Supporting Information

Ultrasensitive chemiluminescence biosensors using nucleic acid-functionalized silver-cysteine nanowires as signal amplifying labels

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Contents

§1. Oligonucleotides sequences used in this work

Table S1. Oligonucleotides Sequences Used in This Work[a]

oligonucleotides	sequences
capture DNA	5'-NH_2-$(CH_2)_6$-GCG CGA ACC GTA TA-3'
signal DNA	5'-TC TAT CCT ACG C-$(CH_2)_6$-NH_2-3'
FITC-signal DNA	5'-FITC-TC TAT CCT ACG C-$(CH_2)_6$-NH_2-3'
target DNA 1	3'-CGC GCT TGG CAT AT AGAT AG ATA GGA TGC G-5'
target DNA 2[b]	3'-CGC GCT AGG CAT AT AGAT AG ATA GGA TGC G-5'
target DNA 3	3'-GCG CGA ACC GTA TA AGAT TC TAT CCT ACG C-5'
aptamer 1	5'-NH_2-poly T(20)-GGT TGG TGT GGT TGG-3'
aptamer 2	5'-NH_2-$(CH2)_6$-AGT CCG TGG TAG GGC AGG TTG GGG TGA CT -3'

[a]Note: target DNA 1, target DNA 2, and target DNA 3 represent the perfectly complementary target DNA, single-base mismatched DNA, and non-complementary DNA, respectively.

[b]The mismatched bases in DNA strands are underlined.

§2. Modification of *p*-SCNWs and PMs with oligonucleotides

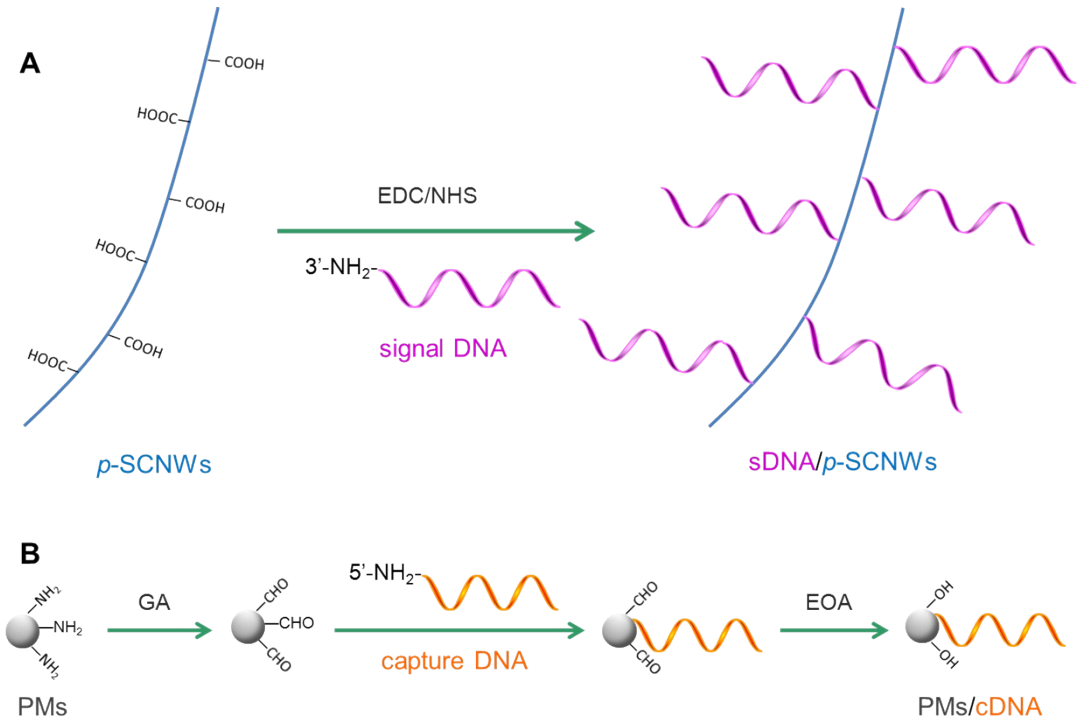

Figure S1. *(A) Modification of p-SCNWs with signal DNA (sDNA), and (B) Immobilization of capture DNA (cDNA) onto amine-actived paramagnetic microspheres (PMs).*

§3. Determination of Surface Coverage of the Prober on the Surface of *p*-SCNWs

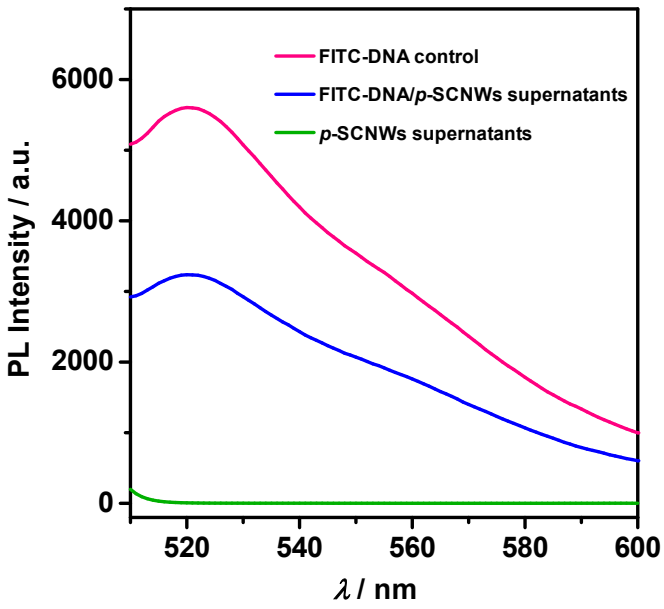

Figure S2. *Fluorescence emission spectra of FITC-DNA (FITC-signal DNA probe, 125 nM) before (red line) and after (blue line) being incubated with p-SCNWs (0.1 mg), and the supernatant of p-SCNWs (0.1 mg) after separated by centrifugation (green line). Fluorescence intensity was recorded at 520 nm with an excitation wavelength of 490 nm.*

§4. Optimization of the DNA Hybridization Reaction Conditions

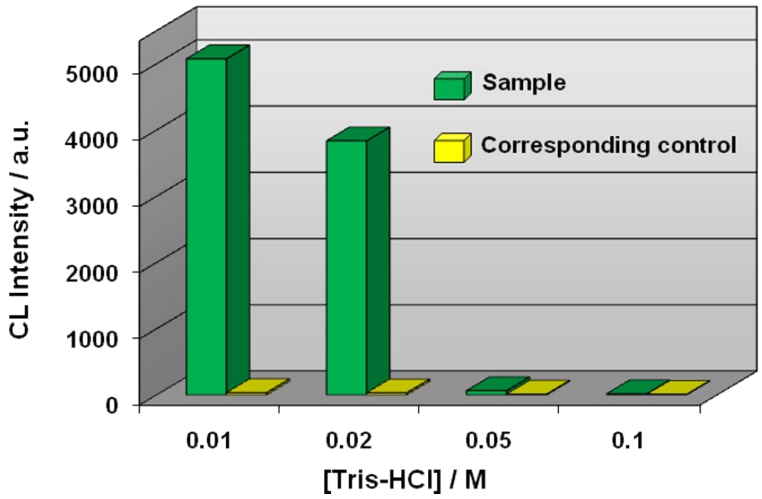

Figure S3. *Effect of the concentration of Tris-HCl buffer on the CL intensities. The final concentration of target DNA was 60 fM. Corresponding control: sample without target DNA.*

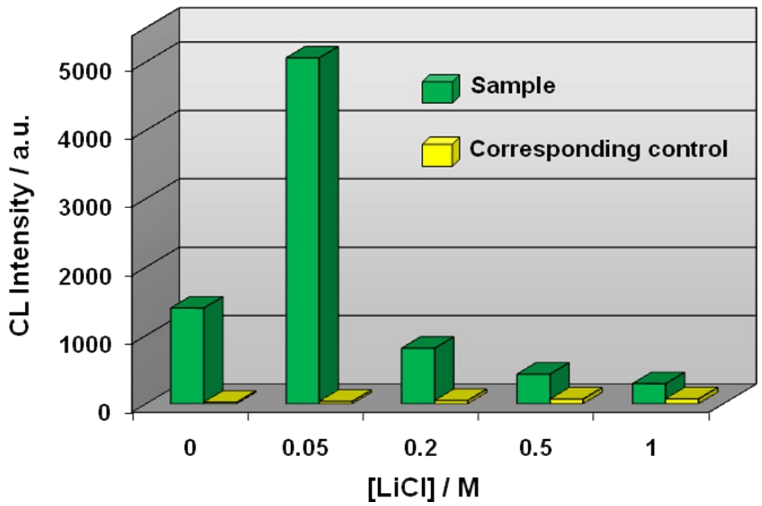

Figure S4. *Effect of the concentration of LiCl in 0.01 M Tris-HCl buffer on the CL intensities. The final concentration of target DNA was 60 fM. Corresponding control: samples without target DNA.*

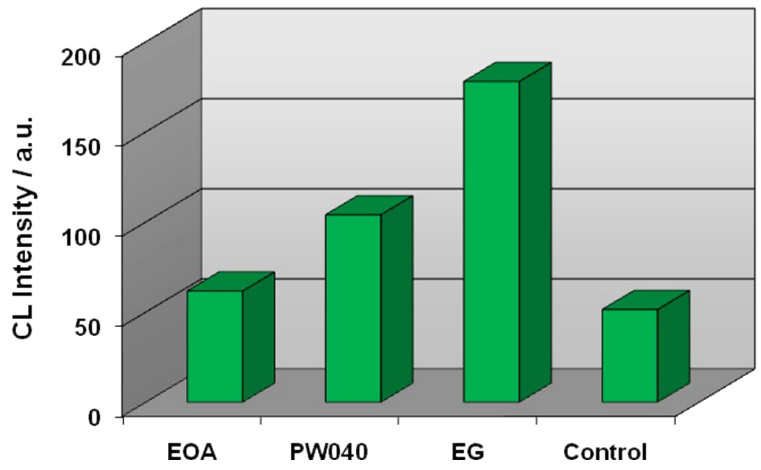

Figure S5. *Effect of different kind of blocking agents on the CL intensities in the DNA assay.*

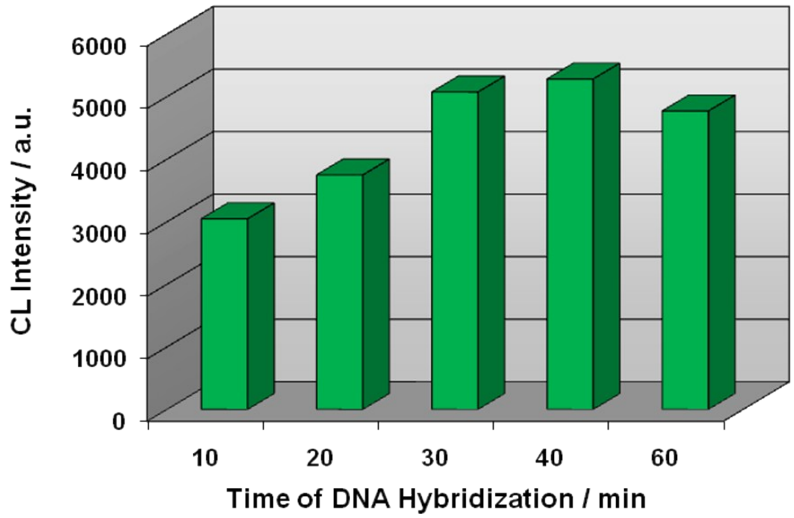

Figure S6. *Effect of DNA hybridization time on the CL intensities. The concentration of target DNA was 60 fM.*

§5. Optimization of the CL reaction conditions

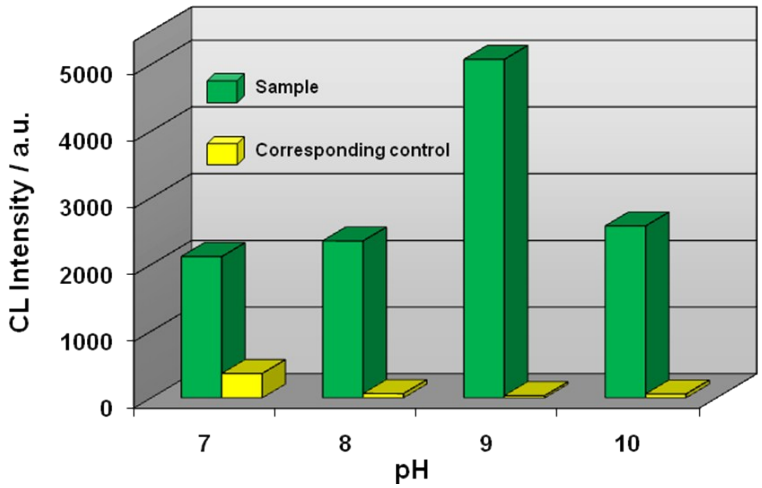

Figure S7. *Effect of pH value of the resultant $KMnO_4$ on the CL intensities. The final concentration of target DNA was 60 fM. Corresponding control: samples without target DNA.*

§6. Determination of DNA in biological samples

Table S2. Recovery of DNA spiked into human serum samples.

Samples	Spiked DNA (10^{-16} M)	Detected DNA (10^{-16} M)	RSD (%, n=5)	Recovery (%, n=5)
1	8.0	7.9	4.7	98.5
2	85.0	84.7	3.2	99.6
3	120.0	126.6	5.0	105.5

§7. Comparison of the Developed CL Assay with Others in the Detection of DNA Hybridization.

Table S3. Comparison of the Developed CL Assay with Others in the Detection of DNA Hybridization.

assay method	label	linear range (M)	LOD (M)	refs
CL[a]	*p*-SCNWs	2×10^{-16}–4×10^{-14}	7.2×10^{-17}	this work
CL	silver nanoparticles (NPs)	1.4×10^{-14}–1.4×10^{-12}	5×10^{-15}	1
CL	CuS NPs and Au NPs	2×10^{-14}–2×10^{-12}	4.8×10^{-15}	2
CL	nucleic acid modified Pt NPs	1×10^{-11}–1×10^{-8}	1×10^{-11}	3
CL	irregular Au NPs	4×10^{-11}–1×10^{-8}	1.3×10^{-11}	4
CRET[b]	hairpin nucleic acid-modified CdSe/ZnS QDs	1×10^{-8}–1×10^{-7}	1×10^{-8}	5
colorimetric	Au NPs	5×10^{-12}–5×10^{-17}	2×10^{-17}	6
spectrophotometry	horseradish peroxidase	1×10^{-14}–1×10^{-9}	1×10^{-14}	7
fluorescence	molecular beacon modified CdTe QDs	5×10^{-10}–2.5×10^{-8}	5×10^{-10}	8
DLS[c]	Au NPs	5×10^{-12}–5×10^{-9}	1×10^{-12}	9
LSPR[d]	label-free	1×10^{-12}–1×10^{-6}	8.03×10^{-13}	10
ECL[e]	$[Ru(bpy)_3]^{2+}$-containing polystyrene microspheres	1×10^{-15}–1×10^{-8}	1×10^{-15}	11
ECL	HRP	1×10^{-8}–1×10^{-17}	8.3×10^{-18}	12
SWSV[f]	ferrocene-functionalized cationic polythiophene	1×10^{-15}–1×10^{-12}	4×10^{-16}	13
ASV[g]	Au NPs modified with bio bar code and PbS NPs	2×10^{-14}–1×10^{-12}	5×10^{-15}	14
potentiometry	alkaline phosphatase	5×10^{-14}–1×10^{-8}	5×10^{-14}	15

[a]Chemiluminescent method.

[b]Chemiluminescence resonance energy transfer.

[c]Dynamic light scattering.

[d]Localized surface Plasmon resonance.

[e]Electrogenerated chemiluminescence.

[f]Square-wave stripping voltammetry.

[g]Anodic stripping voltammetry.

§8. Optimization of thrombin incubation reaction conditions

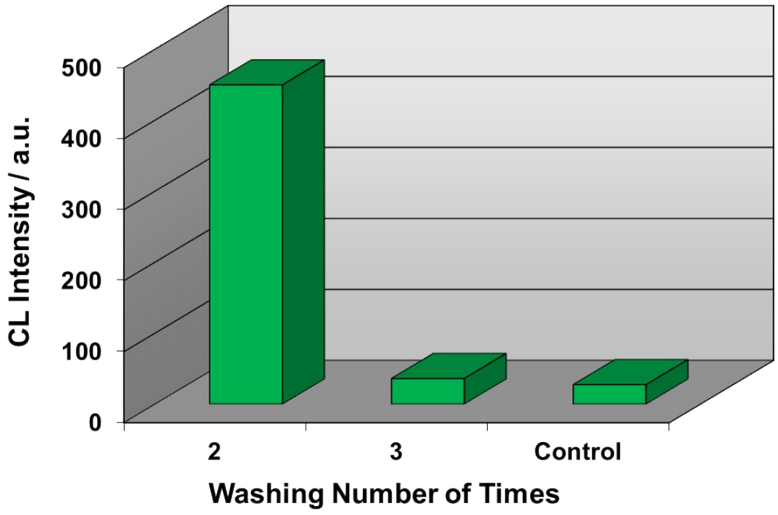

Figure S8. *Effect of washing number of times on the CL intensities. Control: sample without thrombin.*

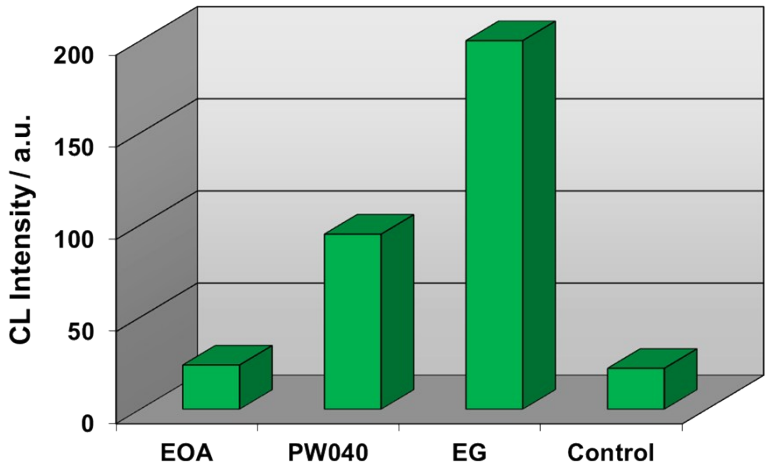

Figure S9. *Effect of different kind of blocking agents on the CL intensities in thrombin assay. Control: sample without thrombin.*

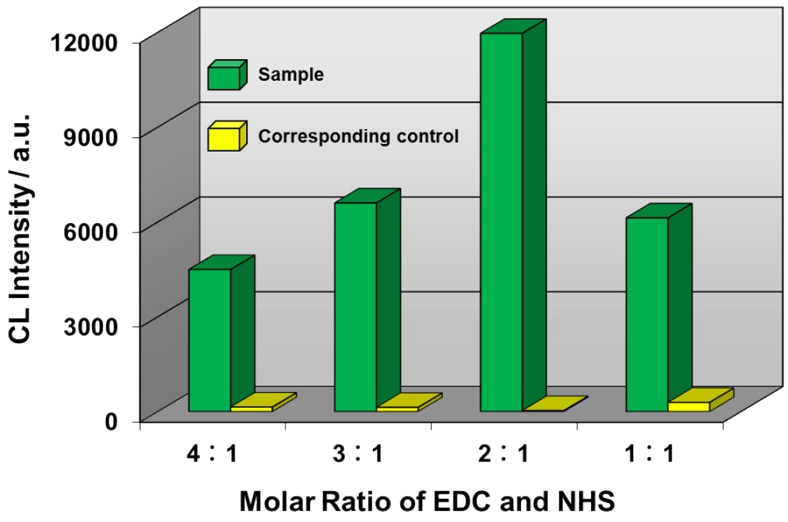

Figure S10. *Effect of the molar ratio of EDC and NHS on the CL intensities. The carboxylic acid-terminated p-SCNWs were activated with different molar ratio of EDC and NHS, while the concentration of NHS was kept 0.1 M. The final concentration of thrombin was 120 pM. Corresponding control: samples without thrombin.*

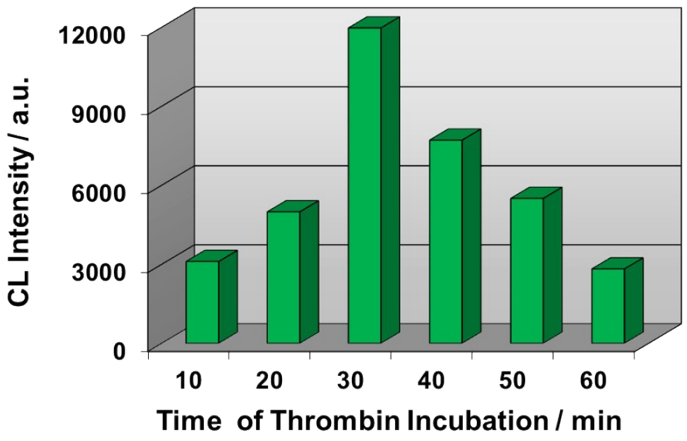

Figure S11. *Effect of the time of thrombin incubation on the CL intensities. The final concentration of thrombin was 120 pM.*

§9. Determination of thrombin in biological samples

Table S4. Recovery of Human α-Thrombin spiked into human serum samples.

Samples	Spiked thromin (10^{-12} M)	Detected thromin (10^{-12} M)	RSD (%, n=5)	Recovery (%, n=5)
1	1.0	0.96	5.4	96.0
2	10.0	10.5	4.6	105.0
3	30.0	30.7	3.0	102.4

§10. Comparison of the Developed CL Assay with Others in the Detection of Thrombin.

Table S5. Comparison of the Developed CL Assay with Others in the Detection of Thrombin.

assay method	label	linear range (M)	LOD (M)	refs
CL	*p*-SCNWs	2.5×10^{-13}–3.5×10^{-11}	4×10^{-14}	this work
CL	Pt nanoparticles	1×10^{-8}–1×10^{-6}	1×10^{-9}	16
CRET	Au nanoparticles	5×10^{-11}–5.5×10^{-10}	1.5×10^{-11}	17
spectrophotometry	Au nanoparticles	2×10^{-8}–1.67×10^{-7}	2×10^{-9}	18
Chromogenic assay	Chromogenic substrates	5×10^{-14}–2×10^{-12}	4×10^{-14}	19
SERS[a]	Crystal violet	1×10^{-10}–1×10^{-8}	2×10^{-11}	20
SPR[b]	Au nanoparticles	1×10^{-17}–1×10^{-15}	1×10^{-18}	21
fluorescence	enzymes	2×10^{-14}–1×10^{-10}	2×10^{-15}	22
ECL	methyl blue	2×10^{-11}–1×10^{-8}	2×10^{-11}	23
ECL	Fe_3O_4@CdSe QDs	1×10^{-12}–5×10^{-9}	1.2×10^{-13}	24
ECL	Pt nanoparticles	1×10^{-8}–1×10^{-6}	1×10^{-9}	25
DPV[c]	Streptavidin-alkaline phosphatase	1×10^{-9}–1×10^{-7}	4.5×10^{-10}	26
DPV	Ferrocene-labeled aptamer	5×10^{-9}–3.5×10^{-8}	5×10^{-10}	27
ECPA[d]	methyl blue	1×10^{-10}–1×10^{-8}	5×10^{-11}	28
ICP-MS[e]	Au nanoparticles	5×10^{-11}–1×10^{-9}	1×10^{-11}	29
EIS[f]	Au nanoparticles	5×10^{-11}–3.5×10^{-8}	1×10^{-13}	30

[a]Surface-enhanced Raman spectroscopy.

[b]Surface plasmon resonance.

[c]Differential pulse voltammetry.

[d]Electrochemical proximity assay.

[e]Inductively coupled plasma-mass spectrometry.

[f]Electrochemical impedance spectroscopy.

§11. References

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