
1 Supporting information for

2 **Silver Iodide-Chitosan Nanotag Induced Biocatalytic Precipitation for**
3 **Self-Enhanced Ultrasensitive Photocathodic Immunosensor**

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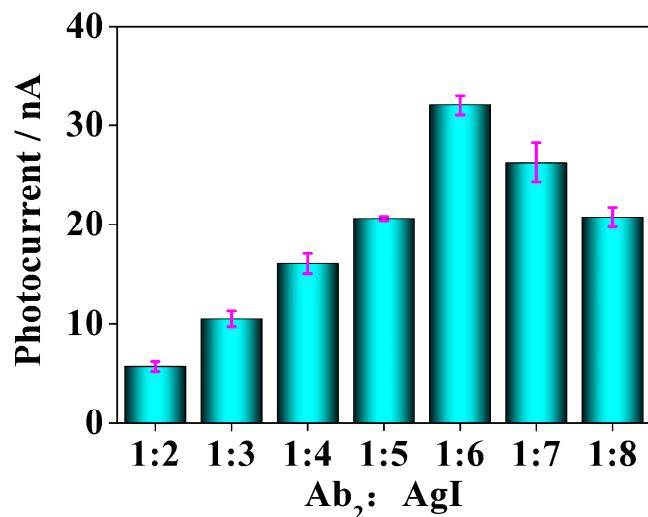
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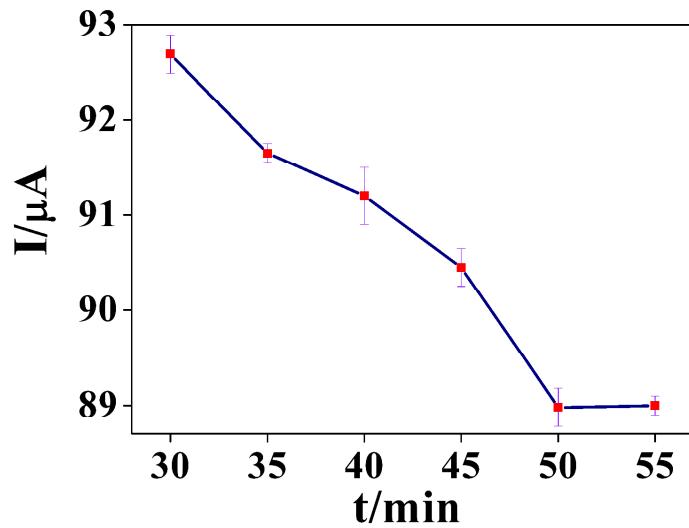
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12 **Calculating method of detection limit.**
13 According the definition of detection limit in ‘IUPAC Compendium of Analytical Nomenclature’, detection limit means that
14 the lowest concentration or quality which could be detected and possessed distinguishing signal value compared with the
15 blank solution. In this work, LOD expressed the lowest concentration (c_L) was derived from smallest measure (x_L) that could
16 be detected by our designed strategy. The value of x_L was obtained by the equation:

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$$x_L = \bar{x}_b \pm 3s_b$$

18 Where \bar{x}_b was the mean of blank measure (without CEA), s_b was the standard deviation of the blank measures ($n=5$).
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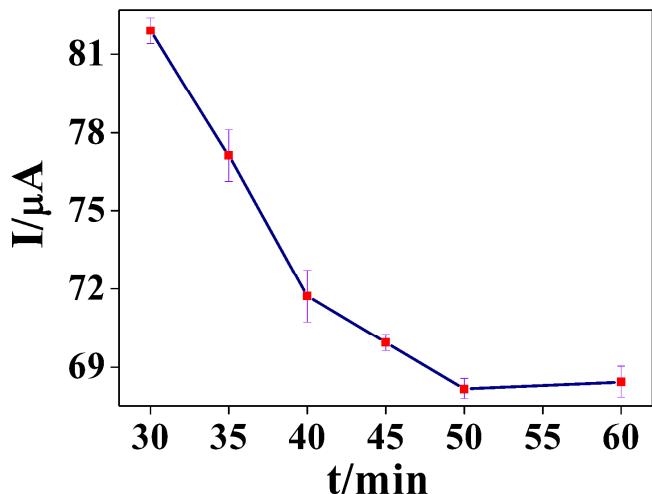


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22 **Figure S1.** The photocurrent responses of different ratio between Ab₂ and AgI in 0.1 M PBS (pH 7.0).



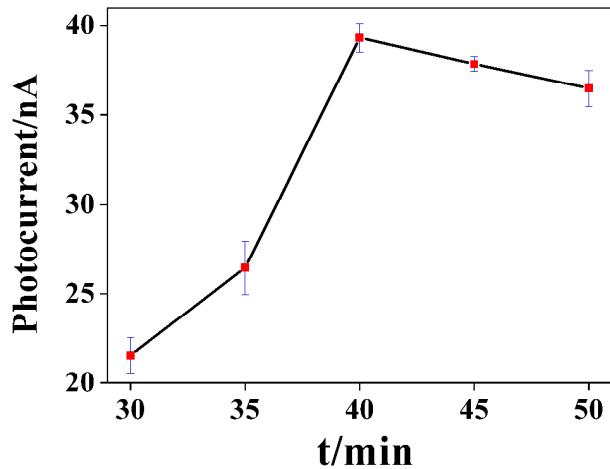
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24 **Figure S2.** The current responses of $\text{Ab}_1/\text{CN-PEI}/\text{GCE}$ with different incubation time of Ab_1 in 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution
25 containing 0.1 M KCl.



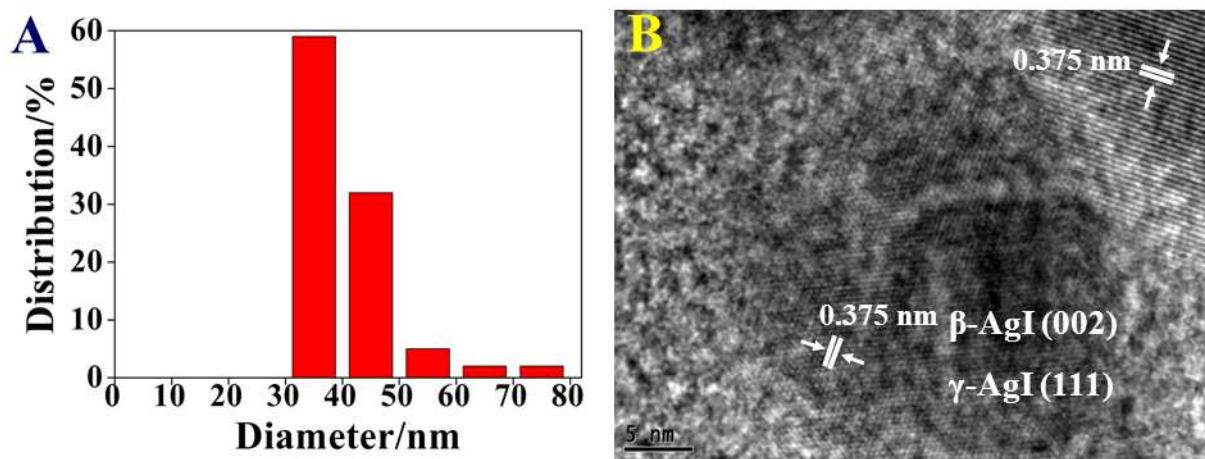
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27 **Figure S3** The current responses of $\text{Ag}/\text{Ab}_1/\text{CN-PEI}/\text{GCE}$ with different incubation time of Ag in 5 mM
28 $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution containing 0.1 M KCl.



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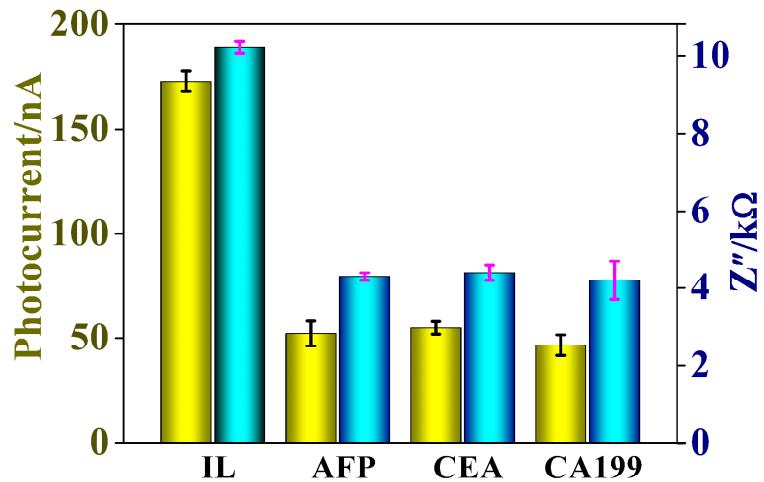
30 **Figure S4** The photocurrent responses of SICNP-Ab₂/Ab₁/CN-PEI/GCE with different incubation time of Ab₁ in 0.1
31 M PBS (pH 7.0).



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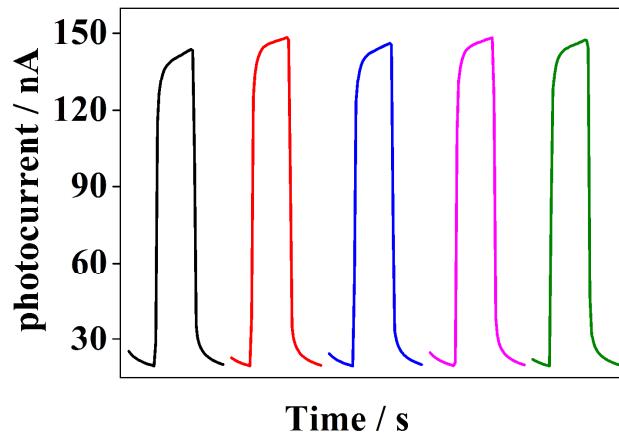
33 **Figure S5** The diameter distribution (A) and HRTEM (B) images of SICNPs.

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36 **Figure S6** The effect of possible interferences.



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38 **Figure S7** The photocurrent responses of the five independent photoelectrochemical immunosensors.

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41 **Table S1 Comparison of analytical performance of different methods and electrode materials for detection of IL-6.**

Methods	Electrode materials	Linear range	LOD	Ref.
		(pg/mL)	(pg/mL)	
PEC	ITO/TiO ₂ /CdS/CS/Ab/Ag-CdSe	1-100000	0.38	[1]
EC	ITO/Au-Grap-Si/Ab ₁ /Ag/Ab ₂ -HRP-Au-CNT@PD	1-40	0.3	[2]
EC	SPCE/MB-Ab ₁ /Ag/Ab ₂ -polyHRP	1.75-500	0.39	[3]
EC	MB-PMMA-Au/Ab ₁ /Ag/Ab ₂ -Au-HRP	5-1000	5	[4]
EC	GCE/UCNP-APTES/AuNPs/Ab/Ag	0.00001-0.1	0.00001	[5]
EC	GCE/Grap/Au/Ab ₁ /Ag/Ab ₂ -PS-Cd	1-1000	0.5	[6]
ECL	TPrA/CNT/Ab ₁ /Ag/Ab ₂ -RuBYP-SiNP	0.01-1000	0.01	[7]
SERS	Ab ₁ /Ag/Ab ₂ -TEG-Au-AgNS	1-1000000	1	[8]
FL	Cr/Au/DSP/Protein A/Ab ₁ /Ag/Ab ₂ -SAF	0.0129-15600	0.0129	[9]
ELISA	Ab ₁ /Ag/Ab ₂ -HRP-PMNPs-poly(MAA-PEGMA)	3.2-1000	1	[10]
EIS	GCE/CN-PEI/Ab ₁ /Ag/Ab ₂ -SICNP	0.000001-90	0.000000479	This work
PEC	GCE/CN-PEI/Ab ₁ /Ag/Ab ₂ -SICNP	0.000001-10	0.000000737	This work

42 **LOD:** Limit of detection; **PEC:** Photoelectrochemistry; **EC:** Electrochemistry; **ECL:** Electrogenerated
 43 chemiluminescence; **SERS:** Surface enhanced Raman scattering; **FL:** fluorescence; **ELISA:** Enzyme-linked
 44 immunosorbent assay; **EIS:** Electrochemical impedance spectroscopy.

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46 **Table S2 The spike and recovery results (n=3) obtained from the designed photocathodic immunosensor for IL-6.**

IL-6 added (pg/mL)	IL-6 found (pg/mL)	RSD (%)	Recovery (%)
5	5.39±0.08	3.4	98.6
10	10.48±0.11	4.5	101.7

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50 **REFERENCES**

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