Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

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Highly chemiluminescent silver nanoclusters with dual catalytic center

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1. Synthesis of GSH@ABEI@AgNCs

GSH@ABEI@AgNCs were synthesized through a one-pot method. In a typical experiment, aqueous $AgNO_3$ (5 mL, 0.035 M) was added to GSH solution (5 mL, 0.035 M) under vigorous stirring. NaOH solution (0.6 mL, 0.5 M) was introduced 10 min later, with subsequent addition of ABEI (2 mL, 4 mM, pH 12) alkaline solution. The reaction was allowed to proceed under vigorous stirring for 24 hrs at room temperature. Finally, the GSH@ABEI@AgNCs were obtained. Methanol precipitation and centrifugation procedures were carried out to remove free reagent molecules. The precipitates were re-dispersed in the ultrapure water for further use.

2. Evidence of completely removement of free ABEI

To make sure that unbound ABEI molecules were completely removed, secondary purification was carried out. First, the synthesized Co^{2+}-GSH@ABEI@AgNCs were centrifuged in methanol and the supernatant was removed. Then weakly acidic B-R buffer solution (pH 4) was added to the bottom precipitate to further remove excess free ABEI. After centrifugation, Co^{2+}-GSH@ABEI@AgNCs were aggregated at the bottom. The UV-vis absorption spectrum of ABEI dissolved in weakly acidic B-R buffer solution (pH 4) (Fig. S1, black line) showed three main characteristic peaks at 243, 281 and 322 nm, absent in the UV-vis absorption spectrum of the supernatant (Fig. S1, red line), which only displayed the characteristic peak at 350 nm belonging to Co^{2+}-GSH@ABEI@AgNCs. The results indicated that the free ABEI could be completely removed just by methanol precipitation and centrifugation.

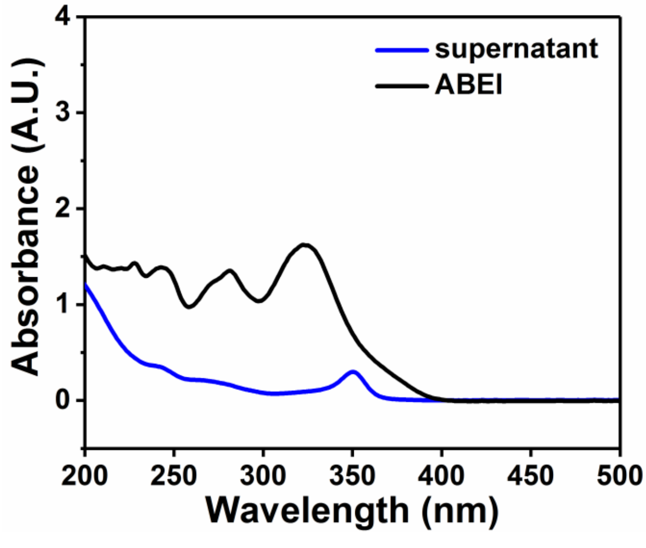

Fig. S1 UV-vis absorption spectra of pure ABEI dissolved in B-R buffer solution (pH 4) (black line) and supernatant after secondary centrifugation (blue line).

3. Calculation of the content of ABEI

When we compared the CL intensity of pure ABEI, GSH@ABEI@AgNCs, ABEI/Co^{2+} and Co^{2+}-GSH@ABEI@AgNCs, the ABEI content in the above systems was normalized to be the same as following: The atomic ratio Co:S:N in Co^{2+}-

GSH@ABEI@AgNCs by XPS was detected to be 1:18.13:59.40 and the molecular formulas of GSH and ABEI are $C_{10}N_3O_6S$ and $C_{14}N_4O_2$, respectively. Therefore the molar ratio of Co^{2+}:ABEI:GSH was calculated to be 1:1.25:18.13. Since the concentration of Co element in Co^{2+}-GSH@ABEI@AgNCs solution by ICP-AES was detected to be 0.23 mM, the concentrations of ABEI and GSH in Co^{2+}-GSH@ABEI@AgNCs solution were calculated to be 0.29 and 4.17 mM, respectively. Therefore, for pure ABEI and ABEI/Co^{2+} systems, the concentration of ABEI should be 0.29 mM. Considering Co^{2+} was coordinated with GSH in Co^{2+}-GSH@ABEI@AgNCs, we added GSH into ABEI/Co^{2+} system to keep a consistent chemical environment.

4. FT-IR spectra of GSH and Co^{2+}-GSH@ABEI@AgNCs

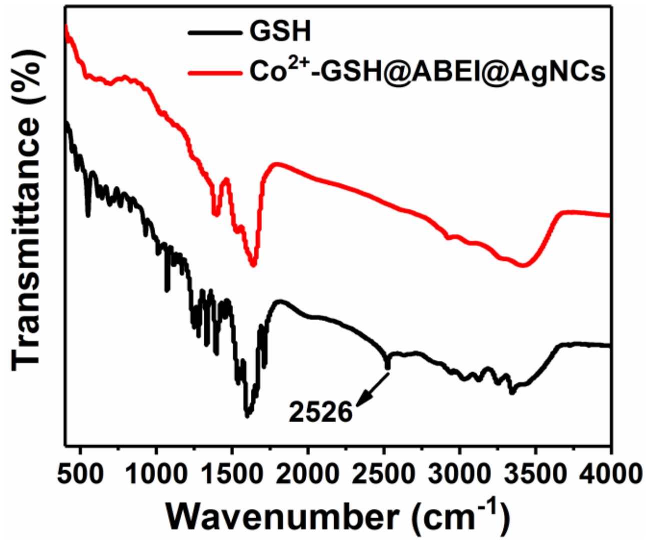

Fig. S2 FT-IR spectra of GSH (black line) and Co^{2+}-GSH@ABEI@AgNCs (red line).

5. Effects of atmosphere, thiourea and SOD on the CL intensity of Co^{2+}-GSH@ABEI@AgNCs

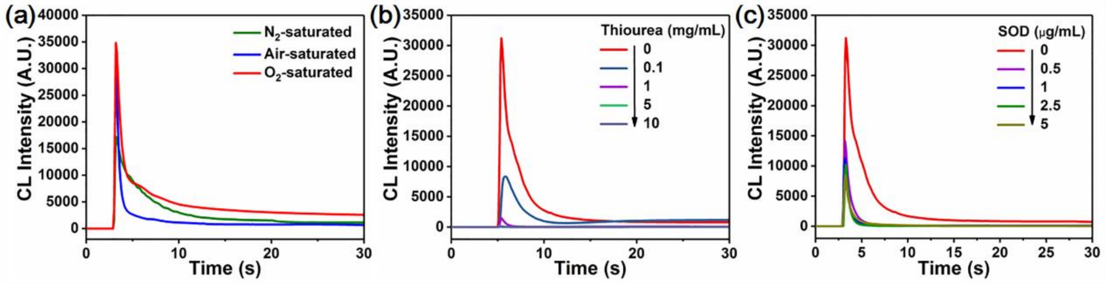

Fig. S3 (a) CL kinetic curves of Co^{2+}-GSH@ABEI@AgNCs-H_2O_2 under nitrogen-saturated (green line), air-saturated (blue line), and oxygen-saturated (red line) solutions, respectively. (b) CL kinetic curves of Co^{2+}-GSH@ABEI@AgNCs-H_2O_2 in the absence (red line) and presence of different concentrations of thiourea: 0.1-10 mg/mL. (c) CL kinetic curves of Co^{2+}-GSH@ABEI@AgNCs-H_2O_2 in the absence (red line) and presence of different concentrations of SOD: 0.5-5 μg/mL. Reaction condition: 1 mM H_2O_2 in 0.01 M NaOH. Photomultiplier tube voltage: -450 V.

6. Stability of Co^{2+}-GSH@ABEI@AgNCs in biological conditions

Phosphate buffered saline (PBS) containing Na_2HPO_4/NaH_2PO_4 (20 mM) and NaCl (40 mM) with pH of 7.4 was used to mimic biological conditions. The precipitates of Co^{2+}-GSH@ABEI@AgNCs were re-dispersed in PBS (pH 7.4) instead of H_2O after methanol precipitation and centrifugation procedures. The stability of Co^{2+}-GSH@ABEI@AgNCs in PBS was investigated by UV-vis absorption, FL and CL measurements within one day and 15 days. The UV-vis absorption spectrum (Fig. S4a) of Co^{2+}-GSH@ABEI@AgNCs in PBS revealed an absorption peak at 350 nm, which was consistent with that of Co^{2+}-GSH@ABEI@AgNCs in H_2O. The relative standard deviation (R.S.D.) of seven replicated UV-vis absorbance signals within a day (Fig. S4b) and fifteen replicated UV-vis absorbance signals in 15 days (Fig. S4c) of Co^{2+}-GSH@ABEI@AgNCs in PBS was 0.77% and 0.88%, respectively. The fluorescent Co^{2+}-GSH@ABEI@AgNCs in PBS had an emission peak centered at 435 nm with excitation wavelength of 370 nm (Fig. S4d). The R.S.D. of seven replicated FL signals within a day (Fig. S4e) and fifteen replicated FL signals in 15 days (Fig. S4f) of Co^{2+}-GSH@ABEI@AgNCs in PBS was 1.74% and 2.46%, respectively. In addition, we detected the CL kinetic curve of Co^{2+}-GSH@ABEI@AgNCs in PBS with alkaline H_2O_2 as shown in Fig. S4g. The R.S.D. of seven replicated CL signals within a day (Fig. S4h) and fifteen replicated CL signals in 15 days (Fig. S4i) of Co^{2+}-GSH@ABEI@AgNCs in PBS was 1.66% and 1.84%, respectively. To be noted, the Co^{2+}-GSH@ABEI@AgNCs were treated the same way as that for UV-vis absorption and FL detections before CL detection. That is, Co^{2+}-GSH@ABEI@AgNCs were re-dispersed and stored in 1xPBS (pH 7.4) before CL detection. Only in the last CL detection step, we used alkaline H_2O_2 as coreactant to produce CL emission. Since all the other procedures (if building bio-probes or sensors by using our Co^{2+}-GSH@ABEI@AgNCs) except for the last CL detection step could be proceeded under biological conditions, the alkaline condition in the last step would not affect the results in the in-vitro tests. All these results supported that Co^{2+}-GSH@ABEI@AgNCs had good stability in biological conditions.

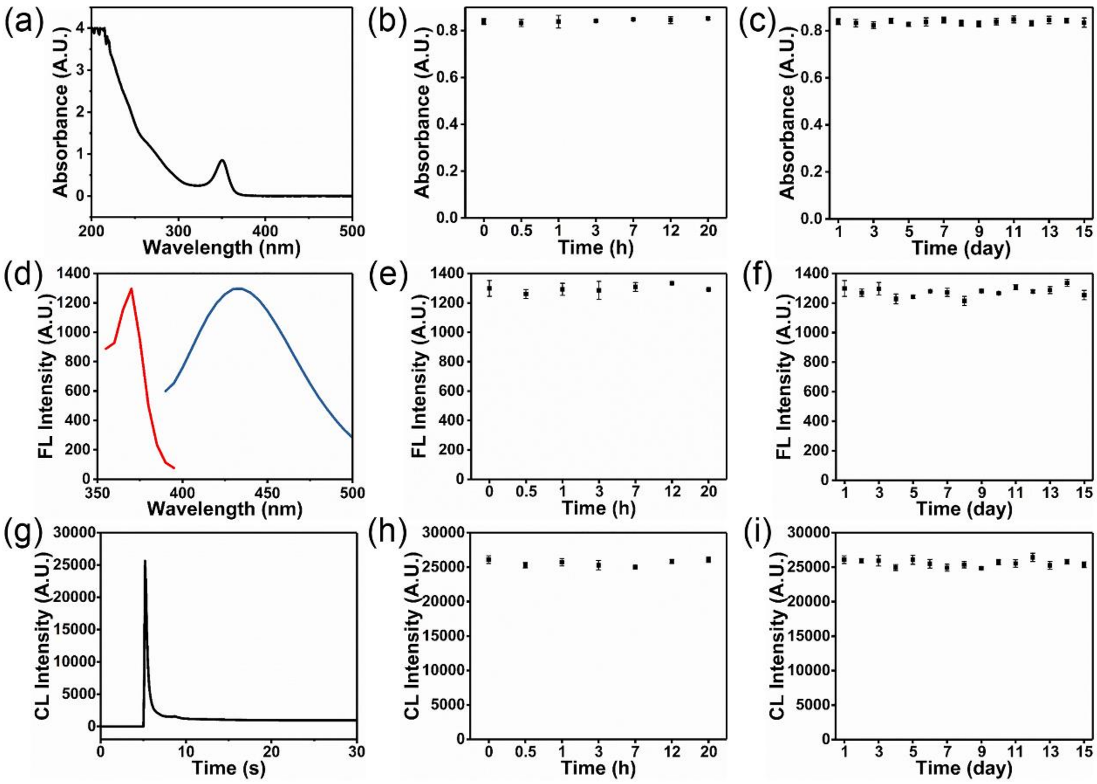

Fig. S4 (a) UV-vis absorption spectrum of Co^{2+}-GSH@ABEI@AgNCs in PBS. (b) Seven replicated UV-vis absorbance measurements in one day and (c) fifteen replicated UV-vis absorbance measurements in 15 days of Co^{2+}-GSH@ABEI@AgNCs in PBS. (d) FL excitation (red) and emission (blue) spectra of Co^{2+}-GSH@ABEI@AgNCs in PBS. (e) Seven replicated FL measurements in one day and (f) fifteen replicated FL measurements in 15 days of Co^{2+}-GSH@ABEI@AgNCs in PBS. (g) CL kinetic curve of Co^{2+}-GSH@ABEI@AgNCs in PBS with H_2O_2. (h) Seven replicated CL measurements in one day and (i) fifteen replicated CL measurements in 15 days of Co^{2+}-GSH@ABEI@AgNCs in PBS. CL reaction condition: 1 mM H_2O_2 in 0.01 M NaOH. Photomultiplier tube voltage: -450 V.