Supporting Information:

From Unimolecular Template to Silver Nanocrystal Clusters: An Effective Strategy to Balance Antibacterial Activity and Cytotoxicity

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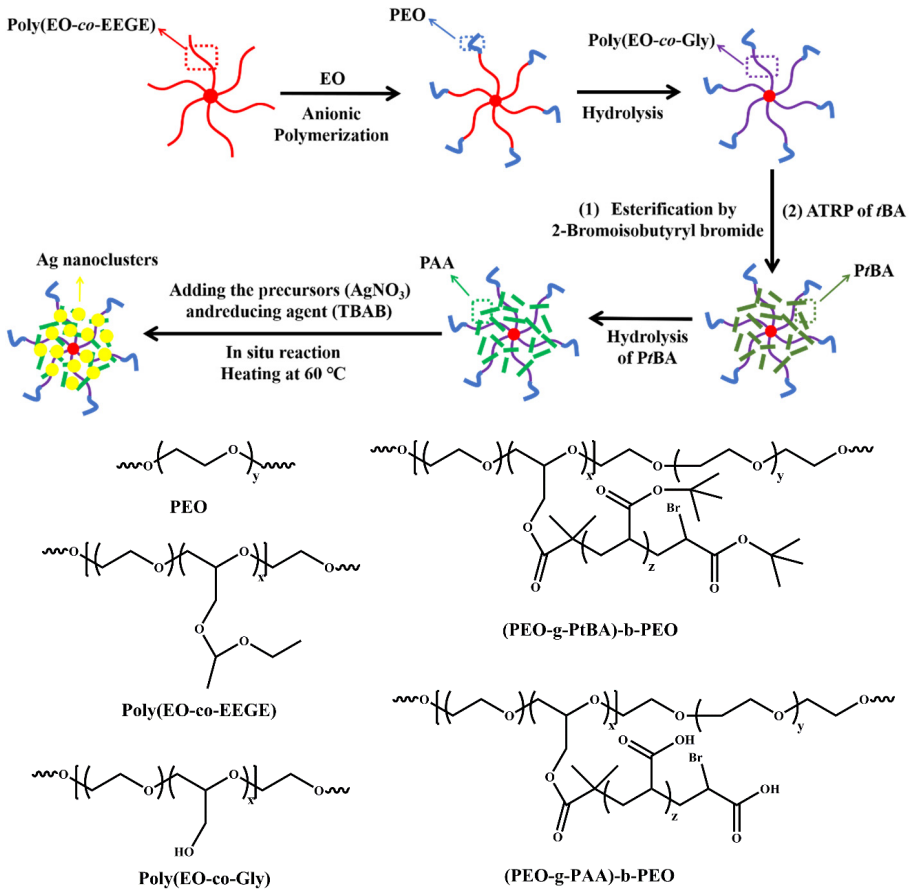
Part 1: Synthesis and Characterization of α-CD-*g*-[(PEO$_{40}$-*g*-PAA$_{50}$)-*b*-PEO$_5$]$_{18}$



Scheme S1. Schematic illustration of the synthesis of water-soluble multi-arm star-shaped brush-like block copolymer α-CD-*g*-[(PEO$_{40}$-*g*-PAA$_{50}$)-*b*-PEO$_5$]$_{18}$.

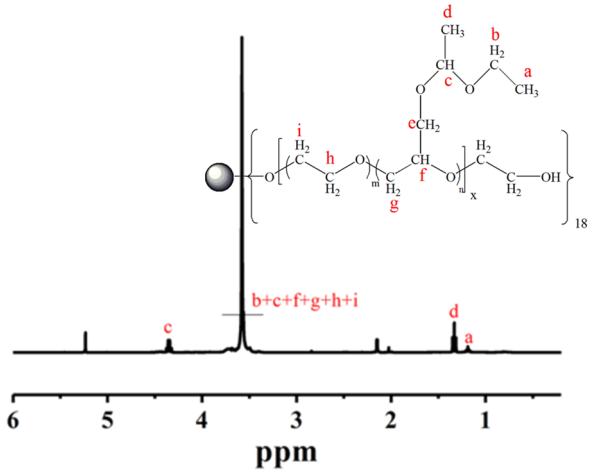


Figure S1. ^{1}H-NMR spectrum of multi-arm star-shaped copolymer poly(EO-*co*-EEGE) ($CDCl_3$).

Figure S1 shows a typical ^{1}H-NMR spectrum of multi-arm starshaped copolymers poly(EO-*co*-EEGE), the quartet at δ=4.69-4.74 ppm is assigned to the methyl protons (H_c) of EEGE moiety, the doublets at δ=1.30, 1.29 ppm and the triplet at δ = 1.21, 1.19, 1.18 ppm are assigned to methyl protons of the EEGE moiety (H_d, H_a), the chemical shift at δ=3.53-3.80 ppm is assigned to protons of the main chain (H_f, H_g, H_h, H_i) and protons of the side chains (H_b, H_e). The copolymer composition can be calculated by using following equation based on the ^{1}H-NMR spectrum:

$$R_T=\frac{4A_c}{A_{sum}-7A_c} \quad (1)$$

where R_T is the molar ratio of EEGE to EO in the resulting multiarm star-shaped copolymers poly (EO-co-EEGE); A_{sum} and A_c represent the peak integral area sum of the protons (b+e+f+g+h+i) and the peak integral areas of the methine protons of the EEGE moiety, respectively. The R_T values of four samples are shown in Table 1, which are nearly equivalent to the monomer feed molar ratio of EEGE to EO. In addition, the average number of protected hydroxyls on each arm could be evaluated by the combination of the theoretical values of molecular weight of each arm and ^{1}H-NMR spectrum using the following eqn (2):

$$N_{EEGE}=\frac{M_{n,arm}}{(146+\frac{44}{R_T})} \quad (2)$$

in which $M_{n,arm}$ is the theoretical value of molecular weight of each arm, 146 and 44 are the molar masses of EEGE and EO, and R_T is the molar ratio of EEGE units to EO units in copolymers, all the data values are listed in Table S1.

Table S1 Summary of multi-arm star-shaped copolymers poly(EO-*co*-EEGE)

Sample	R_f[a]	R_T[b]	PDI[c]	$M_{n,arm}$[d] (g/mol)	N_{EO}[e]
EO-*co*-EEGE	1/20	1/20.7	1.06	2500	40

[a]The feed molar ratio of EEGE to EO.

[b]The unit molar ratio of EEGE to EO in multi-arm star-shaped copolymers poly(EO-*co*-EEGE) measured by ^{1}H-NMR.

[c]The polydispersity (PDI) determined by GPC.

[d]M_n of each CD-*g*-poly(EO-*co*-EEGE) arm calculated from the GPC of M_n.

[e]The number of EO units in multi-arm star-shaped copolymers poly(EO-*co*-EEGE) calculated by the integration of protons from ^{1}H-NMR.

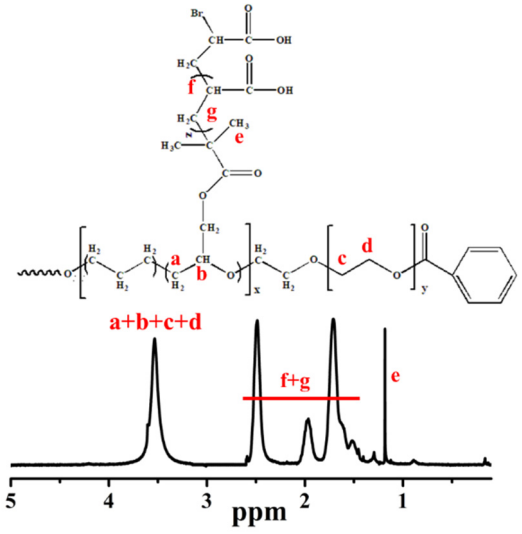


Figure S2. ^{1}H-NMR spectra of α-CD-*g*-[(PEO$_{40}$-*g*-PAA$_{50}$)-*b*-PEO$_5$]$_{18}$. (DMF-d$_7$).

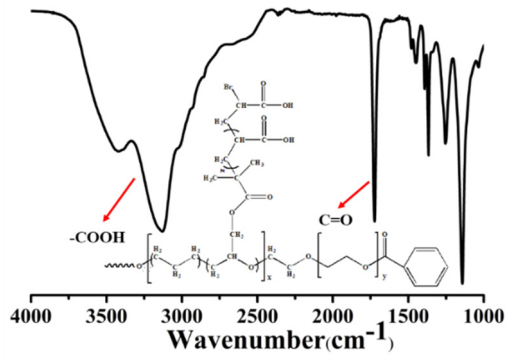


Figure S3. FT-IR spectra of α-CD-*g*-[(PEO$_{40}$-*g*-PAA$_{50}$)-*b*-PEO$_5$]$_{18}$.

DP(x)=N_{EO}=40

DP(z)=$\frac{2(A_{f+g})}{A_e}$=2*25.17=50.34≈50

DP(y)=$\frac{2A_{(a+b+c+d)}}{A_e}$-DP(x)=2*22.59-40=5.18≈5

Thus, the final template is α-CD-*g*-[(PEO$_{40}$-*g*-PAA$_{50}$)-*b*-PEO$_5$]$_{18}$.

Part 2: Synthesis and Characterizations of Ag@Template Nanoclusters

Figure S4. The picture of Ag@Template solution from left to right are Ag@Template-1, Ag@Template-2, Ag@Template-3, Ag@Template-4.

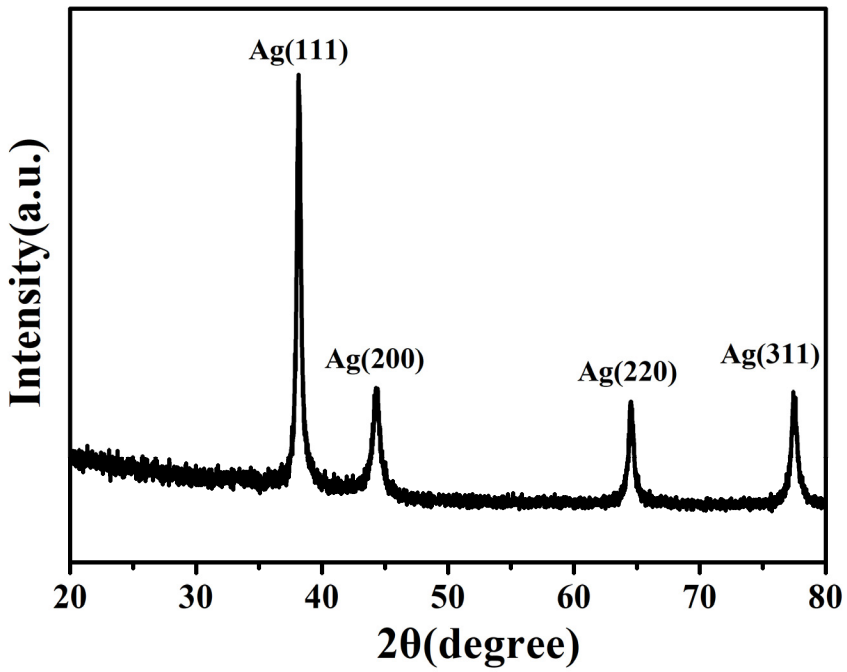


Figure S5. XRD pattern of control Ag NPs.

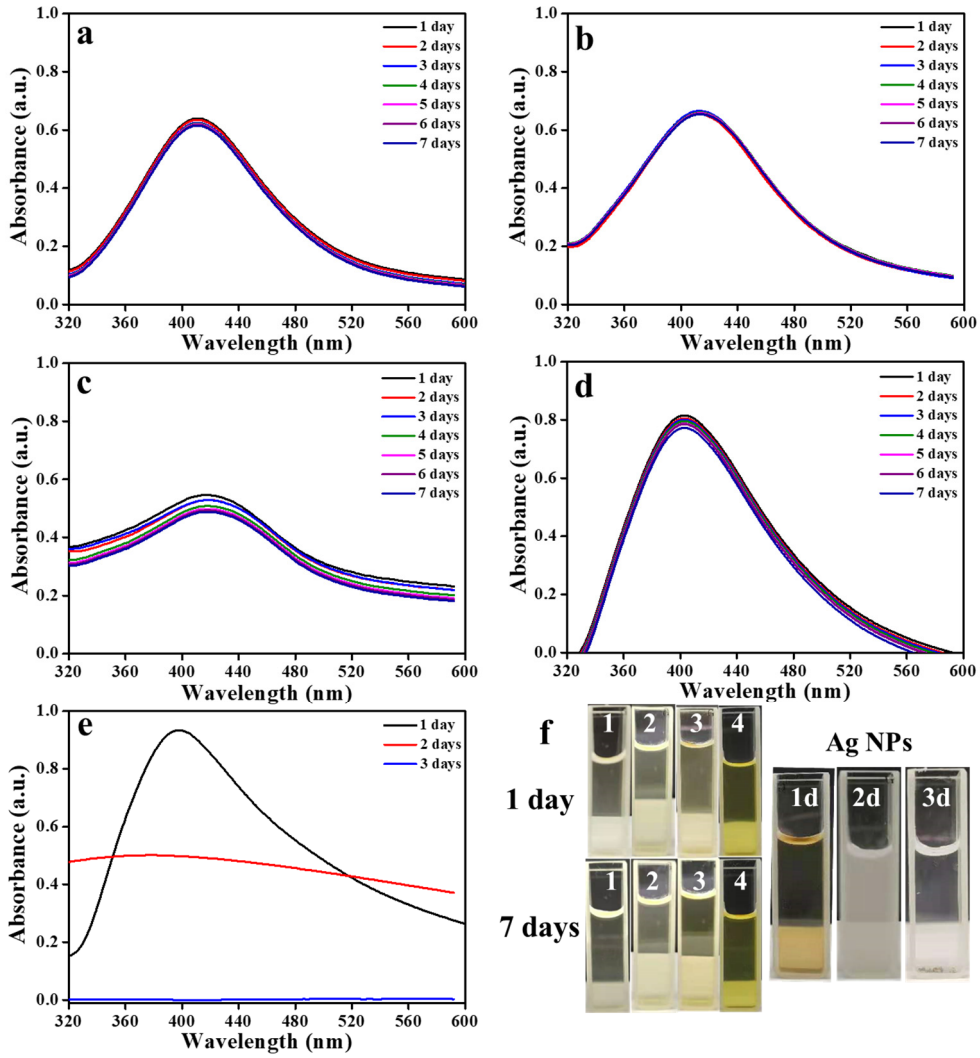


Figure S6. UV-vis absorption spectra of Ag@Template NC dispersion in H_2O (pH=5.5) within a week: Ag@Template-1 NC (a), Ag@Template-2 NC (b), Ag@Template-3 NC (c), Ag@Template-4 NC (d), Ag NPs (e); (f) The photograph of Ag@Template dispersion before (up) and after (down) a week storage, from left to right are Ag@Template-1 NC, Ag@Template-2 NC, Ag@Template-3 NC, Ag@Template-4 NC and Ag NPs.

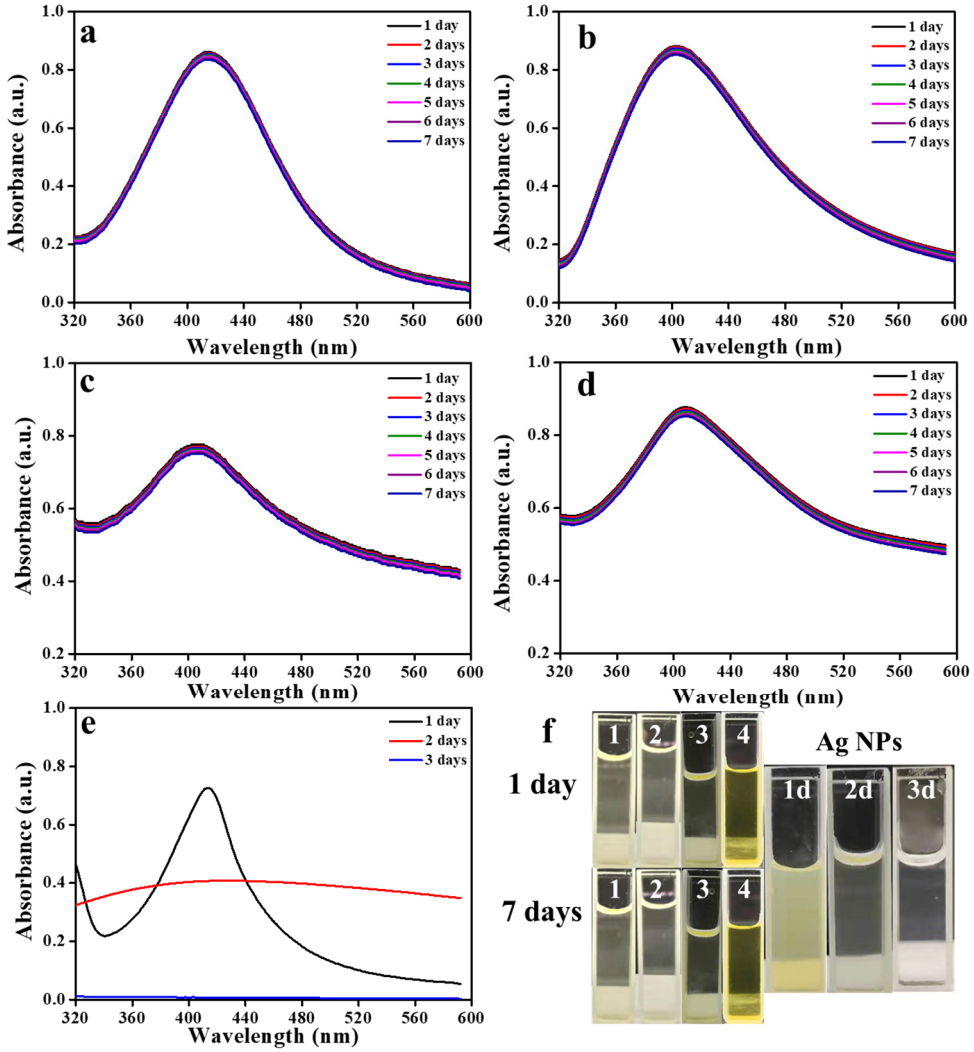


Figure S7. UV-vis absorption spectra of Ag@Template NC dispersion in 0.9% NaCl within a week: Ag@Template-1 NC (a), Ag@Template-2 NC (b), Ag@Template-3 NC (c), Ag@Template-4 NC (d), Ag NPs (e); (f) The photograph of Ag@Template dispersion before (up) and after (down) a week storage, from left to right are Ag@Template-1 NC, Ag@Template-2 NC, Ag@Template-3 NC, Ag@Template-4 NC and Ag NPs.

Table S2. Sizes of Ag@Template in different micrographs (nm)

Samples	DLS	TEM	Grains
Ag@Template-1	64.3	38.2±4.5	1.6±0.3
Ag@Template-2	74.2	32.9±3.1	2.4±0.4
Ag@Template-3	69.8	43.2±6.0	3.4±0.8
Ag@Template-4	73.1	40.4±5.9	5.6±0.9

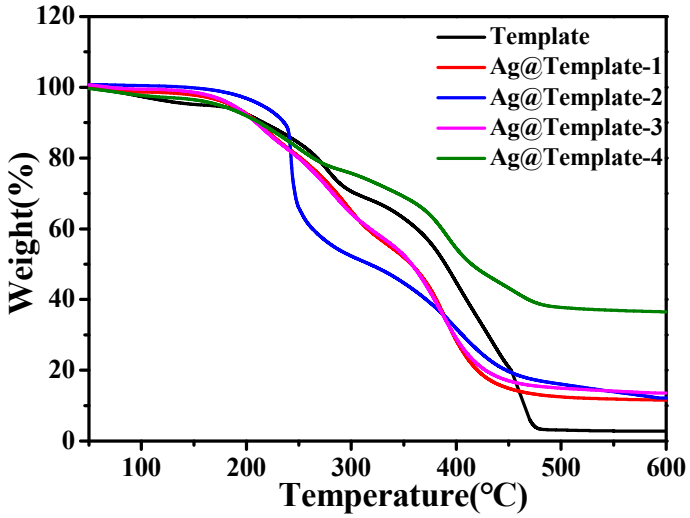


Figure S8. TGA curves of Ag@Template.

Table S3. Content of nanosilver (wt%) in nanoclusters analyzed by TGA

Samples	Residue (%)	Content of Ag (%)
Template	2.60	-
Ag@Template-1	9.80	7.20
Ag@Template-2	12.1	9.50
Ag@Template-3	13.5	10.9
Ag@Template-4	35.4	32.8

Part 3: Property of Ag@Templates Nanoclusters

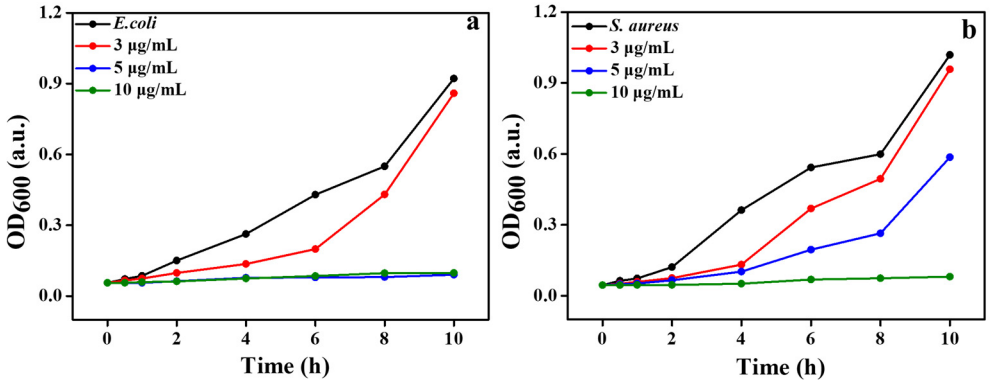


Figure S9. OD_{600} values of *E. coli* (a) and *S. aureus* (b) incubated with Ag@Template-1 at different dosages.

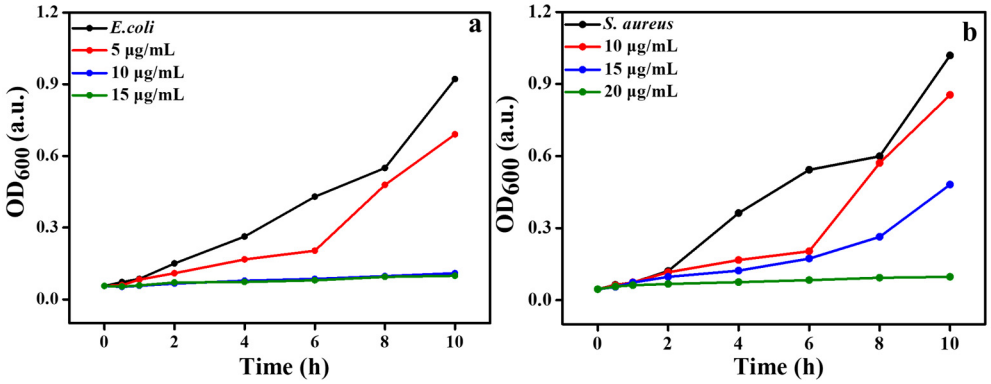


Figure S10. OD_{600} values of *E. coli* (a) and *S. aureus* (b) incubated with Ag@Template-2 at different dosages.

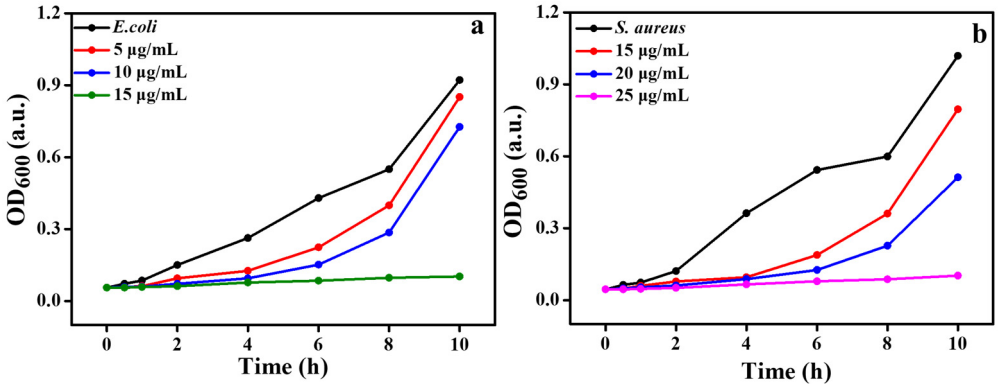


Figure S11. OD_{600} values of *E. coli* (a) and *S. aureus* (b) incubated with Ag@Template-3 at different dosages.

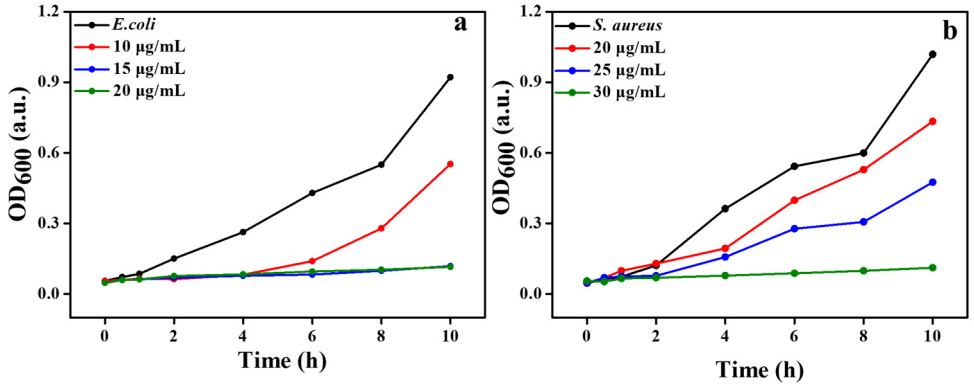


Figure S12. OD_{600} values of *E. coli* (a) and *S. aureus* (b) incubated with Ag@Template-4 at different dosages.

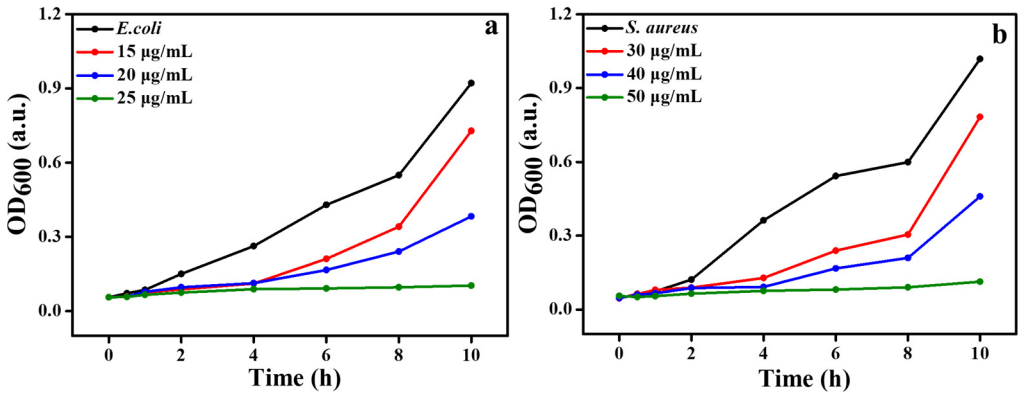


Figure S13. OD_{600} values of *E. coli* (a) and *S. aureus* (b) incubated with Ag NPs at different dosages.

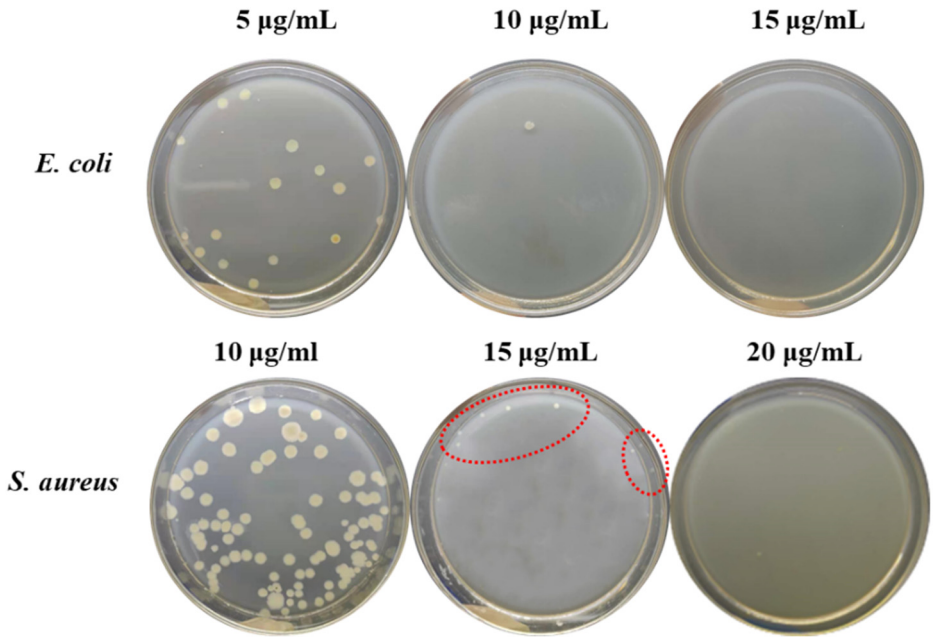


Figure S14. *E. coli* and *S. aureus* plates incubated with Ag@Template-1 at different dosages for 24 h.

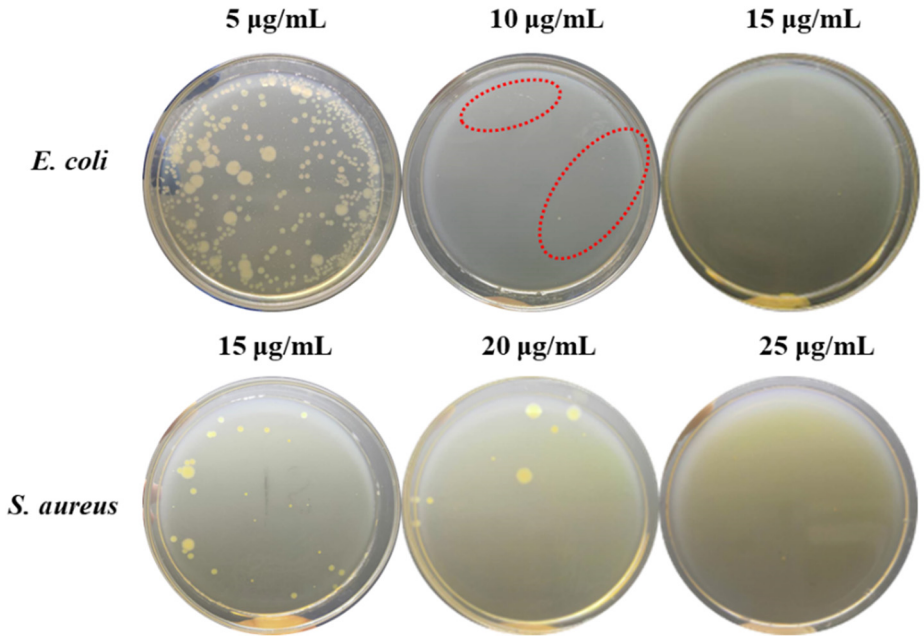


Figure S15. *E. coli* and *S. aureus* plates incubated with Ag@Template-2 at different dosages for 24 h.

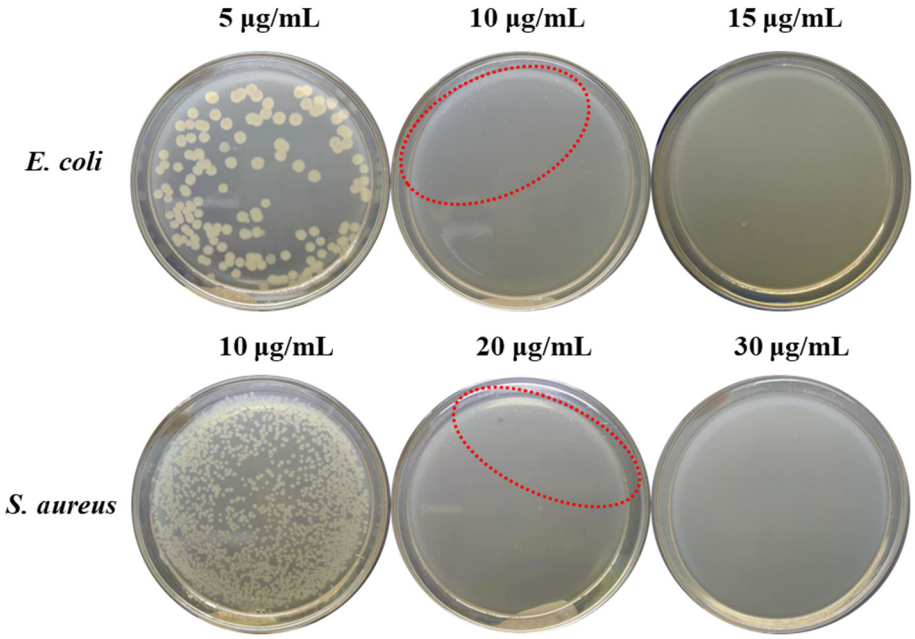


Figure S16. *E. coli* and *S. aureus* plates incubated with Ag@Template-3 at different dosages for 24 h.

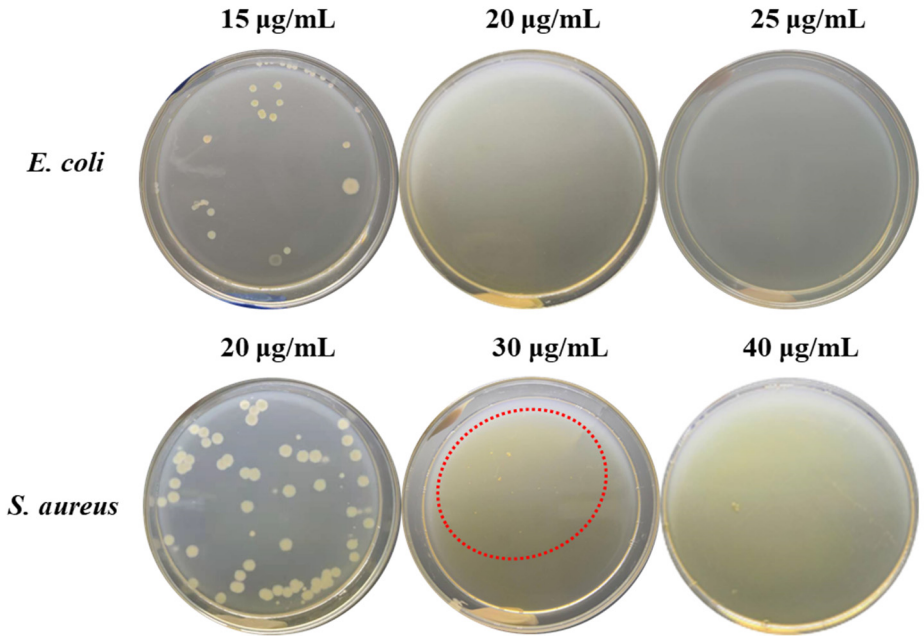


Figure S17. *E. coli* and *S. aureus* plates incubated with Ag@Template-4 at different dosages for 24 h.

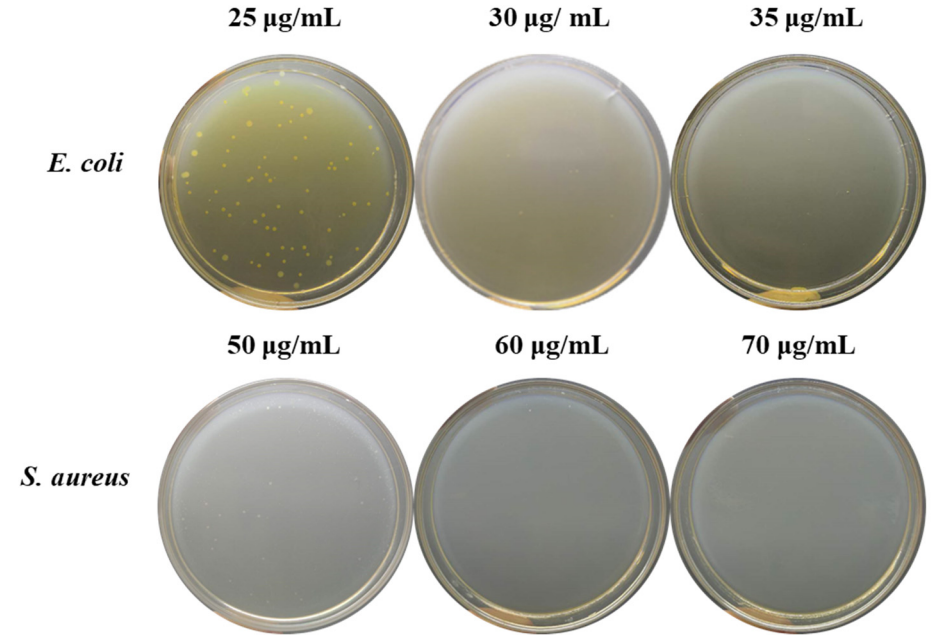


Figure S18. *E. coli* and *S. aureus* plates incubated with Ag NPs at different dosages for 24 h.

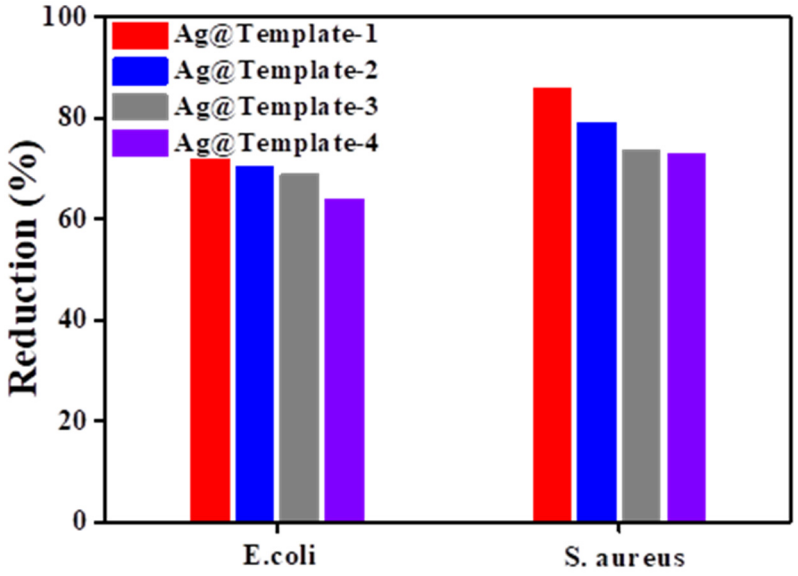


Figure S19. Reduction percentage of bacteria treated with Ag@Template NCs for 4 h (c=10 μg/mL).

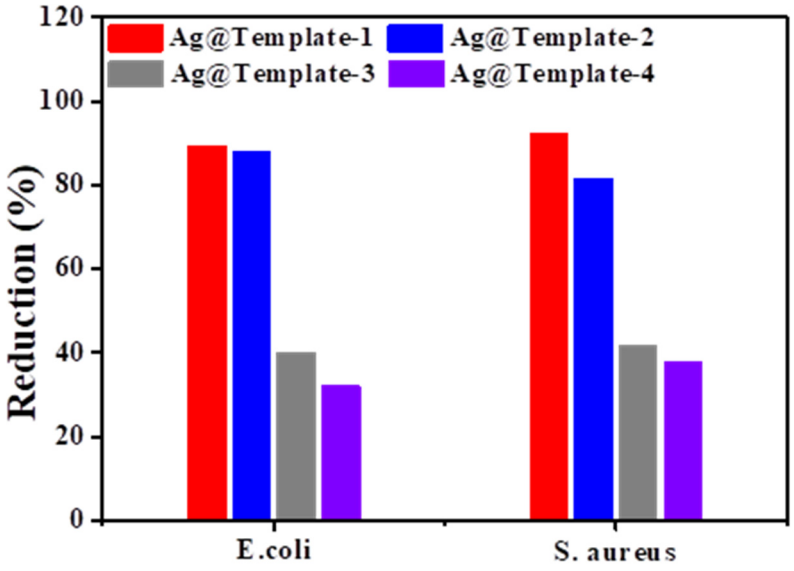


Figure S20. Reduction percentage of bacteria treated with Ag@Template NCs for 10 h (c=10 μg/mL).

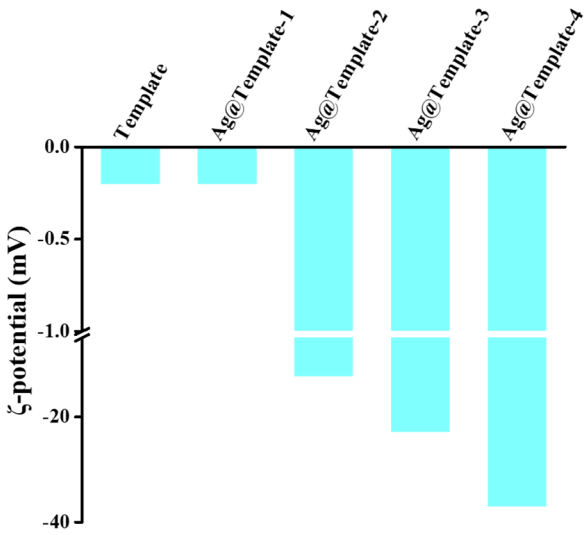


Figure S21. ζ potential of Ag@Template NCs.

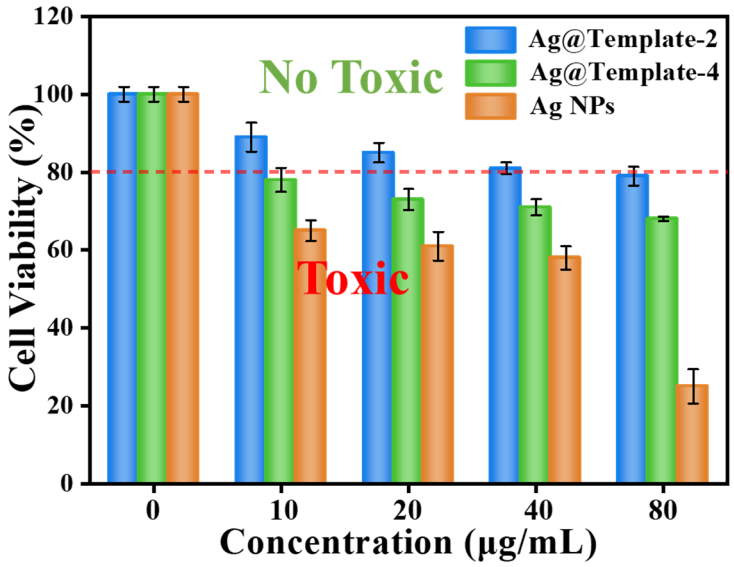


Figure S22. Viability of L02 cells treated with different concentrations of Ag@Template-2, Ag@Template-4 and Ag NPs for 48 h.

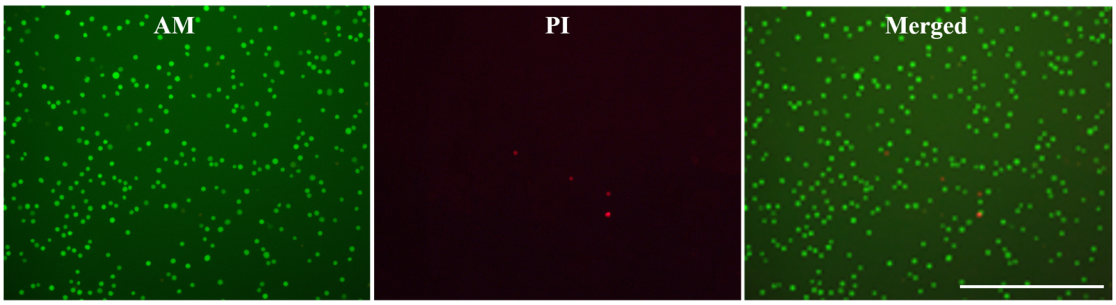


Figure S23. The images of Live/Dead assays of L02 cells (48 h). The scale bar is 10 μm.

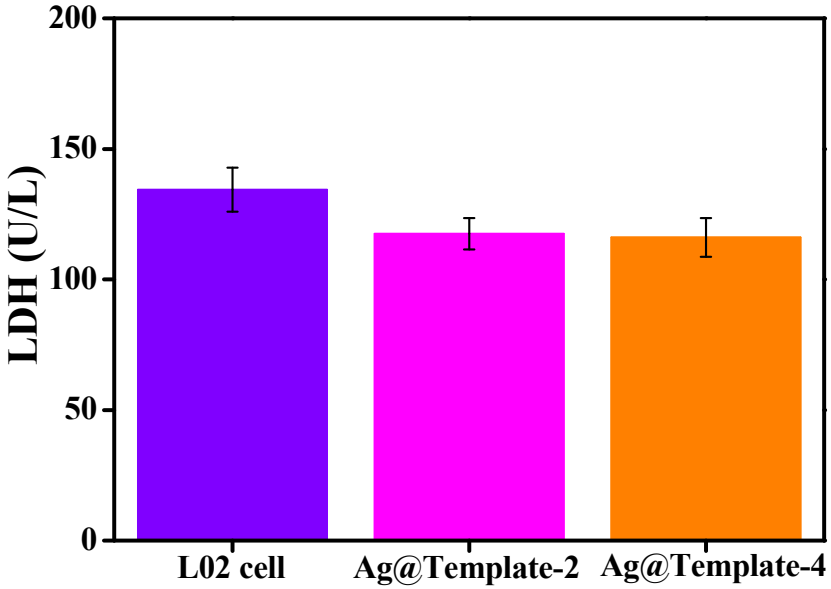


Figure S24. LDH of L02 cells treated at 20 μg/mL concentrations of Ag@Template-2 NC, Ag@Template-4 NC and Ag NPs for 48 h. Error bars represent the standard error of three parallel experiments.

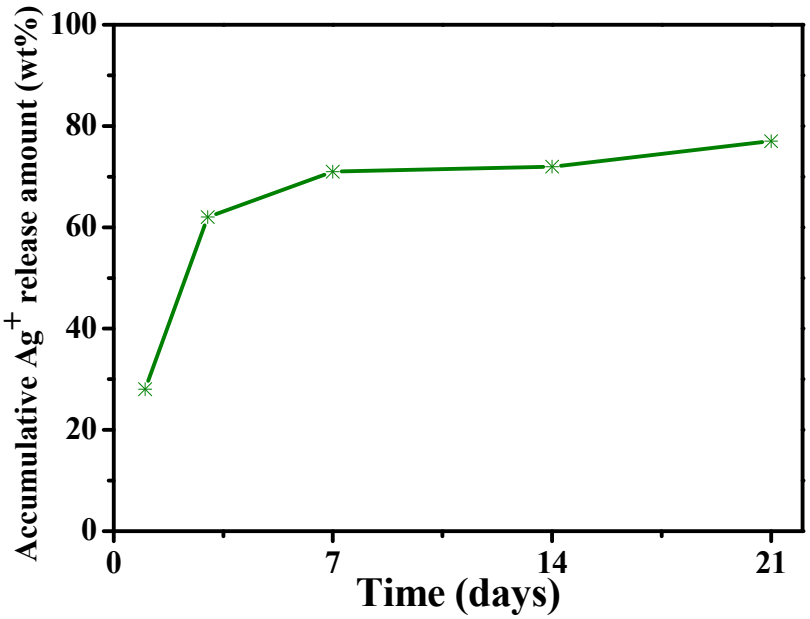


Figure S25. Plots of Ag^+ release concentration vs immersion time in distilled water for different periods.