Supplementary Material

Fabrication of Silk Sericin-Anthocyanin Nanocoating for Chelating and Saturation-Visualization Detection of Metal Ions

Liang Yao, ^{a, 1} Minglu Hao, ^{b, 1} Feng Zhao, ^c Yilin Wang, ^d Yueru Zhou, ^c Zhongyi Liu, ^c Xiaofan An, ^b Zhongfeng Gao, ^b Jun Wang, ^a Tao Zheng, ^e Pu Chen, ^{b, c, *} and Lei Zhang ^{c, *}

^a School of Biotechnology and Sericultural Research Institute, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212018, China

^b School of Advanced Materials Institute, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250014, China

^c Department of Chemical Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

^d Institute of Translational Medicine, Zhejiang University, Hangzhou, Zhejiang 310029, China

^e Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China, 510640

Corresponding Authors:

Department of Chemical Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

* E-mail: 178zhang@uwaterloo.ca (L. Zhang) & p4chen@uwaterloo.ca (P. Chen)

¹ These authors contributed equally.

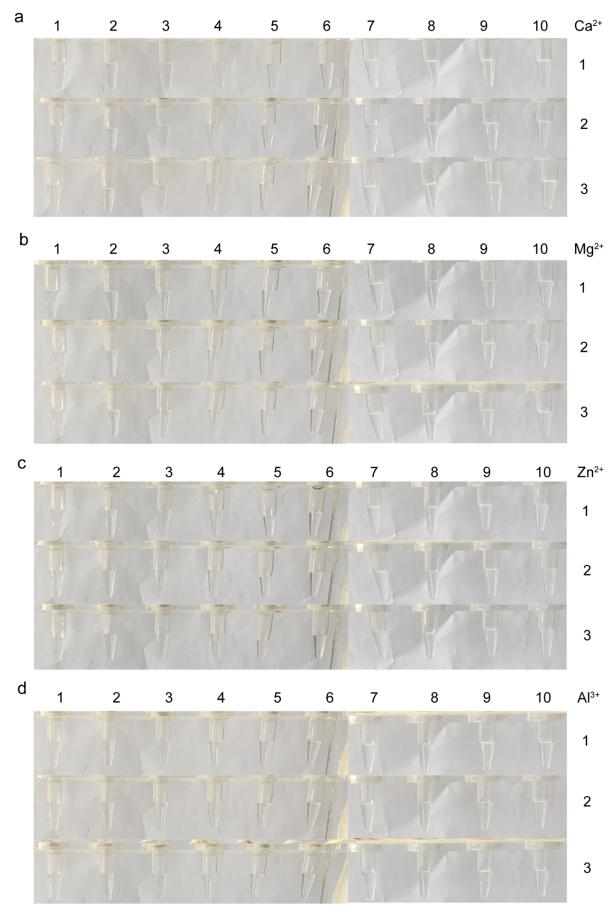


Fig. S1 Images of different concentrations of (a) Ca^{2+} , (b) Mg^{2+} , (c) Zn^{2+} , and (d) Al^{3+} solution.

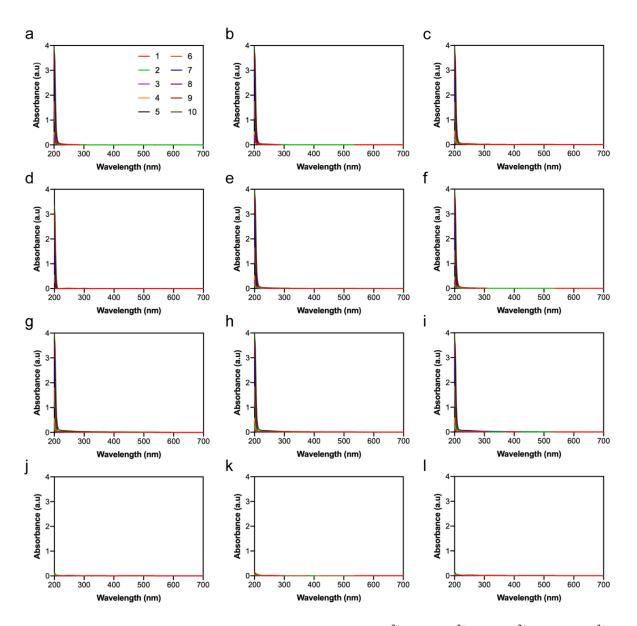


Fig. S2 UV-Vis absorbance of different concentrations of (a-c) Ca^{2+} , (d-f) Mg^{2+} , (g-i) Zn^{2+} , and (j-i) Al^{3+} .

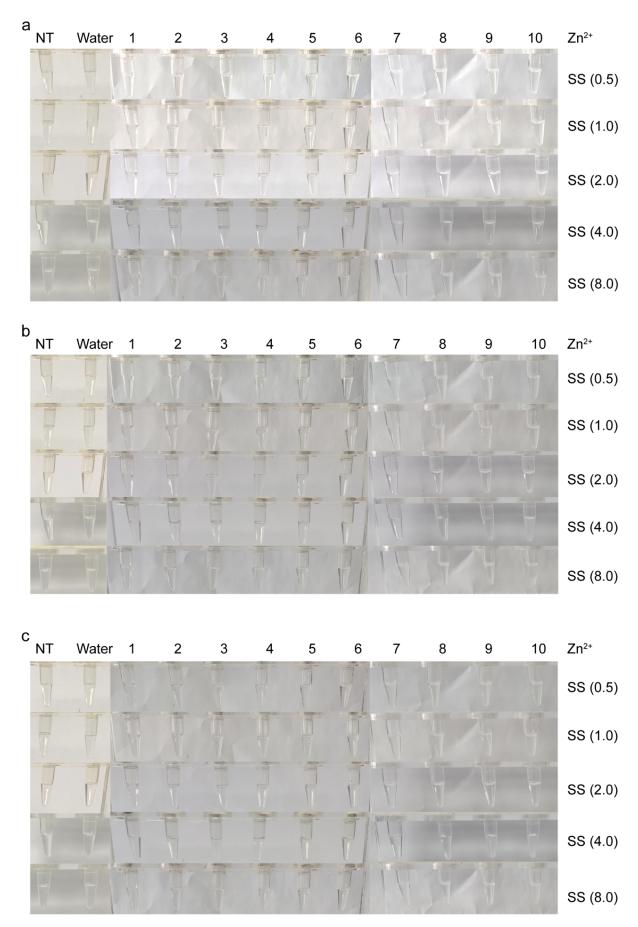


Fig. S3 Images of different concentrations of SS mixed with Zn²⁺.

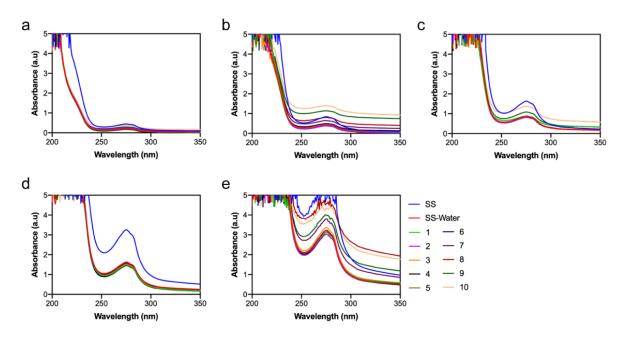


Fig. S4 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Zn^{2+} (Test 1).

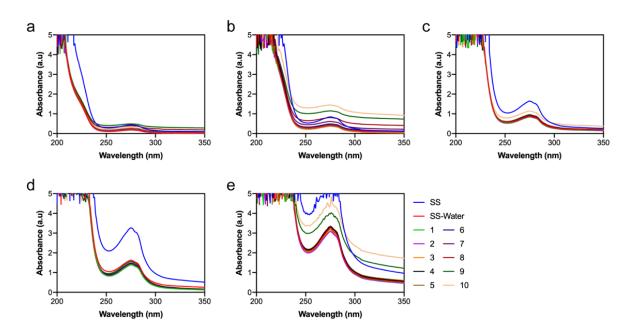


Fig. S5 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Zn^{2+} (Test 2).

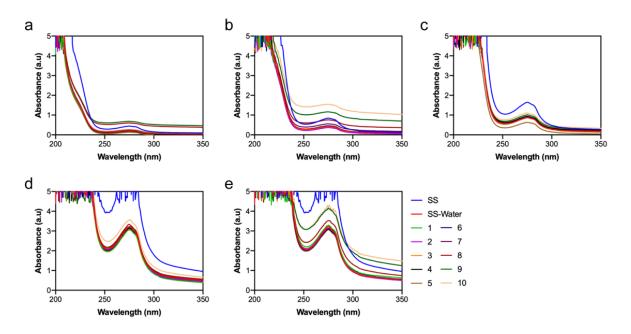


Fig. S6 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Zn^{2+} (Test 3).

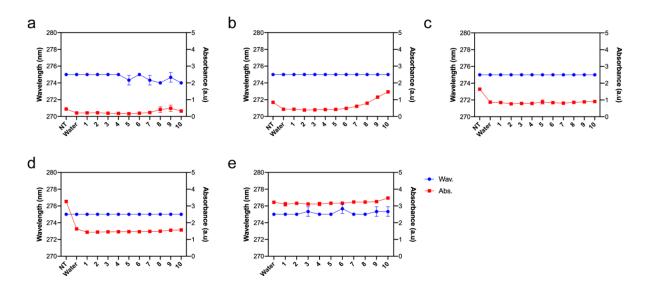


Fig. S7 UV-Vis absorbance change of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Zn^{2+} .

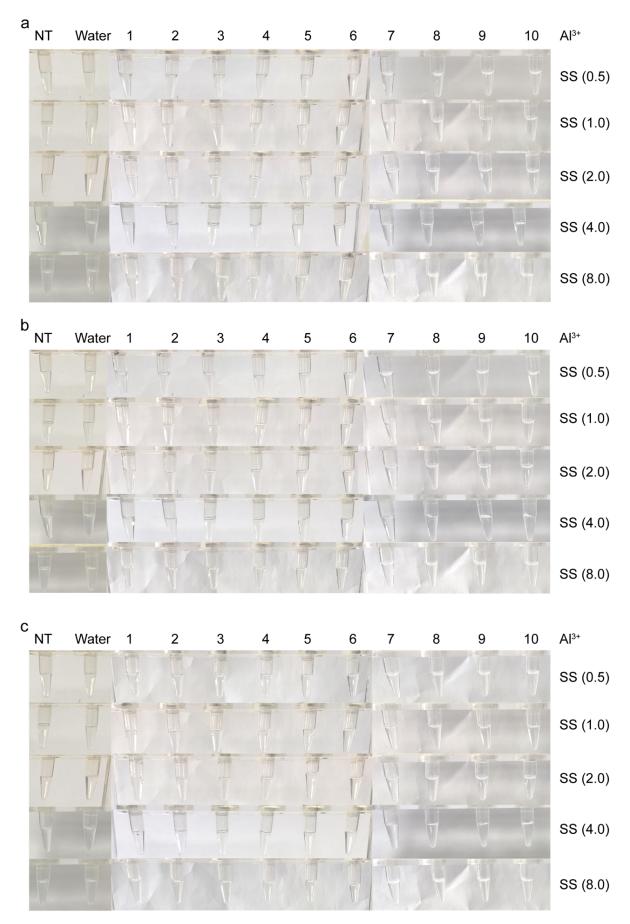


Fig. S8 Images of different concentrations of SS mixed with Al³⁺.

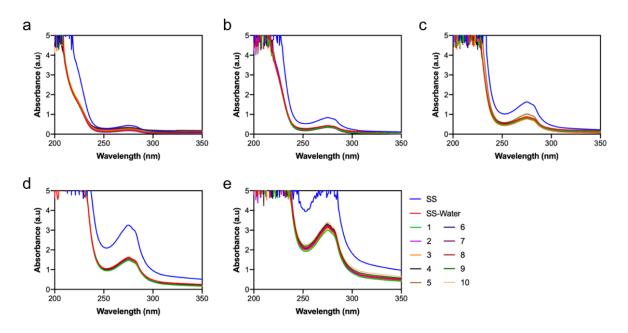


Fig. S9 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Al^{3+} (Test 1).

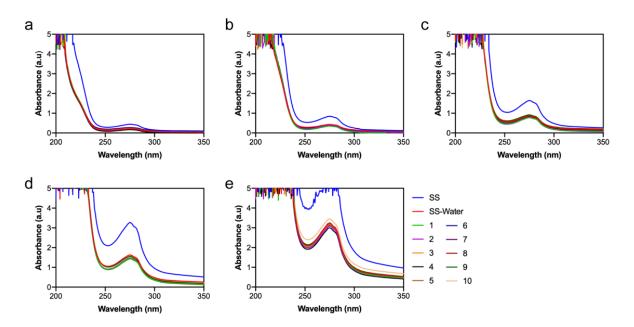


Fig. S10 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Al³⁺ (Test 2).

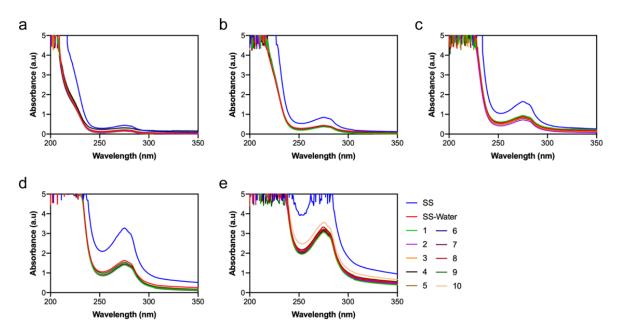


Fig. S11 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Al³⁺ (Test 3).

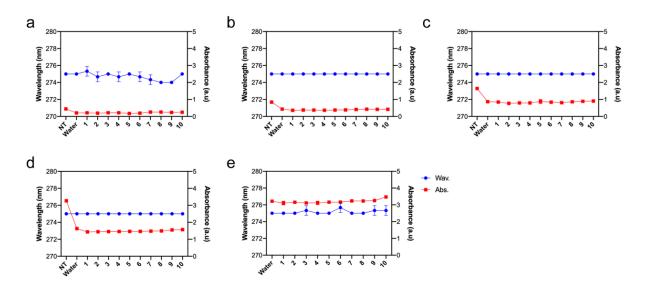


Fig. S12 UV-Vis absorbance change of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Al^{3+} .

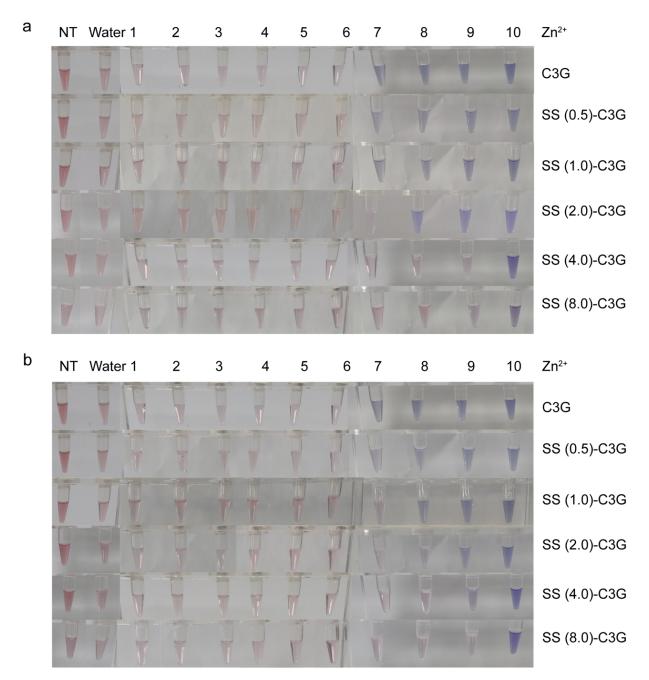


Fig. S13 Images of C3G and SS-C3G nanocomplex after mixing with different concentrations of Zn^{2+} (Repeated tests).

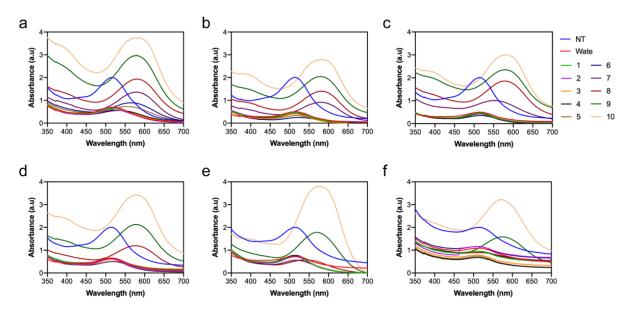


Fig. S14 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Zn^{2+} (Test 1).

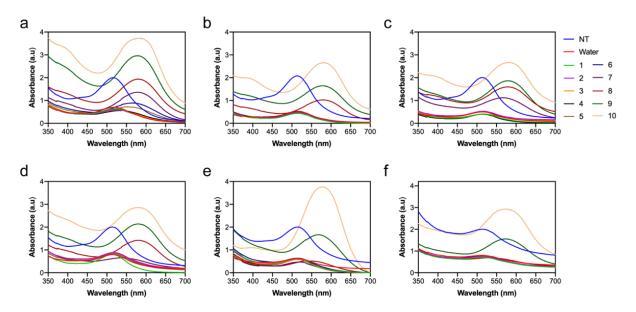


Fig. S15 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Zn^{2+} (Test 2).

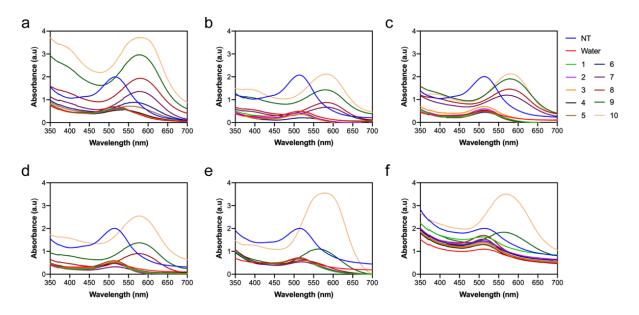


Fig. S16 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Zn^{2+} (Test 3).

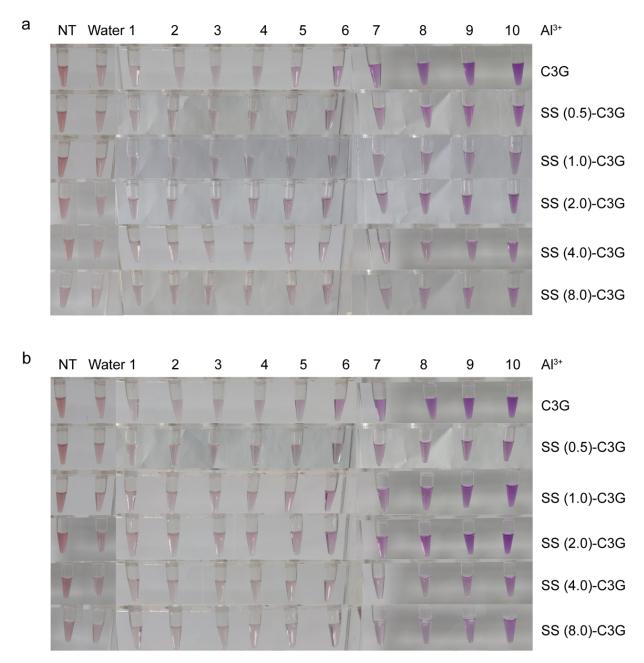


Fig. S17 Images of C3G and SS-C3G nanocomplex after mixing with different concentrations of Al^{3+} (Repeated tests).

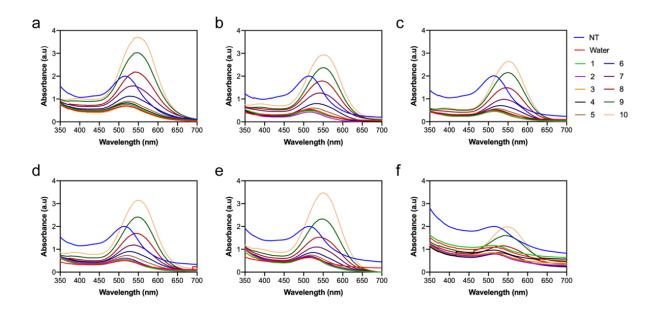


Fig. S18 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Al^{3+} (Test 1).

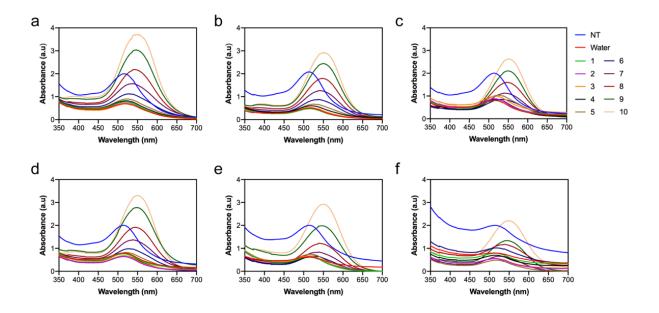


Fig. S19 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Al^{3+} (Test 2).

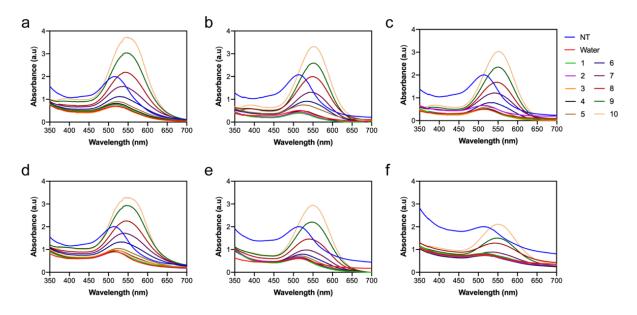


Fig. S20 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Al^{3+} (Test 3).

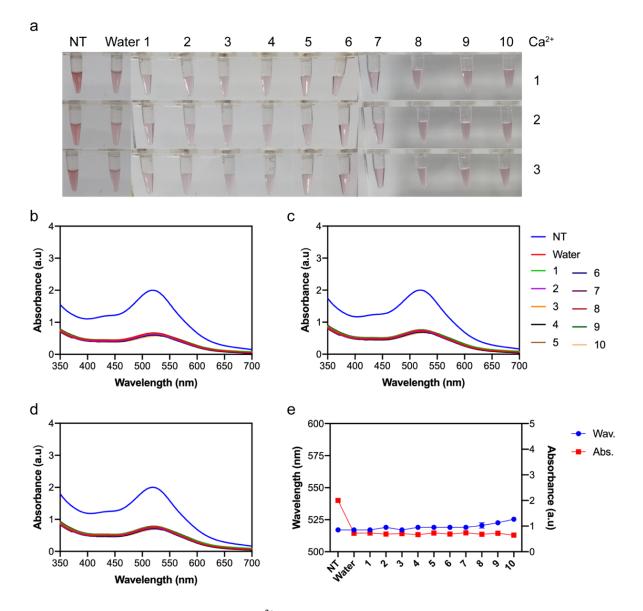


Fig. S21 (a) Images of C3G mixed with Ca^{2+} . (b-c) UV-Vis absorbance and (e) UV-Vis absorbance change of C3G mixed with Ca^{2+} .

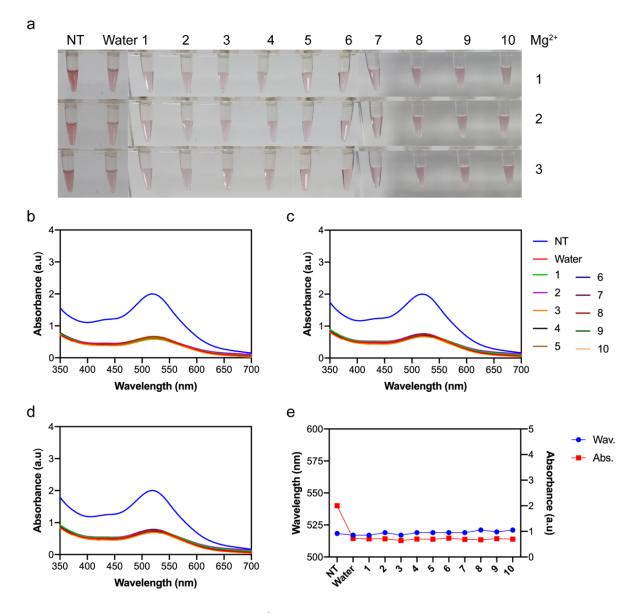


Fig. S22 (a) Images of C3G mixed with Mg^{2+} . (b-c) UV-Vis absorbance and (e) UV-Vis absorbance change of C3G mixed with Mg^{2+} .

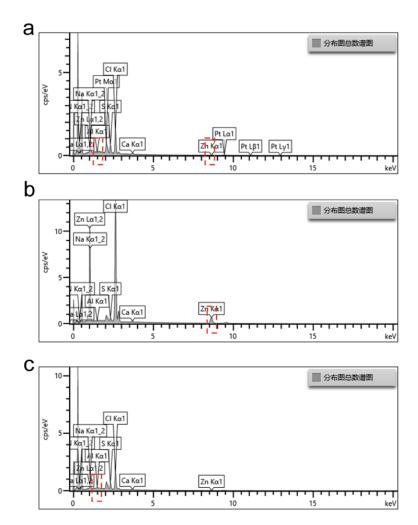


Fig. S23 EDS result of (a) SS (4.0)-C3G, (b) SS (4.0)-C3G-Zn-10, (c) SS (4.0)-C3G-Al-10.

a Water	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
\bigcirc	0	\bigcirc	\bigcirc	\bigcirc	0	\bigcirc	0	0	0	\bigcirc	Water
0		8				0					C3G
•				•		0		•		•	SS (0.5)-C3G
0	•	•	0	•	•		•				SS (1.0)-C3G
	0		0	0							SS (2.0)-C3G
		۲		0							SS (4.0)-C3G
0			0	0		۲					SS (8.0)-C3G
b Water	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
b Water	1	2	3	4	5	6	7	8	9	10	Zn²⁺ Water
b Water	1	2	3	4	5	6	7	8	9	10	
b Water	1	2	3	4	5	6	7	8	9	10	Water
b Water		2	3	4	5	6 0 0	7	8	9	10))))	Water C3G
b Water		2	3	4	5	6 0 0 0	7	8	9		Water C3G SS (0.5)-C3G
b Water		2	3	4	5 ()) ()) ()) ()) ()) ()) ()) ()) ()) ()	6	7	8	9		Water C3G SS (0.5)-C3G SS (1.0)-C3G

Fig. S24 Images of C3G and SS-C3G nanocomplex films (filter paper) after mixing with different concentrations of Zn^{2+} (Repeated tests).

a Water	1	2	3	4	5	6	7	8	9	10	Al ³⁺
0	\bigcirc)	0	\bigcirc		\bigcirc	\bigcirc	0		0	Water
0	0		0	0	0				•		C3G
	0	•	0		•	0			•		SS (0.5)-C3G
			0								SS (1.0)-C3G
0	0			0			0			•	SS (2.0)-C3G
	0	0		0		•		0			SS (4.0)-C3G
		0		0						0	SS (8.0)-C3G
b Water	1	2	3	4	5	6	7	8	9	10	Al ³⁺
b Water	1	2	3	4	5	6	7	8	9	10	Al³⁺ Water
b Water	1	2	3	4	5	6	7	8	9	10	
b Water		2	3 ()) ()) ())	4	5	6	7	8	9	10	Water
b Water		2	3 ()) ()) ()) ()) ()) ())	4	5 ()) ()) ()) ()) ()) ())	6	7 ()) ()) ()) ())	8	9	10	Water C3G
b Water		2	3	4	5 () () () () () () () () () () () () ()	6 0 0 0 0	7 ()) ()) ()) ()) ()) ()) ()) ()) ()) ()	8	9		Water C3G SS (0.5)-C3G
b Water		2	3	4	5 0 0 0 0	6 0 0 0 0 0 0	7 ()) ()) ()) ()) ()) ()) ()) ()) ()) ()	8	9		Water C3G SS (0.5)-C3G SS (1.0)-C3G

Fig. S25 Images of C3G and SS-C3G nanocomplex films (filter paper) after mixing with different concentrations of Al^{3+} (Repeated tests).

а	Water	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
	\bigcirc	\bigcirc	\bigcirc		\bigcirc	\bigcirc	0	\bigcirc	\bigcirc	\bigcirc	0	1
	0	0	0	\bigcirc	0	0	\bigcirc	\bigcirc	0	0	0	2
	0	0	0	5))	\bigcirc	\bigcirc	\bigcirc	\bigcirc	\bigcirc	0	3
b	Water	1	2	3	4	5	6	7	8	9	10	Al ³⁺
b	Water	1	2	3	4	5	6	7	8	9	10	Al ³⁺ 1
b	Water		2	3	4	5	6	7	8	9	10	

Fig. S26 Images of filter paper after mixing with different concentrations of (a) Zn^{2+} and (b) Al^{3+} .

a _{Water}	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
0	0	0	\bigcirc	0	())	()	\bigcirc	0	0	SS (0.5)
0	0	0	\bigcirc	0	0	0	0	0)	0	SS (1.0)
0	0	0	0	0)	0	0	\bigcirc	0	0	SS (2.0)
)	0	0	0	\bigcirc)	0	0	0	0	0	SS (4.0)
\bigcirc	0)	0	0	\bigcirc	\bigcirc	\bigcirc	0	0	0	SS (8.0)
b _{Water}	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
0	0	\mathbf{O}	\bigcirc	\bigcirc	0	\bigcirc	\bigcirc	0	0	0	SS (0.5)
\bigcirc	0	0	0	0	0	\bigcirc	0	0	\bigcirc)	SS (1.0)
\bigcirc	()	0	0	\bigcirc	0	0	\bigcirc	0	\bigcirc	0	SS (2.0)
\bigcirc	()	0	\bigcirc	\bigcirc	0	0)	\bigcirc	0	0	SS (4.0)
)	\bigcirc	0	0		0	0	0	\bigcirc	\bigcirc	0	SS (8.0)
c _{Water}	1	2	3	4	5	6	7	8	9	10	Zn ²⁺
))	0	0	\bigcirc	0	0	0	0	0	0	SS (0.5)
))	0	0	0	0	0	0	0	0	0	SS (1.0)
0)	0	0	0	0	0	0	0	0	0	SS (2.0)
)	0	0	0	0	0	0	0	0	0	\bigcirc	SS (4.0)
0	\bigcirc	\bigcirc	0		0	0	0	0	0	0	SS (8.0)

Fig. S27 Images of SS films (filter paper) after mixing with different concentrations of Zn^{2+} . (Repeated tests).

a _{Water}	1	2	3	4	5	6	7	8	9	10	Al ³⁺
0	0	0)	0	\bigcirc	0	\bigcirc	\bigcirc	0	0	SS (0.5)
0	\bigcirc	0	0	0	-)	0	\bigcirc	0	0	0	SS (1.0)
\bigcirc	0	0	0	0)))	0	\bigcirc)	SS (2.0)
0	\bigcirc)	0	\bigcirc))	0	\bigcirc)	0	SS (4.0)
\bigcirc	0	0	\bigcirc	\bigcirc	()	\bigcirc	0	0	0	0	SS (8.0)
b _{Water}	1	2	3	4	5	6	7	8	9	10	Al ³⁺
)	0	0	0	0	\bigcirc	())	\bigcirc)	0	SS (0.5)
0	0	0	0	0	0	0))	0	0	SS (1.0)
0	0	0	0	0))	\bigcirc	0	\bigcirc	0	SS (2.0)
	0	0	\bigcirc)	\bigcirc	0	()	\bigcirc	\bigcirc	0	SS (4.0)
3		\bigcirc	\bigcirc	\bigcirc		0	0	0	0	0	SS (8.0)
c _{Water}	1	2	3	4	5	6	7	8	9	10	Al ³⁺
0)		0	0	\bigcirc	\bigcirc	\bigcirc	0	\bigcirc)	SS (0.5)
)	\bigcirc	0	0	0	0	\bigcirc	0	0	\bigcirc)	SS (1.0)
\bigcirc	0	\bigcirc	0	0	0	0	0)	0	0	SS (2.0)
0)	\bigcirc	0	0	\bigcirc	0	3	0	0	0	SS (4.0)
0)	0	\bigcirc	0	0	0	0	\bigcirc	0	0	SS (8.0)

Fig. S28 Images of SS films (filter paper) after mixing with different concentrations of Al^{3+} . (Repeated tests).

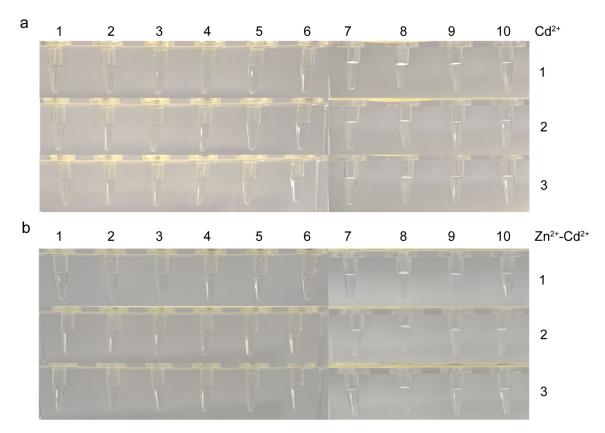


Fig. S29 Images of different concentrations of (a) Cd^{2+} and (b) $Zn^{2+}-Cd^{2+}$ solutions.

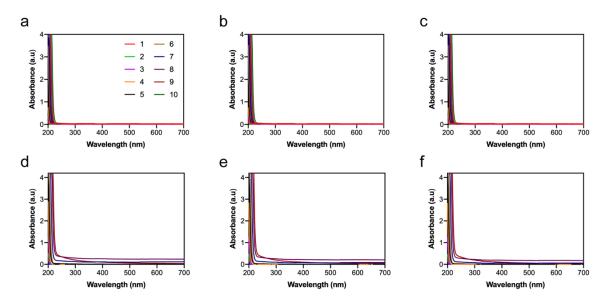


Fig. S30 UV-Vis absorbance of different concentrations of (a-c) Cd^{2+} and (d-f) Zn^{2+} , (g-i) $Zn^{2+}-Cd^{2+}$.

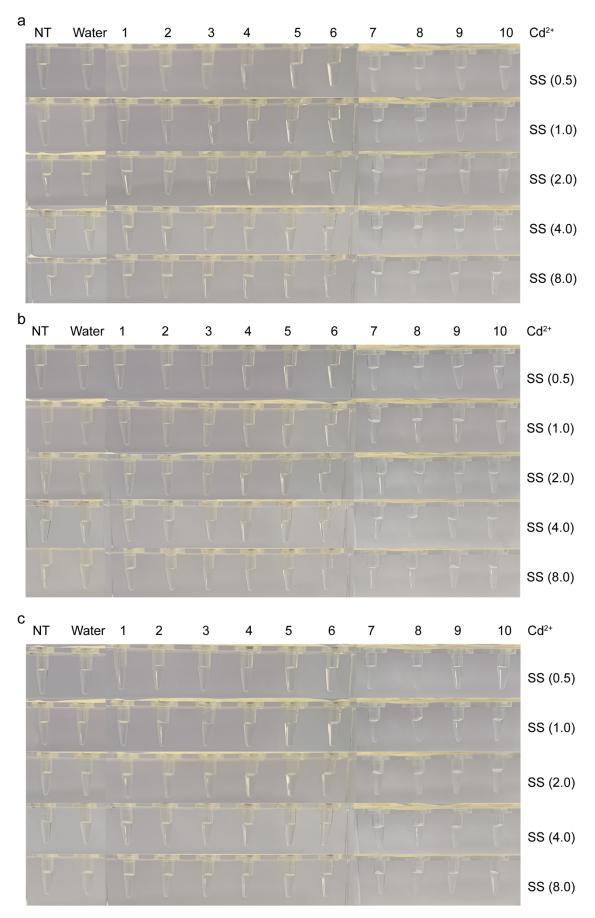


Fig. S31 Images of different concentrations of SS mixed with Cd²⁺.

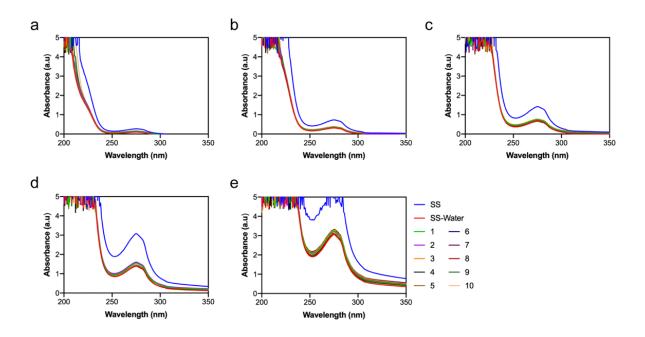


Fig. S32 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Cd²⁺ (Test 1).

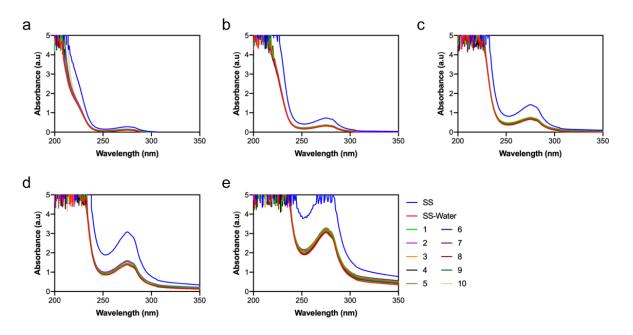


Fig. S33 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Cd²⁺ (Test 2).

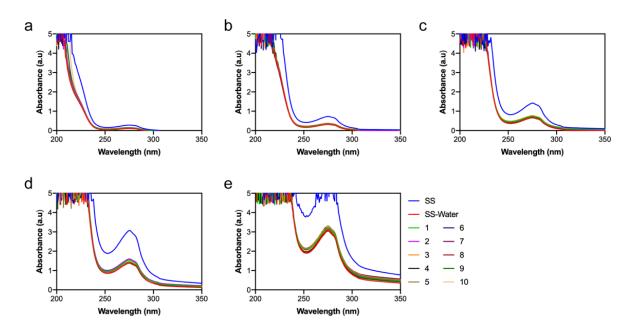


Fig. S34 UV-Vis absorbance of (a) SS (0.5), (b) SS (1.0), (c) SS (2.0), (d) SS (4.0), and (e) SS (8.0) mixed with Cd^{2+} (Test 3).

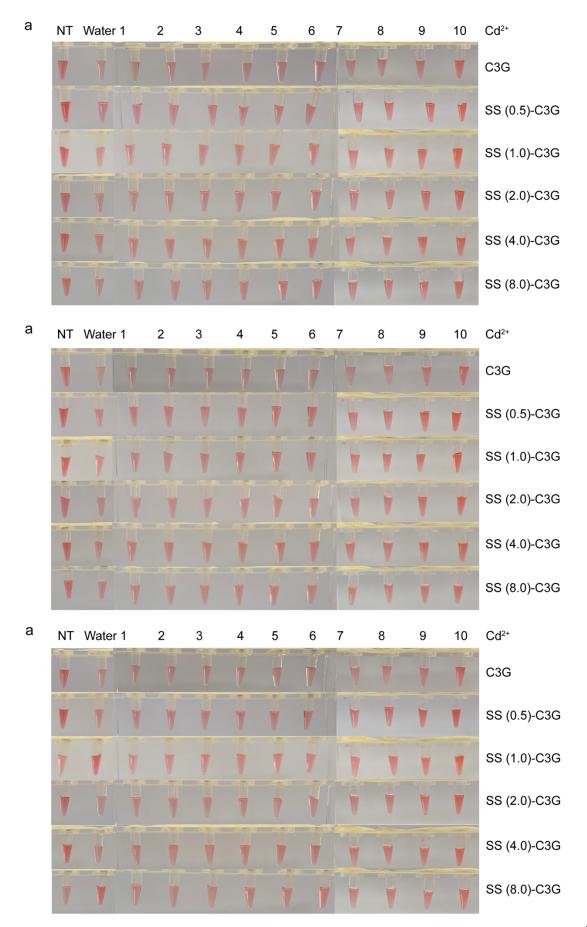


Fig. S35 Images of C3G and SS-C3G nanocomplex after mixing with different concentrations of Cd²⁺.

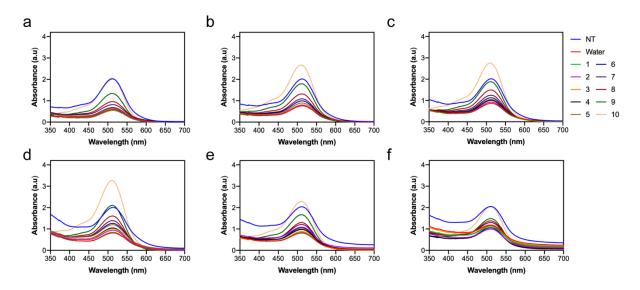


Fig. S36 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Cd^{2+} (Test 1).

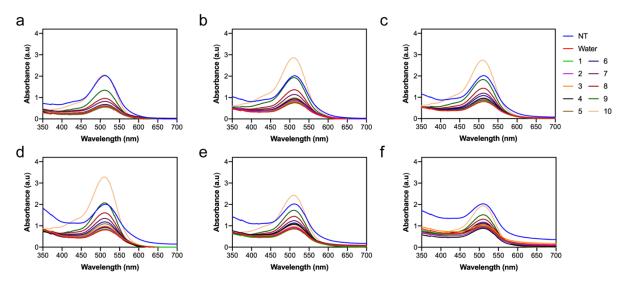


Fig. S37 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Cd^{2+} (Test 2).

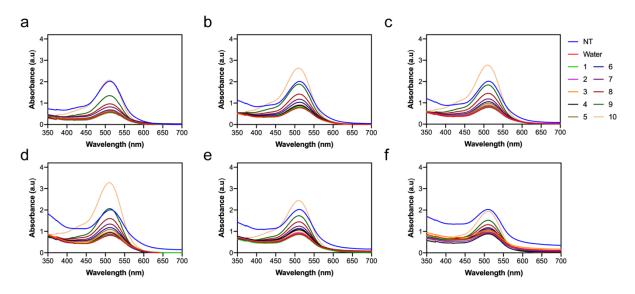


Fig. S38 UV-Vis absorbance (a) C3G, (b) SS (0.5)-C3G, (c) SS (1.0)-C3G, (d) SS (2.0)-C3G, (e) SS (4.0)-C3G, and (f) SS (8.0)-C3G mixed with different concentrations of Cd^{2+} (Test 3).

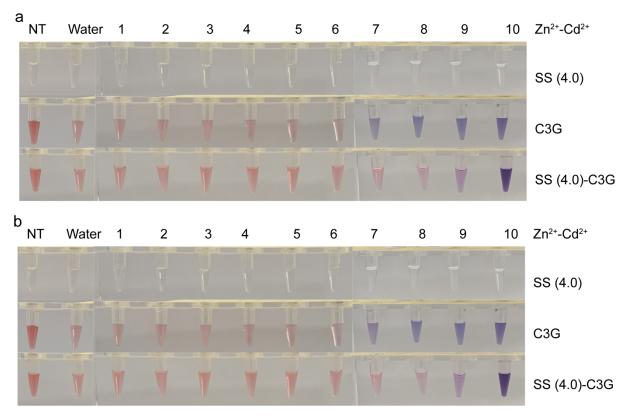


Fig. S39 Images of C3G and SS-C3G nanocomplex after mixing with different concentrations of Zn²⁺-Cd²⁺.

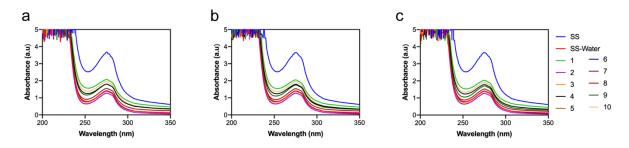


Fig. S40 UV-Vis absorbance SS (4.0) mixed with different concentrations of $Zn^{2+}-Cd^{2+}$.

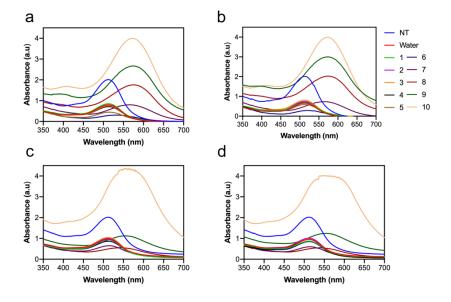


Fig. S41 UV-Vis absorbance (a-b) C3G and (c-d) SS (4.0)-C3G mixed with different concentrations of Zn^{2+} -Cd²⁺.

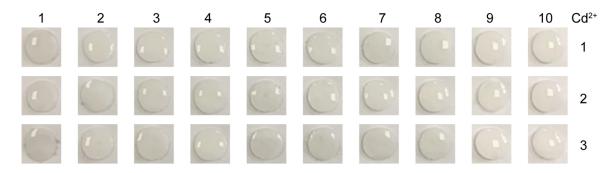


Fig. S42 Images of filter paper after mixing with different concentrations of Cd²⁺.

a Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
0	0	0	0	0		0	0	Cr.	C	0	C3G
	•	0				•	•		0	C	SS (0.5)-C3G
•	0	•	•					•		0	SS (1.0)-C3G
		1		•						۲	SS (2.0)-C3G
	0					•	6			6	SS (4.0)-C3G
۲	1	0	0	0	0			•		۲	SS (8.0)-C3G
b Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
0	0		6				0		O	C	C3G
0	•		•							0	SS (0.5)-C3G
			0						•	0	SS (1.0)-C3G
۲										•	SS (2.0)-C3G
0				0		•	•	0			SS (4.0)-C3G
			0								SS (8.0)-C3G
C Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
•	0	0	0		0	0	0	0		0	C3G
•	•		•			0	0	0		0	SS (0.5)-C3G
	•							•	•	•	SS (1.0)-C3G
۲	۲										SS (2.0)-C3G
0	•	0	0				•		•	0	SS (4.0)-C3G
9			9								SS (8.0)-C3G

Fig. S43 Images of C3G and SS-C3G nanocomplex films (filter paper) after mixing with different concentrations of Cd^{2+} .

а	Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
	\bigcirc	\mathbf{C}	\bigcirc	\bigcirc	C	C	\bigcirc	\bigcirc	C		\bigcirc	SS (0.5)
	\bigcirc	0	C	C	0	C	0	C	C	C	C	SS (1.0)
	0	0	()	0	C	O	0	C	C	C	0	SS (2.0)
	0	0	0	0	0	0	0	0	C	C	C	SS (4.0)
			\bigcirc	0	0	0	0	C	C	C	C	SS (8.0)
b	Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
	\bigcirc	0	\bigcirc	\bigcirc	\bigcirc	-	C	C		C	\bigcirc	SS (0.5)
	C	O	0	0	6	C	0	C	C	C	C	SS (1.0)
	Q.	Ó	0	0	C	C	C	C	0	C	C	SS (2.0)
		0	0	0	0	0	C	0	C	C	C	SS (4.0)
	•	0	O	0	0	0	()	Ch	C	C	0	SS (8.0)
С	Water	1	2	3	4	5	6	7	8	9	10	Cd ²⁺
	0	\bigcirc	C	\bigcirc	\bigcirc	C	6	Ch		C	\bigcirc	SS (0.5)
	0	0	0	0	0	C	C	C	C	C	C	SS (1.0)
	O	0	0	Ó	O	C	C	C	Ci	C	C	SS (2.0)
	$\mathbf{\cdot}$	0	0	9	0	0	C	C	C	C	C	SS (4.0)
	0	0	\bigcirc	O	0	0	0	O	C	0	C	SS (8.0)

Fig. S44 Images of SS films (filter paper) after mixing with different concentrations of Cd^{2+} .

Water	1	2	3	4	5	6	7	8	9	10 Zn ²⁺ -Cd ²⁺
	\bigcirc	0	O	0	0	C	C	C	C	1
O	0	C		0	0	Ó	C	Cor	0	2
0	0	0	\bigcirc	C	G	C	C	C	C	3

Fig. S45 Images of filter paper after mixing with different concentrations of $Zn^{2+}-Cd^{2+}$.

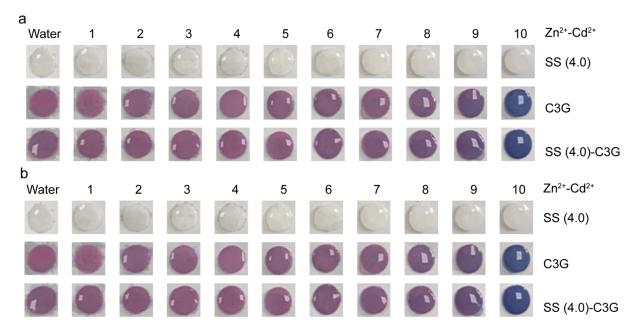


Fig. S46 Images of SS, C3G, and SS-C3G nanocomplex (filter paper) after mixing with different concentrations of Zn^{2+} -Cd²⁺.