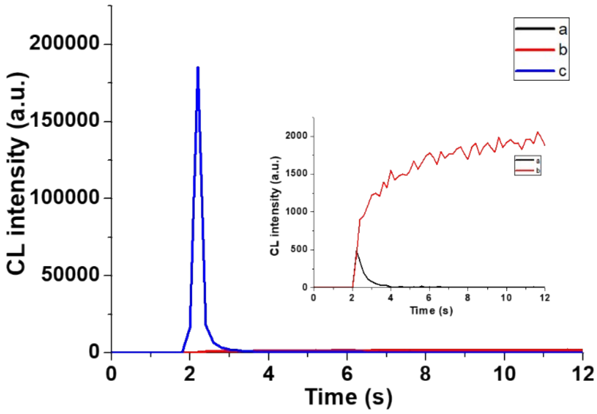


Fig. S12 CL kinetic curves of (a) ABEI/AuNPs/CuZnFeS, (b) ABEI/AuNPs/CuS, (c) ABEI/AuNPs/CoS_2 NWs. Inset: Magnification curves of a and b.

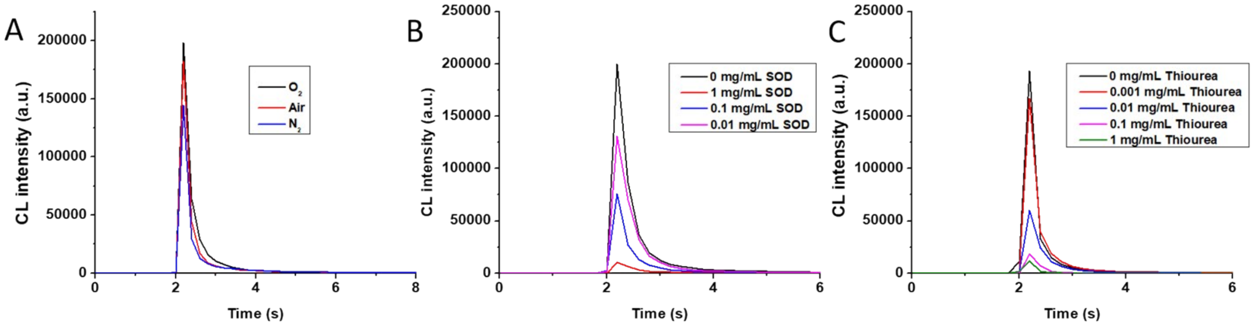


Fig. S13 (A) CL kinetic curves of ABEI/AuNPs/CoS_2 NWs under oxygen-saturated, air-saturated and nitrogen-saturated. CL kinetic curves of ABEI/AuNPs/CoS_2 NWs in the absence and different concentrations of (B) SOD and (C) Thiourea.

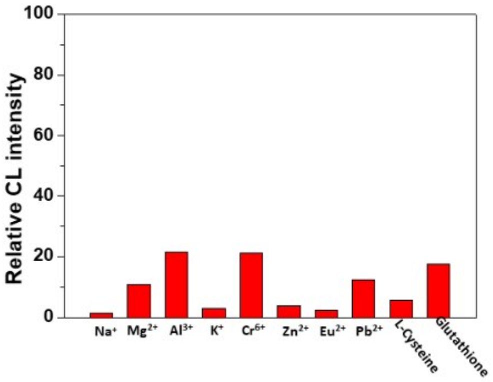


Figure S14 Relative CL intensity response of the proposed method for interferents (10 μM). Reaction conditions: 100μL 10 μM H_2O_2 (pH 12.0) was injected into 100 μL ABEI/AuNPs/CoS_2 NWs solution， including various interferents. Relative CL intensity=$(I_{Blank}-I_{CL})/I_{Blank}$ *100%

Table S1. Comparison of Existing non-enzymatic method detection of H_2O_2.

methods	materials	linear range (μM)	detection limit(μM)	ref
chemically modified electrodes	silver–polyaniline nanotube	100–90000	0.2	3
chemically modified electrodes	PAA/AuSPE	50–500	2	4
chemically modified electrodes	Nafion/EGO/Co3O4/GC	1–100	0.3	5
colorimetry	Gold nanoparticles		2	6
FIA- chemiluminescence	luminol–Cu2+	1-200	0.5	7
chemiluminescence	CTAB–CNSs	5–1000	2.6	8
chemiluminescence	MIL-101(Cr)	3–100	0.5	9
chemiluminescence	ABEI/AuNPs/CoS_2 NWs	1-100	0.3	This work

Table S2. Determination of H_2O_2 concentration in tap water.

Water sample	added (μM)	found (μM)	recovery (%)
1	10	10.4 ± 1.26	104.0
2	10	9.6 ± 0.58	96.0
3	10	9.7 ± 2.13	97.0

Mean ± SD of three measurements.

Table S3. Determination of H_2O_2 concentration in human serum samples.

Water sample	added (μM)	found (μM)	recovery (%)
1	10	9.02± 0.0057	90.2
2	10	9.62 ± 0.0072	96.2
3	15	9.87 ± 0.0058	98.7

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

References

1. Z. Xing, L. Wang and X. Yang, *J. Mater. Chem. B*, 2016, **4**, 2860-2863.
2. D. Tian, H. Zhang, Y. Chai and H. Cui, *Chem. Commun.*, 2011, **47**, 4959-4961.
3. W. He, H. Jia, X. Li, Y. Lei, J. Li, H. Zhao, L. Mi, L. Zhang and Z. Zheng, *Nanoscale*, 2012, **4**, 3501-3506.
4. A. Dalui, B. Pradhan, U. Thupakula, A. H. Khan, G. S. Kumar, T. Ghosh, B. Satpati and S. Acharya, *Nanoscale*, 2015, **7**, 9062-9074.
5. F. Lorestani, Z. Shahnavaz, P. M. Nia, Y. Alias and N. S. A. Manan, *Appl. Surf. Sci.*, 2015, **347**, 816-823.
6. L.-G. Zamfir, L. Rotariu, V. E. Marinescu, X. T. Simelane, P. G. L. Baker, E. I. Iwuoha and C. Bala, *Sens. Actuators B Chem*, 2016, **226**, 525-533.
7. A. A. Ensafi, M. Jafari–Asl and B. Rezaei, *Talanta*, 2013, **103**, 322-329.
8. F. Wang, X. Liu, C.-H. Lu and I. Willner, *ACS Nano*, 2013, **7**, 7278-7286.

9. P. Mahbub, P. Zakaria, R. Guijt, M. Macka, G. Dicinoski, M. Breadmore and P. N. Nesterenko, *Talanta*, 2015, **143**, 191-197.

10. F. Pan, P. Wei, M. Zhang and C. Lu, *Anal. Methods.*, 2015, **7**, 5667-5673.

11. H. Yu and D. Long, *Microchim. Acta*, 2016, **183**, 3151-3157.