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

Supporting Information

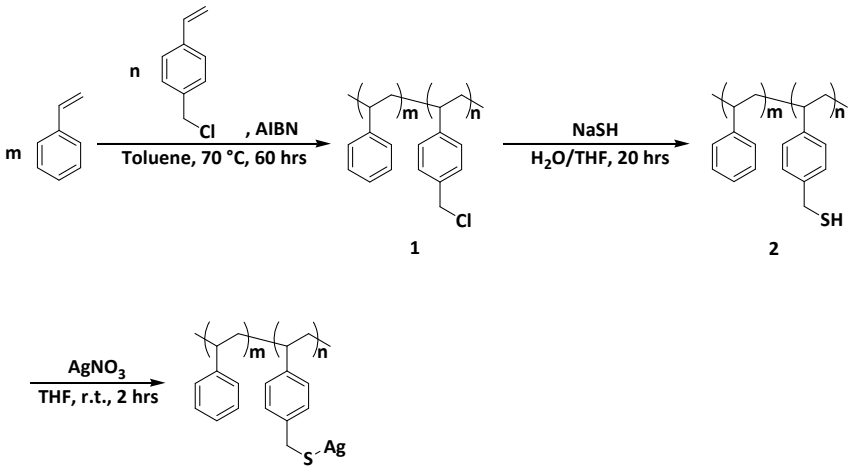
Confinements of silver nanoparticles in polystyrenes through molecular entanglements and their application for catalytic reduction of 4-nitrophenol

Ping-Tsung Huang,*[a] Yu-Ning Chen,[a] Kuan-Chung Chen,[a] Shun-Huei Wu,[a] Ching-Ping Liu*[a]

[a] Department of Chemistry, Fu Jen Catholic University, 510 Zhongzheng Rd., Xinzhuang District, New Taipei City 24205, Taiwan.

* E-mail: 073802@mail.fju.edu.tw; 129723@mail.fju.edu.tw. Fax: 886-2-29023209

Synthetic procedures of PS-Ag NPs



Synthesis of poly(styrene-co-4VBCl)(PS-4VBCl) (1)

Styrene (5.148 g, 49.5 mmol) and 4-vinylbenzyl chloride (0.763 g, 5 mmol) were placed in a 20 mL sample vial containing 3 mL toluene. AIBN (0.005 g, 0.03 mmol) was added to the sample vial and reacted at 70°C for 60 hours. The polymer solution was precipitated from methanol several times to remove unreacted chemicals. The final poly(styrene-co-4VBC) is dried under vacuum at 50°C for overnight. White poly(styrene-co-4VBCl) (2.38 g, 40.2%) powder was collected. The ratio of styrene to vinylbenzylchloride in polymer is about 99:1 as revealed by NMR calculation.

Synthesis of poly(styrene-co-4VBSH) (PS-4VBSH)(2)

Poly(styrene-co-4VBCl) (1 g) was placed in a 250 mL round-bottom flask containing 100 mL THF and 10 mL H_2O. NaSH (0.028 g, 0.5 mmol) was added to the round bottom flask and reacted at 50°C for 20 hours. The polymer solution was precipitated from methanol several times to remove unreacted NaSH. The final poly(styrene-co-4VBSH) is dried under vacuum at 50°C for overnight. White poly(styrene-co-4VBSH) (0.428 g, 42.8 %) powder was collected. [$\bar{M}_n$ =131,300, $\bar{M}_w$ = 244,800].

Synthesis of PS-Ag NPs (3)

Poly(styrene-co-4VBSH) (1 g) was dissolved in a round-bottom flask containing 30 mL THF. Silver nitrate (0.085 g, 0.5 mmol) was dissolved in 10 mL H_2O and added to the poly(styrene-co-4VBSH) solution. The mixed solution was stirred at room temperature for 2 hours and precipitate into H_2O twice. The final PS-Ag NP was dried under vacuum at 50°C for overnight. Lightly grey color PS-Ag NP (0.85 g, 85%) was obtained. The silver content were determined by using ICP-OES.

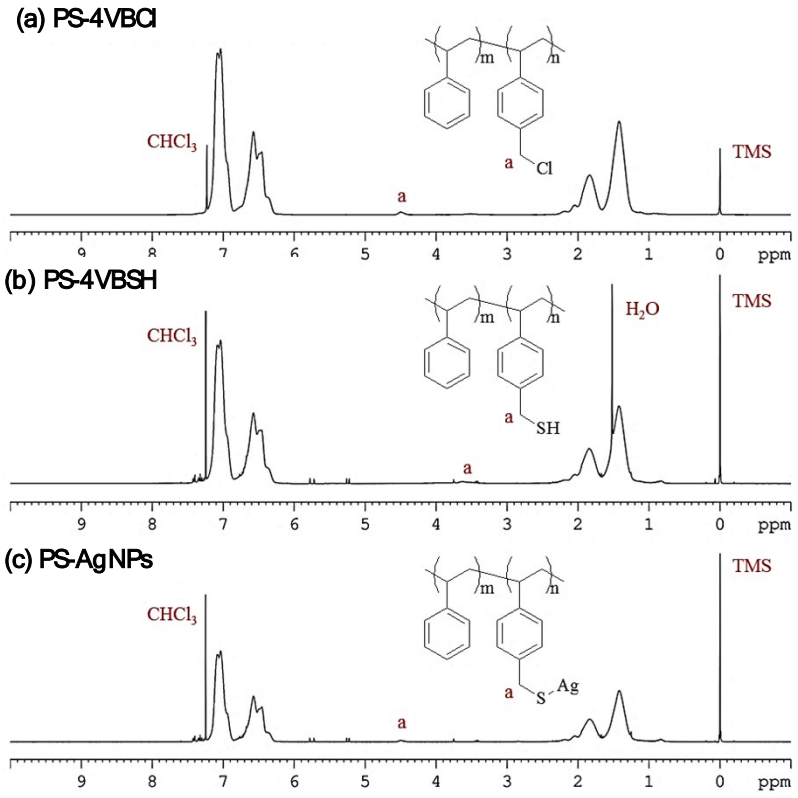


Fig. S1 NMR spectra of (a) PS-4VBCl, (b) PS-4VBSH, and (c) PS-AgNPs.

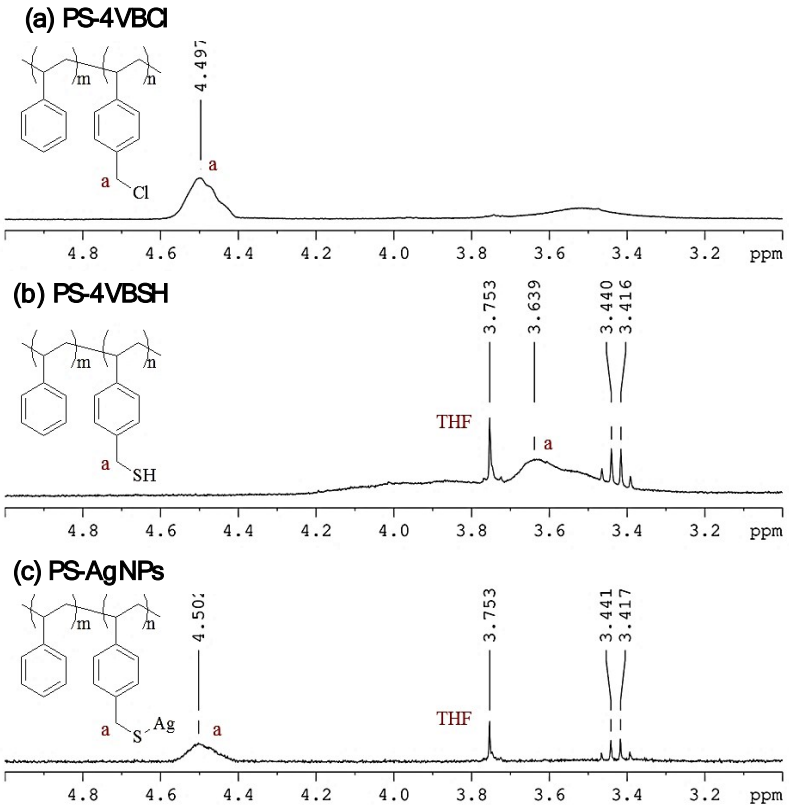


Fig. S2 NMR spectra of (a) PS-4VBCl, (b) PS-4VBSH, and (c) PS-AgNPs between δ = 3~5.

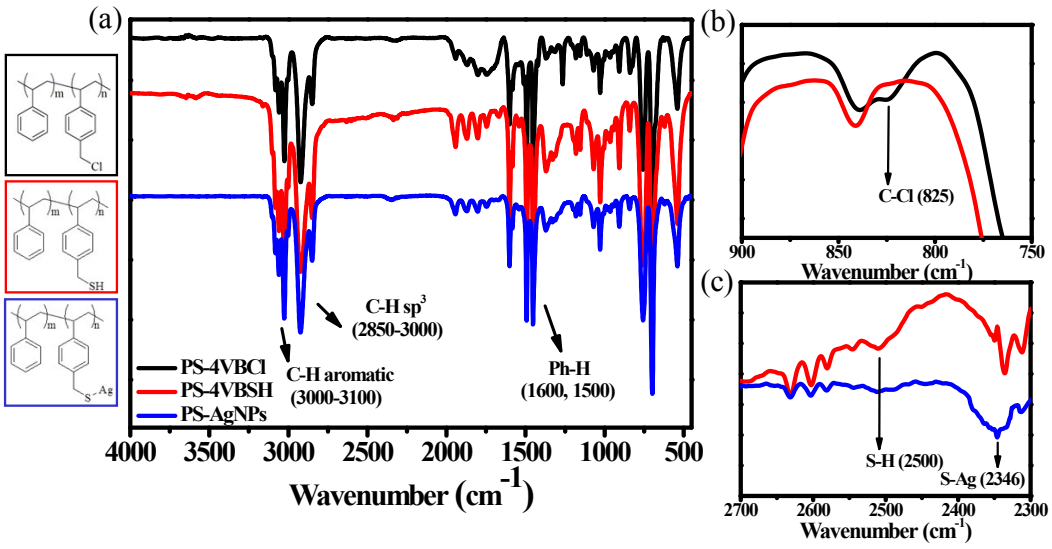


Fig. S3 FT-IR spectra of (a) PS-4VBCl, PS-4VBSH, and PS-AgNPs (b) characteristic peak of C-Cl (c) characteristic peak of S-H and S-Ag.

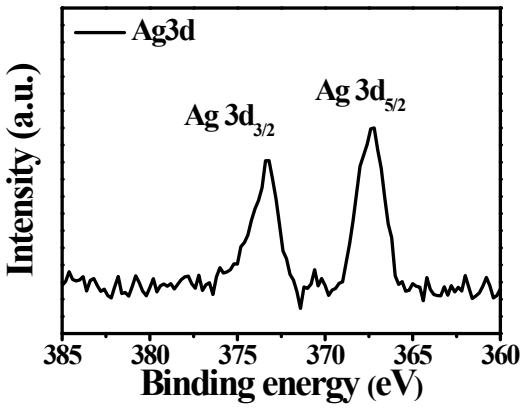


Fig. S4 The XPS spectrum of Ag3d in H-PS-AgNPs.

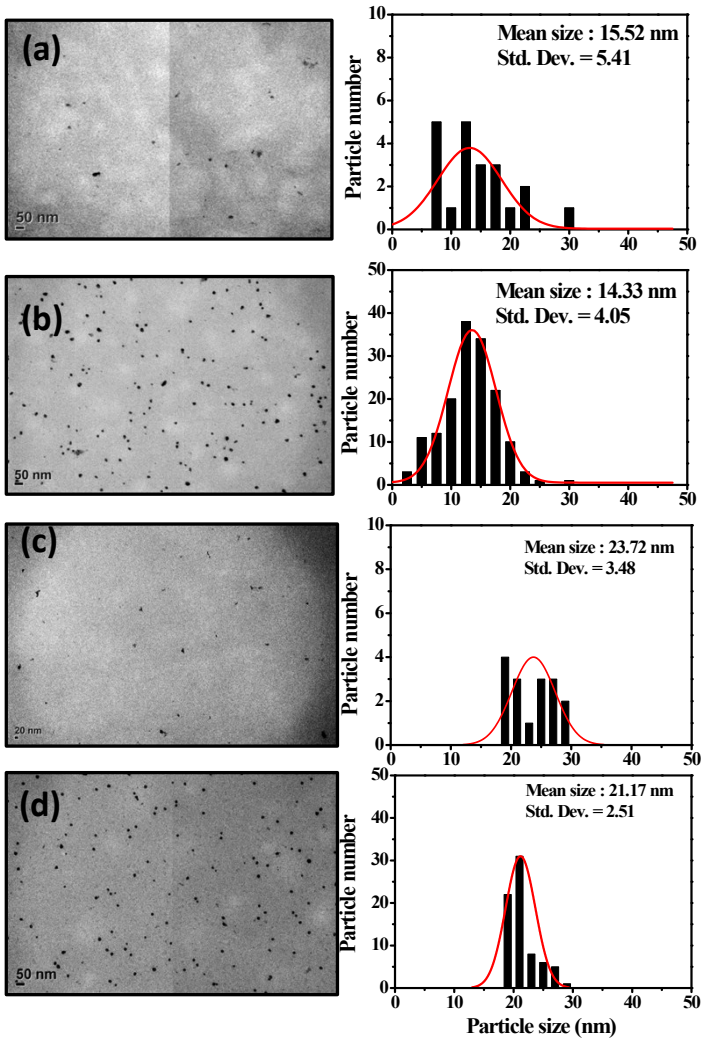


Fig. S5 TEM photos and particle size distribution of (a) as-cast L-PS-AgNPs (0.102 wt%); (b) as-cast H-PS-AgNPs (0.873 wt%); (c) annealed L-PS-AgNPs (0.102 wt%); (d) annealed H-PS-AgNPs (0.873 wt%).

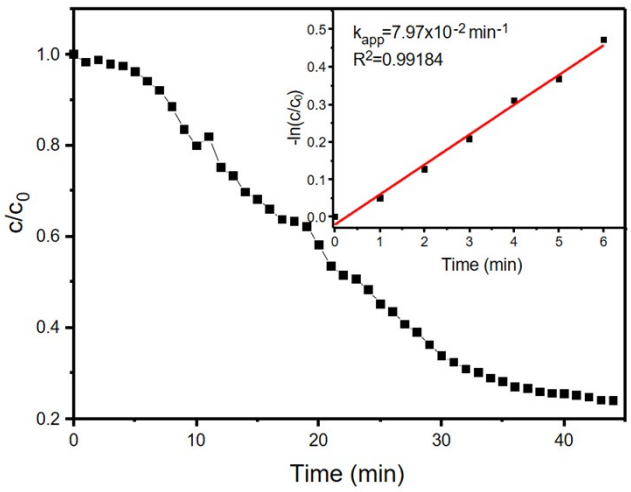


Fig. S6 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by L-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 15 mM; [Ag]= 5.8×10^{-4} mg mL^{-1}.

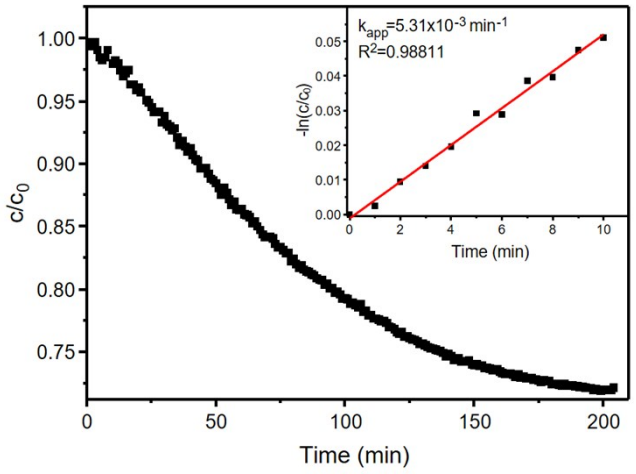


Fig. S7 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by L-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 15 mM; [Ag]= 5.8×10^{-5} mg mL^{-1}.

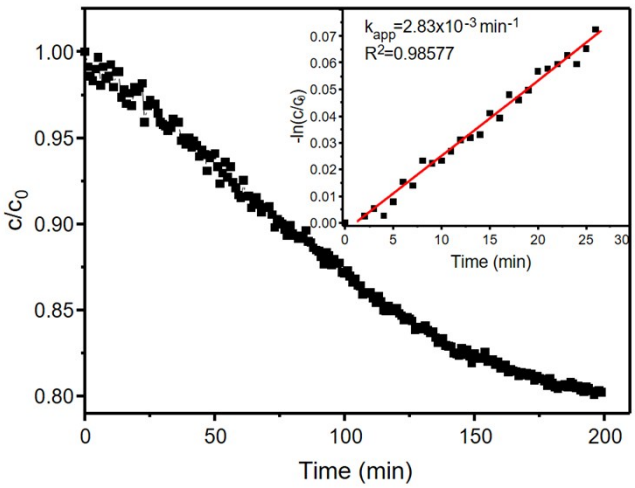


Fig. S8 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by L-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 15 mM; [Ag]=1.16×10^{-5} mg mL^{-1}.

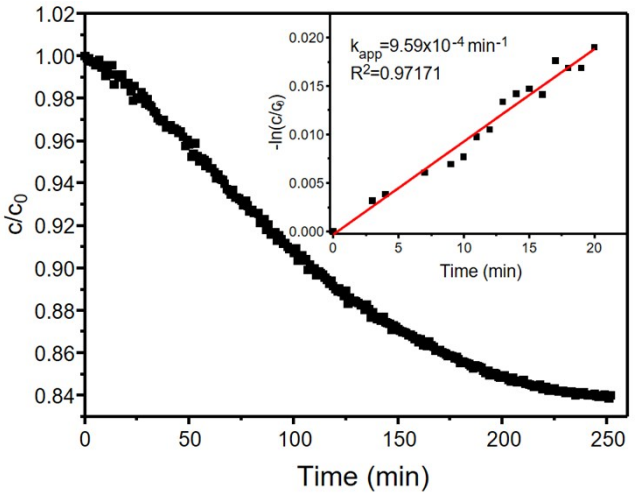


Fig. S9 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by L-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 15 mM; [Ag]=1.16×10^{-6} mg mL^{-1}.

Table S1 Comparison of different AgNP-based nanocomposites as catalysts with their corresponding linear range of [Ag] for the catalytic reduction of 4-NP.

Catalysts	Linear range of [Ag] (mg mL^{-1})	The type of AgNP-based composite	Reference
L-PS-AgNPs	$5.8\times10^{-4}\sim5.8\times10^{-6}$	Covalent bonding	This work
AgNPs@PGMA-SH[a]	$1.3\times10^{-4}\sim5.39\times10^{-2}$		52
PEI-AgNPs[b]	$6.61\times10^{-2}\sim0.343$		66
Chitosan-AgNPs	$5.39\times10^{-2}\sim0.269$		67
AgNPs/Triton	$0.8\sim4$	Encapsulation	*
AgNPs/CA[c]	$0.4\sim1.6$		**
MC-Ag/SiO_2[d]	$3.4\times10^{-4}\sim6.8\times10^{-4}$		53

[a] poly (glycidyl methacrylate) denoted as PGMA.

[b] polyimide denoted as PEI.

[c] calcium alginate denoted as CA.

[d] microcapsule denoted as MC, and k_{app} was proportional to $[Ag]^2$.

* Bano M, Ahirwar D, Thomas M, Naikoo GA, Sheikh MU-D, Khan F, *New J. Chem.* 2016, 40, 6787-6795.

** Saha S, Pal A, Kundu S, Basu S, Pal T, *Langmuir* 2010, 26, 2885-2893.

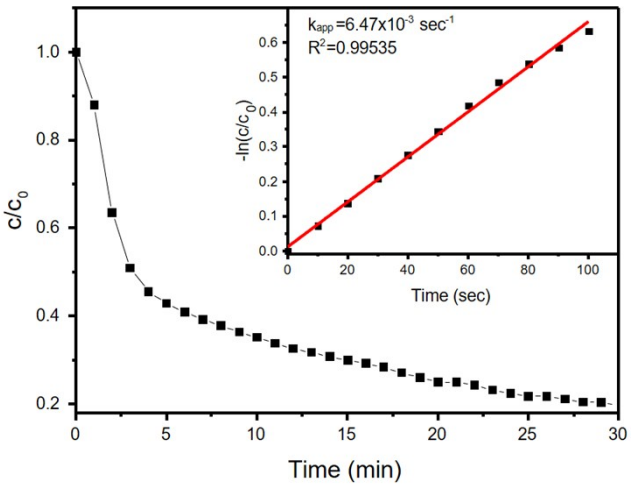


Fig. S10 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by H-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 50 mM; [Ag]=5.0×10^{-4} mg mL^{-1}.

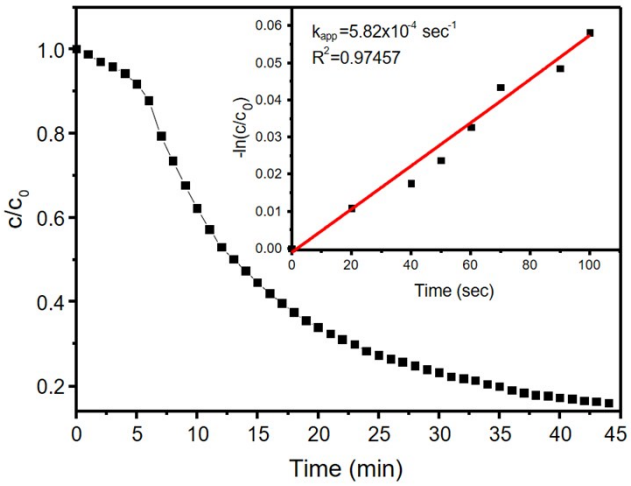


Fig. S11 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by H-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 50 mM; [Ag]=5.0×10^{-5} mg mL^{-1}.

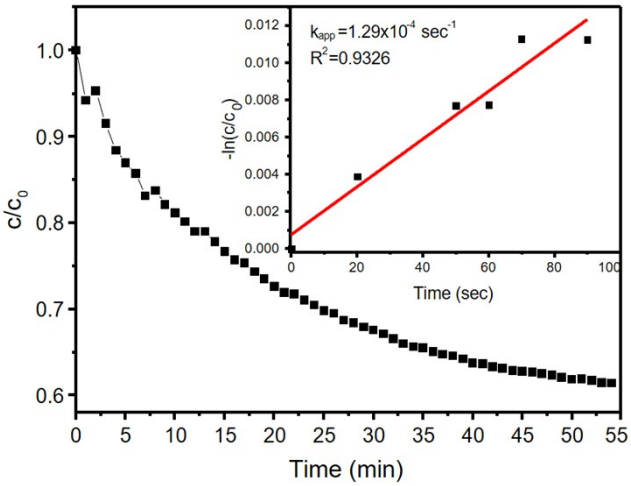


Fig. S12 The plot of c/c_0 versus time for the catalytic reduction of 4-NP by H-PS-AgNPs. The inset exhibited the linear fitting of the first-order kinetics. [4-NP]= 0.125 mM; [$NaBH_4$]= 50 mM; [Ag]=5.0×10^{-6} mg mL^{-1}.

Table S2 The various Ag content in H-PS-AgNPs and L-PS-AgNPs and the corresponding average values of t_0 during the catalytic reaction.

Catalysts	[Ag] (mg mL^{-1})	t_0 (min)
H-PS-AgNPs	5.0×10^{-4}	0.72 ± 0.25
	5.0×10^{-5}	3.67 ± 1.09
	5.0×10^{-6}	3.61 ± 0.96
L-PS-AgNPs	5.8×10^{-4}	15.33 ± 4.73
	2.9×10^{-4}	25.67 ± 9.07
	5.8×10^{-5}	28.67 ± 4.04
	1.2×10^{-5}	43.67 ± 3.79
	5.8×10^{-6}	49.33 ± 3.21